II.D.3 Scale Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

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Subcontractor:
Eastman Chemical Company, Kingsport, TN

Project Start Date: October 1, 2005
Project End Date: September 30, 2010
Phase II will continue till 2012.

Objectives

Develop low-cost hydrogen separation technology which:

- Produces high purity hydrogen from coal-derived synthesis gas (syngas).
- Retains carbon dioxide (CO_2) at coal gasifier pressures.
- Operates near water-gas shift (WGS) conditions.
- Tolerates reasonably achievable levels of coal-derived syngas contaminants.
- Delivers pure H_2 for use in fuel cells, gas turbines, and hydrocarbon processing.
- Meets DOE technical and economic targets in terms of cost-effectiveness compared to alternative technologies for hydrogen separation and carbon capture.

Technical Barriers

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

(K) Durability
(L) Impurities
(N) Hydrogen Selectivity
(P) Flux
(R) Cost

Technical Targets

TABLE 1. Progress toward Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	Current Eltron Membrane
Flux, SCFH/ft^2	200	300	450
Operating Temperature (°C)	300-600	250-500	250-440
Sulfur Tolerance (ppmv)	2	20	20 (prelim.)
System Cost (\$/ft^2)	500	<250	<200
ΔP Operating Capability (psi)	400	800-1,000	1,000
Carbon Monoxide Tolerance	Yes	Yes	Yes
Hydrogen Purity (%)	99.5	99.99	>99.99
Stability/Durability (years)	3	>5	0.9
Permeate Pressure (psi)	N/A	N/A	400

N/A - not applicable

Accomplishments

- Partnered with Eastman Chemical Company to perform scale up testing of Eltron's membranes.
- Continued development of Eltron's membrane system that meets or exceeds the 2010 DOE targets for hydrogen flux and selectivity at the desired operating temperature and pressure ranges and performs well at expected carbon monoxide (CO) concentrations.
- Down-selected tubular membranes for scale up and procured 250' of ½" outside diameter, 500 micron wall tubing.
- Developed electrodeposition techniques for depositing catalyst on the inside and outside surface of tubular membrane up to 5' long.
- Tested tubular membranes between 6" and 2' long under a variety of conditions including pressures up to 600 psig. Hydrogen recoveries as high as 90% were observed.
- Continued development of modeling tools to characterize and design membranes systems.

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Introduction

The objective of this multi-year project is to develop and scale up a membrane-based system enabling >95% carbon capture from an integrated gasification combined cycle (IGCC)-based power plant, while simultaneously producing essentially pure hydrogen at high flux. The system and hydrogen transport membranes are designed to operate under a variety of conditions and gas compositions, allowing flexible process design and engineering. Additionally, the hydrogen transport membranes can operate at the temperatures and pressures of WGS reactors, which enable effective integration with upstream and downstream process units. Particular focus is intended to address low-cost hydrogen separation that demonstrates improved tolerance to CO and syngas impurities, such as sulfur and mercury, as well as considerations for materials selection and mechanical configuration, which will lead to improved design and overall cost reduction when compared to conventional technologies. Process engineering and economic studies show that improved thermal efficiency and cost of electricity for plants incorporating this technology are likely.

Approach

This project will develop, test, and screen membrane compositions, preparation techniques, and structures (membrane, catalyst, disks, and tubes) in bench- to small pilot-scale units. This work includes evaluating commercially applicable manufacturing techniques for these systems. In addition to performance testing, detailed analytical characterization and evaluation of the mechanical characteristics of the membranes will be completed. Performance screening will be conducted at commercially applicable conditions (up to 1,000 psig and 250°C to 440°C) and feed compositions, including CO, water (H_2O), CO_2, and hydrogen (H_2).

Another major area of interest is the modeling of the process – from surface kinetics to mass transport models, to system performance, to fully integrated IGCC process and economic models. These models are used to guide the research and development effort and to ensure that the technology being developed is competitive with conventional and other emerging technologies. The engineering is also being done to design the next phase of the project – evaluation of a sub-scale engineering prototype that will be tested on "live" coal-derived syngas in an operating facility.

