II.G.1 Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

Doug Jack
Eltron Research & Development, Inc.
4600 Nautilus Court South
Boulder, CO 80501
Phone: (303) 530-0263; Fax: (303) 530-0264
E-mail: djack@eltronresearch.com

DOE Technology Development Manager:
Daniel Cicero
Phone: (304) 285-4826; Fax: (304) 285-4292
E-mail: Daniel.cicero@netl.doe.gov

DOE Project Officer: Arun Bose
Phone: (412) 386-4467
E-mail: Arun.Bose@netl.doe.gov

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Objectives

- Develop a low-cost system to produce hydrogen from coal-derived synthesis gas and enable cost-effective capture of CO_2 for sequestration that meets DOE technical and economic targets:
  - System should operate near water-gas shift conditions
  - High purity hydrogen should be delivered
- Obtain engineering scale-up data in 220 lb H_2/day unit using actual coal-derived synthesis gas.
- Design, build and operate 4 ton/day unit as final scale-up step prior to commercialization.
- Ensure system is tolerant to expected levels of coal-derived synthesis gas contaminants.

Technical Barriers

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

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

Technical Targets

Table 1. Progress towards Meeting DOE Targets

Performance Criteria	2010 Target	2015 Target	Current Eltron Membrane
Flux, SCFH/ ft^2	250	300	450
Operating Temperature, °C	300-600	250-500	250-440
Sulfur Tolerance (ppmv)	2	20	20 (prelim.)
System Cost (\$/ft^2)	1,000	<500	~600
ΔP Operating Capability (psi)	400	400-1000	1,000
Carbon monoxide tolerance	Yes	Yes	Yes
Hydrogen Purity (%)	99.99	>99.99	>99.99
Stability/Durability (years)	3	>5	0.9

Accomplishments

- Developed membrane system that meets or exceeds the 2010 DOE targets for flux and selectivity at the desired operating temperature and operating pressure ranges and performs well at expected CO concentrations.
- Developed cermet materials with comparable performance to Pd membranes.
  - Tested for more than 500 hours without loss in permeability.
- Designed, constructed and began operations on high-pressure lifetime skids.
- Improved characterization of membranes leading to better understanding of preparation and performance.
- Developed alloys for membranes and catalysts leading to improved performance and manufacturability.
- Developed modeling tools to characterize and design membranes/systems.
- Improved membrane-based integrated gasification combined cycle (IGCC) flow sheets showing:
  - Carbon capture over 95%
  - Higher heating value (HHV) efficiency ~6% better than conventional technology

– Cost of electricity ~10% better than conventional technology

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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 IGCC-based 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 water-gas shift reactors enabling effective integration with upstream and downstream process units. Particular focus is intended to address low-cost hydrogen separation that demonstrates improved tolerance to carbon monoxide and synthesis gas 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 are showing that improved thermal efficiency and cost of electricity for plants incorporating this technology are likely.

Approach

The approach being taken in this project is to develop and screen membrane compositions, preparation techniques and structures (membrane, catalyst, disks and tubes) in bench to small pilot size 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 are done. Performance screening is done at commercially applicable conditions (up to 1,000 psig and 250-440°C) and feed compositions including CO, H_2O, CO_2, and H_2.

Another major thrust in this effort is 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 synthesis gas in an operating facility.

Results

Eltron has tested dozens of catalyst and membrane alloy compositions during the past year. Membrane alloy compositions were evaluated for their ability to maintain high flux at improved mechanical strength and better resistance to hydrogen embrittlement. Catalyst alloys were assessed for their impact on flux and resistance to impurities. The results of a number of these tests are shown in Figure 1. The large range of fluxes shown in this figure illustrates the importance of proper catalyst and alloy selection on the performance of the membrane. All of the tests were run at 340°C and 400 psig total differential pressure across a 150 micron thick membrane. This work has allowed us to down-select the catalyst composition to be used for scaling up to the next phase of the project.

In addition to the membrane alloy and catalyst alloy work described above, the impact of asymmetric catalyst thicknesses and catalyst compositions (on the feed and permeate side of the membranes) is also being investigated. As would be expected, results show that this also has a significant effect on system performance. These tests will continue so that the ultimate membrane performance can be optimized.

Another important variable affecting the performance of the membranes is temperature. This affects both flux and membrane stability. A number of experiments evaluating performance from 250°C to 440°C were performed. These showed that a temperature range of about 320-360°C gives an optimum performance trading off flux versus membrane stability.

