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ABSTRACT

The objective of this program is to develop a variety of inorganic based high temperature separation membranes. Organic membranes are limited by temperature (<100°C) and chemical environments, and are unsuitable for high temperature applications. The higher temperature stabilities of inorganic materials make them ideal candidates for high temperature membrane applications. Polymers with inorganic backbone structures, such as the polyphosphazenes, are being examined for mid-temperature membrane separation applications (100°C - 350°C). Metallic and ceramic membrane materials are being examined for high temperature separation applications (350°C - 1000°C). The liquid and gas membrane test systems developed for this program are described. Preliminary results on the separation properties of poly[bis(2,2,2 trifluoroethoxy)phosphazene] membranes are reported for dilute aqueous methanol, ethanol, isopropanol, and phenol feedstreams.

INTRODUCTION

The successful application of membrane separation technology for water desalination illustrates the promise that membrane technology could hold for a variety of industrial separation processes. In a recent review of membrane technology several areas in which membranes could provide a substantial enhancement for energy conservation, materials recovery and waste stream processing were identified.(1) Most commercial membranes available today are organic based polymer membranes. These membranes are generally only stable at temperatures below 100°C, narrow pH ranges (neutral, and in the absence of organic solvents and therefore would not be suitable for many industrial processes since they would not survive in the adverse environments encountered in most industrial process streams. There is a need then for the development of membranes which will meet the demands of the industrial process environments. Membranes capable of withstanding the adverse process environments are expected to be based on inorganic materials, since they are generally more resistant to chemical attack and exhibit higher thermal stabilities than organic materials.

The objective of this study is to develop a variety of inorganic based membranes able to survive in high temperatures and various chemical environments. Two membrane systems are being examined: 1) mid-temperature membranes stable up to 350°C, and 2) high-temperature membranes stable from 350°C - 1000°C. In searching for inorganic materials that could survive the harsher environments in these two temperature ranges, it was determined that inorganic based polymers (polyphosphazenes) would be stable in the mid-temperature range, and that metallic and ceramic materials would be stable in the high temperature range. Thus, polyphosphazene materials were chosen for investigation of mid-temperature membrance applications, and metallic and ceramic materials were chosen for investigation of high-temperature membrane separation applications.

The current status of the Idaho National Engineering Laboratory Inorganic Membrane Program is summarized in this paper. In Part A the synthesis, casting, and testing of mid-temperature polyphosphazene membranes is presented. Details of this work are presented elsewhere.(2) The details of initial studies on sputter deposited metallic high-temperature membranes, and the experimental membrane gas test cell apparatus are presented in Part B of this paper.

PART A: POLYPHOSPHAZENE MID-TEMPERATURE MEMBRANES

Background

Inorganic polymer materials, such as the polyphosphazenes, were chosen for initial investigation of mid-temperature membrane separations. The phosphazene polymer consists of a conjugated phosphorous-nitrogen double bond backbone system with two side groups attached to the phosphorous atoms. These polymers can be easily modified with a variety of side groups by nucleophilic substitution and exchange reactions.(3) There are three types of polyphosphazene backbone structures: 1) linear; 2) cyclolinear; and 3) cyclomatrix.(4) The linear organo-substituted polyphosphazene material is synthesized from the ring cleavage polymerization of the cyclic trimer (usually hexachlorocyclotriphosphazene) and subsequent substitution with the desired side group. The other two polymers cyclolinear and cyclomatrix are prepared by reacting the cyclic trimer with a difunctional monomer. The type of polymer obtained is dependent on the mole ratios of the reactants used and available reactive sites on the trimer. The chemical and thermal properties of the polymer are found to be related to both the polymer backbone structure and sidegroups.(3,4) This diversity is attractive for membrane studies since it permits the tailoring of membranes, with certain chemical and physical properties, for specific separations.

The linear polymers were chosen for initial investigation because extensive information on the synthesis and physical properties of the polymers was available in the literature. The first candidate membrane material to be synthesized was the linear poly[bis(2,2,2, trifluoroethoxy)phosphazene] (PTFEP). PTFEP was chosen for the initial study presented in this paper, because it is reported in the literature to be a film former, chemically resistant to various solvents, and has a high melting point (243°C).(5) A summary of the synthesis, casting procedure, and membrane diffusion experiments are presented in the following sections of Part A of this paper.

