APPENDIX B: CARBON DIOXIDE CAPTURE TECHNOLOGY SHEETS

PRE-COMBUSTION MEMBRANES

PILOT-SCALE WATER GAS SHIFT—MEMBRANE DEVICE FOR HYDROGEN FROM COAL

Primary Project Goals

Western Research Institute is building and testing several pilot-scale hydrogen separation devices for use in a gasification product stream. The outcome of the project will be a demonstration of manufacturing practices in addition to the delivery of the engineering for a hydrogen production system ready for testing at large scale.

Technical Goals

- Design a modular water gas shift (WGS)-membrane reactor at 2 lbs hydrogen/day.
- Adapt suitable composite anodized alumina/palladium (Pd) copper (Cu) membranes to fit the reactor design.
- Test the reactor under NETL protocol and coal-derived synthesis gas (syngas) conditions.

Technical Content

Composite ceramic and alloy membranes have physical and chemical characteristics that allow them to be assembled with standard structural steels in easily fabricated constructions. The test data for the composite membranes shows that they eliminate some of the problems seen with metallic foil membranes of Pd or vanadium. By joining the composite membranes to off-the-shelf stainless steel components, complex devices can be designed that remain cost-effective to fabricate. The membrane modules are then inserted into systems that operate similar to heat exchange reactors, the well-established manufacturing capability of an engineering team member. The inclusion of structural monolithic catalysts into the assembly combines a WGS step with the hydrogen separation step to maximize hydrogen production from syngas. This project uses the developments that have been produced over the past five years and builds systems large enough to identify economic and technical issues with potential commercial units for hydrogen production.

Technology Maturity:

Pilot-scale, hydrogen separation in gasification product stream, 2 lbs/day

Project Focus:

Integrated WGS Membrane

Participant:

Western Research Institute

Project Number:

FE0004992

NETL Project Manager:

Darryl Shockley
Darryl.Shockley@netl.doe.gov

Principal Investigator:

Tom Barton
Western Research Institute
tbarton@uwyo.edu

Partners:

Chart Energy & Chemicals, Inc.
Synkera Technologies, Inc.

Performance Period:

9/24/10 – 12/31/11

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd	PdCu
	Materials of fabrication for support layer (if applicable)	AAO	AAO
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	H_2/CO_2	H_2/CO_2
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	1.0×10^{-3} mol/m^{2}sPa$^{0.5}$	1.5×10^{-3} mol/m^{2}sPa$^{0.5}$
	Temperature, °C	400 °C	400 °C
	Bench-scale testing, hours without significant performance degradation	300	1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	0	300
	Maximum pressure differential achieved without significant performance degradation or failure, bar	400 psi	600 psi
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Supported sheet	Supported sheet
	Packing density, m^2/m^3	5	25
	Pressure drop, bar	0.5	0.5
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	\$2,800/ft^2	\$743/ft^2
Product Quality	CO_2 purity, %	90%	97%
	H_2 purity, %	99%	100%

Technology Advantages

- The Pd alloy plugs in the membrane are discontinuous, which greatly reduces embrittlement issues.
- The natural aluminum rim to the composite membrane allows multiple joining technologies, such as brazing and laser welding.
- The volume around the membranes is suited for structural WGS catalyst, which improves hydrogen separation performance.

R&D Challenges

- Electrochemically depositing Pd Cu alloys in the anodized alumina.
- Joining aluminum-rimmed membranes to stainless steel structure.
- Accounting for thermal expansion mismatch during heating and cooling.
- Hydrogen sulfide and other contaminants in coal-derived syngas.

Results To Date/Accomplishments

- Two furnaces were fabricated for testing of components and the 2-lb/day hydrogen unit.
- The slipstream system for the small coal gasifier was refurbished and readied for operation.

- Design of the membrane reactor is completed.
- Laser welding was confirmed by testing to be the best joining technology for the aluminum-rimmed membranes.
- Donut-shaped membranes have been produced in the format suitable for the reactor design.

Next Steps

- Complete fabrication of the 2-lb/day device.
- Development and testing 1-inch Pd-alloys membranes for S-resistance.
- Complete scale-up of fabrication processes and perform trials with 6-inch membranes.
- Preparation for production and delivery of sufficient quantities of scaled membranes to accommodate at least two devices with 2 lb/day of hydrogen output.

Available Reports/Technical Papers/Presentations

The first presentation from this project will be made at the 2011 DOE Annual Hydrogen Review Meeting in Washington, DC, on May 13, 2011.

ADVANCED HYDROGEN TRANSPORT MEMBRANES FOR COAL GASIFICATION

Primary Project Goals

Praxair, Inc is conducting research and development (R&D) on hydrogen transport membranes resulting in the design, fabrication, and testing of a hydrogen separator capable of separating 2-lb/day hydrogen from a coal gasification fuel gas stream.

Technical Goals

- Identify and evaluate a suitable high-temperature, contaminant-resistant, hydrogen transport membrane.
- Fabricate and install hydrogen membrane in a proof-of-concept reactor connected to an operating coal gasifier.
- Test the membrane reactor for separating at least 2 lb/day [approximately 15 standard cubic feet per hour (scfh)] of hydrogen from the coal-derived synthesis gas (syngas).

Technical Content

The membranes must be incorporated into a membrane unit that separates hydrogen from syngas derived from gasification and produces a high-pressure carbon dioxide (CO_2)-rich retentate stream. The project will examine different membrane reactor designs, including use of catalysts and sweep streams, to select the optimum membrane reactor configuration. Reactor modeling will evaluate different configurations and estimate the impact of reactor design on performance. In Phase I, a small proof-of-concept reactor will be built to separate at least 2 lbs/day (about 15 scfh) of hydrogen from coal-derived syngas. In Phase II, a pilot-scale reactor will be built and integrated with an operating gasifier to produce at least 100 lbs/day (about 800 scfh) of hydrogen.

Technology Maturity:

Bench- to pilot-scale, hydrogen separation

Project Focus:

Membrane for H_2 Separation

Participant:

Praxair, Inc.

Project Number:

FE0004908

NETL Project Manager:

Elaine Everitt
Elaine.Everitt@netl.doe.gov

Principal Investigator:

Joseph Schwartz
Praxair, Inc.
Joseph_Schwartz@praxair.com

Partners:

Colorado School of Mines
T3 Scientific, LLC

Performance Period:

9/29/10 – 12/31/11

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd alloy	Pd alloy
	Materials of fabrication for support layer (if applicable)	Ceramic	Ceramic
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	>500 at 100 psi	>500 at 300 psi
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	300 scfh/ft^2 at 100 psi	300 scfh/ft^2 at 100 psi
	Temperature, °C	300–400	300–400
	Bench-scale testing, hours without significant performance degradation	250	500
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	13.79	17.24
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	N/A	25
	Pressure drop, bar	N/A	0.5
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	5,000
Product Quality	CO_2 purity, %	N/A	N/A
	H_2 purity, %	99	99

Technology Advantages

- Thin supported membrane has high flux at low precious metal cost.
- Alloys under development that have shown excellent performance in mixed gas streams including sulfur.

R&D Challenges

- Develop a membrane that matches or exceeds current flux performance in an environment with sulfur and other contaminants from coal or biomass gasification.
- Incorporate membrane treatments to improve contaminant resistance.
- Scale up membrane size and reactor design.

Results To Date/Accomplishments

- A mixed gas test was completed without sulfur. The flux was significantly lower than pure hydrogen at the same feed hydrogen partial pressure, but high hydrogen recovery (86%) was achieved.
- Reactor sizing and design has begun.

Next Steps

- Prepare palladium (Pd) binary alloy membranes with platinum (Pt), as there are indications that Pt may have similar carbon and sulfur inhibition properties as gold (Au).
- The systematic study of ethylenediaminetetraacetic acid (EDTA) will continue with pure gas testing of the Pd membranes prepared using 20 and 40 g/L EDTA in the plating bath.
- Begin testing in sulfur.
- Begin synthesis and testing of Pd/Pt membranes.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

ENGINEERING DESIGN OF ADVANCED H_2-CO_2 PD AND PD/ALLOY COMPOSITE MEMBRANE SEPARATIONS AND PROCESS INTENSIFICATION

Primary Project Goals

Worcester Polytechnic Institute (WPI) is reducing the production of pure hydrogen from the synthesis gas (syngas) to a single unit operation consisting of a composite palladium (Pd) or Pd/alloy water gas shift (WGS) membrane shifter in order to lower the cost of separation.

Technical Goals

- Synthesize thin layer Pd and Pd/gold (Au) membranes with long-term thermal and chemical stability with a special emphasis on long-term stability of hydrogen flux and selectivity.
- Synthesize thin layer Pd, Pd/copper (Cu), and Pd/Au membranes with sulfur poisoning resistance by the use of MembraGuard coating or any other novel techniques.
- Fabricate and testing at the National Carbon Capture Center (NCCC) a membrane module skid consisting of a WGS membrane reactor capable of producing 2 lb of hydrogen (H_2)/day at the competition of Phase I.
- Fabrication and successful operation of a 100-lb-of-H_2/day WGS membrane reactor at the completion of Phase II.
- Full engineering design of a unit capable of producing a minimum for 4 tons/day of H_2 and integration into commercial integrated gasification combined cycle (IGCC) will be complete at the end of Phase III.

Technology Maturity:

Bench-scale (½″ OD, 2.5 ″L),
231 scf H_2/day at ~450 °C,
$\Delta P = 100$ psi ($P_{low} = 15$ psia)

Pilot-scale (1″ OD, 6″ L),
201 scf H_2/day at ~450 °C,
$\Delta P = 15$ psi ($P_{low} = 15$ psia)

Bench and pilot-scale Pd and Pd/alloy membrane,
4 tons H_2 per day

Project Focus:

Pd-Pd Alloy Composite Membrane for H_2 Separation

Participant:

Worcester Polytechnic Institute

Project Number:

FE0004895

NETL Project Manager:

Jason Hissam
Jason.Hissam@netl.doe.gov

Principal Investigator:

Yi Hua Ma
Worcester Polytechnic Institute
yhma@wpi.edu

Partners:

Membrane Technology and Research, Inc.
Siemens Energy, Inc.
T3 Scientific, LLC

Performance Period:

9/20/10 – 12/31/11

Technical Content

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd, Pd/Au, Pd/Cu,	Pd, Pd/Au, Pd coated with S-resistant layer
	Materials of fabrication for support layer (if applicable)	PSS-316L, Inconel-625	PSS-316L, Inconel-625
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	≈ ∞	≈ ∞
	Type of selectivity measurement (ideal or mixed gas)	Ideal, mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	Bench Scale: 3.59 at 450 °C Pilot Scale: 2.91 at 450 °C	DOE 2015 Target: Pilot scale 100 lb H_2 per day Complete design of a 4 ton H_2 per day plant
	Temperature, °C	300–450	250–500
	Bench-scale testing, hours without significant performance degradation	3,550	N/A
	Pilot-scale testing (if applicable), hours without significant performance degradation	850	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	14	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	$1,254 per square foot 744 tonne/day (calculated based on simulation)	$1,000 per square foot
Product Quality	CO_2 purity, %	80.3% (at feed mixed-gas: 37.1% CO_2, 1.2% CO and 61.7% H_2 at 450 °C, 212 psia, GHSV of 1,069 h^{-1} and 92.6% H_2recovery); 83.5% (at feed mixed-gas: 10% CO_2, 23% CO, 22% H_2 and 45% H_2O at 450 °C, 212 psia, GHSV of 4,497 h^{-1}, 83.2% H_2 recovery and 95% CO conversion)	N/A
	H_2 purity, %	>≈99%	—

Other Membrane Parameters

Contaminant Resistance: Pd/Au and Pd/Cu alloy membranes provide some resistance to hydrogen sulfide (H_2S) and are also regenerable.

Technology Advantages

- High-pressure carbon dioxide (CO_2) for carbon capture (low compression costs).
- Low steam requirements compared with traditional WGS reactor.
- High purity hydrogen at the permeate side for fuel cell applications.
- Lower cost operation by combining WGS reaction and separation in the same module.
- Higher energy efficiency.

R&D Challenges

- Inconsistent quality from suppliers of porous metal supports.
- Development of a procedure with fewer steps for industrial production.
- Development of reliable, well reproducible, compatible with support materials, and environmentally friendly to modify support surface in order to overcome support irregularities and surface characteristics inconsistencies.
- Long-term stability selectivity at 450 °C for membranes thinner than 6–8 microns.
- The formulation of defect free membranes material with resistant to sulfur.

Results To Date/Accomplishments

- Completed a new testing rig, fully automatic and remotely controllable, for the study and characterization of pilot-scale (1” OD) membrane under WGS reaction.
- Several composite Pd membranes have been prepared on porous metal supports from Chand Eisenmann Metallurgical. Thicknesses varied from 4 to 28 µm and hydrogen permeances at 450 °C varied for helium (He) leak stable membranes between 13 and 42 scfh/ft^2-psi$^{0.5}$ (with $\Delta P = 14.7$ psi, and Ptube = 14.7 psi).
- Stable membranes were obtained on 0.2 µm PSS 316L supports.
- Pure Pd membranes showed good stability less than 200 parts per million by volume (ppmv) of H_2S for more than 250 hours at 400 °C with MembraGuard coating.
- A prototype for the Phase II membrane reactor module has been designed.
- A complete setup for a WGS reactor capable of producing 2 lb/day of hydrogen at temperature ranging between 350 and 450 °C has been projected.

Next Steps

- Prepare thin and stable composite pure Pd membranes on 1” OD PSS 316L and Hastelloy supports.
- Characterize such membranes in pure hydrogen atmospheres and in WGS reaction conditions.
- The most stable membranes will be sent to MTR for their integration in the skid module.
- Continue equipment preparation for coating deposition on tubular membrane anticipated for next performing period at T3 facilities.
- In the next project performing period, 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.

- Membranes will be sent to T3 so that the H_2S protective coating will be deposited. Such membranes will be tested in sulfur conditions at WPI and then at NCCC under syngas atmospheres.
- The Phase I membrane module skid will be assembled and shipped to NCCC.
- A Phase II membrane reactor module will be fabricated.
- Mounting and leaks testing of the WGS reactor at WPI.
- Pure nitrogen and pure hydrogen tests will be performed in the WGS reactor at WPI in order to reproduce the experimental data obtained with the same membranes in other devices already present in the WPI laboratories.
- Nitrogen-hydrogen mixture experiments at different operative conditions (i.e., different temperatures, hydrogen compositions, and feed flow rates) in the presence of the catalytic bed to perform fluid dynamic analysis and to esteem the mass transport coefficients and the relationship between the dimensionless number characteristic of the system. This analysis can be used in the future to model in a more accurate way the behavior of the system in the presence of the WGS reaction.

Available Reports/Technical Papers/Presentations

Journal Articles:

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

Chen, Chao-Huang and Ma, Yi Hua, "The Effect of H_2S on the Performance of Pd and Pd/Au Composite Membrane," 362(1-2), 535–544(2010).

Pomerrantz, N., Ma, Y. H., "Novel Method for Producing High H_2 Permeability Pd Membranes with a Thin Layer of the Sulfur Tolerant Pd/Cu fcc Phase," J Memb Sci., 370, 97–108 (2011).

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, Accepted for publication.

Augustine; Alexander Sullivan, Kazantzis, Nikolaos K., Ma, Yi Hua, "High pressure palladium-membrane reactor for the high-temperature water-gas shift reaction International Journal of Hydrogen Energy," International J of Hydrogen Energy, Accepted for publication.

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

Chen, C. H. and Ma, Y. H., "The Effect of H_2S on the performance of Pd and Pd/Au composite membrane," Submitted to the **Journal of Membrane Science**.

Pomerantz, N.; Payzant, E.A. and Ma, Y.H. "*Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication*," **AIChE Journal**, In press.

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

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

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 (2009) 430–438.

Conference Proceedings:

Ayturk, M. E. and Ma, Y.H. "*Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability.*" **Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.**, 55(1) (2010).

Chen, C. H. and Ma, Y. H., "*Effect of* H_2S *concentration on hydrogen permeance of a composite Pd/Au hydrogen separation membrane prepared by galvanic displacement*," **Preprint in the Proceedings of 239th ACS Annual Meeting**, March 21–25, 2010, San Francisco, CA, USA.

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

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

Chen, C. H. and Ma, Y. H., "*Characterization of sulfur resistance of Pd/Au hydrogen separation membranes*," Extended abstract in the **Proceedings of the 2008 AIChE Annual Meeting**, November 16–21, 2008, Philadelphia, PA, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "*The effect of* H_2S *on the long-term stability of Pd/Cu membranes and the characteristics of* H_2S *poisoning of electroless deposited Pd,*" Extended abstract in the **Proceedings of the AIChE Annual Meeting 2008**, November 16–21, 2008, Philadelphia, PA, USA.

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. Extended abstract in the **Proceedings of the 10th Intl. Conf. on Inorganic Membranes (ICIM10)**, (2008) Tokyo, Japan.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement," Preprint in the **Proceedings of 234th ACS Annual Meeting**, August 19–23, 2007, Boston, MA, USA.

Pomerantz, N. and Ma, Y.H. "*Effect of* H_2S *poisoning of Pd/Cu membranes on* H_2 *permeance and membrane morphology*," Extended abstract in the **Proceedings of the ACS 234th National Meeting and Exposition**, August 19–23, 2007, Boston, MA, USA.

Presentations:

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

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 DC, USA.

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.

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.

Koc, Reyyan, Kazantzis, Nikolaos and Ma, Yi Hua, "A Process Dynamic Modeling and Control Framework for Performance Characterization and Enhancement of Pd-Based Membrane Reactors," Session: on Membranes for Hydrogen Purification, 10th AIChE Annual Meeting, November 7–12, 2010, Salt Lake City, UT, USA.

Koc, Reyyan, Kazantz, Nikolaosis and Ma, Yi Hua, "A Process Modeling Framework for Performance Assessment of Pd-Based Water-Gas Shift Membrane Reactors," Oral presentation, Session: on Membrane Reactors, AIChE 2010 Annual Meeting, November 7–12, 2010, Salt Lake City, UT, USA.

Augustine, Alexander S., Ayturk, M. Engin and Ma, Yi Hua, "Composite Palladium Membrane Reactor for Hydrogen Production with Syngas Feed," Session on Membranes for Energy Applications, Joint Meeting of North American Membrane Society Annual Meeting and 11th International Conference on Inorganic Membranes, July 17–22, 2010, Washington, DC, USA.

Chen, Chao-Huang and Ma, Y. H., "The Effect of Au Content in Composite Pd/Au Membranes Prepared by Galvanic Displacement On Hydrogen Permeance and H_2S Resistance," Session on Membranes for Hydrogen Purification, AIChE 2010 Annual Meeting, November 17–22, 2010, Salt Lake City, UT, USA.

Ayturk, M. E. and Ma, Y.H. "*Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability*," To be presented at the **ACS Spring National Meeting and Exposition**, March 21–25, 2010, San Francisco, CA, USA.

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

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

Ayturk, M. E. and Ma, Y.H. "*Long-Term Selectivity Stability and High-Pressure Mixed Gas Hydrogen Permeation Testing of Composite Pd/Inconel Membranes*." Presented at the **AIChE Annual Meeting**, November 8–13, 2009, Nashville, TN, USA.

Augustine, A. S.; Ayturk, M.E.; Kazantzis, N. and Ma, Y. H. "*Palladium Membrane Reactor for Water Gas Shift Reaction*." Presented at the **AIChE Annual Meeting**, November 8–13, 2009, Nashville, TN, USA.

Ma, Y. H., Ayturk, M.E., Augustine, 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.

Ayturk, M. E. and Ma, Y. H., "*Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability*," Presented at the **2008 AIChE Annual Meeting**, November 16–21, 2008 Philadelphia, PA, USA.

Chen, C. H. and Ma, Y. H., "Characterization of sulfur resistance of Pd/Au hydrogen separation membranes," Presented at the **2008 AIChE Annual Meeting**, November 16–21, 2008, Philadelphia, PA, USA.

Pomerantz, N.; Payzant, E.A. and Ma, Y.H. "*Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication*," Presented at the **AIChE Annual Meeting 2009**, Nashville, TN, USA, November 8–13, 2009.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "*The effect of* H_2S *on the long-term stability of Pd/Cu membranes and the characteristics of* H_2S *poisoning of electroless deposited Pd*," Presented at the **AIChE Annual Meeting 2008**, November 16–21, 2008, Philadelphia, PA, USA.

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*," Presented at the **10th International Conference on Inorganic Membranes (ICIM10)**, August 18–22, 2008, Tokyo, Japan.

Ayturk, M. E., Kazantzis, N.K. and Ma, Y. H., "*Modeling and Performance Assessment of Pd- and Pd/Alloy-based Catalytic Membrane Reactors for Hydrogen Production*," Presented at the **International Congress on Membranes and Membrane Processes (ICOM 2008)**, July 12–18, 2008, Honolulu, HI, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "XPS studies of H_2S poisoned Pd deposits and the implications on Pd membrane performance." Presented at the **International Congress on Membranes and Membrane Processes (ICOM 2008)**, July 12–18, 2008, Honolulu, HI, USA.

Ma, Y. H., Kazantzis, N., Ayturk, M. E., Pomerantz, N. and Chen, C.-H., "*Composite Pd and Pd/alloy Porous Stainless Steel Membranes for Hydrogen Production, Process Intensification and* CO_2 *Sequestration,*" Presented at the **2008 NHA Annual Hydrogen Conference and Expo: "Ramping up Commercialization,"** March 30-April 03, 2008 Sacramento, CA, USA.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement," Presented at the **2007 ACS Annual Meeting**, August 19–23, 2007 Boston, MA, USA.

Pomerantz, N. and Ma, Y.H. “Effect of H_2S poisoning of Pd/Cu membranes on H_2 permeance and membrane morphology.” Presented at the **ACS 234th National Meeting and Exposition**, August 19–23, 2007, Boston, MA, USA.

Chen, C. H. and Ma, Y. H., “Preparation of Pd/Au hydrogen separation membrane by galvanic displacement,” Presented at the 2007 **North American Membrane Society Annual Meeting**, May 13–16, 2007, Orlando, FL, USA.

EFFICIENT REGENERATION OF PHYSICAL AND CHEMICAL SOLVENTS FOR CO_2 CAPTURE

Primary Project Goals

The University of North Dakota is evaluating the use of composite polymer membranes and porous membrane contactors for the recovery of carbon dioxide (CO_2) from CO_2-rich solvent streams from flue gas and coal gasification synthesis gas (syngas). The development of materials and processes is necessary to reduce the capital and operating costs of the solvent regeneration process, particularly the energy expended in regeneration.

Technical Goals

- Assess the capability of a range of composite polymer membranes and porous membrane contactors to regenerate physical and chemical solvents for CO_2 capture.
- Fabricate a continuous bench-scale test system to measure membrane performance and the effect of several key process parameters: gas flow rate, liquid flow rate, temperature, etc.

Technical Content

This project will investigate the use of two membrane technologies for the recovery of CO_2 from solvents: porous membrane contactors and composite membranes (Figure 1). In both cases a liquid solvent, saturated with CO_2, will flow over the membrane, while either a vacuum or sweep gas will be used to maintain a low partial pressure of CO_2 on the permeate side of the membrane. Porous membranes will rely on surface tension of the solvent to prevent bulk flow of solvent through its pores. Composite membranes will utilize a thin (<50 micron) selective layer to prevent loss of solvent.

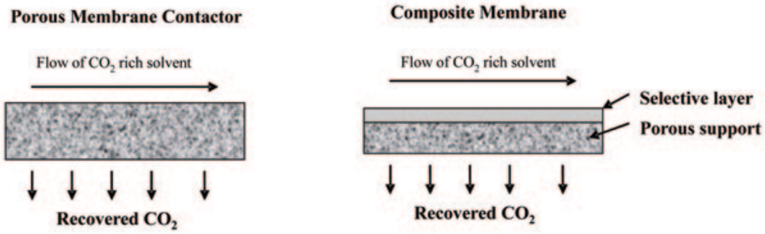


Figure 1: Two Types of Membranes Investigated in this Project

An experimental system has been built to evaluate membrane materials for this application (Figure 2). This system contains an absorber to saturate the solvent at a specified temperature, a pump to circulate the solvent, a heater to heat the solvent to a specified temperature, and a membrane unit. The permeate is analyzed using a gas chromatograph, while samples can be taken from the absorber and after the membrane unit in order to measure the rate of CO_2 recovery.

Technology Maturity:

Bench-scale, CO_2 recovery from flue gas, syngas

Project Focus:

Composite Polymer Membrane

Participant:

University of North Dakota

Project Number:

FE0002196

NETL Project Manager:

Robert Noll
Robert.Noll@netl.doe.gov

Principal Investigator:

Brian Tande
University of North Dakota
briantande@mail.und.edu

Partners:

None

Performance Period:

12/1/09 – 11/30/12

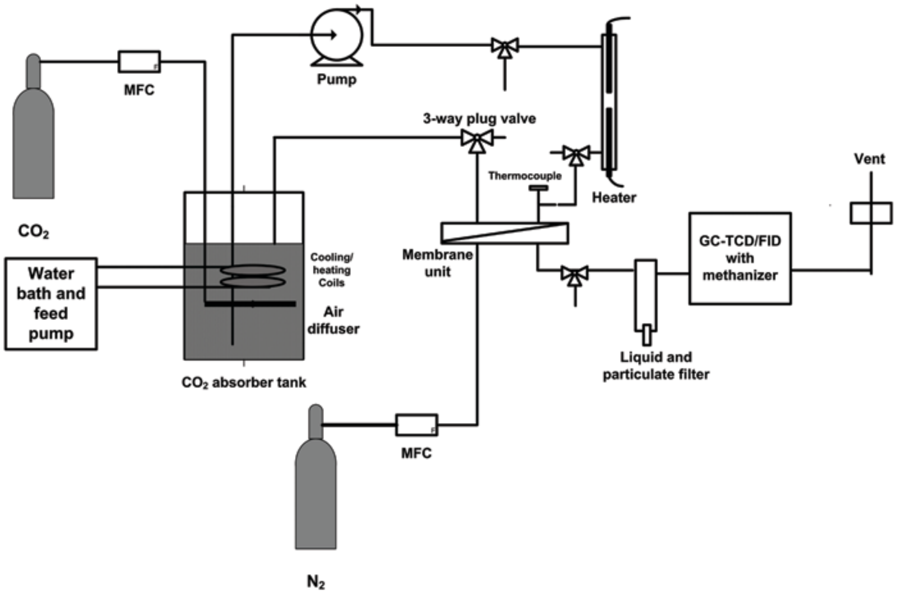


Figure 2: Experimental Apparatus

Technology Advantages

- More mass transfer area per volume than traditional packed or trayed columns.
- Lower operating temperatures than current technology, reducing energy costs, and minimizing amine degradation.
- Potentially wider operating ranges than packed or trayed columns.

R&D Challenges

- Identification of materials with the necessary set of properties.
- Accurate control of temperature and flow rates.
- Measurement of low permeability materials. The gas chromatograph has been calibrated to 100 parts per million (ppm), but a flame ionization detector (FID) with a methanizer may be needed to quantify lower levels of CO_2 in the carrier gas.

Results To Date/Accomplishments

- Recent progress on this project includes the fabrication and commissioning of the test system, as well as the calibration of the gas chromatograph, which is being used to analyze the CO_2 content of the carrier gas so that the CO_2 permeation rate through each membrane material can be determined. Existing methods of determining CO_2 loading of the solvent have also been implemented.
- Porous membrane testing is underway. Early results indicate that polytetrafluoroethylene (PTFE) porous membranes are able to recover as much as 40% of the CO_2 from a saturated monoethanolamine (MEA) solution at a temperature of 95 °C.

Next Steps

- Continue porous membrane testing, which should be complete by end of summer 2011.
- Parametric study for top membrane candidates.
- Commercial feasibility analysis for one of the most promising solvent-membrane candidate systems.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

HYDROGEN SELECTIVE EXFOLIATED ZEOLITE MEMBRANES

Primary Project Goals

The University of Minnesota researchers are further developing exfoliated zeolite coating technology for hydrogen (H_2) separation membranes, including membrane production methodology, and determining the feasibility of integration of the membrane into a water gas shift (WGS) reactor model.

Technical Goals

- Develop and optimize a membrane production method for the exfoliated zeolite coating.
- The membrane must demonstrate high flux, high selectivity, and stable performance.
- Determine the feasibility of integrating these membranes in WGS reactors and integrated gasification combined cycle (IGCC) flow sheets.
- Performing a techno-economic analysis.

Technical Content

This project will further develop a novel silica molecular sieve membrane using exfoliated zeolite coatings with the potential to contribute to carbon capture by high temperature separation of H_2 from carbon dioxide (CO_2) and other gases present in shifted synthesis gas (syngas). The project will establish procedures for the production of the required supply of these layered silicates, first optimizing the synthesis process of the exfoliated zeolite, then the layer-by-layer coating process.

The pore structure of the zeolite that is currently studied (MCM-22) includes ultra-small (potentially H_2-selective) sized pores defined by six SiO_4 tetrahedra (6-Member Ring pores: 6MR) along the c-axis. Therefore, c-out-of-plane oriented films are promising for H_2-separation membranes. MCM-22 has highly anisotropic plate or disk-like crystal shape, thin along the c-crystallographic axis and appropriate for achieving c-oriented films. Among available compositions, an all-silica and potentially hydrothermally stable composition has been reported, which could enable H_2-separations in applications like WGS reactors.

Membrane Microstructures Achieved Currently: MCM-22/silica composite films were fabricated using layer-by-layer deposition towards a nanoscale realization of the selective flake concept. The repetition of appropriate deposition cycles (i.e., particle deposition and subsequent silica coating) led to the gradual increase of separation performance achieving H_2/nitrogen (N_2) ideal selectivity as high as 120. The SEM cross-section image of a five-layer membrane along with its schematic is shown in Figure 1. The aim of the ongoing work is to improve performance using thinner flakes (exfoliated zeolite layers).

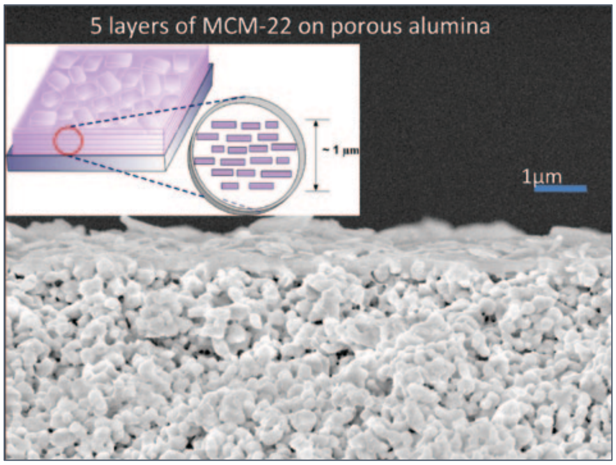


Figure 1: SEM Cross-Section Image of a Five-Layer Membrane Along with its Schematic

The H_2 permeance and selectivity to CO_2 and other gases, as well as hydrothermal stability, will be determined for the developed membrane. A series of tests will determine membrane separation performance. Performance testing configurations will include

Technology Maturity:

Laboratory evaluation using synthetic gases

Project Focus:

Hydrogen Selective Zeolite Membranes

Participant:

University of Minnesota

Project Number:

FE0001322

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

Michael Tsapatsis
University of Minnesota
tsapatsis@umn.edu

Partners:

None

Performance Period:

10/1/09 – 9/30/13

flat alumina supports up to 220 °C; tubular membrane testing using single gases up to 600 °C; tubular membrane testing using simulated feeds up to 600 °C; and high-temperature, high-pressure testing of tubular supports. The membrane stability will be determined in a WGS environment. The three stability test configurations are in steam containing simulated feeds for exfoliated powders; in steam containing simulated feeds for alumina supported films; and in steam containing simulated feeds for stainless steel supported films.

The project will also integrate the membrane into a WGS membrane reactor model, integrate the model in an IGCC flow sheet, and perform techno-economic analysis and operability evaluation and analysis.

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	MCM-22 plate-like crystals	Exfoliated MCM-22 layers
	Materials of fabrication for support layer (if applicable)	Porous alumina discs (homemade)	Porous stainless steel tubes (commercial)
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	20	80–800
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	0.01 mol/m^2-s-bar	0.1–1 mol/m^2-s-bar
	Temperature, °C	200	500
	Bench-scale testing, hours without significant performance degradation	48	250
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3	10
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	N/A	TBD
	Packing density, m^2/m^3	N/A	TBD
	Pressure drop, bar	1–2 atm	10 atm
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	\$3,000/m^2
Product Quality	CO_2 purity, %	N/A	TBD
	H_2 purity, %	N/A	TBD
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	TBD
	Heat requirement, kJ/kg CO_2	N/A	TBD
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	TBD

Other Membrane Parameters

Contaminant Resistance: These materials are crystalline silicates and the main issue is stability to steam. Other contaminants are not expected to create problems.

Flue Gas Pretreatment Requirements: To be determined as project progresses.

Waste Streams Generated: To be determined as project progresses.

Technology Advantages

This membrane technology will form the selective film using a coating process and pre-made components, and will have high selectivity, flux, and stability.

R&D Challenges

- Dispersible exfoliated layers.
- Simple and efficient coatings process.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the September 2013 project completion date.

Available Reports/Technical Papers/Presentations

Maheshwari S., Kumar S., Bates F.S., Penn R.L., Shantz D.F., Tsapatsis M. **Journal of the American Chemical Society 130**, 1507–1516 (2008) *Layer Structure Preservation during Swelling, Pillaring and Exfoliation of a Zeolite Precursor*.

Choi J., Tsapatsis M. **Journal of the American Chemical Society 132(2)**, 448–449 (2010) *MCM-22/Silica Selective Flake Nanocomposite Membranes for Hydrogen Separations*.

PRE-COMBUSTION CARBON DIOXIDE CAPTURE BY A NEW DUAL-PHASE CERAMIC-CARBONATE MEMBRANE REACTOR

Primary Project Goals

Arizona State University is developing a dual-phase, membrane-based separation device which will separate carbon dioxide (CO_2) from typical water gas shift (WGS) mixture feeds and produce hydrogen, which can be introduced into the combustion turbines of integrated gasification combined cycle (IGCC) plants.

Technical Goals

- Synthesize chemically and thermally stable dual-phase, ceramic-carbonate membranes with CO_2 permeance and CO_2 selectivity [with respect to hydrogen (H_2), carbon monoxide (CO), or water (H_2O)] larger than 5×10^{-7}mol/m^2•s•Pa and 500.
- Fabricate tubular dual-phase membranes and membrane reactor modules suitable for WGS membrane reactor applications.
- Identify experimental conditions for WGS in the dual-phase membrane reactor that will produce the hydrogen stream with at least 93% purity and CO_2 stream with at least 95% purity.

