

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

David T. Wickham,<sup>1</sup> Kevin J. Gleason,<sup>2</sup> and Jeffrey R. Engel<sup>3</sup>  
*Reaction Systems, Inc., Golden, Colorado, 80401*

Scott W. Cowley<sup>4</sup>  
*Colorado School of Mines, Golden, Colorado, 80401*

and

Cinda Chullen<sup>5</sup>  
*NASA Johnson Space Center, Houston, Texas, 77058*

The development of a new, robust, portable life support system (PLSS) is currently a high NASA priority 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<sub>2</sub>) concentration in the suit at acceptable levels. The Metal Oxide canister has a finite CO<sub>2</sub> adsorption capacity. To extend mission times, the unit would have to be larger and heavier, which is undesirable; therefore, new CO<sub>2</sub> 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<sub>2</sub> to space but retains oxygen (O<sub>2</sub>). 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<sub>2</sub> over O<sub>2</sub>. 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<sub>2</sub>, O<sub>2</sub>, and water have shown that the CO<sub>2</sub> permeation rate and CO<sub>2</sub>/O<sub>2</sub> 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<sub>2</sub> permeance values have been obtained, while the current CO<sub>2</sub>/O<sub>2</sub> 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.

---

<sup>1</sup> President and Principal Investigator, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.

<sup>2</sup> Senior Engineer, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.

<sup>3</sup> Senior Engineer, 17301 W. Colfax Ave, Suite 160, Golden, CO, 80401.

<sup>4</sup> Professor of Chemistry, Department of Chemistry and Geochemistry, Golden, CO, 80401.

<sup>5</sup> Project Engineer, Space Suit and Crew Survival Systems Branch, Crew and Thermal Systems Division, 2101 NASA Parkway/EC5

## Nomenclature

$^{\circ}\text{C}$	=	degrees Celsius
<i>AP-Mim</i>	=	1-(3-aminopropyl)-3-methylimidazolium
<i>atm</i>	=	atmospheres
<i>cc</i>	=	cubic centimeters
<i>CDRA</i>	=	Carbon Dioxide Removal Assembly
<i>cfm</i>	=	cubic feet per minute
<i>cm<sup>2</sup></i>	=	square centimeters
<i>cm Hg</i>	=	centimeters of mercury
<i>CO<sub>2</sub></i>	=	carbon dioxide
<i>EtOH</i>	=	ethanol
<i>EVA</i>	=	extravehicular activity
<i>ft<sup>3</sup></i>	=	cubic feet
<i>GC</i>	=	gas chromatograph
<i>g</i>	=	grams
<i>h</i>	=	hour
<i>H<sub>2</sub></i>	=	hydrogen
<i>H<sub>2</sub>O</i>	=	water
<i>h-PTFE</i>	=	hydrophobic polytetrafluoroethylene
<i>in-H<sub>2</sub>O</i>	=	inches of water
<i>kg</i>	=	kilogram
<i>kW</i>	=	kilowatts
<i>IL</i>	=	ionic liquid
<i>IP</i>	=	interfacially polymerized
<i>MetOx</i>	=	Metal Oxide
<i>m</i>	=	mass flow
<i>mm Hg</i>	=	millimeters of mercury
<i>mtorr</i>	=	millitorr
<i>NMR</i>	=	nuclear magnetic resonance
<i>N<sub>2</sub></i>	=	nitrogen
<i>O<sub>2</sub></i>	=	oxygen
<i>P</i>	=	power
<i>PLSS</i>	=	portable life support system
<i>psi</i>	=	pounds per square inch
<i>PMP</i>	=	poly-4-methyl pentene
<i>PP</i>	=	polypropylene
<i>PTFE</i>	=	polytetrafluoroethylene
<i>P<sub>1</sub></i>	=	pressure entering pump
<i>P<sub>2</sub></i>	=	pressure exiting pump
<i>P<sub>tot</sub></i>	=	total pressure
<i>R</i>	=	universal gas constant
<i>RCA</i>	=	Rapid Cycle Amine
<i>RH</i>	=	relative humidity
<i>s</i>	=	second
<i>scc</i>	=	standard cubic centimeters
<i>SLM</i>	=	supported liquid membrane
<i>slpm</i>	=	standard liters per minute
<i>T<sub>a</sub></i>	=	absolute temperature
$\Delta P$	=	pressure difference
$\gamma$	=	isentropic expansion factor
$\mu\text{L}$	=	microliter
$\mu\text{m}$	=	micrometers

## I. Introduction

The development of a new, robust, portable life support system (PLSS) is currently a high priority for NASA 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.<sup>1,2</sup> One of the critical PLSS functions is maintaining the carbon dioxide (CO<sub>2</sub>) 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 PLSS. The rate of CO<sub>2</sub> generation varies with the metabolic rate of the crew member. Recent studies of CO<sub>2</sub> control technology have been carried out in which the CO<sub>2</sub> injection rates were varied to match simulated metabolic rates<sup>3,4,5</sup>. The different CO<sub>2</sub> production rates were normalized per metabolic rate and the average CO<sub>2</sub> generation rate over the course of an EVA was estimated to be 93 g/h<sup>6,7</sup>. A study of the physiological effects of CO<sub>2</sub> exposure carried out in 1993 resulted in the recommendation that CO<sub>2</sub> levels be limited during EVA to 3.8 mm Hg for nominal exertion and 7.6 mm Hg for heavy exertion.<sup>8</sup> More recently, the cognitive effects of CO<sub>2</sub> exposure on decision making were studied and it was found that CO<sub>2</sub> levels as low as 0.8 mm Hg could cause a measureable reduction in decision-making capability, whereas levels above 1.5 mm Hg could result in a more severe effects.<sup>9</sup> Based on the most recent findings, NASA has a current interest in reducing the maximum allowable CO<sub>2</sub> concentration in the suit from 7.6 mm Hg to 2.8 mm Hg. Thus, for EVA operation to be safely carried out, the CO<sub>2</sub> 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 8 hours.