Experimental

Synthesis and polymer characterization. A modification of Allcock's procedure was used in the synthesis of PTFEP.(5) Hexachlorocyclotriphosphazene was polymerized in vacuum at 250°C for 48 hours. The polymerized material was then dissolved in dry benzene and added dropwise to a tetrahydrofuran solution of sodium trifluoroethoxide. The mixture was refluxed for 40 hours and upon cooling acidified to a pH of 4-5 with HCl to neutralize any unreacted base. The polymer mixture was then filtered and washed with water and ethanol to dissolve occluded sodium chloride. After the polymer was air dried it was purified with benzene in a Soxhlet extractor for 48 hours (the benzene extraction separated the oligomers from the polymer). Yields of 18-21% of the white fibrous polymer were obtained using the above method (yields are based on a dichlorophosphazene monomeric unit; the best yield obtained was 19.4 g (20.6%) of PTFEP).

A Perkin Elmer series 1420 ratio recording Infrared Spectrometer was used for the IR analysis of PTFEP films. The polymer films were cast from a tetrahydrofuran solution onto sodium chloride crystals. The observed IR vibrations confirmed polymer formation as they agreed very well with those reported in the literature (P-N: 1285 cm^{-1}; P-O-C:885 cm^{-1}, 960 cm^{-1}, 1425 cm^{-1}).(5) A Perkin Elmer Differential Scanning Calorimeter (DSC-2) was used in the thermal analysis of the polymer samples. Polymer samples were heated at a rate of 10°/min in the range of 30°C - 260°C. The two transitions observed at 80°C (first order transition) and 238°C (melting point) agree very well with the thermal characteristics of the polymer reported in the literature.(6)

Casting. The results of a casting study indicated that membranes cast from 1% polymer solutions in ethyl acetate produced dense nonporous uniform membranes which were suitable for the diffusion experiments performed in this study.(2) These membranes were cast using a knife casting apparatus. The knife casting apparatus, shown in Figure 1, consisted of an AO Reichart Microtome (Model 860) with a casting platform and a sage pump drive system for uniform movement of the knife assembly. A vacuum line was installed in the casting platform to hold the casting media in position. Knife height was set by adjustment to the appropriate feeler gauge. Membranes cast with the knife casting apparatus at a knife height of 100 µm with 1% polymer solution in ethyl acetate and tetrahydrofuran were found to be 0.25 µm and 0.47 µm thick, respectively. Film thicknesses were determined gravimetrically on glass cover slide substrates (24 mm x 64 mm) using a Mettler (Model AE163) micro balance.

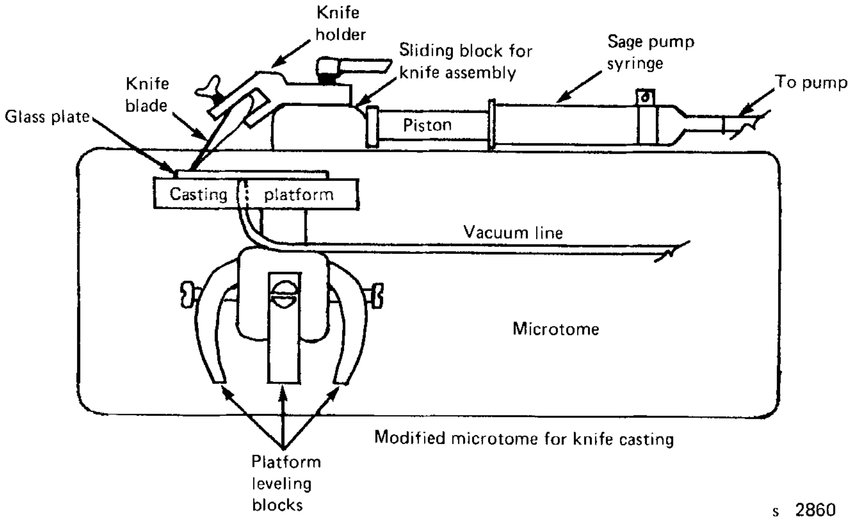

Figure 1. Knife casting apparatus.

