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HIGH TEMPERATURE SIZE SELECTIVE MEMBRANES

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9b.1 High Temperature Size Selective Membranes

CONTRACT INFORMATION

Contract Number	DE-AC21-92MC29245
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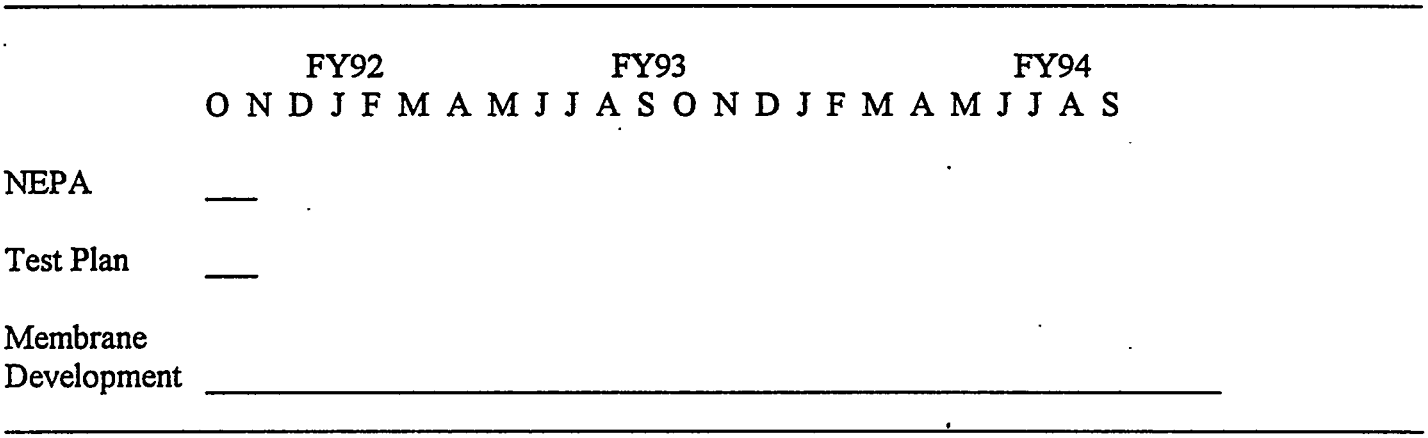
METC Project Manager	Venkat K. Venkataraman
Period of Performance	September 19, 1992 to September 18, 1994

FY94 Program Schedule



OBJECTIVE

The objective of this research is to develop a high temperature size selective membrane capable of separating gas mixture components from each other based on molecular size, using a molecular sieving mechanism. We are evaluating two concepts: a composite of a carbon molecular sieve (CMS) with a tightly defined pore size distribution between 3 and 4 Å, and a microporous supporting matrix which provides mechanical strength and resistance to thermal degradation, and a sandwich of a CMS film between the porous supports. Such a membrane would enable the separation of hydrogen from other gases.

BACKGROUND INFORMATION

Membranes that operate at temperatures higher than 100°C and still possess suitable selectivity and last for a few hundred to a few thousand hours are rare. However, the benefit of performing the separation at reactor temperatures in terms of energy cost, capital cost, and process simplicity has led many to work on developing such membranes. The high temperature membranes we are developing can be used to replace the current low-temperature unit operations for separating gaseous mixtures, especially hydrogen, from the products of the water gas shift reaction at high temperatures. Membranes that have a high selectivity and have both thermal and chemical stability would improve substantially the economics of the coal gasification process. These membranes can also improve other industrial processes such as the ammonia production and oil reform processes where hydrogen separation is crucial.

PROJECT DESCRIPTION

Our CMS membrane is composed of a thin layer of a size selective CMS supported by a microporous ceramic support. The separation of hydrogen from other gases is by a molecular sieving mechanism where the smaller hydrogen molecules (2.96Å) would pass through the pores while the larger molecules such as N_2, CO, and CH_4 are prevented from passing through.

The ceramic support is a fiber reinforced ceramic composite prepared from AlliedSignal's proprietary Blackglas™ resin. The reinforcing fibers can be carbon, glass, ceramic, or metal depending on the end use temperature. The Blackglas material in its resin form can be processed using the conventional polymer processing techniques such as lamination, infiltration, hot molding, casting, and injection molding. We have used hot molding, lamination, and infiltration techniques to make the fiber reinforced ceramic composite support. The Blackglas ceramic support has the potential for high temperature strength/stability with ease of fabrication because of the demonstrated chemical and thermal stability of Blackglas. The coefficient of thermal expansion of the support matches closely that of CMS. Such close match insures mechanical integrity and adhesion when the membrane is subjected to thermal cycles.

