DEVELOPMENT OF INORGANIC MEMBRANES FOR HYDROGEN SEPARATION

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ABSTRACT

This paper presents information and data relative to recent advances in the development at Oak Ridge National Laboratory of microporous inorganic membranes for high-temperature hydrogen separation. These membranes incorporate a metal tubular support with a thin ceramic layer applied to the inside of the support tube. Research emphasis during the last year has been directed toward the development of these high-permeance (high-flux) and high-separation-factor sub 2nm pore-size metal-supported membranes. In addition, improvements were made to our test systems to both increase their operating temperatures and qualify them to work with flammable gases such as hydrogen and propane. Lastly, we have submitted a prototype to DOE for a classification and nonproliferation review (NPR) and received approval for the testing and evaluation of the physical properties and performance characteristics at national labs, universities, and industrial facilities. Performance data for recent membranes are presented and new insights into diffusion mechanisms are included in the discussion.

INTRODUCTION

The U. S. is committed to a future hydrogen economy[1] but hydrogen is not available as an elemental resource. Coal gasification offers one of the most versatile and cleanest ways to convert the energy content of coal into hydrogen. Rather than burning coal directly, gasification breaks down coal or virtually any carbon based feedstock into its basic chemical constituents. Effective recovery of hydrogen from gas mixtures then becomes a central issue.

Inorganic membranes have been employed for well over half a century for separating uranium isotopes. In the early 1980's inorganic membranes began to be applied to the separation of particles from fluids and to the separation of mixtures of fluids, both liquids and gases[2-5]. The smallest pore diameters available in commercial inorganic membranes are about 4 nm.

ORNL has been engaged in the development of microporous membranes for hydrogen separation for several years. Prior to 1999, this effort was directed to very high temperature (i.e., ≥600°C) all-ceramic membranes. As a result of changing system requirements in, for example, coal gasification, the temperature at which hydrogen separation may be conducted is decreased to about 250 to 350°C. The lower temperature operation negates the need for all-ceramic structures and suggests that metal-supported membranes would be an option. Certain advantages accrue from the use of metal-supported membranes. The metal supports provide much greater flexibility in fabrication and in system integration. The support tubes may be equipped with metal end fittings and welded or brazed into the system support structure, usually a tubesheet type arrangement. Ceramic support tubes are, of course, usually much more brittle than metal support tubes and thus are more prone to catastrophic failure. Should a tube fail catastrophically, broken shards and pieces could result in a cascading effect, causing other elements to break. The ORNL membranes are composite structures consisting of a macroporous support tube (pore diameter > 50.0 nm, usually about 2.0–5.0 _m) coated with one or more membrane layers. The layers are thin, about 2.0 _m thick, and, for hydrogen separation, the separative layer pore size is typically < 1.0 nm.

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A microporous membrane is defined by the International Union of Pure and Applied Chemistry (IUPAC) as a membrane with a pore diameter ≤ 2.0 nm. Molecular diffusion, the mode of transport in these membranes, is distinct from the ionic transport in ion-transport membranes and from solution-diffusion transport in palladium membranes. Ion-transport and palladium membranes are fully dense structures, whereas microporous membranes have significant void fractions with open porosity.

For microporous hydrogen-separation membranes, separation occurs by a combination of mechanisms. For gas mixtures containing molecules with significantly different molecular diameters, separation may occur via molecular sieving as is depicted in Fig. 1. Other diffusion mechanisms include Knudsen diffusion, surface diffusion or surface flow, and viscous flow (which has no separation function). Membranes are designed to offer the best combination of flux or volumetric flow rate and selectivity for hydrogen. These designs may differ for different gas mixtures. The focus of the ORNL activity has been toward designing membranes with a pore diameter of less than 1 nm (i.e., approaching a molecular sieve concept).

