II.G.2 Cost-Effective Method for Producing Self-Supporting Pd Alloy Membrane for Use in the Efficient Production of Coal-Derived Hydrogen

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- IdaTech, Bend, OR
- Colorado School of Mines, Golden, CO

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Objectives

- Develop a process methodology for the cost-effective manufacturing of thin (<5 micron thick), dense, self-supporting palladium (Pd) alloy membranes for hydrogen separation from mixed gas streams from coal gasification.
- Reduce Pd membrane thickness by less than 50% over current state-of-the-art and show potential to meet DOE 2010 technical targets.
- Demonstrate viability of ion-assisted, vacuum processing to "engineer" a membrane micro-structure and surface that optimizes hydrogen permeability, separation efficiency, and lifetime.
- Demonstrate efficacy of continuous roll-to-roll manufacturing of membrane material with performance and yields with predefined tolerance limits.
- Establish scale-independent correlations between membrane properties and processing parameters.
- Demonstrate separation efficiency of thin Pd membranes in commercial type fuel processors using mixed gas streams derived from coal gasification.
- Develop a cost model for hydrogen production from coal gasification using Pd membranes.

Technical Barriers

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

(K) Durability
(N) Hydrogen Selectivity
(P) Flux
(R) Cost

Technical Targets

This project is directed at the use of vacuum deposition methods as a cost-effective approach to manufacture palladium alloy membranes for efficient and economical separation of hydrogen from mixed gas streams. A robust, hydrogen selective palladium membrane, has the potential to change the chemical industry by replacing traditional reaction and separation procedures, resulting in sizable savings in energy consumption and capital investment in equipment. Although palladium membranes have potential for efficient and economical separation of hydrogen from mixed gas streams produced by coal gasification, a major shortcoming of palladium as a membrane material is the high and fluctuating cost and the difficulty of fabricating robust, defect-free membranes thinner than 15 microns. In this project, self-supporting Pd-Cu alloy membranes have been produced with thicknesses down to 3 μm and hydrogen permeability rates in excess of the 2010 DOE Targets have been measured as illustrated in Table 1.

TABLE 1. Progress Towards Meeting Technical Targets for Membranes used for Hydrogen Separation and Purification

	2010 DOE Target	2015 DOE Target	SwRI®
Flux (scfh/ft^2)	200	300	242
Cost (\$/ft^2)	200	<100	45.40
Hydrogen Quality	99.95	99.99	99.95
DP Operating Capability	400	400-1,000	400

Accomplishments

- Exceeded DOE Hydrogen Program and 2010 DOE Fossil Energy targets - at 400°C (feed pressure 20 psig) a 2.5 micron Pd-Cu alloy foil (area = 2.6 cm^2) had a pure H_2 permeability of

8x10^{-5} cm^3•cm/cm^2scm $Hg^{0.5}$ and a H_2 Flux = 124 cm^3/cm^2•min (242 scfh/ft^2).

- Delivered more than one dozen full-sized prototype membranes to IdaTech.
- Estimated a total final production cost of \$45.50/ft^2.
- Successfully produced some of the thinnest (3 microns), largest area (110 square inches), and highest performance separation membranes reported.
- A prototype module is complete and ready for assembly if a membrane can be fabricated that is resistant to tearing under high mechanical loads.
- In addition to fabricating several large, nearly pinhole-free membranes for use at Idatech, SwRI® has fabricated novel ternary alloy membranes utilizing small addition of Ru, Rh and Ta.

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Introduction

An affordable, tough, and selective hydrogen separating membrane is needed for separating hydrogen from coal gasification gases or methane. Metal membranes appear to have advantages over ceramic and polymer membranes in terms of manufacturability, lifetime (durability), and ease of sealing, higher operating temperatures, and selectivity for hydrogen. Of the metal membranes, self-supporting, dense palladium alloy membranes have been shown to exhibit extremely high hydrogen selectivity and are able to produce high purity hydrogen feed streams needed for fuel cell applications. Palladium offers other unique benefits in that it can be configured to perform multiple functions and thereby reduce overall reactor costs. For example, as a palladium membrane reactor, catalyzed reactions and product purification can be used to add or remove hydrogen to drive equilibrium restricted reactions to the desired product side. As a result of this added feature, reactor volume and temperature may be lowered, undesirable byproduct formation through side reactions can be reduced, and reduced un-reacted feed sent for recycling; all of these added features ultimately lead to savings on downstream separation requirements, equipment size, and energy usage.

