II.D.6 Supported Molten Metal Membrane (SMMM) for Hydrogen Separation

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Objectives

The overall goal of this project is to develop and test novel supported molten metal membranes (SMMMs) suitable for hydrogen separation in conjunction with a coal gasification plant, based on low-melting, non-precious group metals (non-PGM) or alloys, supported as thin films on an inert porous ceramic, or on a porous metal support with or without an intermetallic diffusion barrier. The specific objectives of the project are to:

- Identify non-PGM molten metals and alloy candidates for membranes that provide good hydrogen dissociation ability, solubility, and diffusivity, and are tolerant to other syngas species such as carbon monoxide, and to poisons such as sulfur.
- Identify porous ceramic and porous metal supports with an intermetallic diffusion barrier that are readily wetted by the molten metals, and allow stable molten metal membranes to be fabricated.
- Develop fabrication procedures for supported molten metal membranes on porous supports that allow inexpensive, rapid, and reproducible membrane synthesis.
- Establish the basic feasibility of the SMMM technique.
- Narrow down the list of promising SMMM candidates based on preliminary permeability experiments.
- Investigate in detail the permeability, selectivity, and durability of the most promising SMMM candidates vis-à-vis DOE technical targets.
- Relate membrane development/optimization to a fundamental experimental and theoretical characterization of the SMMM structure, composition, and mechanism.
- Fully investigate the best SMMM candidate(s) under increasingly realistic conditions based on the DOE Test Protocol and to compare their performance against exceeding the DOE 2010 Technical Targets.

Technical Barriers

This project addresses the following technical barriers within the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan for the Pd-based dense metallic membranes:

- Hydrogen embrittlement at temperatures below 300ºC
- Thermal mismatch between metal membrane and support
- Pinhole formation
- Membrane sintering at higher temperatures
- Poisoning by S, CO, and other trace contaminants in coal derived H_2
- High cost of PGM-based membranes

Technical Targets

The project is currently in its initial stages of identifying molten metal and alloy candidates, porous supports, and in developing the fabrication procedures for these novel membranes. Once these steps are completed, and following initial feasibility investigations, the membranes will be developed further in an effort to meet or exceed the 2010 DOE technical targets listed in Table 1.

Accomplishments

During the first three quarters of Year 1 (Phase I) of this project, the following technical accomplishments have been made:

- The initial candidates for low-melting metals (M_1) have been identified (Sn, In, Ga, and Bi).

TABLE 1. The DOE Technical Targets for Dense Metallic Membranes for Hydrogen Separation

Property	2010 Target	2015 Target
H_2 Flux (std $m^3/m^2.h$)	60	90
H_2 Feed Pressure, $p_{H_2,feed}$ (psia)	150	150
H_2 Permeate Pressure, $p_{H_2,perm}$ (psia)	50	50
Operating $\Delta p_{H_2} = p_{H_2,feed} - p_{H_2,perm}$ (psi)	100	100
Operating Temperature, T (°C)	300–600	250–500
Pressure Tolerance, Δp (psi)	400	800–1,000
Sulfur Tolerance (ppm)	20	>100
CO Tolerance	Yes	Yes
Water-Gas Shift Activity	Yes	Yes
H_2 Purity (%)	99.5	99.99
Cost ($/ft^2)	500	<250
Durability (years)	3	>5

- The initial non-PGM candidates for catalytic metals (M_2) have been identified (Ni, Co, Cu, Fe, Ag, W, Mo, Nb, Ti, and Ta).
- The metallic (Inconel, porous stainless steel) and ceramic (Al_2O_3, ZrO_2, TiO_2, SiC, and Porous Vycor® glass) porous supports have been identified.
- SMMM fabrication procedures have been developed based on electroless- and electro-plating, soldering, and melt imbibition.
- SMMM membrane candidates of Sn and In have been fabricated on porous Inconel and on α- Al_2O_3 supports.
- Initial feasibility studies of these fabricated membranes have been completed.
- The reasons for failure of these first two candidates have been identified. For the case of metal supports, thus, the molten metal diffuses, reacts, and forms a dense non-permeable solid film with the substrate metal. For the ceramic membrane tested so far (α- Al_2O_3), the molten metal is found not to wet it, so that a microporous, rather than a dense, membrane results.
- From these early results, promising support candidates to be tested next have been identified, and include ZrO_2, TiO_2, SiC, Porous Vycor® glass as ceramic support candidates, and porous stainless steel (PSS) with a ZrO_2 layer as a metal support candidate.
- A new permeability apparatus suitable for both tubular and disk (coupon) membranes capable of going up to 650°C and of recording permeation data automatically over an extended period based on LabVIEW® has been designed and built.