Liquid cell test system and diffusion experiments. The liquid cell test system developed at the Idaho National Engineering Laboratory can produce pressures up to 2.07 x 10^7Pa (3000 psi), with a 6.9 x 10^6Pa (1000 psi) pressure drop across the membrane and Inconel porous support, and maintain constant temperature in the test cell up to 350°C. Feed stream flow can range from a few ml/min up to one liter/min (Reynold's number is >2000 to insure turbulent flow). The system is constructed of Inconel and designed to handle a wide range of feedstock solutions. The feed solution is introduced into the cell in a parabolic chamber designed to provide a flow field of uniform velocity. The feed solution passes through a porous flow distributor and across the membrane. The effective area for transport through the membrane is 6.5 cm^2. The permeate side is designed similarly and the permeate is flushed from the cell during diffusion experiments in a continuous mode with a dilution solution.(2)

Membranes were cast on Inconel test cell support plates using the knife technique previously described. The thickness of the membranes tested were approximately 0.25 µm (cast from ethylacetate) and 0.50 µm (cast from tetrahydrofuran). Before the diffusion experiments the membranes were pretested with a pressure differential of 3.5 x 10^5Pa (50 psi) across the membrane, for 20 minutes. Membranes that leaked were rejected. Aqueous feed solutions of 0.1 M methanol, ethanol, isopropanol and phenol were used. The carrier solution was nanopure water. Feed flow rates were approximately 20 ml/min and permeate flow rates were 1.0 ml/min for the diffusion experiments. A positive pressure differential of 3.5 x 10^4Pa (5 psi) was maintained across the membrane and measurements were made at intervals in the range of 25°C - 180°C. The feed and permeate solutions were analyzed using a Perkin Elmer Sigma 1B gas chromatograph to determine the alcohol concentrations.

Results and Discussion

The diffusion flux for each alcohol species was calculated from the experimental measurements using equation (1).

$$F = \frac{C_2 V}{A t} \tag{1}$$

where F is the flux, C_2 is the concentration of the diffusing species on the permeate side, A is the membrane area and V/t is the flow rate of the permeate. The diffusion coefficient can be calculated from Fick's diffusion equation using the calculated flux.(7)

$$F = \frac{D(C_1-C_2)}{\ell} \tag{2}$$

D is the diffusion coefficient for that species, C_1 is the concentration of the diffusing species on the feed side of the membrane and ℓ is the membrane thickness. This assumes diffusion is independent of concentration.

Using the normal temperature dependence of diffusion which for membranes can be derived from the Parlin-Eyring diffusion model, the diffusion coefficient can be represented as a function of temperature and diffusion activation energy of the diffusing species (equation 3).(2,8)

$$D = D_0 \exp(\Delta E_a/kT) \tag{3}$$

where ΔE_a is the activation energy of diffusion for the diffusing species, T is the temperature, k is the Boltzmann constant, and D_0 is a diffusion coefficient constant. The exponential term is generally considered to be the probability of an atom, ion or molecule moving from one stable position to another within the membrane. The activation energy represents the energy barrier the diffusing particle must pass in its movement.

The experimental results and conditions of the PTFEP diffusion studies are presented in Table 1. The flux and the diffusion coefficients calculated (using the data in Table 1) for each alcohol are summarized in Table 2. A logarithmic plot of the diffusion coefficient (log D) vs 1/T is presented in Figure 2 for ethanol. Similar linear plots were also obtained for methanol and isopropanol. The results of these plots show that the three alcohols follow the Parlin-Eyring Model by exhibiting a linear relationship between the log (D_i) vs 1/T (equation 3). The diffusion constant, D_0, and activation energies, ΔE_a, calculated from the y-intercept and slope of the log D_0 vs 1/T plots are presented in Table 3.

TABLE 1

PTFEP Experimental Diffusion Data[a]