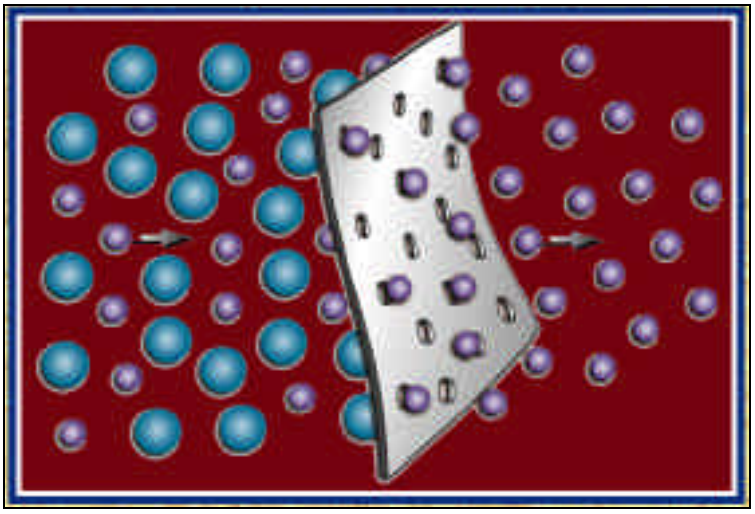

Figure 1 Simplified graphical depiction of a microporous membrane functioning as a molecular sieve.

Recently there has been concerted work to decrease the pore sizes of inorganic membranes to 2 nm or less. Although they are the most well-understood gas separation processes, Knudsen diffusion[6] and surface diffusion fail to describe permeation of gases in membranes having pore sizes below 2 nm, where potentially high separation factors can be achieved.

Inorganic membranes with pore sizes less than 1 nm offer many advantages over thin-film palladium membranes and ion-transport membranes for the separation of hydrogen from mixed-gas streams such as reformed natural gas, coal-derived synthesis gas, and refinery purge gases. In microporous membranes, flux is directly proportional to transmembrane pressure, whereas in palladium membranes, for example, flux is proportional to the square root of transmembrane pressure. Thus, microporous membranes become the preferred option for systems that operate at high pressure (see Fig. 2). The permeance of microporous membranes also increases dramatically as the temperature is increased. Consequently, inorganic membranes have the potential to produce very high fluxes at elevated temperatures and pressures. Because the separation process and transport mechanism are purely physical and thus do not involve ion transport or solution diffusion, the ORNL membranes can be fabricated of almost any combination of materials, such as a ceramic membrane on a metallic support or a ceramic membrane on a ceramic support. Proper material selection is usually based on environmental compatibility, which can ensure that the membrane will have a long lifetime while maintaining high flux and selectivity. The ORNL microporous membranes are low-cost in large measure because their fabrication does not require the use of strategic materials or precious metals, such as palladium.

One disadvantage of microporous iorganic membranes is that they are porous and have a distribution of pore sizes as opposed to having a discrete pore size as is found in zeolites. They can never produce 100% pure gas streams as can thin-film-palladium or ion-transport membranes. In those instances where pure hydrogen is the desired product, that apparent disadvantage can be overcome by coupling microporous membranes with pressure swing adsorption (PSA) to produce pure hydrogen. In such a scenario, PSA would only be required to separate the final 1% of the impurities, which implies a very compact and efficient separation system. Another approach to obtaining very high purity, but not 100% pure, hydrogen is to use two microporous membrane systems in stages or cascades. The impact of staging membranes in this way may be illustrated by considering that a membrane with a relatively low separation factor of 10 will in a single stage enrich a 50:50 mixture of hydrogen with a second gas to ~91% hydrogen. A two-stage system results in an effective separation factor of 100 (i.e., 10^2) and will enrich the initial 50:50 mixture to ~99% hydrogen. Many power generation systems, even hybrid systems using fuel cells, can accommodate less than that purity of hydrogen.

