II.D.1 Advanced Hydrogen Transport Membrane for Coal Gasification

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Contract Number: DE-FE0004908

Subcontractors:
- Colorado School of Mines (CSM), Golden, CO
- T3 Scientific, Blaine, MN

Project Start Date: October 1, 2010
Project End Date: Project continuation and direction determined annually by DOE

Fiscal Year (FY) 2011 Objectives

- Demonstrate hydrogen transport membrane performance in syngas derived from coal or coal-biomass.
- Separate 800 scfh of hydrogen from syngas.
- Design a membrane reactor to separate at least 4 tons/day of hydrogen from a large-scale gasifier.

Technical Barriers

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

(K) Durability
(L) Impurities
(M) Membrane Defects
(P) Flux
(R) Cost

Technical Targets

TABLE 1. Progress towards Meeting Technical Targets for Dense Metallic Membranes for Hydrogen Separation and Purification[a]

Performance Criteria	Units	Status	2010 Target	2015 Target
Flux Rate[b]	scfh/ft^2	>200	250	300
Module Cost (including membrane material)[c]	$/ft^2 of membrane	1,000	1,000	<500
Durability[d]	hr	<8,760	26,280	>43,800
Operating Capability[e]	psi	300	400	400-600
Hydrogen Recovery	%	88	>80	>90
Hydrogen Qualityf	% of total (dry) gas	> 99.98	99.99	>99.99

[a]Based on membrane water-gas shift reactor with syngas.
[b]Flux at 20 psi hydrogen partial pressure differential with a minimum permeate side total pressure of 15 psig, preferably >50 psi and 400°C.
[c]Although the cost of Pd does not present a significant cost barrier due to the small amount used, the equipment and labor associated with depositing the material (Pd), welding the Pd support, rolling foils or drawing tubes account for the majority of membrane module costs. The $1,500 cost status is based on emerging membrane manufacturing techniques achieved by our partners and is approximately $500 below commercially available units used in the microelectronics industry.
[d]Intervals between membrane replacements.
[e]Delta P operating capability is application dependent. There are many applications that may only require 400 psi or less. For coal gasification 1,000 psi is the target.
[f]It is understood that the resultant hydrogen quality must meet the rigorous hydrogen quality requirements. These membranes are under development to achieve that quality. Membranes must also be tolerant to impurities. This will be application specific. Common impurities include sulfur and carbon monoxide.

Most tests have been conducted at higher pressure than 20 psi, but our current test unit is limited to 200 psi. A new reactor is under construction that will allow testing at 450 psi.

FY 2011 Accomplishments

- Demonstrated 90+% of original flux from membranes coated with MembraGuard® in pure gas and mixtures with no sulfur.
- Demonstrated high flux from Pd alloy membranes.
- Determined impact of ethylenediaminetetraacetic acid (EDTA) on membrane performance.
- Improved membrane seal.
- Designed and began construction of new test reactors to test larger membranes with H_2S and at higher pressure and flow rate.
- Coated membranes up to two feet in length.

Introduction

Hydrogen membranes can be used to separate hydrogen from syngas produced by coal gasification and facilitate CO_2 capture and sequestration. Currently, these membranes have not had widespread commercial success because of durability and performance issues, including susceptibility to sulfur contamination.

Approach

The project will examine different membrane alloys and determine the most appropriate alloys for different syngas compositions produced by gasification. The alloy(s) will be selected based on the expected contaminants in the syngas and their resistance to those contaminants. Other methods, such as sorption, will be used to remove contaminants, but employing a contaminant-resistant alloy will help ensure the success of the project. The alloy must be incorporated into a manufactured membrane. The project will examine different membrane architectures and manufacturing techniques to select the optimum membrane based on performance and manufacturing cost. The project will examine different manufacturing methods to select the most reliable low-cost production method that can produce large membranes on a commercial scale.

The membranes must be incorporated into a membrane unit that separates hydrogen from syngas. The project will examine different membrane reactor designs, including use of catalysts and sweep streams, to select the optimum membrane reactor configuration. Reactor modeling will evaluate different configurations and estimate the impact of reactor design on performance. In Phase I, a small proof-of-concept reactor will be built to separate at least 2 lbs/day (about 15 scfh) of hydrogen from coal-derived syngas. In Phase II, a pilot-scale reactor will be built and integrated with an operating gasifier to produce at least 100 lbs/day (about 800 scfh) of hydrogen. The reactors must be incorporated into a membrane process that produces hydrogen and power at a lower cost than competing processes. The project will examine different integrated process designs to select the most economical process based on the total cost of power and hydrogen produced. In Phase III, this process will be used as the basis for designing a commercial-scale hydrogen transport membrane unit capable of producing at least 4 tons per day of hydrogen.

