

IV.C.5 Hydrogen Separation

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Objectives

- Task 1. Water-Gas-Shift (WGS) Membrane Reactors — the objective is to demonstrate that a Pd-Cu membrane reactor (MR) can enhance CO conversion of the WGS reaction and recover H₂ in the permeate in the presence of sulfur.
- Task 2. Pd-Cu Membranes — the objectives are to a) determine the degree of sulfur resistance of Pd-Cu membranes, and b) determine the effects of other gas impurities on permeability.
- Task 3. Novel H₂ Production and Separation — the objective is to conduct exploratory research in new areas related to hydrogen.

Technical Barriers

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

- L. Durability
- M. Impurities
- N. Defects
- O. Selectivity
- P. Operating Temperature
- Q. Flux
- S. Cost

The project also addresses Section 5.1.5.1., Technical Barriers – Central Production Pathway in the Hydrogen from Coal – Research, Development and Demonstration Plan of the DOE Office of Fossil Energy. This includes WGS reaction barriers and hydrogen separation barriers.

Approach

- Conduct testing of Pd and Pd-Cu materials in a membrane reactor configuration to determine the feasibility of a high-temperature WGS reaction with no added catalyst.
- Conduct permeability and surface exposure tests to determine the characteristics of Pd-Cu alloys for hydrogen separation in the presence of sulfur.
- Examine alternatives to membranes for separating CO₂ and H₂, conduct performance testing of external membranes, and develop novel materials as separation membranes.

Technical Targets

Table 1 lists the targets that the project will attempt to meet during its implementation.

Table 1. Technical Targets: Dense Metallic Membranes for Hydrogen Separation and Purification

Performance Criteria	Units	Calendar Year			
		2003 Status ^a	2005 Target	2010 Target	2015 Target
Flux Rate	scfh/ft ²	60	100	200	300
Membrane Material and All Module Costs	\$/ft ² of membrane	\$2,000	\$1,500	\$1,000	<\$500
Durability	hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	100	200	400	400-1,000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity	% of total (dry) gas	>99.9	>99.9	>99.95	99.99%

^aBased on membrane shift reactor with syngas

Accomplishments

- Evaluated the influence of WGS gas components on the permeability of an 80-wt% Pd-Cu membrane.
- Determined the H₂ permeance and surface effects as a function of H₂S exposure time.
- Fabricated a novel ternary metal membrane, and screened with regard to hydrogen flux.
- Fabricated and tested CO₂-selective membranes based on ionic liquids.
- Conducted performance testing of novel prototypes from external membrane developers to develop a baseline or validate results.

Future Directions (FY 2006)

- Task 1 – Determine temperature at which pitting occurs in the presence of high concentrations of steam, and conduct WGS reactions in 100 μm, 80-wt% Pd-Cu disk MR.
- Task 2 – Investigate the nature of the H₂S interaction with Pd-Cu membrane alloys via spectroscopic and reflectivity studies of Pd-Cu surface chemistry, and develop improved Pd-based membrane alloys for gasification applications.
- Task 3 – Solve the sealing problems for the ANL-3e-4 Cermet membranes and conduct reproducibility tests, and conduct extensive testing of Oak Ridge National Laboratory's (ORNL's) inorganic porous membrane in support of their scale-up demonstration project.
- Task 4 – Initiate work in support of “Low Cost Hydrogen Production from Biomass Using a Novel Membrane Gasifier” (Gas Technology Institute) and “High Flux Metallic Membranes for Hydrogen Recovery and Membrane Reactors” (REB Research & Consulting).

Introduction

Next-generation fuel and power plants are likely to be based on gasification technology. In this process, coal, biomass, or other carbon-containing materials would be fed to a gasifier, which would convert this feed material into synthesis gas, or

syngas – a mixture of hydrogen and carbon monoxide, small amounts of carbon dioxide, light hydrocarbons, and associated impurities. From this point, the syngas could be burned directly for power, made into chemicals, or shifted to essentially all hydrogen and carbon dioxide. A hydrogen-carbon dioxide separation step would yield product

hydrogen, available as an energy carrier or for advanced electric power production via fuel cell technology, and a concentrated carbon dioxide stream available for sequestration. The best possible solution to the separation issue would be a membrane reactor. An appropriately designed reactor could combine the shift and separation steps into one, enabling a significant leap forward in efficiency and lowered cost of hydrogen produced. In a WGS membrane reactor, syngas and water are fed to the inlet of the membrane reactor and separated streams of hydrogen and carbon dioxide (with associated impurities) are removed from the product side. A number of potential membrane materials have shown good hydrogen permeation at high pressures and temperatures. However, tolerance to impurities found in fossil fuel gasification streams is an important prerequisite for the deployment of membrane reactors that has not been widely investigated. Hydrogen sulfide is arguably the most significant impurity in a fossil fuel gasification stream due to its ability to poison catalysts and corrode metal surfaces. Palladium-copper alloys were chosen as the subject of the current study due to reports that they continue to possess good hydrogen permeation characteristics in the presence of sulfur-containing gases.