Technical Content

A membrane separation device consisting of a porous metal phase and a molten carbonate phase can conduct carbonate ion (CO_3^{2-}) at a high rate. The metal-carbonate membranes only conduct electrons, and oxygen (O_2) should be mixed with CO_2 in the feed in order to convert CO_2 to $CO_3^=$ ions. However, the presence of O_2 can also oxidize the metallic support and reduce its electronic conductivity, and thus CO_2 permeability. The problem can be solved by the proposed dual-phase, ceramic-carbonate membrane configuration consisting of a porous ionic conducting ceramic phase and a molten carbonate phase.

At the upstream surface, CO_2 reacts with oxygen ions supplied from the ceramic phase to form $CO_3^=$, which transports through the molten carbonate phase towards the downstream surface of the membrane. On the downstream surface, the reverse surface reaction takes place, converting $CO_3^=$ to CO_2, with $O^=$ released and transported back through the ceramic phase towards the upstream surface of the membrane. The net effect is permeation of neutral CO_2 through the membrane driven by the CO_2 pressure gradient. The dual-phase membrane will be made of continuous thin meso-porous oxygen ionic conducting ceramic layer filled with a molten carbonate, supported on porous stainless steel or other metal, with an intermediate layer of sub-micron, pore-sized oxygen ionic conducting material.

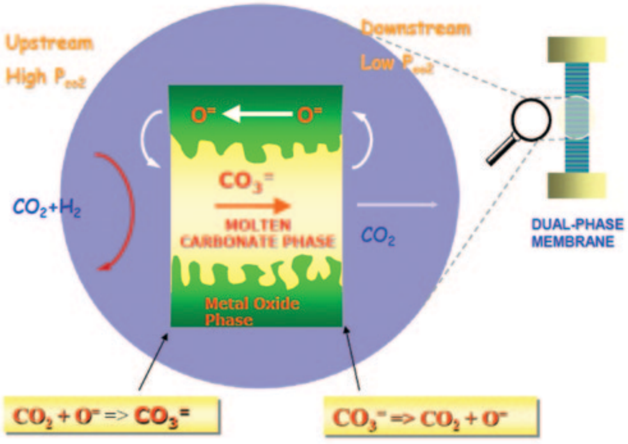


Figure 1: Concept of Dual-Phase Membrane

Technology Maturity:

Bench-scale using simulated syngas

Project Focus:

Dual-Phase Ceramic-Carbonate Membrane Reactor

Participant:

Arizona State University

Project Number:

FE0000470

NETL Project Manager:

Arun Bose
Arun.Bose@netl.doe.gov

Principal Investigator:

Jerry Y.S. Lin
Arizona State University
Jerry.Lin@asu.edu

Partners:

None

Performance Period:

10/1/09 – 9/30/13

Development of this dual-phase membrane will be divided in to two phases. Phase I work will include identifying optimum conditions for synthesis of adequate membrane supports and the dual-phase membranes in disk geometry and studying gas permeation properties of the membranes. The second part of the Phase I work will be focused on fabrication of the dual-phase membranes in tubular geometries and the study of permeation, chemical, and mechanical stability of the tubular membranes relevant to their uses in membrane reactors for WGS reaction.

Phase II work will be directed towards studying the dual-phase membrane reactor performance for WGS reaction for hydrogen production and CO_2 capture. The work includes synthesis and kinetic study of a high-temperature WGS catalyst and experimental and modeling study of WGS reaction on the dual-phase membrane reactors. The experimental data will be compared with modeling results to identify optimum operating conditions for WGS reaction. The project will perform an economic analysis using the dual-phase membrane as a WGS reactor for hydrogen production and CO_2 capture for an IGGC plant.

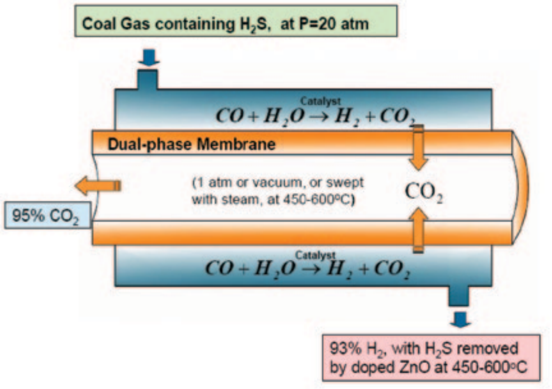


Figure 2: Proposed Membrane Reactor for WGS Reaction

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Li_2/K_2CO_3	Doped Li_2/K_2CO_3
	Materials of fabrication for support layer (if applicable)	Porous stainless steel	Fast-ionic conductors (doped ZrO_2)
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	20	>300
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	200 GPU	1,500 GPU
	Temperature, °C	800	500
	Bench-scale testing, hours without significant performance degradation	N/A	1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disk	Shell-and-tube
	Packing density, m^2/m^3	10	60
	Pressure drop, bar	0.2	10
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	N/A	$\$1,500–\$3,000/m^2$
Product Quality	CO_2 purity, %	N/A	95
	N_2 purity, %	N/A	N/A
	Other contaminants, %	N/A	N/A
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	N/A
	Heat requirement, kJ/kg CO_2	N/A	N/A
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	N/A

Other Membrane Parameters

Contaminant Resistance: The membrane to be stable in 0.1–1% atmosphere containing hydrogen sulfide (H_2S).

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: N/A.

Technology Advantages

- WGS reaction at one temperature (about 400 °C).
- Separation of CO_2 and H_2 mixture in one step.
- Production of high-pressure hydrogen stream.

R&D Challenges

- Failure to obtain sufficiently high CO_2 permeance due to a rate-limiting surface reaction.
- Undesired surface properties of ceramic supports resulting in instability of the carbonate in the support pores.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the September 2013 project completion date.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

DESIGNING AND VALIDATING TERNARY PD ALLOYS FOR OPTIMUM SULFUR/ CARBON RESISTANCE

Primary Project Goals

Pall Corporation is developing an economic, high temperature and pressure, hydrogen (H_2) separation membrane system for carbon dioxide (CO_2) capture, while resisting moderate levels of contaminants using a ternary palladium (Pd)-alloy. A membrane module prototype will be fabricated and will undergo long-term testing in actual coal gasification conditions. The final objective is a pilot-scale membrane system with a product plan for commercialization of the technology.

Technical Goals

- Create an advanced Pd-alloy for optimum H_2 separation performance using combinatorial material methods for high-throughput screening, testing, and characterization.
- Demonstrate durability under long-term testing of a pilot membrane module at a commercial coal gasification facility.
- Understand long-term effects of the coal gasifier environment on the metallurgy of the membrane components by comparing controlled diffusion studies with in-service membranes.

Technical Content

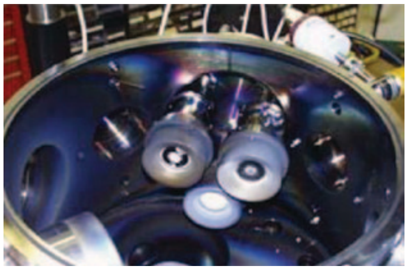


Figure 1: A Co-Sputtering Chambe

The project will develop an advanced Pd-alloy for optimum H_2 separation performance and to demonstrate long-term durability under coal synthesis gas (syngas) conditions. Ternary Pd-alloys with potential for favorable performance will be selected based on a literature search. This large set of ternary Pd-alloys will undergo combinatorial alloy spreads on thin film support disks. These disks will be tested in a syngas environment using in-situ Raman spectroscopy to measure H_2 separation factor and permeability, as well as characterize sulfur and carbon resistance of best candidate alloys. These alloys will be compared to baseline tests of traditional Pd-gold (Au) alloy membranes.

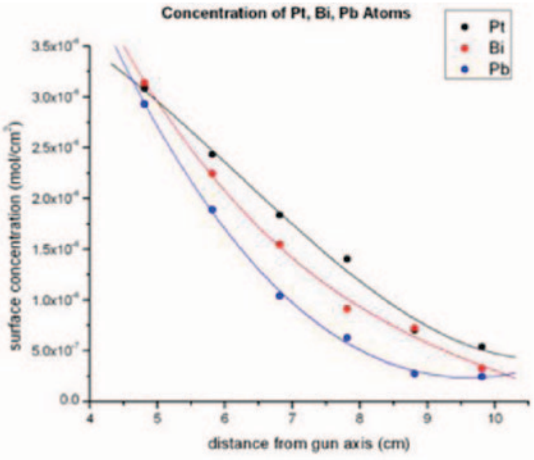


Figure 2: Graph of Atom Concentration as a Function of Distance from the Gun Axis for Pt, Bi, and Pb Targets

The best alloys will be fabricated into 15-cm^2 tubular membranes and tested. As with the combinatorial disks, the 15-cm^2 active area tubes will be exposed to conditions representative of a coal gasifier environment: high temperature and high pressure in the presence of contaminating species. Emphasis will be placed on identification and characterization of membrane defects, surface analysis of the regions affected by the contaminants, and assessment of the surface quality of the ceramic substrate.

Technology Maturity:

Pilot-scale using actual syngas

Project Focus:

Ternary Palladium-Alloy
Hydrogen Separation
Membranes

Participant:

Pall Corporation

Project Number:

FE0001181

NETL Project Manager:

Patricia Rawls
Patricia.Rawls@netl.doe.gov

Principal Investigator:

Daniel Henkel
Pall Corporation
Daniel_Henkel@pall.com

Partners:

Cornell University
Georgia Institute of Technology
Oak Ridge National Laboratory
Southern Company

Performance Period:

10/1/09 – 9/30/12

Using the best candidate alloys, the 15-cm^2 membranes will be scaled up by a factor of 5–75 cm^2. After a series of performance tests and membrane characterization, a module of 75-cm^2 tubes, made with the best performing alloy, will be assembled. The module will be subjected to 500-hour service tests at a commercial coal gasification facility.

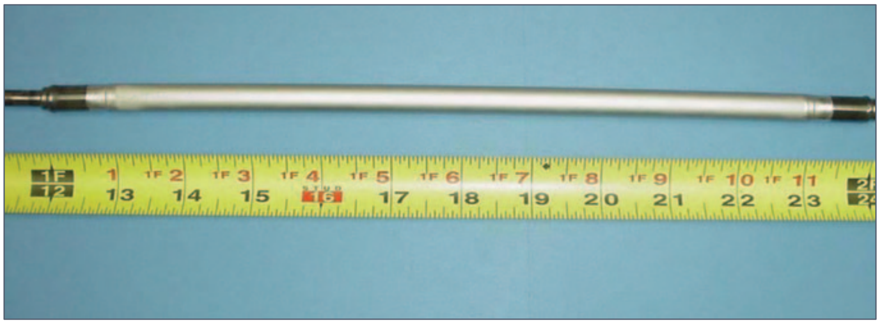


Figure 3: A 75-cm^2 Membrane

Technical Targets:

- Membrane would be tolerant of up to 20 parts per million (ppm) hydrogen sulfide (H_2S).
- Hydrogen flux of 200 ft^3/hr/ft^2 at 400 °C and 20 pounds per square inch (psi) H_2 partial pressure differential.
- Total pressure differential operating capability 400 psi.
- The membrane cost must be in the range of \$500/ft^2.
- Permeate H_2 purity should be at a level of 99.5%.
- The membrane must be resistant to coking with relatively low steam-to-carbon ratio.
- The system should be stable for a minimum of three years in service.

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Palladium-gold alloys	N/A
	Materials of fabrication for support layer (if applicable)	Zirconia coated porous stainless steel tubes	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	>5,000 of H_2/CO_2	>10,000
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Ideal
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	72 scfh/ft^2 psi$^{0.5}$	N/A
	Temperature, °C	400	N/A
	Bench-scale testing, hours without significant performance degradation	500 hours with syngas	5,000 hours with syngas
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	300 psi
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %	N/A	N/A
	H_2 purity, %	N/A	N/A

Other Membrane Parameters

Contaminant Resistance: Pd-based alloy membranes should tolerate moderate levels of coal gas contaminants after advanced hot syngas cleanup. Primary contaminants include H_2S and carbon monoxide (CO). A typical hot gas cleanup process can bring residual level of sulfur into the range of 0.5–20 parts per million volume (ppmv). After a single-stage water gas shift (WGS) reactor, CO can be as low as a few percent.

Flue Gas Pretreatment Requirements: No flue gas pretreatment is required since it is pre-combustion CO_2 capture technology (i.e., coal is converted to syngas by partial combustion/gasification process).

Waste Streams Generated: No waste streams are generated since H_2 is extracted by a Pd-alloy membrane system with primarily CO_2 and water (H_2O) left at high pressure. After steam is condensed, CO_2 is sent for sequestration.

Technology Advantages

- Researchers will use a proprietary process to create ultrathin, economical, Pd-alloy membranes in virtually any alloy system.
- The project will apply combinatorial methods to continuous ternary alloy spreads and use a novel characterization method to rapidly scan the alloys after syngas exposure to identify the most resistant compositions.
- A customized composite substrate from Pall will be used to deposit ultrathin Pd-alloy membranes. The substrate is porous stainless steel tubes with ceramic coating on the outside surface as a diffusion barrier. Thus membrane elements can be assembled into the module by a conventional welding technique.

R&D Challenges

- Hydrogen separation performance may not achieve target performance by membrane design alone. Supplements such as additional gas reforming capabilities may be required either upstream or downstream of the membrane module.
- Scaleup of the Pd-alloy surface area from 15 to 75 cm^2; although the membrane fabrication process has been designed for 75 cm^2 on tubular substrates, the actual scaleup has not been attempted.
- Membrane durability during thermal cycling and its effect on stability; the stability of the ceramic coated support has been demonstrated but not the long-term stability with a Pd-alloy membrane in place.

Results To Date/Accomplishments

A dozen binary and ternary alloy spreads were fabricated. Six have been exposed to high-temperature syngas, representative of actual coal gas conditions. Four of the ternary spreads had shiny areas after exposure that indicate exceptional carbon and sulfur tolerance (170 ppm H_2S). Raman spectroscopy of shiny areas show little or no sulfides or carbon compounds present on Pd-alloy surface. DFT modeling of binding energies of sulfur/carbon compounds are in agreement with observations. Hydrogen permeance through high-potential alloys has not yet been quantified.

Next Steps

Final test results will not be available until the September 2012 project completion date.

Available Reports/Technical Papers/Presentations

Five quarterly reports and two milestone reports have been submitted to NETL. A presentation was made at the NETL Technology Conference in Pittsburgh on September 16, 2010.

PRESSURE SWING ABSORPTION DEVICE AND PROCESS FOR SEPARATING CO_2 FROM SHIFTED SYNGAS AND ITS CAPTURE FOR SUBSEQUENT STORAGE

Primary Project Goals

The New Jersey Institute of Technology (NJIT) is developing, via laboratory-scale experiments, a pressure swing absorption-based (PSAB) device using a non-dispersive membrane-based gas-liquid contactor which produces hydrogen at high pressure for integrated gasification combined cycle (IGCC) and a carbon dioxide (CO_2) stream between 1 and 5 atm containing at least 90% of the CO_2 from a feed gas at ~200 °C and 300 pounds per square inch gauge (psig).

Technical Goals

- Develop, via laboratory experiments, an advanced PSAB device and a cyclic process to produce helium (He) (a surrogate for hydrogen) at high pressure from low-temperature post-shift reactor synthesis gas (syngas) and a CO_2 stream containing at least 90% of the CO_2 and suitable for sequestration.
- Provide data and analysis of the cyclic process and device to facilitate subsequent scale up.
- Develop a detailed analysis for the process and device to allow economic evaluation for potential larger-scale use.

Technical Content

In the first phase of research, an experimental set up will be developed for studying the PSAB process. NJIT will work with Media and Process Technology, Inc. and Applied Membrane Technologies (AMT), Inc. to develop ceramic tubule-based and Polytetrafluoroethylene (PTFE) hollow fiber-based absorption devices. The absorption device will be explored on a preliminary basis for performance of PSAB separation of a moist CO_2-He gas mixture at 150–200 °C and 200–300 psig, simulating a low-temperature post-shift reactor syngas stream.

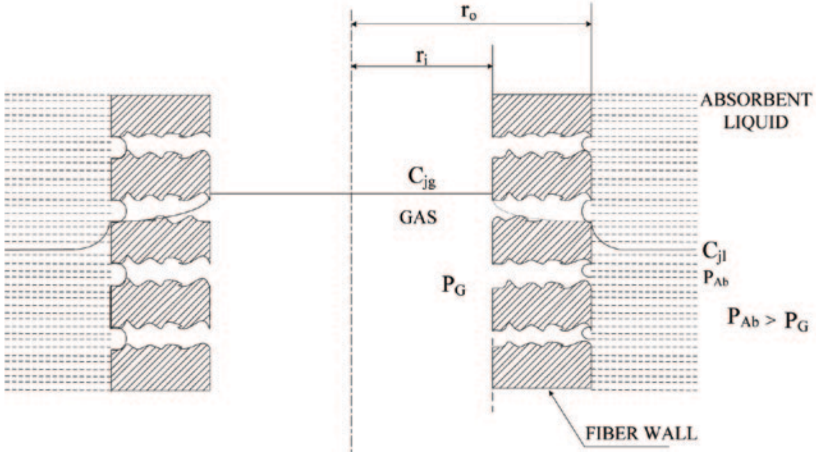


Figure 1: Concentration Profile of Absorbed Species in Gas and Liquid Phases

Technology Maturity:

Laboratory-scale using simulated syngas

Project Focus:

Pressure Swing Absorption with Membrane Contactor

Participant:

New Jersey Institute of Technology

Project Number:

FE0001323

NETL Project Manager:

Norman Popkie
Norman.Popkie@netl.doe.gov

Principal Investigator:

Dr. Kamalesh Sirkar
New Jersey Institute of Technology
sirkar@njit.edu

Partners:

Applied Membrane Technologies
Media and Process Technology, Inc.
Techverse

Performance Period:

10/1/09 – 9/30/12

In phase two, NJIT will explore in detail the purification and separation performance of the PSAB process for selected absorbents vis-à-vis purification of the feed gas stream to obtain a high-pressure purified He stream and a low-pressure purified CO_2 stream. Experimental setups will be developed to measure the solubility and diffusion coefficients of CO_2 and He at the appropriate ranges of temperature and pressure for selected absorbents. Researchers will develop a mathematical model of the PSAB device and process.

In phase three, NJIT will generate experimental data on the solubility and diffusion coefficient for CO_2 and He for the selected absorbents. This will allow comparison of the results of simulation of the mathematical model with the observed purification and separation in the PSAB process and device for selected absorbents. Simulations of the model will be performed to explore scale up of the process and facilitate process evaluation. The extent of loss/deterioration of the absorbents over extended periods of operation will be determined.

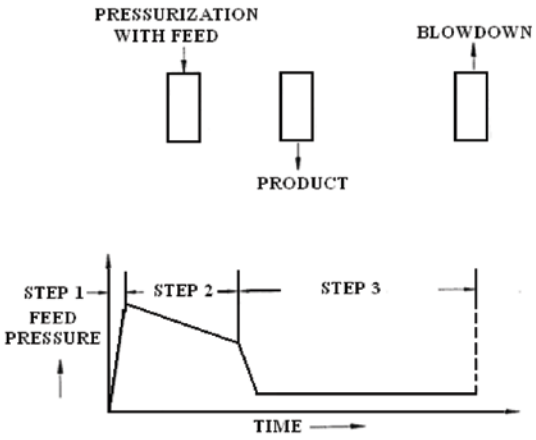


Figure 2: Pressure vs. Time Profile in Bore of Tubule or Hollow Fiber

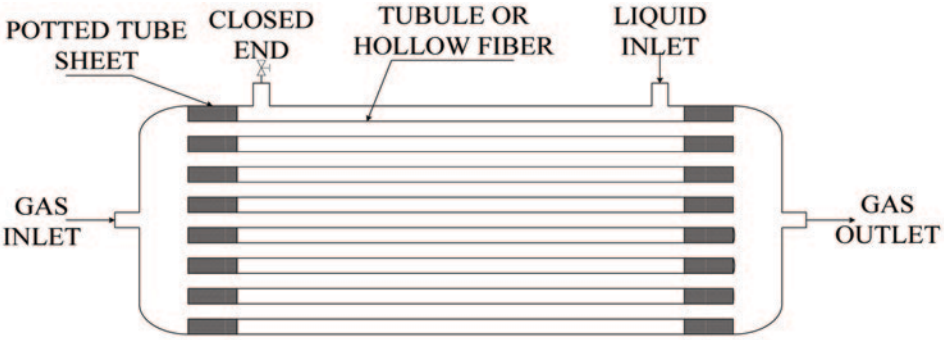


Figure 3: Schematic of Absorber Containing Ceramic Tubules or Hollow Fibers

Table 1: Liquid-Sorbent Bed Parameters

	Parameter	Current R&D Value	Target R&D Value
Liquid Sorbent Properties	Type of sorbent	Ionic liquid	
	Molecular weight	200–300	
	Boiling point (°C)	>500	
	Viscosity, cP	~33	
	Heat of absorption (kJ/mole CO_2)	N/A	
	CO_2 loading/working capacity, wt%	—	N/A
	Cycle time (fixed bed), minutes	—	0.4–2 min
	Pressure drop (fixed bed), psia	—	1–2
Operating Conditions	Absorption temperature, °C	—	150–200
	Absorption pressure, atm	—	13–20
	CO_2 capture efficiency, %	—	>90
	H_2 recovery, %	—	N/A
	Regeneration method	—	Pressure swing
	Regeneration temperature, °C	—	150–200
	Regeneration pressure, atm	—	1–5

Table 1: Liquid-Sorbent Bed Parameters

	Parameter	Current R&D Value	Target R&D Value
Miscellaneous	Sorbent replacement rate, kg/kg CO_2	—	N/A
Product Quality	CO_2 purity, %	—	>90
	H_2 purity, %	—	N/A
Process Performance	Electricity requirement, kJ/kg CO_2	—	N/A
	Heat requirement, kJ/kg CO_2	—	N/A
	Total energy (electricity equivalent), kJ/kg CO_2	—	N/A

Table 2: Membrane-Contactor Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	—	Fluoropolymer
	Materials of fabrication for support layer (if applicable)	—	Ceramic, teflon, PEEK
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	—	30–100+
	Type of selectivity measurement (ideal or mixed gas)	—	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	—	N/A
	Bench-scale testing, hours without significant performance degradation	—	100–200
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	—	13–20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	—	Hollow-fiber Shell-and-tube
	Packing density, m^2/m^3	—	Ceramic: 900 Teflon: 2,000 PEEK: 5,000
	Pressure drop, bar	—	N/A
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	—	100–500 $\$/m^2$

Other Membrane Parameters

Contaminant Resistance: Hydrogen Sulfide (H_2S) will not affect the ceramic substrate; it will not affect the fluoropolymer coating on ceramic and PEEK materials; the Teflon hollow fibers will remain unaffected also. PEEK material is also unlikely to be affected.

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: Degraded absorption solvent.

Technology Advantages

- High solubility selectivity of novel selected liquid absorbents, high purification ability of the PSA process, and high gas-liquid contacting surface area per unit device volume.
- Compact, membrane-like device.
- Will deliver highly purified hydrogen (H_2) at nearly its partial pressure and temperature in the post-shifted reactor syngas feed.
- Purified CO_2 stream (>90% CO_2) will be available at 1–5 atm.

R&D Challenges

- Leakage of absorbent through microporous PTFE hollow fibers having a plasma polymerized microporous fluorosilicone coating.
- Capability of the hydrophobic coatings on ceramic tubules to hydrophobize them sufficiently (avoid defects) to eliminate leakage of absorbent into the tube side.
- Effect of module diameter and length on He purification ability.
- Achieve a steady state in the cyclic process by preventing a drift in the composition and amount of two purified product streams obtained.

Results To Date/Accomplishments

Results from the project are not yet available

Next Steps

Final test results will not be available until the September 2012 project completion date.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

HIGH TEMPERATURE POLYMER-BASED MEMBRANE SYSTEMS FOR PRE-COMBUSTION CARBON DIOXIDE CAPTURE

Primary Project Goals

Los Alamos National Laboratory is developing and demonstrating polymer-based membrane structures, deployment platforms, and sealing technologies that achieve the critical combination of high selectivity, high permeability, chemical stability, and mechanical stability all at elevated temperatures (>150 °C) and packaged in a scalable, economically viable, high area density system amenable to incorporation into an integrated gasification combined cycle (IGCC) plant for pre-combustion carbon dioxide (CO_2) capture. The project is focused on the optimization of a technology that could be positioned upstream or downstream of one or more of the water gas shift reactors (WGSRs), or integrated with a WGSR.

Technical Goals

- Development and demonstration of high temperature m-polybenzimidazole (PBI)-based membrane chemistries and morphologies for carbon capture and hydrogen purification from a coal-derived shifted synthesis gas (syngas) IGCC process stream.
  - Operation at/near water gas shift (WGS) conditions.
  - Stability in the presence of anticipated concentrations of primary coal-derived syngas components and impurities.
- Development of the capability to deposit/fabricate in situ thin membrane selective layers on microporous substrates with the goal of hollow fiber membrane fabrication where the membrane selective layer is comprised of the PBI-based polymers of interest.
- Development of the materials and techniques required to successfully mount (pot) the produced fibers into a cartridge/module. A barrier/potting material, along with a sealing technique that is compatible with the target process' thermal, chemical, and mechanical environments, must be developed or the fibers produced will not be useful.
- All of the aforementioned developments must be utilized together to ultimately achieve a module package that can be tested for permselectivity character in simulated and ultimately real process environments.

Technical Content

Los Alamos National Laboratory (LANL) work to-date has demonstrated that PBI and other benzimidazole-based materials show promise as membranes for pre-combustion-based capture of CO_2. The ultimate achievement in the area of CO_2 capture is the production of a CO_2-rich stream at pressure using methods compatible with the overall DOE NETL Carbon Sequestration Program goals of 90% CO_2 capture at less than 10% increase in the cost of energy services. The work that this project team is pursuing is aligned directly with these capture goals and utilizes a pre-combustion capture approach focused on the continued development of high-temperature polymer-based membranes that will ultimately be integrated into an advanced IGCC process.

Technology Maturity:

Pre-pilot testing, prototype development, manufacturing methodology development/optimization

Project Focus:

High-Temperature Polymer-Based Membrane

Participant:

Los Alamos National Laboratory

Project Number:

FE13-AC24

NETL Project Manager:

Robie Lewis
Robie.Lewis@netl.doe.gov

Principal Investigator:

Kathryn A. Berchtold
Los Alamos National Laboratory
berchtold@lanl.gov

Partners:

None

Performance Period:

10/1/09 – 9/30/12

PBI, the membrane selective layer, is a high-temperature polymer that is stable to temperatures approaching 500 °C. PBI possesses excellent chemical resistance, a very high glass transition temperature (~460–500 °C), good mechanical properties, and an appropriate level of processability. The PBI-based membranes developed by this project team have demonstrated operating temperatures significantly higher than 150 °C (up to 400–450 °C) with excellent chemical, mechanical, and hydrothermal stability.

The commercial viability of a membrane separation process is ultimately driven by selectivity, permeability (throughput), and stability in the process environments of interest (Figure 1). The goal is to utilize materials that exhibit the important and often elusive combination of high selectivity, high permeability, and chemical and mechanical stability all at temperatures significantly above 25 °C. Stability goals are focused on tolerance to the primary syngas components and impurities at various locations in the process. As process stream compositions and conditions (temperature and pressure) vary throughout the IGCC process, it is essential to incorporate all aspects of system integration into any plan. To that end, the work is aimed at evaluation of the PBI-based membrane over a broad temperature range (ambient: 400 °C), trans-membrane pressure range (10–450 psid), and in the presence of the primary syngas components [hydrogen (H_2), CO_2, nitrogen (N_2), methane (CH_4), carbon monoxide (CO), hydrogen sulfide (H_2S), and water (H_2O)].

A previous programmatic effort was focused on the utilization of the PBI formulations as a selective layer deposited on and supported by a unique porous metal substrate (fabricated by Pall Corporation). Systems, economic, and commercialization analyses conducted by NETL, LANL, and others, combined with in- and out-of-laboratory testing, established the technical viability of the technology and indicated the strong potential for the membrane-based capture technology to meet and exceed the DOE Sequestration Program goals. However, these analyses also made clear the need to cut the costs of the support material and increase the area density realized by the ultimate module design in order to realize the desired step-change in both performance and cost of CO_2 capture associated with the use of this membrane-based capture technology. One promising option for achieving a substantial increase in active membrane area density and mitigating the cost of a metal or inorganic material-based support is the use of a hollow fiber membrane platform. A hollow fiber module is the membrane configuration with the highest achievable packing density (i.e., the highest membrane selective area density). Hollow fiber modules have been fabricated to obtain a density as high as 30,000 m^2/m^3. This affords the opportunity to achieve several orders of magnitude improvement over the density achievable with the previous polymeric-metallic membrane platform (ca. 250 m^2/m^3). Realization of such a step change in area density with the materials previously developed by this team would lead to substantial economic and technical benefits.

Current and future work is aimed at continued development and demonstration of the membrane based pre-combustion hydrogen purification/carbon capture technology developed by LANL. A major aspect of that work involves developing the capability, materials, and methods to realize a high area density membrane platform with a selective layer comprised of the PBI-based polymers of interest. Furthermore, development of the materials and techniques required to successfully mount (pot) the produced fibers into a cartridge/module is essential. Finally, all of the aforementioned developments must be utilized together to ultimately achieve a module package that can be tested for permselectivity character in simulated and ultimately real process environments.

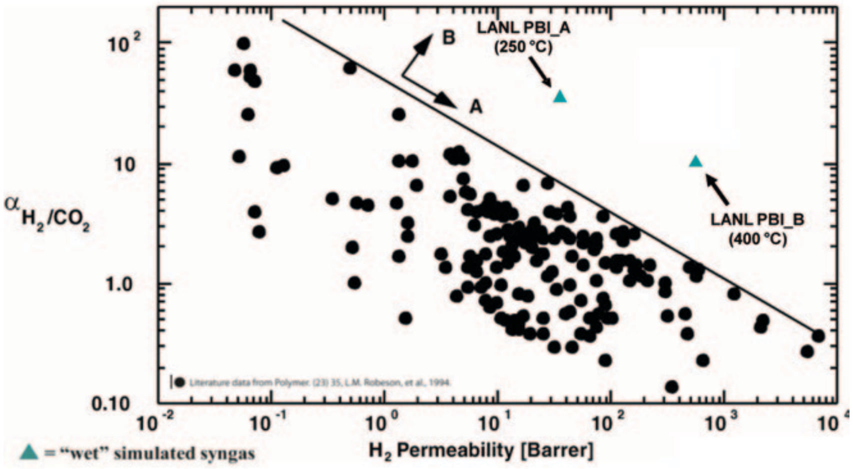


Figure 1: Trade-Off Plot Between H_2 Permeability and H_2/CO_2 Selectivity

Literature data are for polymeric membranes at ambient temperature and are represented by the filled circles below the upper bound. The data points for PBI reflect measurements made at elevated temperature in a "wet" simulated syngas environment. Most of the literature materials would be degraded by the process relevant test temperatures presented for PBI.

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	High T_g polymer	High T_g polymer
	Materials of fabrication for support layer (if applicable)	Metallic composite	High T_g polymer
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	43	≥25
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	150	>100
	Temperature, °C	100–400[1]	250
	Bench-scale testing, hours without significant performance degradation	8,400 (at 250 °C)	—
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	31	>20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Hollow-fiber
	Packing density, m^2/m^3	250	2,000–30,000
	Pressure drop, bar	2.3	—[2]
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	—	<$\$200/m^2$
Product Quality	CO_2 purity, %	90% capture[3]	90% capture[3]
	H_2 purity, %	—[2]	—[2]

Notes:

1. Presented data at 250 °C.
2. Highly dependent on system configuration, including: utilized sweep gas flows, staging, and turbine inlet specs.
3. Highly dependent requirements including: syngas composition treated, pipeline/transportation specs, system configuration.

Technology Advantages

- Broad accessible membrane operating temperature range (150–300 °C) facilitating increased opportunity for process integration/optimization.
- Demonstrated long-term hydrothermal stability, sulfur tolerance, and overall durability of selective layer materials.
- Membrane-based technology competitive advantages: modularity, low-maintenance operations, small footprint, low/no waste process, and flexible design opportunities.

R&D Challenges

- Design, control, prediction, and synthesis of tailored material morphologies.
- Realizing defect-free gas separation viable hollow fibers of optimized material chemistries and morphologies.
- Realizing barrier/potting materials and processes and defect sealing methods compatible with the target materials' and process' thermal, chemical, and mechanical characteristics/environments.

Results To Date/Accomplishments

- Successful demonstration of hollow fiber potting materials and methods that allow for testing of hollow fibers up to 250 °C at laboratory scale in simulated syngas environments.
- Successful demonstration of a hollow fiber membrane with permselectivity characteristics matching that of the shell and tube composite membranes.
- Successful testing of the high T_g polymer-based membrane in simulated syngas environments containing H_2, CO_2, CH_4, N_2, CO, H_2O, and H_2S from 25 to 400 °C. Demonstration of the membrane's thermal stability via 300+ days in operation at 250 °C.

Next Steps

Continued Materials, Methods, and Process Development.

Available Reports/Technical Papers/Presentations

K.A. Berchtold, et al., "High Temperature Polymer-Based Membranes for Hydrogen Purification and Carbon Capture," North American Membrane Society Annual Meeting, Charleston, SC (2009).

HIGH-TEMPERATURE, HIGH-PRESSURE MEMBRANES FOR HYDROGEN SEPARATION

Primary Project Goals

Ceramatec is producing a prototype membrane that will separate hydrogen from coal-derived synthesis gas (syngas) at operating conditions found at a typical coal gas facility without the use of precious metals. This research will enhance performance and efficiency as well as reduce the cost of hydrogen separation membrane technology.

Technical Goals

- Hydrogen flux of greater than 200 standard cubic feet per hour per square foot (scfh/ft^2).
- Hydrogen purity >99.5%.
- Manufacturing cost of less than \$100/ft^2.
- Efficient operation at relevant conditions.