T (°C)	Perm Flow (ml/min)	V (ml)	ℓ (μm)	Permeate Analysis (PPM) C_{2m}	C_{2e}	C_{2i}	Feed Analysis (PPM) C_{1m}	C_{1e}	C_{1i}
24.4	0.90	18.00	0.47	3.5	5.4	5.0	3480	4889	6203
24.6	0.92	18.40	0.47	2.4	4.3	3.1	3620	5100	6430
24.7	0.94	18.80	0.47	3.0	4.6	3.1	3693	5203	6537
52.7	0.94	18.80	0.47	13.1	23.6	32.2	3692	5202	6693
52.8	0.93	18.60	0.47	11.6	20.9	26.9	3747	5552	6958
52.8	0.94	18.80	0.47	10.3	20.0	23.8	2939	4470	5809
73.3	0.95	19.00	0.47	8.1	15.5	18.8	3784	5506	7025
73.4	0.96	19.20	0.47	9.6	17.5	21.7	3696	5346	6807
73.7	0.91	18.20	0.47	13.0	24.4	31.4	3542	5212	6689
97.2	1.01	20.20	0.25	216.0	309.0	398.0	3452	5434	6829
97.5	1.01	20.20	0.25	287.0	410.0	532.0	3333	4902	6166
97.9	1.01	20.20	0.25	287.0	412.0	536.0	3040	4342	5534
98.4	0.88	17.60	0.47	18.1	25.5	28.7			
98.6	0.94	18.80	0.47	21.2	29.6	34.9	3683	5343	6671
99.4	0.94	18.80	0.47	23.5	31.5	35.7	3322	4817	6136
100.5	0.97	19.40	0.25	41.7	56.8	73.2	3848	5755	7159
100.9	0.95	19.00	0.25	59.0	80.5	107.7	3261	4723	5878
101.0	0.95	19.00	0.25	52.3	72.7	95.1	3666	5437	6800
121.7	1.01	20.20	0.25	311.0	453.0	538.0	3885	5805	6918
121.9	1.05	21.00	0.25	397.0	590.0	704.0	4135	6254	7522
122.0	0.99	19.80	0.25	253.1	444.0	389.0	3712	5945	7019
123.0	0.97	19.40	0.47	135.4	192.1	239.8	3524	5013	6403
123.4	0.97	19.40	0.47	127.7	181.2	224.8	3526	4997	6349
123.7	0.96	19.20	0.47	129.0	182.7	226.9	3471	4983	6376
150.2	1.05	21.00	0.47	35.6	48.0	59.1	3561	5112	6527
150.6	1.07	21.40	0.47	39.2	55.6	71.1	3471	5102	6484
177.6	0.96	19.20	0.47	195.0	281.0	360.0	3463	5099	6419
179.3	1.00	20.00	0.47	473.0	678.0	892.0	3491	5174	6526
179.5	0.91	18.20	0.47	330.0	472.0	611.0	3503	5204	6537

[a] Membrane area = 6.5cm^2; T = temperature; V = sample volume; ℓ = membrane thickness; C_2 = permeate concentration (PPM); C_1 = feed concentration (PPM); m = methonol; e = ethanol; i = isopropanol.

The activation energies of the three alcohols tabulated in Table 3 are all small. This suggests that there is little binding energy between the PTFEP membrane and the diffusing species. The activation energies of the three alcohols are also quite close thus it is concluded that there is little steric hinderance between the alcohols and the PTFEP membrane during diffusion through the membrane. In other words these results indicate that the diffusion pathways within the membrane are larger than the diffusing species (methanol, ethanol and isopropanol). This can be easily seen when the activation energies for diffusion of each alcohol in PTFEP are compared with the activation energies for diffusion of various atoms, molecules and ions in solid potassium chloride.

The activation energies for the ions diffusing through KCl in Table 4 are higher than the activation energies calculated for the alcohols in PTFEP. One would expect higher energy barriers for diffusion through an ionic crystal than a polymer because of the higher degree of order and packing in the crystal. It is interesting to

TABLE 2

Summary of Diffusion Calculations[a]

T	Flux (moles/cm^{2}s)				Diffusion Coefficient (cm^2/s)			
(°C)	$\bar{F}_m$	$\bar{F}_e$	$\bar{F}_i$	$\bar{F}_p$	$\bar{D}_m$	$\bar{D}_e$	$\bar{D}_i$	$\bar{D}_p$
24.6	2.27E-10	2.54E-10	1.52E-10	NA	9.53E-11	1.09E-10	6.75E-11	NA
52.8	9.10E-10	1.17E-09	1.15E-09	NA	3.99E-10	5.02E-10	5.02E-10	NA
73.5	7.97E-10	1.04E-09	9.95E-10	NA	3.30E-10	4.23E-10	4.14E-10	NA
100.8	4.06E-09	3.87E-09	3.90E-09	2.76E-09	9.31E-10	8.67E-10	9.16E-10	5.91E-10
121.9	2.72E-08	2.93E-08	2.47E-08	1.76E-08	6.04E-09	6.11E-09	5.59E-09	5.14E-09
150.4	3.30E-09	3.18E-09	3.07E-09	NA	1.43E-09	1.36E-09	1.34E-09	NA
178.8	2.66E-08	2.66E-08	2.65E-08	NA	1.29E-08	1.24E-08	1.29E-08	NA

[a] T = Temperature; m = methanol; e = ethanol; i = isopropanol; p = phenol; $\bar{F}$ and $\bar{D}$ are average flux and diffusion coefficient values.

