II.A.2 Integrated Ceramic Membrane System for Hydrogen Production

Joseph Schwartz (Primary Contact), Prasad Apte, Raymond Drnevich, Ashok Damle
Praxair, Inc.
175 East Park Drive
Tonawanda, NY 14150
Phone: (716) 879-7455; Fax: (716) 879-7567; E-mail: 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

Subcontractor: Research Triangle Institute, Research Triangle Park, NC

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
- 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 under simulated reactor conditions
- 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. Operation and Maintenance
- C. Feedstock and Water Issues
- E. Control and Safety
- Z. Catalysts
- AA. Oxygen Separation Technology
- AB. Hydrogen Separation and Purification

Approach

- Update literature review
- Develop substrate
- Develop membrane
- Confirm membrane performance through tube testing
- Update process economics

Accomplishments

- Determined that the two-stage integrated ceramic membrane process could be cost-competitive if the membranes can be developed
- Produced Pd-Ag alloy membranes that are leak-tight and have reasonable flux
- Flux has doubled in the last six months
- Substrate pore size reduced from > 50 μm to < 5 μm
- Film thickness reduced from > 20 μm to < 10 μm
- Initial economic analysis indicates that the cost of Pd will not be a significant part of the total capital cost for the HTM unit

Future Directions

- Determine the cost of hydrogen production using palladium alloy membranes
- Decide whether to continue the project based on membrane performance and projected costs
- If continued, demonstrate membrane performance in a water gas shift reactor
- Build a multi-membrane prototype unit

Introduction

Hydrogen can be produced from natural gas. 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, which could significantly reduce the capital cost of producing hydrogen and, consequently, reduce the price of hydrogen to the consumer. Because of the way that 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.

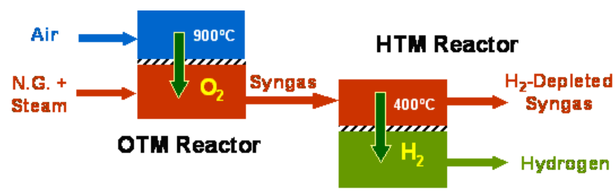

Figure 1. Integrated Membrane Reactor System

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 was 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 been produced with satisfactory performance. Their performance has continuously improved and is still improving.

Approach

The first step in developing the hydrogen purifier was to determine possible materials for the membrane based on available results in the technical literature. Some membrane compositions examined in the past have been unable to resist contamination caused by other materials in the syngas, such as CO or sulfur. Other compositions have failed because they were made of materials with different thermal expansion characteristics so that when the final membrane was heated, the layers separated, destroying the membrane. Possible membrane compositions that are expected to be sufficiently resistant to contaminants and not separate when heated were identified.

The next step in the project was to make and test the membrane to confirm its performance. Porous substrates using ceramic materials have been made based on our expertise in producing ceramic membranes for other applications. These substrates have been coated with palladium, and the resulting membranes have been analyzed. Controlling the pore size and porosity of the ceramic substrate is critical to ensuring that the coating will be leak-free and uniform while being sufficiently thin to provide adequate performance at a reasonable cost. The porous substrates have shown continuous improvement because of improved techniques designed to control the pore size and porosity of the substrates. Membranes were tested to measure hydrogen flux under different operating temperatures and pressures.

The final step in the current phase is to revise the economic assessment performed in Phase I based on the test results. If the integrated ceramic membrane process still appears to be a low-cost hydrogen generation process, we will advance to the next part of the project, which is testing the membrane in a water gas shift reactor.

Results

The preferred substrate material and alloy, Pd-Ag, were selected based on the results of the literature review and preliminary screening tests. Most of the effort in the past year has been focused on optimizing the substrate and membrane properties and performance.

In the initial testing, the pore size of the substrates was too large. Reducing pore size is critical because it affects the thickness of the final Pd-Ag alloy film. As the pore size increases, the thickness of the film must also increase to enable a leak-tight film that spans the pores. Because our goal is a final film of less than 5 μm, the pore size must be small. High porosity is important because it allows a greater fraction of the film surface area to be used. Obviously, areas of the film in direct contact with the dense substrate material, as opposed to pores, are not available for hydrogen transport.

Reducing the pore size while maintaining high porosity was the critical task and most significant accomplishment achieved. Table 1 shows the progress made in substrate tube production.

Table 1. Progress in Substrate Development

Substrate Fabrication Date	Pore Size (mm)	Nitrogen Leak Rate 25ºC (ccm/cm^2)	Hydrogen Flux 40 psi, 550ºC (ccm/cm^2)
February 2003	> 50		N/A
March-April	50		N/A
April – June	20	20 at 10 psid	N/A
June – August		3 at 5 psid	N/A
September – November	5-10	1 at 30 psid	18.8
December – May 2004	< 5	< 1 at 30 psid	33

Most of the progress in the early stages of Phase IIA came from decreasing the size of the pore formers. The use of small pore formers alone was not sufficient to further reduce the pore size to below 5 μm, so other techniques are being developed. These methods have allowed us to further reduce the pore size to below 5 μm consistently.

Several Pd-Ag composite membrane tubes have been prepared and tested for hydrogen flux. Figure 2 shows the results for a representative tube made in 2004.