Technical Content

Modern gasifier and water gas shift (WGS) reactor technology produce syngas, a mixture primarily of hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). By using a pressure-driven hydrogen separation membrane, the high-pressure CO_2 is retained and thus amenable for capture and sequestration. Ceramic perovskite membranes show very high hydrogen separation efficiency. Because of their low electronic conductivity, ceramic-metal composites have been investigated as a potential pressure-driven membrane. Thermochemical instability of the perovskite in syngas and processing incompatibilities between ceramic and metal components has hampered effective use of ceramic-metal composites. Ceramatec has demonstrated a ceramic-ceramic composite material that shows excellent stability in syngas at the desired membrane operating temperature range. The use of an all ceramic membrane allows employing conventional ceramic processing for the manufacture of low-cost membrane devices.

The membrane consists of barium cerate as the proton conducting composition with ceria as the electron conducting composition. The technical bench mark criteria that are set for Year 1 of the project are:

1. Demonstration of effective membrane proton conductivity of 0.02 S/cm, corresponding to >150 scfh/ft^2 wafer hydrogen separation.
2. Preliminary membrane design (layer thickness, channel dimensions) showing <\$200/ft^2 fabrication feasibility.

Technology Maturity:

Bench-scale, hydrogen separation

Project Focus:

Ceramic Membrane for H_2 Separation

Participant:

Ceramatec

Project Number:

FE0001045

NETL Project Manager:

Arthur Baldwin
Arthur.Baldwin@netl.doe.gov

Principal Investigator:

S. Elangovan
Ceramatec
elango@ceramatec.com

Partners:

CoorsTek
Sandia National Laboratories

Performance Period:

10/1/09 – 9/30/12

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Barium cerate + ceria	Barium cerate + ceria
	Materials of fabrication for support layer (if applicable)	Barium cerate + ceria	Barium cerate + ceria
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	100% for H_2	100% for H_2
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	N/A	—
	Temperature, °C	800 °C	600–700 °C
	Bench-scale testing, hours without significant performance degradation	N/A	—
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	N/A	—
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Flat plate stack	Flat plate stack
	Packing density, m^2/m^3	N/A	—
	Pressure drop, bar	N/A	—
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	~$\$150/ft^2$	$\$100/ft^2$
Product Quality	CO_2 purity, %	—	—
	H_2 purity, %	N/A	>99.5

Technology Advantages

- All ceramic composite is amenable to low-cost ceramic fabrication technology.
- Membrane has 100% selectivity to hydrogen.

R&D Challenges

- Fabrication technology development for thin supported membrane.
- Optimizing membrane composition for high hydrogen conductivity.
- Stability of contaminants, especially sulfur.

Results To Date/Accomplishments

- Composition showing proton conductivity of 0.02 S/cm at ~600 °C demonstrated.
- Cost model shows a pathway for achieving target cost.

Next Steps

- Demonstration of hydrogen flux corresponding to measure proton conductivity.
- Fabrication development for thin membrane.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

PRE-COMBUSTION CARBON CAPTURE BY A NANOPOROUS, SUPERHYDROPHOBIC MEMBRANE CONTACTOR PROCESS

Primary Project Goals

The Gas Technology Institute (GTI) is developing cost-effective separation technology for carbon dioxide (CO_2) capture from synthesis gas (syngas) based on a hollow-fiber membrane contactor.

Technical Goals

- Design an energy-efficient CO_2 recovery process which minimizes hydrogen loss.
- Tailor highly chemical inert and temperature stable, superhydrophobic, hollow-fiber poly (ether ether ketone) (PEEK) membrane for pre-combustion CO_2 capture.
- Manufacture a low-cost integrated membrane module.

Technical Content

The membrane contactor is a novel gas separation technology based on a gas/liquid membrane concept. The membrane contactor is an advanced mass transfer device that operates with a liquid on one side of the membrane and gas on the other. Unlike gas separation membranes where a differential pressure across the membrane provides the driving force for separation, the membrane contactor can operate with pressures that are almost the same on both sides of the membrane. The driving force is the chemical potential of CO_2 absorption into the liquid. This process is thus easily tailored to suit the needs for pre-combustion CO_2 capture.

The hollow fiber membrane is manufactured from an engineered material called PEEK by PoroGen Corporation using a patented process. Some key characteristics which make PEEK attractive for this process are: high heat resistance, high rigidity, high dimensional stability, good strength, excellent chemical resistance, excellent hydrolytic stability, an average pore size of 1–50 nm, an average porosity of 40–70%, and an 800 pound per square inch (psi) water breakthrough pressure.

The PEEK hollow-fiber membrane is nanoporous and can be surface modified to achieve super-hydrophobicity, fiber OD can range from 200 µm to 1 mm, and fibers can be made with very thin wall (<25 µ) due to the strength of PEEK. The PEEK membrane pore size can be controlled from 1 to 50 nm, and asymmetric membrane structures can be utilized for high performance. The hollow fiber has a high burst pressure of greater than 500 pounds per square inch gauge (psig), and a high collapse pressure of greater than 1,000 psig.

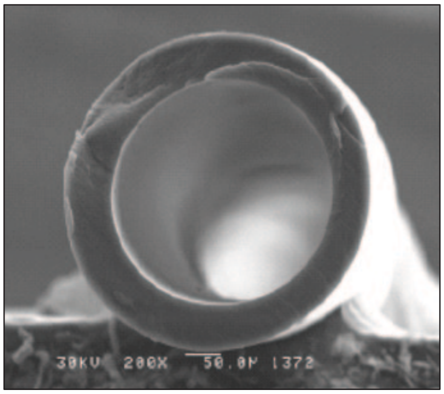


Figure 1: PEEK Hollow Fiber

The advanced hollow-fiber module is constructed by computer-controlled helical winding. The modules exhibit favorable flow dynamics with minimal pressure drop, high uniform packing density, and thermodynamically efficient counter-current flow configuration.

Technology Maturity:
Bench-scale using simulated syngas

Project Focus:
Nanoporous, Superhydrophobic Membranes

Participant:
Gas Technology Institute

Project Number:
FE0000646

NETL Project Manager:
Arun Bose
Arun.Bose@netl.doe.gov

Principal Investigator:
Howard Meyer
Gas Technology Institute
Howard.Meyer@gastechnology.org

Partners:
PoroGen Corporation

Performance Period:
10/1/09 – 9/30/11

The project is divided into two phases. The activities of the first phase will be the development of hollow-fiber membranes suitable for the membrane contactor application with improved mass transfer, establishing feasibility of the proposed technology for syngas CO_2 separation, and performing initial process design and economic analysis based on test data.

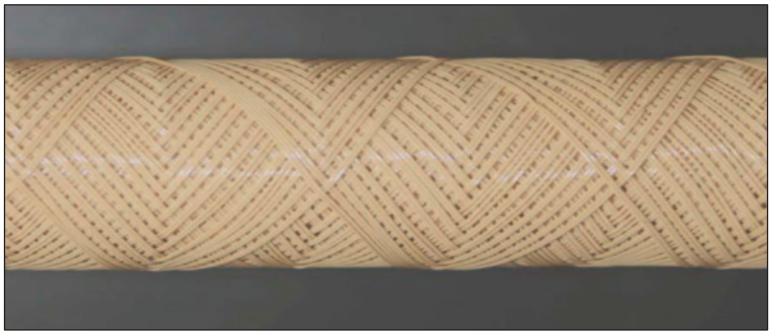


Figure 2: Advanced Hollow-Fiber Module Design

The focus of the phase two activity is to scale up the process from lab to bench scale. This includes scale up of the membrane module fabrication process so that membrane modules of the size suitable for large-scale application can be manufactured; bench-scale testing of the membrane contactor process stability and sensitivity to process variations; and refinement of the process economics based on bench-test data.

Table 1: GTI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Perfluoro-oligomer	Perfluoro-oligomer/polymer
	Materials of fabrication for support layer (if applicable)	PEEK	PEEK
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	Solvent dependent	Solvent dependent
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	300	700
	Temperature, °C	50	Maximize
	Bench-scale testing, hours without significant performance degradation	TBD	TBD
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	3.4	Maximize
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow-fiber	Hollow-fiber
	Packing density, m^2/m^3	500–1,000	500–1,000
	Pressure drop, bar	0.4	Minimize
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	$100	$40
Product Quality	CO_2 purity, %	—	—
	H_2 purity, %	—	—

Other Membrane Parameters

Contaminant Resistance: Membrane is resistant to all contaminants. Absorbents will be affected by contaminants to a lesser extent than a conventional packed or tray column.

Flue Gas Pretreatment Requirements: N/A.

Waste Streams Generated: None.

Technology Advantages

- Counter-current flow allows for the most efficient mass transfer, thermodynamically.
- Computer-controlled winding provides structured packing to enable enhanced turbulence flow at fiber surface.
- High temperature stability for the desorption step.
- High liquid breakthrough pressure (no liquid wet out), high membrane integrity.
- High membrane productivity.

R&D Challenges

- Membrane hydrophobic properties change with solvent contact causing leakage.
- Mass transfer coefficient not sufficiently high for gas absorption in the membrane contactor.

Results To Date/Accomplishments

Results from the project are not yet available.

Next Steps

Final test results will not be available until the September 2011 project completion date.

Available Reports/Technical Papers/Presentations

S. James Zhou, Howard Meyer, Ben Bikson and Yong Ding, “Hybrid Membrane Absorption Process for Post Combustion CO_2 Capture.” AIChE Spring Meeting, San Antonio, TX, March 21–25, 2010.

INTEGRATED WATER GAS SHIFT MEMBRANE REACTORS UTILIZING NOVEL, NON-PRECIOUS METAL MIXED-MATRIX MEMBRANES

Primary Project Goals

The University of Texas at Dallas (UTD) is preparing novel, non-precious metal mixed-matrix membranes (MMMs) in flat, tubular, and hollow fiber geometries based on polymer composites with nanoparticles of zeolitic imidazolate frameworks (ZIFs). Membrane performance to separate hydrogen from synthesis gas (syngas) [e.g., hydrogen (H_2), carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O)] generated during coal gasification will be evaluated in an integrated water gas shift (WGS) membrane reactor. The goal is to exploit the high surface areas, adsorption capacities, and sieving capabilities of the nanoporous ZIF additives to achieve unprecedented, selective transport of hydrogen.

Technical Goals

- To prepare novel, non-precious metal MMMs in flat, tubular, and hollow fiber geometries based on polymer composites with nanoparticles of ZIFs in an integrated WGS membrane reactor.
- To prepare a high-performance membrane to separate hydrogen from syngas (e.g., H_2, CO, CO_2, H_2O) generated during coal gasification that will be evaluated in an integrated WGS membrane reactor using NETL test protocols.

Technical Content

The utilization of coal as a clean source of energy relies on the successful development and implementation of carbon capture and sequestration (CCS) technologies with a minimal impact on energy generation costs. The efficient conversion of coal into H_2 and CO_2 requires membranes that are stable at high temperatures and pressures (300–500 °C, 15–30 bar, Table 1) with an H_2/CO_2 separation selectivity that provides H_2 with >99% purity. A minimum temperature of 250–300 °C is required to maintain catalyst activity for the efficient conversion of syngas (>95% with commercial low temperature $CuO\text{-}ZnO\text{-}Al_2O_3$ catalyst), while a high H_2 flux across the membrane ($>300\ ft^3_{stp}/ft^2\bullet h$) drives the reaction.

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H = -41\ kJ/mol$$

MMMs combine the polymers' processability with the ZIFs' superior permselective properties for H_2/CO_2 separations. Selected polymer membranes (Figure 1) displayed increased H_2 and CO_2 permeabilities (up to a 45-fold increase) at 300 °C and up to 30 bar (Figure 2). Hydrogen sorption isotherms of selected ZIFs showed H_2 adsorption up to 350 °C and 100 bar, while the integrity of the framework was maintained.

The UTD Membranes Team has fabricated robust, defect-free MMMs with good metal organic framework (MOF)/polymer interfaces with MOF loadings up to 80% (w/w). Hydrogen-selective ZIFs (an MOF subfamily) and thermally stable polymers, such as polyimides (synthesized 6FDA-based polymers and commercial VTEC PI-1388), polybenzimidazole (PBI), and Polymers

Technology Maturity:

Bench- to pilot-scale, non-precious metal membranes for hydrogen separation

Project Focus:

Integrated WGS Non-Precious Membrane

Participant:

University of Texas at Dallas

Project Number:

FE0001293

NETL Project Manager:

Jason Hissam
Jason.Hissam@netl.doe.gov

Principal Investigator:

John P. Ferraris
University of Texas at Dallas
Ferraris@utdallas.edu

Partners:

Santa Fe Science & Technology, Inc.

Performance Period:

9/30/09 – 9/29/12

of Intrinsic Microporosity-1 (PIM-1) were fabricated into MMMs. These MMMs demonstrated increased H_2 permeability, and crosslinking polyimides further increased the H_2/CO_2 selectivity (Figure 3). These membranes will be tested under WGS reaction conditions (300 °C, 15–30 bar) in a membrane reactor.

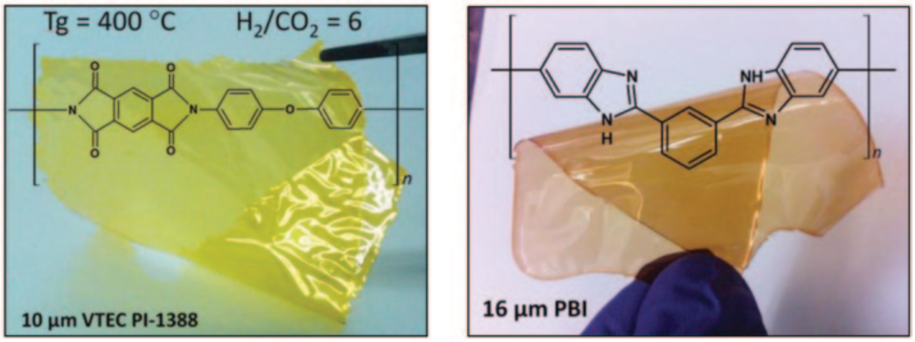


Figure 1: Polymer Membranes Annealed at 250 °C (Left: VTEC PI-1388; Right: Polybenzimidazole, PBI)

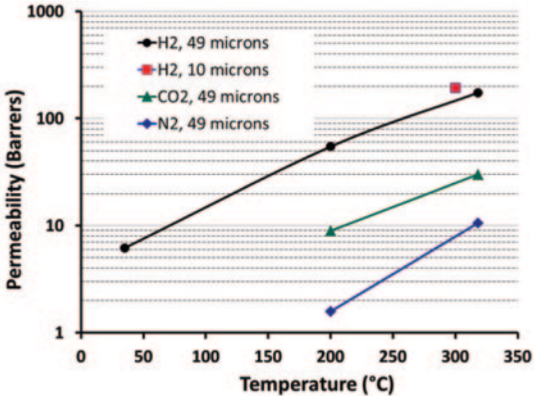


Figure 2: VTEC Polymer Gas Permeability at High Temperatures and up to 30 atm

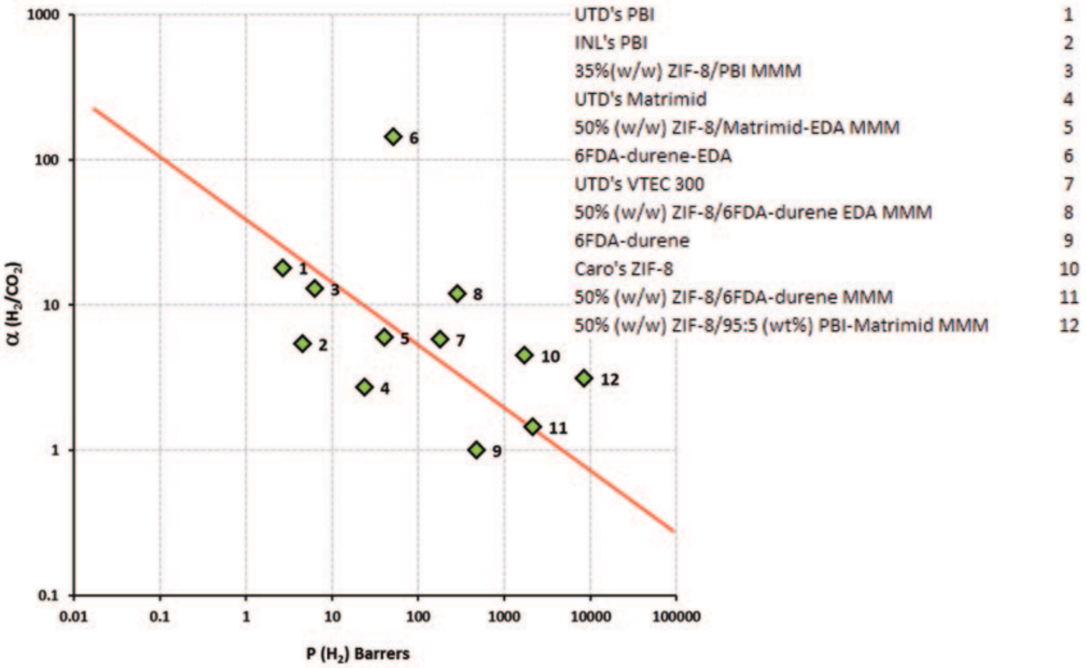


Figure 3: Robeson Upper Bound for H_2/CO_2 Separations

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	ZIF/polymer	ZIF/polymer
	Materials of fabrication for support layer (if applicable)	Polymer, ZIF/polymer	Polymer, alumina
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	6–102	99
	Type of selectivity measurement (ideal or mixed gas)	Ideal selectivity	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	20 GPU	120 GPU
	Temperature, °C	300	300
	Bench-scale testing, hours without significant performance degradation	>120	120
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	>15	15
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	N/A	—
	Packing density, m^2/m^3	N/A	—
	Pressure drop, bar	N/A	—
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	N/A	—
Product Quality	CO_2 purity, %	N/A	—
	H_2 purity, %	85%	99.5%

Other Membrane Parameters

- Membranes did not fail up to 33 bar.
- The thicknesses of the flat membranes tested were 10 and 49 μm, with an exposed area of 0.5 cm^2.
- In a hollow fiber configuration, a <1-μm thick layer is expected to provide the target flux (300 $ft^3_{stp}/ft^2•h$).

Technology Advantages

- Low cost, low carbon footprint, readily available materials for ZIF, polymer, and membrane preparation: Non-precious metals (i.e., zinc, copper, and aluminum) can be easily obtained or, for organic compounds, synthesized from commercially available materials.
- Membrane fabrication follows simple procedures: mix and cast. Dispersions of ZIFs and polymer solutions are easily prepared without the use of expensive equipment. Casting solvents can be re-utilized.
- Membrane geometry can be adapted to different module types: flat, spiral wound, hollow fiber, or tubular.

R&D Challenges

- Obtaining defect-free polymer/ZIF interfaces remains a challenge for MMMs.
- Obtaining required gas fluxes in MMMs.

Results To Date/Accomplishments

- Thermally and chemically stable nanosized ZIFs with high affinity and selectivity for H_2 and CO_2 were synthesized based on reported procedures and used in MMMs. Robust polyimides (Matrimid®, VTEC PI-1388, and 6FDA-based PIs), PBI, and PIM-1 were employed.
- High-performance polymers (VTEC polyimide and polybenzimidazole, PBI) were tested for gas permeation [H_2, CO_2, and nitrogen (N_2)]. VTEC was tested up to 30 bar and 300 °C.
- Measurement of hydrogen sorption in thermally stable molecular sieve ZIFs showed H_2 adsorption up to 350 °C and 100 bar, while retaining the ZIF's integrity.
- ZIF/PBI MMMs exhibited a 130% increase in H_2 permeability with a 28% reduction in H_2/CO_2 selectivity at 35 °C and 3 bar.
- The measured H_2/CO_2 selectivity ($\alpha = 144$) for 6FDA-durene treated with ethylenediamine (EDA) results from a reduction in polymer chain mobility, which is accompanied by a dramatic decrease in permeability compared to the pure polymer. Incorporation of ZIFs into MMMs is known to increase permeability. ZIF-8/polymer (Matrimid® and 6FDA-durene) MMMs were crosslinked in an attempt to retain selectivity while increasing permeability (Figure 3).
- A membrane reactor was designed to meet DOE target conditions for the H_2/CO_2 separation at 300 °C and 15 atm, considering a gas flux across the membrane of 300 ft^3_{stp}/ft^2•h and currently under construction.

Next Steps

- Testing of select ZIF/polymer MMMs at 300 °C and up to 30 bar.
- Preparation of tubular ZIF/polymer mixed-matrix membranes for testing under WGS reaction conditions.
- Testing of the WGS membrane reactor.

Available Reports/Technical Papers/Presentations

Molecular sieving realized with ZIF-8/Matrimid® mixed-matrix membranes, Ordoñez, M. J. C.; Balkus Jr, K. J.; Ferraris, J. P.; Musselman, I. H., *J. Membr. Sci*. **2010**, *361*, 28–37.

The PIs presented for the U.S. Department of Energy National Energy Technology Laboratory Strategic Center for Coal's Advanced Fuels Peer Review October 18–22, 2010, in Morgantown, WV.

Perfluorocyclobutyl (PFCB) Polymers for Gas Separation Applications, **G. D. Kalaw**, K. J. Balkus, Jr., I. H. Musselman, J. P. Ferraris (Poster), 2010 NAMS annual meeting, Washington, D.C.

ZIF-8/6FDA-Durene Mixed-Matrix Membranes for Gas Separations, **S. N. Wijenayake**, K. J. Balkus, Jr., I. H. Musselman, J. P. Ferraris (Poster), 2010 NAMS annual meeting, Washington, D.C.

ZIF-7/Matrimid® Mixed-Matrix Membranes for Gas Separations, **Zhang, Z.**, K. J. Balkus, Jr., J. P. Ferraris, I. H. Musselman (Poster), 2010 NAMS annual meeting, Washington, D.C.

Metal-Organic Framework Mixed-Matrix Membranes for Gas Separations, **K. J. Balkus, Jr.**, J. P. Ferraris, I. H. Musselman (Talk), 16th International Zeolite Conference, Sorento, Italy, 2010.

Perfluorocyclobutyl (PFCB) Polymer/Basolite® Z1200 Mixed-Matrix Membranes (MMMs) for Gas Separation Applications (Poster and talk), **G. D. Kalaw**, K. J. Balkus, Jr., I. H. Musselman, J. P. Ferraris, 240th ACS National Meeting, Boston, MA, 2010.

Mixed-matrix membranes (MMMs) comprising metal organic frameworks and novel perfluorocyclobutyl-based polymers or high temperature polyimides for gas separations, J. P. Ferraris; **K. J. Balkus**; I. H. Musselman; G. J. Kalaw; M. C. Ordoñez; S. N. Wijenayake, PacifiChem 2010. Honolulu, HI.

Polymer-based mixed-matrix membranes containing zeolitic imidazolate frameworks for gas separations, **I. H. Musselman**; M. C. Ordoñez; Z. Zhang; K. J. Balkus; J. P. Ferraris, PacifiChem 2010. Honolulu, HI.

ADVANCED PALLADIUM MEMBRANE SCALE-UP FOR HYDROGEN SEPARATION

Primary Project Goals

United Technologies Research Center (UTRC), in collaboration with Power+Energy, Inc. (P+E) and the Energy and Environmental Research Center at the University of North Dakota (UNDEERC), is demonstrating the membrane-based separation of H_2 from coal-derived synthesis gas (syngas) at the pre-engineering/pilot scale using an improved palladium (Pd) -based membrane technology.

Technical Goals

- Construct, test, and demonstrate a Pd copper (Cu) metallic tubular membrane micro-channel separator capable of producing 2 lb/day of H_2 at ≥95% recovery when operating downstream of an actual coal gasifier.
- Quantify the impact of simulated gas composition and temperature on separator performance.
- Compare the performance and durability of a surface-modified higher H_2 flux PdCu membrane with the baseline PdCu tubular membrane.
- Evaluate various materials of construction for the separator structural parts to ensure durability under harsh gasifier conditions.

Technology Maturity:

Bench- to pilot-scale, hydrogen separation

Project Focus:

Membrane for H_2 Separation

Participant:

United Technologies Research Center

Project Number:

FE0004967

NETL Project Manager:

Jason Hissam
Jason.Hissam@netl.doe.gov

Principal Investigator:

Sean Emerson
United Technologies Research Center
emersosc@utrc.utc.com

Partners:

Power+Energy, Inc.
University of North Dakota EERC

Performance Period:

9/24/10 – 12/31/11

Technical Content

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd, Cu	Pd, Cu
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	999,999	999,999
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	50 $ft^3ft^{-2}h^{-1}$ for 200 psia H_2	300 $ft^3ft^{-2}h^{-1}$
	Temperature, °C	250–600	250–500
	Bench-scale testing, hours without significant performance degradation	1,031 h	43,829 h
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	13.8 bar	—
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	—
	Packing density, m^2/m^3	157	—
	Pressure drop, bar	—	—
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	—	—
Product Quality	CO_2 purity, %	—	—
	H_2 purity, %	99.9999	99.99

Technology Advantages

- The PdCu alloy has stronger resistance to sulfur compared to traditional membranes, resulting in improved CO_2 capture efficiency.
- A PdCu alloy-based CO_2 capture membrane is able to better withstand the corrosion and wear associated with membranes constructed of other materials.
- Less corrosion means the membrane does not need to be replaced as often, resulting in a lower overall operating cost for the power plant.

R&D Challenges

- Membrane resistance to coal gasifier exhaust such as carbon monoxide, sulfur, arsenic, and mercury.
- Corrosion and metal dusting resistance of non-membrane materials of construction.
- Separation of 2 lb/day of H_2 operating downstream of an actual coal gasifier.

Results To Date/Accomplishments

- Delivery of first two 0.1 ft^2 separators.
- Prepared samples of eight alloys for corrosion testing (SS-316, SS-309, C-22, C-276, SS-310, HR-120, and Oak Ridge National Laboratory OC-10 and OC-11 alloys).
- Evaluated the gas impurity resistance of the first 0.1-ft^2 separator.

Next Steps

- Corrosion testing of metal alloy coupons at 500 °C.
- Evaluate the performance of PdCu separators with improved surface coating.
- Conduct durability studies under DOE protocol test conditions of 2-lb/day H_2 separators.
- Conduct pilot-scale testing of a 2-lb/day H_2 separator at UNDEERC's coal gasifier.

Available Reports/Technical Papers/Presentations

Emerson, S.C., et al. *Experimental Demonstration of Advanced Palladium Membrane Separators for Central High Purity Hydrogen Production, DOE Award Number DE-FC26-07NT43055*. East Hartford, CT: United Technologies Research Center, 2010. Final Report.

Advanced Palladium Membrane Scale-up for Hydrogen Separation, invited presentation at Advancing the Hydrogen Economy Action Summit III. Emerson, S.C. Grand Forks, ND: University of North Dakota EERC's National Center for Hydrogen Technology, 2010.

Opalka, S.M., Løvvik, O.M., Emerson, S.C., Vanderspurt, T.H. Electronic Origins for Sulfur Interactions with Palladium Alloys for Hydrogen-Selective Membranes, submitted to J. Membrane Sci. 2010.

SUPPORTED MOLTEN METAL MEMBRANE FOR HYDROGEN SEPARATION

Primary Project Goals

Worcester Polytechnic Institute (WPI) is developing and testing novel supported molten metal membranes (SMMMs) for hydrogen separation that meet DOE's targets in terms of cost, operating conditions, permeability, selectivity, robustness, and longevity. These membranes would be based on low-melting, non-precious group metals [e.g., tin (Sn), indium (In), gallium (Ga), bismuth (Bi)] and their alloys, supported as thin films on an inert porous ceramic or a porous metal support with or without an intermetallic diffusion barrier.

Technical Goals

- Selection of molten metals and their supports and develop membrane fabrication protocols, and establish feasibility to the SMMM technique.
- Select and optimize final SMMM candidates and investigate in term of permeability, selectivity, and susceptibility to poisons, as well as microstructural, solubility, and diffusion characteristics.
- Investigate best SMMM candidate under increasingly realistic conditions.

Technical Content

Experiments were continued in an effort to fabricate dense and stable SMMMs on oxidized porous metal and/or ceramic supports. Ceramic disk membranes were found to lack wettability as well as the strength needed for effective sealing at higher temperatures.

Coupon studies indicated that porous stainless steel (PSS) oxidized at the usual temperature (700 °C) does not provide an effective diffusion barrier that holds up to the liquid metals tested (In, Ga, Sn). PSS membranes oxidized at a higher temperature seem to provide a firmer barrier and may work. A porous Ni disk when oxidized provides a diffusion barrier that is effective. Therefore, oxidized porous Ni and porous Inconel supports should be effective as membrane supports.

Technology Maturity:

Bench-scale, SMMM hydrogen membranes

Project Focus:

Supported Molten Metal Membrane for H_2 Separation

Participant:

Worcester Polytechnic Institute

Project Number:

FE0001050

NETL Project Manager:

Jason Hissam
Jason.Hissam@netl.doe.gov

Principal Investigator:

Ravinda Datta
Worcester Polytechnic Institute
rdatta@wpi.edu

Partners:

None

Performance Period:

9/23/09 – 9/29/11

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	In, Ga, Sn	Non-PGM
	Materials of fabrication for support layer (if applicable)	NiO, ZrO_2, TiO_2	Durable
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	N/A	10,000
	Type of selectivity measurement (ideal or mixed gas)	—	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	N/A	1 sccm/psi.cm^2
	Temperature, °C	300–400	300–600
	Bench-scale testing, hours without significant performance degradation	—	—
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	—	100 psi
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	—	Shell-and-tube, Plate-and-frame
	Packing density, m^2/m^3	—	—
	Pressure drop, bar	—	—
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	\$5,400/m^2
Product Quality	CO_2 purity, %	—	—
	H_2 purity, %	N/A	99.99

Technology Advantages

- The SMMM comprises non precious-group metal membranes and, thus, has a cost advantage.
- Its range of operating temperatures is potentially wider than conventional palladium (Pd)-based membranes.
- Thermal mismatch issues between metal and support are absent and is potentially self-repairing of pinholes.
- It potentially has better tolerance to other synthesis gas (syngas) components.

R&D Challenges

- The SMMM is conceptually a novel idea and there is a lack of prior work/recipe in the literature, thereby leading to a lack in guidance.
- Molten metals are highly reactive and are likely to infiltrate the support, making the naked porous metal supports unsuitable.
- Most ceramics are too fragile to allow compressive sealing at higher temperatures.
- Thinning of the tubular liquid metal membrane upon heating.

Results To Date/Accomplishments

- It was found that wettability and chemical inertness are competing requirements. Thus, ceramic supports (e.g., zirconia) possess good inertness but poor wettability, while naked metal supports (e.g., PSS), while readily wetted, react with molten metals at elevated temperatures to form impermeable solid alloys and intermetallic compounds.
- Ceramic supports are fragile and crack at sealing pressures necessary for effective sealing at higher temperatures. Thus, efforts were focused on developing interfacial layers on porous metal substrates that provide an appropriate combination of wettability and inertness and experiments were performed using disks and tubular supports.
- Coupon studies indicated that PSS oxidized at the usual temperature (700ºC) that works for Pd membranes does not provide an effective diffusion barrier that holds up to the liquid metals tested (In, Ga, Sn).
- It appears that porous nickel (Ni) (and Inconel) supports when oxidized appropriately may provide an adequate diffusion barrier needed for the stability of the molten metal membrane.
- Despite persistent sealing leaks in the disk permeator, it was found that the hydrogen (H_2)/helium (He) selectivity of several tested membranes is higher than ideal selectivity of Knudson diffusion.
- Two alternate procedures have been developed for depositing a second metal (Pd for now) to alloy with the base liquid metal deposited on a tubular support in order to obtain membranes with melting point in the range of 300–400 °C.

Next Steps

- Fabricate dense and stable SMMMs with porous Ni, porous Inconel, and porous Itanium supports.
- Investigating if the wettability can also be improved by sputtering a nanoscale layer of these elements at the interface.
- Resolving sealing issues of disk permeator setup, to get accurate idea of hydrogen flux and selectivity through SMMMs.
- Improve the wettability of the membrane so that there is a stronger bond between membrane and support.
- Utilize liquid membranes with melting points not significantly below the operating temperature of 400 °C or above, so that liquid thinning at high temperatures is less of an issue.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

NANOPOROUS, METAL CARBIDE, SURFACE DIFFUSION MEMBRANE FOR HIGH TEMPERATURE HYDROGEN SEPARATIONS

Primary Project Goals

The Colorado School of Mines (CSM) is fabricating, characterizing, and optimizing transition metal carbide, composite membranes to separate hydrogen (H_2) from gas mixtures at high temperatures and pressures representative of gasification of carbon feedstocks such as coal or biomass. Supports will be either dense BCC metals [vanadium (V), niobium (Nb), tantalum (Ta), etc.] or porous stainless steel filters from Pall Corporation.

Technical Goals

- Pore size, carbide formation conditions, and the thickness of the carbide layer will be varied to study the effects on the performance of the metal carbide composite membranes.
- Investigate the effect of synthetic water-gas shift product mixtures on permeance and selectivity of nanoporous, metal carbide/sulfide, composite membranes.
- Determine if metal carbide layers can catalyze the dissociation of hydrogen on dense, Group V, BCC metal membranes (V, Nb, Ta, or their alloys).

Technical Content

CSM will fabricate, characterize, and optimize novel, high-temperature membranes for hydrogen separation based on metal [molybdenum (Mo) or tungsten (W)] carbides and sulfides. These membranes could be used in water gas-shift environments for the simultaneous generation of pure H_2 and a stream enriched in carbon dioxide (CO_2) at high pressure for subsequent capture. These membranes contain no platinum group metals (PGMs) such as ruthenium (Ru), rhodium (Rh), palladium (Pd), osmium (Os), iridium (Ir), or platinum (Pt). The membrane selective layer will be either a mesoporous carbide layer on a porous support (see Figure 1) or a thin carbide layer on a dense BCC metal (V, Nb, Ta, or their alloys) as shown in Figure 2.

The CSM synthesis strategy consists of the use of a low-temperature, plasma-enhanced chemical vapor deposition (PECVD) process to form a dense metal oxide layer on tubular, stainless steel filtration membrane from Pall Corporation. The dense metal oxide layer will then be converted to a carbide phase containing small nanopores (2–3 nm) via a reduction process in a hydrocarbon/hydrogen environment. Tests will be used to identify membranes with larger pores that will subsequently be repaired to eliminate non-selective transport by viscous flow. Robust, porous stainless steel substrates will be used which will facilitate high-temperature sealing and can be scaled up as they have been modularized for industrial-scale filtration by Pall Corporation.

In addition to the experiments with porous molybdenum carbide (Mo_2C) to obtain a surface diffusion membrane, its use as a catalyst on crystalline, dense Group V metal membranes (e.g., V, Nb, Ta) was also examined. In these experiments, an Mo_2C target was used to apply catalytic layers by sputtering on both sides of dense vanadium foils. This approach is shown schematically in Figure 2.