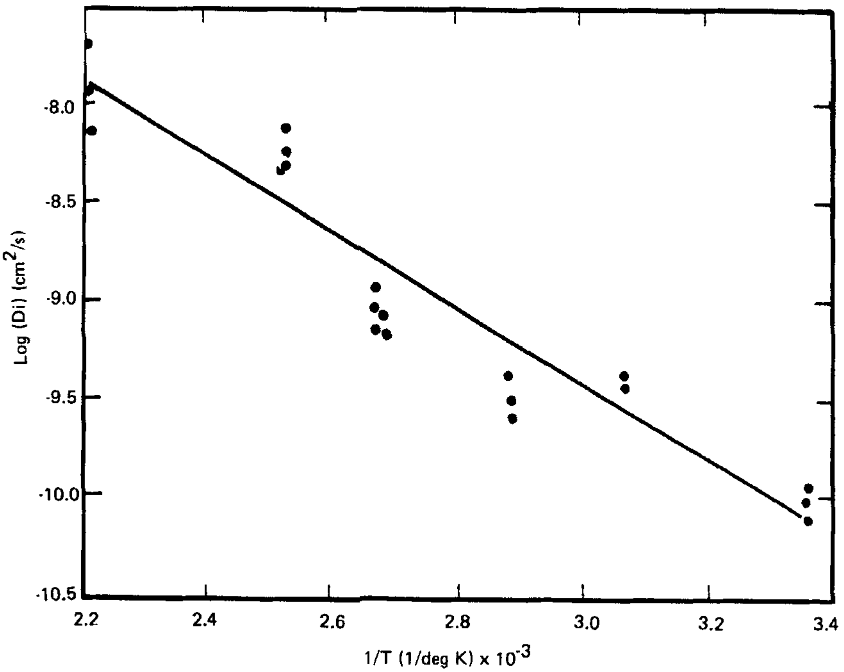

Figure 2: Measured diffusion coefficient for ethanol and linear fit to data.

TABLE 3
Activation Energy Data for Diffusing Species in PTFEP

Alcohol Species	ΔE_a (eV)	D_0 (cm^2/sec)
Methanol	0.38	2.2×10^{-4}
Ethanol	0.37	1.2×10^{-4}
Isopropanol	0.39	2.8×10^{-4}

TABLE 4
Comparison of Activation Energies for Diffusion in
Poly bis(trifluoroethoxy)phosphazene and KCL.

Substrate	Diffusant	ΔE_a (eV)	Ionic or Molecular radii (Å)
PTFEP	CH_3OH	0.38	1.4[a]
PTFEP	CH_3CH_2OH	0.36	1.7[a]
PTFEP	$CH_3CH(CH_3)OH$	0.39	2.1[a]
KCl	Kr	2.1	1.69
KCl	H_2O	0.80	1.36
KCl	Li^+	1.52	0.60
KCl	Na^+	1.75	0.95
KCl	K^+	2.15	1.33
KCl	Cd^{2+}	0.54	0.97
KCl	Pb^{2+}	1.18	0.84
KCl	Ce^{3+}	1.03	1.03
KCl	Cl^-	2.25	1.81

[a] Molecular radii were calculated using covalent bond lengths and covalent radii; cylindrical shapes were assumed and the smallest molecular radius of the alcohol is given.

note that the ions diffusing through KCl have radii comparable to the cylindrical radii calculated for the alcohols. This would suggest then that the lower activation energies for diffusion through PTFEP are attributed to the packing structure and defects within the polymer membrane. The loose packing structure and defects (relative to an ionic crystal would create large pathways for the diffusion of the alcohols through the membrane.(2)

Table 5 gives the ratio of methanol diffusion coefficients to ethanol, isopropanol and phenol in the temperature range of 25-179°C (only two temperatures are reported for phenol).