Results

A Pd-Au membrane was tested for H_2 flux over a temperature range of 300-400°C and a pressure range of 20-200 psid as shown in Figure 1. The membrane showed H_2 fluxes of 96 and 511 scfh/ft^2 at 400°C and 20 and 200 psid, respectively. This is a very encouraging result because a high H_2 flux with a high Au content is expected to provide acceptable performance and resistance to contamination due to impurities including sulfur. The best fit for the H_2 flux showed a pressure dependence of 0.56, indicating that the Pd-Au film is responsible for most of the resistance to hydrogen permeation.

The membrane was then tested in a mixed gas stream with CO (1%), CO_2 (30%), H_2 (50%), and H_2O (19%) and a feed flow rate of 6.2 slpm. As shown in Figure 2, the hydrogen recovery increased with pressure and reached 82% at a feed pressure of 200 psi. The composition of H_2 in the retentate decreased from 57 to 33% while the composition of CO_2 increased from 41 to 64% as the feed pressure increased from 50 to 200 psia.

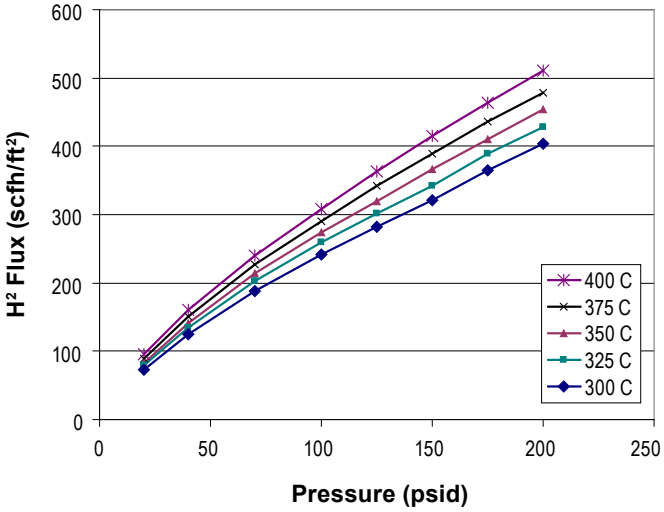

FIGURE 1. Flux Test Results for a Binary Pd-Au Membrane at 300-400°C

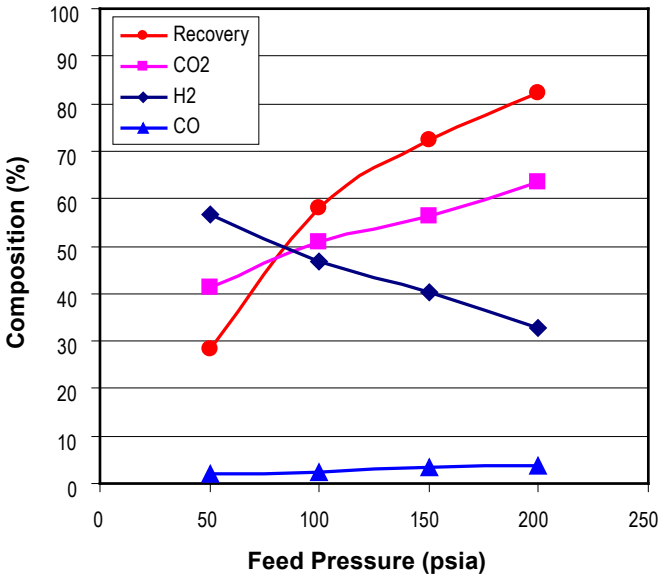

FIGURE 2. H_2 Recovery and Dry Gas Composition on the Retentate Side for a Pd-Au Membrane in a Mixed Gas Test

Other experimental work focused on understanding the effect of EDTA on hydrogen permeation in pure Pd films. EDTA is a bath stabilizer utilized to keep Pd ions in solution and to prevent formation of Pd particles during electroless plating of Pd. EDTA is added to the standard Pd electroless plating solution in amounts that bracket literature values. The plating temperature, hydrazine amount, and length of time in the plating bath were all held constant to understand the effect of EDTA on plating kinetics, which were shown to decrease as the amount of EDTA increased. Pure gas hydrogen permeation tests were completed and are discussed in detail in the following.

Effects of EDTA

The amount of EDTA added to the Pd electroless plating solution for the study was 0–80 g/l, spanning the amount used in the literature. The average amount of EDTA currently being used in the membrane literature is about 40 g/L EDTA. The single-gas permeation results are compared with Pd membranes made without EDTA as seen in Figure 3.