Technology Maturity:

Bench-scale composite membranes H_2 separation

Project Focus:

Nanoporous Metal Carbide Membrane for H_2 Separation

Participant:

Colorado School of Mines

Project Number:

FE0001009

NETL Project Manager:

Robie Lewis
Robie.Lewis@netl.doe.gov

Principal Investigator:

J. Douglas Way
Colorado School of Mines
dway@mines.edu

Colin A. Wolden
Colorado School of Mines
cwolden@mines.edu

Partners:

Pall Corporation

Performance Period:

9/23/09 – 9/30/12

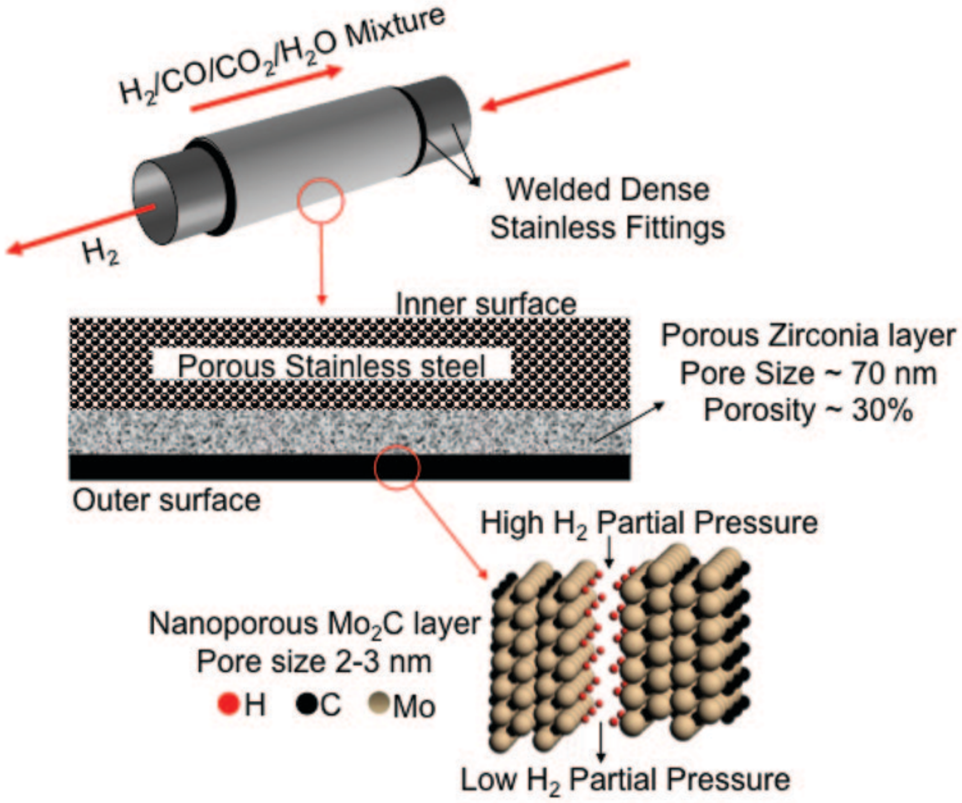


Figure 1: Schematic Diagram of Metal Carbide, Surface Diffusion Membrane Concept

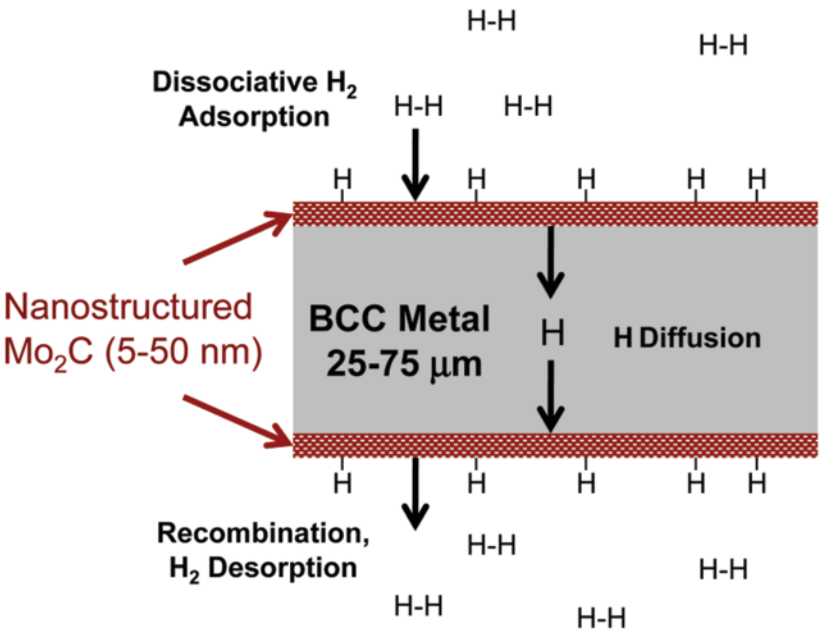


Figure 2: Schematic Diagram of Mo$_2$C Coated, Group V (Nb, V, Ta), BCC Metal Composite Membrane

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	65 nm thick Mo_2C on 50 micron thick V	—
	Materials of fabrication for support layer (if applicable)	—	—
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	H_2/N_2 ideal selectivity is infinite	—
	Type of selectivity measurement (ideal or mixed gas)	Ideal	—
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	Pure H_2 permeance = 5.97×10^{-4} mole/m^2•s•Pa$^{0.5}$	Pure H_2 permeance = 2.63×10^{-3} mole/m^2•s•Pa$^{0.5}$
	Temperature, °C	700 °C	250–500 °C
	Bench-scale testing, hours without significant performance degradation	168 hours	>5 years
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	100 psia = 6.8 bar	800–1,000 psi
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	N/A	—
	Packing density, m^2/m^3	—	—
	Pressure drop, bar	—	—
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	—	—
Product Quality	CO_2 purity, %	—	—
	H_2 purity, %	100%	99.99%

Technology Advantages

No Platinum Group Metals needed, materials costs of Mo_2C/BCC metal membranes are a fraction of an equivalent Pd or Pd alloy membrane. For example, Mo costs more than 300 times less than Pd, while V is more than 800 times cheaper than Pd.

R&D Challenges

- Stability of Mo_2C/BCC metal membrane in mixed gases representative of a water-gas shift equilibrium product mixture.
- Determination of rate limiting step(s) in hydrogen permeation through carbide/BCC composite membranes.
- Improve selectivity of metal carbide surface diffusion membranes.
- Increase hydrogen flux of Mo_2C/BCC metal membranes to meet 2015 DOE NETL target value of 300 standard cubic feet per hour (SCFH)/ft^2 for a hydrogen differential pressure of 100 pounds per square inch (psi).

Results To Date/Accomplishments

- After carburization, the best Mo_2C surface diffusion membrane, GTC 5, achieved a pure hydrogen flux of 367 SCFH/ft^2 at a feed pressure of only 20 pounds per square inch gauge (psig). The corresponding H_2/nitrogen (N_2) separation factor was 4.1.
- The new PECVD reactor system was used to deposit molybdenum oxide (MoO_3) coatings on three porous alumina tubes and multiple Mott porous stainless steel disks. The N_2 leak rate for a typical alumina tube was reduced from approximately 1 liter/minute to essentially zero.

- TEM images after permeation testing confirm that a dense, 65-nm thick layer of Mo_2C was deposited on the V foil, and that there was no evidence of reduction of the Mo_2C layer or diffusion into the V foil after extended testing at 700 °C.
- Experiments on Mo_2C/V composite membranes produced a pure H_2 flux as high as 93.7 SCFH/ft^2 at 700 °C and 100 psig, with no detectable inert gas permeance during the testing period. The pure H_2 flux was stable for 168 hours equals one week. This flux is approximately the same as pure Pd at the same membrane thickness and test conditions.

Next Steps

- Coat Pall AccuSep and GTC substrate tubes with MoO_3 using pulsed PECVD.
- Perform in-situ carburization followed by permeation tests with H_2 and UHP N_2 to investigate the causes of the observed H_2 flux decline.
- Vary the thickness of the V foil to determine the effect on the H_2 flux (25–75 microns). If bulk diffusion controls, then the flux should vary with the reciprocal of the membrane thickness.
- Reduce the thickness of the Mo_2C catalyst layer on the V foil membranes and vary its morphology through control of sputter parameters.
- Perform further analysis of the TEM sample using in-situ selected area diffraction.
- Develop techniques for in-situ reduction of pore size in substrates prior to deposition, and likewise to repair defects that may develop during carburization.
- Continue to optimize parameters associated with conversion of oxides to carbides with a focus on the use of higher flow rates to mitigate mass transfer limitations.

Available Reports/Technical Papers/Presentations

Wolden, C. A., Pickerell, A., Gawai, T., Parks, S., Hensley, J. and J. D. Way, “Synthesis of β-Mo_2C Thin Films,” *ACS Applied Materials and Interfaces*, 2011, 3, 517–521.

AMORPHOUS ALLOY MEMBRANE FOR HIGH-TEMPERATURE HYDROGEN SEPARATION

Primary Project Goals

Southwest Research Institute (SwRI) is modeling, fabricating, and testing thin film amorphous alloy membranes which separate hydrogen (H_2) from a coal-based system with performance meeting the DOE 2015 targets of flux, selectivity, cost, and chemical and mechanical robustness, without the use of platinum group metals (PGMs). This project will use a combination of theoretical modeling, advanced physical vapor deposition fabricating, and laboratory and gasifier testing to develop amorphous alloy membranes.

Technical Goals

- Use density functional theory (DFT) methods to predict H_2 flux through amorphous zirconium (Zr)-based alloys as functions of operating temperature, H_2 feed pressure, membrane thickness, and trans-membrane pressure drop to advance testing of heuristics for alloy selection.
- Fabricate amorphous alloy membranes using magnetron sputtering with compositions consistent with those identified by H_2 flux modelling that are mechanically robust for application in a hydrogen separation unit.
- Test and establish thermal stability, pure gas [H_2 and nitrogen (N_2)] and mixture [H_2/carbon monoxide (CO) and H_2/hydrogen sulphide (H_2S)] permeation performance, and gasifier testing on optimized amorphous alloy membrane materials.

Technical Content

Thin film amorphous alloy membranes are a nascent but promising new technology for industrial-scale hydrogen gas separations from coal-derived syngas. This project uses a combination of theoretical modeling, advanced physical vapor deposition fabricating, and laboratory and gasifier testing to develop amorphous alloy membranes that have the potential to meet DOE targets in the testing strategies outlined in the NETL Membrane Test Protocol. The project is on schedule with SwRI, Georgia Institute of Technology (GT), and Western Research Institute (WRI) all operating independently and concurrently. GT has applied the computational methodology to investigate a series of candidates with relatively high crystallization temperatures (>700K). GT performed extensive calculations for ternary element additions to zirconium copper (ZrCu), specifically for $Zr_{30}Cu_{60}T_{10}$ [T = scandium (Sc), yttrium (Y), niobium (Nb), molybdenum (Mo), technetium (Tc), ruthenium (Ru), rhodium (Rh), silver (Ag), tantalum (Ta), tungsten (W), rhenium (Re), osmium (Os), iridium (Ir), platinum (Pt), gold (Au)]. The selection of 30:60:10 composition is because $Zr_{30}Cu_{60}Ti_{10}$ showed good results in previous calculations. Among these materials, Sc, Ta, and Y have been identified as good ternary elements for $Zr_{30}Cu_{60}T_{10}$. To achieve fast surface H_2 dissociation process, a thin layer of palladium (Pd) is normally added on the amorphous film's surface as a catalytic layer. It is thus interesting to see the hydrogen properties in $Zr_{30}Cu_{60}Pd_{10}$ due to Pd diffusion into the host lattice. Hydrogen permeability through $Zr_{30}Cu_{60}Pd_{10}$ is not favorable compared to either Pd, $Zr_{54}Cu_{46}$, or $Zr_{30}Cu_{60}Ti_{10}$. Ni_xZr_{1-x} coatings with x ranging from 0.71 to 0.93 were deposited by magnetron co-sputtering process. It was found that as-deposited films are more amorphous with an increase of Zr content starting from x = 0.9 and reaching an X-ray diffraction (XRD)-amorphous state at x >0.88.

Figure 1: A Cross Section of a Ni93Zr7 Deposited Alloy

Technology Maturity:

Bench-scale

Project Focus:

Amorphous Alloy Membrane for H_2 Separation

Participant:

Southwest Research Institute

Project Number:

FE0001057

NETL Project Manager:

Steven Markovich
Steven.Markovich@netl.doe.gov

Principal Investigator:

Kent Coulter
Southwest Research Institute
kent.coulter@swri.org

Partners:

The Georgia Institute of Technology
Western Research Institute

Performance Period:

9/23/09 – 9/29/11

Mechanical properties of these coatings are strongly correlated with their composition. Amorphous films with higher Zr content have retained their XRD measured amorphous state after one hour of annealing in an argon/2% hydrogen atmosphere at 300 °C. The partial re-crystallization in films with the highest Zr content occurs after 24 hours of annealing. The precise deposition of metal coatings by magnetron sources was demonstrated for deposition of CuZr and CuZrTi coatings. In these coatings, the Cu:Zr ratio was varied to line up with the previously calculated permeability data. The CuZr and CuZrTi all are amorphous as deposited, but none have survived 24 hours at 350 °C. The species that form are not consistent with standard XRD spectra for CuZr species.

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Amorphous Zr-based alloys	Amorphous Zr-based alloys
	Materials of fabrication for support layer (if applicable)	Stainless steel	Stainless Steel
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	TBD	99.99
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	TBD	H_2-200 SCFH/ft^2
	Temperature, °C	300	300–600
	Bench-scale testing, hours without significant performance degradation	1	120
	Pilot-scale testing (if applicable), hours without significant performance degradation	TBD	120
	Maximum pressure differential achieved without significant performance degradation or failure, bar	TBD	6.9
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Plate-and-frame
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	TBD	4.8
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	TBD	\$10,764/m^2
Product Quality	CO_2 purity, %	N/A	N/A
	H_2 purity, %	N/A	N/A

Technology Advantages

- GT has developed a detailed DFT and a heuristic lattice model that is appropriate for rapidly characterizing hydrogen solubility and diffusion in the search for new promising alloys for membranes. This approach can be used as an initial tool for screening materials prior to using more expensive experimental investigations.
- The advanced vapor deposition methods used to construct the amorphous alloy membranes provide unique advantages compared to other membrane fabrication techniques. The high-power, pulsed magnetron sputtering and plasma-enhanced magnetron deposition methods are able to rapidly produce membranes of almost any alloy composition, providing excellent flexibility in terms of the materials and properties used in a membrane.

R&D Challenges

Since they are thermodynamically metastable, amorphous alloys have the distinct disadvantage that they have a tendency to crystallize when heated to sufficiently high temperatures. This property places limits on the operating conditions at which amorphous membranes can be used.

Results To Date/Accomplishments

- To achieve fast surface H_2 dissociation process, a thin layer of Pd is normally added on the amorphous film's surface as a catalytic layer. It is thus interesting to see the hydrogen properties in $Zr_{30}Cu_{60}Pd_{10}$ due to Pd diffusion into host lattice. Hydrogen permeability through $Zr_{30}Cu_{60}Pd_{10}$ is not favorable compared to either Pd, $Zr_{54}Cu_{46}$, or $Zr_{30}Cu_{60}Ti_{10}$.
- SwRI has demonstrated the precise deposition of metal coatings by magnetron sputtering for deposition of CuZr and CuZrTi coatings.
- GT performed extensive calculations for ternary element additions to ZrCu, specifically for $Zr_{30}Cu_{60}T_{10}$ (T = Sc, Y, Nb, Mo, Tc, Ru, Rh, Ag, Ta, W, Re, Os, Ir, Pt, Au). The selection of a 30:60:10 composition is because $Zr_{30}Cu_{60}Ti_{10}$ showed good results in previous calculations.
- WRI has conducted all X-ray powder crystallography, elemental composition tests, and thermal annealing tests. The ternary NiZrNb coatings have demonstrated superior thermal stability during 24 hours of annealing at 300 °C in Ar/2%H_2 as compared to the binary NiZr coatings having similar Zr concentration.

Next Steps

- GT will perform both solubility and diffusion calculations on selected membranes.
- SwRI will fabricate amorphous alloys for testing.
- WRI will continue thermal stability testing in air and reducing environments and begin permeability testing.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

AMORPHOUS ALLOY MEMBRANES PREPARED BY MELT-SPIN METHODS FOR LONG-TERM USE IN HYDROGEN SEPARATION APPLICATIONS

Primary Project Goals

University of Nevada's main objective is to produce amorphous ribbons from non-precious metal alloys. These amorphous membranes are expected to work towards meeting all 2015 separation targets, such as of flux (300 $ft^3/hr/ft^2$), temperature (200–500 Â°C), sulfur tolerance [>100 parts per million by volume (ppmv)], and cost (<\$100/ft^2). The project consists of developing multiple metal-alloy ribbon membranes for evaluation and down selection.

Technical Goals

- Screening of amorphous alloys and selection of potential alloys, which gives comparable performance in terms of hydrogen flux, thermal stability, etc.
- Determine hydrogen solubility, permeation, and recrystallization temperatures.

Technology Maturity:

Bench-scale, hydrogen separation

Project Focus:

Amorphous Alloy Membrane for H_2 Separation

Participant:

University of Nevada

Project Number:

FE0000998

NETL Project Manager:

Steven Seachman
Steven.Seachman@netl.doe.gov

Principal Investigator:

Dhanesh Chandra
University of Nevada, Reno
dchandra@unr.edu

Partners:

CSIRO, Division of Energy Technology
TDA Research, Inc.

Performance Period:

9/22/09 – 9/30/12

Technical Content

Table 1: Membrane Process Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd	Ni-Nb-Zr Ni-Nb-Zr-Ta
	Materials of fabrication for support layer (if applicable)	—	—
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	H_2	H_2
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units		300 $ft^3/hr/ft^2$
	Temperature, °C	400	250–500
	Bench-scale testing, hours without significant performance degradation	100	500
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	—	55–69
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Plate-and-frame
	Packing density, m^2/m^3	—	150[1]
	Pressure drop, bar	—	—
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	Ni-Nb-Zr foil only: <$\$50/m^2$ Pd-coated foil: <$\$300/m^2$ Module containing membrane: <$\$500/m^2$ (2)	<929
Product Quality	CO_2 purity, %	Depends on H_2 yield through membrane: 85% H_2 yield gives CO_2 purity of ~90%	—
	H_2 purity, %	100	100

Notes:

1. Based on 2,000 mm × 100 mm × 10 mm planar, dual-sided membrane modules with compressive seals inside cylindrical containment vessel with diameter 2,000 mm and packing density of 0.80.
2. Costs based on module of above dimensions, taking into account containment vessels, materials, machining, membrane manufacture, etc.

Technology Advantages

- Drastic reduction in overall cost compared to conventional palladium (Pd) alloy membranes system.
- Tolerent to carbon monoxide (CO) poisoning.
- High-volume, reliable, and inexpensive manufacturing process.

R&D Challenges

- Defects during fabrication of rubust amorphous alloy membranes.
- Thermal cycling.
- Membrane stability/embrittlement.

- Loss of membrane structural integrity/performance.
- Wide operating temperature range.

Results To Date/Accomplishments

Permeability

- Completed permeability testing of the $(Ni_{0.6}Nb_{0.4})_{100-x}Zr_x$ and $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ (where x = 0, 10, 20 or 30) series of amorphous alloy membranes.
- The partial substitution of niobium (Nb) with tantalum (Ta) resulted in slightly lower permeability. Alloys with ≤10 wt% zirconium (Zr) content had very low permeabilities; <2 × 10-9 mol m-1 s-1 Pa-0.5.
- Thermal stability results showed a rapid decrease in hydrogen flux with time at 400 or 450 °C for alloys containing higher Zr contents; details included in this report.
- The addition of Ta showed modest increase in the thermal stability of the amorphous nickel (Ni)-Nb-Zr alloy with only a slight impact on hydrogen permeability.
- Alloys containing little or no Zr displayed very stable, but low, hydrogen permeabilities throughout 100-hour tests.
- Fracture due to embrittlement decreased with increasing Zr content.
- Ta substitution in the $(Ni_{0.6}Nb_{0.4})_{70}Zr_{30}$ alloy embrittled significantly, but $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{70}Zr_{30}$ clearly decreased the susceptibility to hydrogen embrittlement at 400 °C.

Solubility

- Completed solubility testing of $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{90}$ Zr_{10} and $(Ni_{0.6}Nb_{0.4})_{100-x}Zr_x$ (where x = 0, 10, 20 or 30) series of amorphous alloy membranes.
- Results show that higher Zr content gives higher hydrogen solubility at all the temperatures in the 200–400 °C range.
- All the membranes showed higher solubility at lower temperatures.
- In case of $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{90}Zr_{10}$, Ta addition resulted in lowering the solubility at all the temperatures.
- In all the cases, Sievert's Law is being violated (positively), which is being understood to be a general trend in case of amorphous alloys.
- We observed a hook effect in case of lower Zr content alloy membranes (x = 10,20), which we are trying to analyze.

Crystalization Kinetics

- Completed crystallization temperature and kinetics of a series of $(Ni_{0.6}Nb_{0.4})_{100-x}Zr_x$ and $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ (where x = 0, 10, 20 or 30) amorphous alloy membranes.
- The crystallization temperature increases with decreasing Zr content or increasing Ta content.
- The Jonson-Mehl-Avrami (JMA) equation was applied to the isothermal analysis: the main crystallization process of the Ni-Nb-Zr alloy is governed by diffusion-controlled three-dimension growth.
- The activation energies of the crystallization of amorphous alloy membranes were determined by Kissinger and Ozawa analyses: (i) the activation energy of crystallization increases with decreasing Zr content, and (ii) the addition of Ta increase the activation energy of the amorphous Ni-Nb-Zr alloy.

Next Steps

- Complete ongoing solubility testing of rest of $(Ni_{0.6}Nb_{0.3}Ta_{0.1})_{100-x}Zr_x$ (where x = 20 or 30) series of amorphous alloys membranes, and also the amorphous alloy membranes of both the series without Pd coating to get more information to analyze the hook effect.
- Continue crystallization kinetics studies for amorphous alloy membranes with various transition metal substitutions.
- Begin testing a new series of Ni-Nb-Zr amorphous alloy membrane materials with various transition metal substitutions.
- Continue testing various surface catalytic coatings to replace Pd and increase chemical and thermal stability.
- Continue micro-structural analysis studies for membrane and coating optimization using SEM, XRD, and XPS/AES.

Available Reports/Technical Papers/Presentations

Presentations at the Meetings:

"Effect of tantalum substitution on the crystallization kinetics and hydrogen permeability of Ni-Nb-Zr amorphous alloys," *S.-M. Kim, **N. K. Pal**, D. Chandra, M. D. Dolan, W.-M. Chien, J. Lamb, A. Talekar, S. N. Paglieri, and T. B. Flanagan*. Presented at the TMS 2011 Meeting, Feb 27-March 3, San Diego, CA, USA.

"Hydrogen permeability and crystallization kinetics in amorphous Ni-Nb-Zr alloys," *S.-M. Kim, **N. K. Pal**, W.-M. Chien, J. Lamb, M. D. Dolan, A. Talekar, D. Chandra, S. N. Paglieri, T. B. Flanagan and Jim Reilly*, Presented at the "International Conference on Renewable Energy (ICRE 2011), Jan. 17–21, 2011, Jaipur, India.

"*Crystallization Kinetics and Hydrogen Solubility in Ni-based Amorphous Alloys for Hydrogen Permeability*," Sang-Mun Kim, Narendra K. Pal, Wen-Ming Chien, Joshua H. Lamb, Anjali Talekar, Dhanesh Chandra, Michael D. Dolan and Stephen N. Paglieri, **NAMS/ICIM 2010 Conferences**, July 17–22, 2010, Washington, D.C., USA.

"*Ni-Nb-Zr Amorphous Alloy Membranes for Hydrogen Separation*," Stephen N. Paglieri, Michael D. Dolan, David P. Moore, Kevin M. Hubbard, Sang-Mun Kim, Narendra K. Pal, Wen-Ming Chien, Joshua H. Lamb, Anjali Talekar, Dhanesh Chandra, Sarah J. DeVoss and Gokhan O. Alptekin, **2010 AIChE Annual Meeting**, November 7–12, 2010, Salt Lake City, UT, USA.

"*Ni-Nb-Zr and Ni-Nb-Zr-Ta Amorphous Alloy Membranes for Hydrogen Separation*," Stephen N. Paglieri, Sarah J. DeVoss, Gökhan O. Alptekin, Tyler B. Gleditsch, Michael D. Dolan, Kevin M. Hubbard, David P. Moore, Sang-Mun Kim, Narendra K. Pal, Joshua H. Lamb, Wen-Ming Chien, and Dhanesh Chandra, **NAMS/ICIM 2010 Conference**, July 17–22, 2010, Washington, D.C., USA.

Manuscripts: Submitted and Prepared:

"Hydrogen permeability, thermal stability and hydrogen embrittlement of Ni-Nb-Zr and Ni-Nb-Ta-Zr amorphous alloy membranes," *S. N. Paglieri, N. K. Pal, M. D. Dolan, S-M Kim, W-M Chien, J. Lamb, and D. Chandra*. **Journal of Membrane Science**, 2011. In review.

"Hydrogen permeability and crystallization kinetics in amorphous Ni-Nb-Zr alloys," **S.-M. Kim, W.-M. Chien, M. D. Dolan, N. K. Pal, A. Talekar, J. Lamb, D. Chandra, S. N. Paglieri, and T. B. Flanagan**, **International Journal of Hydrogen Energy**, 2011. In review.

"Glass transition and crystallization kinetics of melt-spun $Ni_{60}Nb_{20}Zr_{20}$ amorphous alloy," *Sang-Mun Kim, Wen-Ming Chien, Michael D. Dolan, Narendra Kumar Pal, Joshua Lamb, Anjali Talekar, Dhanesh Chandra, Stephen N. Paglieri, Ted B. Flanagan*. (Prepared the manuscript for **Journal Publication**).

"Effect of tantalum substitution on the crystallization kinetics and hydrogen permeability of Ni-Nb-Zr amorphous alloys," *S.-M. Kim, D. Chandra, M. D. Dolan, W.-M. Chien, N. K. Pal, J. Lamb, A. Talekar, S. N. Paglieri, and T. B. Flanagan*. (Prepared the manuscript for submission to the **Met. Trans A.** 2011).

NOVEL POLYMER MEMBRANE PROCESS FOR PRE-COMBUSTION CO_2 CAPTURE FROM COAL-FIRED SYNGAS

Primary Project Goals

Membrane Technology and Research, Inc. (MTR) is developing a new polymer membrane and membrane separation process to capture carbon dioxide (CO_2) from shifted synthesis gas (syngas) generated by a coal-fired integrated gasification combined cycle (IGCC) power plant.

Technical Goals

- Investigate novel high-temperature-stable polymers identified by Tetramer for use in hydrogen (H_2)/CO_2 selective membranes.
- Prepare composite polymer membranes and bench-scale modules that have H_2/CO_2 selectivities of 10 or higher and hydrogen permeances of greater than 200 gas permeation units (GPU) at syngas cleanup temperatures of 100–200 °C.
- Optimize membrane process designs, investigate the sensitivity of different proposed processes to membrane performance, and assess the optimal integration of a membrane system into the syngas cleanup train.
- Conduct bench-scale testing of optimized membranes and membrane modules at Membrane Technology and Research, Inc.'s (MTR) laboratories with simulated syngas mixtures to evaluate membrane performance and lifetime under expected operating conditions.
- Prepare a comparative evaluation of the cost of the polymer membrane-based separation process versus current cleanup technologies (Rectisol®, Selexol®, and PSA) and proposed future membrane reactors.

Technical Content

The thrust of this project is development of polymer membranes that currently show mixture H_2 permeances up to 200 GPU and H_2/CO_2 selectivities of 10 at 100–200 °C. These membranes can be fabricated into robust, inexpensive modules of the type currently used commercially in the refinery and natural gas industries to separate gas mixtures at high pressures. Experience from these industries shows that membrane selectivity requirements often depend on the process design. Calculations utilizing new polymer membranes and innovative process schemes indicate that membranes with current properties can approach DOE CO_2 capture goals. Further improvements in performance and reductions in energy penalty are possible with membrane optimization.

This program will consist of two 12-month phases. The first phase will focus on materials development with an emphasis on identifying high-temperature polymers with desirable H_2/CO_2 separation properties. Promising polymers will be fabricated into industrial flat-sheet composite membranes and tested with simulated WGS mixtures. Parametric data from these tests will be used in a systems analysis to identify the optimal membrane design for syngas cleanup. Researchers will confirm that composite membranes made from novel membrane selective layers give hydrogen permeances of at least 200 GPU and H_2/CO_2 selectivities of greater than 10 in bench-scale tests using model syngas mixtures. These actual membrane performance data will be used to demonstrate that a membrane process shows progress toward meeting DOE pre-combustion CO_2 capture program targets.

Technology Maturity:

Bench-scale using simulated syngas and membrane stamp field tests using actual syngas slipstream

Project Focus:

Polymer Membranes

Participant:

Membrane Technology and Research, Inc.

Project Number:

FE0001124

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

Tim Merkel
Membrane Technology and Research, Inc.
tcmerkel@mtrinc.com

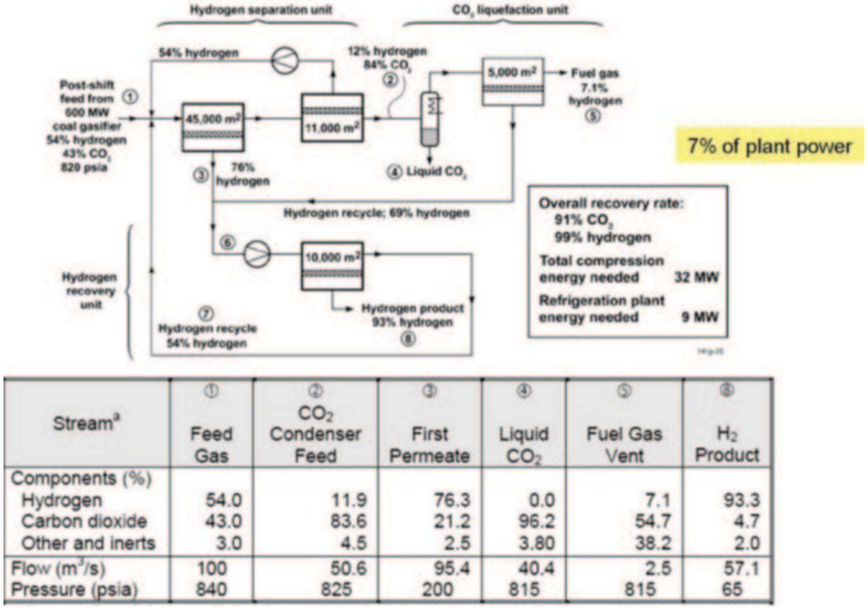
Partners:

Southern Company
Tetramer Technologies, LLC

Performance Period:

9/14/09 – 9/10/10

In the second phase of the project, optimized membrane materials will be down-selected and fabricated into composite membranes on commercial-scale equipment. These membranes will be formed into laboratory-scale, spiral-wound modules, each containing about 1 m^2 of membrane. The modules will be tested with simulated syngas mixtures to provide performance and lifetime data and demonstrate module performance and lifetime consistent with small-scale membrane stamp studies. This information will allow cost estimates of the membrane CO_2 capture process to be prepared to determine the overall technical and economic competitiveness of the proposed process as compared to alternative technologies and the DOE program targets.



Stream[a]	① Feed Gas	② CO_2 Condenser Feed	③ First Permeate	④ Liquid CO_2	⑤ Fuel Gas Vent	⑧ H_2 Product
Components (%)						
Hydrogen	54.0	11.9	76.3	0.0	7.1	93.3
Carbon dioxide	43.0	83.6	21.2	96.2	54.7	4.7
Other and inerts	3.0	4.5	2.5	3.80	38.2	2.0
Flow (m^3/s)	100	50.6	95.4	40.4	2.5	57.1
Pressure (psia)	840	825	200	815	815	65

Figure 1: A Possible Membrane Process Design to Capture 90% CO_2 from Shifted Syngas that Recovers >99% of the Hydrogen in Syngas at >93% Purity

An H_2/CO_2 selectivity versus H_2 permeance trade-off curve is presented in Figure 2. All data points below the upper bound are for polymeric membranes from literature and have been translated from pure-gas permeability at 25 °C assuming a selective layer thickness of 1 micron. Polymeric composite hydrogen-selective membranes are being developed in this project. The pure- and mixed-gas performance of the membranes is shown in Figure 2. For the mixed-gas measurement, the feed gas is an H_2/CO_2 (50:50 vol%) mixture at 50 pounds per square inch gauge (psig) and 150 °C. The mixed-gas performance target set in the proposal (hydrogen permeance = 200 GPU, H_2/CO_2 selectivity = 10 at 150 °C) is also included for comparison.

Figure 3 shows a test skid installed by MTR at the National Carbon Capture Center (NCCC) managed by the Southern Company. The skid will be used to test membrane and module candidates with coal-derived syngas throughout this project. Initial tests of both hydrogen-selective and CO_2-selective membranes during November and December of 2009 showed stable performance that exceeded project targets.

