

CARBON DIOXIDE SELECTIVE SUPPORTED IONIC LIQUID MEMBRANES: THE EFFECT OF CONTAMINANTS

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Introduction

The integrated gasification combined cycle (IGCC) is widely viewed as a promising technology for the large scale production of energy in a carbon constrained world. The cycle, which can include gasification, contaminant removal, water-gas shift, CO₂ capture and compression, and combustion of the reduced-carbon fuel gas in a turbine, has significant thermal efficiency advantages over conventional combustion technologies. A CO₂ selective membrane capable of maintaining performance at conditions approaching those of low temperature water-gas shift (260°C) could facilitate the production of carbon-neutral energy by simultaneously driving the shift reaction to completion and concentrating CO₂ for sequestration.

Supported ionic liquid membranes (SILMs) have been previously evaluated for this application. Early attempts suffered from support failures due to plasticization (1), but with improved supports, SILMs were determined to be physically and chemically stable to temperatures in excess of 300°C. These membranes were based on ionic liquids which interacted physically with CO₂ and diminished considerably in selectivity at higher temperatures. To alleviate the problem of diminishing selectivity, the original ionic liquids were replaced with ionic liquids able to form chemical complexes with CO₂. These complexing ionic liquid membranes have a local maximum in selectivity which is observed at increasing temperatures for more stable complexes. Similar results have been published by Matsuyama and coworkers (2). Efforts are currently underway to develop ionic liquids with selectivity maxima at temperatures greater than 75°C, the best result to date, but other practical concerns must also be addressed if the membrane is to be function under water-gas shift conditions.

A CO₂ selective membrane must function not only at high temperature, but also in the presence of all the reactants and contaminants likely to be present in coal-derived fuel gas, including water, CO, CH₄, COS, and H₂S. A study has been undertaken which examines the effects of some of these gases on SILMs.

Experimental

Porous films 25mm in diameter and approximately 152µm in thickness of amphoteric nylon-6,6 (Biodyne[®]A, Pall Corporation) or polysulfone (Tuffryn[®], Pall Corporation) (PSF) were used as supports for the ionic liquid membranes. These substrates have 75-85% void volume with nominal pore sizes of 0.2µm. The supported ionic liquid membranes were made by placing supports in a container and depositing ionic liquid on top of the membrane with a pipette. Enough ionic liquid was added to completely cover the surface of the substrate, and the membrane was allowed to absorb the ionic liquid for at least eight hours. The SILMs were then removed from the container and excess ionic liquid was removed by blotting. Finished membranes were placed on the permeate side of a Millipore[®] filter holder and a polymer

substrate identical to the one used to prepare the membrane was placed against the membrane on the feed side to reduce mechanical stress. The active sample area for the holder is 2.2 cm².

Steady state performance measurements were made in a flow system in which the permeate and retentate gas compositions were measured using a HP 5890 gas chromatograph with twin TCD detectors and Alltech Hayesep D 100/120 packed columns. Entering gas flows were controlled with rotameters and exiting flows were measured with a digital, bubble flow meter. Temperature was measured by a Type K thermocouple in contact with the surface of the testing cell and controlled using a Lindberg/Blue M tube furnace with integrated PID controller. Feed rate to the sample cell was 2-7 ml/min. Feed gases were purchased premixed and varied according to the experiment: CO₂ (2.00%), CH₄ (2.50%), and argon (balance) with a feed rate of 2 ml/min; CO₂ (19.95%), H₂ (20.01%), H₂S (0.888%) and argon (balance) with a feed rate of 7 ml/min; CO₂ (20.00%), H₂ (19.90%), CO (5.00%), and argon (balance) with a feed rate of 7 ml/min; and CO₂ (19.97%), H₂ (20.02%), H₂O (97ppm) and argon (balance) with a feed rate of 7 ml/min. A sweep of argon (99.999%) was passed over the opposing (permeate) membrane face at a flow of 6-10 ml/min. The total pressure was approximately 108 kPa for the feed and the permeate pressure was less than 105 kPa. After introduction of a feed, the system was allowed to reach steady state and data were then recorded for approximately 4 hours before ramping to the next temperature. Temperature changes were carried out at a rate of 1°C/min for a temperature difference equal to or less than 20°C and 1°C/ 2 min for temperature differences greater than 20°C.

