Continued Advancement of Supported Liquid Membranes for Carbon Dioxide Control in Extravehicular Activity Applications

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The Development of a new, robust, portable life support system (PLSS) is currently a high NASA priority in order to support longer and safer extravehicular activity (EVA) missions that will be necessary as space travel extends to near-Earth asteroids and eventually Mars. One of the critical PLSS functions is maintaining the carbon dioxide (CO_2) concentration in the suit at acceptable levels. The Metal Oxide (MetOx) canister has a finite CO_2 adsorption capacity and therefore in order to extend mission times, the unit would have to be larger and heavier, which is undesirable; therefore new CO_2 control technologies must be developed. While recent work has centered on the use of alternating sorbent beds that can be regenerated during the EVA, this strategy increases the system complexity and power consumption. A simpler approach is to use a membrane that vents CO_2 to space but retains oxygen(O_2). A membrane has many advantages over current technology: it is a continuous system with no theoretical capacity limit, it requires no consumables, and it requires no hardware for switching beds between absorption and regeneration. Conventional gas separation membranes do not have adequate selectivity for use in the PLSS, but the required performance could be obtained with a supported liquid membrane (SLM), which consists of a microporous film filled with a liquid that selectively reacts with CO_2 over oxygen (O_2). In a recently completed Phase II Small Business Innovative Research project, Reaction Systems developed a new reactive liquid that has effectively zero vapor pressure, making it an ideal candidate for use in an SLM. Results obtained with the SLM in a flat sheet configuration with representative pressures of CO_2, O_2, and water (H_2O) have shown that the CO_2 permeation rate and CO_2/O_2 selectivity requirements have been met. In addition, the SLM vents moisture to space very effectively. The SLM has also been prepared and tested in a hollow fiber form, which will be necessary to meet size requirements in the PLSS. In initial tests, the required CO_2 permeance values have been obtained, while the current CO_2/O_2 selectivity values are somewhat lower than needed. However, the performance of the SLM is a strong function of the method used to impregnate the sorbent in the hollow fiber walls and rapid progress is being made in that area.

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Nomenclature

°C	=	degrees Celsius
AP-Mim	=	1-(3-aminopropyl)-3-methylimidazolium
atm	=	atmospheres
Btu/h	=	British thermal units per hour
cc	=	cubic centimeters
cm^2	=	square centimeters
cm-Hg	=	centimeters of mercury
CO_2	=	carbon dioxide
EVA	=	extravehicular activity
ft^3	=	cubic feet
GC	=	gas chromatograph
g/h	=	grams per hour
H_2O	=	water
h-PTFE	=	hydrophobic polytetrafluorethyleen
IL	=	ionic liquid
L	=	liter
kDa	=	kilodalton
MetOx	=	Metal Oxide
MHz	=	megahertz
m^2	=	square meters
m^3	=	cubic meters
mm	=	millimeters
mmHg	=	millimeters of mercury
mtorr	=	millitorr
NMR	=	nuclear magnetic resonance
O_2	=	oxygen
PLSS	=	portable life support system
PTFE	=	polytetrafluoroethylene
P_{tot}	=	total pressure
RC	=	regenerated cellulose
RCA	=	Rapid Cycle Amine
RH	=	relative humidity
s	=	second
scc	=	standard cubic centimeters
SLM	=	supported liquid membrane
slpm	=	standard liters per minute
T	=	temperature
μL	=	microliter
μm	=	micrometers

I. Introduction

The development of a new, robust, portable life support system (PLSS) is currently a high priority for NASA in order to support longer and safer extravehicular activity (EVA) missions as it carries out more and more difficult missions, including flights to near-Earth asteroids, the Moon, and eventually Mars.[1,2]. One of the critical PLSS functions is maintaining the carbon dioxide (CO_2) concentration in the suit at acceptable levels. New space suits must be able to accommodate longer EVAs without increasing the size or weight of the portable life support system (PLSS). The rate of CO_2 generation varies with the metabolic rate of the crew member. Recent studies of CO_2 control technology have been carried out in which the CO_2 injection rates were varied to match simulated metabolic rates. The different CO_2 production rates were normalized per metabolic rate and the average CO_2 generation rate over the course of an EVA was estimated to be 93 g/h[3,4]. A study of the physiological effects of CO_2 exposure carried out in 1993 resulted in the recommendation that CO_2 levels be limited during EVA to 3.8 mmHg for nominal exertion and 7.6 mmHg for heavy exertion.[5] More recently, the cognitive effects of CO_2 exposure on decision making were studied and it was found that CO_2 levels as low as 0.8 mmHg could cause a measureable reduction in decision making

capability, while levels above 1.5 mmHg could result in a more severe effects[6]. Based on the most recent findings, NASA has a current interest in reducing the maximum allowable CO_2 concentration in the suit from 7.6 mmHg to 2.8 mmHg. Thus, for EVA operation to be safely carried out, the CO_2 control system must be sized to handle at least average production rates for the duration of the EVA, which likely will last in excess of eight hours.

Currently, the Metal Oxide (MetOx) system is being used for CO_2 control during EVA. The MetOx employs a metal oxide sorbent, which reacts with CO_2 at low temperatures to produce the metal carbonate. Although it has worked well, it has a finite CO_2 adsorption capacity. Consequently, the unit would have to be larger and heavier to extend EVA times. Therefore, new CO_2 control technologies must be developed to meet mission objectives without increasing the size of the PLSS. While the Rapid Cycle Amine (RCA) system in which the sorbent can be regenerated during the EVA has shown good promise for the next generation technology, the strategy increases the system complexity and power consumption. A simpler approach is to use a membrane that vents CO_2 to space while retaining oxygen (O_2).

An effective membrane system would have several significant advantages over the other methods of CO_2 control. It would be a continuous system with no limit on the amount of CO_2 removed during a single mission. It could also be very simple and not require any moving parts and should have low power demand. In addition unlike the RCA, the O_2 losses with a membrane are independent of metabolic output. However, the CO_2 flux through the membrane scales with CO_2 concentration, which will help prevent crew exposure to high CO_2 concentrations during periods of increased CO_2 generation.

The successful application of a membrane requires that some difficult challenges be met. First, the permeation rate of CO_2 through the membrane must be high enough that a reasonably sized membrane module can control an average metabolic CO_2 generation rate. In addition, the membrane must have good selectivity for CO_2 over O_2 to prevent unacceptably high O_2 losses. Recent estimates suggest that in order to control the average CO_2 production rate the CO_2 permeance would need to be 1.04E-4 scc/(cm^2 s cmHg), where scc is standard cubic centimeters of CO_2, cm^2 is the surface area of the membrane, s is time in seconds and cmHg is the differential CO_2 partial pressure across the membrane[3,4]. If we assume that the low pressure side of the membrane is exposed to space vacuum, then cmHg is the partial pressure of CO_2 on the crew side of the suit. Finally, in order to maintain O_2 losses no greater than the existing leak rates of the suit, 4.2 g/h [7], the CO_2/O_2 selectivity must be at least 1180.

Unfortunately, conventional polymeric gas separation membranes, which rely on the differences in solubility and diffusional properties between gas molecules, have not been able to meet the requirements outlined above because of the inherent trade-off between selectivity and permeability. For example, poly(dimethyl)siloxane has adequate CO_2 permeability but has a CO_2/O_2 selectivity of only about five.

Another approach is to take advantage of the difference in chemical properties of CO_2 and O_2 by immobilizing a reacting compound into the membrane to produce a supported liquid membrane (SLM). In this application, the immobilized liquid would form a metastable complex with CO_2 on the crew side of the membrane. Because CO_2 is an acidic compound, a basic liquid could be an effective reagent. The complex would then diffuse through the liquid contained in the membrane pores, ultimately reaching the vacuum side of the membrane where the absence of gas phase CO_2 would shift the equilibrium, thereby resulting in the decomposition of the metastable complex, the release of the CO_2, and the regeneration of the sorbent (Figure 1). This process is frequently referred to as facilitated transport. On the other hand, because O_2 does not have acidic properties, it should not react with the liquid, resulting in potentially high CO_2/O_2 selectivity.