Currently, the Metal Oxide (MetOx) system is being used for CO<sub>2</sub> control during EVA. The MetOx employs a metal oxide sorbent, which reacts with CO<sub>2</sub> at low temperatures to produce the metal carbonate. Although it has worked well, it has a finite CO<sub>2</sub> adsorption capacity. Consequently, the unit would have to be larger and heavier to extend EVA times. Therefore, new CO<sub>2</sub> control technologies must be developed to meet mission objectives without increasing the size of the PLSS. Although 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<sub>2</sub> to space while retaining oxygen (O<sub>2</sub>).

An effective membrane system would have several significant advantages over the other methods of CO<sub>2</sub> control. It would be a continuous system with no limit on the amount of CO<sub>2</sub> 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<sub>2</sub> losses with a membrane are independent of metabolic output. However, the CO<sub>2</sub> flux through the membrane scales with CO<sub>2</sub> concentration, which will help prevent crew exposure to high CO<sub>2</sub> concentrations during periods of increased CO<sub>2</sub> generation.

The successful application of a membrane requires that some difficult challenges be met. First, the permeation rate of CO<sub>2</sub> through the membrane must be high enough that a reasonably sized membrane module can control an average metabolic CO<sub>2</sub> generation rate. In addition, the membrane must have good selectivity for CO<sub>2</sub> over O<sub>2</sub> to prevent unacceptably high O<sub>2</sub> losses. Recent estimates suggest that to control the average CO<sub>2</sub> production rate, the CO<sub>2</sub> permeance would need to be 1.04E-4 scc/(cm<sup>2</sup> s cm Hg), where scc refers to CO<sub>2</sub>, cm<sup>2</sup> is the surface area of the membrane, and cm Hg is the differential CO<sub>2</sub> partial pressure across the membrane.<sup>6,7</sup> If we assume that the low pressure side of the membrane is exposed to space vacuum, then cm Hg is the partial pressure of CO<sub>2</sub> on the crew side of the suit. Finally, the membrane must minimize O<sub>2</sub> losses. Although a simple membrane system would likely have multiple system benefits that could make up for increased O<sub>2</sub> losses, a simple first cut approach to estimate a reasonable selectivity requirement is to set losses to be no greater than the existing leak rates of the suit, 4.2 g/h<sup>10</sup>. Using this approach, the ratio of CO<sub>2</sub> permeance to O<sub>2</sub> permeance, or CO<sub>2</sub>/O<sub>2</sub> selectivity, for a membrane should 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<sub>2</sub> permeability but has a CO<sub>2</sub>/O<sub>2</sub> selectivity of only about five.

Another approach is to take advantage of the difference in chemical properties of CO<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub> on the crew side of the membrane. Because CO<sub>2</sub> 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<sub>2</sub> would shift the equilibrium, thereby resulting in the decomposition of the metastable complex, the release of the CO<sub>2</sub>, and the regeneration of the sorbent (Figure 1). This process is frequently referred to as facilitated transport. On the other hand, because O<sub>2</sub> does not have acidic properties, it should not react with the liquid, resulting in potentially high CO<sub>2</sub>/O<sub>2</sub> 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.

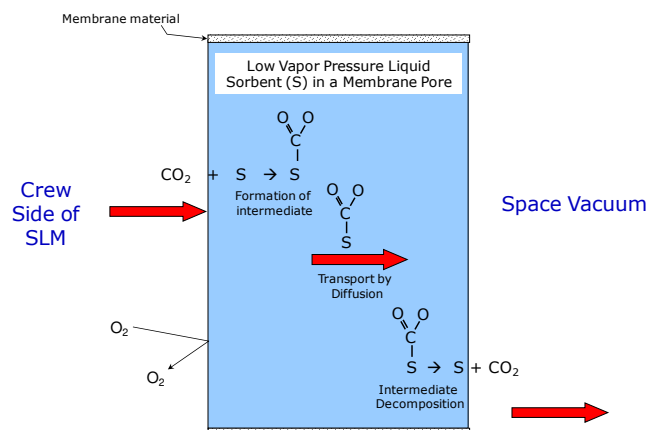
Amines have been shown to possess excellent reversible CO<sub>2</sub> absorption capacity. Amines are commonly used to absorb CO<sub>2</sub> out of industrial gas streams and are currently being evaluated in a cycling bed configuration to control CO<sub>2</sub> in EVA<sup>11,12</sup>. The affinity of an amine for CO<sub>2</sub> depends on its structure. Primary amines bind CO<sub>2</sub> strongly, usually requiring that the sorbent be heated for regeneration. On the other hand, secondary and tertiary amines do not bind CO<sub>2</sub> 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 be 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<sub>2</sub> permeance and improved CO<sub>2</sub>/O<sub>2</sub> selectivities relative to polymeric membranes.<sup>6,7</sup> The more recent work demonstrated that an SLM containing a primary amine functionalized ionic liquid, AP-Mim (Figure 2) sorbent in a layered, flat sheet configuration met the CO<sub>2</sub> permeance and CO<sub>2</sub>/O<sub>2</sub> selectivity targets established above and that the membrane rapidly vented moisture as well.<sup>7</sup> The layered membrane consisted of two thin, large pore polytetrafluorethylene (PTFE) membranes. The layer on the high pressure side was treated with a surfactant to make it hydrophilic (h-PTFE), while an untreated PTFE layer, which is hydrophobic, was placed on the low pressure side. The sorbent was loaded into the h-PTFE layer and the presence of the hydrophobic layer on the low pressure side prevented the sorbent from being forced out of the pores when exposed to a differential pressure. 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.

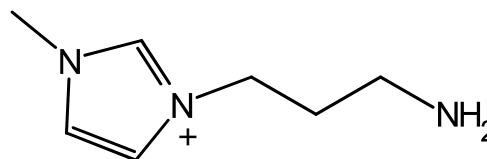
## II. Experimental Methods

### 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 an 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. Although this compound is a primary amine, it binds CO<sub>2</sub> less strongly than conventional primary amines and therefore can be regenerated at room temperature. However, the best membrane performance obtained to date has been at elevated temperatures, approximately 75°C. 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.<sup>6,7</sup>



**Figure 1. Schematic of facilitated CO<sub>2</sub> transport within a membrane pore.**



**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.<sup>6,7</sup> 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<sup>6,7</sup> 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<sub>2</sub> or O<sub>2</sub> 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

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 is impregnated with the sorbent and the process flow is 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 3/8-inch compression fitting ports and one 1/4-inch male-NPT pipe threaded fitting port) connected using a 3-inch-long piece of 3/8-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<sub>2</sub> from O<sub>2</sub> 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; tests to verify the seal quality are described below.