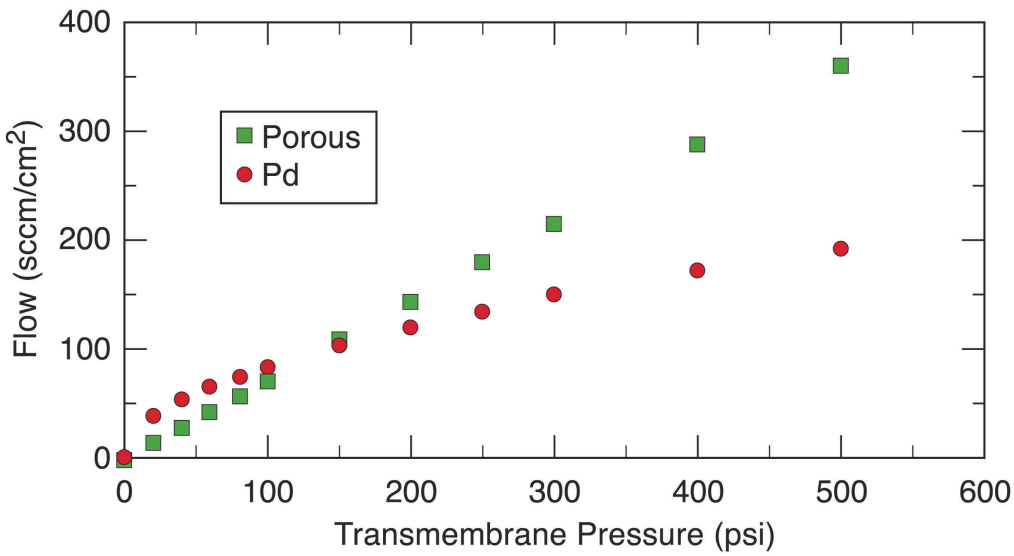

Figure 2 Hydrogen flows as a function of transmembrane pressure (_P) for an ORNL microporous membrane and a palladium membrane.

DISCUSSION OF CURRENT ACTVITIES

MEMBRANE FABRICATION

The permeance of a homogeneous membrane is inversely proportional to the membrane thickness. To be effective for gas separations, the mean pore diameter should be 2 nm or less. With such small pores, the membrane must be very thin, preferably less than 2 µm, in order to have the highest flux at the lowest transmembrane pressure. Such a thin membrane is too weak to support itself and must be applied as a layer onto a strong, porous support material, either metal or ceramic. It is preferable that the separative layer be applied to the inside of the tube. This provides for protection of the membrane from damage incidental to handling. Metal was chosen for the support tube for the reasons discussed earlier.

The primary or separative membrane layer can be applied directly to the support tube or to an intermediate layer. A layer having an intermediate pore size applied to the support tube first can provide a better surface for the primary separative layer, resulting in a thinner and more uniform membrane. The intermediate layer should be as thin as possible (usually less than 5 µm thick) and have a mean effective pore diameter of 10 nm or less and preferably as small as 2 nm. Once the primary layer is in place, various chemical treatments can be used to reduce the effective pore diameter to the desired value (as low as 0.5 nm). A photomicrograph of a microfilter (Fig. 3) shows the typical intermediate layer thickness, in this case an approximately 3-µm-thick layer of zirconia on a stainless steel support.

It is extremely difficult to fabricate a membrane with absolutely no defects. Fabricated membranes are evaluated by combining measurements made on them with a model[3] to estimate the percentage of flow through the defects and to estimate the amount that the separation factor would be lowered by their presence. Because a defect can allow the unimpeded flow of both the desired product gas and the undesired gases, the number of defects must be minimized in order to achieve a high separation factor. Several methods have been developed to reduce the effective pore diameter of a defect or to eliminate the defect altogether. These defect repair methods do not significantly reduce the number of small pores and thus do not lower the flux rate of hydrogen through the membrane.

