II.B.4 A Photopolymerization/Pyrolysis Route to Microstructured Membranes

Kathryn A. Berchtold (Primary Contact), Jennifer S. Young
Los Alamos National Laboratory
MST-7, MS E549
Los Alamos, NM 87545
Phone: (505) 665-7841; Fax: (505) 667-8109; E-mail: Berchtold@lanl.gov

DOE Technology Development Manager: Arlene Anderson
Phone: (202) 586-3818; Fax: (202) 586-9811; E-mail: Arlene.Anderson@ee.doe.gov

Objectives

Develop inexpensive ceramic membranes for hydrogen purification that are significantly more robust than existing ceramic membranes and that meet the stated targets of the HFCIT Program's Multi-Year RD&D Plan

- Provide a rational approach to the design of synthesis processes for robust ceramic membranes with high gas permselectivity
- Develop economically and technically viable synthesis process for non-oxide containing ceramic membranes
- Optimize ceramic precursor chemistries and processing conditions to optimize permselectivity and material properties of the resultant ceramic 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:

- A. Fuel Processor Capital Costs
- D. Carbon Dioxide Emissions
- AB. Hydrogen Separation and Purification

Approach

- Implement statistical experimental design to rationally investigate the multi-variable space
- Develop formulations and procedures for synthesis of non-oxide containing polymer derived ceramic thin film membranes
- Develop procedures for evaluation of non-oxide containing polymer derived ceramic thin film membranes
- Establish membrane testing capability at conditions and with streams relevant to hydrogen production
- Synthesize and evaluate preceramic polymer films

Accomplishments

- Established membrane synthesis capability through the proposed route
- Synthesized non-oxide containing preceramic polymer films
- Established membrane testing capability at conditions of interest (temperatures up to 800°C; gas testing with streams relevant to hydrogen production including H_2, CO, CO_2, CH_4, and H_2S; fixturing for ceramic films)
- Safety protocols and work plans for materials synthesis, gas permeation testing (including toxic and flammable gasses), and materials evaluations are in place and all work authorizations have been obtained.

Future Directions

- Evaluate single-gas permeation and selectivity characteristics on Gen1 membranes
- Optimize photopolymerization and pyrolysis processing conditions on selected Gen2 materials
- Conduct single- and mixed-gas ceramic membrane testing of Gen2 materials using industrially relevant gas mixtures
- Evaluate temperature stability of Gen2 materials
- Conduct cost analysis (flux, scfh/$)

Introduction

A recurring theme in the production of hydrogen is the separation of hydrogen from carbon dioxide or carbon monoxide and other minority components. This work is focused on the development of robust ceramic membranes for gas separations at 1000°C or higher for $5/ft² or less. We will do this by producing non-oxide containing ceramic membranes using commonly employed polymer processing techniques. The non-oxide ceramics are much more stable to process conditions than their oxide containing counterparts. Because we start with preceramic polymer precursors that can be photopolymerized into tough polymer films and then pyrolyzed to form the ceramic membrane, we can employ polymer processing techniques that are routinely used to make millions of square feet of polymer films and hollow fibers. We are confident that the resulting ceramic membranes will have high fluxes (as do other ceramic membranes[1]), but will be much more robust in terms of their chemical, thermal, and mechanical stability. There are a number of variables to be explored in the development of these membranes, including initial preceramic polymer chemistry, photopolymerization conditions, and pyrolysis conditions.

In the initial phase of this work, we are focusing on understanding the interaction of the variables important to membrane formation and, correspondingly, their impact on gas permeation and selectivity. With this fundamental understanding, we can then tailor membrane properties for a given set of conditions (gas composition, temperature, and pressure). This accomplishment will represent a revolutionary step in high-temperature membrane technology, enabling production of economically viable membrane modules that would address and provide a path towards the milestones outlined in the DOE HFCIT Program Multi-Year RD&D Plan, 2003. Concurrently, this work also addresses and significantly benefits many of the key areas highlighted by the National Research Council ("The Hydrogen Economy: Opportunities, Costs, Barriers, and R&D Needs," 2004) as important to the Hydrogen Fuel Initiative (HFI). Specifically, the research described here represents a pathway to the successful development of robust and inexpensive high-temperature membranes for energy-efficient H_2 purification in applications that span from distributed and centralized generation utilizing transitional fuels such as natural gas to the longer-term HFI interests surrounding generation using coal and biomass. It is also clear that the chemistries and synthetic routes to be explored support the incorporation of a water-gas shift catalyst, providing an opportunity for membrane separation coupled with chemical conversion. Additionally, the development of these membrane materials would lead to a purification scheme that leaves CO_2-rich streams at pressure, thereby readily enabling sequestration while reducing costs associated with compression to pipeline pressures.

Approach

Polymer-derived ceramics (PDCs) is a relatively young research area[2]. With this technique, new types of ceramic materials for high-temperature applications can be processed at relatively low temperatures (compared to traditional ceramic fabrication methods[3]). Specifically, this development enables the production of non-oxide containing ceramic membranes via pyrolysis of thin polymer films. These types of ceramic materials, e.g., Si-C-N, are not amenable to the traditional membrane fabrication techniques and, thus, have not previously been formed into membranes. These non-oxide ceramics should prove quite thermally,