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 shell side of 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.

### 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.<sup>6,7</sup> The mixed gas test rig system included a flow loop connected to a flow-

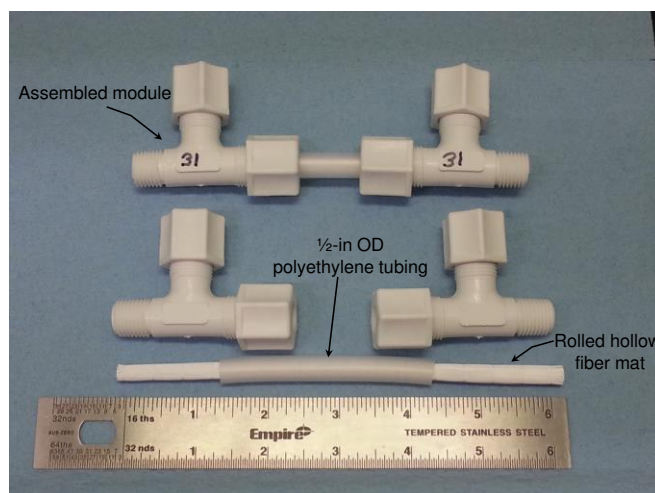
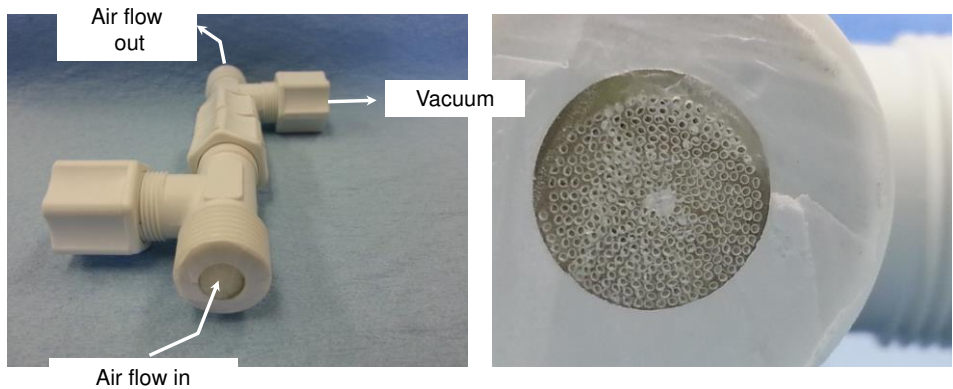


Figure 3. Photograph of the hollow fiber module.

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<sub>2</sub> and CO<sub>2</sub>, a diaphragm pump to circulate the mixture, analytical instrumentation to measure the changes in CO<sub>2</sub> and water (H<sub>2</sub>O) concentrations, and an 8-liter reservoir. Water was introduced with a



**Figure 4. Photograph of the assembled module.**

Chemyx Fusion 100 syringe pump so that water could be added on a continual basis at a representative rate. A Vaisala relative humidity (RH) sensor was used to monitor the RH in the mixed gas and the CO<sub>2</sub> 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.

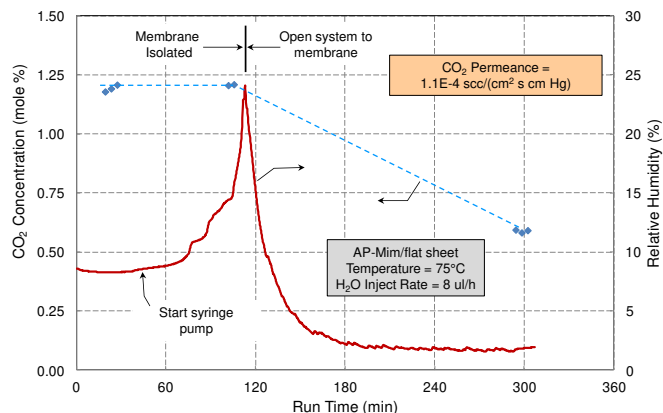
To conduct gas permeation tests, the system was first evacuated to less than 50 mtorr and then the membrane was isolated from the rest of the system. The loop and reservoir were then charged to 0.4 atm with a mixture consisting of between 0.75% and 2.5% CO<sub>2</sub> in O<sub>2</sub>, which corresponded to CO<sub>2</sub> partial pressure from 1.9 mm Hg up to 7.6 mm Hg. The circulation pump was started directing flow through the loop and the module by-pass line and the syringe pump was activated, injecting H<sub>2</sub>O 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<sub>2</sub> concentration in the loop were made through the course of the experiment and used to calculate CO<sub>2</sub> permeance. The test was stopped when the CO<sub>2</sub> concentration dropped to approximately half the original starting concentration. The O<sub>2</sub> 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

#### A. 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<sup>7</sup> are included in Figure 5 and Figure 6. In Figure 5, the CO<sub>2</sub> concentration and RH are plotted against the test or run time. From time zero up until 118 minutes, the flow loop was isolated from the membrane; during this period, the CO<sub>2</sub> concentration was stable and the RH increased due to the constant moisture addition from the syringe



**Figure 5. CO<sub>2</sub> concentration (blue diamonds) and moisture (red line) as a function of time with the AP-Mim flat sheet SLM.**