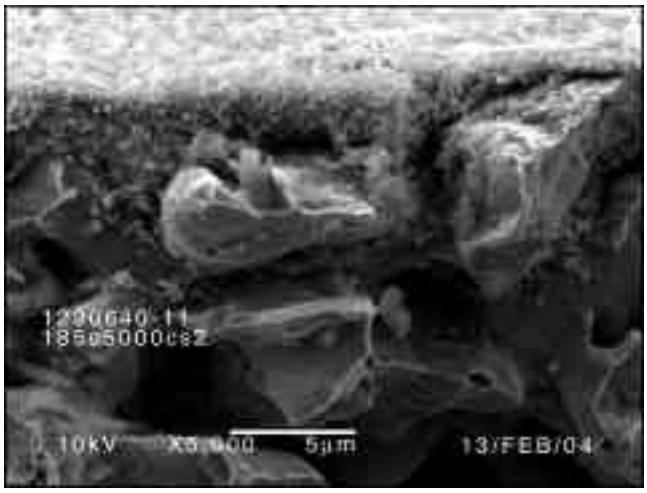

Figure 3 Photomicrograph of a porous zirconia membrane on a porous stainless steel support tube.

TECHNICAL APPROACH

In order to evaluate the separation of H_2 from a gas mixture relevant to applications where various hydrocarbons and combustion products may be present, a number of test gases were selected including propane (C_3H_8) and carbon dioxide (CO_2) which were chosen because of their relevance to needed separation applications. Helium was included also, both for benchmarking with previous work and because it is of interest in itself in connection with our membranes having potential for improved recovery of helium from gas mixtures. Initially, SF_6 was also included for benchmarking with earlier work. However, tests at higher temperatures indicated that SF_6 could be interacting with and modifying the properties of the membranes, so measurements using this gas were discontinued. Two existing gas permeation test systems were modified for use with the flammable gases H_2 and C_3H_8. The required safety documentation was completed and approved.

In order to help determine the fundamental operating mechanisms of gas separation, it is essential that data be obtained over a wide range of temperatures, with the maximum temperature as high as possible. Therefore, the membrane sealing mechanism for one of these systems was modified for operation up to and above 400 °C. Previous membrane seals using this system limited testing to temperatures below 275 °C. Most of the work was carried out on this system and consisted of sequential permeation measurements on individual gases. The ratios of permeances of the individual gases give the selectivity or ideal separation factor for the membrane in question. In addition, however, this system provides the capability to measure the actual separation of hydrogen from mixtures of two or more gases. Mixed gas measurements, using hydrogen and propane, were carried out for one membrane during the research reported here. This capability will be utilized in future work.

The test system, capable of operating at 400 °C and above, consisted of a stainless steel membrane holder, surrounded by a clamshell furnace connected to gas feed, permeate, and retentate lines. Tubular separation membranes were sealed into the holder using graphite ferrules. Each membrane was tested using the gases H_2, He, CO_2, and C_3H_8 for each temperature from 100 to 400 ºC (see Fig. 4). Tests at room temperature were also carried

out for H_2 and He. Most of the work consisted of permeation measurements on individual gases. The ratios of permeances of the individual gases give the selectivity or ideal separation factor. In addition, the system provides the capability to measure the actual separation of hydrogen from mixtures of two or more gases.