The liquid sorbent must meet several criteria to have adequate performance. First, because the membrane operates at constant temperature, the liquid must be fully regenerable by exposure to space vacuum and not require any temperature change to increase capacity. Second, the liquid must have low viscosity so the complex can diffuse quickly from one side of the membrane to the other. Third, and perhaps most important, the liquid reactant must have effectively zero vapor pressure so it is not lost by evaporation to space.

Amines have been shown to possess excellent reversible CO_2 absorption capacity. Amines are commonly used to absorb CO_2 out of industrial gas streams and are currently being evaluated in a cycling bed configuration to control CO_2 in EVA. The affinity of an amine for CO_2 depends on
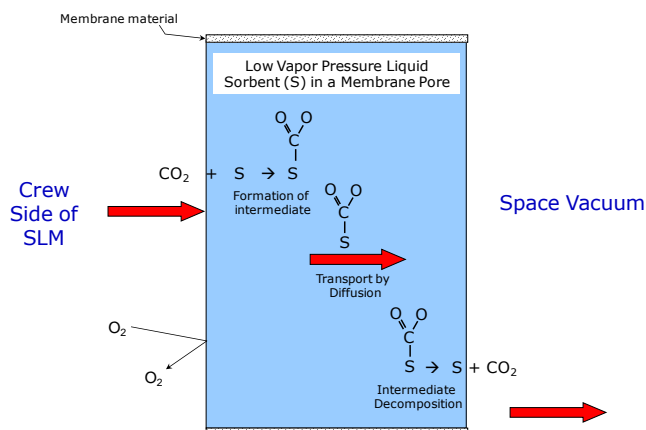
**Figure 1. Schematic of facilitated CO_2 transport within a membrane pore.**

its structure. Primary amines bind CO_2 strongly, usually requiring that the sorbent be heated for regeneration. On the other hand, secondary and tertiary amines do not bind CO_2 as strongly and therefore some can be regenerated by simply reducing pressure, a requirement for use in a membrane. Unfortunately, the vapor pressures of conventional amines are too high to prevent loss when exposed to space vacuum, and therefore must be modified. In the RCA system, the amines are anchored to an ion exchange bead; however, this approach would not suitable for use in a membrane.

Another potentially effective way to reduce the amine vapor pressure and retain it in a liquid form is to incorporate the amine functional group into an ionic liquid. Ionic liquids are well-suited for this application because they have effectively zero vapor pressure and are not lost to space. Recent work has shown that ionic liquids containing all three types of amines can be synthesized and then used in SLMs that have good CO_2 permeance and improved CO_2/O_2 selectivities relative to polymeric membranes[3,4]. The more recent work demonstrated that an SLM containing a primary amine functionalized ionic liquid sorbent in a flat sheet configuration met the CO_2 permeance and CO_2/O_2 selectivity requirements established above.[4] In this paper, we present additional results of the SLM after it has been converted into a modular, hollow fiber form that will be necessary to meet size requirements in the PLSS.

II.   Experimental Methods

A. Compound Synthesis and Characterization

The sorbents used in this work consist of ionic liquids functionalized with an amine group. Ionic liquids are relatively low molecular weight hydrocarbon-based compounds that can have low viscosity and effectively zero vapor pressure. Thus, they are excellent choices for use in a SLM where one side will be exposed to space vacuum. In this work, we discuss results obtained with one containing a primary amine function group, 1-(3-aminopropyl)-3-methylimidazolium or AP-Mim (Figure 2). Once the sorbent was prepared, it was characterized by nuclear magnetic resonance (NMR) spectroscopy to verify its chemical structure. The methods used to synthesize and characterize this compound were described previously[3,4]
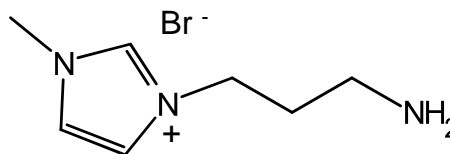
Figure 2. Structure of the AP-Mim functionalized ionic liquid sorbent.

B. Membrane   Permeation   Rate   Measurements

1. Flat Sheet Membrane Impregnation

The methods used to prepare the membranes were described in detail previously[3],[4]. Briefly the SLMs were prepared by impregnating a layered porous membrane material with the ionic liquid sorbent. The layer on the high pressure side was hydrophilic, and easily wetted by the ionic liquid sorbent while the layer on the low pressure side was hydrophobic and resisted wetting by the sorbent. This configuration effectively contained the ionic liquid sorbent inside the hydrophilic layer. The impregnation was done by contacting the membrane with the ionic liquid sorbent and cycling the membrane between vacuum (50 mtorr) and atmospheric pressure to remove air from the pores.

The membrane housing was also described previously[3,4] and consisted of two aluminum flanges with flow passages and O-ring seals machined into each. The flange on the low pressure side was connected to a vacuum pump to simulate the vacuum of space. Two different top flange configurations were used. In single gas tests, one port on the top flange was opened to either pure CO_2 or O_2 and the permeance of each was measured by monitoring the rate at which the pressure decreased on that side of the membrane. In mixed gas tests, we used a two-port top flange that circulated the process flow into the housing, over the membrane surface, and then out of the cell housing.
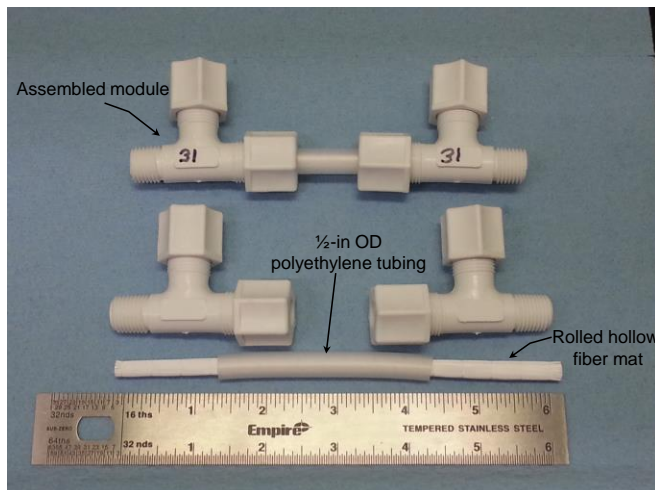
2. Hollow Fiber Module Development

In order to meet size requirements, the SLM must be contained in hollow fibers, which have much greater surface area to volume ratios compared to membranes in a flat sheet configuration. In this configuration, the wall of the hollow fiber will be impregnated with the sorbent and the process flow would be directed through the inside or lumen of the fiber, while the outside of the fiber is exposed to vacuum.

We designed the hollow fiber module so that the potting material sealing the hollow fibers was in contact with a male-NPT polypropylene fitting that would allow good adhesion with the potting material. A photograph showing the individual pieces and the assembled module for this potting configuration is shown in Figure 3. The design for the
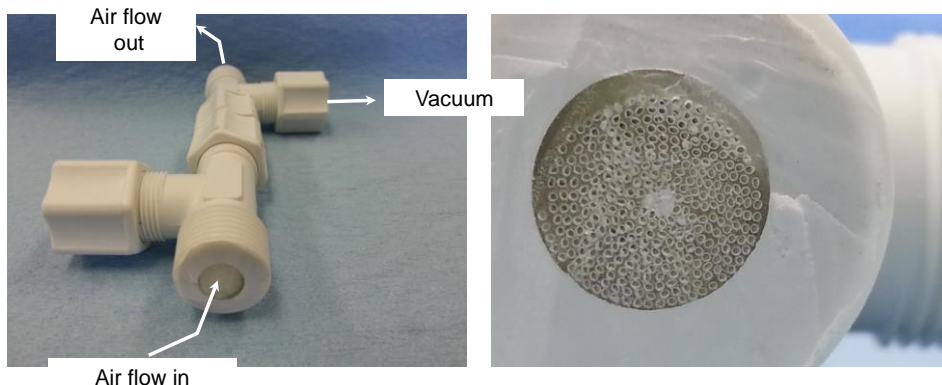
small hollow fiber module uses two polypropylene run-tee fittings (containing two ⅜ inch compression fitting ports and one ¼ inch male-NPT pipe threaded fitting port) connected using a 3 inch long piece of ⅜ inch polyethylene tubing as the casing for the module and a two part polyurethane as the potting material. The module incorporated a rolled-up hollow fiber mat 2.5 inches x 6.25 inches (fiber length).