In the temperature range of 25°C - 73°C methanol diffuses slower than the other alcohols. In the range 100°C - 179°C methanol diffuses faster than the other alcohols. PTFEP undergoes a first order crystalline transition at about 83°C. The change in the diffusion coefficient ratio of methanol to the other alcohols appears to be affected in the temperature range where the polymer undergoes a transition from a crystalline state to a mesomorphic state. At this time, because further studies are needed, no reasons are given for the cause of this phenomena. The ratio of diffusion coefficients for phenol is higher than the ethanol and isopropanol ratios. This could indicate that the phenol molecular cross-sectional area is approaching the size of the interstitial spaces in the polymer available for diffusion. Larger species (i.e., sugar) should be tested to see if their diffusion is inhibited and to determine whether a PTFEP membrane would be useful in the separation of large molecules.

TABLE 5
Ratio of Diffusion Coefficients[a]

Temp (°C)	D_m/D_e	D_m/D_i	D_m/D_p
25	0.88	1.4	NA
53	0.80	0.80	NA
73	0.78	0.79	NA
100	1.1	1.1	1.4
123	1.0	1.1	1.1
129	1.0	1.0	NA

[a] m = methanol; e = ethanol; i = isopropanol; p = phenol

Conclusions

Based on the results of the diffusion experiments the following conclusions are made:

1) Poly bis(trifluoroethoxy)phosphazene is a stable membrane material up to 180°C for at least five hours.

2) PTFEP is highly permeable to methanol, ethanol, isopropanol, and phenol. High diffusion coefficients and low activation energies were observed.

3) Interstitial sites within the membrane are larger than the methanol, ethanol and isopropanol molecules since no selectivity was demonstrated in the diffusion experiments.

PART B: METALLIC HIGH TEMPERATURE MEMBRANES

Background

The use of membranes in separation processes with extreme conditions of temperature, pressure and with aggressive mixtures (chemical, abrasive, and even micro-biological) are becoming increasingly important. Due to the high temperatures (350°C - 1000°C) and pressures involved in many of the envisioned separation processes, metallic and ceramic membranes appear to be the only materials capable of surviving under these conditions. Much of the experimental work dealing with metals has been concerned with the permeation and diffusion of gases in connection with their applications in various areas of vacuum technology and as vacuum vessel materials for use in fusion energy devices. Some of these topics were discussed in a review article by Perkins.(9) Refractory metals such as tungsten and molybdenum, and many of the more permeable metals such as copper, nickel, iron and alloys containing these metals have been widely studied. Generally, they have been studied only in the context of their potential use as vacuum materials, and in most cases for the permeation and diffusion of hydrogen and its isotopes, oxygen, nitrogen, and in some cases carbon monoxide. Palladium and palladium-silver alloys are widely used to purify hydrogen, and silver is quite permeable to oxygen; however, very little work has been done on the development of metal membranes to separate more complex process streams. Ceramic based membranes are only now beginning to be developed as membranes used to separate more complex multicomponent gas streams. It would appear that the preparation of crack-free metallic and ceramic films with ultra-fine pores and with controllable, narrow pore size distribution is a major obstacle to overcome in order to prepare membranes possessing the desired separation selectivity. Work to date has been directed toward the preparation of thin metal films by sputter deposition techniques which possess microstructures potentially suitable for use as membranes.

The motivation for investigating the use of thin films as membranes arose from the recognition that various film microstructures can occur as a result of the conditions used during the sputter deposition of the thin film. Certain of these microstructures may lead to the desirable situation wherein a controllable, small pore size structure with a narrow size distribution may be created in the film which would act in turn as a microstructural mechanism to achieve membrane selectivity. The microstructure of the film is determined by the nucleation and subsequent growth of the film by the sputter deposited atoms. Nucleation of the impinging atoms will depend on the atom-substrate interactions and their surface mobility. Growth in turn is also determined by the surface mobility of the depositing atoms, their atomic arrangement on condensation and any subsequent rearrangement of the structure. For films which have become continuous, when the mean free path between collisions of the depositing atoms is large and their surface mobility is low, the growth of the deposit will be controlled by the geometry of the surface. Deposition on the high spots and shadowing of the low spots will produce a columnar microstructure consisting of very fine grains of the material. This is often referred to as Zone 1 in the zone model proposed by Movchan and Demchishin.(10) This zone forms at low T/T_m values where T is the temperature of the substrate, and T_m is the melting point of the film material.(11) It is also promoted by an elevated pressure of the gas used to induce sputtering of the cathode target (usually argon). The columnar structures usually consist of tapered crystals with domed tops which are separated by voided boundaries. It is the diameter, area number density and uniformity of these voided boundaries which will be varied, controlled and exploited for the preparation of the thin film membranes.