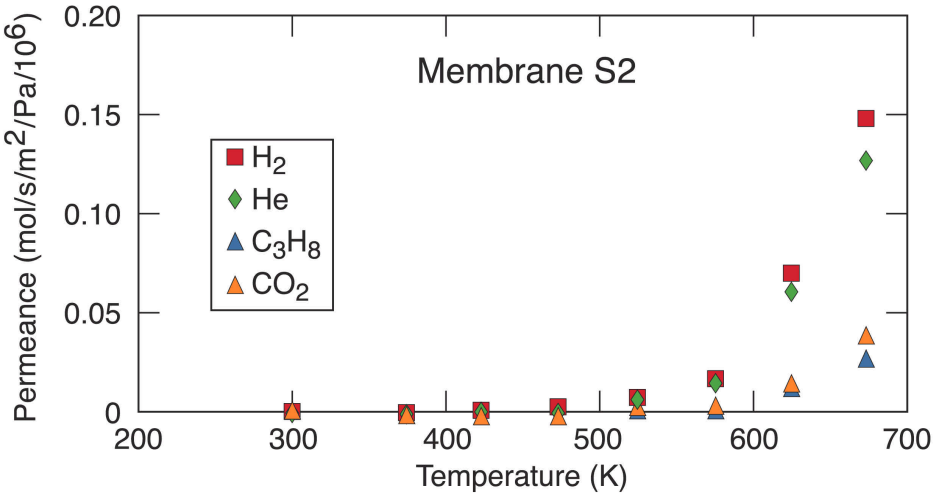

Figure 4. Measured permeance with respect to temperature. At room temperature, only He and H_2 were measured. At other temperatures all four gases were measured.

RESULTS AND ACCOMPLISHMENTS

Measurements were carried out on eight different membranes, here designated as S1 through S8 (see Table 1). The membranes tested consisted of stainless steel tubes supporting various ceramic membrane separation layers. The tube holder was also constructed of stainless steel. Each membrane had different permeance and separation properties based on different processing parameters during membrane fabrication.

Table 1

	H_2/C_3H_8 Ideal Separation Factor*						
Membrane	**100 °C**	**150 °C**	**200 °C**	**250 °C**	**300 °C**	**350 °C**	**400 °C**
S1	***2.55***	***4.10***	**5.70**	**6.79**	**6.74**	**6.48**	***3.37***
S2	**18.26**	**19.87**	**31.39**	**22.71**	**10.59**	**6.69**	**5.45**
S3	**6.59**	**8.86**	**9.30**	**11.88**	**8.14**	**6.22**	**4.85**
S4	***4.42***	***3.82***	**5.78**	**5.63**	**6.02**	**4.93**	**4.70**
S5	**5.34**	No Data	**5.14**	**5.07**	**5.49**	**5.65**	No Data
S6	**7.73**	No Data	**9.20**	**12.41**	**11.58**	**6.08**	No Data
S7	***1.87***	***3.63***	**4.94**	**5.69**	No Data	No Data	No Data
S8	***2.73***	***2.65***	***3.43***	***4.00***	***4.46***	No Data	No Data

* Values in Blue/Bold indicate an ideal separation factor higher than expected for Knudsen diffusion and values in Red/Italics indicate an ideal separation factor less than expected for Knudsen diffusion. Ideal separation factors for membrane S7 were determined at 100, 150, 175, 225, and 275 °C. The highest temperature data for membrane S8 were obtained at 275 °C.

Figures 5 and 6 show the permeance and selectivity, respectively, for membrane S2. This is the membrane that showed the highest product of selectivity and permeance for H_2 with respect to C_3H_8. This product is generally accepted as a figure of merit to assess membrane performance. At 200 ºC the measured selectivity of hydrogen with respect to propane was 31.39. The corresponding number for helium with respect to propane was 32.69. These numbers are 6.71 and 9.85 times the Knudsen selectivity, respectively, and indicate that the pore diameters in this

membrane are on the order of one nanometer. The corresponding permeance at the highest temperature of 673 K was approximately 1.5 x 10^{-7} mol/s/m^2/Pa.

There was some variation in the properties of the membranes with time at temperature. This is illustrated in Figure 5. Here the results of repeated permeation measurements of H_2 on membrane S2 are shown. It is evident that the permeation of hydrogen increased by about 30 %between the first and the last measurement at 400 ºC.