Significant efforts to improve the chemical and physical characterization of the membrane have also been undertaken. These have allowed us to optimize the preparation techniques for making the membranes, understand differences in performance between membranes, and will ultimately allow us to set quality

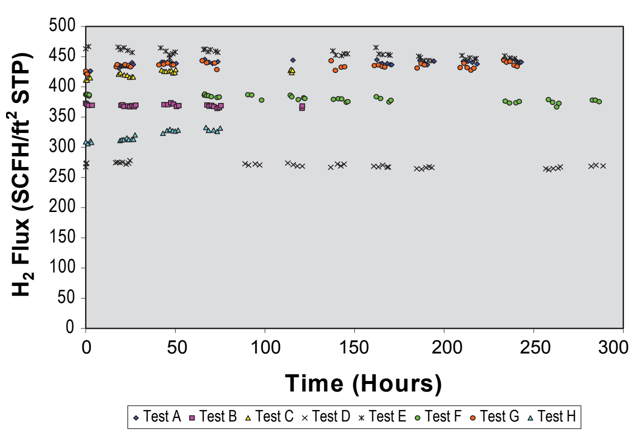

FIGURE 1. Membrane Alloy and Catalyst Alloy Permeation Data

control standards for commercial manufacture of membranes.

Two high-pressure, lifetime testing systems were designed, constructed and started up during the past year. A photo of that skid is shown in Figure 2. This skid contains two trains that are capable of operating under conditions expected in a commercial IGCC power plant. The system will operate up to 450°C, 1,000 psig, and use full water-gas shift feed (including the steam). These will mainly be used to run long life tests of thousands of hours in duration to establish that the membranes perform stably over time. This is the last major technical target to be achieved for Eltron's membrane system.

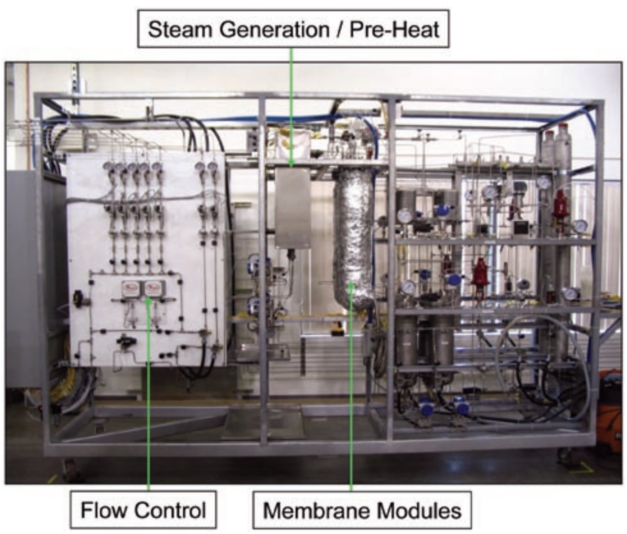

FIGURE 2. Lifetime High-Pressure System

A mass transport model was developed that examines the contribution of the different mass transfer resistances to hydrogen transport. The model includes resistances from the boundary layer between the catalyst and the bulk gas phase (on feed and permeate), transport through the catalyst layer (feed and permeate), resistance at the buried interface between the catalyst and the membrane (feed and permeate), and transport through the membrane. Detailed experiments are underway allowing the quantitative contributions of each resistance to the overall mass transport of hydrogen through the system are underway.

Process and economic modeling of an IGCC plant incorporating Eltron's technology has been done along with similar modeling for conventional technology for comparison. A block flow diagram representing one of the myriad of cases examined is shown in Figure 3. For this case, Eltron's membrane technology is paired with warm gas cleaning technology (to remove sulfur and other contaminants from the synthesis gas). The synthesis gas is generated using a high-pressure General Electric gasifier. Comparison of this flow sheet with one using a Selexol-based synthesis gas cleaning technology shows several significant benefits. These are illustrated in the table shown as Table 2. This table shows a comparison of three cases: the first column is an IGCC plant with no carbon capture as a reference. The second is for pre-combustion capture of CO_2 using Selexol. The third column represents the base case shown in Figure 3. As can be seen, the thermal efficiency is improved by more than 6% over conventional technology, while the cost of electricity is improved by about 8%.