The CMS membrane is produced by controlled pyrolysis of polymeric precursors on the surface or in the pores of the support. Alternatively, a free standing CMS film can be made without the support and combined with a support structure in a later stage to form the membrane. The pore size of the CMS membrane can be modified by post-treatments.

The composite membrane will be tested for its permeation properties at 550°C or higher. Thermal, mechanical and chemical stability of the membrane will be assessed.

RESULTS

<u>Supported Membrane</u>

We have produced fiber reinforced ceramic microporous supports from Blackglas™ resin and carbon, glass, and ceramic fibers. The polymer composite is converted to a ceramic composite by pyrolysis under inert atmosphere (nitrogen). Repeated infiltration and pyrolysis steps are used to increase the density and decrease the porosity of the support. The resulting supports are tested for mechanical strength, pore size and pore size distribution at room temperature. The results are summarized in Tables 1 and 2.

Sample #	YIELD STRESS (psi)	YIELD STRAIN (%)	Modulus (psi)
1	1457	0.36	500500
2	3163	0.39	1031000
3	3709	0.29	1482000
4	5640	0.33	1984000

Table 1. Flexural Test Results

Sample #	MEDIAN PORE DIAMETER (μm)	POROSITY (%)
1	2.4077	23.8
2	1.1787	13.79
3	0.6216	7.02
4	0.2596	3.62

Table 2. Mercury Intrusion Results

The stress and strain results shown in Table 1 suggest that the supports are not only strong but also non-brittle as indicated by the yield strain of 0.3 to 0.4%. The pore size of the supports can also be changed to suit our needs as shown by the results presented in Table 2. The pore size distribution of the support is narrow.

SEM micrography of the porous ceramic support structure shows that the pores are formed by microcracks in the composite matrix. These microcracks come from the shrinkage associated with the pyrolysis of Blackglas resin. Thus, the pores generally have an elongated slit structure. Other pore size controlling techniques can also be used to modify the pore size and pore structure of the support.

We have also measured the flow rate of nitrogen through the support at room temperature. The results are given in Figure 1. This figure shows that the resistance of the support to gas flow is small even at room temperatures and that the flow rate is a function of the support pore size.

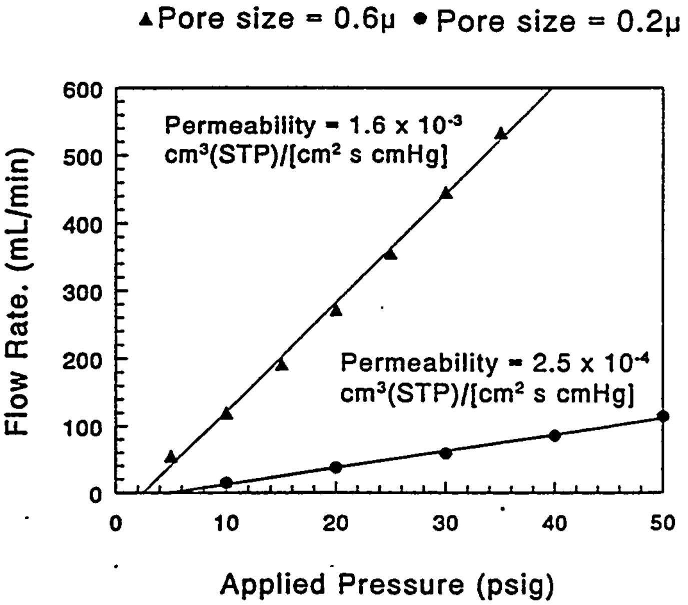


Figure 1. **Nitrogen Flow Rate Through Porous Blackglas Supports**

Our CMS membranes are prepared by a coating method where a CMS precursor polymer solution is coated on the microporous support and carbonized in nitrogen or helium. Repeated coating may be necessary to eliminate defects and cracks formed during carbonization because of the shrinkage of the polymer coating. The CMS is formed within the pores and on the surface of the porous support.

We have measured the flow rate and selectivity of nitrogen, hydrogen, and methane through the CMS membranes at both room temperature and at elevated temperatures up to 700°C and at pressures up to 60 psig. The results of these measurements are summarized in Figures 2 and 3. These figures show that the flow rate through the membrane (disk shape with effective diameter of 2.5 inches) increases with increasing temperature as expected. The ideal H_2/N_2 and H_2/CH_4 selectivities are not a strong function of temperature, and have values close to the Knudsen diffusion limit. These figures also show that the flux of all gases are high. The ideal selectivities obtained from the current study are comparable to those obtained by Koresh and Sofer [1,2] on unsupported CMS membranes prepared from cellulose material. The ideal selectivities reported are 20 and 8 for He/O_2 and O_2/N_2 before heat treatment and 2.8 and 0.92 after heat treatment, respectively. Hatori et al. [3] have also reported the following ideal selectivities for an unsupported carbon membrane made from Kapton polyimide: $He/N_2 = 19.6$, $He/O_2 = 4.3$, and $He/CO_2 = 0.4$. These results may suggest that the pore size of the current CMS membrane is still too large or simply that there are still defects in the membrane. Recently, SEM has confirmed the presence of micro defects on the surface of the CMS membranes we made. Moreover, the permeabilities of our CMS membrane is about two orders magnitude higher than those reported.