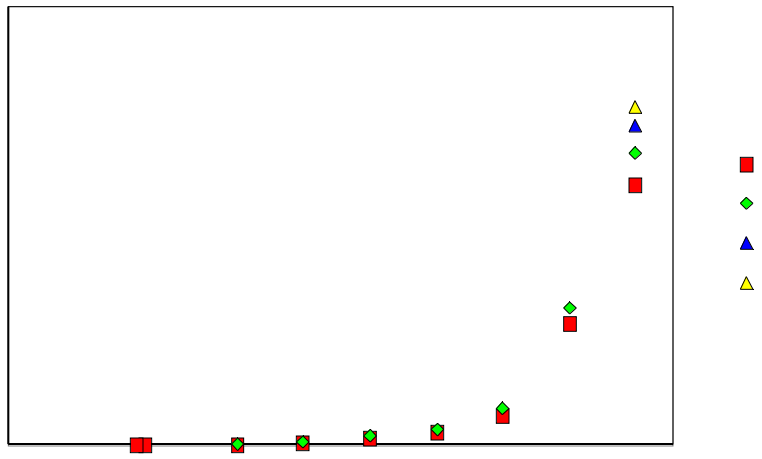

Figure 5. Results of repeated measurements of H_2 permeance for Membrane S2 at each temperature. H_2 permeance was first measured at a given temperature and then again after the permeance measurement for each of the other gases, for a total of four H_2 measurements at each temperature.

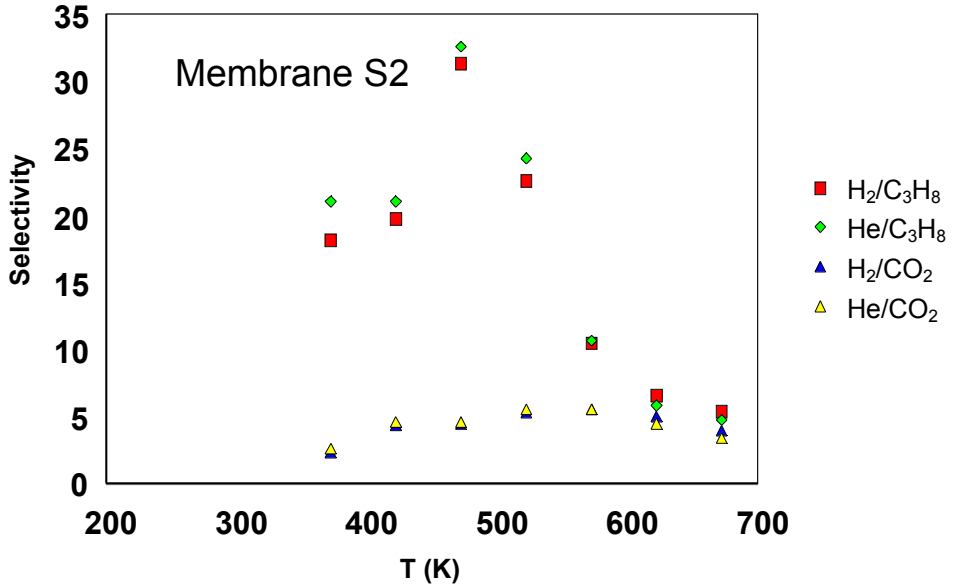

Figure 6. Measured selectivity for Membrane S2 with respect to temperature of the four gas combinations indicated.

Generally, for pore diameters > 2nm, the dominant permeation mechanisms in operation are Knudsen diffusion and surface transport, together with molecular diffusion and viscous flow (Poiseuille or laminar flow) at larger pore diameters. For pore diameters of about 1nm and smaller, other mechanisms, which are covered by the term "nanopore diffusion," become operative. Several mechanisms of gas transport through a membrane are summarized in Table 2. Key parameters include temperature (T), pressure (P), molecular mass (m), kinetic molecular diameter (d_m), pore diameter (d_p), molecular collision free path (λ), and several thermal activation energies. The latter are H_a, the heat of gas adsorption, E_s, the activation energy for surface diffusion, and E_d, the activation energy for nanopore diffusion. Expressions for selectivity and permeance also are given in the table for those cases where the dependencies on important variables can be expressed in simple form.

