IV.B.6 Cost-Effective Method for Producing Self-Supporting Pd Alloy Membrane for Use in the Efficient Production of Coal-derived Hydrogen

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Subcontractors:
IdaTech, Bend, OR
Colorado School of Mines, Golden, CO

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Objectives

- Develop a 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.
- Demonstrate the viability of ion-assisted vacuum processing to "engineer" a membrane micro-structure and surface that optimize hydrogen permeability, separation efficiency and lifetime.
- Demonstrate the efficacy of continuous roll-to-roll manufacturing of membrane material with performance and yields within pre-defined tolerances.
- Establish scale-independent correlations between membrane properties and processing parameters.
- Demonstrate separation efficiency of thin Pd membranes in commercial 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 following technical barriers from the Hydrogen Production section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- L. Durability
- M. Impurities
- N. Defects
- O. Selectivity
- P. Operating Temperature
- Q. Flux

- R. Testing and Analysis
- S. Cost

The project also addresses one or more of the barriers described in Section 5.1.5.1., Technical Barriers – Central Production Pathway in the Hydrogen from Coal – Research, Development, and Demonstration Plan of the DOE Office of Fossil Energy.

Technical Targets

Table 1 lists the targets that the project will attempt to meet during its implementation.

Table 1. Technical Targets: Ion Transfer Membranes for Hydrogen Separation and Purification[a]

Performance Criteria	Units	2003 Status	2005 Target	2010 Target	2015 Target
Flux Rate	scfh/ft^2	60	100	200	300[b]
Cost	\$/ft^2	2,000	1,500	1,000	<\$500
Durability	Hours	<8,760	8,760	26,280	>43,800
ΔP Operating Capability	psi	100	200	400	400-1000
Hydrogen Recovery	% of total gas	60	>70	>80	>90
Hydrogen Purity	% of total (dry) gas	>99.9	>99.9	>99.95	99.99

[a] Targets are derived from Table 3.1.5. from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan, March 2005.

[b] Flux upper limit for ion transport membranes.

Approach

- Conduct research into the fabrication of dense, free-standing Pd alloy membranes up to an order of magnitude thinner than the current state-of-the-art membranes.
- Deposit the membranes onto flexible supports that can be chemically removed or separated using a water-soluble release agent and recycled after use.
- Explore production of novel compositions of Pd-Cu alloy systems with the objective of producing a thermally stable, nano-crystalline grain structure that will result in a membrane material with improved hydrogen separation characteristics.
- Conduct testing of experimental membranes as well as design and modeling of novel alloy composite structures.
- Finally, complete real-world bench testing and the analysis of Southwest Research Institute (SwRI)-manufactured membranes.

Accomplishments

- Completed fabrication of an initial series of Cu and Pd-Cu alloy membranes in the range of 1-10 μm in thickness by depositing samples onto polymeric substrates of ~20 sq. in. in area.
- Investigated the variation of deposition rate, argon flow, and other parameters in order to optimize film density and stress and minimize pinholes in the membranes.
- Completed initial investigation of backing removal methods and determined which method (dissolvable or release-coated backing layer) merits further development.
- Demonstrated deposition and removal of Pd alloy membranes on polymer sheets approximating 75 sq. in. in area.

- Completed the down-selection of a backing removal method for large-area membrane devices manufacturing.

Future Directions

- Study influence of alloying additions, such as Sn, Y, and V for phase segregation and ZrO_2 for grain refinement, on the hydrogen permeation in Pd-Cu base alloy; study pressure rating and gas separation properties of optimized Pd-Cu compared to pure Pd-Cu.
- Complete design and initial construction of specialized hydrogen separation modules incorporating SwRI's manufactured membranes.
- Initiate performance and characterization studies of membrane devices of approximately 75 sq. in. surface area.

Introduction

An affordable, tough, and selective hydrogen separation membrane is needed for separating hydrogen from coal-derived synthesis gas or methane. Polymer membranes are economical in some applications, but the higher temperatures of most chemical reactions and many waste gas and reforming processes (i.e., coal gasification/natural gas reforming) preclude their use. Considerable research in the area of inorganic membranes for hydrogen gas separation has taken place in recent years. Of the two general classes of high-temperature membranes available (ceramic and metal), ceramic membranes have been developed and commercialized to a greater extent for gas separation. Such materials, however, pose key challenges from several perspectives. Typically, the ceramics must exhibit an extremely fine, highly controlled pore size that can be difficult to fabricate over large areas.