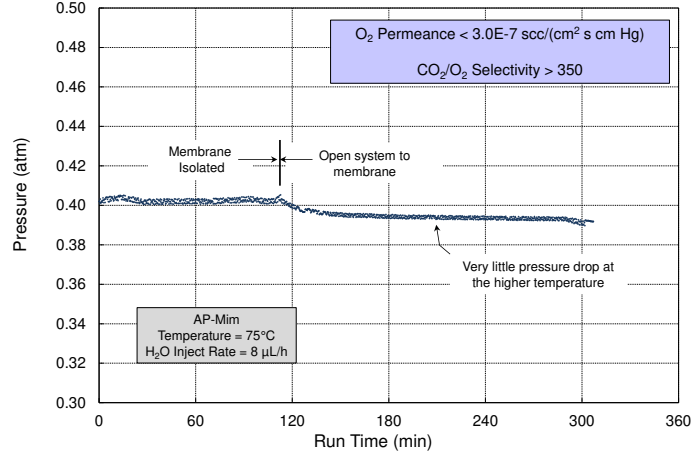


pump. The RH dropped rapidly after the flow loop was exposed to the membrane, and reached a steady-state concentration of about 2% to 3%. In addition, the figure shows that the CO<sub>2</sub> concentration dropped from 1.21% to 0.58% over the duration of the run, resulting in a permeance of 1.1E-4 scc/(cm<sup>2</sup> s cm Hg). Data obtained in other tests have shown that the drop in CO<sub>2</sub> concentration is linear with time when the manifold is open to the membrane and that the CO<sub>2</sub> permeance is unaffected by water vapor.<sup>7</sup> Since continual CO<sub>2</sub> sampling reduces the overall pressure in the manifold which affects the O<sub>2</sub> permeance measurement, CO<sub>2</sub> was only measured in this test at the end of the test period. The permeance of 1.1E-4 scc/(cm<sup>2</sup> s cm Hg) meets the performance goal established earlier. Therefore, once the SLM is converted into a hollow fiber form, a unit sized to control the average CO<sub>2</sub> production from a crew member could be contained in a module that is no larger than 0.25 ft<sup>3</sup>, which is the size of the RCA system, the next generation technology for CO<sub>2</sub> control in the PLSS.

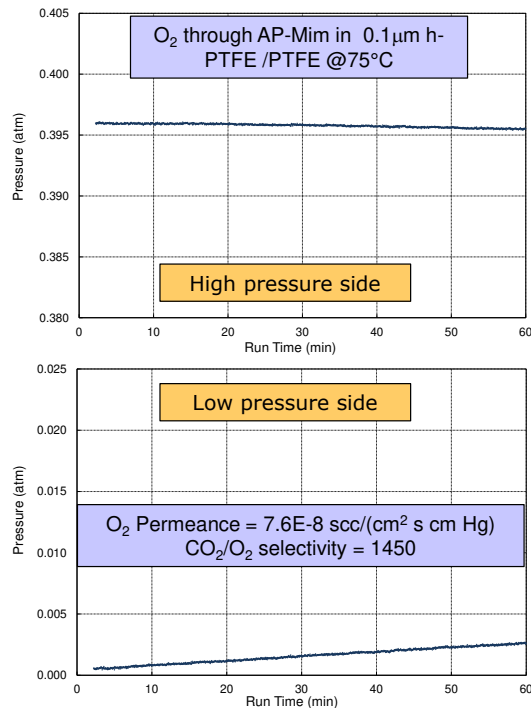
The total pressure measurement for this test is shown in Figure 6. In this case, very little pressure drop occurred after the loop was exposed to the membrane. Once again, immediately after the loop was opened to the membrane, a noticeable pressure drop occurred, due primarily to the loss of water vapor, as shown in Figure 5. However, after that change, the pressure remained constant. For example, Figure 6 shows that the pressure was 0.394 atm at 170 minutes and decreased by only 0.0020 atm after being on line for 2 hours. 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<sup>2</sup> s cm Hg). Combining this value with the CO<sub>2</sub> permeance reported above results in a CO<sub>2</sub>/O<sub>2</sub> 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<sub>2</sub>/O<sub>2</sub> selectivity target. Although a selectivity of greater than 350 is encouraging, the O<sub>2</sub> permeance was less than our detection limit in this test rig. Therefore, we repeated the O<sub>2</sub> permeance test in the single-gas test rig, which for O<sub>2</sub> permeance has a lower detection limit than the mixed gas test rig.

The results of the static tests for O<sub>2</sub> with the modified AP-Mim are shown in Figure 7. The figure shows that the pressure in the upper reservoir decreased from 0.3959 atm to 0.3954 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 0.00044 atm to 0.00262 atm over the same time period. The data resulted in a calculated O<sub>2</sub> permeance of 7.6E-8 scc/(cm<sup>2</sup> s cm Hg); using this value along with the CO<sub>2</sub> permeance reported in Figure 5, we calculated that CO<sub>2</sub>/O<sub>2</sub> 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<sub>2</sub> permeation and CO<sub>2</sub>/O<sub>2</sub> selectivity levels that we established. These results demonstrate the potential feasibility of using a supported liquid membrane for CO<sub>2</sub> control. Although the temperature required to achieve this performance currently is 75°C, it is



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



**Figure 7. O<sub>2</sub> permeation results obtained for AP-Mim in the flat sheet membrane at 75°C.**

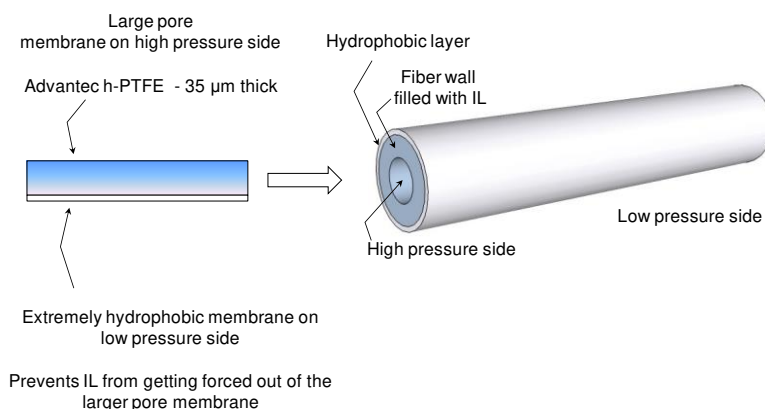
possible with further development of the ionic liquid that this temperature can be reduced. Nonetheless, since there are no other power demands with the membrane system, it is likely that it could be operated at an elevated temperature without an unacceptable power requirement.