Figure 4 shows photographs of a completed module. The photograph on the left side shows that the process flow goes through the fiber lumen (inside of the fiber) and that the low pressure is applied to the shell side of the fiber bundle. Thus, the separation of CO_2 from O_2 is accomplished in the walls of the fiber. The photograph on the right side shows the ends of the fibers after the end of the potted section has been sliced off. The photograph shows the open fibers completely sealed by the urethane to the outer wall of the module. The integrity of the seal is important and tests to verify the seal quality are described below.

Figure 3. Photograph of the hollow fiber module.

After the potting process was complete and the urethane had set, we carried out tests with water to verify the integrity of the seal around the edge of the fibers and inner wall of the module housing. To conduct the test, we connected one of the side ports on the module to a water tap and pressure gage and allowed water to flow through the module. The water pressure was set to 20 psi to prevent exceeding the burst pressure of the fiber (45 psi). We then closed off the exit port and monitored the pressure with the gage. Since water will not penetrate the fibers, the outer shell is sealed in this configuration and we simply observed the ends of the module to verify that water was not leaking through voids in the urethane layer at the end of the module.

Figure 4. Photograph of the assembled module

3. Permeation Test Rigs

Gas permeation tests were conducted in two types of test rigs, one for mixed gas tests and one for single gas tests and each has been described previously [3,4]. The mixed gas test rig system included a flow loop connected to a flow-through test cell or hollow fiber module, an oil-less scroll pump to evacuate the loop, a gas manifold to charge the loop with representative pressures of O_2 and CO_2, a diaphragm pump to circulate the mixture, analytical instrumentation to measure the changes in CO_2 and H_2O concentrations, and an 8-liter reservoir. Water was introduced with a Chemyx Fusion 100 syringe pump so that water could be added on a continual basis at a representative rate. A Vaisala relative humidity sensor was used to monitor the relative humidity (RH) in the mixed gas and the CO_2 concentration in the gas mixture was monitored with a gas chromatograph (GC). Finally, the system used LabVIEW software and National Instruments hardware for control and data acquisition.

To conduct gas permeation tests, the system was first evacuated to less than 50 mtorr and then the loop and reservoir were charged to 0.4 atm with a mixture consisting of between 0.75 and 2.5% CO_2 in O_2, which corresponded to CO_2 partial pressure from 1.9 mmHg up to 7.6 mmHg. The circulation pump was first started and then the syringe pump was activated, injecting H_2O at a rate of 8.0 μL/h to bring the humidity level up to the desired set point. When the RH reached the desired starting point of about 25%, initial GC analyses were obtained and then the process flow

was switched from the membrane bypass loop to the flow-through cell, exposing the process flow to the SLM. Measurements of CO_2 concentration in the loop were made through the course of the experiment and used to calculate CO_2 permeance. The test was stopped when the CO_2 concentration dropped to approximately half the original starting concentration. The O_2 permeance was calculated by monitoring total pressure and correcting for the loss of humidity and losses from the GC sampling.

The single gas test rig contains high and low pressure manifolds separated by the SLM. To conduct a test, the high pressure manifold containing a 1 liter reservoir was first evacuated and then charged with the desired pressure of the test compound. The low pressure manifold, which is connected to the low pressure side of the SLM and contains a 150 cc reservoir was also evacuated and then isolated from the vacuum pump. When pressures in each manifold were stable, a valve opening the high pressure reservoir to the SLM was opened. The rate at which the test compound permeated through the membrane was monitored by recording the pressure decrease on the high pressure side and the pressure rise on the low pressure side of the SLM.

III.   Results

C. Mixed Gas Test Results with Constant Water Addition Rate

The performance of the membrane in the flat sheet configuration met the permeance and selectivity objectives outlined earlier. Test results with this membrane, which were presented previously[4] are included in Figure 5 and Figure 6. In Figure 5, the CO_2 concentration and relative humidity (RH) are plotted against the test or run time. From time zero up until 118 minutes the flow loop was isolated from the membrane and during this period, the CO_2 concentration was stable and the RH increased due to the constant moisture addition from the syringe pump. After the flow loop was exposed to the membrane, the RH dropped rapidly and reached a steady-state concentration of about 2% to 3%. In addition, the figure shows that the CO_2 concentration dropped from 1.21% to 0.58% over the duration of the run, resulting in a permeance of 1.1E-4 scc/(cm^2 s cmHg). This value meets the performance goal established earlier. Therefore once the SLM is converted into a hollow

Figure 5. CO_2 concentration (blue diamonds) and moisture (red line) as a function of time with the AP-Mim SLM.

fiber form, a unit sized to control the average CO_2 production from a crew member could be contained in a module that is no larger than 0.25 ft^3.

The total pressure measurement for this test is shown in Figure 6. In this case, there was very little pressure drop after the loop was exposed to the membrane. Once again, immediately after the loop was opened to the membrane, there was a noticeable pressure drop, which was due primarily to the loss of water vapor, as shown in Figure 5. However, after that change, the pressure remained constant. For example, Figure 6 shows that the pressure was 0.3949 atm at 180 minutes; however, at 300 minutes or 2 hours later, the pressure had only dropped to 0.3929 atm. This difference is very small and is right at the resolution of our pressure transducer. Therefore, we estimated that the permeance obtained during this run was less than 3E-7 scc/(cm^2 s cmHg). Combining this value with the CO_2 permeance
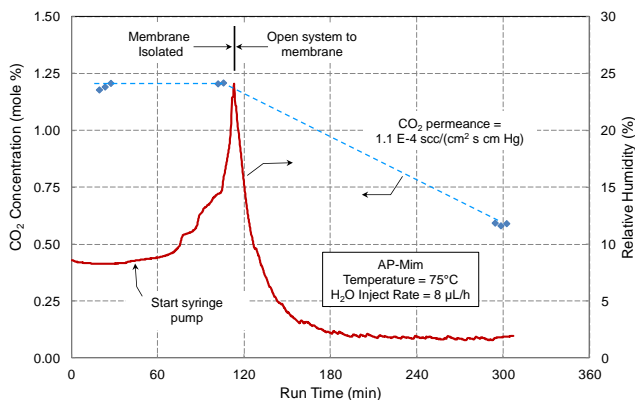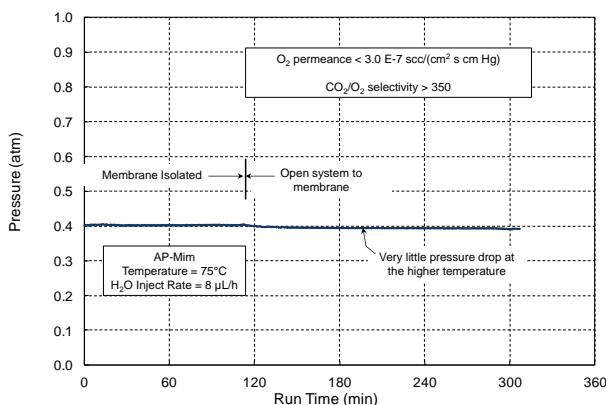

Figure 6. Total pressure as a function of time with the AP-Mim SLM at 75°C.

reported above results in a CO_2/O_2 selectivity of greater than 350.

