II.B Separations

II.B.1 Defect-Free Thin Film Membranes for H_2 Separation and Isolation

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Objectives

- Synthesize defect-free thin film zeolite membranes for H_2 isolation and purification.
- Use as water management membranes in polymer electrolyte membranes (PEMs).
- Replace existing expensive and fragile Pt catalysts.
- Test the separations of light gases (pure and mixtures) through the membranes.
- Demonstrate effective light gas separations and commercialization potential of zeolite 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
- B. Operation and Maintenance (O&M)
- C. Feedstock and Water Issues
- E. Control and Safety
- AB. Hydrogen Separation and Purification

Approach

- Synthesize and optimize defect-free thin film zeolite membranes.
- Model/simulate permeation of light gases through various frameworks/pores for optimized performance.
- Analyze flux and permeation of pure, binary and industrially relevant mixed gases through membranes on unique in-house permeation unit.
- Validate modeling/simulation with actual permeation data to optimize membranes synthesized.
- Foster industrial contacts and collaborations.

Accomplishments

- Synthesized defect-free zeolite membranes with different selectivities for various gas molecules; selectivity is based upon a combination of molecular sieving through the pores and adsorption of the various composition frameworks.
- Compared permeation through all silica and aluminosilicate zeolite membranes, both on alumina supports and on composite oxide-coated stainless steel supports.

- Modified our unique in-house permeation unit to test H_2S gas in addition to the traditional reformate gases. The unit can test both disk and tube membranes, with multiple pure or mixed gases, in a temperature range of 25-500°C.
- Synthesized new unidentified silicotitanate zeolite membrane phase that shows selectivity for H_2.

Future Directions

- Synthesize and characterize thin films and bulk novel microporous phases including aluminosilicate (Al/Si) zeolite thin films doped and/or ion-exchanged with other elements and unsupported aluminosilicate zeolite membranes.
- Use atomic layer deposition to deposit catalytic metals on top of zeolite membranes.
- Synthesize membranes on oxide-coated porous stainless steel (commercially viable) supports.
- Model and simulate the movement of gas molecules through the various molecular sieve thin films. Then compare the calculated data with actual permeation data for validation of models and prediction capabilities.
- Study the permeation and flux of pure, binary and industrially relevant mixed gases (H_2, CO, CO_2, CH_4, H_2S, N_2, and SF_6), through membranes studied from room temperature to 500°C.
- Build a partnership with a membrane company. Initiate an agreement for product development with an industrial partner.

Introduction

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. In particular, we are interested in (1) separating and isolating H_2 from H_2O and CH_4, CO, CO_2, O_2, N_2 gases; (2) water management in PEMs; and (3) replacing expensive Pt catalysts needed for PEMs. Current hydrogen separation membranes are based on Pd alloys or on chemically and mechanically unstable organic polymer membranes. The use of molecular sieves brings a stable (chemically and mechanically stable) inorganic matrix to the membrane [1-3]. The crystalline frameworks have "tunable" pores that are capable of size-exclusion separations. The frameworks are made of inorganic oxides (e.g., silicates, aluminosilicates, phosphates) that bring different charge and electrostatic attraction forces to the separation media. The resultant materials have high separation abilities plus inherent thermal stability over 600°C and chemical stability. Furthermore, the crystallographically defined (<1 Å deviation) pore sizes and shapes allow for size exclusion of very similarly sized molecules. In contrast, organic polymer membranes are successful based on diffusion separations, not size exclusion. We envision positive impacts from this project in the near-term with hydrocarbon fuels, and long-term with biomass fuels.

Approach

The approach for this project in FY 2004 is the development of defect-free thin film zeolite membranes and new bulk microporous phases for the selective separation of light gases. The development of these membranes includes membranes synthesis, modeling/simulation of gas movement through the membranes, and permeation studies of the separation and isolation of H_2. The modeling and simulation work helps determine improved pore size and composition for sieving. The validation is the iteration of modeling/simulation data with actual permeation values to improve upon the membranes synthesized.