Results

During the past year Eltron Research & Development, Inc. has partnered with Eastman Chemical Co. to scale up Eltron's hydrogen membrane technology for pilot plant testing in a gasified coal feed stream. This partnership will result in a pilot plant demonstration of a hydrogen membrane reactor integrated with warm gas cleaning run on a gasified coal slip-stream. During the proposed work plan Eltron and Eastman will design, construct, and operate two different scale-up reactors. First, a 12 lbs/day hydrogen membrane reactor will be designed, constructed, and operated to demonstrate membrane performance on real syngas. Second, a 250 lbs/day reactor will be integrated with appropriate sorbent beds or with Eastman's warm gas cleaning pilot unit and operated.

Eltron down-selected tubular membranes and procured 250' of membrane substrate tubing from 2 different suppliers. This tubing was down-selected by Eltron based on performance and engineering considerations. The tubing is ½" outside diameter with a 500 micron wall thickness. Tubing received from one supplier is shown in Figure 1.

Eltron scaled up the equipment and techniques for depositing catalyst on tubular membranes. Catalyst was successfully deposited onto both the inside and outside

FIGURE 1. Digital image of as-received tubular membranes. A yardstick is included on the right side of the picture for reference.

surfaces of five foot long tubes. Figure 2 shows the surface of the tube with catalyst compared to an as-received tube.

Tubular membranes up to two feet long have been tested under a variety of conditions. Tubes were tested under simulated WGS gas compositions at temperatures between 300 and 400°C and at feed stream pressures up to 700 psig. Figure 3 shows data collected for a membrane tested up 600 psig feed pressure in a 100% H_2 feed stream. Flux rates up to 175 SCFH/ft^2 were observed at these high hydrogen partial pressures.

Once it was demonstrated that tubes could survive high hydrogen partial pressures, Eltron tested longer tubular membranes. The longest tube that Eltron can test in our facilities in Boulder, CO is a two foot tubular membrane. Eltron successfully tested a two foot long membrane in two separate tests. Each test was performed at pressures up to 600 psig. The first test utilized a feed stream mixture containing H_2 and N_2 and the second tested was conducted under a simulated WGS feed stream. Results showed that in both cases the two foot long tubular membranes were limited by the low flow rates of gases relative to the high surface area of the membranes. High hydrogen recoveries were observed up to 85% H_2 recovery; however, low flux rates were observed. This was attributed to bulk diffusion limitations on the feed side of the membrane.

FIGURE 2. Surface of tubular membrane before and after catalyst deposition. An as-received tube is shown on the bottom and a tube with deposited catalyst is shown on the top.

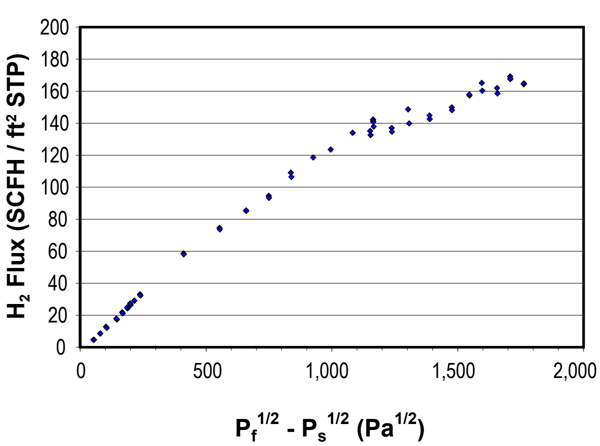

FIGURE 3. H_2 flux vs. the difference in the square roots of the hydrogen partial pressure of the feed and sweep sides of a six inch long tubular membrane.

To determine the effect of impurities on membrane performance, planar and tubular membranes were exposed to a live gasified coal feed streams. Eltron membranes were sent to Eastman and exposed to gasified coal syngas that had passed through a ZnO sorbent bed. This exposure was performed at 340°C and 700 psig. Following exposure the membranes were sent back to Eltron for characterization and permeation testing. The exposed membranes were tested in a 50% H_2/50% He stream at 300 psig and 340°C. Permeation results for exposed membranes were compared to membranes that had not been exposed, as shown in Figure 4.

