

## II.A.5 Integrated Ceramic Membrane System for Hydrogen Production

Joseph Schwartz

Praxair, Inc.  
175 East Park Drive  
PO Box 44  
Tonawanda, NY 14151  
Phone: (716) 879-7455; Fax: (716) 879-7567  
Email: joseph\_schwartz@praxair.com

DOE Technology Development Manager:  
Arlene Anderson

Phone: (202) 586-3818; Fax: (202) 586-9811  
E-mail: Arlene.Anderson@ee.doe.gov

DOE Project Officer: Jill Gruber

Phone: (303) 275-4961; Fax: (303) 275-4753  
E-mail: Jill.Gruber@go.doe.gov

Contract No. DE-FC36-00GO10534.

Start Date: May 1, 2000  
Projected End Date: September 30, 2008

### Objectives

Project – Develop a low-cost reactive membrane-based hydrogen production system

- Use existing natural gas infrastructure
- Demonstrate improved thermal efficiency when compared to conventional systems
- Develop a reactor to serve both the transportation and industrial markets
  - Industrial market provides immediate opportunities
  - Gain valuable operating experience before fuel cells are widely used

Phase III – Integrate hydrogen transport membrane (HTM) with water-gas shift (WGS)

- Low-cost hydrogen production, separation, and purification
- Demonstrate HTM performance in reactive environments
- Develop a versatile system that can be combined with any syngas generation method for improving hydrogen production, especially at a distributed scale

### Technical Barriers

Hydrogen Separations

(K) Durability

(M) Membrane Defects

(P) Flux

(R) Cost

### Technical Targets

	2006	2010	2015
Flux (scfh/ft <sup>2</sup> )	>200	250	300
Cost (\$/ft <sup>2</sup> )	1,500	1,000	<500
Durability (years)	<1	3	>5
ΔP Operating Capability	200	400	400-600
Hydrogen Recovery	60	>80	>90
Hydrogen Quality	99.98	99.99	>99.99

### Accomplishments

- Increased flux by a factor of seven by improving the substrate design
- Increased membrane reliability and improved substrate coating process
- Developed a model to predict membrane and reactor performance
- Completed initial cost estimates to develop targets for substrate cost and membrane thickness
- Completed construction of integrated HTM/WGS test reactors



### Introduction

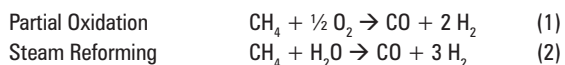
Capital costs account for 70-85% of the total hydrogen cost for on-site systems that produce less than about 50 kg/h. As a result, the opportunity exists to substantially reduce product hydrogen costs by introducing advanced technology that can reduce the number of unit operations and capital cost. The focus of this project is to develop an integrated system for the production of hydrogen at 2.4-12 kg/h. The design is based on replacing the WGS reactor(s) and pressure swing adsorption (PSA) unit with a single integrated shift reactor/membrane system. This will reduce the number of unit operations and vessels in the system, and consequently, could reduce the capital cost. Another potential advantage is that the membrane will remove hydrogen in the shift reactor, which will shift the equilibrium toward increased hydrogen production. Therefore, this system also offers the added benefit of increased hydrogen production efficiency when

compared to conventional technology. This project emphasizes the development of membrane technology and the development of a reactor design to use the membranes. Praxair is responsible for making the membranes, testing them, and developing the reactor design. Research Triangle Institute was an important partner in the previous phase.

## Approach

Phase I of the project determined that sequential reactors are preferable to a single integrated oxygen transport membrane (OTM)/HTM reactor. A schematic diagram of the sequential membrane reactor system is shown in Figure 1. The system comprises two reactors, one containing an OTM and the other containing an HTM. This project focuses exclusively on developing the HTM reactor. The OTM reactor is being pursued in other projects. Successful development of the HTM reactor is not dependent on developing the OTM reactor. Therefore, it can be used with other syngas reactors, so it can be used independently. This includes the possibility that the HTM reactor could be commercialized before development of the OTM reactor is complete.

Air at low pressure (a few psig) is fed to the retentate side of the OTM and compressed natural gas (200-400 psig) and steam are fed to the permeate side of the OTM. Oxygen is transported across the OTM to the permeate side, where it reacts with natural gas to form syngas (Reaction 1). A portion of natural gas also reacts with steam to form syngas. A catalyst is incorporated in the reactor to promote steam reforming (Reaction 2) on the permeate side.