Previous work at Sandia has successfully shown the ability to grow defect-free aluminosilicate and phosphate-based molecular sieve membranes. The continued focus is on the enhancement and optimization of the type of molecular sieve for separation, the methodology of film growth, the type of supports upon which to grow membranes (and

remain commercially viable), the upgrade of our permeation unit for high-temperature and steady-state permeation experiments, and the establishment of industrial partners for eventual commercialization.

We are studying and comparing silicate and aluminosilicate frameworks to better determine the relationship between adsorption, sieving and permeation. To study the effect and compatibility of support types, we are studying and comparing unsupported film growth with film growth on ceramic supports. We are beginning studies on newly available ceramic-coated stainless steel supports which allow for phase match with the ceramic and have the durability of stainless steel. With all materials synthesized, we will perform characterization in-house to better understand structure-permeability relationships. Characterization methods include X-ray diffraction, thermal analyses, elemental analysis and permeation studies. Our in-house permeation unit is capable of fitting both disk and tubular membrane supports, and either ceramic oxide or stainless steel materials. We are upgrading our permeation capabilities to include a new unit that can be run from room temperature to elevated temperatures (500C), and in both steady-state and pressurized modes. The new unit will be attached to a gas chromatograph/mass spectrometer (GC/MS), enabling us to monitor and quantify the concentrations of gases present in the permeate stream. We also are able to leverage end sealant technology patented through Sandia. The gases we plan to test for in this project include H_2, He, CH_4, CO, CO_2, CH_4, O_2, N_2, H_2S, SF_6, and binary and industrially relevant mixtures of these gases.

Results

In the area of thin film membranes, we have successfully synthesized micron-thick silicalite (all-silica ZSM-5) and aluminosilicate ZSM-5 zeolite membranes on both pure alumina and composite oxide-coated stainless steel disks (see Figure 1). Our permeation testing (see Figure 2) of the material shows that these membranes can be synthesized with minor intracrystalline defects or defect-free. Defect-free implies permeation selectivity owing to size exclusion by molecular sieving through the zeolite pores and not through crystalline defect sites, pinholes, or crystallite mismatches (pores of this

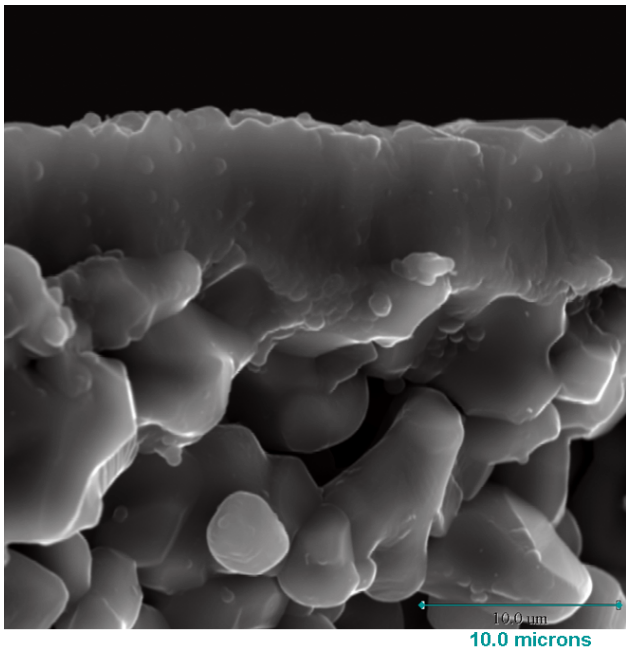

Figure 1. Cross-Section View by Scanning Electron Microscope of a 10 Micron Thick Silicalite Zeolite Membrane on an Oxide-Coated Stainless Steel Porous Support