The ionic liquid tested, 1-n-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([HMIM][Tf₂N]), was synthesized by the Brennecke research group at the University of Notre Dame using standard procedures (3,4). Impurity levels of halide (Br⁻) were measured using an Oakton Ion 510 meter with Cole-Palmer Ion Specific Probes (27502-05) and were less than 10 ppm.

Results and Discussion

Membranes consisting of the ionic liquid [HMIM][Tf₂N] supported on porous nylon-6,6 had CO₂ permeabilities increasing from 498 to 1165 Barrer over the temperature range 37-300°C with a reasonably strong Arrhenius dependency ($R^2=0.9581$). The CO₂/H₂ selectivity, as determined by the ratio of the permeabilities of the two gases when both are simultaneously diffusing through the membrane, varied from 9.0 to 1.3 over the same temperature range and showed a somewhat stronger Arrhenius correlation ($R^2=0.9687$). The data are shown in Figure 1.

In the presence of 5.00% CO, membranes consisting of the ionic liquid [HMIM][Tf₂N] supported on porous nylon-6,6 had CO₂/H₂ selectivity decreasing from 7.6 to 2.4 over the temperature range 37-125°C with a strong Arrhenius dependency ($R^2=0.9995$). The data are shown in Figure 2. The CO concentration is between that of shifted and unshifted fuel gas. Based on these results it may be suggested that the 1% CO typical of fully shifted fuel gas would have little or no effect on the membrane performance, but further tests will be necessary to determine whether or not the higher concentrations found in unshifted fuel gas will present more of a problem.

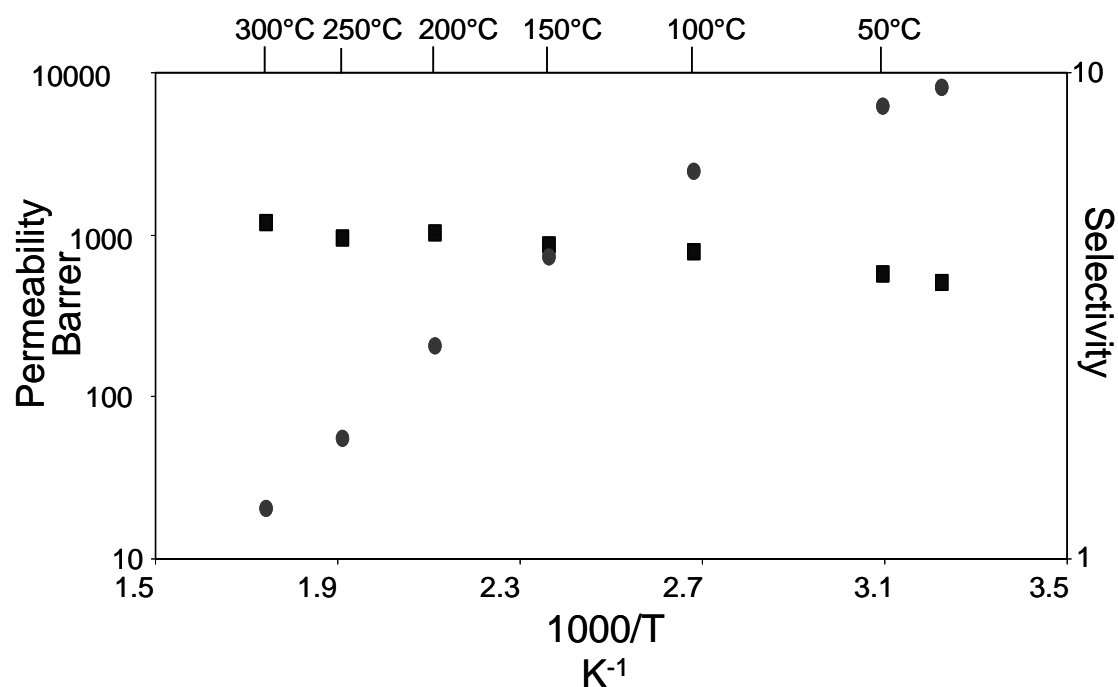


Figure 1. CO₂ permeability (■) and CO₂/H₂ selectivity (●) of a membrane composed of the ionic liquid [HMIM][Tf2N] supported on porous nylon-6,6 as a function of temperature.

