

II.D.2 Scale-Up of Hydrogen Transport Membranes for IGCC and FutureGen Plants

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Project Start Date: October 1, 2005
 Project End Date: September 30, 2009.
 Planned Phase II will continue till 2014.

Objectives

Develop low-cost hydrogen separation technology which:

- Produces high purity hydrogen from coal-derived synthesis gas (syngas).
- Retains carbon dioxide (CO₂) at coal gasifier pressures.
- Operates near water-gas shift (WGS) conditions.
- Tolerates reasonably achievable levels of coal-derived syngas contaminants.
- Delivers pure H₂ for use in fuel cells, gas turbines, and hydrocarbon processing.
- Meets U.S. Department of Energy (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 Hydrogen, Fuel Cells and Infrastructure 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

- Developed a 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.
- Developed ceramic-metallic (cermet) blend materials with comparable performance to palladium (Pd) membranes and 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 a better understanding of preparation and performance.
- Developed alloys for membranes and catalysts leading to improved performance and manufacturability.
- Manufactured and tested 10 high flux and low-cost alloys.
- Demonstrated tolerance to 20 ppm hydrogen sulfide (H₂S) at 340°C and ambient pressure.

- Developed modeling tools to characterize and design membranes/systems.
- Improved membrane-based integrated gasification combined cycle (IGCC) flow sheets showing:
 - Carbon capture >95%.
 - Thermal efficiency 32% for cold gas cleaning and 33.6% for warm gas cleaning; ~6% better than conventional technology.
 - Cost of electricity ~10% better than conventional technology.



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 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 CO₂, water (H₂O), CO₂, and hydrogen (H₂).

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 process development unit that will be tested on “live” coal-derived syngas in an operating facility.

Results

Eltron has tested dozens of catalyst and membrane alloy compositions during the course of the project. Membrane alloy compositions were evaluated for their ability to maintain high flux at improved mechanical strength and enhance resistance to hydrogen embrittlement. Catalyst alloys were assessed for their impact on flux and resistance to impurities. This work allowed down-selecting the catalyst composition to be used for scaling up to the production 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. Results show that this also has a significant effect on system performance. These tests will continue so that the 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 in the range of 250°C to 440°C were performed; these experiments showed that a temperature range of about 320°C to 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, allowing for the optimization of preparation techniques for making the membranes and understanding the differences in performance between membranes. This enables the project team to set quality control standards for the commercial manufacturing of membranes.

Two high-pressure, lifetime testing systems were designed, constructed, and started. Figure 1 shows H₂ fluxes across the selected membrane at T=340°C and ΔP=400 and 600 psi. Figure 2 is a photo of the skid. 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 WGS 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.

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.

Process and economic modeling of an IGCC power plant incorporating Eltron’s technology has been completed along with similar modeling for comparison to conventional technology. 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 syngas). The syngas is generated using a high-pressure General Electric gasifier. Comparison of this flow sheet with the one using a Selexol-based syngas cleaning technology shows several significant benefits, which are illustrated in 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 column is for pre-combustion capture of CO₂ using Selexol. The third column represents the base case shown in Figure 3. As