The results presented in Figure 5 and Figure 6 demonstrated that we have reached the required value for permeance and are also approaching the CO_2/O_2 selectivity target. Although a selectivity of greater than 350 is encouraging, the O_2 permeance was less than our detection limit in this test rig. Therefore, we repeated the O_2 permeance test in the single-gas test rig, which for O_2 permeance has a lower detection limit than the mixed gas test rig.

The results of the static tests for O_2 with the modified AP-Mim are shown in Figure 7. The figure shows that the pressure in the upper reservoir decreased from 0.3960 atm to 0.3955 atm over a period of 50 minutes. Likewise, the pressure in the lower reservoir, which has only 1/6 the volume of the large reservoir, increased from 0.002 atm to 0.004 atm over the same time period. The data resulted in a calculated O_2 permeance of 7.6E-8 scc/(cm^2 s cmHg) and using this value along with the CO_2 permeance reported in Figure 5, we calculated that CO_2/O_2 selectivity of this ionic liquid at a temperature of 75°C is 1450. This value is greater than our initial target value of 1180; therefore, these results show that we have achieved the target CO_2 permeation and CO_2/O_2 selectivity requirements that we established. These are very positive results and demonstrate the potential feasibility of using a supported liquid membrane for CO_2 control.
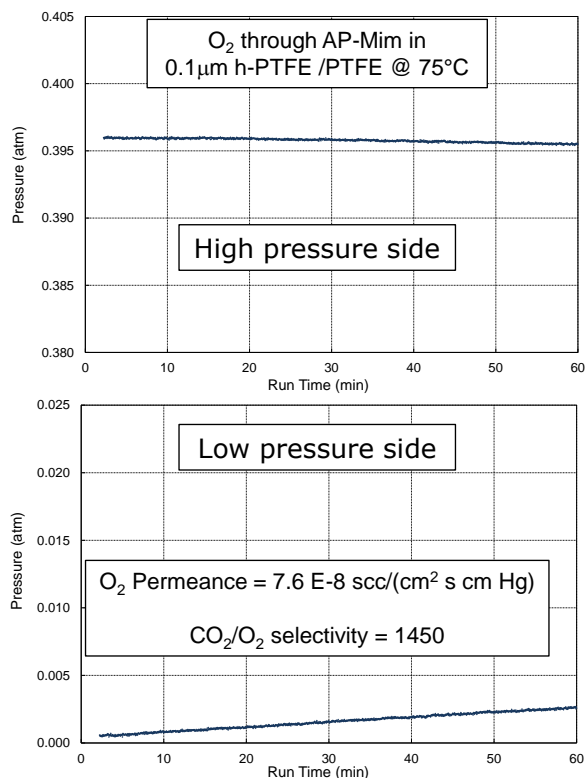

Figure 7. O_2 permeation results obtained for AP-Mim in the layered membrane at 75°C.

D. Tests with the Hollow Fiber Modules

In order to meet the volume requirements for a CO_2 control system in the PLSS, the SLM membrane must be incorporated into a hollow fiber module form. As pointed out above, we achieved the required performance in a two layered membrane system consisting of a hydrophilic membrane on the high pressure side and a hydrophobic membrane on the low pressure side. The functionalized ionic liquid was contained in the hydrophilic membrane and the presence of the hydrophobic membrane on the low pressure side kept the liquid from being forced out the membrane. Therefore, in order to achieve the same performance in the hollow fiber form, an analogous layered hollow fiber was needed.

Figure 8 illustrates the layered membrane in both the flat sheet and hollow fiber configurations. The left side shows the layered membrane that produced the results described above On the right side we have shown a desired, analogous configuration in a hollow fiber form. In this configuration, the inside of the fiber wall contains the ionic liquid, while a hydrophobic layer on the outside of the wall prevents the liquid from being forced out to the shell side of the membrane. The process flow is directed through the center of the hollow fiber (or lumen) while the shell side is
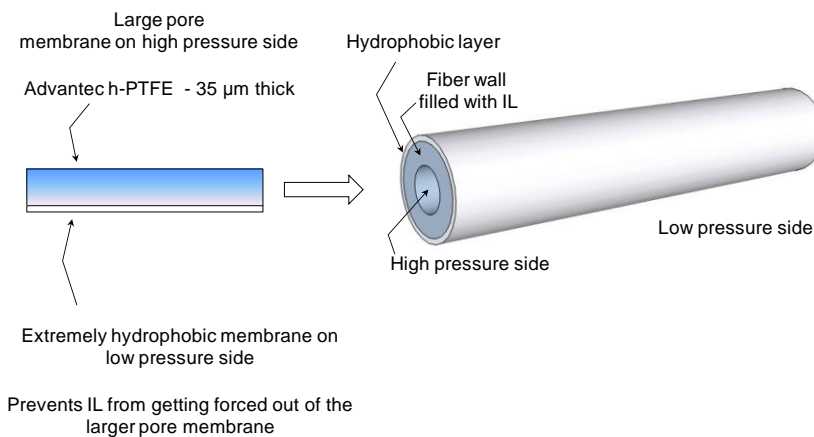
Figure 8. Two layer flat sheet membrane (left side) and the analogous two layer form in a hollow fiber (right side).

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exposed to vacuum. Thus, as the CO_2 contained in the air flows through the fiber, it is absorbed by the functionalized ionic liquid in the wall and then diffuses to the outside of the fiber where it desorbs into the vacuum.

Several types of fibers were used in this work: one fiber was used that did not contain a barrier layer on the outside of the fiber, while two types of hollow fibers contained a thin layer on the outside of the wall to prevent IL from being forced out of the fiber. Result obtained with these fibers are presented in the following sections.

1. Mixed Gas Tests with Polypropylene Fibers with No Polymerized Layer Test Rig

Several tests were carried out in polypropylene (PP) hollow fibers that did not contain a resistive barrier layer. This was done for two reasons. One reason was to determine the maximum permeance that is potentially available from these fibers when no additional layer was present. The second reason was to determine if it is possible to conduct tests with non-polymerized fibers without having the ionic liquid forced out of the fibers from the pressure differential. In this case, the fibers were impregnated with a mixture of 74% ionic liquid sorbent, 13% ethanol (EtOH), and 13% H_2O. This ratio was found to reduce the viscosity and surface tension of the ionic liquid so that it readily wet the fiber walls and filled the pores effectively. We used four injections and obtained a loading of 0.878 g IL in the hollow fiber after the EtOH and H_2O solvents were removed by evacuation.

The results of this test are shown in **Figure 9**. The CO_2 permeance is 2.81E-5 scc/(cm^2 s cm Hg), which is about a factor of four lower than that needed to module size requirements outlined above. The figure also shows that the O_2 permeance is 2.81E-5 scc/(cm^2 s cm Hg) resulting in a CO_2/O_2 selectivity of 400. Although the permeance and CO_2 selectivity values are lower than were obtained with the flat sheet, they nonetheless are very positive because they show that we have been successful in transitioning the SLM technology from the flat sheet to a hollow fiber module form.