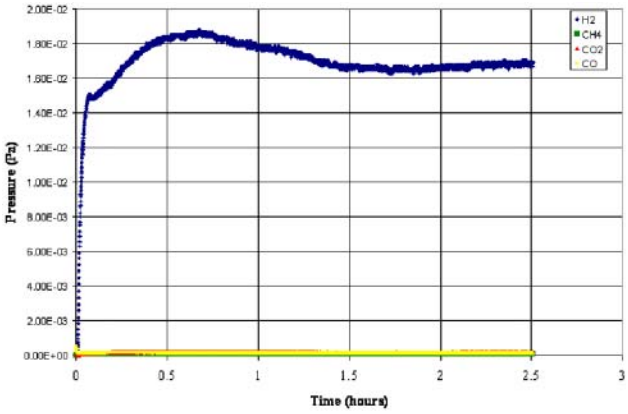

Figure 2. Permeation Graphics of ZSM-5 Membrane with the Reformate Gas Mixture (16 psig pressure)

zeolite are 5.5 Å). Molecules used for this test are He (kinetic diameter = 2.6 Å) and SF_6 (kinetic diameter = 5.5 Å). We currently run our experiments at room temperature. However, we have done preliminary permeation studies at 80 and 120°C on both silicalite and aluminosilicate ZSM-5 membranes.

Once the membrane is determined to be defect-free, testing on pure gases vital to the steam reforming cycle for natural gas to hydrogen fuels can begin. In the past years, we have shown that the Sandia

aluminosilicate membranes have fluxes on the order of 10^{-6} mole/(m^2Pa sec) and separations of H_2/N_2 61, H_2/CO_2 80, H_2/CH_4 = 7, CH_4/CO_2 11 [4].

This project year, we have completed preliminary pressure-driven (16 psig) permeation studies on binary and mixed gas streams [5]. The permeation characteristics of several silicalite and ZSM-5 zeolite membranes grown on porous α-alumina supports via hydrothermal synthesis have been tested using gas mixtures. Gas mixtures of 50/50 H_2/CO_2, 50/50 H_2/CH_4 and a simulated reformate stream mixture of 76.2% H_2, 13.6% CO_2, 6.8% CO, and 3.4% CH_4 were tested as well as the pure gases present during methane reforming processes (H_2, CO_2, CH_4, CO, N_2 and O_2). For the ZSM-5 membrane, the ideal selectivity for H_2 calculated from the pure gas data was between two and four for all the gas species. High selectivities for H_2 were recorded on the same membrane for all three gas mixtures, between 13 and 28 depending on the gas mixture. The selectivities were concentration-dependant; the highest selectivity recorded was from the gas mixture with an H_2 concentration of 76.2 mol%. For the silicalite membranes with the 50/50 H_2/CO_2 gas mixture, competitive adsorption overwhelmed the CO_2 selectivity calculated from the pure gas results. The silicalite membranes exhibited H_2 selectivity over CO_2 of 22.59, which was less than the ZSM-5 selectivity for H_2 over CO_2. The extremely high H_2 selectivity over CO_2, CO, and CH_4 of both membranes suggests these membranes will be useful for industrial H_2 separations and purification (see Figure 2).

Contaminant gases are of interest and concern for H_2 purification from reformate streams. Our initial studies with H_2S (200 ppm in N_2, approximate concentration found in reformate streams) do indicate that H_2S permeates through a ZSM-5 membrane. There is no indication of damage to the membrane, though longer-term studies are necessary. Furthermore, residual H_2S in H_2 streams will be damaging to any fuel cell apparatus.

Although we are still working to understand them, these results indicate that we can tune the membrane materials to have selectivity for various light gases. This is even more valuable as it is with crystalline inorganic zeolite membranes that are chemically, thermally and mechanically robust and stable. In comparison to Pd alloy films, the zeolite membranes perform well. According to the literature [6], Pd on alumina had relative ratios of light gas separations of H_2/N_2 = 110 at elevated temperature of 350C. The flux was also low (2×10^{-7} mole/m^2Pa sec). Furthermore, we have synthesized defect-free aluminosilicate zeolite thin films supported on commercially available oxide-coated stainless steel supports (SS316); industry requires stainless steel to make membranes an economically viable technology. Early economic analysis has shown that for an installed Pd membrane complete with permeation module, the cost is estimated up to \$200/ft^2. In comparison, zeolite membranes plus modules are currently estimated at \$200/ft^2 (importantly, this value is before mass commercialization price reductions) [7].