Figure 4 shows that the membrane that had been exposed to gasified coal syngas had a hydrogen flux rate ~50% lower than a membrane that had not been exposed. Scanning electron microscopy and X-ray diffraction analysis showed that this drop in flux was due to the presence of sulfur, arsenic, and mercury on the surface of the membrane.

Eltron and Eastman have completed design and construction of a 12 lbs/day membrane reactor. Design specifications for the reactor included:

- 300 SCFH coal-derived syngas
- 450–900 psig feed pressure
- 500°C maximum operating temperature
- 85% H_2 recovery

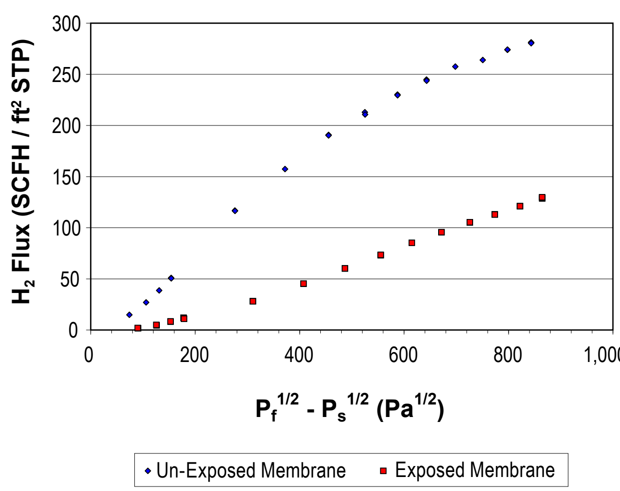

FIGURE 4. H_2 Flux vs. the difference in the square roots of the hydrogen partial pressure on the feed and sweep sides of the membrane for two planar membranes: one membrane that was not exposed to gasified coal syngas (blue diamonds) and one membrane that was exposed to gasified coal syngas (red squares).

The reactor will contain ten feet of Eltron's tubular membrane. Engineering design activities included preparation of piping and instrumentation diagrams, associated interlock narratives, and a process hazards analysis. Equipment was specified and procured and the reactor skid was constructed by Continental Technologies.

Conclusions and Future Directions

Eltron's hydrogen membranes met or exceeded most DOE 2010 targets in bench-scale operations. Process economic evaluations have shown that they provide significant improvements over conventional technologies for capturing CO_2 and providing high purity hydrogen for an IGCC power plant. Future work required to bring these to commercial reality includes:

- Construct and operate 12 lbs/day H_2 membrane reactor on gasified coal slip-stream.
- Design, construct, and operate 250 lbs/day H_2 membrane reactor integrated with warm-gas cleaning on a gasified coal slip-stream.
- Continue life and impurity testing on new materials as required.
- Maintain and improve techno-economic models.

Special Recognitions & Awards/Patents Issued

1. Hydrogen Transport Membranes – Published U.S. Patent Application No. 11/141/250.

FY 2010 Publications/Presentations

1. Hydrogen Separation Using Dense Composite Membranes, Part 1: Fundamentals. Michael. V. Mundschau, *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York, 125-154, 2009.

2. Hydrogen Separation Using dense Composite Membranes, Part 2: Process Integration and Scale-up for H_2 Production and CO_2 Sequestration. David H. Anderson, Carl R. Evenson IV; Todd H. Harkins; Douglas S. Jack; Richard Mackay; Michael. V. Mundschau; *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York; 155-172, 2009.

3. Carl Evenson. Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants. 2010 DOE Hydrogen Program Annual Merit Review . Washington, D.C. June 8, 2010.

4. David Anderson. Carl Evenson. John Faull. Doug Jack. Scale-up of Membranes for Separation of Hydrogen from Syngas for Carbon Capture. AIChE 2010 Annual Meeting. Salt Lake City. November 7–12, 2010.