II.C.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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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.
- Demonstrate viability of ion-assisted, vacuum processing to "engineer" a membrane micro-structure and surface that optimizes hydrogen permeability, separation efficiency, and life time.
- Demonstrate efficacy of continuous roll-to-roll manufacturing of membrane material with performance and yields with pre-defined 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.

Introduction

An affordable, tough, and selective hydrogen separating membrane is needed for separating hydrogen from coal gasification gases or methane. Polymer membranes are economical in some applications, but the higher temperatures of coal gasification/natural gas reforming reactions 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), 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 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, 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 unreacted feed sent for recycling; all of these added features 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 (CSM) 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's 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 small-scale purification system, from testing at IdaTech, and several novel Pd-alloy membrane compositions.

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.
- Complete design and initial construction of specialized hydrogen separation modules incorporating SwRI-manufactured membranes.

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.
- Initiate performance and characterization studies of membrane devices of approximately 75 sq. in. surface area.
- Complete membrane composition optimization studies and select membrane alloy compositions for further development and scale-up.
- Complete prototype module assembly and membrane testing.
- Complete development of cost models for hydrogen production using membranes developed in this project and suggest follow-on scale-up R&D work plan in the final report.
- Complete pressure and purification testing of pilot-manufactured membranes for testing in prototype assembly and further scale-up.