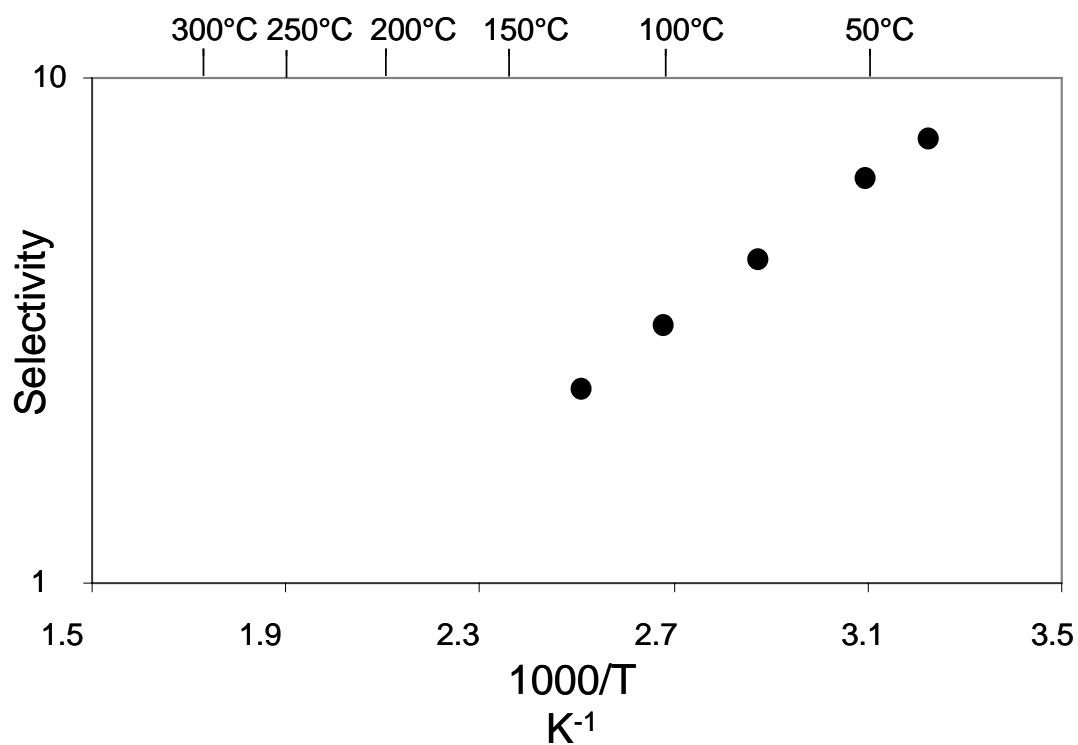


Figure 2. CO₂/H₂ selectivity (●) of a membrane composed of the ionic liquid [HMIM][Tf2N] supported on porous nylon-6,6 as a function of temperature in the presence of 5% CO.

In the presence of 0.89% H₂S, membranes consisting of the ionic liquid [HMIM][Tf2N] supported on porous nylon-6,6 had CO₂ permeabilities increasing from 400 to 1030 Barrer over the temperature range 37-200°C with a strong Arrhenius dependency ($R^2=0.969$). The CO₂/H₂ selectivity decreased from 7.2 to 1.1 over the same temperature range and showed a very strong Arrhenius correlation ($R^2=0.999$). The data are shown in Figure 3. At 37°C, both CO₂ permeability and CO₂/H₂ selectivity are reduced by about 20 percent from the values observed in the absence of contaminants. The change is appreciable, but not a serious degradation in the effectiveness of the membrane. It should also be noted that 0.89% H₂S is a higher concentration than would be encountered in most gasification schemes since a sulfur removal step would most likely occur before the CO₂ membrane.