Metal membranes, however, appear to have significant advantages over ceramic and polymer membranes in terms of manufacturability, lifetime (durability), 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 permselectivity 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, in a palladium membrane reactor, the palladium membrane can both catalyze reactions and purify the product, adding or removing 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 the amount of unreacted feed sent for recycling can be reduced; all of these benefits ultimately lead to savings on downstream separation requirements, equipment size, and energy usage.

Approach

Southwest Research Institute (SwRI) will utilize its expertise in large-area vacuum deposition methods to conduct research into the fabrication of dense, free-standing Pd alloy membranes up to an order of magnitude thinner than the current state of the art, which is approximately 25 μm in thickness and more than 20 in^2 in area. The membranes will be deposited onto flexible supports that can be chemically removed or separated using a water-soluble release agent and recycled after use. Using these methods, the production of novel compositions of Pd-Cu alloy systems will be explored with the objective of producing a thermally stable, nano-crystalline grain structure that will result in a membrane material with improved hydrogen separation characteristics. Researchers at the Colorado School of Mines will support the effort with testing of experimental membranes as well as design and modeling of novel alloy composite structures. IdaTech will provide real-world bench testing and the analysis of SwRI-manufactured membranes. The anticipated deliverables for the project include test data on the performance of experimental membranes fabricated by vacuum deposition, either stand-alone or as part of a smallscale purification system, from testing at IdaTech, and several novel Pd alloy membrane compositions.

Results

SwRI completed the fabrication of an initial series of Cu and Pd-Cu alloy membranes in the range of 1-10 μm in thickness by depositing samples onto polymeric substrates of ~20 sq. in. in area (see Figure 1). An investigation of the variation of deposition rate, argon flow, and other parameters was conducted in order to optimize film density and stress and minimize pinholes in the membranes. Initial investigation of backing removal methods was completed, and which method merits further development (dissolvable or release-coated backing layer) was determined. Deposition and removal of Pd alloy membranes on polymer sheets approximating 75 sq. in. in area were demonstrated. A backing removal method for large-area membrane devices manufacturing was down-selected.

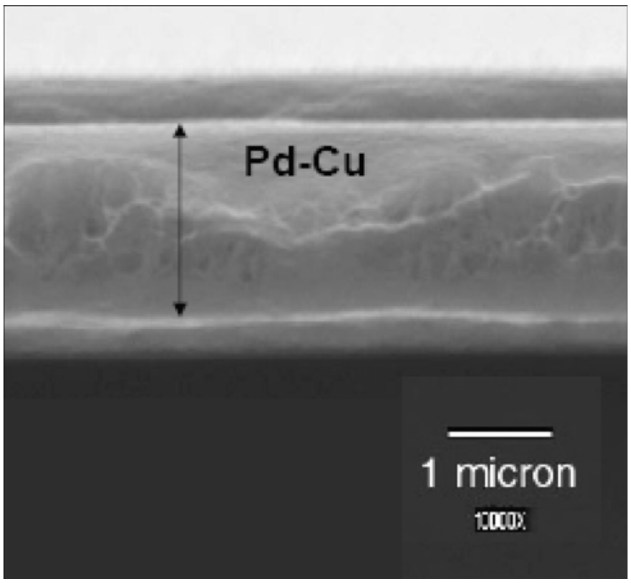

Figure 1. Pd-Cu Membrane

Conclusions

Dense-phase Pd alloy membranes can be competitive with other technologies for H_2 separation if their thickness can be reduced from the current 25 microns to <5 microns. For coal-based applications, Pd/Cu alloy is the preferred choice because of its sulfur tolerance. It is also stronger physically due to smaller swelling from H_2 dissolution.

FY 2005 Publications/Presentations

1. International Conference on Metallurgical Coatings and Thin Films, Advanced Surface Engineering Division of AVS, May 2-6, 2005, San Diego, CA; "Fabrication of Self-Supported Pd-Alloy Membranes Using Vacuum Deposition Methods."