Introduction

Coal gasification is promising for the centralized co-production of electric power and hydrogen via integrated gasification combined-cycle (IGCC) technology, when combined with carbon dioxide sequestration. For this, the main commercial technologies available for separating H_2 from other syngas components, i.e., pressure-swing adsorption (PSA) and cryogenic distillation, however, are expensive and energy intensive. Thus, membrane separation of H_2 is being investigated. The current dense metallic membranes based on Pd, however, are expensive, and still fall short of the desired permeability, selectivity, low cost, chemical and mechanical robustness, and durability. Hence, novel dense membranes based on non-PGM metals are sought that might overcome these barriers.

Thus, we have proposed a novel dense membrane technology for the separation of H_2 from syngas based on non-PGM SMMMs, comprising of a thin film (< 25 μm) of a liquid metal or alloy, with a melting point in the range of 200-500°C, and supported on a porous ceramic or porous metal support. The proposed membranes would be less expensive, more robust to species such as CO, and resistant to poisons such as sulfur. In addition, they would obviate issues related to solid dense membranes, i.e., sintering, H_2 embrittlement, thermal mismatch between the membrane and the support, and formation of pin-holes.

Approach

Figure 1 shows a schematic of the proposed SMMM. It comprises of a porous ceramic/metal support on which a thin but dense layer of a molten metal or molten metal alloy is deposited. Further, an oxide/ceramic layer is interposed in the case of a porous metallic support to

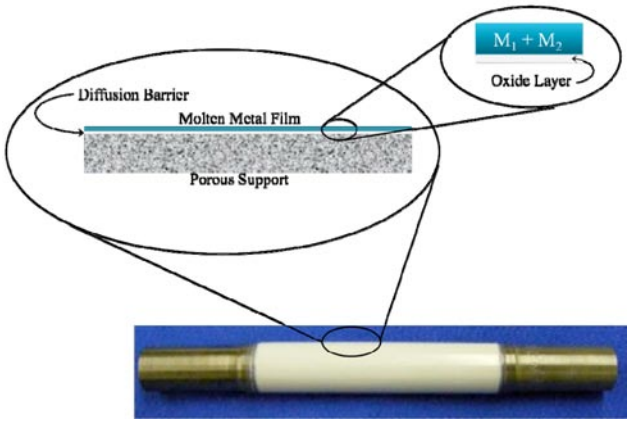

FIGURE 1. Schematic of SMMM on ZrO_2-PSS Support

avoid any diffusion and alloying reaction between the molten metal and the porous metal support.

The dense molten metal membrane comprises of two components: 1) a low-melting metal (M_1) to provide an open and fluid lattice desirable for ready dissolution and diffusion of hydrogen atoms, H; and 2) a non-precious group transition, or other catalytic, metal (M_2), to facilitate dissociation of hydrogen molecules at the membrane surface, in keeping with the accepted mechanism of hydrogen diffusion through a dense metallic membrane, wherein the H_2 molecule first dissociates and adsorbs on the surface, followed by ingress into the lattice, and subsequent diffusion through it, both of which steps are presumably facilitated by lattice defects and vacancies present in a liquid metal film.

Results

Due to the novelty of the proposed membranes, the work had to start from scratch, namely, identification of initial metal and support candidates, and development of the fabrication procedures for the membranes. Thus, as a start, it was decided to pick Sn as our initial choice for the molten metal M_1, since it has a large liquidus range (melting point [M.P.] = 232ºC, boiling point [B.P.] = 2,602ºC), and is relatively resistant to sulfur and carbonaceous deposits. This choice was subsequently supplemented with In (M.P. = 157ºC, B.P. = 2,072ºC), also abundant and nontoxic like Sn. As our initial choices for the porous supports, we picked: 1) a porous Inconel support as a porous metal support; 2) a porous alumina support as the porous ceramic support; and 3) a PSS with a ZrO_2 layer obtained from Pall Corporation. With the initial choice of the molten metal and the porous supports in hand, the next focus of the work was on developing a protocol for the fabrication of the SMMM. The various techniques investigated were: 1) electroless plating, 2) electroplating, 3) molten metal imbibition, and 4) soldering.

During the deposition of Sn on porous Inconel support, it was found that Sn is not conducive to thick deposits via electroless plating, because of the self-passivating nature of the metal, i.e., unlike, Pd, or Cu, for instance, it has low catalytic activity for the reductant oxidation reaction at room temperature. Thus, the plating stops once an impenetrable self-passivating layer of the metal has been deposited on the substrate. As a result, only a thin layer of Sn on porous Inconel could be obtained via electroless plating. Consequently, in order to deposit thicker tin layers, electro-plating was utilized. The electrodeposition experiment was carried out using four electrodes configuration in a cylindrical cell. The porous Inconel tube support was the cathode. The three cleaned tin rods were used as the anodes and symmetrically placed around the cathode to obtain uniform deposition. In this manner, any deposit thickness could be readily obtained. However, it was found that Sn electrodeposition is prone to whisker formation. However, these could be readily scraped off. The resulting Sn/Inconel membrane is shown in Figure 2.

However, when this membrane was tested for hydrogen/helium permeability above the M.P. of Sn, it was found that it was rendered virtually impermeable. The membrane post permeability testing is shown in Figure 3.