Testing of these metallic membranes at temperatures up to 1000°C and pressures to 3.5×10^6Pa (500 psi) necessitates careful design and special materials selection. The wide range of experimental work in the area of gas permeation at near ambient temperatures has resulted in a wide variety of apparatus for measuring the transport parameters. Hwang(12) has presented an overview of various designs. The American Society For Testing Materials (ASTM) has a recommended apparatus design, originally proposed by Stern(13) in their standard for gas permeation measurements (ASTM D-1434-11). Two test systems have been designed, one for preliminary scoping studies and a second more complex system for detailed transport study. These systems and the preliminary results of initial membrane fabrication studies are discussed in the following sections.

Experimental

Membrane preparation. The current sputter deposition system consists of a Kurt J. Lesker Co. Model KJL-UCV-18/6 oil diffusion pumped vacuum system which houses an Enerjet, Inc. Torus-10 gun assembly. One of the high temperature, low pressure membrane test systems was designed using VCR couplings (Cajon Company), and thus the membrane substrate (i.e., the substrate onto which the metal membrane was directly sputter deposited) consisted of an SS-16-VCR-2-0.5M VCR filter gasket. This is a nominal one inch (3.6cm; 1.41 in. OD) stainless steel gasket into which a 0.5 micron pore size stainless porous filter (2.3cm; 0.89 in. OD) has been fusion bonded. One side of the porous filter was machined even with the gasket surface in order to provide a flat surface on which to deposit the metal film. Essentially this assembly provides a porous mechanical support for the film which allows the application of a differential pressure across the metal film. It also provides a convenient means of sealing the metal membrane into the test cell.

Films of vanadium and aluminum of 1 to 10 microns in thickness (as monitored by a quartz crystal oscillator) have been deposited on the VCR filter gasket assembly to determine their adherence, microstructure and He leak-rate (as determined using a He vacuum leak detector). Preliminary results indicate that pin-hole-free thin films of vanadium at a 1 micron thickness level can be prepared. However, the vanadium film when exposed to laboratory air over a period of a week has been observed to flake off the substrate. This has similarly been observed for the aluminum films. Work is continuing on the reproducible preparation of the thin supported films. Determining their microstructure as a function of the sputter deposition parameters and their effectiveness as membranes for gaseous separations is planned.

Membrane test cells. The membrane test cells and support systems closely follow the major design characteristics of previous systems(2), with the exception that temperatures up to 1000°C and pressures to 3.5×10^6Pa (500 psi) can be accomodated. A simple system for performing preliminary scoping studies has been constructed with commercially available Cajon VCR stainless steel fittings. This system provides an overpressure on the feed side of the membrane and can provide a vacuum on the permeate side. Material properties limit the system to approximately 1.0×10^7Pa at 500°C. The effective transport area of the cell is 4 cm^2 of porous stainless steel. The cell is heated with a small clam-shell furnace.

A second, more versatile system is currently being constructed. This system is designed to provide closely controlled temperatures up to 1000°C and pressures to 3.5×10^6Pa (500 psi), to maintain gas concentration and to accommodate corrosive gases. Figure 3 shows a schematic diagram of the system.