The absence of the polymer layer did not produce a rapid loss of IL from the fiber. However, the sorbent was detected in the shell side of the module after it was removed from the test rig. Thus, in the next tests, these fibers were coated with a polymeric layer to prevent IL loss. The coating process is described in the following section.
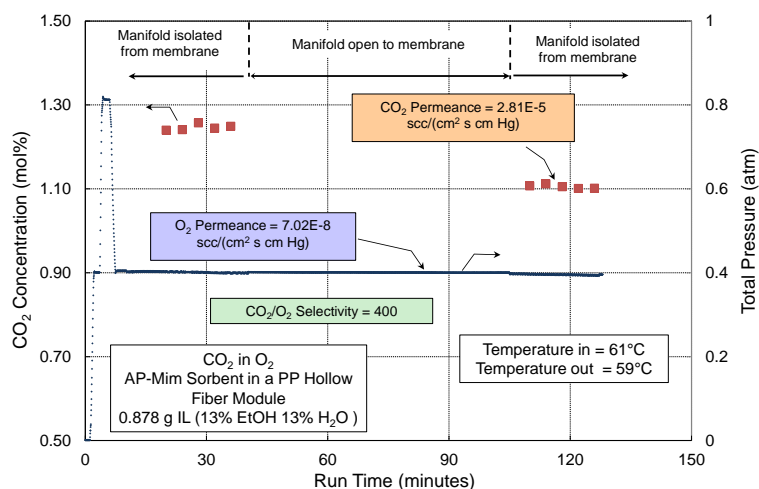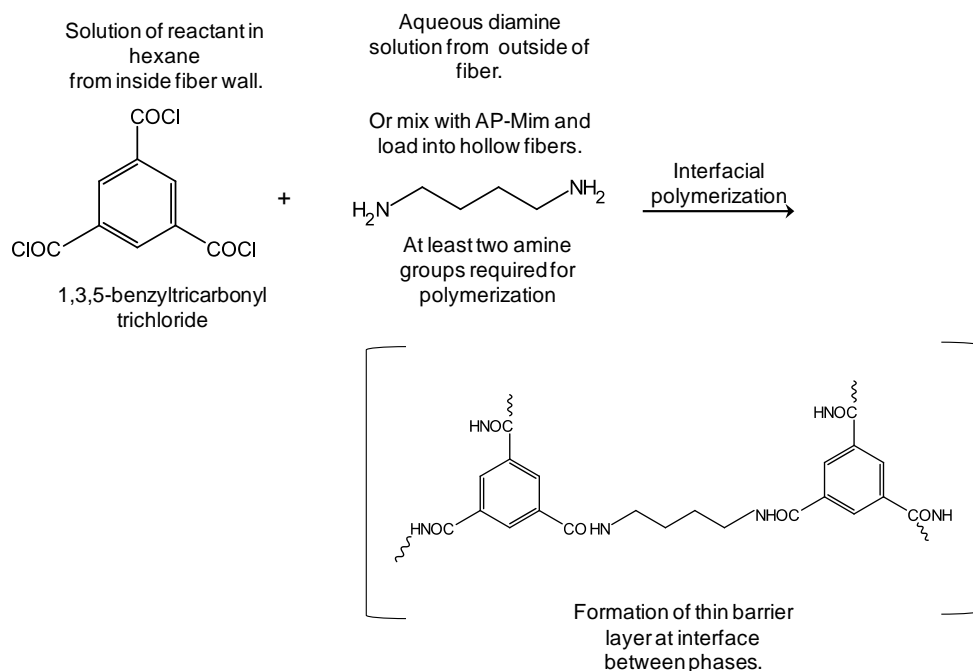

Figure 9. CO_2 concentration and total pressure in the mixed gas tests with CO_2 in O_2 using polypropylene fibers without a polymer layer.

2. Addition of an IL Barrier to the Outer Skin of the Hollow Fiber

We used a method that had been published previously to add the polymer layer to the outside of the fiber and generate a layered structure in-situ[8]. The process is based on an interfacial the polymerization reaction that occurs between an acid chloride and a compound containing at least two primary amine groups. An example of such a reaction is shown in Figure 10. In this case, 1,3,5-benzyltricarbonyl trichloride reacts with butyldiamine and generates a polyamide. The 1,3,5-benzyltricarbonyl is contained in an organic phase such as hexane while the diamine is contained in an aqueous phase. These solutions are not miscible and thus when they are brought into contact, the reaction can only occur at the interface between the solutions.

The method to incorporate the polymer into the hollow fiber is illustrated Figure 11. The figure on the left shows a cross section of an empty hollow fiber. We first flowed the aqueous solution containing the butyldiamine through the shell side of the module. The fibers are not easily wetted with water so this solution will not penetrate into the wall of the fiber. Once the shell side was filled, we then flowed the hexane solution containing the 1,3,5-benzyltricarbonyl trichloride through the inside of the fibers. These fibers are easily wetted by organic solvents such as hexane and therefore the solution will fill the fibers with reactant (center illustration). However, the two solutions will contact
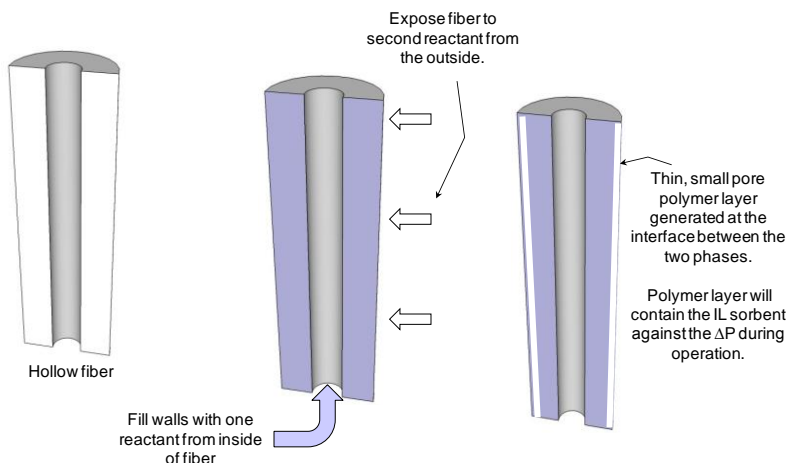
Solution of reactant in hexane from inside fiber wall.

COCl

ClOC   COCl

1,3,5-benzyltricarbonyl trichloride

+

Aqueous diamine solution from outside of fiber.

Or mix with AP-Mim and load into hollow fibers.

H_2N NH_2

At least two amine groups required for polymerization

Interfacial polymerization →

HNOC   HNOC

HNOC   CO HN   NHCO   CONH

Formation of thin barrier layer at interface between phases.

Figure 10. Polymerization reaction between an acid chloride and a diamine.

each other at the outside edge of the fiber, and as illustrated by the diagram in the right side of **Figure 11**, a polymer layer will form at that location. Moreover, Morgan and Kwolek[8] show that the polymer layer tends to grow into the organic side so it will be formed inside the polymer layer but at the outside edge as shown in the figure.

After preparation a modified hollow fiber module was placed in the mixed gas test rig for CO_2 and O_2 permeance measurements. The results of this test are shown in **Figure 12**. The GC data show that CO_2 is being removing from the circulation loop. Between times of 30 and 90 minutes before the loop contents are exposed to the module, the CO_2 level is stable, and averages 1.24 mole%. At a time of 90 minutes, the circulating flow is then directed through the module and immediately the GC data show that the concentration drops steadily over the next 240 minutes, eventually reaching a concentration of 1.17%. The data were used to calculate a CO_2 permeance of 5.92 E-6 scc/(cm^2-s cm Hg),

which is well below the permeance values needed and obtained with other SLMs. The figure shows that after 90 minutes when the flow was directed through the module, the pressure drops slowly, reaching a value of 0.384 atm at the conclusion of the test, resulting in O_2 permeance of 1.06E-7 scc/(cm2-s cmHg) which results in a selectivity of 56.

Unfortunately, while the interfacial polymerization process showed good promise, we were not able to develop the method to the point that we could consistently achieve the needed CO_2 permeance values. In order to assess if this was due to inconsistent interfacially polymerized (IP) coating thickness, we measured the N_2 permeance of the interfacially

Expose fiber to second reactant from the outside.

Thin, small pore polymer layer generated at the interface between the two phases.

Polymer layer will contain the IL sorbent against the ΔP during operation.