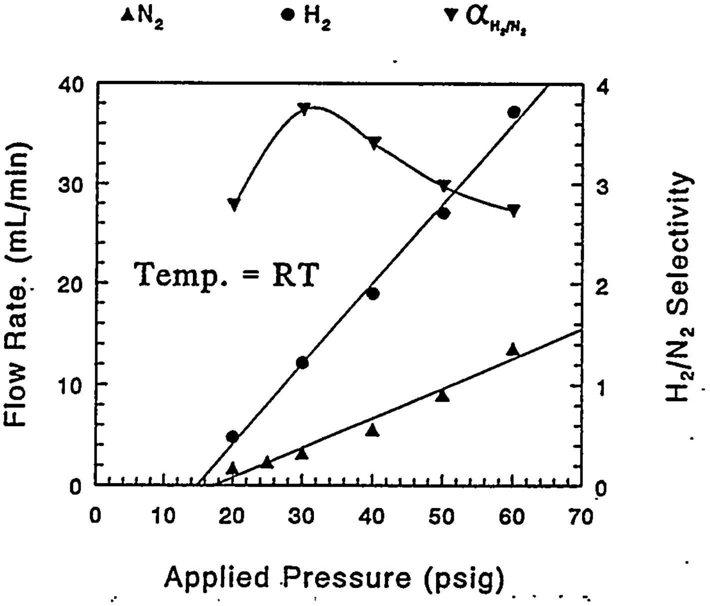


Figure 2. **Nitrogen and Hydrogen Flow Rate and Selectivity at Room Temperature**

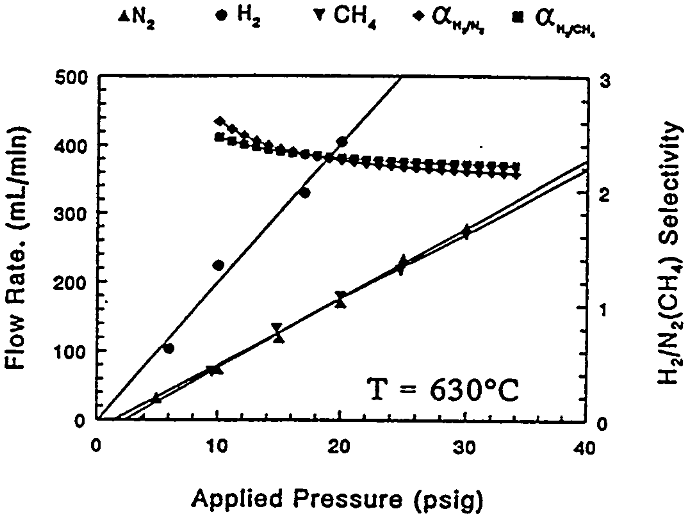


Figure 3. **Nitrogen, Methane and Hydrogen Flow Rate and Selectivity at Elevated Temperature.**

Unsupported Carbon Film

We have developed methods for the carbonization of polymer precursor into continuous, defect-free, hydrogen impermeable, carbon films. During carbonization, the films lose 40% of their precursor weight and the isotropic shrinkage is 20%.

A carbon film prepared from the pyrolysis of 3 mil polymer precursor was sealed in epoxy and placed in a membrane test cell. A pressure of 320 psig of hydrogen was applied to one side of the membrane and a pressure of 290 psig of argon was applied to the other side. The static gas pressures were blocked off and allowed to remain for two hours. At the end of two hours the argon was collected and analyzed by gas chromatography for hydrogen. No hydrogen was observed and the limits of detection of the method used were 1000 ppm, which means that the maximum possible flux constant could not have exceeded about $2x10^{-10}$ [cm^3(STP) cm]/[cm^2 s cmHg]. In a similar experiment, a 5 mil film was configured such that a differential pressure of 60 psig of hydrogen was applied to one side and allowed to stand for several hours. Flux exceeding 10^{-11} [cm^3(STP) cm]/[cm^2 s cmHg] was not observed.