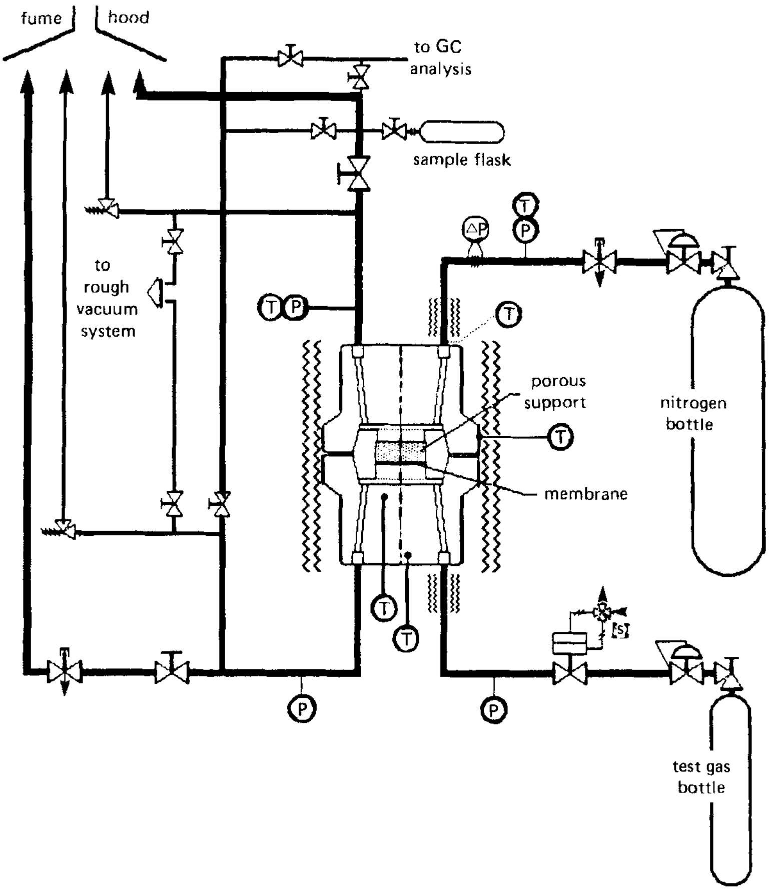

Figure 3. High temperature, high pressure gas system for membrane characterization.

The feed stream can provide either a fixed gas flow rate or a stagnate volume. The feed gas is preheated prior to entering the test cell and within the test cell the temperature is controlled with a computer based feedback system. The test cell is contained within an isothermal chamber surrounded by a blast shield. The cell is constructed of Inconel and is based on a Greylock fitting design. The membrane support is a porous metal disc set into the Greylock sealing gasket. The flow area of the membrane support is $5cm^2$. Gas sampling ports are located on the feed, retentate and permeate streams. The permeate stream includes a dilution (flush) gas system to maintain constant concentration and can operate under vacuum. The absolute and differential pressure across the membrane is measured and controlled. A small process computer is used for monitoring, control, and data acquisition.

PART C: SUMMARY AND FUTURE STUDIES

Polyphosphazene Membranes

Poly[bis(2,2,2 trifluoroethoxy)phosphazene] was successfully synthesized and cast into sub-micron thin films. The results of a prior casting study(2) indicated that dense homogeneous thin films suitable for membrane diffusion experiments were obtained when cast from ethyl acetate - PTFEP solutions. PTFEP membranes were found to be highly permeable to methanol, ethanol, isopropanol, and phenol and stable up to 179°C.

Future studies include the synthesis, casting, and testing of other linear organo-substituted polyphosphazene membranes which have higher thermal stabilities and different chemical affinities (i.e., aryloxy phosphazenes polymers). In addition a variety of cyclolinear and cyclomatrix polymers will be investigated for membrane applications. These polymers generally have higher thermal stabilities and increased chemical inertness over their linear counterparts, thus it is envisioned that novel casting techniques will have to be developed. Some of the techniques being considered are: 1) glow discharge polymerization and in situ deposition of polymer films; 2) in situ photopolymerization of monomer films; and 3) in situ solid-liquid and solid-gas chemical polymerization of monomer films.

Metallic Membranes

Initial studies on the preparation of thin, crack-free metal membranes, using sputter deposition techniques have been most encouraging. The film thickness and homogeneity of the metallic or alloy membranes produced by the sputter deposition technique could be easily controlled. The ability to vary and control the morphology of the thin film and its influence on the separation selectivity of the membranes appears promising but needs further study. The study of the gas molecule/membrane material physical and chemical interactions is also being pursued in the design of the metal membranes. These interactions directly influence the adsorption, desorption and transport of the gas molecules through the membrane. Corrosive interactions between the gas mixture and the membrane not only effect the longevity of the membrane but it will also effect the chemical/physical interactions governing the transport of the gas molecules through the membrane. The influence of these effects will be studied by surveying the separation selectivity of a number of different metal membranes with various gas mixtures. The two membrane gas test cell systems previously described will be used to conduct these studies. Both low and high pressure gas mixtures in conjunction with high temperatures will be used.

Future studies will involve the preparation of ceramic membranes using sol/gel techniques to cast thin layers of ceramic materials with controlled micro-porosity. Direct sputter deposition of ceramic films will also be studied. The ability to prepare crack-free homogeneous films possessing controllable pore size and a narrow pore size distribution will be one of the major goals of this effort.

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