As the amount of EDTA used in the plating bath increases, the hydrogen permeability decreases. The percent differences from the estimated value of 0 g/L EDTA (linear fit trend line) are 2.6%, 5.7%, 14.3%, and 31.7% for the 20, 40, 60, and 80 g/L EDTA films, respectively. All of the films were exposed to air at 300°C for a minimum of five hours at 5 psi. Exposure to air provides a boost in hydrogen flux, more for membranes containing EDTA than for those that do not. As a result of air exposure, the flux for 0 g/L EDTA increased by a factor of 1.5, while it increased by factors of 1.8, 2.0, 2.42, and 3.1 for 20, 40, 60, and 80 g/L EDTA, respectively. This increase in flux did not allow EDTA membranes to be equivalent to those made without EDTA. A possible explanation is that although the carbon on the surface may have been cleared off with the air, there is still carbon left in the bulk and/or grain boundaries that is inhibiting the hydrogen transport.

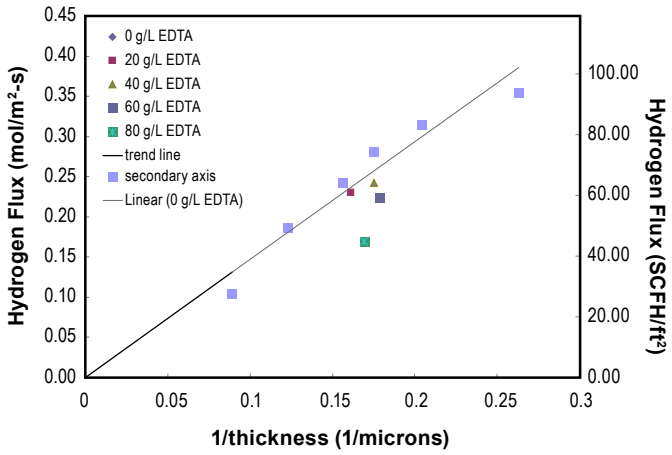

FIGURE 3. Hydrogen Flux of Pd Membranes Made With and Without EDTA at 400°C and 20 psi

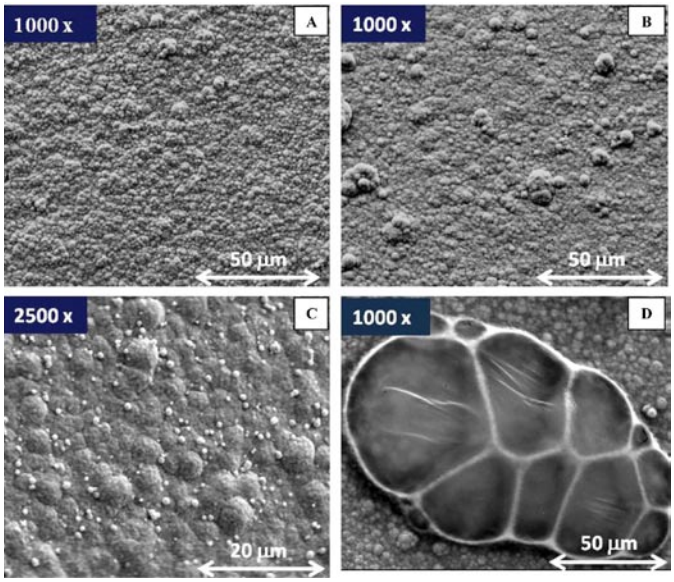

FIGURE 4. SEM micrographs of films made with EDTA. 20 g/L EDTA (A), 40 g/L EDTA (B), 60 g/L EDTA (C), and 80 g/L EDTA (D)

All of the membranes were examined with scanning electron microscopy (SEM)/energy dispersive X-ray spectroscopy (EDS) after testing. Interestingly, as the amount of EDTA decreases, the films begin to resemble ones made without EDTA in that the surface is connected, bubbly, and "cauliflower" like. SEM micrographs of these films can be seen in Figure 4.

The 60 and 80 g/L EDTA films had noticeable carbon enrichment on the surface. In the case of 60 g/L, this can be seen in the small, white spheres (Figure 4C), which were identified by EDS in the peak magnitude of the carbon as compared to the larger, darker bubbles. In the case of 80 g/L EDTA, contamination could be seen with the naked eye and looked like black tar on the membrane surface. The micrograph in Figure 4D is a close up of one of the spots.

Future work with the EDTA membranes will have the objective to try to understand why the hydrogen permeation is suppressed. As hydrogen is transported through a palladium membrane using a solution-diffusion mechanism, permeability, P, is a function of solubility, S, and diffusivity, D, as seen in equation 1:

$$P = D \cdot S \quad (1)$$

Conclusions and Future Directions

- High flux has been demonstrated using Pd and Pd alloy membranes that are expected to have good resistance to contaminants, including H_2S.
- Future research will focus on demonstrating performance with H_2S contamination.

- Small-scale gasifier testing has begun at Colorado School of Mines.
- Future research will focus on integrating a membrane test unit with the gasifier to demonstrate performance in coal-derived syngas.

FY 2011 Publications/Presentations

1. DOE Annual Hydrogen Review Meeting.