## B. Tests with the Hollow Fiber Modules

The SLM membrane must be incorporated into a hollow fiber module form to meet the volume requirements for a CO<sub>2</sub> control system in the PLSS. 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, an analogous layered hollow fiber was needed to achieve the same performance in the hollow fiber form.

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.

The process flow is directed through the center of the hollow fiber (or lumen) while the shell side is exposed to vacuum. 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 of the membrane. Thus, as the CO<sub>2</sub> 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.



**Figure 8. Two layer flat sheet membrane (left side) and the analogous two layer form in a hollow fiber (right side).**

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 ionic liquid from being forced out of the fiber. The flat sheet testing clearly showed that water penetrated the ionic liquid SLM rapidly. Therefore in the initial tests with the modules, we did not add moisture to the system. Results 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 whether 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<sub>2</sub>O. 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 ionic liquid in the hollow fiber after the EtOH and H<sub>2</sub>O solvents were removed by evacuation. In these initial tests, the weight of ionic liquid loaded into the fiber bundle was used to compare the relative loading from one module to the next and provide an indication of what quantity of liquid will be necessary in larger modules.

The results of this test are shown in Figure 9. The CO<sub>2</sub> permeance is 2.81E-5 scc/(cm<sup>2</sup> s cm Hg), which is about a factor of four lower than that needed to meet the module size requirement outlined above. The figure also shows that the O<sub>2</sub> permeance is 7.02E-8 scc/(cm<sup>2</sup> s cm Hg) resulting in a CO<sub>2</sub>/O<sub>2</sub> selectivity of 400. Although the permeance and CO<sub>2</sub> selectivity values are lower than were obtained with the flat sheet, they nonetheless they show that we have been able to transition the SLM technology from the flat sheet to a hollow fiber module form.



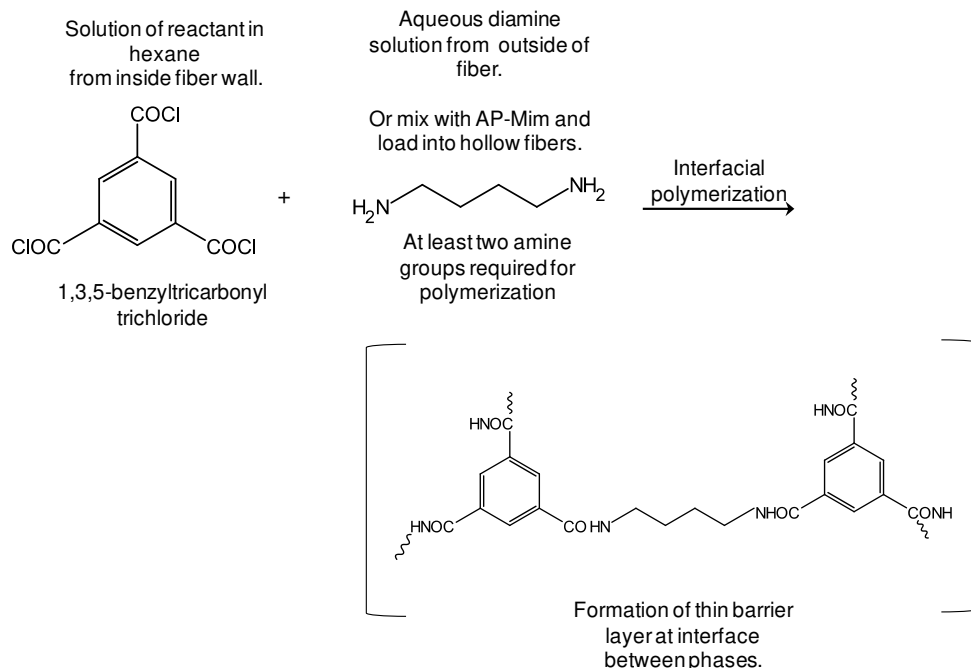
The absence of the polymer layer did not produce a rapid loss of IL from the fiber. However, the sorbent was detected in the shell side of the module after it was removed from the test rig. Thus, in the next tests, these fibers were coated with a polymeric layer to prevent IL loss. The coating process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

## 2. Addition of a Polymer Barrier to the Outer Skin of the Hollow Fiber

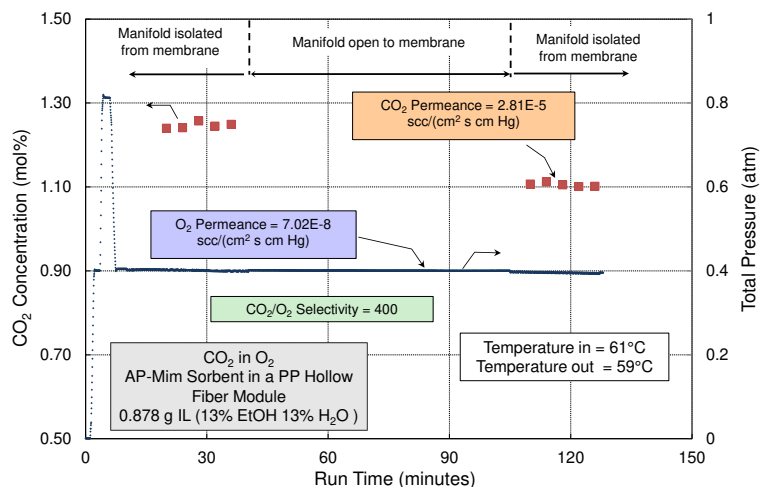
We used a method that had been published previously to add the polymer layer to the outside of the fiber and generate a layered structure in-situ.<sup>13</sup> The process is based on an interfacial polymerization (IP) reaction that occurs between an acid chloride and a compound containing at least two primary amine groups. An example of such a reaction is shown in Figure 10. In this case, 1,3,5-benzyltricarboxyl trichloride reacts with butyldiamine and generates a polyamide.