As can be seen from Figure 2, increasing the hydrogen partial pressure difference or increasing the

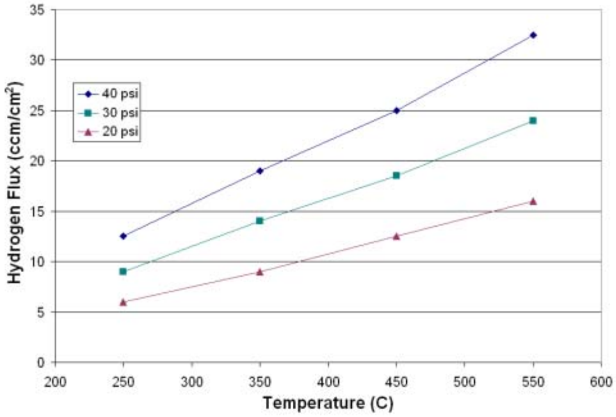

Figure 2. Hydrogen Flux for a Pd-Ag Membrane with a 5-µm Film

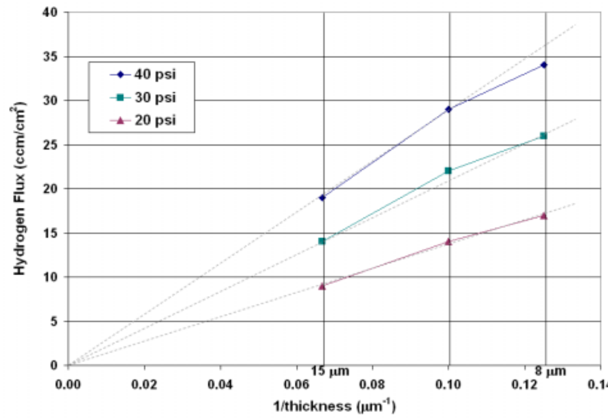

Figure 4. Hydrogen Flux Increased as Membrane Thickness Decreased

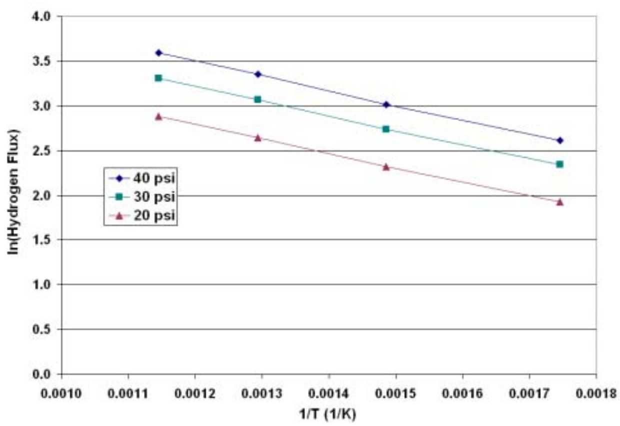

Figure 3. Arrhenius Plot Showing Apparent Activation Energy

temperature over the range studied (250-550ºC) increased the hydrogen flux. In order to quantify the effect of temperature, the data from another tube were used in the Arrhenius plot shown in Figure 3.

In each case, the correlation was very good, with each line showing $r^2 > 0.999$. The apparent activation energy was 3.2 kcal/mol, showing a consistently strong temperature dependence. Because these measurements were done with significant flux, this is not the actual activation energy, but merely an apparent activation energy to help quantify the observed temperature dependence. The dependence of flux on the square root of the hydrogen partial pressure was also confirmed.

The effect of Pd-Ag layer thickness was also examined using three different tubes tested under identical conditions. Figure 4 shows the effect of membrane thickness on flux.

As expected, the hydrogen flux increased in inverse proportion to the membrane alloy layer thickness. This is a good indication that the alloy layer is the rate-determining step in hydrogen flux for layers of at least 8 µm using our substrate. Eventually, the thickness of the layer will become low enough that other resistances will become more important, so decreasing the layer thickness beyond that level will have less benefit than might be expected. At this time, finding ways to decrease the membrane layer thickness below 8 µm will have a significant effect on the hydrogen flux. If this trend is extrapolated, the alloy layer thickness will have to be about 2 µm in order to reach the DOE target flux using the current substrates. Because a 2-µm film is unlikely to be leak-tight, some additional improvement in the substrate structure is necessary. However, this improvement appears to be well within reach considering the progress made in the development project over the last year. The most likely method to reach the DOE target flux will be to improve the substrate microstructure and to decrease the film thickness. There has already been substantial progress made in both these areas, and we expect that progress to continue.

The final effort in this phase will be to update the process economics from Phase I. During Phase I, the dual reactor approach appeared to have potential to be the low-cost hydrogen production method at 2000 SCFH. Since Phase I was completed, there has been significant progress made in distributed hydrogen production, so that conclusion will need to be reevaluated.

The cost of the Pd that is required for the current membranes for a unit producing 2000 SCFH of hydrogen is less than $2500, assuming a Pd price of $300/ounce. Improvements in membrane microstructure and performance will drive this down further. This shows that the Pd cost of the final unit is likely to be less than 1% of the total unit cost. In other words, even though Pd is very expensive, the total cost of the Pd for a hydrogen production unit is small because Pd can be deposited in very thin films and the hydrogen flux through thin films is high.

Conclusions

- Palladium alloy membranes have been produced that have reasonable flux.
- Membrane performance has continuously improved thoughout the year because of improvements made in the alloy and substrate.

FY 2004 Publications/Presentations

1. "Integrated Ceramic Membrane System for Hydrogen Production," Joseph Schwartz, Raymond Drnevich, Prasad Apte, and Ashok Damle. Presentation at the DOE Annual Merit Review Meeting, May 2004.

2. "Integrated Ceramic Membrane System for Hydrogen Production," Joseph Schwartz, Raymond Drnevich, Prasad Apte, and Ashok Damle. Semi-Annual Progress Report submitted to DOE.