Figures 4 and 5 indicate an increase in permeance with increasing temperature. If Knudsen diffusion were dominant the permeances would decrease with temperature. The increase with temperature of the permeances indicates the possibility of thermally activated behavior. This characteristic is similar to the diffusion of defects or atoms in the solid state in the presence of traps[7], with activation energy E_d. Physically this is plausible, because delay time and activation energy have a one-to-one correspondence in a trapping model. Here the jump distance is determined by the pore diameter rather than the crystal lattice dimension, however, the lower limit on size of a pore must correspond to interatomic spacing in the solid state.

Table 2 Expressions for key membrane gas-transport mechanisms.

Mechanism	Pore	Selectivity	Permeance
Viscous Flow	$\lambda < d_p$	None	$d_p^2 P T^{-1}$
Molecular Diffusion	$\lambda < d_p$	None	
Knudsen diffusion	$\lambda > d_p$	$m^{-1/2}$	$m^{-1/2} d_p T^{-1/2}$
Surface Transport	All d_p	Variable	$d_p^{-1} P \exp[(H_a! - E_s)/RT]$
Capillary Condensation	f(P)	Variable	
Nanopore Diffusion	$3 d_m > d_p$	Highest	$m^{-1/2} d_p T^{-1/2} \exp[!-E_d/RT]$

STATUS OF APPROVAL OF MEMBRANES FOR COMMERCIALIZATION AND USE

Legacy classified technology issues impose the requirements for classification and nonproliferation reviews of membranes fabricated by ORNL's Inorganic Membrane Technology Laboratory. A hydrogen membrane classification and nonproliferation review package was submitted for review on January 16, 2004. These membranes were determined to be unclassified and ORNL obtained approval from DOE on July 9, 2004. The implications of this approval are that the membranes may be distributed to outside laboratories for characterization and testing, and scale-up, pilot testing, and demonstration of the membranes may be accomplished. Hydrogen membranes approved as unclassified are those with any type 300 or 400 stainless steel, Hastelloy X, or iron aluminide support tube; a membrane layer of alumina; and a final separative layer of any oxide of aluminum, zirconium, titanium, or silicon.

SUMMARY AND CONCLUSIONS

Much of the work during the past year has been directed toward modifying test systems and membrane sealing mechanisms so that evaluations with flammable gases, such as hydrogen and propane, could be accomplished at temperatures of 400 °C and higher. Eight membranes were examined, six of which demonstrated selectivity higher than for Knudsen diffusion. Selectivities of hydrogen and helium with respect to propane and carbon dioxide were demonstrated as high as 30. Membranes of this type have excellent potential for application to separation of hydrogen from hydrocarbons and combustion products. It is also apparent that the best membranes showed an increase of permeance with increasing temperature, of a form that is consistent with a thermally activated gas transport mechanism.

Also, membrane prototypes were designed, fabricated, and submitted for a Classification and Nonproliferation Review on January 16, 2004. These membranes were determined to be unclassified and ORNL obtained approval from DOE on July 9, 2004 so that the physical properties and performance characteristics of the ORNL membranes could be tested and evaluated at other national labs, universities, and industrial facilities.

Future work will include characterizing the membranes using high resolution electron microscopy at the High Temperature Materials Laboratory (HTML) and comparing the physical characteristics with flow data. Also, we will continue to expand the temperature range of our permeance and separations tests and perform a more comprehensive thermal stability study of the membranes. Data over a wider range of temperatures will help us to better understand thermally activated diffusion so that we can develop a model which will predict the performance of the membranes and how the thermally activated diffusion can be taken advantage of to improve the overall membrane performance.

ACKNOWLEDGMENTS

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