The 1,3,5-benzyltricarboxyl trichloride reacts with butyldiamine and generates a polyamide. The 1,3,5-benzyltricarboxyl 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-benzyltricarboxyl trichloride through the inside of the fibers. These fibers are easily wetted by organic solvents such as hexane and



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



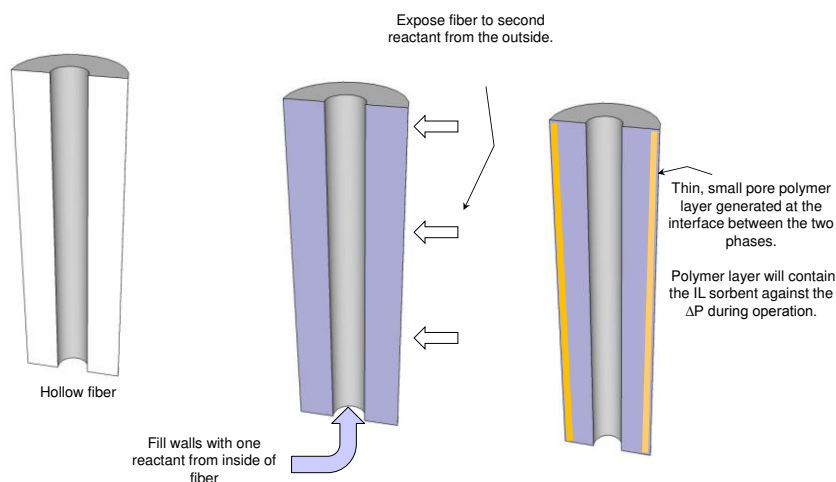
**Figure 9.  $\text{CO}_2$  concentration and total pressure in a mixed gas test with  $\text{CO}_2$  in  $\text{O}_2$  using polypropylene fibers without a polymer layer.**

therefore the solution will fill the fibers with reactant (center illustration). However, the two solutions will contact 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<sup>13</sup> 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.

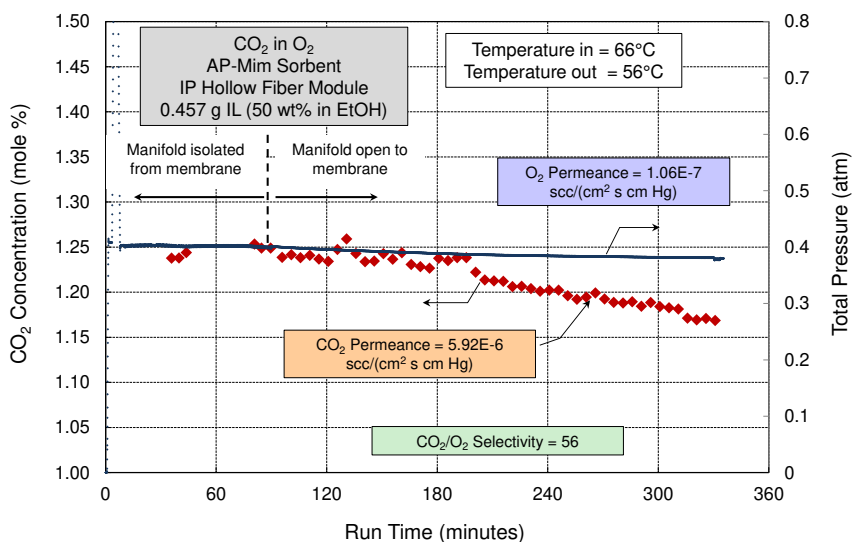
After preparation, an IP-modified hollow fiber module was placed in the mixed gas test rig for CO<sub>2</sub> and O<sub>2</sub> permeance measurements. The results of this test are shown in Figure 12. The GC data show that CO<sub>2</sub> was being removed from the circulation loop. Between times of 30 and 90 minutes before the loop contents were exposed to the module, the CO<sub>2</sub> level was stable, and averaged 1.24 mole%. At a time of 90 minutes, the circulating flow was then directed through the module and immediately the GC data show that the concentration dropped steadily over the next 240 minutes, eventually reaching a concentration of 1.17%. The data were used to calculate a CO<sub>2</sub> permeance of 5.92 E-6 scc/(cm<sup>2</sup>-s cm Hg), which is well below the permeance values needed and obtained with other SLMs. The figure shows that when the flow was directed through the module, the total pressure dropped from 0.40 atm to 0.384 atm at the conclusion of the test. The change in pressure resulted in O<sub>2</sub> permeance of 1.06E-7 scc/(cm<sup>2</sup>-s cm Hg), which produced 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<sub>2</sub> permeance values. To assess whether this was due to inconsistent interfacially polymerized coating thickness, we measured the nitrogen (N<sub>2</sub>) permeance of the IP-coated fibers before they had been impregnated with the ionic liquid sorbent. The results of N<sub>2</sub> 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<sup>2</sup> s cm Hg) to a low of 1.1E-7 scc/(cm<sup>2</sup> 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 contain a gas permeable, dense integral skin on the outside of the fiber. These skinned fibers consist of poly-4-methyl pentene (PMP). To compare the “as-received” PMP fibers to the polypropylene fibers that contained the IP layer, we likewise measured the N<sub>2</sub> 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.



**Figure 11. Method to add a polymer layer on the shell side using IP.**



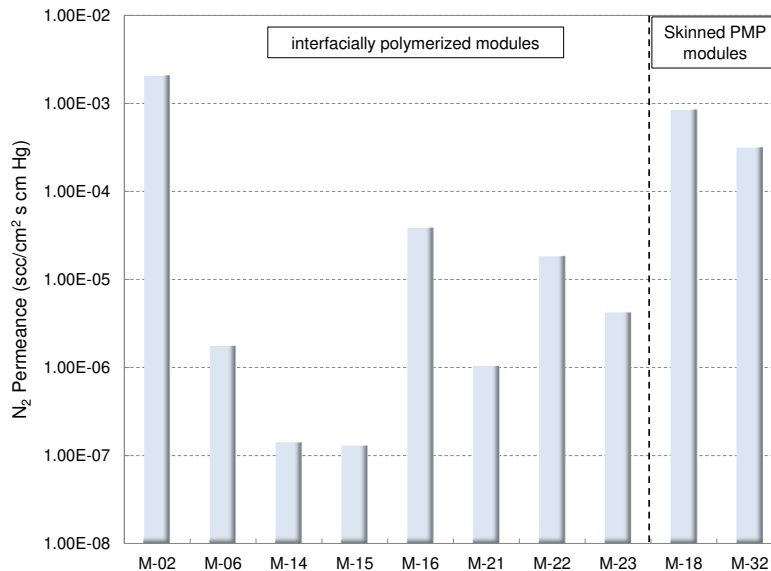
**Figure 12. CO<sub>2</sub> concentration and total pressure data in a mixed gas test with the AP-Mim SLM in a hollow fiber with a polymerized outer layer.**

The figure shows that the  $N_2$  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.