It appears thus that an alloying reaction has taken place between the Sn and Inconel, possibly forming a solid, dense, impermeable layer. Post-mortem microscopic characterization via scanning electron microscopy (SEM)/energy dispersive X-ray (EDX) is planned to confirm the alloying and formation of a dense solid film. It, thus, appears that porous metal supports without an intermetallic diffusion barrier are unsuitable for SMMM due to the ingress and reaction of the molten metal with the porous metal substrate.

Since porous metal supports are not, thus, suitable for SMMM, the fabrication of a Sn/α-Al_2O_3 ceramic support membrane was undertaken. A thin 2-μm layer of Sn/Cu was first predeposited on the α- Al_2O_3 support via electroless plating, over which, subsequently, a thick layer of Sn was deposited via electroplating at a low current density. The predeposition of the Sn/Cu layer is, of course, essential to allow the support to be used as an electrode. The resulting membrane is shown in Figure 4.

When this membrane was subjected to permeability testing at elevated temperatures, a very high flux and low selectivity between H_2 and He were found, characteristic of a microporous membrane (Figure 5) rather than a dense membrane. In other words, upon melting, only a thin microporous layer of Sn remained on the Cu/α-Al_2O_3 porous substrate. It was, thus, determined that α-Al_2O_3 is not wetted by the molten Sn.

FIGURE 2. A 20 μm Dense Layer of Sn on the Porous Inconel Support before Permeability Test

FIGURE 3. The used Sn/Inconel Membrane after Permeation Experiments up to 600°C

FIGURE 4. The Sn/Cu/α-Al_2O_3 Porous Ceramic Membrane before Permeability Testing

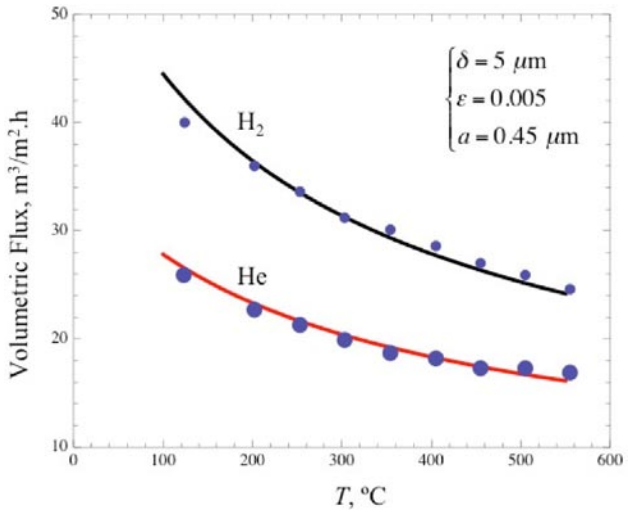

FIGURE 5. Relation between Flux and Temperature for Microporous Sn/Cu/α-Al_2O_3 Membrane

Figure 5 also shows the agreement between theory and experiments, with all theoretical parameters with the exception of those mentioned in the figure, and exhibits a curious inverse relationship between flux and temperature, not widely reported, and explicable via the dusty-gas model involving Knudsen diffusion and flow of a gas within a microporous membrane, with its viscosity coefficient increasing with temperature (Figure 5).

A new permeation apparatus for testing the He and H_2 permeability, selectivity, and durability of the SMMM membranes, capable of going up to 650°C, and capable of recording permeation data automatically over an extended period based on LabVIEW® was also designed and built.

Conclusions and Future Directions

In summary, we are still working on fabricating a dense supported molten metal membrane, and hope to accomplish this shortly. The following work is planned for the upcoming year (Year 2):

- We will test the suitability of other ceramic supports (ZrO_2, SiC, TiO_2, Vycor® glass), along with metal supports with intermetallic diffusion barrier ceramic layers, for forming stable molten metal membranes.
- Once molten metal membranes with our initial choice for M_1 are thus fabricated and tested for basic permeability, the next step would be to alloy them with the catalytic metal M_2, and narrow down the selection to a handful of final SMMM candidates.
- The most promising SMMM candidates hence fabricated will be subjected to H_2 permeability, selectivity, and durability testing under increasingly realistic conditions of temperature, pressure, gas composition, poisons.
- The best SMMM membranes will be subjected to detailed physical, microstructural, and chemical characterization before and after the permeation test.
- We will develop a detailed kinetic/diffusion theoretical model for SMMM, including dynamics of all the sequential steps including dissociative adsorption/desorption and diffusion, so that no arbitrary assumptions are necessary regarding the rate-limiting step.

In the third and final year of the project, we will fully investigate the best SMMM candidate(s) under increasingly realistic conditions based on the DOE test protocol and compare their performance against exceeding the DOE 2010 targets (Table 1).

FY 2010 Publications/Presentations

1. Datta, R., Ma, Y.H., "Supported Molten Metal Membrane for Hydrogen Separation," presented at the 2010 DOE Hydrogen Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting, June 2010, Washington, D.C.