Approach

- Task 1. WGS Membrane Reactors – The approach will include the following actions: a) determine the optimum MR configuration, heater design, and sweep rate for steady-state testing; b) evaluate the performance of Pd and Pd-Cu MRs over a range of feed conditions and compositions; c) examine the effect of H₂S on MR performance.
- Task 2. Pd-Cu Membranes – The approach will be to integrate a) computational modeling of sulfur and hydrogen on Pd and Pd-Cu surfaces; b) treatment of membrane surfaces via gas exposure and temperature with both concomitant and subsequent surface analysis; and c) steady-state permeability testing of membranes over a wide range of conditions.
- Task 3. Novel H₂ Production and Separation – The approaches include CO₂-permeable membranes for separating CO₂ and H₂, binary and ternary membrane materials that are

contaminant-resistant, metal organic framework and carbon nanotube membranes, and performance testing of novel membranes from external membrane developers.

Results

Task 1. WGS Membrane Reactors – Tests were conducted with an 80-wt% Pd-Cu membrane in high H₂O, CO, and CO₂ atmospheres over a 350 – 900°C temperature range and 75 – 210 psig pressure range to determine the effect of these syngas components on hydrogen permeability. H₂ permeance appears not to be affected by H₂O over the temperature range of study. However, a dramatic roughening of the Pd-Cu surface was observed after exposure to steam. Such pitting may impact the viability of ultra-thin membrane reactors (1-10 μm). At <565°C and >765°C, H₂ permeance appears to be only slightly affected by CO; however, an appreciable decline in permeance was observed at 635°C. This decrease is likely due to carbon deposition on the membrane surface because of the prevalence of the Boudouard reaction at that temperature. Pitting at 635°C appears to be a result of increased catalytic activity of the membrane surface, as the CO-reduction reaction results in the formation of C and H₂O.

Task 2. Pd-Cu Membranes – Membrane alloy exposure tests were conducted to determine the effect of sulfur on hydrogen permeance. Membranes were exposed to 1000 ppm H₂S in H₂ under a selected temperature-time profile to determine permeance changes. Used membranes were then characterized via X-ray diffraction and scanning electron microscopy to determine phases present and morphological changes. Preliminary results indicate that the various alloys have different responses to sulfur with regard to either permeance or surface effects. In addition, alloy coupon exposure tests are in progress where 100-μm thick alloy coupons are exposed to flowing 1000-ppm H₂S in H₂ for set times at set temperatures to determine the sulfide growth rate/sulfide phases formed on the surface.

Task 3. Novel H₂ Production and Separation – A novel binary/ternary metal membrane was fabricated and screened with regard to flux. The preliminary data compared favorably with Pd and Pd-Cu results. In addition, several types of CO₂-

selective membranes based on ionic liquids were prepared and tested, but no valid data have been collected yet due to difficulties with sealing the membrane assemblies. Finally, several novel prototypes from external membrane developers were tested in an effort to develop a baseline or validate results, including prototypes from ORNL, Argonne National Laboratory (ANL), Synkera, and Eltron.

Special Recognitions & Awards/Patents Issued

1. B. Howard, B. Morreale – submitted Record of Invention last year for discovery of correlation between S tolerance and crystalline structure of Pd-Cu. DOE Patent Office preparing Patent Application, 06/05
2. Osemwengie Iyoha, representing the project, received the Best Student Paper Award at the Spring AIChE Meeting in Atlanta, GA, in April 2005.

FY 2005 Publications and Presentations

1. K. Rothenberger et al., “High-P Permeance of Porous Stainless Steel Coated with a Thin Pd Film via Electroless Plating”, *J. of Membrane Science*, Vol. 244, pp. 55-68, 11/04

2. F. Bustamante et al., “Kinetics of the Hi-T fWGS Reaction in an Empty Quartz Reactor and Quartz Reactors Packed w/ Inconel, Pd or Pd-Cu,” *AIChE Jour.*, Vol. 51, No. 5, 03/05
3. P. Kamakoti et al., “1st Principles Predictions of H₂ Flux Thru Sulfur-Tolerant Dense Binary Alloy Membranes,” *Science*, Vol. 307, 01/28/05
4. K. Rothenberger et al., “An Analytical Scheme for Evaluation of H₂ Perm. in Metals at High T&P,” poster only – PITTCON 2005, Orlando, FL, 02/05
5. K. Rothenberger et al., “Pd-Cu Alloy Membrane Performance Under Continuous H₂S Exposure,” NHA Conference, Washington, DC, 03/05
6. M. Ciocco et al., “Water-Gas Shift Membrane Reactors: Effect of Contaminants,” Coal Utilization Conference, Clearwater, FL, 04/05
7. O. Iyoha et al., “High Temperature and Pressure Pd-Cu Based H₂ Purification in the Presence of CO, CO₂, and H₂O,” *AIChE Spring Meeting*, Atlanta, GA, 04/05
8. O. Iyoha et al., “Effect of H₂S, CO, CO₂, and H₂O on the H₂ Permeability of Pd-Cu Alloys,” *NACS 2005*, Philadelphia, PA, 05/05
9. R. Killmeyer et al., “Hydrogen Separation,” poster only – DOE H₂ Review Meeting, Arlington, VA, 05/05