Conclusions

There is a great need for robust, defect-free, highly selective molecular sieve (zeolite) thin film membranes for light gas molecule separations in hydrogen fuel production from CH_4 or H_2O sources. They contain an inherent chemical, thermal and mechanical stability not found in conventional membrane materials. Our goal is to utilize those zeolitic qualities in membranes for the separation of light gases, and to eventually partner with industry to commercialize the membranes. To date, we have successfully:

- Demonstrated (through synthesis, characterization and permeation testing) both the ability to synthesize defect-free zeolitic membranes and use them as size-selective gas separation membranes; zeolites include aluminosilicates and silicates.
- Built and operated our in-house light gas permeation unit; we have amended it to enable testing of H_2S gases and mixed gases and at high temperatures. We are initiating further modification by designing and building an upgraded unit that will allow for temperatures up to 500°C, steady-state vs. pressure-driven permeation, and mixed gas resolution through GC/MS analysis.
- Shown in preliminary experiments high selectivity for H_2 from binary and industrially

relevant mixed gas streams under low operating pressures of 16 psig.

- Synthesized membranes on commercially available oxide and composite disks (this is in addition to successes we have had in synthesizing zeolitic membranes on tubular supports [8]).
- Shown through modeling and simulation that silicotitanate zeolites (i.e., ETS-4 and Zorite) would be highly selective molecular sieving membranes for H_2 over CH_4 [9].

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9. Mitchell, M.; Gallo, M.; Nenoff, T. M. Molecular Dynamics Simulations of Binary Mixtures of Methane and Hydrogen in Titanosilicates. *J. Phys. Chem*., **2004**, in press.

FY 2004 Presentations

1. M. Mitchell, M. Gallo, T. M. Nenoff, Molecular Dynamics Simulations of Binary Mixtures of Methane and Hydrogen in Titanosilicates, Fall National ACS Meeting, New York City, NY, September 2003.

2. T. M. Nenoff, M. E. Welk, F. Bonhomme, Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation, Fuel Cell Symposium, Miami, FL, November 2003.

3. T. M. Nenoff, M. E. Welk, Defect-Free Thin Film Membranes for H_2 and CO_2 Separation and Isolation, Spring National ACS Meeting, Anaheim, CA, March 2004.

4. T. M. Nenoff, M. E. Welk, Defect-Free Thin Film Membranes for H_2 Separation and Isolation, 14^{th} International Zeolite Conference, Cape Town, South Africa, April 2004.

FY 2004 Publications

1. Bonhomme, F.; Welk, M. E.; Nenoff, T. M. "CO_2 Selectivity and Lifetimes of High Silica ZSM-5 Membranes." *Micro. & Meso. Materials*, **2003,** *66*, 181.

2. Mitchell, M.; Gallo, M.; Nenoff, T. M. "Molecular Dynamics Simulations of Binary Mixtures of Methane and Hydrogen in Titanosilicates." *J. Phys. Chem*., **2004**, in press.

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4. Welk, M. E.; Nenoff, T. M. Mixed Gas "Permeation Studies through ZSM-5 and Silicalite Zeolite Membranes." *J. Membrane Sci*., **2004**, in prep.

Special Recognitions & Awards/Patents Issued

1. Reed, S. G.; Stone, R. G.; Nenoff, T. M.; Trudell, D. E.; Thoma, S. G. "Gas Impermeable Glaze for Sealing a Porous Ceramic Surface." US Patent 6,716,275, April 6, 2004.