Hollow fiber

Fill walls with one reactant from inside of fiber

Figure 11. Method to add a polymer layer on the shell side using interfacial polymerization.

polymerized (IP) coated fibers before they had been impregnated with the ionic liquid sorbent. The results of N_2 permeance measurements on eight IP-coated modules are shown on the left side of Figure 13 and ranged from a
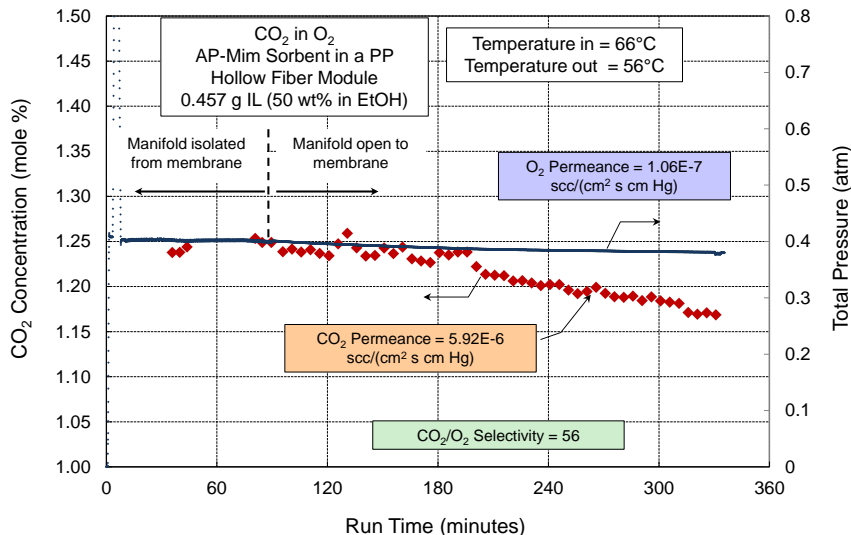
maximum of 1.3E-3 scc/(cm^2 s cm Hg) to a low of 1.1E-7 scc/(cm^2 s cm Hg), which represents a variation by a factor of over 10,000 and underscores the inconsistent results we achieved with the IP-coated SLM modules.
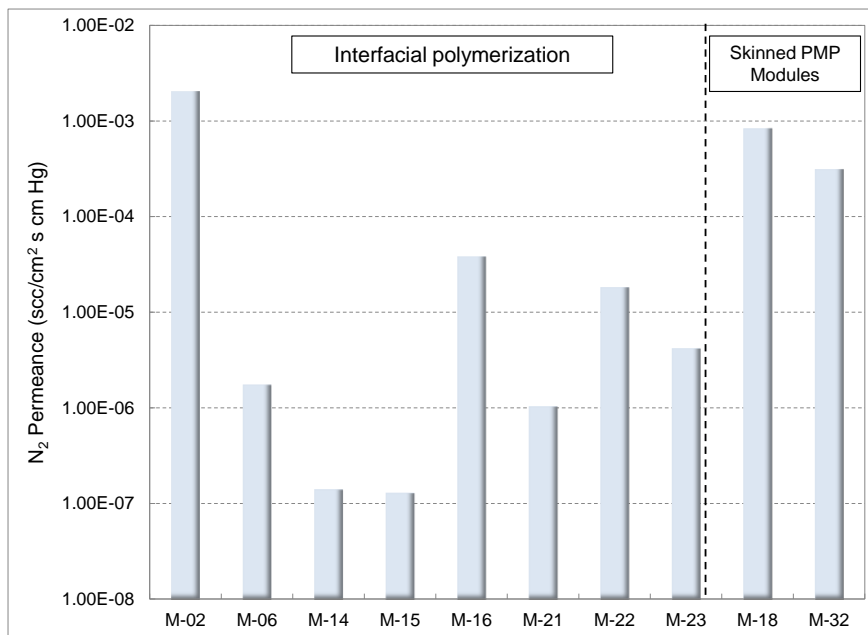
We then identified a commercial source of hollow fibers that contained a high gas permeable dense integral skin on the outside of the fiber. In order to compare the "as-received" fibers to the PP fibers that contained the IP layer, we likewise measured the N_2 permeance of the "as-received" fibers before they had been impregnated with the ionic liquid sorbent. These results are shown on the right side of Figure 13. The figure shows that the N_2

Figure 12. CO_2 concentration and total pressure data in the mixed gas tests with CO_2 in O_2 with the AP-Mim SLM.

permeances for the skinned fibers are higher than all but one of the IP-coated modules and that the values, at least for those two, are relatively consistent. Results of tests with these fibers impregnated with ionic liquid are included in the following section.

3. Tests with a Skinned Hollow Fiber

We carried out several tests with modules containing AP-Mim impregnated in the PMP skinned hollow fibers and the results of four tests are shown in Figure 14, Figure 15, Figure 16, and Figure 17. Figure 14 shows results obtained with a loading of 0.209 g of AP-Mim impregnated into the hollow fiber walls using the mixture of 25% ethanol and 75% IL. The figure shows that prior to exposing the contents of the manifold to the membrane, the total pressure was constant at 0.4 atm and the CO_2 concentration was stable at 1.3%. At this pressure, the CO_2 concentration correlates to a CO_2 partial pressure of 3.9 mm Hg. After the manifold was exposed to the membrane, the total pressure dropped slowly, but at a time of 105 minutes or 65 minutes of membrane exposure, the CO_2 concentration had dropped to 0.87%. By contrast, with the polypropylene membrane the concentration decreased from

Figure 13. N_2 permeation results for the PP modules following the interfacial polymerization process and for two as-received skinned fiber modules.
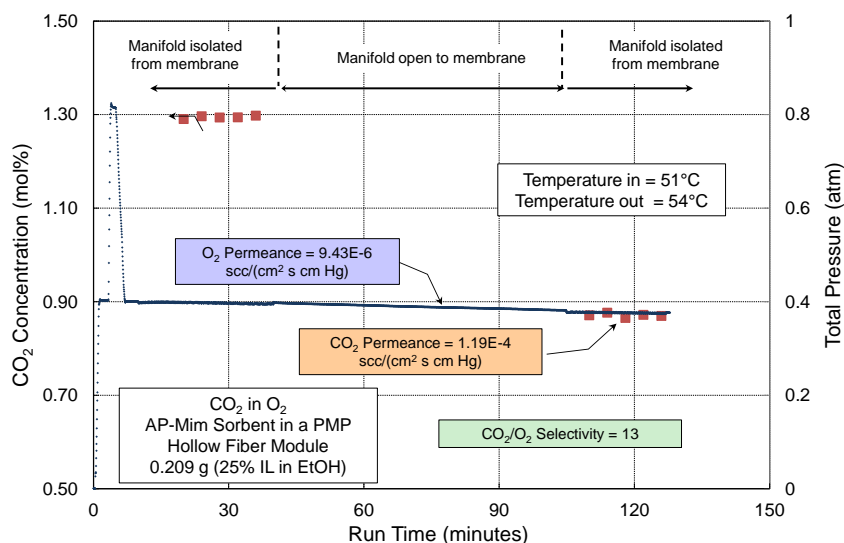
1.25% to 1.11% in over 90 minutes of exposure time (see **Figure 9**). These results were used to calculate a CO_2 permeance of 1.19E-4 scc/(cm² s cm Hg). This result is about 50 times greater than the results obtained with the polypropylene membrane and meets the value required to fit in the PLSS. The figure also shows that the O_2 permeance is 9.43E-6 scc/(cm² s cm Hg), which is higher than the results obtained in the PP fiber modules containing the polymer layer. This increase dropped the CO_2/O_2 selectivity to 13, which is below the value needed to prevent substantial O_2 losses through the membrane.

Figure 15 shows the effect of raising the temperature exiting the module from 54°C to 59°C.