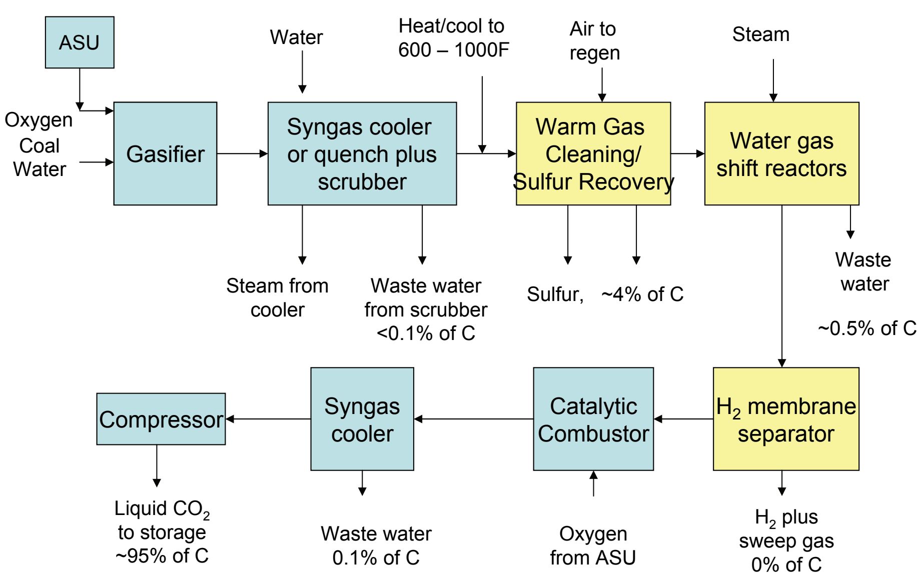

FIGURE 3. Pre-Combustion CO_2 Capture with Eltron Hydrogen Membrane Technology

The fourth column in the table is an attempt to evaluate the Eltron technology on an incremental basis versus the Selexol case. This can give a better picture of the improvements possible since the synthesis gas cleaning and CO_2 capture technologies are only a small part of the capital cost of an IGCC facility; yet capital costs dominate the economics of the plant. Again, it is easily seen that with over 95% carbon capture, or 5% more than the conventional technology, Eltron's hydrogen membrane

TABLE 2. Technology Comparison

CO_2 Capture Method	None[1]	Pre-combustion Selexol	Eltron WGCU & Membrane	Δ Selexol vs. Eltron WGCU & Membrane
Coal Feed (tpd)	5,876	3,258	3,526	268
Net Power (MW)	640	239	318	79
HHV Efficiency	38.2%	27.4%	33.6%	6.2%
% CO_2 Captured	0%	91.3%	95.3%	4.0%
Cost of Electricity ($/MWh)	78.0	115.5	106	77.32
Plant Cost ($/kW)	1,813	2,434	2,292	1,863[2]

[1] NETL Report, "Cost and Performance Baseline for Fossil Energy Plants," May 2007
[2] Cost applicable only to the incremental net power produced
WGCU - Warm gas cleaning unit

is superior from both a capital and a thermal efficiency viewpoint.

Conclusions and Future Directions

Eltron's hydrogen membranes met or exceeded most DOE 2015 targets in bench-scale operation. 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 plant. Future work required to bring these to commercial reality includes:

- Life testing (>3,000 hours) of membranes at commercially applicable conditions.
- Continued work with commercial suppliers for manufacture of full-size alloy membranes.
- Delineation of impact of contaminants on membrane performance and impact on process integration.
- Design, construct and operate a sub-scale engineering prototype on "live" coal-derived synthesis gas.

Special Recognitions & Awards/Patents Issued

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

FY 2008 Publications/Presentations

1. CO_2 Capture and Hydrogen Production in IGCC Power Plants – Evenson, Carl – presented at the CTSI Conference on Clean Technology and Sustainable Industries, Boston, MA, June 1-4, 2008.

2. Low Cost IGCC Pre-Designed for Cost-Effective CO_2 Capture – Rollins, William S.; Armstrong, Phillip A.; Stein, Vaneric E.; Jack, Doug S. – presented at PowerGen International 2007, New Orleans, LA, December 11-13, 2007.

3. Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants - Jack, Doug - NETL H2-from-Coal Separations Project Reviews National Energy Technology Laboratory, Morgantown, WV, April 29 – 30, 2008.

4. Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants – Jack, Doug - 2008 DOE Hydrogen Program Annual Merit Review, Arlington, VA, June 9-13, 2008.