IV.A.8 Integrated Ceramic Membrane System for Hydrogen Production

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Objectives

- Develop an integrated ceramic membrane system using an oxygen transport membrane (OTM) in the first stage to produce syngas and a hydrogen transport membrane (HTM) in the second stage to produce hydrogen at a low cost on a scale of 1000-5000 SCFH; OTM development is being done outside this project
- Develop a palladium-based HTM that can meet performance goals for flux, selectivity, life, and cycling on a bench scale
- Develop the substrate materials, coating materials, and appropriate manufacturing technology
- Confirm membrane performance
- Confirm that the process is cost-competitive for distributed hydrogen production

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:

- A. Fuel Processor Capital Costs
- B. Fuel Processor Manufacturing
- C. Operation and Maintenance
- F. Control and Safety
- L. Durability
- M. Impurities
- N. Defects
- O. Selectivity
- P. Operating Temperature
- Q. Flux

- S. Cost
- T. Oxygen Separation Technology

Technical Targets

	Praxair Status	2005 DOE Target	2010 DOE Target
Flux (scfh/ft^2)	60-100 scfh/ft^2 at 20 psid and 400°C	100	200
Cost (\$/ft^2)	<\$1000/ft^2	1500	1000
Durability (yrs)	demonstrated 600 hours, test stopped as planned	1	3
ΔP Operating Capability	demonstrated 40 psi, working on higher-pressure reactor design	200	400
Hydrogen Recovery	N/A	>70	>80
Hydrogen Quality	>99.9%	99.9	99.95

Approach

- Develop hydrogen transport membrane
  - Prepare low-cost substrate tubes with high porosity and small pore size at the interface
  - Develop alloy coating process to produce thin, leak-free films
  - Demonstrate flux, life, and cycling
  - Produce larger membranes
- Develop HTM process
  - Design and build test reactors
  - Select appropriate water-gas-shift catalyst
  - Demonstrate HTM performance
- Develop conceptual design for Integrated Ceramic Membrane System (ICMS)
- Update process economics
  - Revise performance and cost targets
  - Define manufacturing process for HTM and ICMS
  - Compare cost of hydrogen production using ICMS with using other methods

Accomplishments

- Produced thin, leak-free HTM that surpasses the DOE cost targets and matches the performance targets
- Increased flux by a factor of 5 in the last 18 months without significantly increasing projected cost
- Reduced pore size to less than 5 μm and film thickness to less than 10 μm
- Demonstrated resistance to H_2S and CO contaminants
- Completed Phase IIA

Future Directions

- Continue to improve HTM performance
- Develop conceptual design for commercial-scale ICMS
- Update process economics to determine the cost of hydrogen and compare to hydrogen produced using other methods

Introduction

Natural gas is one of the primary resources for production of hydrogen. Natural gas is mixed with steam, oxygen, air, or a combination of these to produce syngas, which contains hydrogen. One potentially low-cost, efficient way to produce syngas is to use a ceramic membrane to separate oxygen from air. The separated oxygen reacts with natural gas and steam over a catalyst to produce syngas. The membrane, which can be integrated into the syngas generator, eliminates the need for a large, expensive air separation plant. (The work on oxygen membranes is being done in a different project.) Implementing those membranes to produce hydrogen is one of the goals of this project. To produce hydrogen, the product syngas is typically sent to another reactor, where most of the CO and some of the steam in the syngas react to produce additional hydrogen. Using conventional existing technology, the hydrogen in the product stream from the second reactor must be purified using additional large, expensive equipment. The goal of the current phase of this project is to simplify hydrogen production by combining the second reactor and the hydrogen purification into a single step in a single vessel. This process could significantly reduce the capital cost of producing hydrogen, and consequently, reduce the price of hydrogen to the consumer. Because of the way the reaction and separation are combined, it is also possible to produce more hydrogen than would be possible using the conventional two-step approach, providing additional benefit to the consumer. A diagram of the process is shown in Figure 1.

Phase I of this project analyzed and compared several different processes. Based on projected cost, efficiency, and likelihood of success, a two-stage process wherein each stage is comprised of a membrane reactor was selected. The analysis indicated that this process has the potential to be the least expensive hydrogen production method of those evaluated. Phase II has focused on developing the hydrogen purifier to put this process into practice. Membranes have achieved satisfactory performance and continue to improve.