Alternatively, other conventional syngas production methods including steam reforming, autothermal reforming, and partial oxidation could be used. These methods have the added benefit that they are more amenable to using renewable liquid feedstocks. The syngas product is cooled and fed to the retentate side of the HTM, where a catalyst is used to promote the water gas shift reaction (Reaction 3). Hydrogen product is transported through the HTM to the permeate side driven by a hydrogen partial pressure difference. Additional hydrogen is formed by the water gas shift

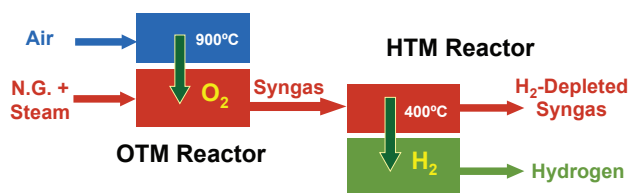
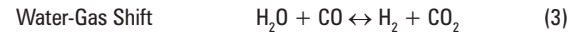


FIGURE 1. Integrated Membrane Reactor System

reaction because hydrogen removal by the HTM shifts the equilibrium toward hydrogen production.



As much hydrogen as possible is recovered from the reactor by the HTM. Eventually, a pinch partial pressure difference between the reaction zone and the permeate side is reached and no more hydrogen can be recovered. The retentate, which includes a significant amount of hydrogen, is recycled or used in another process.

## Results

### Membrane Testing

There has been significant progress in HTM development. As shown in Figure 2, the flux of the membranes has improved by a factor of seven since the start of the project. We have been able to decrease the pore size on the surface of the substrate by grading the porosity so that the pores in the bulk of the substrate are still large. These improvements in the substrate have enabled thinner coatings, and consequently, higher flux. Now that the project has restarted, further improvements are expected as the porosity grading technique is optimized. Moving the tube coating and testing to the same location as the substrate manufacturing should allow for increased synergy, shorter turnaround time, and faster improvement. Substrate pore size has been decreased using new techniques to modify the surface pore structure. Substrate porosity has increased because smaller pores exist only on the surface. The pores are significantly smaller at the interface with the membrane. This allows a thinner film to span the pores without producing any pinholes.

### Membrane Modeling

A membrane simulation has been developed. The simulation predicts flows of hydrogen, carbon monoxide, carbon dioxide, and water through the integrated

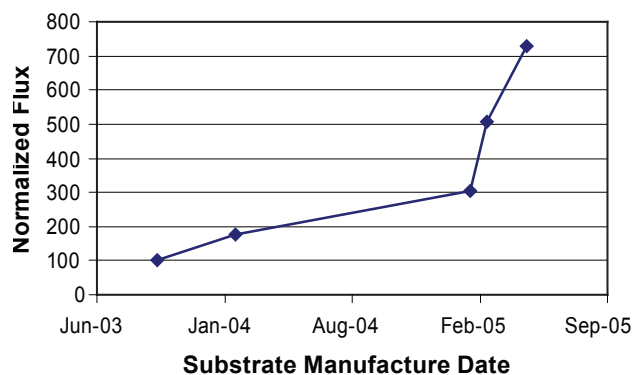


FIGURE 2. Hydrogen Flux Improvement

HTM/WGS. The basic principal of the integrated reactor is that hydrogen is continuously removed, so the gas composition changes to convert CO and water to hydrogen and CO<sub>2</sub>. This allows for increased CO conversion, increased hydrogen production, and improved process efficiency. Figure 3 shows the results of a typical membrane reactor simulation run. This particular case looked at typical syngas flows from a steam methane reformer designed to produce 2,000 scfh of hydrogen, which is the baseline size for comparing the membrane reactor to conventional technology. At very large sizes, conventional technology will be more economical than membrane reactors because the cost of the membrane scales linearly with increased hydrogen production. However, this can be an advantage at smaller sizes. One object of the economic analysis is to determine the size range in which the membrane reactor has an advantage.

The simulation shows some important points regarding the membrane reactor system. Hydrogen removal leads to increased hydrogen production. The curves shown in Figure 3 show hydrogen recovery up to 100% based on the inlet hydrogen feed. Even at “complete” recovery, there is still a significant amount of hydrogen in the reactor. If one is willing to run the reactor at very low permeate hydrogen partial pressure or at relatively low hydrogen flux for some of the membrane area, it is possible to recover more hydrogen than was fed because of the shift reaction. A typical PSA system will recover less than 80% at this scale. Hydrogen flux drops as recovery increases. This means that the marginal cost of additional hydrogen production increases because more membrane area is required to produce the next incremental amount of hydrogen. This can be seen by looking at the decreasing slope of the hydrogen recovery curve as area increases. Balancing the additional marginal cost against the benefit of increased production is another goal of the economic analysis portion of the project. At high hydrogen recovery, the concentration of hydrogen and CO can get quite low. This leads to an environment that could