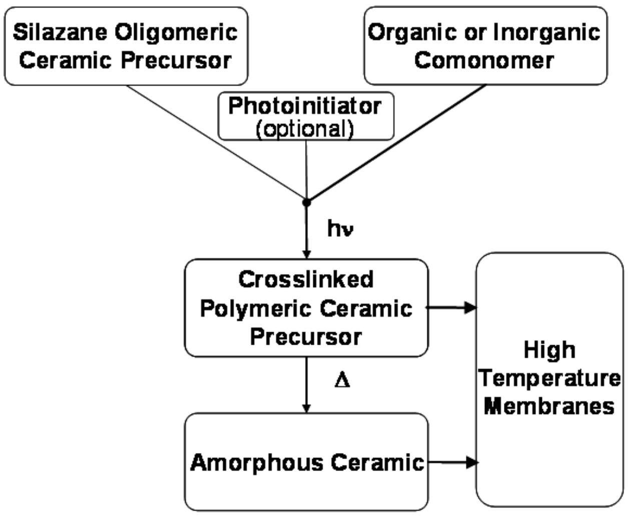

Figure 1. Pathway for Membrane Preparation

mechanically, and chemically stable. One would expect, based on their oxide counterparts[1], that these membranes will have useful permselectivities. Thus, this work represents a significant improvement in high-temperature membrane technology.

Fabrication of a membrane from PDCs (Figure 1) begins with the combination of a ceramic precursor with an organic or organic-inorganic comonomer. A thin film is formed on a substrate and is subsequently photopolymerized to form a crosslinked preceramic polymer film. This film is then pyrolyzed under the appropriate conditions to form a ceramic membrane with the desired chemical functionality and transport characteristics. The composition and architecture of the crosslinked polymeric film and, correspondingly, the resultant ceramic film can be tailored through variations of the initial monomer chemistries, comonomer compositions, and polymerization and pyrolysis conditions.

During the initial pyrolysis of these polymeric preceramic materials, amorphous structures are formed which exhibit atomically homogenous elemental distributions. In the bulk, these amorphous materials demonstrate excellent creep, corrosion, chemical, radiological, and oxidation resistance. These properties are complimented by high tensile strength and hardness characteristics as well as outstanding temperature stability. In fact, amorphous-phase thermal stabilities as high as 1800°C have been achieved with this new class of materials! These materials have not, however, been characterized as thin films such as those useful in membrane applications. Such high thermal stabilities in bulk indicate that these materials are excellent candidates for high-temperature gas separation applications.

While one normally thinks of ceramics as brittle, we are employing a step-growth photopolymerization using comonomer chemistries that provide a novel and powerful means for producing homogeneous crosslinked networks that, when pyrolyzed, result in a much stronger and more flexible material suitable for membrane applications than is currently obtainable. Other advantages of photopolymerization processes include rapid curing at room temperature, low energy requirements, chemical versatility, solvent-free processing, and low environmental impact, all of which significantly reduce the manufacturing costs for these membranes.

Results

Work on this project was initiated in Q2 FY 2004 (February). Initial efforts focused on establishing the membrane synthesis capability through the proposed processing route with the selected materials. This capability includes all processing steps and experimental protocols necessary to produce, characterize, and test a ceramic membrane as it is fabricated from inorganic/organic photoactive precursors. While Los Alamos National Laboratory (LANL) had a substantial infrastructure in place to support this work prior to the project's inception, notable augmentation in terms of high-temperature and toxic and reactive gas processing and testing was completed. Pyrolysis and gas permeation testing equipment is located in California hoods to allow a large degree of flexibility in processing conditions. Pyrolysis operations can be conducted over a broad temperature range (ambient to 1700°C) and in multiple atmospheres, including inert and reactive environments (e.g., ammonia). Gas permeation operations can also be conducted over a broad temperature range (ambient to 800°C) and with a broad spectrum of industrially relevant gases and gas mixtures, including H_2, CO, CO_2, CH_4, and H_2S. Extension of the temperature range to 1000°C is still in progress. All processes and their associated safety protocols have been reviewed and approved through the LANL Integrated Safety Management process.

Gen1 materials, including control materials, have been selected. A coarse grained experimental approach towards both material selection and evaluation has been taken to facilitate screening of materials and process conditions, leading to optimization to Gen2 materials and processing in FY 2005. Thin films of Gen1 materials have been cast and photopolymerized to form non-oxide containing preceramic polymer films. Free-standing polymer films and polymer films on various substrates are being evaluated and subsequently pyrolyzed to form Gen1 ceramic membranes. A high-temperature fixture for gas permeation evaluation of these membranes has been designed and fabricated. Fabrication and testing of Gen1 ceramic membranes is currently underway.

Conclusions

A new synthetic route for high-temperature non-oxide ceramic membranes is being developed to address the shortcomings of current hydrogen separation membranes as well as the shortcomings associated with using pressure swing adsorption for hydrogen purification. This new route employs novel preceramic polymer chemistries in combination with a photopolymerization and pyrolysis fabrication route. This synthesis route not only opens the door to a new class of ceramic membrane materials—specifically, non-oxide containing ceramics—but also provides opportunities to tailor the permselectivity and material property characteristics of membranes fabricated within a specific class of materials.

References

1. Lin, Y., I. Kumakiri, B. Nair, H. Alsyouri, Separation and Purification Methods, 31, 229 (2002).
2. Kroke, E, Y.L. Li, C. Konetschny, E. Lecomte, C. Fasel, R. Riedel, Materials Science & Engineering R-Reports, 26(4-6), 97-199 (2000).
3. Bengisu, M., Engineering Ceramics, Springer-Verlag: Berlin (2001).

FY 2004 Publications/Presentations

1. K.A. Berchtold and J.S. Young, "A Photopolymerization/Pyrolysis Route to Microstructured Membranes," 2004 Hydrogen Program Review, Philadelphia, PA (2004).

Patent Disclosures

1. Berchtold, K.A. and J.S. Young, "A Novel Approach to Robust, High Temperature Ceramic Membranes for Gas Separations," Los Alamos National Laboratory Invention Disclosure No. LAD-2003-065.