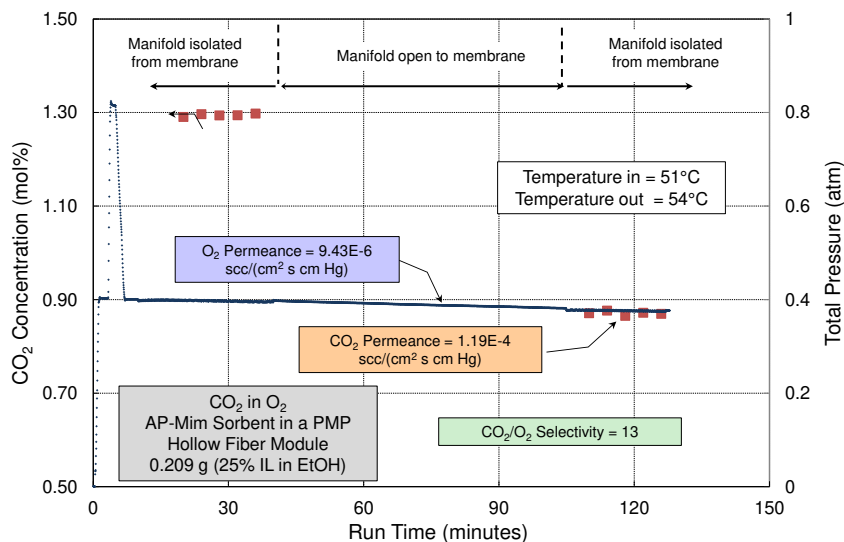
### 3. Tests with a Skinned Hollow Fiber

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% ionic liquid. 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 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  $1.19E-4$   $sc/(cm^2 s cm Hg)$ . 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  $9.43E-6$   $sc/(cm^2 s cm Hg)$ , which is higher than the results obtained in the polypropylene 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  $54^\circ C$  to  $59^\circ C$ . 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 had a substantial effect on the  $CO_2$  permeance as it increased the value from  $1.19E-4$   $sc/(cm^2 s cm Hg)$  to  $1.78E-4$   $sc/(cm^2 s cm Hg)$ , which represents a 50% improvement.



**Figure 13.  $N_2$  permeation results for the polypropylene modules following the interfacial polymerization process and for two as-received skinned fiber modules.**



**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.**

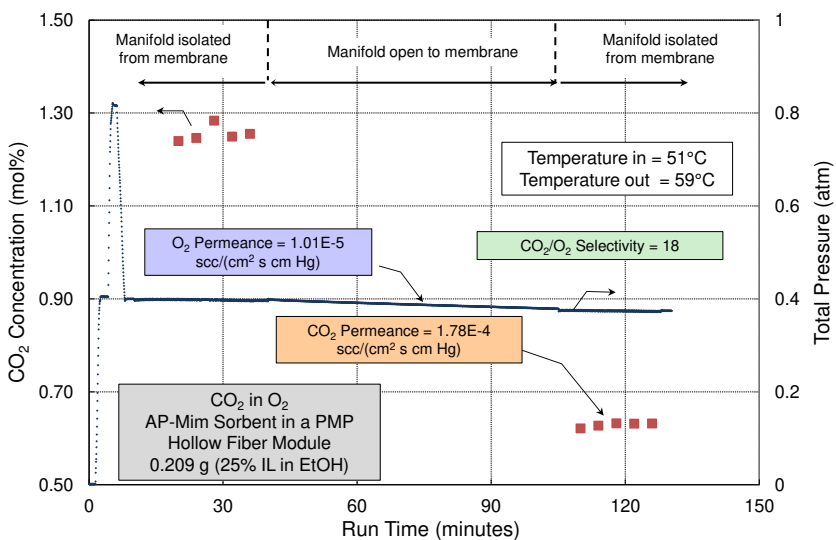
Not surprisingly, the O<sub>2</sub> permeance also increased; however, it only increased by 7% and therefore the increase in temperature also increased the CO<sub>2</sub>/O<sub>2</sub> selectivity from 13 to 18.

The results obtained with the skinned module show that while the CO<sub>2</sub> permeance has more than met the required values, the CO<sub>2</sub>/O<sub>2</sub> selectivity is well below the values needed to prevent excessive O<sub>2</sub> loss through the membrane. One of the concerns regarding the PMP material was that the material itself had high permeance values for both CO<sub>2</sub> and O<sub>2</sub>, which could reduce the membrane selectivity. To minimize that effect, we added more AP-Mim to reduce the exposure of the gases to the uncoated fiber material.

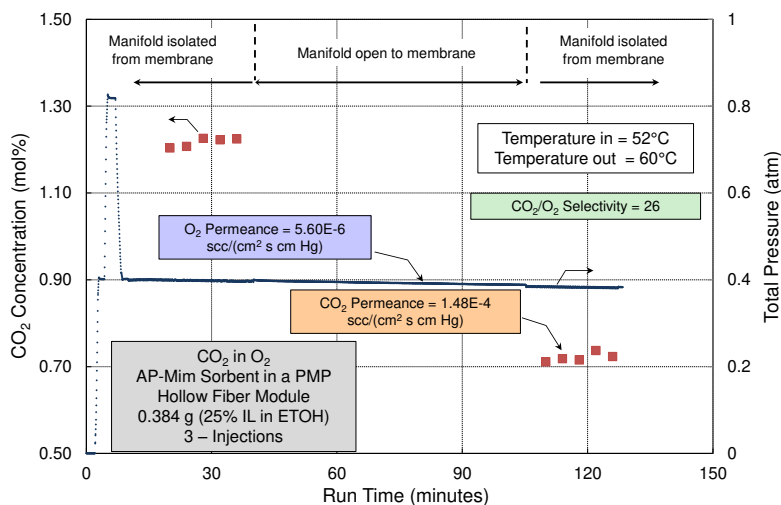
In this case, we used three separate injections, resulting in a loading of 0.384 g ionic liquid, almost two times the quantity contained in the module used to obtain the data shown in the previous two figures. The results of tests obtained with this module are shown in Figure 16. In this case, we maintained 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<sub>2</sub> permeance decreased from 1.78E-4 scc/(cm<sup>2</sup> s cm Hg) to 1.48 E-4 scc/(cm<sup>2</sup> s cm Hg) or by 17%. However, the O<sub>2</sub> permeance decreased from 1.01E-5 scc/(cm<sup>2</sup> s cm Hg) to 5.60E-6 scc/(cm<sup>2</sup> s cm Hg) or by 44%. Therefore, the CO<sub>2</sub>/O<sub>2</sub> selectivity increased from 18 to 26.