Figure 14. CO_2 concentration and total pressure data in a mixed gas test with a skinned fiber module impregnated with 0.209 g of AP-Mim.

This was accomplished by raising the power on the heater that is attached to the module. The figure shows that increasing the temperature by a small amount has a substantial effect on the CO_2 permeance as it increased the value from 1.19E-4 scc/(cm² s cm Hg) to 1.78E-4 scc/(cm² s cm Hg), which represents a 50% improvement. Not surprisingly, the O_2 permeance also increased; however it only increased by 7% and therefore the increase in temperature also increased the CO_2/O_2 selectivity from 13 to 18.

The results obtained with the skinned module show that while the CO_2 permeance has more than met the required values, the CO_2/O_2 selectivity is well below the values needed to prevent excessive O_2 loss through the membrane. One of the concerns regarding the PMP material was that the material itself had high permeance values for both CO_2 and O_2, which could reduce the membrane selectivity. In order to minimize that effect, we added more AP-Mim in order to reduce the exposure of the gases to the uncoated fiber material.

In this case, we used three separate injections, resulting in a loading of 0.384 g IL, almost two times the quantity contained in the module used to obtain the data shown in the previous two figures. The results of tests obtained with this module are shown in Figure 16. In this case we maintained temperatures similar to the profile shown in the previous figure where the gas entered the module at 52°C and exited at 60°C. The figure shows that, compared to the data in the Figure 15, the CO_2 permeance decreased from 1.78E-4 scc/(cm² s cm Hg) to 1.48 E-4 scc/(cm² s cm Hg) or by 17%. However, the O_2 permeance decreased from
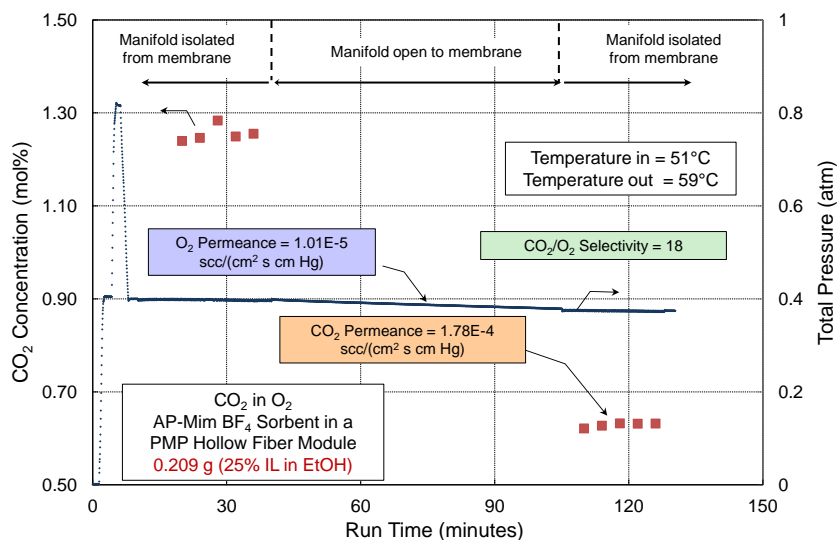
Figure 15. CO_2 concentration and total pressure data in a mixed gas test with the skinned fiber impregnated with 0.209 g of AP-Mim.

$1.01E-5$ scc/(cm² s cm Hg) to $5.60E-6$ scc/(cm² s cm Hg) or by 44%. Therefore the CO_2/O_2 selectivity increased from 18 to 26.
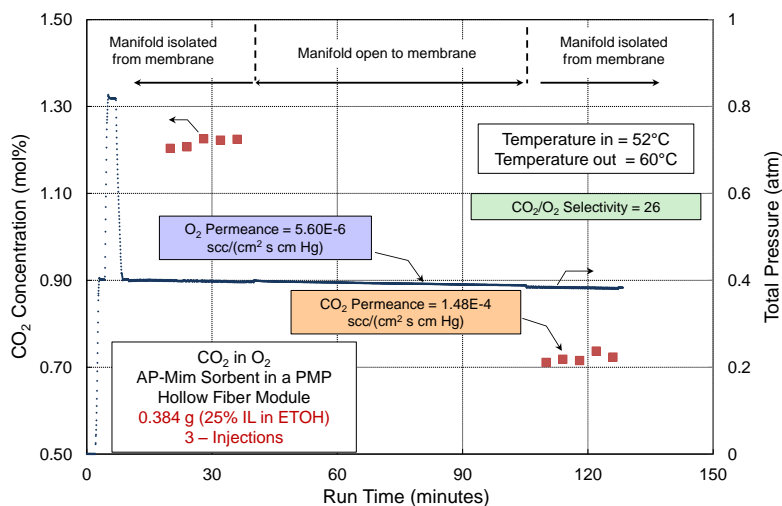
The next module, was impregnated with a mixture of AP-Mim, 13 wt% H_2O and 13 wt% ethanol and the loading was increased to 0.854 g of AP-Mim. The results of permeation testing with this module carried out at similar temperature as the last test are shown in Figure 17. The results show that the CO_2 permeance has increased slightly from $1.48E-4$ scc/(cm² s cm Hg) to $1.63 E-4$ scc/(cm² s cm Hg). However, the most significant change is the decrease in O_2 permeance. With the new module the O_2 permeance dropped to $1.04E-6$ scc/(cm² s cm Hg), which is over a factor of five reduction compared to the previous data. Combining the drop in O_2 permeance with the increase in CO_2 permeance results in a CO_2/O_2 selectivity of 157, which is a substantial increase over previous results.

Figure 16. CO_2 concentration and total pressure data in a mixed gas test with a skinned fiber module containing 0.384 g of AP-Mim.

In addition to the high selectivity obtained, the results of the last tests are encouraging because they show that the methods we are using to dissolve the ionic liquid and inject it into the hollow fiber walls still has a substantial effect on the membrane performance. Since these represent initial results, it is highly likely that the process of loading the IL into the hollow fiber walls is not optimized, and therefore further improvements in performance is still very possible with the current sorbent AP-Mim and the PMP hollow fiber modules that we are currently using. Moreover, once the process has been optimized, it is likely that it can be scaled up easily because the addition of the barrier polymer layer is not necessary. these hollow fibers.
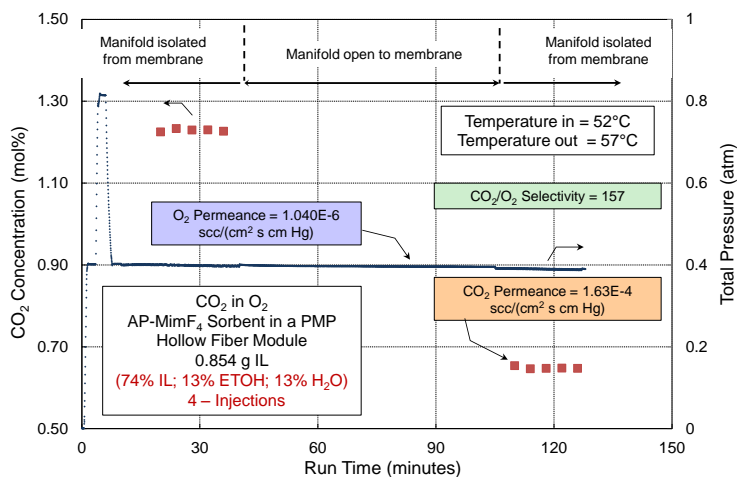
Design of a Full Scale Module

We developed a numerical model to estimate the performance of a module that would be large enough to control CO_2 produced by an astronaut on an EVA based on the CO_2 and O_2 permeance values reported in **Figure 17**. The model allows for the CO_2 partial pressure to be set coming into the module and then uses the relation between CO_2 pressure and permeance we established previously[4] to calculate the CO_2 permeance at the particular partial pressure. The model allow us to calculate performance as a function of a number of variables including length and diameter of the modules along with flow rate and CO_2 partial pressure. We used the physical dimensions of the skinned PMP hollow fibers that were used in the test results reported in Figure 9 to estimate the total surface area as a function of module diameter and length.