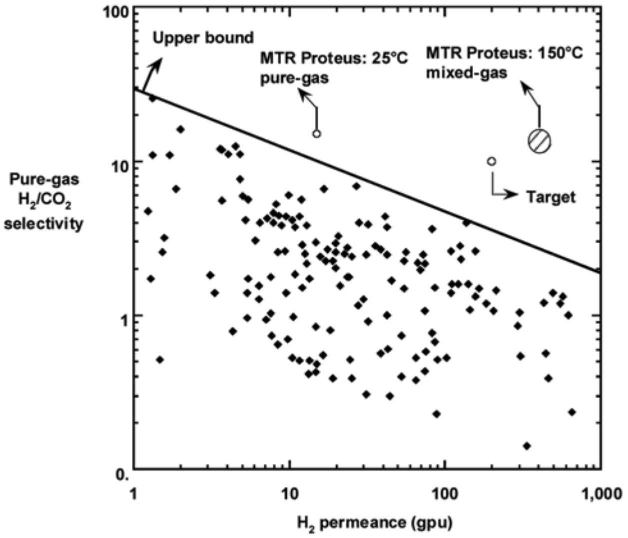


Figure 2: Tradeoff Plot of H_2/CO_2 Selectivity versus H_2 Permeance

Figure 3: MTR Membrane Test Skid at the National Carbon Capture Center

Table 1: Membrane-Based CO_2 Separations

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Polymer	Polymer
	Materials of fabrication for support layer (if applicable)	Polymer	Polymer
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	15–25	>10
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	200–400 GPU	>200 GPU
	Temperature, °C	120–150	150
	Bench-scale testing, hours without significant performance degradation	20 hours	>100
	Pilot-scale testing (if applicable), hours without significant performance degradation	500 hours	500
	Maximum pressure differential achieved without significant performance degradation or failure, bar	50 bar	50 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Spiral-wound	Spiral-wound
	Packing density, m^2/m^3	700	700
	Pressure drop, bar	0.5	0.5
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	2.0	0.5
Product Quality	CO_2 purity, %	N/A	97+
	H_2 purity, %	N/A	93+ or 40–45% in fuel
	Other contaminants (H_2S if it is not removed upstream of the membrane process), %	N/A	<25 ppm in H_2 fuel
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	<100
	Cooling requirement (electricity equivalent), kJ/kg CO_2	N/A	<150
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	<250

Other Membrane Parameters

Contaminant Resistance: The greatest concern would be fouling of the membrane surface due to residual particulate matter or heavy hydrocarbons/tars. Preliminary results from tests at NCCC suggest that existing syngas filters upstream of the membranes will be sufficient to protect the membranes from such surface fouling.

Syngas Pretreatment Requirements: As described above, existing syngas filters should be adequate protection for the membranes. Current temperature limitations on the polymeric membranes require the syngas to be cooled to ~150 °C prior to treatment.

Waste Streams Generated: The membrane process will not generate any waste streams. Periodic module replacement (expected lifetime of three years) will produce a small amount of solid waste. Typically, for the large membrane applications like sea water desalination by reverse osmosis, these membrane modules are sent to a landfill.

Technology Advantages

- Membranes developed in this project are based on polymer materials that show higher hydrogen permeance and higher H_2/CO_2 selectivity than conventional polymer materials. These membranes can be fabricated into robust, stable, and inexpensive modules of the type currently used commercially in the refinery and natural gas industries to separate gas mixtures at high pressures.
- The process design using hydrogen permeable membranes will create a high-pressure CO_2 stream capturing >90% of CO_2 in post-shift syngas and a 93 mol% purity hydrogen stream, and could use as little as about 7% of the plant's power output.
- Membranes offer the advantages of simple, passive operation; no use of hazardous chemicals and the subsequent waste handling and disposal issues; no stream use; and a small footprint.

R&D Challenges

- Polymer materials that are used in the selective layer and the support layer need to be thermally stable at high operating temperatures.
- Membrane modules to be developed for this application have to endure the extended long-term operations at high temperatures (~150 °C). All the module components, including feed and permeate spacers, support papers, and glues, require new development for this application.
- There is little membrane operational experience with real coal-derived syngas.

Results To Date/Accomplishments

- The first project milestone (membrane permeance and selectivity targets) was met ahead of schedule.
- The second and third project milestones (process design study and module fabrication, respectively) were accomplished on schedule.
- Three 500-hour slipstream tests of membrane stamps with coal-derived syngas have been completed at NCCC. The membranes show stable performance treating syngas containing up to 780 parts per million (ppm) hydrogen sulfide (H_2S). The average membrane performance (H_2/CO_2 selectivity of 15–25 and H_2 permeance of 200–300 GPU) exceeds project targets.

Next Steps

- A module test with a coal syngas slipstream is scheduled at NCCC in May 2011.
- Final test results and a report will be available by the September 2011 project completion date.

Available Reports/Technical Papers/Presentations

T. C. Merkel, S. Thomas, M. Zhou, H. Lin, A. Serbanescu, *Novel Polymer Membrane Process For Pre-Combustion CO_2 Capture From Coal-Fired Syngas*, DOE 2010 Carbon Dioxide Capture Technology Meeting.

M. Zhou, S. Thomas, H. Lin, A. Serbanescu, T. Merkel, *Polymer Membranes For Pre-Combustion CO_2 Capture*, 2010 NAMS Annual Meeting and International Conference on Inorganic Membranes.

M. Zhou, S. Thomas, H. Lin, A. Serbanescu, T. Merkel, *Polymer Membranes For Pre-Combustion CO_2 Capture*, 2010 AIChE Spring Meeting and 6th Global Congress on Process Safety.

T. C. Merkel, M. Zhou, and R. W. Baker; *Carbon Dioxide Capture with Membranes at an IGCC Power Plant*; manuscript in preparation.

EXPERIMENTAL DEMONSTRATION OF ADVANCED PALLADIUM MEMBRANE SEPARATORS FOR CENTRAL HIGH-PURITY HYDROGEN PRODUCTION

Primary Project Goals

United Technologies Research Center (UTRC) is developing a palladium copper (PdCu) trimetallic alloy hydrogen (H_2) separator for central H_2 production from coal gasification-derived synthesis gas (syngas).

Technical Goals

- Test the high stability and resistance of a PdCu trimetallic alloy to carbon and carbide formation, sulfur, halides, and ammonia (NH_3).
- Develop a sulfur-, halide-, and NH_3-resistant alloy membrane with a projected H_2 permeance of 25 $m^3m^{-2}atm^{-0.5}h^{-1}$ at 400 °C and capable of operating at pressures of 120 atm (12.1 MPa).
- Construct and experimentally validate the performance of PdCu trimetallic alloy membranes operating at an H_2 separation rate of 0.1 kg/day at feed pressures of 20 atm (2 MPa) in the presence of hydrogen sulfide (H_2S), NH_3, and hydrogen chloride (HCl). The performance of the best separator candidate will be demonstrated for a minimum of 2,000 hours of operation.

Technical Content

Figure 1 depicts one of the membrane separators developed for this project. The purpose of the separators is to house the membrane and receive the flue gas stream from combustion. The membrane allows the H_2 to pass through it, following the H_2 permeate path in the diagram. The remaining gas stream then exits the membrane system for further processing.

Figure 2 illustrates the path of the gas stream through the separation mechanism's structure. The gas stream enters through the PdCu alloy pipes, which allow the H_2 present in the gas stream to permeate through the alloy walls into the secondary level of the structure (shown as the white area within the blue outer-shell), while containing the remaining gases [carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), and nitrogen (N_2)]. The H_2 and other gases can then be separately processed once they exit the separator mechanism.

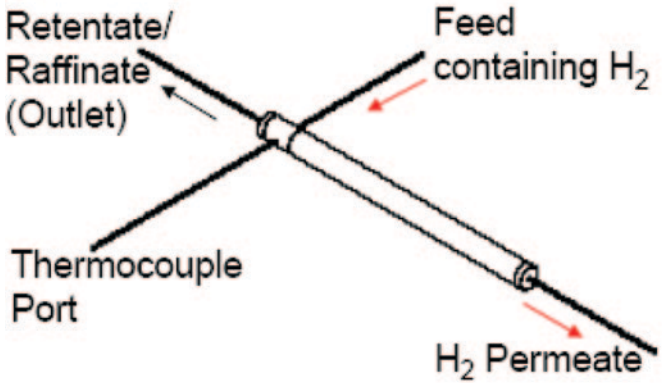


Figure 1: Tubular Membrane Separator

Technology Maturity:

Bench-scale, 0.1 kg/day of H_2

Project Focus:

Palladium-Copper Trimetallic Alloy Membranes

Participant:

United Technologies Research Center

Project Number:

NT43055

NETL Project Manager:

Jason Hissam
Jason.Hissam@netl.doe.gov

Principal Investigator:

Sean Emerson
United Technologies Research Center
emersonsc@utrc.utc.com

Partners:

Metal Hydride Technologies, Inc.
Pall Corporation
Power+Energy, Inc.

Performance Period:

6/15/07 – 6/14/09

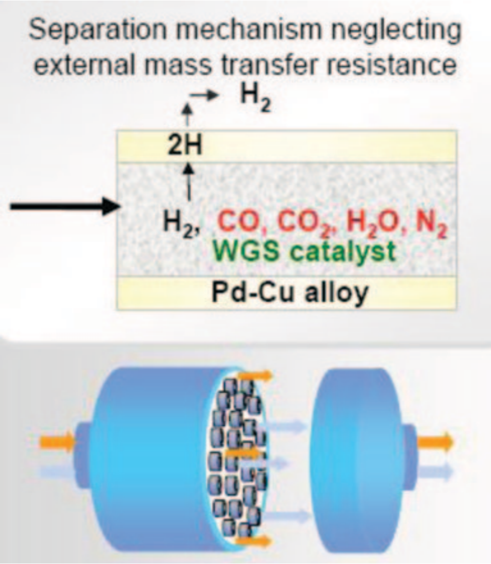


Figure 2: Configuration of Larger Assembly

Table 1: UTRC Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd,Cu	Pd,Cu
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	999,999	999,999
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	61 $ft^3ft^{-2}h^{-1}$ for a feed containing 100 psig H_2 and 100 psig N_2	200 $ft^3ft^{-2}h^{-1}$
	Temperature, °C	350–600 °C	350–600 °C
	Bench-scale testing, hours without significant performance degradation	527 h	527 h
	Pilot-scale testing (if applicable), hours without significant performance degradation	—	—
	Maximum pressure differential achieved without significant performance degradation or failure, bar	13.8 bar	13.8 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	157	157
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	N/A	N/A

Technology Advantages

A PdCu alloy-based CO_2 capture membrane is able to better withstand the corrosion and wear associated with membranes constructed of other materials. Less corrosion means the membrane does not need to be replaced as often, resulting in a lower overall operating cost for the power plant. The PdCu alloy also has a stronger resistance to sulfur compared to traditional membranes, resulting in an improved CO_2 capture efficiency.

R&D Challenges

Tests have shown that the fcc PdCu alloy produced by Power+Energy is capable of meeting all of the program goals, except the H_2 flux target. The UTRC ternary alloy tubes tested to date have not been able to exceed the fcc PdCu alloy flux, primarily due to surface compositional variations. Work is in progress to identify ways to change the surface properties of the tubes.

Results To Date/Accomplishments

The PdCu alloy separators were tested for their H_2 separation performance and the membranes have not yet met all of the DOE 2010 targets. The highest H_2 flux obtained in these experiments was 61.03±0.01 $ft^3h^{-1}ft^{-2}$ at a feed pressure of 7.8 atm [100 pounds per square inch gauge (psig)]. The alloy has not yet met the H_2 flux goal of 200 $ft^3h^{-1}ft^{-2}$. Tests also showed that the alloy's sulfur resistance exceeded the project's designated target of 20 parts per million by volume (ppmv). The membranes themselves are still costly to make compared to the desired cost of use on the commercial scale, and they still do not meet the required average lifespan of three years. Overall, the PdCu alloy testing has successfully met performance requirements for operating temperature (350–600 °C), sulfur tolerance (20 ppmv), operating pressure [27 atm (400 psi) max], CO tolerance, and the production of at least 99.5% pure H_2.

In addition:

- Initial technical and economic models are complete.
- Advanced membrane property simulations by atomistic and thermodynamic modeling calculations are complete.
- Hydrogen solubility tests using various alloys for 6–12 separators and H_2 permeability performance tests are complete.

Next Steps

- Conduct a durability study on the Pd alloy membrane separators in a high-pressure reformer test rig.
- Continue to work with Power+Energy to develop and test better ternary alloy tubes for use in the new hydrogen separator units.
- Complete revisions to the technical and economic models to better define the feasibility of using these membranes on an industrial scale.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

NOVEL HYDROGEN PURIFICATION DEVICE INTEGRATED WITH PEM FUEL CELLS

Technology Maturity:

Bench-scale, 80 kg H_2/day

Project Focus:

Palladium Alloy Membranes

Participant:

Praxair, Inc.

Project Number:

NT43054

NETL Project Manager:

Arthur L. Baldwin
Arthur.Baldwin@netl.doe.gov

Principal Investigator:

Joseph Schwartz
Praxair, Inc.
Joseph_Schwartz@praxair.com

Partners:

Boothroyd-Dewhurst
Colorado School of Mines

Performance Period:

6/1/07 – 5/31/10

Primary Project Goals

Praxair is developing a palladium (Pd) alloy membrane capable of concentrating carbon dioxide (CO_2) effluent from technologies, such as coal gasification plants, by efficiently removing high purity hydrogen (H_2) for subsequent use as a fuel.

Technical Goals

- Develop simulation models to predict H_2 flux based on membrane composition.
- Design a Pd membrane capable of operating at lower than typical temperatures.
- Develop the necessary membranes, seals, and other required components for a cost-effective H_2 purification device.
- Research and select a suitable substrate material that compliments the membrane's thermal expansion properties.
- Develop production practices capable of producing consistently high-quality membrane substrates at low cost.

Technical Content

Development of a Pd alloy membrane capable of operating at lower temperatures to efficiently separate H_2 at low cost from various sources, including synthesis gas (syngas) from coal gasification units. The removal of H_2 from syngas would result in a stream of concentrated CO_2 ready for further purification and sequestration.

A porous ceramic substrate that has graded porosity has been produced. This grading permits the coating of the microporous surface without significant defects while the rest of the tube has open porosity that poses minimal resistance to flow. The Pd alloy coating is achieved by use of the electroless plating method.

Preliminary results have shown that the Pd alloy membranes tested maintain structural integrity after several periods of thermal cycling, which is an important attribute for use in processes where process temperatures are not constant, such as coal gasification.

Several tests have been completed in order to determine H_2 flux through the membrane at various pressures and temperatures. It was found that at 225 °C and 0.7 atm [10 pounds per square inch (psi)], the flux is approximately 40 scfh/ft^2, increasing with both temperature and pressure up to 400 °C and 4.8 atm (70 psi) where the flux was approximately 300 scfh/ft^2. This demonstrates the membrane's stability at both low and high temperatures, making it a versatile product.

In order to maximize efficiency, a model of H_2 transport through the membrane has been developed. All steps of the entire process are considered in the model, which is used to determine the rate determining step for different membrane compositions and thicknesses. This model will be used to provide guidance for alloy selection and for optimizing membrane properties.

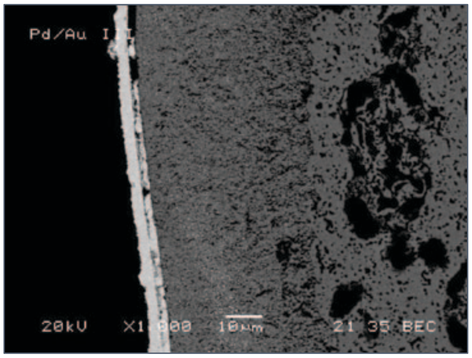


Figure 1: Image of Pd-Au Structure

Table 1: Praxair Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd, Pd-Au, Pd-Ru, Pd-Au-Ru, Pd-Ag, Pd-Cu	Pd, Pd-Au, Pd-Ru, Pd-Au-Ru, Pd-Ag, Pd-Cu
	Materials of fabrication for support layer (if applicable)	Modified ZrO_2	Modified ZrO_2
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	>100	>1,000
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	965 scfh/ft^2 at 400 °C and 200 psi 134 scfh/ft^2 at 400 °C and 20 psi	1,000 150
	Temperature, °C	225	200
	Bench-scale testing, hours without significant performance degradation	264 with planned shutdown	250
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	168
	Maximum pressure differential achieved without significant performance degradation or failure, bar	14	14
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	N/A	3.07
	Pressure drop, bar	N/A	14
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	H_2 purity, %	N/A	N/A

Technology Advantages

Palladium alloy membranes have:

- High structural stability at both high and low temperatures and through thermal cycling.
- High flux and selectivity.
- Low production costs.

R&D Challenges

- Structural failure occurs for Pd-gold (Au) membranes at 200 °C.
- Ethylenediaminetatraacetic acid (EDTA) has been found to remain in the membrane after completing the plating bath, producing carbon contamination and compromising performance.
- Production of the substrate by protrusion produces defects that are difficult to repair.

Results To Date/Accomplishments

- Economic analysis based on technical work done in Phase I and Phase II indicates the expected cost for the membrane purifier will be lower than the cost of alternative purification methods.
- A Pd-ruthenium (Ru) membrane had a flux of 965 scfh/ft^2 at 200 psi and 400 °C.
- A method to produce substrate tubes by extrusion was developed. Extrusion allows for larger substrates to be produced and for larger quantities of substrates to be produced.
- A model was developed to determine alloy structures using cluster expansion and a model has been developed to calculate flux based on all steps of the overall process; when combined, the models will assist in finding potential candidate alloys to synthesize and test.
- A multi-tube prototype reactor has been designed and is currently being built with testing scheduled for later this year.

Next Steps

Perform mixed gas permeation tests with H_2, carbon monoxide (CO), CO_2, steam (H_2O), methane (CH_4), and nitrogen (N_2).

Available Reports/Technical Papers/Presentations

"Novel Hydrogen Purification Device Integrated with PEM Fuel Cells." http://www.netl.doe.gov/technologies/hydrogen_clean_fuels/refshelf/presentations/2008Reviews/Praxair-NETL%20Review%20080429.pdf

COMPOSITE PD AND PD ALLOY POROUS STAINLESS STEEL MEMBRANES FOR HYDROGEN PRODUCTION AND PROCESS INTENSIFICATION

Primary Project Goals

Worcester Polytechnic Institute (WPI) is developing an advanced synthesis gas (syngas) cleanup system and an integrated, cost-effective, hydrogen (H_2) production and separation process using a unique H_2 separation composite palladium (Pd) and alloy membrane for water gas shift (WGS) reactors. WPI is also developing advanced technologies that offer the potential to consolidate two or more unit processes/units, such as gas separation processes in one module for process intensification, which would be integrated downstream of a coal gasification system designed to produce a pure stream of H_2 with high-pressure carbon dioxide (CO_2) for sequestration.

Technical Goals

- Synthesis of composite Pd and Pd/alloy porous Inconel membranes for WGS shift 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 (R&D) of advanced gas clean-up technologies for sulfur removal to reduce the sulfur compounds to <2 parts per million (ppm) (Sub, ARI).
- Development of a systematic framework towards process intensification to achieve higher efficiencies and enhanced performance at a lower cost.

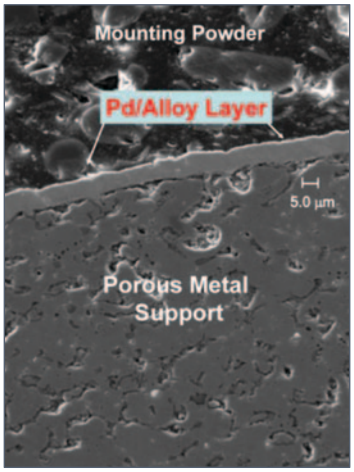


Figure 1: Illustration of WPI's Pd/Alloy Layer

- 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 Content

WPI's unique, patented technology to synthesize robust composite thin Pd and Pd/alloy membranes on porous sintered metal substrates uses an electroless plating process to produce membranes that are stable in the range of 300–450 °C. In addition, the novel aspects of WPI's membrane technology can be summarized as follows:

Technology Maturity:

Bench-scale (½′′ OD, 2.5′′L), 231 scf H_2/day at ~450 °C, $\Delta P = 100$ psi ($P_{low} = 15$ psia)

Pilot-scale (1′′ OD, 6′′L), 201 scf H_2/day at ~450 °C, $\Delta P = 15$ psi ($P_{low} = 15$ psia)

Project Focus:

Palladium-Based Membranes

Participant:

Worcester Polytechnic Institute

Project Number:

NT43058

NETL Project Manager:

Daniel Driscoll
Daniel.Driscoll@netl.doe.gov

Principal Investigator:

Yi Hua Ma
Worcester Polytechnic Institute
yhma@wpi.edu

Partners:

Adsorption Research, Inc.

Performance Period:

5/7/07 – 5/6/10

- It is made with a patented novel intermetallic diffusion barrier to prevent loss of permeance at high temperatures.
- It is plated on a porous metal support for mechanical strength at high pressures, low Pd/alloy layer thickness, and good chemical resistance to the feed gases.
- It is made of Pd/alloys that avoid H_2 embrittlement and crack formation during cycling.
- It is scalable and modular to accommodate small to large diameter and length tubular dimensions by connecting sections with commercial welding techniques.
- It can be easily integrated into a WGS reactor to effect one-step H_2 production from coal gas at small to large scales.

Further refinement and/or advancement of the aforementioned fabrication approaches and synthesis techniques were successfully reported in the quarterly progress reports submitted to DOE.

Table 1: WPI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd	Pd/Au
	Materials of fabrication for support layer (if applicable)	PSS-316L, PSS-310, Inconel-625	PSS-316L, PSS-310, Inconel-625
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	∞	∞
	Type of selectivity measurement (ideal or mixed gas)	Ideal	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units (scfh/ft^2-psi at ΔP = 100 psi H_2 partial pressure with P_{low} = 15 psia)	Bench scale: 3.59 at 450 °C Pilot scale[1]: 2.91 at 450 °C	DOE 2015 Target: 3
	Temperature, °C	300–450	250–500
	Bench-scale testing, hours without significant performance degradation	3,550	N/A
	Pilot-scale testing (if applicable), hours without significant performance degradation	850	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	14	N/A
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3 (for ½′′ OD, 2.5′′ L or 1′′ OD, 6′′ L assemblies)	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	CO_2 purity, %, of the retentate stream (>99.9% hydrogen purity at the permeate side)	80.3% (at feed mixed-gas: 37.1% CO_2, 1.2% CO and 61.7% H_2 at 450 °C, 212 psia, GHSV of 1,069 h^{-1} and 92.6% H_2 recovery); 83.5% (at feed mixed-gas: 10% CO_2, 23% CO, 22% H_2 and 45% H_2O at 450 °C, 212 psia, GHSV of 4,497 h^{-1}, 83.2% H_2 recovery and 95% CO conversion)	
	Other contaminants, % CO (feed gas: 10% CO_2, 23% CO, 22% H_2 and 45% H_2O at 450 °C, 212 psia, GHSV of 4,497 h^{-1}, 83.2% H_2 recovery and 95% CO conversion)	2.9% at the retentate (dry basis) 0% at the permeate	N/A

Note:

1. Computed pressure normalized flux. Experiments were conducted at a ΔP = 15 psi H_2 partial pressure (P_{low} = 15 psia) due to the large membrane surface area and feed hydrogen demand.

Other Membrane Parameters

Contaminant Resistance: Pd/gold (Au) and Pd/copper (Cu) alloy membranes provide some resistance to hydrogen sulfide (H_2S) and also regenerable.

Flue Gas Pretreatment Requirements: Pressure Swing Adsorption (PSA) for removal of sulfur compounds (Sub, ARI).

Waste Streams Generated: None.

Technology Advantages

The H_2 separation membrane can deliver CO_2 at high-pressure, significantly reducing compression costs associated with transporting the CO_2 and recompression for sequestration. The membrane also reduces the steam requirement associated with a traditional WGS reactor, thus improving overall plant efficiency. WPI's unique Pd alloy membranes provide high fluxes, proved high selectivity of separation, provide the ability to operate at temperatures around 300–450 °C, and allow high-purity H_2 production from the WGS membrane reactor. In addition, by combining reaction, separation, and purification in a single-unit operation, the Pd/alloy-based membrane reactor is markedly more efficient than the conventional technology and also economical by combining the high- and low-temperature shift reactors and preferential oxidation reactor, as well as the H_2 separator (i.e., PSA), into a single-unit operation, allowing for process intensification.

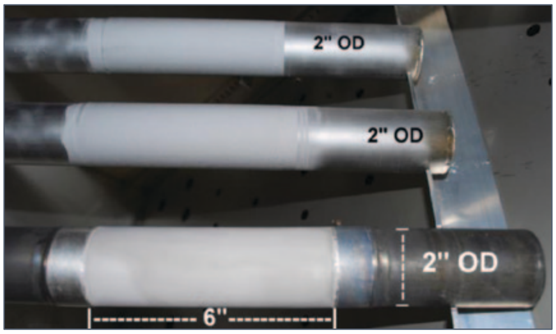


Figure 2: WPI Pd/Inconel H_2 Separation Membranes

R&D Challenges

- The formulation and synthesis of defect-free membrane materials, which are resistant to sulfur.
- Long-term selectivity stability.
- Support metals with uniform pore size distribution and minimum mass transfer resistance.

Results To Date/Accomplishments

- Achieved excellent long-term H_2/helium (He) selectivity stability of essentially infinite over a total testing period of ~3,550 hours (>147 days) at 300–450 °C and at a DP of 15–100 pounds per square inch (psi) [P_{low} = 15 pounds per square inch absolute (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 30–90 days.
- Flux of ~359 scfh/ft^2, which exceeded DOE's 2010 and 2015 H_2 flux targets [T = 442 °C and DP of 100 psi (with P_{low} = 15 psia)].
- Conducted an additional ~3,000 hours of mixed gas permeation experiments [61.7% H_2, 37.1% CO_2 and 1.2% carbon monoxide (CO) with and without 19% steam].
- Reduced the number of synthesis steps for the large-scale 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 catalytic membrane reactor (CMR) operated at ~350 °C, ΔP = 200 psi (P_{low} = 15 psia) $H_2O/CO = 1.44$ and $GHSV_{stp} = 150\ h^{-1}$, exceeding equilibrium conversion of 93.4% and traditional packed bed conversion of 92.7%.

- Successfully completed steady-state MSR and WGS reaction modeling studies and initiated process intensification analysis.
- Successfully completed unsteady-state WGS reaction modeling studies and implemented process control strategies.
- Successfully completed a two-dimensional model for WGS tube and shell membrane reactors.
- Successfully used the two-dimensional model to calculate CO conversion and H_2 recovery for different configurations of MR integration into integrated gasification combined cycle (IGCC) plants.
- Completed capital and operation and maintenance costs of an IGCC-MR plant.
- Completed net present value (NPV) analysis of IGCC, IGCC-PBR, IGCC-MR, and SC-PC plants.
- Completed property and isotherm measurements for the selected adsorbents (Sub, ARI).
- Completed the PSA system construction and initiated PSA testing at 200 °C and a feed pressure of 200 psia (with $P_{low} = 1$ atm) (Sub, ARI).

Next Steps

Since the grant will be completed on May 6, 2011, the planned activities will be in conjunction with the grant, which are listed in the following:

- Prepare thin and stable composite pure Pd membranes on 1” OD PSS 316L and Hastelloy supports.
- Characterize such membranes in pure hydrogen atmospheres and in WGS reaction conditions.
- The most stable membranes will be sent to MTR for their integration in the skid module.
- Continue equipment preparation for coating deposition on tubular membrane anticipated for next performing period at T3 facilities.
- In the next project performing period, conduct DOE Test 2A (simulated effluent of WGS reactor) on MembraGuard-coated Pd membrane to further confirm stability under WGS reaction conditions.
- Membranes will be sent to T3 so that the H_2S protective coating will be deposited. Such membranes will be tested in sulfur conditions at WPI and then at National Carbon Capture Center (NCCC) under syngas atmospheres.
- The Phase I membrane module skid will be assembled and shipped to NCCC.
- A Phase II membrane reactor module will be fabricated.
- Mounting and leaks testing of the WGS reactor at WPI.
- Pure nitrogen and pure hydrogen tests will be performed in the WGS reactor at WPI in order to reproduce the experimental data obtained with the same membranes in other devices already present in the WPI laboratories.
- Nitrogen-hydrogen mixtures experiments at different operative conditions (i.e., different temperatures, hydrogen compositions, and feed flow rates) in the presence of the catalytic bed to perform fluid dynamic analysis and to esteem the mass transport coefficients and the relationship between the dimensionless number characteristic of the system. This analysis can be used in the future to model, in a more accurate way, the behavior of the system in the presence of the WGS reaction.

Available Reports/Technical Papers/Presentations

Journal Articles:

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

Chen, Chao-Huang and Ma, Yi Hua, "The Effect of H_2S on the Performance of Pd and Pd/Au Composite Membrane," 362(1-2), 535–544 (2010).

Pomerrantz, N., Ma, Y. H., "Novel Method for Producing High H_2 Permeability Pd Membranes with a Thin Layer of the Sulfur Tolerant Pd/Cu fcc Phase," J Memb Sci., 370, 97–108 (2011).

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," Accepted for Publication.

Augustine; Alexander Sullivan, Kazantzis, Nikolaos K., Ma, Yi Hua, "High pressure palladium-membrane reactor for the high-temperature water-gas shift reaction International Journal of Hydrogen Energy," International J of Hydrogen Energy, Accepted for publication.

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

Chen, C. H. and Ma, Y. H., "The Effect of H_2S on the performance of Pd and Pd/Au composite membrane," Submitted to the **Journal of Membrane Science**.

Pomerantz, N.; Payzant, E.A.; and Ma, Y.H. "*Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication*," **AIChE Journal**, In press.

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

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

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 (2009) 430–438.

Conference Proceedings:

Ayturk, M. E. and Ma, Y.H. "*Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability.*" **Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.**, 55(1) (2010).

Chen, C. H. and Ma, Y. H., "*Effect of H_2S concentration on hydrogen permeance of a composite Pd/Au hydrogen separation membrane prepared by galvanic displacement*," **Preprint in the Proceedings of 239th ACS Annual Meeting**, March 21–25, 2010, San Francisco, CA, USA.

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

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

Chen, C. H. and Ma, Y. H., "*Characterization of sulfur resistance of Pd/Au hydrogen separation membranes*," Extended abstract in the **Proceedings of the 2008 AIChE Annual Meeting**, November 16–21, 2008, Philadelphia, PA, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "*The effect of* H_2S *on the long-term stability of Pd/Cu membranes and the characteristics of* H_2S *poisoning of electroless deposited Pd,*" Extended abstract in the **Proceedings of the AIChE Annual Meeting 2008**, November 16–21, 2008, Philadelphia, PA, USA.

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. Extended abstract in the **Proceedings of the 10th Intl. Conf. on Inorganic Membranes (ICIM10)**, (2008) Tokyo, Japan.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement," Preprint in the **Proceedings of 234th ACS Annual Meeting**, August 19–23, 2007, Boston, MA, USA.

Pomerantz, N. and Ma, Y.H. "*Effect of* H_2S *poisoning of Pd/Cu membranes on* H_2 *permeance and membrane morphology*," Extended abstract in the **Proceedings of the ACS 234th National Meeting and Exposition**, August 19–23, 2007, Boston, MA, USA.

Presentations:

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

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 DC, USA.

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.

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.

Koc, Reyyan, Kazantzis, Nikolaos and Ma, Yi Hua, "A Process Dynamic Modeling and Control Framework for Performance Characterization and Enhancement of Pd-Based Membrane Reactors," Session: on Membranes for Hydrogen Purification, 10th AIChE Annual Meeting, November 7–12, 2010, Salt Lake City, UT, USA.

Koc, Reyyan, Kazantz, Nikolaosis and Ma, Yi Hua, "A Process Modeling Framework for Performance Assessment of Pd-Based Water-Gas Shift Membrane Reactors," Oral presentation, Session: on Membrane Reactors, AIChE 2010 Annual Meeting, November 7–12, 2010, Salt Lake City, UT, USA.

Augustine, Alexander S., Ayturk, M. Engin and Ma, Yi Hua, "Composite Palladium Membrane Reactor for Hydrogen Production with Syngas Feed," Session on Membranes for Energy Applications, Joint Meeting of North American Membrane Society Annual Meeting and 11th International Conference on Inorganic Membranes, July 17–22, 2010, Washington, DC, USA.

Chen, Chao-Huang and Ma, Y. H., "The Effect of Au Content in Composite Pd/Au Membranes Prepared by Galvanic Displacement On Hydrogen Permeance and H_2S Resistance," Session on Membranes for Hydrogen Purification, AIChE 2010 Annual Meeting, November 17–22, 2010, Salt Lake City, UT, USA.

Ayturk, M. E. and Ma, Y.H. "*Hydrogen Production via Composite Palladium Membranes with Long-Term Selectivity Stability*," To be presented at the **ACS Spring National Meeting and Exposition**, March 21–25, 2010, San Francisco, CA, USA.

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

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

Ayturk, M. E. and Ma, Y.H. "*Long-Term Selectivity Stability and High-Pressure Mixed Gas Hydrogen Permeation Testing of Composite Pd/Inconel Membranes*." Presented at the **AIChE Annual Meeting**, November 8–13, 2009, Nashville, TN, USA.

Augustine, A. S.; Ayturk, M.E.; Kazantzis, N. and Ma, Y. H. "*Palladium Membrane Reactor for Water Gas Shift Reaction*." Presented at the **AIChE Annual Meeting**, November 8–13, 2009, Nashville, TN, USA.

Ma, Y. H., Ayturk, M.E., Augustine, 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.

Ayturk, M. E. and Ma, Y. H., "*Defect-Free Composite Pd Membranes with High Temperature Long-Term Stability*," Presented at the **2008 AIChE Annual Meeting**, November 16–21, 2008 Philadelphia, PA, USA.

Chen, C. H. and Ma, Y. H., "Characterization of sulfur resistance of Pd/Au hydrogen separation membranes," Presented at the **2008 AIChE Annual Meeting**, November 16–21, 2008, Philadelphia, PA, USA.

Pomerantz, N.; Payzant, E.A. and Ma, Y.H. "*Isothermal Solid-State Transformation Kinetics Applied to Pd/Cu Alloy Membrane Fabrication*," Presented at the **AIChE Annual Meeting 2009**, Nashville, TN, USA, November 8–13, 2009.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "*The effect of* H_2S *on the long-term stability of Pd/Cu membranes and the characteristics of* H_2S *poisoning of electroless deposited Pd*," Presented at the **AIChE Annual Meeting 2008**, November 16–21, 2008, Philadelphia, PA, USA.

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*," Presented at the **10th International Conference on Inorganic Membranes (ICIM10)**, August 18–22, 2008, Tokyo, Japan.

Ayturk, M. E., Kazantzis, N.K. and Ma, Y. H., "*Modeling and Performance Assessment of Pd- and Pd/Alloy-based Catalytic Membrane Reactors for Hydrogen Production*," Presented at the **International Congress on Membranes and Membrane Processes (ICOM 2008)**, July 12–18, 2008, Honolulu, HI, USA.

Pomerantz, N.; Shaw, E. and Ma, Y.H. "XPS studies of H_2S poisoned Pd deposits and the implications on Pd membrane performance." Presented at the **International Congress on Membranes and Membrane Processes (ICOM 2008)**, July 12–18, 2008, Honolulu, HI, USA.

Ma, Y. H., Kazantzis, N., Ayturk, M. E., Pomerantz, N. and Chen, C.-H., "*Composite Pd and Pd/alloy Porous Stainless Steel Membranes for Hydrogen Production, Process Intensification and* CO_2 *Sequestration,*" Presented at the **2008 NHA Annual Hydrogen Conference and Expo: "Ramping up Commercialization,"** March 30-April 03, 2008 Sacramento, CA, USA.