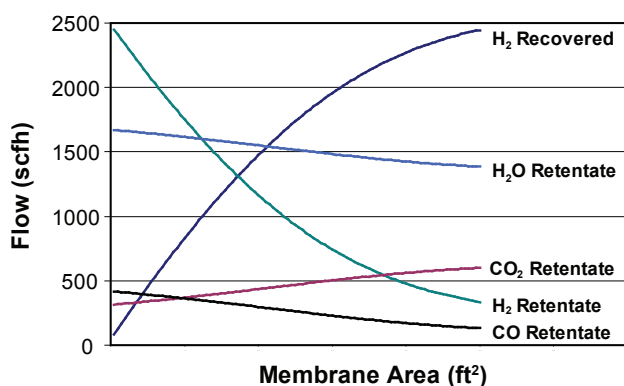


FIGURE 3. Membrane Reactor Simulation Results

potentially oxidize the water gas shift catalyst. The catalyst, or at least the catalyst near the reactor outlet, must be selected so that it can operate properly using the unusual gas compositions produced in a membrane reactor.

The membrane simulation can also examine the effects of cocurrent and countercurrent purge streams. Purge streams allow the hydrogen partial pressure on the permeate side to be very low, but introduce the additional cost of further separation because the hydrogen must be separated from the purge stream. This is another important consideration when doing economic analysis. The membrane simulation will be an essential tool for the economic analysis to be conducted in Phase III.

### Economic Analysis

One important target to establish is the required thickness of the membrane to be able to meet the DOE goals. The 2010 DOE flux target is 250 scfh/ft<sup>2</sup>. The DOE cost target is \$1,000/ft<sup>2</sup>. The goal of our project is to minimize the cost of producing hydrogen. Therefore, these two targets are combined into one. The cost target is \$4/scfh capital cost. This combines two components of the cost that are interrelated. For example, a membrane that met both targets would lead to a capital cost of \$4/scfh while a membrane that had a flux of 200 scfh/ft<sup>2</sup>, short of the DOE target, and a capital cost of \$500/ft<sup>2</sup> would have a hydrogen cost of \$2.50/scfh. Even though the second membrane does not meet the flux target, it would be a better fit for the goals of this project because it reduces the cost of hydrogen. This analysis assumes that the cost of the substrate, seals, membrane fittings, and reactor housing is \$250/ft<sup>2</sup> of membrane area, the cost of palladium is \$375/oz and the cost of silver is \$13.32/oz. Both prices are based on market prices as of June 19, 2007. This means that the cost of Pd/Ag for a 75% Pd membrane is about \$10 per square foot per micron of membrane thickness. The analysis also assumes a membrane flux of 200 scfh/ft<sup>2</sup> for a 5-micron membrane and that the flux is inversely proportional to membrane thickness, as has been verified in membrane testing. Figure 4 shows the results of this analysis including the revised target of \$4/scfh, or \$8,000 for a 2,000 scfh system. This analysis indicates that the project cost target can be met using a membrane that is less than about 10 microns. We have produced membranes that are less than 10 microns, so this is an achievable target.

### Conclusions and Future Directions

- Reducing the surface pore size by grading the porosity has allowed the membrane thickness to be reduced and significantly improved membrane performance.

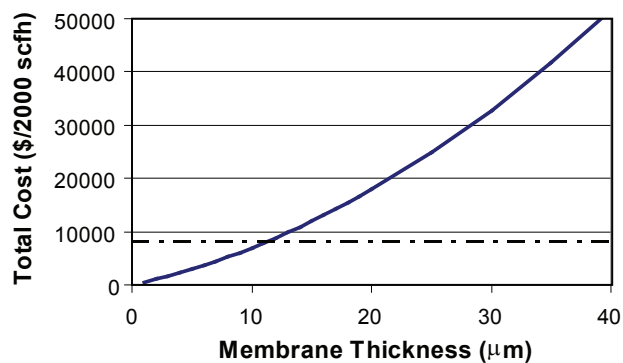


FIGURE 4. Capital Cost as a Function of Membrane Thickness

- The capital cost and performance targets should be combined into a single cost target if the goal is to minimize the cost of producing hydrogen.
- Future economic analysis will define the performance break points between membranes and PSA and define the optimum hydrogen recovery in the unit. The membrane reactor simulation will be an important tool in this analysis.
- Future membrane development and testing will be done at the same location so that improvements can be made more rapidly.
- Phase III will focus on continuing to improve the membrane, reduce its cost, and demonstrate its performance when integrated in a water gas shift reactor.

### FY 2007 Publications/Presentations

1. A poster was presented at the DOE Annual Merit Review Meeting (May 2007).