We have developed a method for determining the B.E.T. surface area of materials using hydrogen as a probe gas at 19.7 K. The development of the hydrogen B.E.T. method resulted in part from recent developments in temperature control at the condensation temperature of hydrogen using a Janis Research Super Varitemp cryostat. The recently developed hydrogen B.E.T. method can be used in conjunction with the existing and well-established carbon dioxide B.E.T. method. By using both methods, we can directly compare the properties of surface interaction such as surface adsorption between hydrogen and carbon dioxide, the gases of principal interest in this project. In particular, we can study the effects of varying carbonization and activation conditions on the pore structure and it influence on the adsorption of the gases onto the carbon material. The ability to make direct comparisons between the two gases is a tool we can use to tune the pore structure and adsorption properties through variations in our synthetic procedures. Figure 4 shows a pore-size distribution determined with carbon dioxide as probe gas.

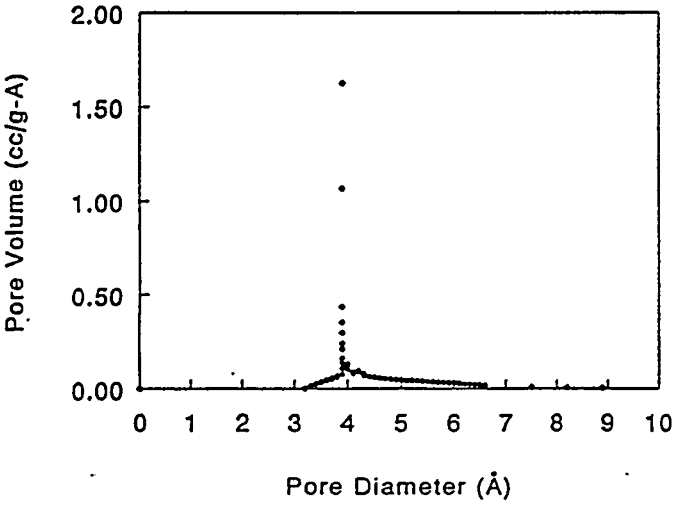


Figure 4. **Pore-size Distribution of CMS Film Using CO_2 as Probe Gas**

Surface areas depend on carbonization and activation. Variations in carbonization conditions can be used to control pore size and median pore diameter from 4.2 to 5.1 Å and pore volumes up to 0.20 cm^3/g. Surface areas as high as 400 m^2/g have been measured. The thickness of the polymer film influences the surface area. In particular, the thicker the polymer film, the lower the overall surface area. These observations strongly suggest that an impermeable, non-porous "dead" layer exists within the film. The overall composition of the film may be such that porosity exists in a higher concentration near the surface of the film. We anticipate that development of thinner carbon films may produce a hydrogen permeable material since a thinner film would have less or no dead layer material. Figure 5 shows the measured surface area as a function of precursor film thickness for both hydrogen and carbon dioxide probe gases. Also, activation has been shown to increase the surface adsorption selectively in such a way that the hydrogen pore volume (cc/g) increased from 0.10 to 0.19 but the carbon dioxide pore volume increased from 0.15 to 0.18.

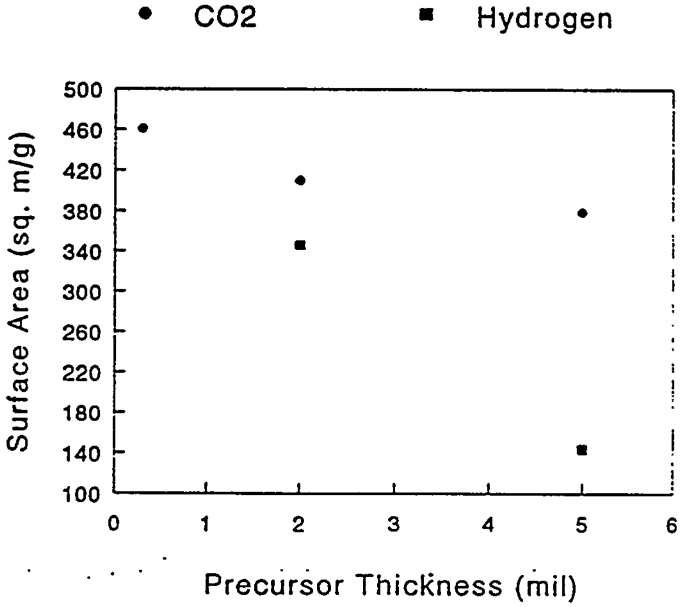


Figure 5. **Surface Area vs. Precursor Thickness**

FUTURE WORK

We are working on eliminating the micro defects on the CMS membrane surface to improve selectivity using several techniques. We are also putting efforts into making the CMS membrane just inside the pore mouth of the support, such that the CMS is constrained within the pores, eliminating any possible defects from the fabrication process and from late thermal cycling. The membranes made will be tested at high temperatures for gas permeability and selectivity. The surfaces and the interior of the membrane will also be examined by an SEM method to better understand the development of defects and ways of eliminating them. In addition to obtaining membrane permeabilities for the various gases, we will obtain information on the stability of the membrane for extended hours of operation at elevated temperatures in the reducing environment of the gases.

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