Chen, C. H. and Ma, Y. H., "Permeation of composite Pd/Au hydrogen separation membrane prepared by galvanic displacement," Presented at the **2007 ACS Annual Meeting**, August 19–23, 2007 Boston, MA, USA.

Pomerantz, N. and Ma, Y.H. "Effect of H_2S poisoning of Pd/Cu membranes on H_2 permeance and membrane morphology." Presented at the **ACS 234th National Meeting and Exposition**, August 19–23, 2007, Boston, MA, USA.

Chen, C. H. and Ma, Y. H., "Preparation of Pd/Au hydrogen separation membrane by galvanic displacement," Presented at the 2007 **North American Membrane Society Annual Meeting**, May 13–16, 2007, Orlando, FL, USA.

CARBON MOLECULAR SIEVE MEMBRANE AS A TRUE ONE-BOX UNIT FOR LARGE-SCALE HYDROGEN PRODUCTION

Primary Project Goals

Media and Process Technology, Inc. is developing a one-box process for hydrogen (H_2) production based on carbon molecular-sieve (CMS) membranes. Gas cleanup will be combined with a water gas shift membrane reactor (WGS-MR) in a single processing unit.

Technical Goals

- Develop and test a one-box (gas cleanup and the WGS-MR), H_2 production process that integrates the four major technology components for synthesis gas (syngas) cleanup and conditioning into a single unit.
- Demonstrate the one-box process at bench-scale at the University of Southern California (USC); followed by a single-tube slipstream test at the Power Systems Development Facility (PSDF). Upon successful completion of this testing, a pilot-scale unit will be developed and tested with a stream from a gasifier.
- A mathematical model will be verified with the bench- and pilot-scale test results, and then used to conduct a techno-economic analysis.
- Evaluate the CMS membrane deposited on a ceramic substrate for candidate selection in future full-scale demonstrations.

Technical Content

The one-box process under investigation combines the gas cleanup and WGS-MR for H_2 production. Figure 1 displays how the one-box process will be incorporated following the gasification of a coal-based feedstock. Syngas cleaning will consist of a water quench, particulate removal, WGS, and CMS membrane to produce an H_2 gas stream and a carbon dioxide (CO_2) stream ready for sequestration. The one-box process will remove the sulfur and other contaminants from the H_2 product stream via the molecular sieving mechanism of the H_2-selective CMS membrane. If a high-purity H_2 product is necessary, an optional palladium (Pd) membrane can be installed for post-treatment of this sulfur-removed H_2 product stream. Table 1 compares the one-box process to a conventional H_2 purification processes.

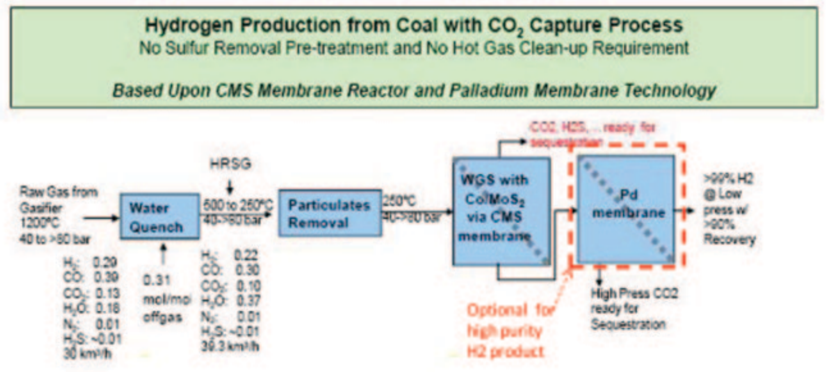


Figure 1: Incorporation of One-Box Process Following the Gasification of a Coal-Based Feedstock

Technology Maturity:

Bench-scale

Project Focus:

Carbon Molecular Sieve Membranes

Participant:

Media and Process Technology, Inc.

Project Number:

NT43057

NETL Project Manager:

John Stipanovich
John.Stipanovich@netl.doe.gov

Principal Investigator:

Paul K.T. Liu
Media and Process Technology, Inc.
pliu@mediaandprocess.com

Partners:

Power Systems Development Facility
University of Southern California

Performance Period:

5/2/07 – 5/1/12

Media and Process Technology, Inc. — Carbon Molecular Sieve Membranes

Table 1: One-Box Process Versus a Conventional Hydrogen Purification Processes

Performance Criteria	Conventional WGS with PSA	One-Box Process
H_2 product pressure, psig	High pressure, 200–400	Low pressure, e.g., 5 to >100 psig
H_2 product purity, %	>99.9	>99.9
H_2 product yield, %	60 to 80	>90
CO conversion, %	90 to 97	>97
H_2O/CO ratio for WGS	3–4	~1.5
CO_2 Stream Pressure, psig	Low pressure, 5–10	High pressure, i.e., gasifier pressure

Within the one-box unit, a colbalt sulfide (CoS_2)/molybdenum disulfide (MoS_2) catalyst will be used to perform the WGS reaction. As shown in Figure 2, the CMS membrane will incorporate a candle filter configuration that has a high resistance to hydrogen sulfide (H_2S), which allows the H_2 to permeate through the membrane and create an H_2-rich stream. After the H_2 permeates through the CMS membrane, a CO_2-rich stream will remain outside the membrane at a high pressure ready for transportation.

Figure 2: Candle Filter Configuration for CMS Membrane and Module (pilot scale)

Figure 3 shows the permeance of the membrane under investigation for separation of H_2 and CO_2.

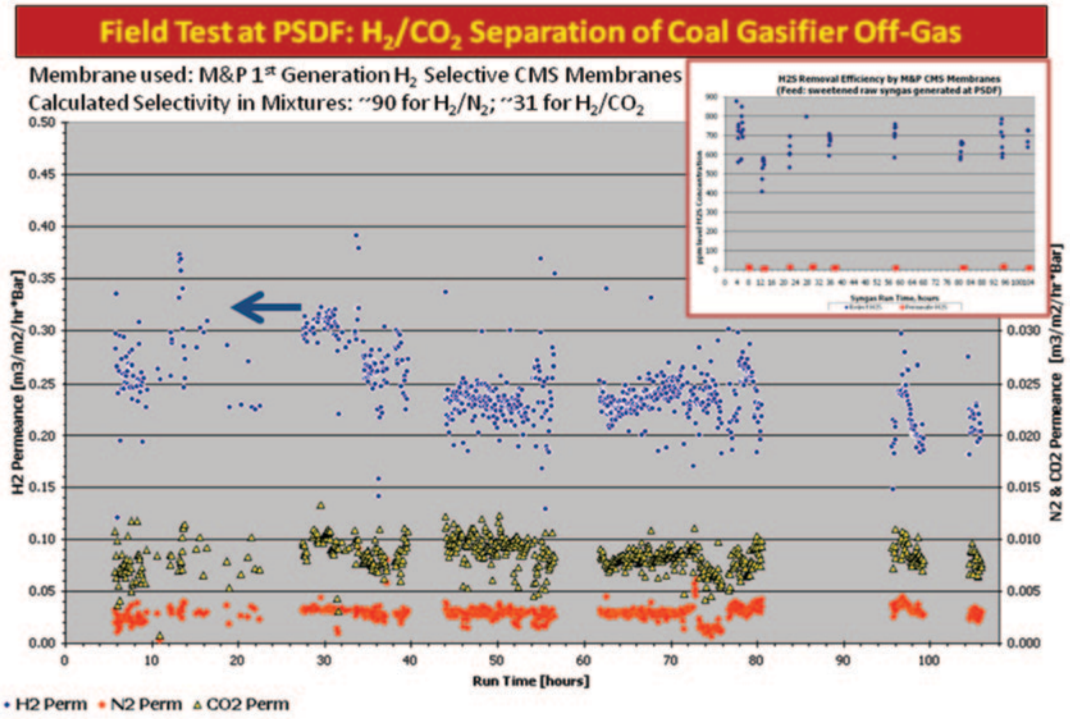


Figure 3: Permeances of Membranes for Separation of H_2 and CO_2 from Coal Gasifier Off-Gas Generated at PSDF

Table 2: Media and Process Technology Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Carbon	Carbon
	Materials of fabrication for support layer (if applicable)	Ceramic	Ceramic
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	25–30 (50 to >100 for H_2/CO)	25–30 (50 to >100 for H_2/CO)
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	925 GPU	1,295 FPU
	Temperature, °C	250	>600
	Bench-scale testing, hours without significant performance degradation	>500	>1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	100	>250
	Maximum pressure differential achieved without significant performance degradation or failure, bar	>50	>50
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube in candle filter configuration	Shell-and-tube in candle filter configuration
	Packing density, m^2/m^3	250	500
	Pressure drop, bar	<0.1	<0.1
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	$\$1,000/m^2$	$<\$500/m^2$
Product Quality	CO_2 purity, %	80	85
	N_2 purity, %	2	2
	Other contaminants, %	18	13
Process Performance	Electricity requirement, kJ/kg CO_2	Minimal (theoretical 0)	Minimal (theoretical 0)
	Heat requirement, kJ/kg CO_2	Minimal (theoretical 0)	Minimal (theoretical 0)
	Total energy (electricity equivalent), kJ/kg CO_2	Minimal (theoretical 0)	Minimal (theoretical 0)

Technology Advantages

- Produces a high-pressure CO_2 stream for sequestration.
- Achieves nearly complete carbon monoxide (CO) conversion, increases H_2 recovery from the gasification stream.
- Reduces the steam required for the WGS reaction, improving plant efficiency.
- Removes sulfur contaminants and uses an existing Pd membrane to filter >99.9% H_2.

R&D Challenges

- Scaling the one-box process from laboratory scale to larger scales.
- The one-box process produces a H_2 stream product at a high pressure.
- Increase H_2 recovery rate at a high purity hydrogen.

Results To Date/Accomplishments

- Performed a membrane performance field test for >100 hours using a slipstream test at the PSDF facility.
- Completed an evaluation of the CoS_2/MoS_2 catalyst for WGS of simulated coal gasifier off-gas.
- Established the separation efficiency of key contaminants in a simulated stream.
- Experimentally determined the performance of the one-box process in a bench-scale unit.
- Evaluated the outside coated CMS membrane and compared its performance with the existing membrane.

Next Steps

- Fabricate the ceramic membrane/module for the pilot testing unit and conduct an examination analysis of the ceramic membrane.
- Refine the mathematical model of the one-box H_2 production process from the bench-scale unit.
- Assemble a slipstream testing unit and perform slipstream tests at PSDF.
- Evaluate the performance of the pilot-scale testing unit.
- Complete the simulation, optimization, and economic analysis of the one-box process.
- Assess the ceramic-based, one-box H_2 production unit.

Available Reports/Technical Papers/Presentations

Hydrogen Production from Syngas, Using a Catalytic Membrane Reactor, Mitra Abdollahi, Hyun Hwang, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, NAMS 2009.

Integrated One Box Process for Hydrogen Production From Syngas, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, AIChE 2009.

Process Intensification in Hydrogen Production From Syngas, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Muhammad Sahimi, Theodore T. Tsotsis, ISCRE 2010.

Hydrogen Production from Coal-Derived Syngas Using a Catalytic Membrane Reactor-Based Process, Mitra Abdollahi, Jiang Yu, Paul K.T. Liu, Rich Ciora, Muhammad Sahimi, Theodore T. Tsotsis, Journal of Membrane Science, submitted.

HIGH PERMEABILITY TERNARY PALLADIUM ALLOY MEMBRANES WITH IMPROVED SULFIDE AND HALIDE TOLERANCE

Primary Project Goals

Southwest Research Institute (SwRI) is employing an iterative modeling, rapid fabrication, and testing approach to develop and demonstrate an ultra-thin (<5 micron), durable ternary palladium (Pd)-alloy membrane with excellent resistance to sulfur and halogen attacks while meeting or exceeding the hydrogen (H_2) permeability performance established by DOE. A secondary benefit is to support the process of carbon dioxide (CO_2) gas sequestration.

Technical Goals

- Investigate the performance of a variety of ternary Pd-copper (Cu)-M alloys to identify which experimental alloys show improved H_2 permeance compared to a baseline Pd alloy.
- Develop the necessary methods for the fabrication of high-performance, thin Pd-alloy membranes using advanced physical vapor deposition methods.
- Experimentally determine the H_2 and nitrogen (N_2) permeation rates of the alloys under a range of pressures from 1.3 to11 atm [5–150 pounds per square inch gauge (psig) feed pressure] and temperatures (200–500 °C).
- Characterize the alloy membranes using binary mixture permeation tests, electron microscopy (to observe structure and morphology), X-ray diffraction (for purity of the film and crystal structure), atomic force microscopy (for surface structure), and energy-dispersive X-ray spectroscopy (for alloy composition).
- Test the performance of the alloy membranes in the presence of a single- and multi-contaminant synthesis gas (syngas).

Technical Content

The project team consisting of SwRI, Georgia Institute of Technology (GT), the Colorado School of Mines (CSM), TDA Research, and IdaTech, LLC was focused on developing a robust, poison-tolerant, hydrogen-selective free standing membrane to produce clean hydrogen. The project completed on schedule and on budget with SwRI, GT, CSM, TDA, and IdaTech all operating independently and concurrently. GT has developed a robust platform for performing extensive Density Functional Theory (DFT) calculations for H in the bulk of Pd, binary alloys, and ternary alloys of Pd. In GT's work, the idea of describing the binding sites with a series of well-defined geometric configurations via a cluster expansion (CE) method was introduced. In order to select the best CE model, the Leave One Out (LOO) analysis was introduced. With the CE-LOO analysis, the DFT data sets were taken and models developed that could accurately define the binding sites, these models were then used in subsequent analysis of the solubility and diffusion of H in the bulk of the ternary alloys. SwRI deposited and released more than 160 foils of binary and ternary Pd alloys. There was considerable work on characterizing and improving the durability of the deposited foils using new alloy compositions, post annealing, and ion bombardment. The 10- and 25-µm thick films were sent to CSM, TDA, and IdaTech for characterization and permeation testing. CSM conducted more than 60 pure gas permeation tests with binary and ternary alloy

Technology Maturity:

Bench-scale

Project Focus:

Ternary Palladium Alloy Membranes

Participant:

Southwest Research Institute

Project Number:

NT43056

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

Kent Coulter
Southwest Research Institute
kent.coulter@swri.org

Partners:

Colorado School of Mines
The Georgia Institute of Technology
IdaTech
TDA Research, Inc.

Performance Period:

5/2/07 – 5/1/10

membranes. The Pd-gold (Au) and PdAu-platinum (Pt) membranes exhibited the best performance at temperatures in the range of 423–773 °C, and their performance correlates well with the predictions from GT. TDA completed testing under the DOE testing guidelines on more than 16 membranes; of particular interest is the PdAuPt alloys that exhibited only a 20% drop in flux when sulfur was added to the gas mixture and the flux was completely recovered when the sulfur flow was stopped. IdaTech tested binary and ternary membranes on simulated flue gas streams and experienced significant difficulty in mounting and testing the sputter deposited membranes. IdaTech was able to successfully test PdAu and PdAuPt membranes and saw similar sulfur tolerance to what TDA found.

Table 1: SwRI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd ternary alloys	Pd ternary alloys
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	99.99	99.99
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	H_2-242 scfh/ft^2	H_2-200 scfh/ft^2
	Temperature, °C	400	300–600
	Bench-scale testing, hours without significant performance degradation	250	120
	Pilot-scale testing (if applicable), hours without significant performance degradation	24	120
	Maximum pressure differential achieved without significant performance degradation or failure, bar	6.9	6.9
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate-and-frame	Plate-and-frame
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	4.8	4.8
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	\$16,146/m^2	\$10,764/m^2
Product Quality	CO_2 purity, %	N/A	N/A
	H_2 purity, %	N/A	N/A

Technology Advantages

GT developed a detailed DFT and a heuristic lattice model that is appropriate for rapidly characterizing H solubility and diffusion in the search for new promising alloys for membranes. This approach can be used as an initial tool for screening materials prior to using more expensive experimental investigations. The advanced vapor deposition methods used to construct the Pd-alloy membranes provide unique advantages compared to other membrane fabrication techniques. The high-power, pulsed magnetron sputtering and plasma-enhanced magnetron deposition methods are able to rapidly produce membranes of almost any alloy composition, providing excellent flexibility in terms of the materials and properties used in a membrane. These methods also generate alloy compositions with good uniformity over areas up to 645 cm^2 (100 in^2).

R&D Challenges

The mechanical durability of membranes fabricated using magnetron sputtering are inferior compared to cold rolled membranes, and is it currently not ready for industrial environments.

Results To Date/Accomplishments

- Developed a rigorous strategy for predicting H_2 permeability through ternary alloys using complex calculations.
- Coated more than 160 thin (5–25 micron) membranes of PdCu, PdAg, Pd-ruthenium (Ru), PdAu, Pd-thulium (Tm), PdCu-silver (Ag), PdCuAu, PdCuPt, PdCu-nickel (Ni), PdCuRu, PdCuAu, PdAuAg, and PdAuPt for structural and composition measurements and permeation testing.
- Determined pure gas H_2 and N_2 permeation rates for a range of pressure differentials [1.3–11 atm feed pressure (5–150 psig)] and temperatures ranging from 200 to 500 °C for more than 60 membranes.
- Under DOE specified test conditions, evaluated 16 membranes.
- More than 10 presentations at national and international conferences were made, four papers were published (two additional papers in progress) in technical journals, and three students completed their Ph.D. using results generated during the course of the program.
- The three major findings of program were: (1) the DFT modeling was verified as a predictive tool for the permeability of Pd-based ternary alloys; (2) while magnetron sputtering is useful in precisely fabricating binary and ternary alloys, the mechanical durability of membranes fabricated using this technique are inferior compared to cold rolled membranes and sputtered membranes are not currently ready for industrial environments; and (3) based on both modeling and experimental verification in pure gas and mixed gas environments, PdAu and PdAuPt alloys were found to have the combination of the highest permeability and tolerance to sulfur.
- The program met all the deliverables on schedule and on budget.

Next Steps

- Program completed on December 31, 2010.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.

FABRICATION AND SCALE-UP OF POLYBENZIMIDAZOLE MEMBRANE-BASED SYSTEM FOR PRE-COMBUSTION BASED CAPTURE OF CARBON DIOXIDE

Primary Project Goals

SRI International is developing a high-temperature polymer membrane and designing a membrane module for pre-combustion capture of carbon dioxide (CO_2) from integrated gasification combined cycle (IGCC)-derived synthesis gas (syngas).

Technical Goals

- Design, construct, and test a pre-combustion-based CO_2 capture system (50 kWth) skid using polybenzimidazole (PBI) membranes developed by Los Alamos National Laboratory (LANL).
- Evaluate the effectiveness of the membrane elements for CO_2 separation in relation to permeability and selectivity.
- Perform a techno-economic analysis of an IGCC system employing PBI membranes for carbon capture and sequestration (CCS).

Technical Content

The membrane under development consists of hollow-fiber PBI, which is chemically and thermally stable at temperatures up to 450 °C and pressures up to 55 atm [800 pounds per square inch gauge (psig)]. This characteristic permits the use of a PBI membrane without requiring additional cooling after the water gas shift (WGS) section of an IGCC system including carbon capture. Further gas cooling is not required before the PBI membrane, increasing plant efficiency. In addition, the CO_2 is recovered at high pressure, decreasing CO_2 compression requirements.

PBI-based hollow fibers, as seen in Figure 1 and Figure 2, offer a considerable advantage over stainless steel-coated tubes. They require as much as 24 times less membrane surface area and 305 times less membrane volume when using a 0.1–0.5 micrometer separation layer.

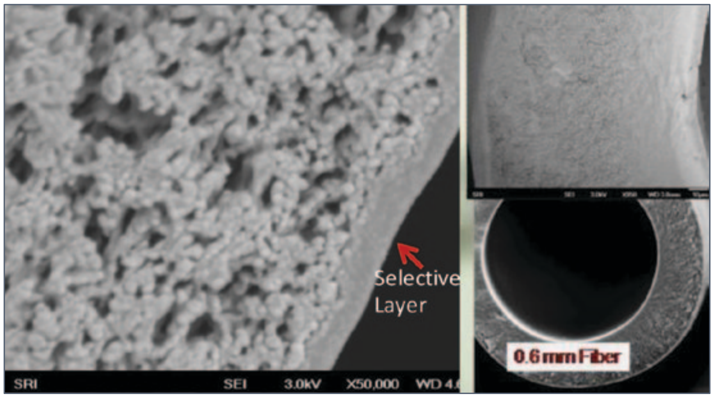


Figure 1: Image of PBI-Based Hollow Fibe Produced at SRI

Technology Maturity:

Prototype, 0.4 tonnes CO_2/day

Project Focus:

High-Temperature Polymeric Membranes

Participant:

SRI International

Project Number:

NT43090

NETL Project Manager:

Robie Lewis
Robie.Lewis@netl.doe.gov

Principal Investigator:

Gopala Krishnan
SRI International
Gopala.Krishnan@sri.com

Partners:

BP
Enerfex
LANL
Visage Energy
Whitefox

Performance Period:

3/30/07 – 3/31/12

The durability of narrow, single-bore, PBI-based hollow fibers has been shown to be considerable, with near constant levels of permeability and selectivity over the course of 330 days while in the presence of hydrogen (H_2), carbon monoxide (CO), methane (CH_4), nitrogen (N_2), CO_2, and hydrogen sulfide (H_2S) at 250 °C.

Figure 2: Image of a Bundle of PBI-Based, Asymmetric Hollow Fibers

Table 1: LANL PBI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	—	—
	Materials of fabrication for support layer (if applicable)	PBI	PBI
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	40	>40
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	130	130
	Temperature, °C	250	250
	Bench-scale testing, hours without significant performance degradation	1,000	1,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	10	20
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Hollow-fiber	Hollow-fiber
	Packing density, m^2/m^3	N/A	2,292
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	N/A	161
Product Quality	CO_2 purity, %	90	90
	N_2 purity, %	N/A	<1
	Other contaminants, %	N/A	<0.01
Process Performance	Electricity requirement, kJ/kg CO_2	N/A	281
	Heat requirement, kJ/kg CO_2	N/A	0
	Total energy (electricity equivalent), kJ/kg CO_2	N/A	281

Other Membrane Parameters

Contaminant Resistance: Sulfur tolerance.

Gas Pretreatment Requirements: No pretreatment of the gas stream from WGS is required.

Waste Streams Generated: No waste stream.

Technology Advantages

- The use of PBI offers several advantages over Selexol and conventional polymeric membranes, including reduced CO_2 compression costs due to the ability to deliver the concentrated CO_2 stream at pressures up to 55 atm (800 psig).
- PBI is thermally stable up to 450 °C and sulfur tolerant.
- Highest demonstrated operating temperature (400 °C) of a polymer-based membrane with permeabilities and selectivities of interest.

R&D Challenges

- Designing and synthesizing materials structure and configuration.
- Obtaining desired selectivity, productivity, chemical resistance, and durability at elevated temperatures and pressures by overcoming the limitations of current state-of-the-art technology.
- Understanding and optimizing mass transfer and the interaction with heat transfer.
- Scale up of the technology from laboratory to larger scales.
- Integration and optimization of systems.

Results To Date/Accomplishments

- Developed an IGCC process simulation model.
- Performed and analyzed several membrane separation scenarios under various temperatures, pressures, and gases, which showed:
  - PBI membrane-based, high-temperature CO_2 separation is competitive with the Selexol system.
  - COE for CO_2 capture may approach the DOE goal under optimized membrane performance.
- Fabricated both single- and multi-bore, hollow-fiber PBI membrane configurations.
- Determined that multi-bore configuration offers increased selective layer area density while single bore provides higher mechanical stability.
- Completed characterization using scanning electron microscope (SEM) and X-ray tomography.
- Identified a sealant for short-term testing.
- Completed permeability measurements with both single- and mixed-gas environments.
- Achieved an H_2 permeability of >100 GPU with an H_2/CO_2 selectivity of 40 at 250 °C. Long-term performance evaluation data-selectivity and H_2 permeance are given in Figure 3.

- Determined that the PBI membrane has a high permeability for steam.
- Determined that PBI hollow-fiber configuration provides the most compact membrane module.
- Established the fabrication of PBI substrate with interconnected pores.
- Performed risk management analysis to identify several system-level questions pertaining to the PBI technology.
- Developed and refined mitigation strategies that considered all stakeholder needs and requirements.
- Completed successful testing of the polymeric-metallic composite membrane in dry gas environments containing H_2, CO_2, CH_4, N_2, CO, and H_2S from 25 to 400 °C.
- Completed successful testing of the polymer-based membrane on fully hydrated natural gas reformate up to 300 °C.

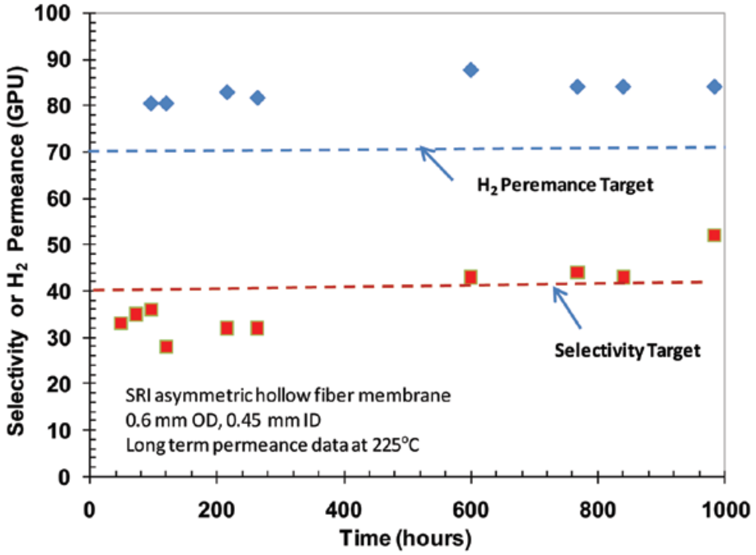


Figure 3: PBI-Based Hollow-Fiber Performance Data

Next Steps

- Complete subcomponent design and evaluation.
- Construct membrane modules using the selected asymmetric hollow fibers fabricated at SRI.
- Integrate the membrane module with commercially available skids, control systems, and connectors.
- Evaluate the complete system.
- Develop feasible approaches for commercializing the technology in the designated markets and sectors, along with possible routes for technology transfer.

Available Reports/Technical Papers/Presentations

Krishnan, Gopala et al., "Fabrication and Scale-up of Polybezimidazole (PBI) Membrane Based Capture of CO_2," 2010 NETL CO_2 Capture Technology Conference, September 16, 2010, Pittsburgh, PA.

Krishnan, Gopala et al., "Simulation of a Process to Capture CO_2 From IGCC Syngas Using a High Temperature PBI Membrane," http://www.sciencedirect.com/science/article/B984K-4W0SFYG-MR/2/a10e288aa794a1a71db6123e6 ddde6c8

DEVELOPMENT OF LOW-COST MEMBRANES FOR $H_2/CO_2/CO$ SEPARATION FOR WGS REACTORS

Primary Project Goals

Grambling State University is developing low temperature bimetallic nanocatalysts for use in the water gas shift (WGS) reaction for hydrogen (H_2) production from a carbon monoxide (CO) and steam mixture, along with development of low-cost metal/ceramic membranes for H_2/carbon dioxide (CO_2) separation.

Technical Goals

- Develop micro/mesoporous ceramic membrane disks, composed of tantalum (Ta)/niobium (Nb) alloys, for optimum H_2 separation.
- Examine the effect of alloying the Ta/Nb ceramic membranes with other metals to reduce H_2 embrittlement and promote cathodic protection.
- Develop cellulose acetate interlayers between two micro/mesoporous ceramic disks for optimum H_2 and CO_2 separation.
- Examine the effects of plasticizers on CO_2 permeability.
- Prepare and optimize nano-bimetallic nickel (Ni)/molybdenum (Mo), cobalt (Co)/cerium (Ce), copper (Cu)/Ni, and iron (Fe)/Mo catalysts supported on mesoporus γ-Al_2O_3 and Al_2O_3/SiO_2 granules for the WGS reaction.
- Develop and demonstrate a prototype reactor based on novel low-cost metal (Ta/Nb)/ceramic and cellulose acetate membranes to separate H_2 and CO_2.
- Examine the performance of Ta/Nb and cellulose acetate/ceramic membranes under WGS conditions.

Technical Content

The WGS will utilize Cu-Ni-Ce/alumina granular nanocatalysts that react CO and steam to produce H_2 and CO_2. Figure 1 represents the chemical reaction inside the WGS as the gas stream is exposed to the catalyst and converts the CO to CO_2. The Cu-Ce catalyst converts approximately 69% of the CO, while Cu-Ce-Ni converts approximately 83% during a 10-hour reaction period.

Table 1 displays different compositions of metal catalysts investigated for promoting the WGS reaction. Four catalyst compositions (rows 3, 4, 9, and 10 in Table 1) are evaluated for high-temperature shift (HTS) reactions with optimum temperature between 350 and 400 °C and six compositions (1, 2, 5, 6, 7, and 8 in Table 1) for low-temperature shift (LTS) reactions with optimum temperatures between 150 and 300 °C obtained using a Gas Phase Dynamic Flow Reactor Study.

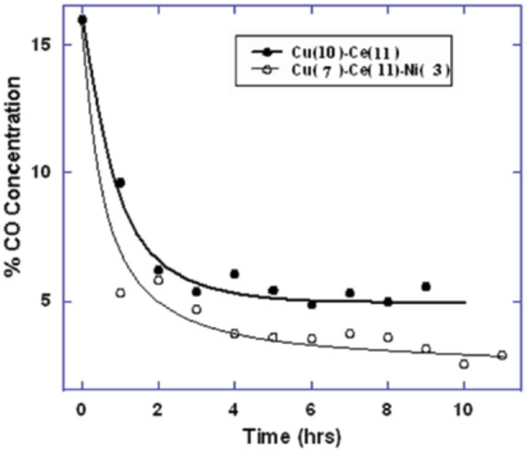


Figure 1: Catalytic Conversion of CO to CO_2

Technology Maturity:

Laboratory-scale

Project Focus:

Catalysts for Use in Membrane Reactors

Participant:

Grambling State University

Project Number:

NT43064

NETL Project Manager:

Daniel Driscoll
Daniel.Driscoll@netl.doe.gov

Principal Investigator:

Seetala V. Naidu
Grambling State University
naidusv@gram.edu

Partners:

Louisiana Tech University

Performance Period:

12/20/06 – 1/1/10

Table 1: Compositions of Metal Catalysts Under Investigation for Promoting WGS Reaction

Catalyst Composition											
CU (%)	NI (%)	Ce (%)	% Metal	$Ni(NO_3)_2$ •$6H_2O$ (g)	Wt. (g)	Wt. CuO (g)	Wt. Cu (g)	Wt. CeO_2 (g)	Wt. Ce (g)	Wt. Fe_2O_3 (g)	Wt Fe (g)
10		11	20.96	0.00	0.00	0.46	0.37	0.52	0.42	0.00	0.00
7	3	11	20.70	0.54	0.11	0.33	0.26	0.48	0.39	0.00	0.00
5	5	11	21.31	0.93	0.19	0.24	0.19	0.49	0.40	0.00	0.00
3	7	11	21.29	1.31	0.26	0.14	0.11	0.48	0.39	0.00	0.00
	10	11	21.32	1.86	0.38	0.00	0.00	0.46	0.38	0.00	0.00
	10	9	19.15	1.80	0.36	0.00	0.00	0.37	0.30	0.00	0.00
	10	6	16.09	1.75	0.35	0.00	0.00	0.24	0.19	0.00	0.00
	10	3	13.04	1.69	0.34	0.00	0.00	0.11	0.09	0.00	0.00
	10		10.00	1.64	0.33	0.00	0.00	0.00	0.00	0.00	0.00
7	9	13	28.39	1.93	0.39	0.35	0.28	0.54	0.45	0.00	0.00
Fe(10%) Ce(11%)			21.05	0.00	0.00	0.00	0.00	0.51	0.41	0.54	0.38

The optimum reaction temperatures obtained from gas-phase flow reactor, and the CO conversion and CO_2 production obtained from a gas-phase batch reactor at optimum temperatures for Ni-Cu-Ce/alumina LTS and HTS catalysts, are summarized in Table 2.

Table 2: Optimum Reaction Temperature, CO Conversion, and CO_2 Production after 13 Hours of Reaction for LTS and HTS Ni-Cu-CE/Alumina Catalysts

Catalyst	Optimum Temp. (°C)	CO conversion (% moles)	CO_2 production (% moles)
Low Temperature Shift (LTS) catalysts			
Ni(10%)Ce(3%)	300	92.72	29.09
Ni(10%)Ce(9%)	250	77.2	61.81
Ni(10%)Ce(11%)	250	73.63	71.81
Ni(10%)Ce(6%)	300	72.72	43.63
Cu(10%)Ce(11%)	200	48.18	62.72
Ni(3%)Cu(7%)Ce(11%)	200	47.09	17.27
High Temperature Shift (HTS) catalysts			
Ni(10%)	400	98.18	17.2
Ni(5%)Cu(5%)Ce(11%)	350	80.09	100.0
Ni(7%)Cu(3%)Ce(11%)	350	59.09	90.9
Fe(10%)Ce(11%)	350	7.27	17.2

After the WGS reaction takes place, the H_2 will be separated from the CO_2 using an outer shell ceramic membrane of Ta/Nb metal that will be used to separate H_2 from the rest of the constituents. A membrane consisting of cellulose acetate (CA) with 75% triethyl citrate plasticizer is used to separate the CO_2. The CA will be located between two mesoporous ceramic disks. Figure 2 shows a blank ceramic disk on the left (a) and the ceramic disk on the right (b) sputter coated with Nb. The metal film coating the disk is approximately 400 nanometers thick and the coatings will be applied through sputtering (physical) techniques or aluminothermic (chemical) methods. The parameters for Ta/Nb membranes are given in Table 3 and those for CA membranes are given in Table 4.