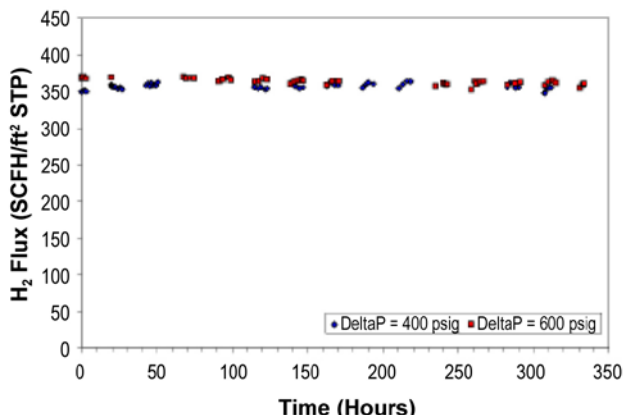


FIGURE 1. Membrane Alloy Permeation Data at T=340°C and ΔP=400 and 600 psig

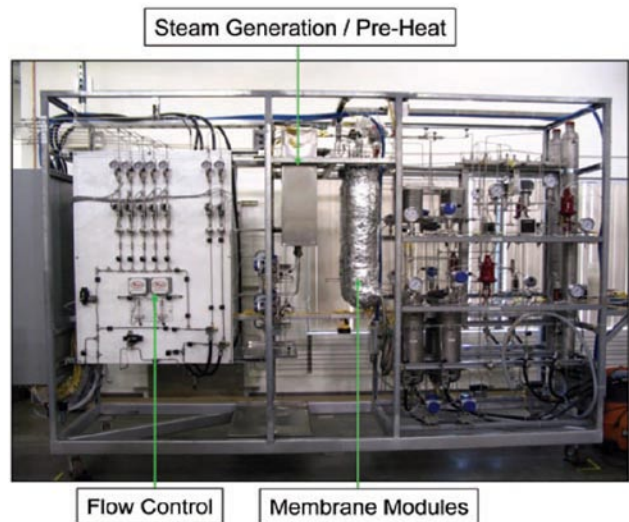


FIGURE 2. Lifetime High-Pressure System

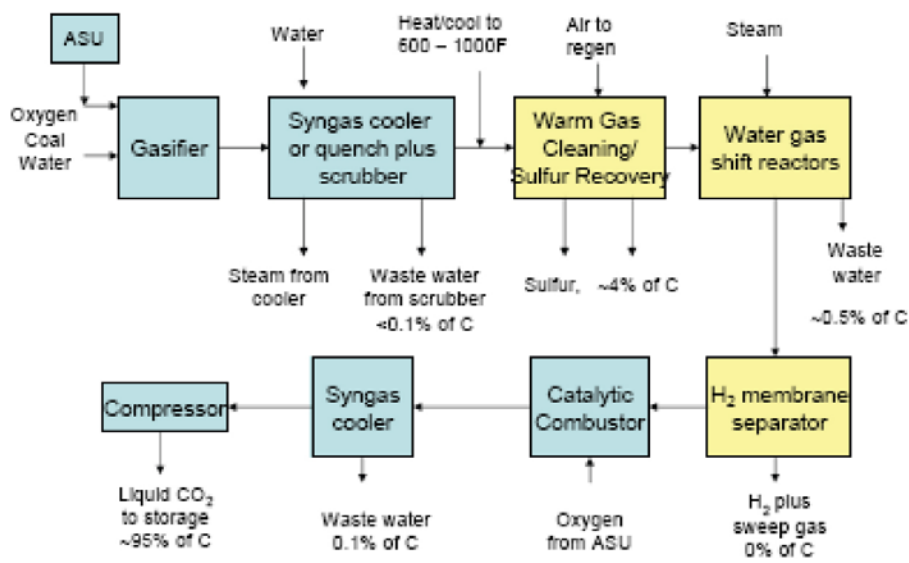


FIGURE 3. Pre-Combustion CO₂ Capture with Eltron Hydrogen Membrane Technology

can be seen, the thermal efficiency is improved by more than 6% over conventional technology, while cost of electricity is improved by about 8%.

TABLE 2. Technology Comparison

CO ₂ Capture Method	None	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

WGCU - warm gas cleaning unit; HHV - higher heating value

The fourth column in the table is an attempt to evaluate the Eltron technology on an incremental basis versus the Selexol case. This provides a view of the possible improvements since the syngas cleaning and CO₂ 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 shown that with over 95% carbon capture, or 5% more than the conventional technology, Eltron's hydrogen membrane is superior from both a capital and a thermal efficiency viewpoint.

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 CO₂ and providing high purity hydrogen for an IGCC power plant. Future work required to bring these to commercial reality includes:

- Focus near-term on scale-up work with commercial suppliers on the manufacturing of full-size alloy membranes.
- Perform life testing on new materials as required.
- Understand the impacts of contaminants.
- Maintain and improve techno-economic models.
- Design, build, and operate a 220 lb/day process development unit – planned 2010+ goal.

Special Recognitions & Awards/Patents Issued

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

2009 Publications/Presentations

1. CO₂ Capture and Hydrogen Production in IGCC Power Plants, Jack, Doug, Gasification Technologies Conference, October 5–8, 2008.
2. Hydrogen Separation Using Dense Composite Membranes, Part 1: Fundamentals. Michael V. Mundscha, *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York, 125-154, 2009.
3. Hydrogen Separation Using dense Composite Membranes, Part 2: Process Integration and Scale-up for H₂ Production and CO₂ Sequestration. David H. Anderson, Carl R. Evenson IV; Todd H. Harkins; Douglas S. Jack; Richard Mackay; Michael V. Mundscha; *Inorganic Membranes for Energy and Fuel Applications*; Arun C. Bose, Editor: Springer: New York; 155-172, 2009.