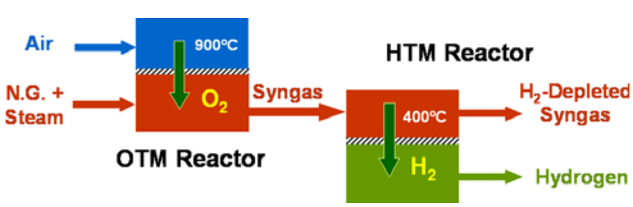

Figure 1. Integrated Membrane Reactor System

Approach

This phase has emphasized developing a hydrogen membrane that will have a much lower cost than competing membranes while providing acceptable performance. Praxair's experience and expertise in making porous ceramic membrane substrates will be applied to making substrates for Pd membranes. This requires applying the techniques used for other materials to produce substrates from materials that have thermal expansion properties very similar to the Pd alloy to avoid thermal stress when cycling. To keep the total cost down, the membranes must be thin because of the high cost of Pd, and the substrates must be produced using simple processes that can be easily scaled up to produce large quantities. The goal is to maximize HTM performance while restricting ourselves to low-cost, scalable substrate production methods. Once these membranes are made, they will be tested under ideal, realistic, and harsh conditions to determine their performance. The actual HTM performance will be used to develop a conceptual reactor design and determine the cost of producing hydrogen at a scale appropriate for distributed, on-site production.

Results

There has been significant progress in HTM development. As shown in Figure 2 , the flux of the membranes has improved by a factor of five in the last 18 months. In particular, a step-change improvement in substrate manufacturing was made earlier this year. Improvements in the substrate have enabled thinner coatings and, consequently, higher flux.

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. Figure 3 shows the pores of the substrate and a cross-section of the alloy film. The pores are significantly smaller at the interface with the membrane. This allows a thinner film to span the pores without producing any pinholes. The adhesion of the metal alloy to the substrate can also be seen in the photo due to the degree of penetration of the metal into the substrate.

The mixing of the Pd and Ag in the alloy has been excellent. The electroless plating procedure used to deposit the alloy allows for a uniform composition in the film. Figure 4 shows a normal cross-section view of the membrane and substrate followed by elemental analysis. As can be seen in the figure, the Pd and Ag mix well and penetrate the substrate enough to adhere properly, but do not fill the pores. The substrate contains Zr.

Another important goal of the testing is to determine the effects of potential contaminants, such as H_2S and CO. Figures 5 and 6 show the effect of H_2S on both Pd-Ag and Pd-Cu membranes. Testing on the effect of CO is in progress. There is an initial loss of performance with H_2S introduction, but performance can be recovered after feeding hydrogen and performing a thermal cycle. Thermal cycling and pure hydrogen were not tried with the Pd-Cu membrane, but it recovered more than half of the lost flux simply upon removal of the H_2S from the feed stream. The Pd-Ag sample also passed the 500-hour goal for a life test and demonstrated three complete thermal cycles. Demonstrating life and cycling are important goals of the test project. Figure 5 shows the effect of 45 ppm H_2S exposure for three hours and subsequent recovery (shaded portions of Figure 5). This test also completed three thermal cycles.

Figure 6 shows the effect of H_2S on Pd-Cu membranes. As expected, the flux through the Pd-Cu