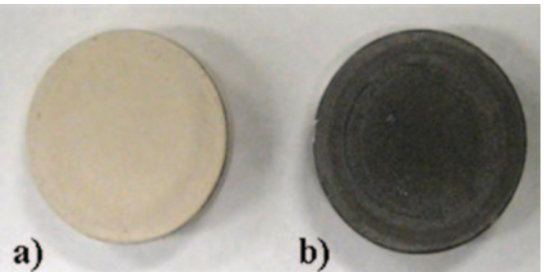


Figure 2: Uncoated and Coated Ceramic Disks

Table 3: Grambling Parameters for Ta/Nb Membranes

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Ta/Nb 400 µm thin films	Ta/Nb 400 µm thin films
	Materials of fabrication for support layer (if applicable)	Ceramic or asbestos	Ceramic or asbestos
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	70%	90%
	Type of selectivity measurement (ideal or mixed gas)	Permeability (indirect)	Permeability (direct)
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	N/A	N/A
	Temperature, °C	350 °C	400 °C
	Pilot-scale testing (if applicable), hours without significant performance degradation	1 week	1 month.
	Maximum pressure differential achieved without significant performance degradation or failure, bar	5 bar	15 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Film	Film
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	<1 bar	<1 bar
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	~$10,000	$4,000
Product Quality	CO_2 purity, %	N/A	N/A
	H_2 purity, %	70% indirect	90% direct

Table 4: Grambling Parameters CA Membrane

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	500 nm	500 nm
	Materials of fabrication for support layer (if applicable)	Cellulose/filter paper	Cellulose/filter paper
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	60%	90%
	Type of selectivity measurement (ideal or mixed gas)	Permeability	Permeability
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	N/A	N/A
	Temperature, °C	25 °C	25 °C
	Pilot-scale testing (if applicable), hours without significant performance degradation	4 days	1 month.
	Maximum pressure differential achieved without significant performance degradation or failure, bar	x bar	x bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Film	Film
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	<1 bar	<1 bar
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	~$500	<$500
Product Quality	CO_2 purity, %	60%	90%
	H_2 purity, %	N/A	N/A

Technology Advantages

Ceramic/asbestos membranes incorporating low-cost metals (Ta/Nb) could lower H_2 production costs.

R&D Challenges

- Lower Ta/Nb H_2 separation efficiencies.
- The WGS reaction time is longer than desired.

Results To Date/Accomplishments

- Prepared the bimetallic Ni/Cu nanoparticles/sol-gel supported Ce promoted catalysts.
- Fabricated Ta/Nb-ceramic and asbestos membranes and studied for H_2 separation.
- Fabricated cellulose acetate-ceramic membranes and studied CO_2 separation.
- Ni(10%)Ce(11%) catalyst was found to be the best WGS catalyst among the LTS catalysts, while Ni(5%)Cu(5%)Ce(11%) was found to be the best among HTS catalysts.

Next Steps

- Design a WGS reactor and complete the catalytic studies.
- Integrate system evaluation using the prototype WGS reactor with H_2/CO_2 separation membranes.

Available Reports/Technical Papers/Presentations

“Water gas shift reaction nano-catalysts for hydrogen production; and metal/ceramic and polymer membranes for $H_2/CO/CO_2$ gas separation,” N. Seetala, U. Siriwardane, and T. Kudale, Invited talk at the International Conference on Green Chemistry and Sustainable Environment, 7–8, July 2010, Tiruchirappalli, India. To be published in the Proceedings.

“Nanoparticle metal oxide (MgO, CaO, and ZnO) heterogeneous catalysts for biodiesel production,” N. Seetala, U. Siriwardane, R. Forester, and R. Talathi, International Conference on Green Chemistry and Sustainable Environment, 7–8, July 2010, Tiruchirappalli, India.

“Positron lifetime/free volume and gas diffusion studies of cellulose acetate membranes with triethyl citrate as plasticizer for drug delivery systems,” N. Seetala, R. Bhandaria, T. Kudaleb, and U. Siriwardane, International Conference - Bangalore India Bio 2010, June 2–4, 2010.

“Nb/Ta Thin Film Coated Micro-Porous Alumina Membranes for Hydrogen Separation from WGS Reaction Products,” N. Seetala, U. Siriwardane, R. Jayasingha, and J. Bass, World Journal of Engineering, Vol. 7 (No. 3), pp. 62–66, 2010.

“Development of Metal (Ta, Nb)/Ceramic and Cellulose Acetate Membranes for Cu-Ni-Ce/Alumina WGS Catalytic Reactor,” N. Seetala, U. Siriwardane, T. Kudal, R. Foreste, and A. Pokhare, ACS Fuel Chemistry Division Preprints 2010.

“Fabrication of cellulose acetate membranes (CA) and their $CO/CO_2/H_2$ permeabilities”, T. V. Kudale, N. V. Seetala, and U. Siriwardane, LAS Meeting, Alexandria, Feb. 2010.

“Preparation and characterization of nanoparticle metal oxide (MgO, CaO, and ZnO) heterogeneous catalysts for biodiesel production,” R. Forester, S. Brown, U. Siriwardane and N. V. Seetala, LAS Meeting, Alexandria, Feb. 2010.

"Development of Low Cost Membranes for H_2/CO_2 Separation for WGS Reactors," University Coal Research/Contractors Review Conference, Morgan Town, June 2009.

"Sol-gel Synthesis, Characterization and Activities of Alumina Supported Nanoparticle CuO-NiO-CeO_2 Catalysts for Water-Gas-Shift (WGS) Raction," N. Seetala, U. Siriwardane, R. Garudadri, and J. Bass, Invited Talk presented at the International Conference on Nano-Composites Engineering (ICCE-17), Honolulu, HI, July 26-Aug. 1, 2009; World Journal of Engineering, Vol. 6, Supplement 2009, pp. 903–906.

"Bimetallic Nanocatalysts for Water-Gas-Shift Reaction," Naidu V. Seetala, Invited talk at the Inorganic Chemistry Seminar, LSU-Baton Rouge, LA, Feb. 10, 2009.

"Sol-gel Prepared Cu-Ce-Ni Nanoparticle Alumina Catalysts for WGS Hydrogen Production," N. V. Seetala, J. Bass, A. M. R. Jayasingha, R. Garudadri, and U. Siriwardane, Microscopy and Microanalysis, Vol. 14, Suppl. 2, (2008) 308.

"Microreactors for Syngas Conversion to Higher Alkanes: Effect of Ruthenium on Silica-Supported Iron-Cobalt Nanocatalysts," S. Zhao, V. S. Nagineni, N. V. Seetala, and D. Kuila, Ind. Eng. Chem. Res., 47 (2008) 1684.

"Development of Low Cost Membranes for H_2/CO_2 Separation for WGS Reactors," University Coal Research/Contractors Review Conference, Pittsburgh June 10–11, 2008.

"Sol-gel synthesis and characterization of alumina supported Cu-Ni-Ce catalysts for water-gas-shift (WGS) reaction," R. S. Garudadri, R. A.M. Jayasingha, N. V. Seethala and U. Siriwardane, 235th ACS National Meeting, New Orleans, LA, April 6–10, 2008.

"Preparation and characterization of alumina porous membranes coated with Nb/Ta thin films for the separation of $H_2/CO_2/CO$," R. A. M. Jayasingha, R. S. Garudadri, N. V. Seethala and U. Siriwardane, 235th ACS National Meeting, New Orleans, LA, April 6–10, 2008.

"Microreactors for Syngas Conversion to Higher Alkanes: Effect of Ruthenium on Silica-Supported Iron-Cobalt Nanocatalysts," Ind. Eng. Chem. Res., 47 (2008) 1684.

"Preparation and characterization of sol-gel alumina supported bimetallic nanocatalysts for WGS reaction," J. Bass, N.V. Seetala, A.M.R. Jayasingha, R.K. Garudadri, and U. Siriwardane, Louisiana Academy of Sciences Meeting, Northwestern State University, Natchitoches, LA, March 14, 2008.

"Development of Low Cost Membranes for H_2/CO_2 Separation for WGS Reactors," University Coal Research/HBCU-MI Contractors Review Conference, Pittsburgh June 5–7, 2007.

HIGH FLUX METALLIC MEMBRANES FOR HYDROGEN RECOVERY AND MEMBRANE REACTORS

Primary Project Goals

REB Research and Consulting is developing a carbon dioxide (CO_2)/hydrogen (H_2) separation membrane that utilizes a base metal in place of more expensive palladium (Pd).

Technical Goals

- Fabricate metallic alloys for coupon testing to determine permeation and inter-diffusion properties along with material embrittlement.
- Conduct more thorough evaluation of the most promising membranes in harsher conditions, and evaluate drawability, cladability, and brazability.
- Fabricate an H_2 purifier and membrane reactor units, and perform H_2 permeation, shock resistance, and longevity tests on modules under simulated operating conditions.

Technical Content

The project is investigating a more economic metal to replace Pd for use in an H_2 membrane. The current focus is on B2 alloys. These are similar to the BI alloys (also known as BCC) metals of the 4B and 5B element region (columns) on the periodic table—metals like vanadium (V), niobium (Nb), and tantalum (Ta) that are reasonably good at H_2 purification. These metals have a high H_2 sorption, high H_2 diffusivity, and are flexible enough for membrane fabrication; however, even when alloyed with a moderator, they tend to embrittle. Further, in the B1 form, stress creep and Pd-substrate interdiffusion are a problem. B2 (CP2) metals have similar structure and properties to the B1 metals, but should be much more resistant to creep and interdiffusion. Several membranes of the B2 structure have been developed and tested, and so far as predicted, they have passed H_2 and have been durable. Figure 1 depicts the membrane structure. The B2 intermetallic alloy substrate is coated with a thin layer of Pd alloy for catalytic activity and oxidation protection. These improved membranes so far have been hard to fabricate as tubes.

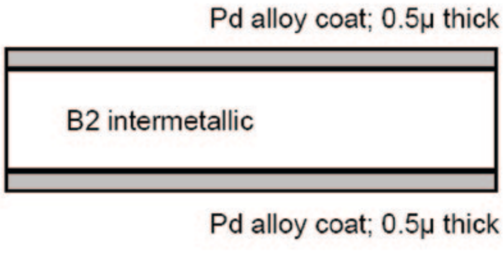


Figure 1: Typical B2 Allot Coated with Pd-Alloy

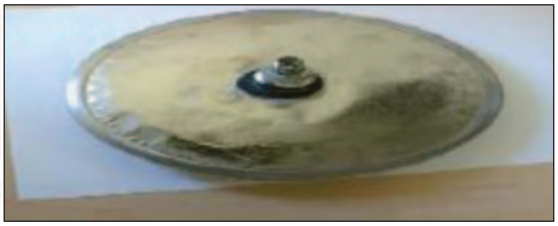


Figure 2: Hydrogen Permeation Disk

Figure 2 displays the disc configuration that has been developed for use with B2 membrane materials and Figure 3 displays how the B2 alloy discs (H_2 permeation discs) will be assembled into a purifier or membrane reactor.

Technology Maturity:

Pilot-scale, 8 tonnes CO_2/day

Project Focus:

High-Flux Metallic Membranes and Reactors

Participant:

REB Research and Consulting

Project Number:

NT42400

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

Robert Buxbaum
REB Research and Consulting
buxbaum@rebresearch.com

Partners:

G&S Titanium Co.
Iowa State University, Ames Laboratory
Los Alamos National Laboratory
Western Research Institute

Performance Period:

10/1/05 – 3/31/09

A version of this reactor/separator has been tested using a coal gasifier slipstream at the Western Research Institute at Laramie, WY. A device with one catalytic doughnut and two membrane discs produced 2.28 standard cubic feet per hour (scfh) of pure H_2 from a 90 pound per square inch (psi) slip-stream at 400 °C. The total membrane surface area was 0.947 ft^2 and the coal gas had a dry composition of 37% H_2, 27% carbon monoxide (CO), 30% CO_2, 3% methane (CH_4), and 100 parts per million (ppm) hydrogen sulfide (H_2S) (2.41 scfh/ft^2). There was excess steam in the gas. Calculations suggest that a scaled up version of this purifier should allow economical H_2 from coal-gas, where the H_2 permeates through the metal and leaves behind a high-pressure CO_2-rich stream. The high-pressure, CO_2-rich gas stream is sequestration ready.

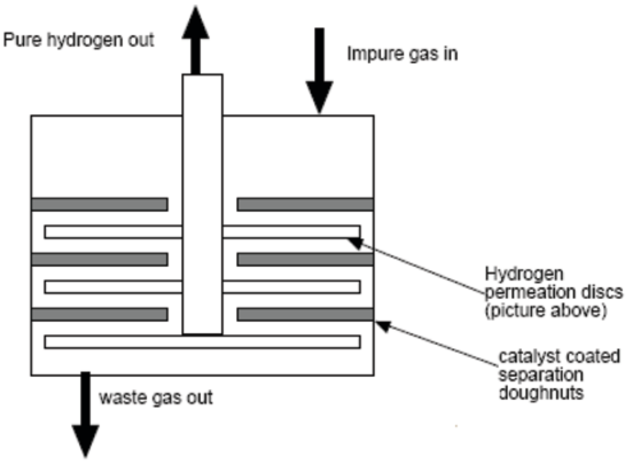


Figure 3: Membrane Reactor Design

Table 1: REB Research Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	B2 alloys	B2 alloys
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	100%	100%
	Type of selectivity measurement (ideal or mixed gas)	Helium leak	Helium leak, CO/CO_2 in H_2 stream for larger units
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	0.2 mol /m^{2}s (51 scfh/ft^2) at $\Delta P = 44$ psi	Same, but for gas mixtures
	Temperature, °C	350–400 °C	350–400 °C
	Bench-scale testing, hours without significant performance degradation	1,500	1,500
	Pilot-scale testing (if applicable), hours without significant performance degradation	75	200
	Maximum pressure differential achieved without significant performance degradation or failure, bar	6 bar	20 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disc and doughnut	Disc and doughnut
	Packing density, m^2/m^3	135 m^2/m^3	135 m^2/m^3
	Pressure drop, bar	N/A	<1bar
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	\$1,200/m^2	\$1,200/m^2
Product Quality	CO_2 purity, %	80%	80%
	H_2 purity, %	>99%	>99%

Membranes, when copper (Cu)-Pd coated, resisted poisoning from 50 hours with 100 ppm H_2S; better resistance is expected with gold (Au)-Pd coated membranes. Dust from the coal-gas built up at the seals; scaled up operation will require dust filtering. Waste gas was a high-pressure, CO_2-rich stream suitable for sequestration (or perhaps, for sale).

Technology Advantages

- B2 alloys should extend the life of the separator, effectively making it cost-competitive.
- Membranes have similar selectivity and flux to Pd.
- Projected life of the material to be 15+ years.
- Low embrittlement.
- Base metal costs \$1,080/m^2 (\$100/ft^2), while Pd costs \$32,300/m^2 (\$3,000/ft^2).

R&D Challenges

There can be difficulty in fabricating membranes to the shapes and tolerances needed. More potential problems can arise, fabricating durable purifiers and membrane reactors with the new alloys (seals). Some alloys are much cheaper than Pd, but exhibit higher embrittlement.

Results To Date/Accomplishments

- Demonstrated suitable lifespan and flux in accelerated tests at target costs.
- Demonstrated acceptable brazing behavior.
- Lowered the cost/flux of H_2 permeation membranes, thus lowering the cost of H_2.
- Identified several new B2 alloys with potential use in other applications, such as nuclear reactor fabrication.

Next Steps

- Fabricate and test B2 metal-metal matrix membranes in hopes that these membranes will work as well but will be easier to fabricate.
- Conduct disc membrane reactor tests with coal-gas for the new alloy membranes at a higher pressure with revised seals and flow path.

Available Reports/Technical Papers/Presentations

S. N. Paglieri (AET-3), Y. Wang (MST-8), T. J. Venhaus (AET-3), H. Oona (AET-3), R. E. Buxbaum, K. S. Rothenberger, B. H. Howard, R. P. Killmeyer, "Characterization of V-6Ni-5Co Membranes for Hydrogen Separation." International Symposium on Metal- Hydrogen Systems (MH-2006) held October 1–6, 2006, in Maui, HI.

Low-cost Coal to Hydrogen for Electricity with CO_2 Sequestration, Dr. Robert E. Buxbaum, MI Catalysis Soc. Talk, April 2009.

Development of membranes for hydrogen separation: Pd coated V-10Pd, Paglieri, S.N.; Wermer, J.R.; Buxbaum, R.E.; Ciocco, M.V.; Howard, B.H.; Morreale, B.D., Volume 3, Number 3, September 2008 , pp. 169–176(8).

Development of Group V Based Metal Membranes for Hydrogen Separation, **Stephen N. Paglieri**, Micheal V. Ciocco, Robert E. Buxbaum, Bryan D. Morreale. AIChE meeting, November 20, 2008, Paper 701f.

DEVELOPMENT OF PALLADIUM-SILVER COMPOSITE MEMBRANE FOR SEPARATION OF HYDROGEN AT ELEVATED TEMPERATURE

Primary Project Goals

North Carolina A&T State University is developing hydrogen (H_2)-selective, palladium (Pd)-silver (Ag) composite membranes in microporous substrates for use in the production and separation of H_2 and carbon dioxide (CO_2) at elevated temperature.

Technical Goals

- Fabricate thin film, Pd-Ag alloy composite membranes.
- Evaluate the long-term integrity and stability of the fabricated membranes under thermal cycling.
- Optimize the electroless plating process for co-deposition of Pd-Ag in microporous stainless steel (MPSS) substrate.
- Conduct H_2 permeation studies for disc membranes.
- Fabricate a tubular diffusion cell reactor.
- Conduct H_2 permeation studies for tubular membranes.
- Conduct methanol stream-reforming experiments.

Technical Content

A reactor-separator is a device that utilizes a catalyst and a membrane. Incorporating a membrane in the reactor permits the removal of H_2 from the reaction zone, which increases the efficiency by allowing a greater conversion rate. Additionally, the removal of H_2 produces a waste stream with high concentrations of CO_2 for subsequent filtration and containment.

North Carolina A&T State University has been developing a Pd-Ag alloy thin film composite membrane capable of withstanding high temperatures for use in a reactor-separator; specifically, the reforming of liquid hydrocarbons and methanol by equilibrium shift to produce H_2 for subsequent use as fuel.

Figure 1 is a diagram of a reactor-separator used to convert methanol to H_2. The methanol was fed into the reactor with steam to prevent catalyst degradation and promote additional H_2 production via a water gas shift (WGS) reaction.

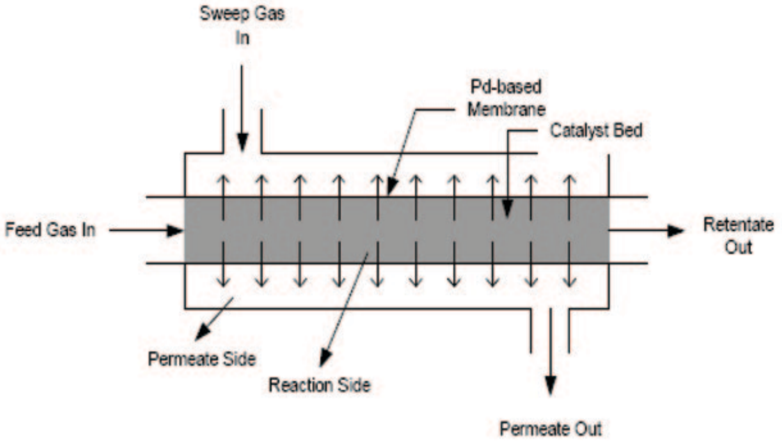


Figure 1: Schematic of Reactor Separato

Technology Maturity:

Laboratory-scale

Project Focus:

Palladium/Silver Composite Membranes

Participant:

North Carolina A&T State University

Project Number:

NT42492

NETL Project Manager:

Arun Bose
Arun.Bose@netl.doe.gov

Principal Investigator:

Shamsuddin Ilias
North Carolina A&T State University
ilias@garfield.ncat.edu

Partners:

None

Performance Period:

9/1/05 – 2/28/09

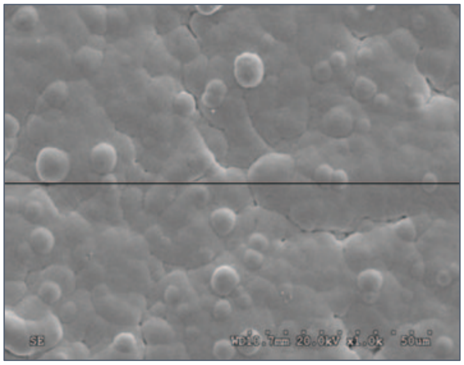


Figure 2: Image of Membrane

Technology Advantages

Inorganic membrane reactors:

- Have significantly higher H_2 flux [1.791×10^{-6} mol/(m•s•$Pa^{0.56}$)] with high selectivity (~75%) compared to other commercially available membranes.
- Are capable of operating at high temperatures, which allows for the combining of the reaction and separation into a single step.
    - Eliminates the need for additional equipment, which reduces capital costs and lowers energy requirements.
    - Allows for the immediate removal of H_2, which shifts the equilibrium in favor of the desired conversion and consequently increases efficiency.

R&D Challenges

- Developing an H_2 selective thin solid film that is thermally, chemically, and mechanically stable at high temperatures.
- Designing and fabricating effective seals at high temperature and high pressure.

Results To Date/Accomplishments

- Installed an electroless plating bath with digital continuous monitoring of temperature.
- Fabricated Pd membranes.
- Conducted permeability measurements of H_2 through Pd membranes.
- Developed a 2-D steady state membrane reactor-separator model to describe the reactive reforming process with effective radial concentration gradients due to H_2 permeation across the membrane cylindrical surface.
- Simultaneous production and separation of H_2 in a Pd-MPSS membrane reactor has been demonstrated using steam methanol reforming (SMR) reactions as an example.

Next Steps

This project is complete.

Available Reports/Technical Papers/Presentations

"Development of Pd-Ag Composite Membrane for Separation of Hydrogen at Elevated Temperature." http://www.netl.doe.gov/publications/proceedings/06/ucr/abstracts/ILIAS.pdf (Accessed 06/04/2009).

Ilias, Shamsuddin. "Development of Pd-Ag Composite Membrane for Separation of Hydrogen at Elevated Temperatures." http://www.netl.doe.gov/publications/proceedings/08/ucr/abstracts/ILIAS2_Abstract.pdf (Accessed June 4, 2009).

SCALE-UP OF HYDROGEN TRANSPORT MEMBRANES FOR IGCC AND FUTUREGEN PLANTS

Primary Project Goals

Eltron is developing an advanced membrane technology for separating and purifying hydrogen (H_2) from carbon dioxide (CO_2).

Technical Goals

Develop and H_2/CO_2 separation system that:

- Delivers pure H_2 for use in fuel cells, gas turbines, or hydrocarbon processing.
- Retains CO_2 at coal gasifier pressures.
- Operates near water gas shift (WGS) conditions.
- Tolerates coal-derived impurities (e.g., sulfur).

Technical Content

Hydrogen separation membranes are being developed that will be compatible with high-temperature WGS reactors employed in coal gasification-based H_2 production and combined-cycle power plants. The membranes will operate in the range of approximately 320–440 °C. A typical feed gas composition is 41 mol% H_2, 37% steam (H_2O), 17.8% CO_2, and 3.3% carbon monoxide (CO), and will also contain residual impurities from coal gasification that have not been removed upstream of the WGS reactors. The membranes function at pressures set by coal gasifier operations of 30 atm [450 pounds per square inch (psi)] to 70 atm (1,000 psi).

The membranes under investigation will use a dense metal or metal alloy. Metallic membranes have been developed that exhibit high mechanical strength, little distortion in the presence of high temperatures and pressures, and resistance to fracture. The membrane unit may be operated solely as an H_2/CO_2 separation device, or be integrated within the WGS reactor and perform the dual function of separation and conversion of CO and H_2O to additional H_2 and CO_2 using surface exchange catalysis.

Figure 1 illustrates Eltron's H_2 membrane. Hydrogen is separated by a multilayer dense membrane, leaving a CO_2-rich stream at high pressure ready for geological storage. The membrane can be operated without a sweep gas for pure H_2 production, or with a nitrogen sweep gas for H_2 turbine power production.

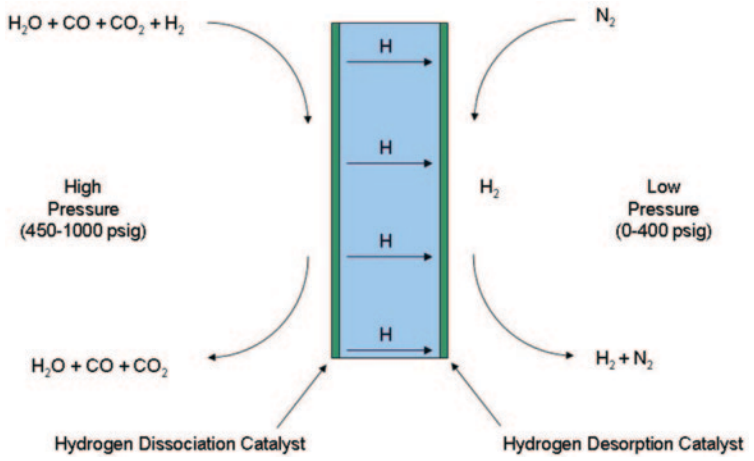


Figure 1: Eltron Hydrogen Membran

Technology Maturity:

Pilot-scale, 100 kg/day H_2 production

Project Focus:

Hydrogen Transport Membranes

Participant:

Eltron Research, Inc.

Project Number:

NT42469

NETL Project Manager:

Arun Bose
Arun.Bose@netl.doe.gov

Principal Investigator:

Carl Evenson
Eltron Research, Inc.
cevenson@eltronresearch.com

Partners:

Eastman Chemical Co

Performance Period:

8/16/05 – 9/30/08

Table 1: Eltron Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Metal alloy	Metal alloy
	Materials of fabrication for support layer (if applicable)	N/A	N/A
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	100% selective	100% selective
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	4×10^{-4} $mol/m^2/s/Pa^{1/2}$	8×10^{-4} $mol/m^2/s/Pa^{1/2}$
	Temperature, °C	320–440 °C	320–440 °C
	Bench-scale testing, hours without significant performance degradation	1,000	3,000
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	69 bar	69 bar
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Shell-and-tube	Shell-and-tube
	Packing density, m^2/m^3	85.2	85.2
	Pressure drop, bar	0.06	0.06
	Estimated cost of manufacturing and installation, $\$/m^2$-GPU or equivalent	6,140	6,140
CO_2 Quality	CO_2 purity, %	95.9	95.9
	N_2 purity, %	3.2	3.2
	Other contaminants, %	0.9	0.9
H_2 Purity	H_2 purity	99.99%	99.99%
	H_2 delivery pressure (psig)	400	400
	H_2 recovery	65%	95%

The membrane is expected to be contaminant resistant; it also produces H_2 product and CO_2 at high pressures for efficient carbon capture.

Technology Advantages

Dense metallic membranes have a high flux and produce essentially pure H_2. They can be operated at the desired application pressures and temperatures, producing a residual CO_2 stream at higher pressures than competing technologies and minimizing CO_2 compression requirements for sequestration.

R&D Challenges

Major challenges include low membrane tolerance of feed gas impurities, such as hydrogen sulfide (H_2S), and high costs for materials and fabrication of the membrane modules.

Results To Date/Accomplishments

- Improved composition and properties of the membrane leading to better understanding of fabrication and improved separation performance.
- Demonstrated more stable membrane performance at lower temperatures.
- Developed modeling tools to characterize and design membranes modules and systems.
- Improved membrane-based integrated gasification combined cycle (IGCC) flow sheets, achieving carbon capture greater than 95%, plant efficiencies greater than 6%, and a cost of electricity 10% lower than for conventional technology.

Next Steps

- Evaluate membrane materials from seven different manufacturers for: H_2 flux, lifetime stability, mechanical strength, scalability, and cost.
- Develop design basis for scale up to 100 kg H_2/day process development unit (PDU).
- Continue to work with commercial suppliers on developing techniques to manufacture full-size alloy membranes.
- Conduct durability tests.
- Conduct further experiments to understand and improve tolerance of contaminants.
- Continue techno-economic analyses relating to process optimization and scale up.

Available Reports/Technical Papers/Presentations

Advanced Power Systems Peer Review Presentation, July 2007.

Eltron Presentation, June 13, 2008.

Hydrogen Separation Using Dense Composite Membranes, In *Inorganic Membranes for Energy and Fuel Applications*; Arun Bose, Editor; Springer: New York, 2009; 125–172.

INTEGRATION OF A STRUCTURAL WATER GAS SHIFT CATALYST WITH A VANADIUM ALLOY HYDROGEN TRANSPORT DEVICE

Primary Project Goals

Western Research Institute (WRI) is developing and designing a membrane reactor for processing coal gasification-derived synthesis gas (syngas) that integrates water gas shift (WGS) and hydrogen (H_2) separation functions.

Technical Goals

- Develop a structural WGS catalyst capable of withstanding high-pressure differentials.
- Develop vanadium alloy H_2 separation membrane.
- Integrate the WGS catalyst and metallic membranes into a device and test under simulated gasifier conditions.
- Fabricate a modular WGS/membrane integrated device capable of producing 10,000 L H_2/day from coal-derived syngas.

Technical Content

The membrane reactor under development promotes the reaction of carbon monoxide (CO) with water, by use of a WGS catalyst, to produce carbon dioxide (CO_2) and H_2, and then separates the H_2, by use of a metallic membrane. Hydrogen produced can be used for electricity generation. The concentrated stream of CO_2 produced can be further purified and sequestered.

Figure 1 shows a schematic of a possible configuration for the membrane reactor. In this configuration, there are alternating stages of membrane disks and catalyst doughnuts.

By integrating the WGS and the gas separation into one unit, the WGS conversion is increased due to the continuous removal of H_2.

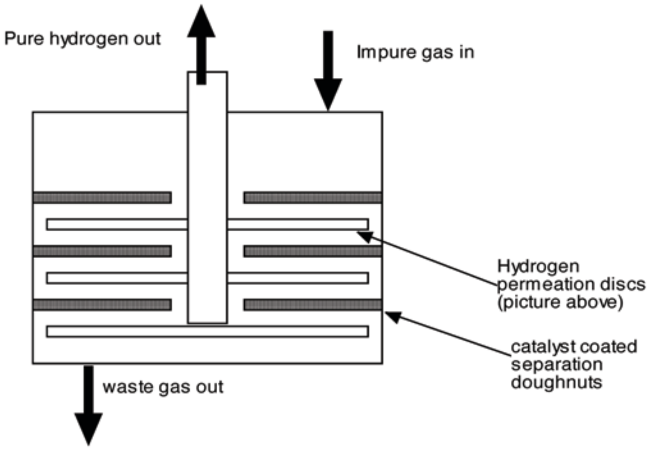


Figure 1: Schematic of Disk and Donut Integrated Device Desig

Technology Maturity:

Prototype, 10,000 L H_2/day

Project Focus:

Water Gas Shift Catalyst with Vanadium Alloy Membrane

Participant:

Western Research Institute

Project Number:

NT42454

NETL Project Manager:

Paula B. Flenory
Paula.Flenory@netl.doe.gov

Principal Investigator:

Tom Barton
Western Research Institute
tbarton@uwyo.edu

Partners:

Chart Energy and Chemicals
REB Research and Consulting
University of Wyoming
U.S. DOE Ames Laboratory

Performance Period:

7/1/05 – 12/30/08

Table 1: WRI Membrane Parameters

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	V-Pd	V-Pd
	Materials of fabrication for support layer (if applicable)	304 SS	304SS
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	100% H_2	100% H_2
	Type of selectivity measurement (ideal or mixed gas)	Mixed	Mixed
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	52 scfh/ft^2	52 scfh/ft^2
	Temperature, °C	400 °C	400 °C
	Bench-scale testing, hours without significant performance degradation	100	100
	Pilot-scale testing (if applicable), hours without significant performance degradation	40	40
	Maximum pressure differential achieved without significant performance degradation or failure, bar	200 psig	200 psig
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Plate	Plate
	Packing density, m^2/m^3	10	10
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	\$2,100/m^2	\$2,100/m^2

The project is completed so current and target values are identical. The membrane reactor ran at baseline flux levels for 40 hours in a coal-derived syngas mixture with 125 parts per million (ppm) hydrogen sulfide (H_2S) and 30% CO. Other low-level contaminants were not quantified but were also not removed from the gas mixture.

Technology Advantages

Combining the WGS catalyst with H_2 separating membrane increases production of H_2 by removing it from the reaction zone and reduces capital cost of the plant by eliminating the need for additional gas separation.

R&D Challenges

Consistent production of vanadium 9 wt% palladium (Pd) alloy is difficult due to persistent cracking of the alloy during rolling.

Results To Date/Accomplishments

The focus of the chemistry of the WGS catalyst has been on iron (Fe), aluminum (Al), chromium (Cr), copper (Cu), and cerium (Ce) -based systems, including:

- Tested catalysts by impregnation into porous mullite substrates and cordierite monoliths.
- Determined highest activity and stability for 75Fe-15Al-8Cr-2Cu.
- Identified among the Fe-Cr-Cu-Ce-oxygen (O) catalysts, those with 4 wt% ceria are the most active and stable for WGS.
- Determined that producing high surface area monoliths of this catalyst series may be problematic due to sintering at higher operational temperatures.

- Obtained and tested multiple vanadium alloys for brazing performance with Cu.
- Developed guidelines based on the brazing tests and analysis of the literature to anticipate the performance of vanadium alloys with respect to H_2 transport and fabricability based on alloying elements.
- Determined elements that are potentially positive to both H_2 transport performance and brazing performance include Ce, Cu, Fe, manganese (Mn), molybdenum (Mo), nickel (Ni), and zinc (Zn).
- Identified alloying elements that can be sufficiently used to overcome their detrimental effect on brazing.
- Determined that brazing with vanadium and structural alloys, including mild steel, 304 stainless steel, and 9Cr 1Mo steel, were generally excellent.
- Produced an integrated WGS membrane device which produced 10,000 liters per day of H_2 under coal-derived syngas.

Next Steps

Project work was recently completed.

Available Reports/Technical Papers/Presentations

Barton Tom, Morris Argyle. "Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device." http://www.hydrogen.energy.gov/pdfs/review07/pd_18_barton.pdf (Accessed June 2009).

Barton Tom, Morris Argyle. "The Integration of a Structural Water Gas Shift Catalyst with a Vanadium Alloy Hydrogen Transport Device." http://www.hydrogen.energy.gov/pdfs/progress08/ii_g_4_barton.pdf (Accessed June 2009).

SULFUR-TOLERANT PD/CU AND PD/AU ALLOY MEMBRANES FOR H_2 SEPARATION WITH HIGH-PRESSURE CO_2 FOR SEQUESTRATION

Primary Project Goals

Worcester Polytechnic Institute (WPI) is designing and developing sulfur-tolerant composite palladium (Pd)/copper (Cu) and Pd/gold (Au) alloy membranes on porous stainless steel substrates for separating hydrogen (H_2) from coal gases and producing high-pressure, sequestration-ready carbon dioxide (CO_2) streams.