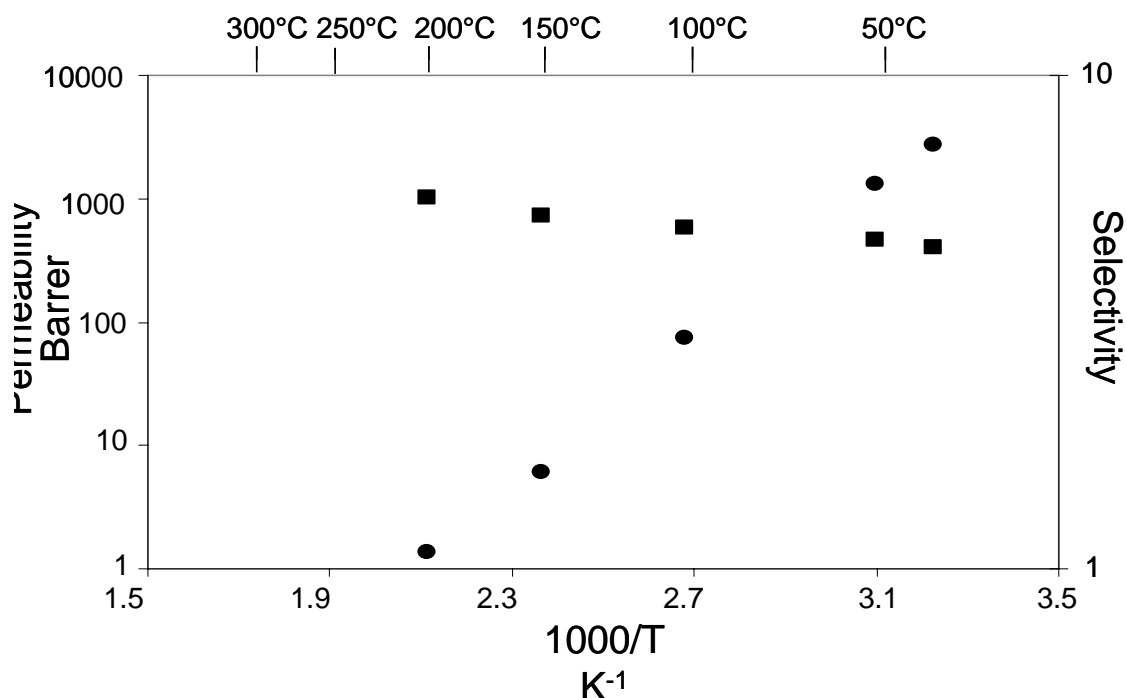


Figure 3. CO₂ permeability (■) and CO₂/H₂ selectivity (●) of a membrane composed of the ionic liquid [HMIM][Tf2N] supported on porous nylon-6,6 as a function of temperature in the presence of 0.89% H₂S.

Information about the possible role of another fuel gas component may be gleaned from the results of experiments evaluating the applicability of the membrane to natural gas sweetening. The membranes had been tested for CO₂/CH₄ separation performance. Comparing the CO₂ permeabilities measured in the presence of 2.5% CH₄ to the permeabilities in the absence of methane, an ideal selectivity may be calculated. As with H₂S, the presence of methane results in appreciable but not critical reduction in both permeability and selectivity.

Table 1. CO₂ permeability of a membrane composed of the ionic liquid [HMIM][Tf2N] supported on porous nylon-6,6 in the presence of 2.5% CH₄.

	37°C	60°C
CO ₂ Permeability (Barrer)	378	416
CO ₂ /H ₂ Selectivity (Ideal)	6.8	4.3

Membranes consisting of the ionic liquid [HMIM][Tf2N] supported on porous PSF had been previously studied. The support was abandoned because it lacked the thermal stability required to perform at water-gas shift reaction conditions. Membranes fabricated using the PSF support showed higher permeability and slightly lower selectivity than those which employ the nylon-6,6 support owing to the lesser contribution of gas diffusion through the polymer rather than the ionic liquid in the nylon-6,6 membrane. The support should have little bearing on contaminant effects since those will be confined to alternation of the ionic liquid rather than the support. A comparison of the performance of this membrane in the presence and absence of 97 ppm water is shown in Table 2. The changes in performance are small, leading to the conclusion that at low concentrations water does not play a significant role in membrane performance.

Table 2. CO₂ permeability and CO₂/H₂ selectivity of a membrane composed of the ionic liquid [HMIM][Tf2N] supported on porous PSF under dry conditions and in the presence of 97ppm H₂O.

	Dry		Wet	
	37	100	37	100
Temperature (°C)				
CO ₂ Permeability (Barrer)	840	1040	742	1060
CO ₂ /H ₂ Selectivity	7.0	3.0	6.8	2.9

Examining the results above, it is possible to suggest that in the short term common fuel gas contaminants will not seriously deteriorate the performance of non-complexing ionic liquid membranes. Additional tests are required to determine what the long term effect of these contaminants may be, to examine how performance changes in the presence of multiple contaminants, to conduct investigations under realistic pressures, and to explore the effect of contaminants on chemically complexing ionic liquids.

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Disclaimer

Reference in this report to any specific commercial product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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