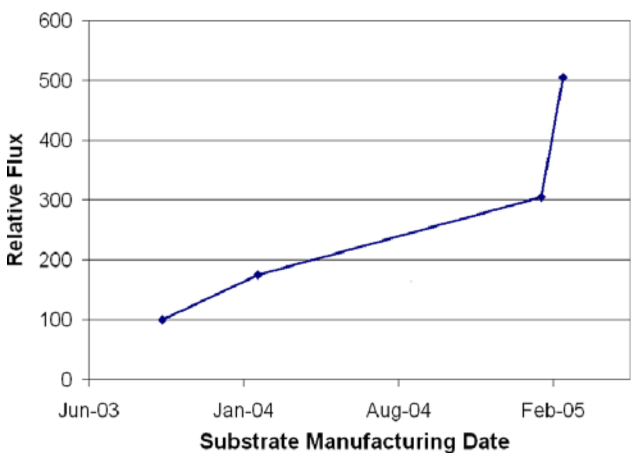

Figure 2. Hydrogen Flux Improvement

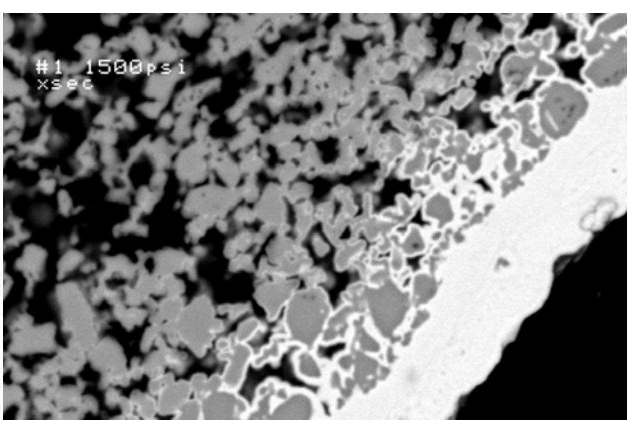

Figure 3. Cross-Section of Pd Alloy Membrane and Substrate

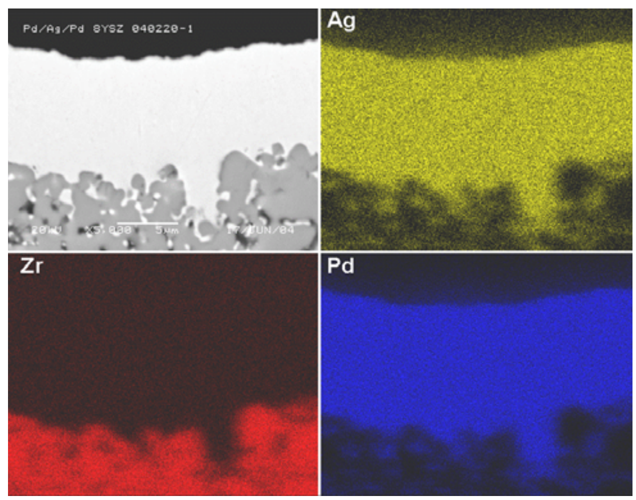

Figure 4. Elemental Analysis of the Membrane

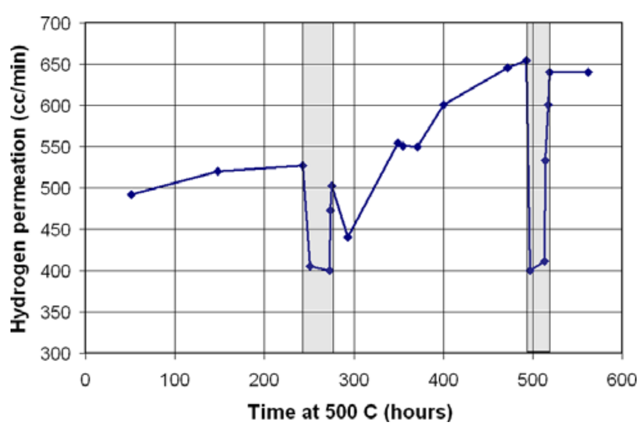

Figure 5. Effect of H_2S on Pd-Ag Membrane

membrane is lower than the flux through a Pd-Ag membrane, but the Pd-Cu membrane is more resistant to sulfur as shown by the fact that much more sulfur is required to reduce the flux by 20% (250 ppm vs. 45 ppm).

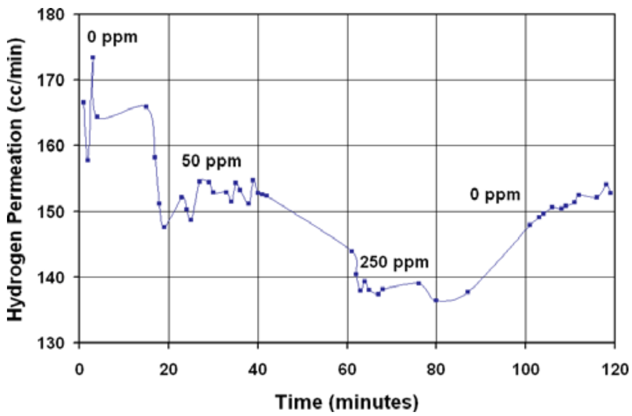

Figure 6. Effect of H_2S on Pd-Cu Membrane

Conclusions

- Pd-based membrane tubes can be produced at a relatively low cost using Praxair's substrates and manufacturing techniques.
- Membrane and substrate properties have continuously and significantly improved, but do not yet meet the 2010 DOE goals.
- The 2010 cost goal of $5/scfh will be difficult to achieve.
- The HTM must provide advantages by integration with the water-gas-shift reactor to beat low-cost pressure swing adsorption for hydrogen purification and production.

FY 2005 Publications/Presentations

1. 2005 DOE Annual Review Meeting

Special Recognitions & Awards/Patents Issued

1. Patent applications are being prepared to cover the substrate production process