Approach

SwRI® has utilized its expertise in large-area vacuum deposition methods to conduct research into the fabrication of dense, freestanding Pd-alloy membranes that are 3-5 microns thick and over 100 in^2 in area. The membranes are centered around the Pd-Cu system and were deposited onto flexible and rigid supports that were subsequently removed and separated using novel techniques developed over the course of the project. Researchers at the Colorado School of Mines (CSM) supported the effort with extensive testing of experimental membranes as well as design and modeling of novel alloy composite structures. IdaTech provided commercial bench testing and analysis of SwRI®-manufactured membranes.

Results

The novel feature of the SwRI® approach was to prepare freestanding, thin membranes by vacuum deposition on to a suitable temporary substrate that was easily and cleanly removed. The materials also had to have decent thermal stability and be inexpensive (relative to the membrane), reusable, and/or recyclable. Based on these requirements, two initial approaches were investigated; 1) deposition of the membrane onto a polymeric substrate, which was subsequently chemically dissolved and 2) deposition onto a rigid substrate with and without pretreatment of a thin release coating.

The initial alloy coatings deposited on to polymers showed a tendency to exhibit pinhole defects most of which were attributed to the presence of dust particles. Pd-Cu alloy membrane films were deposited onto smooth, silicon wafers. Particulate and other contaminants were more readily controlled on a silicon surface in comparison to plastic, and was considerably smoother than plastic. In general, the key factors that affected formation of a thin, dense, defect-free, Pd-Cu alloy films were surface energy, roughness, and oxygen/moisture content of the backing material. Correspondingly, using vacuum processing conditions that were optimized to minimize intrinsic film stress, pinhole-free Pd-Cu alloy films over large areas at thicknesses below 5 µm were produced.

An example of a successful membrane was a 12.7 µm thick foil with a composition slightly off the ideal $Pd_{60}Cu_{40}$ (i.e., slightly higher palladium weight fraction). The membrane was heated to 250°C, and the hydrogen permeability at this temperature was determined to be 3.8•10-5 cm^3(STP)•cm/cm^2•s•cm $Hg^{0.5}$. This is good agreement given that the palladium composition of the foil sample is higher than 60 mass% and that the H_2 permeability declines sharply for higher Pd contents. A range of palladium compositions and thicknesses were tested at CSM under typically 400°C and 20 psi trans-membrane pressure.

While CSM was able to measure a significant number of thin foils using their experimental gasket set-up, IdaTech was not able to successfully assemble a module that would meet IdaTech's allowable leak rate requirements and did not pursue assembly of a fuel processor with the SwRI® membrane. Fabrication of a module utilizing the SwRI® foils will require significant development of a new gasket compression process or alternative module design.

Of the elements that comprise a hydrogen purification module, the membrane is presumed to be by far the most significant cost contributor. The total cost for manufacturing is based on the raw materials cost, annual equipment depreciation, labor costs, utilities and maintenance, and throughput. Using industry accepted rates, a total cost of $45.40 per square foot for a vacuum deposited membrane was calculated. Even if the rates for throughput, equipment, or labor costs are significantly underestimated, this estimate is more than an order of magnitude lower than the DOE 2010 target.

Conclusions and Future Directions

In this project, self-supporting Pd-Cu alloy membranes have been produced with thicknesses down to 3 µm. Hydrogen permeability rates in excess of the 2010 DOE Targets have been measured and self-supporting membranes that exhibit long life at temperatures above 300°C were produced. It has been shown to be feasible to produce membranes below 5 µm in thickness that are competitive with other methods for hydrogen separation in energy applications. The project is well positioned for pilot-scaling and membrane incorporation in commercial separation units. Potential areas for development include fine tuning the membrane fabrication, modularization and long term testing.

FY 2008 Publications/Presentations

1. B.R. Lanning, O. Ishteiwy, J.D. Way, D. Edlund and K. Coulter, Un-supported Palladium Alloy Membranes for the Production of Hydrogen, Inorganic Membranes for Energy and Fuel Applications, Springer, in press.

2. Self-Supporting Pd-Cu Alloy Membranes for Production of Coal-Derived Hydrogen, 137th Annual Meeting, TMS, New Orleans, LA, March 10, 2008.

3. Cost Effective Method for Producing Self Supporting Pd Alloy Membrane for Use in the Efficient Production of Coal Derived Hydrogen, 2008 DOE Hydrogen Program Merit Review and Peer Evaluation Meeting, Washington, D.C., June 13, 2008.