Figure 17. CO_2 concentration and total pressure data in a mixed gas test with a skinned fiber module containing 0.854 g AP-Mim.

The results obtained with a 12-in diameter module for several different flow rates are shown in Figure 19. In all cases we are assuming a CO_2 partial pressure at the inlet of the module of 10 mm Hg and therefore changing the flow
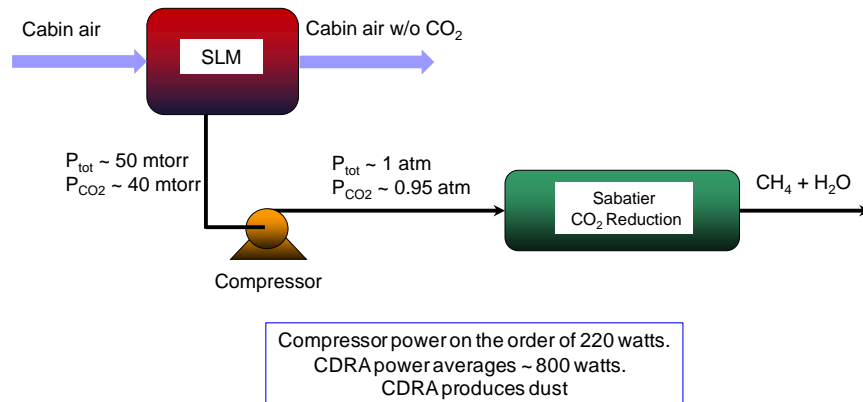
rate affects the total load on the system and these values are included in the figure. Overall the figure shows that the module will remove a substantial fraction of the inlet CO_2 even at the highest flow rate. At 50 standard liters per minute (slpm), the CO_2 flow rate entering the module is 120 g/hr, which is greater than the average CO_2 generation rate. In this case the concentration exiting the module is 3 mm Hg, which is above the targeted upper limit. At 40 slpm the rate is 109 g/h, the concentration exiting the module is predicted to be 2.2 mm Hg, while at the lowest flow rate the model predicts that the module will reduce the concentration down to 1 mm Hg, well below the target value of 2 mm Hg.
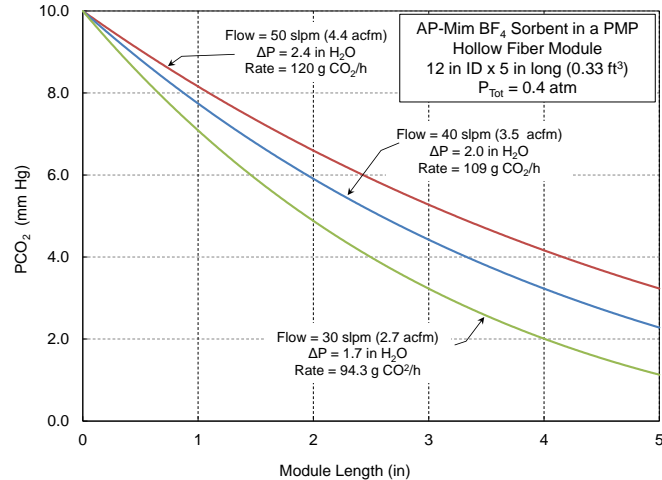
Figure 19. Predicted CO₂ concentrations exiting a skinned hollow fiber module at flow rates of 2.7. 3.5 and 4.4 cfm.

Potential for use in Cabin

Although the focus of this work is on EVA applications where the low pressure side of the membrane is exposed to space vacuum and the CO_2 that passes through the membrane is lost to space, the SLM could be transitioned into CO_2 control and O_2 recovery on space craft. In this case, a small vacuum pump could be installed on the low pressure side of the membrane in place of space vacuum as shown in **Figure 18**. Although the pump represents additional mass and power consumption, both of these factors will be less than those required for the Carbon Dioxide Removal Assembly on the International Space Station. Moreover, with the SLM, there is no potential to produce dust. An estimate of the pump power consumption is included in the following section.

The nominal and upper values for generation of metabolic CO_2 in EVA are 41.6 and 93.3 grams per hour per crew member respectively. For sizing calculations, we assume that the overall average value is halfway between these values or 67 grams CO_2 per hour per crew member, and for a crew of six, the total CO_2 generation rate is 402 g/h. The CO_2 flow through the membrane must be equal to the total CO_2 generation rate of 402 g/h if the CO_2 is maintained at a constant value. Using the measured CO_2/O_2 selectivity obtained in the flat sheet tests and relative O_2/N_2 permeance of 2, we calculate that in addition to CO_2, the O_2 flow will be 16.1 g/h and the N_2 flow will be 7.0 g/h, resulting in a total flow of 425 g/h.

Figure 18. Schematic of an SLM system used for control of cabin CO₂ and O₂ recovery.

The total pressure on the low pressure side of the pump must be low enough to maintain a high driving force across the membrane. With the above flows of CO_2, O_2, and N_2, the mole fraction of CO_2 is 0.92 and therefore if the pressure on the low pressure side of the SLM is 50 mtorr or 6.58E-5 atm, then the CO_2 partial pressure on the low pressure side of the membrane is 6.08 E-5 atm. On the high pressure side of the membrane a CO_2 partial pressure of 2.8 mm Hg is equivalent to 3.68E-3 atm and therefore the pressure differential is 3.62E-3 atm or very nearly the same pressure differential that would be encountered if the low pressure side of the membrane was exposed to space vacuum. We assume the pressure of the flow exiting the pump is one atmosphere and therefore we can calculate the power needed to operate the pump. The relationship between pump flow rate and pressure differential is shown by:

$$P = m \, \gamma/(\gamma-1) \, R \, T \, [(P_2/P_1)^{(\gamma-1)/\gamma} -1] \qquad\qquad \text{Eq. 1}$$

Where P is power in kW, m is the mass flow, γ is the heat capacity ratio, R is the gas constant, T is absolute temperature, P_2 is the pressure at the compressor outlet and P_1 is the pressure on the low pressure side of the compressor[9]. Using these results we obtained a power requirement of 215 watts. This is well below the continual CDRA power requirement of 800 watts. If the total power including fans is assumed to be 300 watts, the difference is 500 watts, which can be converted to an Equivalent System Mass (ESM) savings of 118 kg using the factor of 237 kg/kW_e. [10] The flow exiting the pump can then be directed into the CO_2 reduction system where it could be combined with H_2 and converted to CH_4 and H_2O in a Sabatier reactor or to C and H_2 in a Bosch system.

IV.   Summary and Conclusions

Overall, the results reported here show that SLMs containing custom amine-functionalized ionic liquids have the potential to separate CO_2 from O_2 in EVA applications. We have prepared a new sorbent that has low viscosity and good reversible CO_2 absorption capacity. Perhaps most important, the new sorbent has effectively zero vapor pressure, so it can be exposed to the vacuum of space without being lost by evaporation. We demonstrated that impregnating a thin, layered membrane with the AP-Mim sorbent produced permeation rates that are high enough that if contained in a hollow fiber module would meet the volume limitation of 0.25 ft^3. Moreover, we achieved a CO_2/O_2 selectivity of 1450; therefore, the O_2 losses through the membrane would be less than the expected leak rate in suit. We also demonstrated that the membrane could be transitioned into a hollow fiber form and obtained permeance values that exceeded the size criteria. Although the CO_2/O_2 selectivity is lower than needed, we demonstrated that the parameter is a strong function of methods used to impregnate the fiber and have made good progress in this areas in a very limited amount of time. Finally, we showed that SLM could be transitioned to control CO_2 in the cabin with power demands that are well below the CDRA.

Acknowledgments

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