Technical Goals

- Synthesize a sulfur-tolerant composite Pd/Cu and Pd/Au alloy porous stainless steel membrane with a thin intermediate oxide layer.
- Develop an understanding of the kinetics of Pd/Cu and Pd/Au alloy formations.
- Conduct permeation studies in order to characterize the membrane performance and its relation to the changes in nanostructure properties of the alloy.
- Test the membrane at lab scale using simulated coal gases to develop low-cost, high-flux, ultra-thin, sulfur-tolerant Pd/Cu and Pd/Au membranes for simultaneous H_2 separation from coal gases and production of sequestration-ready CO_2.

Technical Content

Coal gasification processes with shift reactions, such as integrated gasification combined cycle (IGCC), produce synthesis gas (syngas), a mixture of H_2 and CO_2. WPI is developing a Pd membrane to separate H_2 from syngas at practical rates to produce high-purity H_2 for later use as a combustible, while simultaneously leaving high-pressure, sequestration-ready CO_2 in the waste stream.

However, Pd alone is not sufficient for a membrane intended for use in coal-related processes due to the sulfur composition of coal. Hydrogen sulfide (H_2S), formed during the burning of coal, reacts with Pd to form palladium sulfide (Pd_4S), which drastically reduces the membranes permeability and creates small holes, reducing its selectivity. The plating of Pd with Cu or Au has been shown to reduce the reaction with H_2S, therefore increasing the membranes chemical stability.

Palladium/copper membranes were tested for H_2 permeability under 45–55 parts per million (ppm) H_2S. It was found that approximately 80% of the H_2 permeance was lost due to the formation of H_2S. However, exposing the membrane to a stream of pure H_2 recovered some of the H_2 permeance, showing that the reaction is partially reversible. Conversely, the amount of irreversible poisoning increased with the increasing time of H_2S exposure.

Palladium/gold membranes offered even greater permeance than that of Pd/Cu membranes. However, as with Pd/Cu membranes, they exhibited a sharp decline in H_2 permeance when exposed to H_2S. Unlike Pd/Cu membranes, the permeance was nearly fully recovered in pure H_2, indicating that the poisoning was reversible. Also, a longer H_2S exposure time did not increase the permeance decline, as it only slowed the permeance recovery rate.

Technology Maturity:
Laboratory-scale

Project Focus:
Sulfur-Tolerant Palladium Alloy Membranes

Participant:
Worcester Polytechnic Institute

Project Number:
NT42194

NETL Project Manager:
Arun Bose
Arun.Bose@netl.doe.gov

Principal Investigator:
Yi Hua Ma
Worcester Polytechnic Institute
yhma@wpi.edu

Partners:
None

Performance Period:
9/28/04 – 9/30/08

In both Pd/Cu and Pd/Au membranes, the permeation and chemical resistance to sulfur increased with increasing temperatures, and decreased with decreasing temperatures. Experiments were run at temperatures up to 600 °C, demonstrating the thermal stabilities of these membranes.

The damaging effects of H_2S on Pd membranes can be observed by comparing Figure 1 (no exposure) to Figure 2 (exposed to 54.8 ppm H_2S/H_2 gas mixture for 24 hours at 350 °C).

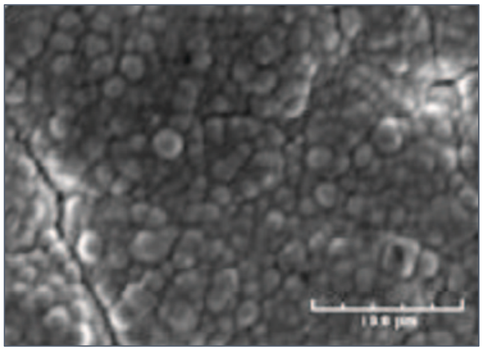


Figure 1: Micrograph of PD as Deposited (No Exposure to H_2S)

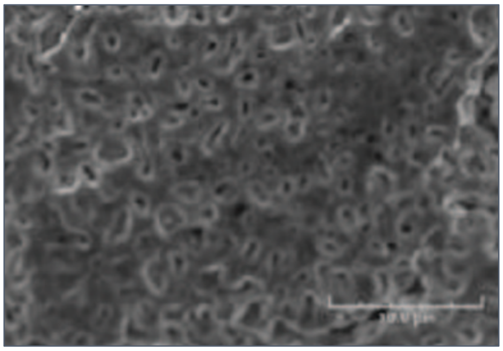


Figure 2: Micrograph of PD Exposed to a 54.8 ppm H_2S/H_2 Gas Mixture for 24 Hours at 350 °C

Technology Advantages

- Permeation lost to the formation of H_2S is recoverable by exposing the Pd/Cu or Pd/Au membrane to a stream of pure H_2.
- Selective properties of Pd/Cu and Pd/Au membranes are retained despite the formation of H_2S.
- Membranes with an oxide and additional Pd/Ag inter-metallic diffusion barrier display additional stability in H_2 permeance.
- Palladium/gold and Pd/Cu membranes show significant gains in chemical stability and sulfur resistance compared to Pd membranes.

R&D Challenges

- Palladium/gold membranes showed an almost instantaneous sharp decline of the H_2 permeance when exposed to H_2S.
- Palladium/copper membranes showed a permeance decline of approximately 80% when exposed to H_2S.
- With extended exposure to H_2S, the amount of Pd/Cu that was regenerable with pure H_2 decreased.

Results To Date/Accomplishments

- Synthesized Pd/Cu and Pd/Au alloy porous stainless steel membranes with a thin intermediate oxide layer.
- Conducted permeation studies and observed the membrane performance and its relation to the changes in nanostructure properties of the alloy.
- Conducted studies to determine the effects of H_2S on Pd/Cu and Pd/Au membranes.

Next Steps

This project is complete.

Available Reports/Technical Papers/Presentations

"Sulfur-Tolerant Pd/Cu and Pd/Au Alloy Membranes for Hydrogen Separation with High Pressure CO_2 for Sequestration."
http://www.netl.doe.gov/publications/proceedings/07/ucr/Poster-Abstract/Ma_Poster_Abstract.pdf

"Effect of H_2S on the Performance and Long-Term Stability of Pd/Cu Membranes."
http://pubs.acs.org/doi/abs/10.1021/ie801947a

MIXED MATRIX MEMBRANES FOR CO_2 AND H_2 GAS SEPARATIONS USING METAL-ORGANIC FRAMEWORKS AND MESOPOROUS HYBRID SILICAS

Primary Project Goals

The University of Texas at Dallas is applying metal organic frameworks (MOFs) and mesoporous hybrid silicas in polymer-based mixed-matrix membranes (MMMs) for the separation of hydrogen (H_2) and carbon dioxide (CO_2).

Technical Goals

The technical goal of this project is to exploit the high surface areas, adsorption capacities, and selectivities of microporous additives for membrane-based separations.

Technical Content

Matrimid is a widely used polyimide (a polymer) that has both attractive thermal and gas transport properties. When combined with microporous organic-inorganic hybrid nanocrystals for the preparation of polymer-based MMMs, the time and steps required for membrane preparation is reduced compared to inorganic additives.

The following materials have been synthesized and combined with Matrimid to form MMMs: MOF-5, Copper(II) biphenyldiacetate triethylenediamine metal organic framework (Cu-MOF), metal organic polyhedral 18 (MOP-18), zeolitic imidazolate framework 8 (ZIF-8), zeolite socony mobil 5 (ZSM-5), carbon aerogel, carbon aerogel-zeolite composites, single-walled carbon nanotube (SWNT), Copper(II) bipyridine hexafluorosilicate metal organic framework (Cu-BPY-HFS), and periodic mesoporous organosilicas (PMOs). Experiments have also been conducted to determine the selectivity and permeability of microporous additives with Matrimid MMMs. MOF-5, Cu-MOF, MOP-18, and ZIF-8 were found to be stable up to 350 °C, 300 °C, 300 °C, and 400 °C, respectively. Carbon aerogels, carbon aerogel-zeolites, and PMOs showed similar mechanical resistance.

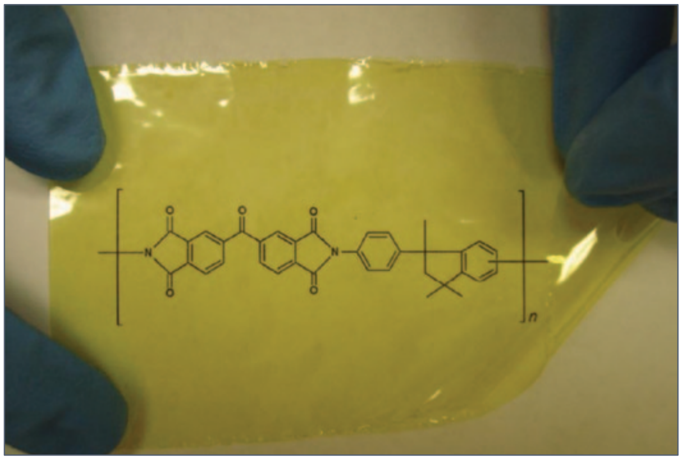


Figure 1: Flat Matrimid Membrane Cast From Chloroform

Technology Maturity:

Bench-scale

Project Focus:

Mixed Matrix Membranes for H_2/CO_2 Separations

Participant:

University of Texas at Dallas

Project Number:

NT42173

NETL Project Manager:

Edgar Klunder
Edgar.Klunder@netl.doe.gov

Principal Investigator:

Inga Holl Musselman
University of Texas at Dallas
imusselm@utdallas.edu

Partners:

None

Performance Period:

8/26/04 – 8/31/08

Technology Advantages

- Addition of substances, such as MOF-5, Cu-MOF, MOP-18, ZIF-8, ZSM-5, carbon aerogel, carbon aerogel-zeolite, functional SWNT and SWNT-short, Cu-BPY-HFS, and PMOs, may provide benefits, such as increased selectivity, permeability, and increased mechanical and thermal stability.
- Incorporation of organic functionalities in frameworks improves dispersion in a polymer matrix.
- Inclusion of these substances reduces time and steps required for membrane preparation. Organic character of the crystals facilitates the dispersion and improves the interfacial contact with the polymer matrix.

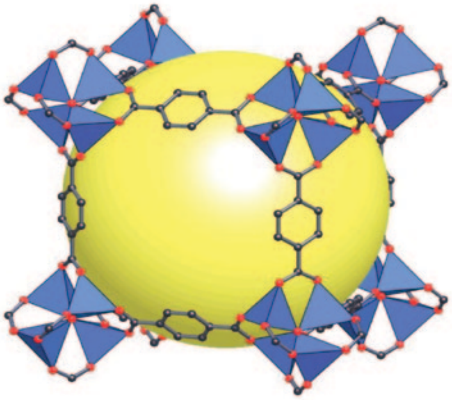


Figure 2: Model of MOF-5

R&D Challenges

- Obtaining selectivities high enough to achieve effective separation.
- Obtaining permeabilities high enough to achieve efficient separation.
- Developing membrane pores resistant to contamination.

Results To Date/Accomplishments

- Synthesized MOF-5, Cu-MOF, MOP-18, ZIF-8, ZSM-5, carbon aerogel, carbon aerogel-zeolite, functional SWNT and SWNT-short, Cu-BPY-HFS, and PMOs.
- Fabricated all synthesized materials with Matrimid MMMs.
- Completed permeability studies.

Next Steps

This project is complete.

Available Reports/Technical Papers/Presentations

Musselman, Inga H. et al., "Mixed-Matrix Membranes for CO_2 and H_2 Separations Using Metal-Organic Frameworks and Mesoporous Hybrid Silicas." http://www.netl.doe.gov/publications/proceedings/05/UCR_HBCU/pdf/papers/Musselman.pdf

MEMBRANES FOR USE IN PALLADIUM MEMBRANE REACTOR TECHNOLOGY FOR PRODUCTION OF HYDROGEN FROM COAL GAS

Primary Project Goals

Los Alamos National Laboratory (LANL) is designing and developing a composite palladium (Pd) membrane reactor (PMR) capable of extracting hydrogen (H_2) from fossil fuels, resulting in near capture-ready concentrations of carbon dioxide (CO_2) in the effluent stream.

Technical Goals

- Identify and develop sulfur-tolerant water gas shift (WGS) catalysts and membranes.
- Develop methods of fabricating PMRs with thin, active Pd-alloy surfaces on porous substrates.
- Determine the performance of the PMRs at elevated pressures.
- Determine the influence impurities impose on the functionality of PMRs.
- Develop Pd alloys resistant to effects of impurities.
- Determine optimal PMR operating pressure and temperature.

Technical Content

Current methods of extracting H_2 from hydrocarbons have low efficiency due to limitations imposed by reaction equilibrium. A PMR has been developed that combines the WGS reaction with H_2 separation. By doing so, the H_2 product of the reaction is removed from the reaction zone, driving the reaction towards completion and significantly increasing the efficiency of the process. Additionally, the extraction of H_2 leaves behind a near capture-ready concentration of CO_2 in the effluent stream.

The removal of H_2 from the reaction zone increases the reaction rate by freeing up active reaction sites on the catalyst. This results in reaction rates equal to conventional reforming technology at lower temperatures. For instance, conventional methane reforming is carried out at temperatures ranging from 800 to 1,000 °C, whereas equivalent results are obtained in a PMR at temperatures near 450 °C.

Additionally, the pressure required to carry out the reaction is reduced by the removal of H_2 from the reaction zone. It is estimated that approximately 60–80% of the feed hydrogen (in the form of water and fuel) will be recovered at an inlet pressure of 10 atm. At 20 atm, the anticipated recovery increases to 80–95%. However, while higher pressures are not required, the permeation rate decreases significantly with decreasing pressures. Therefore, operating at the optimal pressure is important.

Figure 1: Unheated, Broken Pd-Cu/αAlumina Composite Membrane

Technology Maturity:

Bench-scale employing simulated syngas

Project Focus:

Palladium-Based Membrane Reactor

Participant:

Los Alamos National Laboratory

Project Number:

FWP-FE99002-4A24A

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

Stephen Birdsell
Las Alamos National Laboratory
Steve.Birdsell@lanl.gov

Partners:

Ames Laboratory

Performance Period:

10/1/05 – 6/22/07

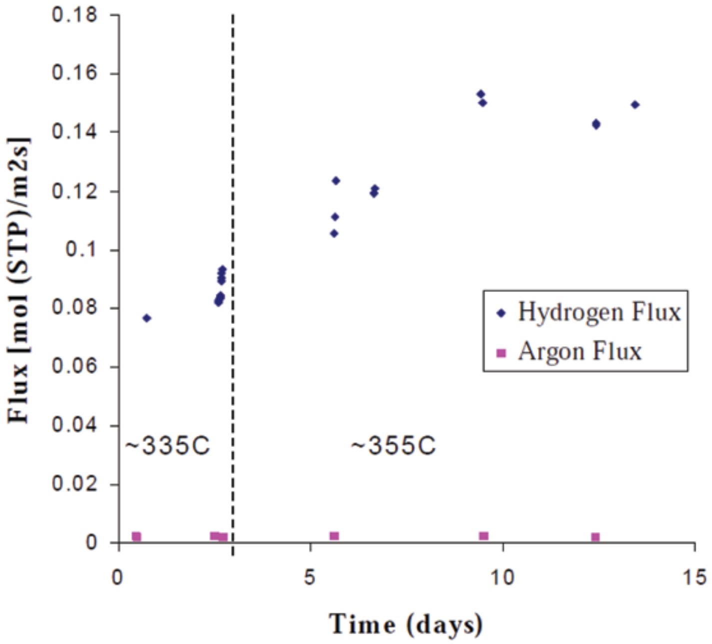


Figure 2: Flux Data for Pd-Cu/αAlumina Composite Membrane

Coal gas contains impurities, such as hydrogen sulfate (H_2S), which de-activate and degrade Pd membranes. It is expected that the level of degradation will be proportional to the concentration of H_2S present. However, much of the damage should be reversible and simple to alleviate by methods like exposure to steam or air. Also, by combining Pd with copper (Cu) or gold (Au), the amount of sulfur poisoning is reduced significantly.

In order to reduce the cost of membranes and increase the flux of H_2 through the membranes, ultra-thin (<10 microns), Pd-alloy films are applied to H_2-permeable supports to form composite metal membranes. One such membrane has been developed—a vanadium (V) or tantalum (Ta) metal foil coated on both sides with Pd. This membrane has demonstrated fluxes more than 10 times greater than other Pd composite membranes.

Technology Advantages

In comparison to existing methods of H_2 extraction, PMRs have:

- Nearly 10 times greater flux.
- Reduced capital costs.
- Lower temperatures (450 °C), pressures (<20 atm), and amounts of excess water.
- Resistance to hydrogen embrittlement.
- Prolonged physical and chemical stability.

R&D Challenges

- Thick membranes have fluxes lower than desired that result in higher capital costs and greater space requirements.
- Impurities, such as H_2S, degrade the functionality of Pd consisting apparatus.

Results To Date/Accomplishments

- Characterized the performance of PMRs with respect to inlet conditions, temperature, geometry, and catalyst type.
- Developed mechanistic model of PMR incorporating information gathered through experimentation.
- Investigated WGS reaction, as well as the reforming of methane, methanol, ethanol, octane, and gasoline with the PMR.
- Fabricated membranes consisting of modified porous supports deposited with thin layers of composite Pd alloys.

Next Steps

This project has been completed.

Available Reports/Technical Papers/Presentations

S. N. Paglieri, D. R. Pesiri, R. C. Dye, and R. C. Snow. Palladium-Coated Vanadium Alloy Membranes for Hydrogen Separation. *Proceedings of the 19th Annual Conf. on Fossil Energy Mater*. Knoxville, TN; May 9–11, 2005.

S. N. Paglieri, I. E. Anderson, R. L. Terpstra, R. E. Buxbaum, M. V. Ciocco, and B. H. Howard. A $Pd_{60}Cu_{40}$/Porous Iron Aluminide Membrane for Hydrogen Separation. *Proceedings of the 21st Annual Conf. on Fossil Energy Mater.*, Knoxville, TN; Apr. 30-May 2, 2007.

S. N. Paglieri, I. E. Anderson, R. L. Terpstra, T. J. Venhaus, Y. Wang, R. E. Buxbaum, K. S. Rothenberger, and B. H. Howard. Metal Membranes for Hydrogen Separation. *Proceedings of the 20th Annual Conf. on Fossil Energy Mater.* Knoxville, TN, June 12–14, 2006.

S. N. Paglieri. "Palladium Membranes" in *Nonporous Inorganic Membranes*. Edited by A.F. Sammells and M. V. Mundschau, Miley-VCH, pp. 77–106 (2006).

S. N. Paglieri, Y. Wang, T. J. Venhaus, H. Oona, R. C. Snow, B. P. Nolen, R. E. Buxbaum, K. S. Rothenberger, B. H. Howard, and R. P. Killmeyer. Characterization of V-6Ni-5Co Membranes for Hydrogen Separation. Proceedings of the 9th *Int. Conf. on Inorganic Membranes*, Lillehammer, Norway, June 25–29, 2006.

DEVELOPMENT OF DENSE CERAMIC MEMBRANES FOR HYDROGEN SEPARATION

Primary Project Goals

Argonne National Laboratory is developing a dense ceramic or cermet (ceramic/metallic composite) membrane for separating hydrogen (H_2) from synthesis gas (syngas) generated during coal gasification, resulting in a high concentration carbon dioxide (CO_2) stream.

Technical Goals

Develop a membrane that is:

- Chemically stable in the presence of steam, carbon monoxide (CO), CO_2, methane (CH_4), hydrogen sulfide (H_2S), ammonia (NH_3), mercury (Hg), and halides.
- Mechanically stable under high pressures, high temperatures, and temperature cycles.
- Capable of providing industrially significant fluxes at desired levels of H_2 selectivity.

Technical Content

During coal gasification, large volumes of H_2 and CO_2 are produced. Dense ceramic and cermet membranes are being developed for use with coal gasification process to separate H_2 from CO_2. These membranes must be capable of achieving a high flux and selectivity in order to reduce the surface area required to process the high volumes of gas produced. Reducing a membrane thickness can increase H_2 flux; however, to maintain selectivity, the membrane must remain defect free. Dense ceramic and cermet membranes are capable of providing reduced thickness while avoiding the formation of defects.

High density membranes are achieved by sintering the cermet at high temperatures. Sintering aids have been developed that prevent delamination of the cermet from the porous ceramic substrate. Figure 1 shows a cermet membrane with cobalt nitrate as the sintering aid on a TZ-3Y [zirconium dioxide (ZrO_2) partially stabilized with yttrium oxide (Y_2O_3)] substrate.

The chemical stability of the membranes is also important for their use in the corrosive syngas stream produced from coal gasification. Hydrogen sulfide is a particularly corrosive contaminant to membranes containing palladium (Pd). When H_2S reacts with Pd, palladium sulfide (Pd_4S) forms on the surface of the membrane, which greatly reduces H_2 permeation through the membrane. Therefore, it is important to identify the temperatures and pressures at which the membrane is stable. The Pd-containing cermets being developed are stable between about 430 and 680 °C (700 K and 950 K) in stable a gas containing 73% H_2 with between approximately 60 and 400 parts per million (ppm) H_2S. When the gas contains only 10% H_2, the membrane is stable for H_2S concentrations between approximately 8 and 50 ppm.

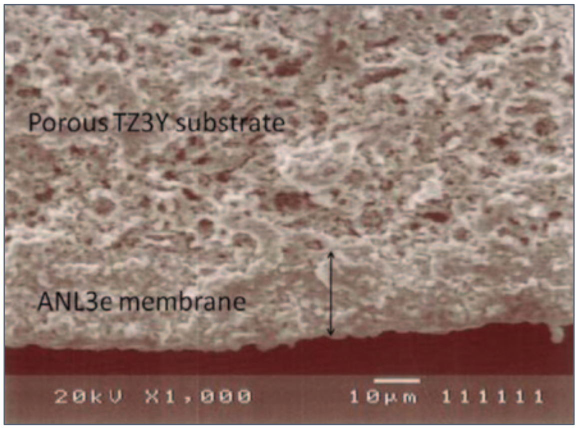


Figure 1: Cross-Sectional View of ANL-3e Thin Film Membrane Sintered at 1,160 °C on Porous TZ-3Y Substrate

Technology Maturity:

Laboratory- and bench-scale

Project Focus:

Dense High-Temperature Ceramic Membranes

Participant:

Argonne National Laboratory

Project Number:

FWP-49601

NETL Project Manager:

Richard Dunst
Richard.Dunst@netl.doe.gov

Principal Investigator:

U. (Balu) Balachandran
Argonne National Laboratory
balu@anl.gov

Partners:

None

Performance Period:

3/31/98 – 9/30/13

Table 1: ANL Membrane Parameter

	Parameter	Current R&D Value	Target R&D Value
Membrane Properties	Materials of fabrication for selective layer	Pd/TZ-3Y cermet	Pd/TZ-3Y cermet and/or non-precious metal
	Materials of fabrication for support layer (if applicable)	Alumina/zirconia	Metal/alloy
	Selectivity of key gas components: H_2/CO_2 for pre-combustion technology	150	10,000
	Type of selectivity measurement (ideal or mixed gas)	Mixed gas	Mixed gas
	Pressure normalized flux (permeance for linear materials) for more selective gas component, GPU or equivalent units	5.0 scc/min/cm^2 at 400 °C with hydrogen feed pressure of 7.4×10^5 Pa (7.3 atm) and hydrogen sweep pressure of 3.0×10^3 Pa (0.03 atm)	75
	Temperature, °C	400–600	250–500
	Bench-scale testing, hours without significant performance degradation	1,200 hr	1,200 hr
	Pilot-scale testing (if applicable), hours without significant performance degradation	N/A	N/A
	Maximum pressure differential achieved without significant performance degradation or failure, bar	12.2	20.4
Module Properties	Module configuration: hollow-fiber, spiral-wound sheet, shell-and-tube, plate-and-frame, other	Disk/short tube (≈3 in)	Long tubes (≈12 in)
	Packing density, m^2/m^3	N/A	N/A
	Pressure drop, bar	N/A	N/A
	Estimated cost of manufacturing and installation, \$/m^2-GPU or equivalent	N/A	N/A
Product Quality	H_2 purity, %	99.8	99.99

Other Membrane Parameters

Contaminant Resistance: The membrane is tolerant to H_2S between 430 and 680 °C in gas containing 73% H_2 and approximately 60–400 ppm H_2S.

The membrane is tolerant to ≈15 mol% CO and ≈20 mol% steam in the temperature range of 400–700 °C.

Technology Advantages

- Ceramic phase of the cermet membrane provides 3-D mechanical support that can blunt or deflect crack propagation through the metallic phase.
- Dense ceramic membranes operate at high pressures and temperatures.
- Dense ceramic membranes have no interconnected porosity; therefore, selectivity for H_2 is high.
- Dense ceramic membranes remove H_2 from H_2 and CO_2 mixtures, resulting in a concentrated stream of CO_2 that is near sequestration-ready.

R&D Challenges

- Reducing membrane thickness increases flux, but can lead to pin-holes in the membrane, which reduces H_2 selectivity. Therefore, reducing defects in thinner membrane is desired.
- Developing low-temperature sintering methods to avoid loss of Pd to evaporation during sintering at high temperatures.
- Determining stability restrictions in order to limit the reaction of Pd with H_2S, which forms Pd_4S and reduces H_2 flux.
- Understanding chemical stability in the presence of NH_3, Hg, and halides.
- Increasing the resistance to the effects of particulates impacting the membrane surface.
- Developing leak-proof metal/ceramic seals at high pressures under thermal cycling.
- Reducing the cost of the membrane by employing non-precious metals/alloys to form the cermet membrane.

Results To Date/Accomplishments

- Developed dense, cermet membranes that non-galvanically separate H_2 from mixed-gas streams.
- Achieved an H_2 flux of 52 $cm^3/min\text{-}cm^2$ measured on an 18-µm thick membrane composed of Pd and TZ-3Y using a feed of 1 atm H_2.
- Achieved H_2 permeation exceeding 150 cm^3/min (0.32 scfh) measured in short, 8-cm long tubular membranes at 600 °C and ambient pressures.
- Demonstrated durability of membrane during cycling in temperature and H_2 concentration.
- Maintained flux stability for 1,200 hours in feed stream with 400 ppm H_2S at 900 °C.
- Achieved regeneration of sulfur-poisoned, cermet membrane.
- Long-term (≈4 months) flux measurements showed that cermet membranes are stable in NETL Test Protocol test 1 gas mixtures.

Next Steps

- Develop methods for eliminating pin-holes in thinner membranes for high purity and high selectivity for H_2.
- Fabricate and test tubular membranes at high flow rates and changing flow directions to overcome the external transport phenomena that are limiting the H_2 flux at the boundary layer.
- Continue testing of membranes as per test protocols established by NETL.
- Fabricate/test membrane performance in a gasifier syngas slip stream.
- Perform experiments integrating H_2 separation and shift reaction.
- Make long-term flux measurements and demonstrate reliability and durability of membranes under high-pressure conditions.

Available Reports/Technical Papers/Presentations

Balachandran, u., et al., "Hydrogen Separation Membranes Annual Report for FY2010," publication date January 30, 2011, http://www.osti.gov/bridge

GASIFICATION OF LIGNITES TO PRODUCE LIQUID FUELS, HYDROGEN, AND POWER

Primary Project Goals

The University of North Dakota Energy and Environment Research Center (UNDEERC) is conducting research to determine the effects of lignite coal on gas cleanup processes used for coal gasification; including hydrogen (H_2)/carbon dioxide (CO_2) separation membranes, as well as the removal of condensed vapors, particulates, mercury, and sulfur.

Technical Goals

- Construct an entrained-flow gasifier (EFG), and perform shakedown on the EFG.
- Demonstrate the gasification lignite, and monitor the composition and concentration of synthesis gas (syngas) produced.
- Perform testing of membranes and other gas cleanup processes.

Technical Content

Lignite coal is an attractive fuel for gasification because of its calcium and sodium concentrations, which are known to catalyze the gasification reactions. This permits lower operating temperatures with increased carbon conversion efficiency. However, the composition of lignite, mainly sodium and chlorine, causes damaging effects to H_2/CO_2 membrane separators. Research is ongoing on the effectiveness of H_2/CO_2 membrane separators, specifically palladium (Pd)/copper (Cu) membranes, for use in lignite coal-fueled gasification processes.

The gas cleanup configuration can be found in Figure 1, where the syngas is delivered from a transport reactor development unit (TRDU). The waste gas from the separation membrane contains high concentrations of CO_2 that can be further purified and sequestered.

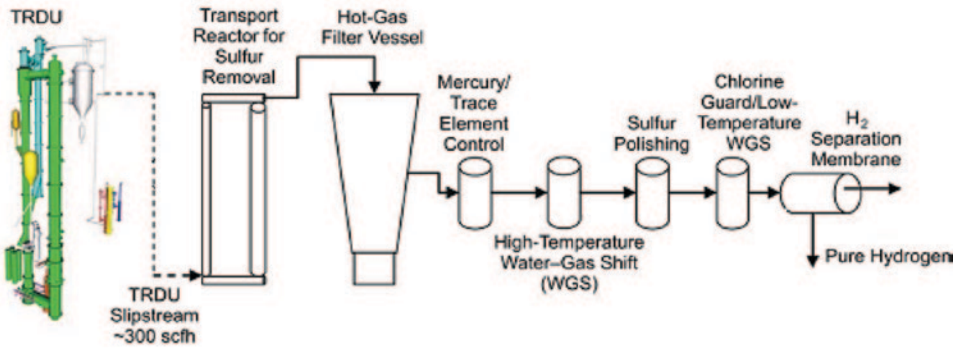


Figure 1: Gas Cleanup Configuration Schematic

Figure 2 is a plot of H_2 flux through the tested membrane over time. The oxygen (O_2)-blown run contained H_2 at higher partial pressures as a result of reduced nitrogen levels, which resulted in higher H_2 flux. This demonstrates that higher-pressure differentials will yield greater quantities of H_2.

Technology Maturity:

Bench, 2 lb/day H_2; 45 lb/day CO_2

Project Focus:

H_2/CO_2 Separation Membranes

Participant:

UNDEERC

Project Number:

NT42465-1.2

NETL Project Manager:

Edgar Klunder
Edgar.Klunder@netl.doe.gov

Principal Investigator:

Joshua J. Stanislowski
University of North Dakota
Energy and Environmental
Research Center
jstanislowski@undeerc.org

Partners:

EPRI
Great River Energy
Luminant
North American Coal Corporation
North Dakota Industrial Commission
Porviar Filtration Group
Rio Tinto

Performance Period:

6/23/05 –5/31/11

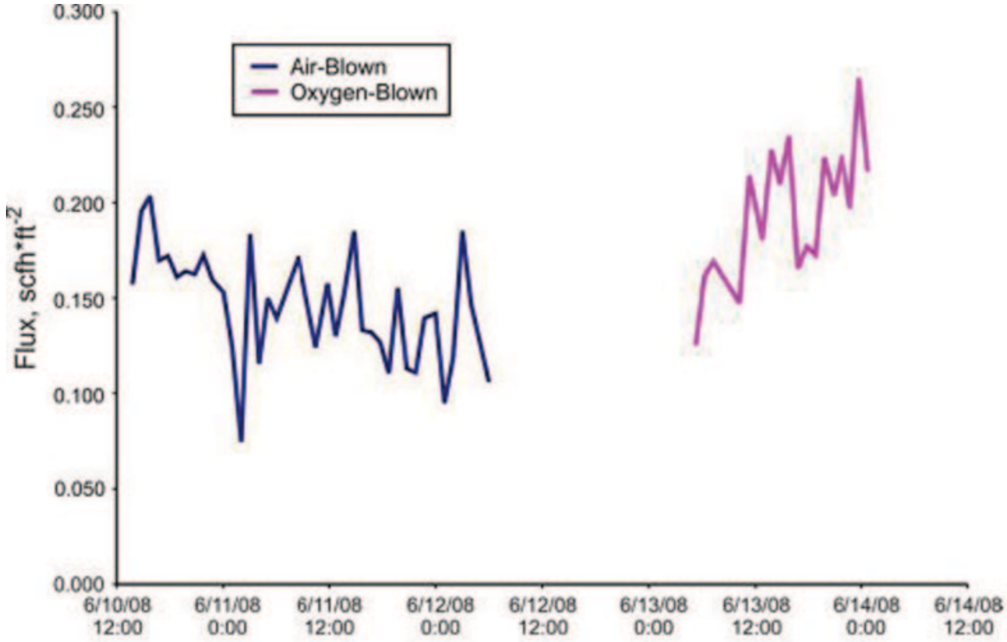


Figure 2: Hydrogen Flux of Air- and Oxygen-Blown Syngas

The permeate stream contained greater than 99.9% H_2, demonstrating the selectivity of the membrane and its ability to be utilized in gasification processes fueled by lignite coal.

To date, Pd-Cu-based membranes developed by Wah-Chang and TDA Research have been tested in the UNDEERC's gasification facilities. Both membranes have shown high hydrogen purities, but flux measurements were low because of low partial pressure across the membrane. Additional testing with these and other membranes is planned to occur in 2010. Gasifiers capable of producing syngas at pressures up to 1,000 pounds per square inch (psi) will be used in conjunction with the membranes, resulting in high dP and improved hydrogen flux.

Technology Advantages

- The calcium and sodium concentrations of lignite coal catalyze the gasification reaction, which permits lower operating temperatures with increased carbon conversion efficiency.
- Pd/Cu membranes produce high purity hydrogen and a separate stream of CO_2 that remains at high pressure and is ready for sequestration.

R&D Challenges

- Lignite's high calcium, sodium, mercury, and chlorine composition cause operation issues, such as bed agglomeration and ash deposition, as well as damage to water gas shift (WGS) catalysts.
- Pd/Cu membranes have a low tolerance for sulfur, so gas cleanup systems must remove the hydrogen sulfide (H_2S) and carbonyl sulfide (COS) to subparts per million levels.

Results To Date/Accomplishments

- Completed feedstock characterization.
- Completed bench-scale testing of gas desulfurization and H_2 and CO_2 purification concepts.
- Completed construction of the EFG, as well as gasification test runs on the EFG.
- Conducted testing to determine optimum warm- or hot-gas cleanup to remove impurities, such as condensed vapors and particulates, as well as control trace elements like mercury.
- Conducted testing of high-efficiency sulfur removal techniques.
- Performed testing of H_2/CO_2 separation membranes.

Next Steps

- Perform advance characterization analysis of lignites and ash materials.
- Issue final report to project sponsors.
- Continue membrane development work through additional test programs at UNDEERC.

Available Reports/Technical Papers/Presentations

No reports, technical papers, or presentations are yet available.