The next module was impregnated with a mixture of AP-Mim, 13 wt% H<sub>2</sub>O 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<sub>2</sub> permeance has increased slightly from 1.48E-4 scc/(cm<sup>2</sup> s cm Hg) to 1.63 E-4 scc/(cm<sup>2</sup> s cm Hg). However, the most significant change is the decrease in O<sub>2</sub> permeance. With the new module the O<sub>2</sub> permeance dropped to 1.04E-6 scc/(cm<sup>2</sup> s cm Hg), which is over a factor of five reduction compared to the previous data. Combining the drop in O<sub>2</sub> permeance with the increase in CO<sub>2</sub> permeance results in a CO<sub>2</sub>/O<sub>2</sub> selectivity of 157, which is a substantial increase over previous results.

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 ionic liquid into the hollow fiber walls is not optimized; therefore, further improvements in performance is still very possible with the current sorbent



**Figure 15. CO<sub>2</sub> concentration and total pressure in a test with the skinned fiber impregnated with 0.209 g of AP-Mim at a higher temperature .**



**Figure 16. CO<sub>2</sub> concentration and total pressure data in a mixed gas test with a skinned fiber module containing 0.384 g of AP-Mim.**

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.

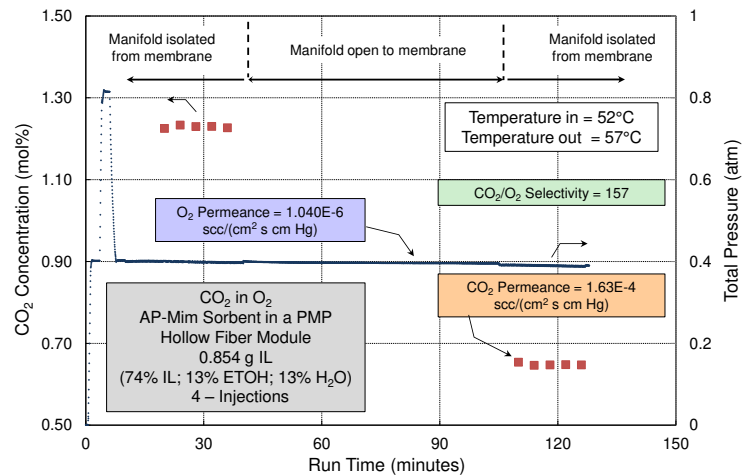
### C. Design of a Full Scale Module

We developed a numerical model to estimate the performance of a module that would be large enough to control CO<sub>2</sub> produced by an astronaut on an EVA based on the CO<sub>2</sub> and O<sub>2</sub> permeance values reported in Figure 17. The model allows for the CO<sub>2</sub> partial pressure to be set coming into the module and then uses the relation between CO<sub>2</sub> pressure and permeance we established previously<sup>7</sup> to continually update CO<sub>2</sub> permeance as the partial pressure decreases through the module. 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<sub>2</sub> partial pressure. We used the physical dimensions of the skinned PMP hollow fibers and data reported in Figure 17 to estimate the total surface area as a function of module diameter and length.

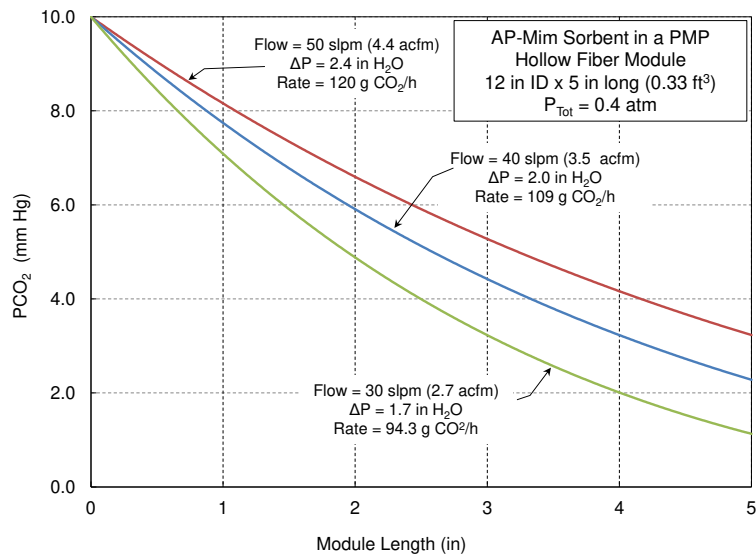
The results obtained with a 12-inch diameter module for several different flow rates are shown in Figure 18. In all cases, we are assuming a CO<sub>2</sub> partial pressure at the inlet of the module of 10 mm Hg; therefore, changing the flow rate affects the total load on the system, and these values are included in the figure. Overall, the figure shows that the module will remove a substantial fraction of the inlet CO<sub>2</sub>, even at the highest flow rate. At 50 standard liters per minute (slpm), the CO<sub>2</sub> flow rate entering the module is 120 g/hr, which is greater than the average CO<sub>2</sub> 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.

### D. 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<sub>2</sub> that passes through the membrane is lost to space, the SLM could be transitioned into CO<sub>2</sub> control and O<sub>2</sub> recovery on spacecraft. 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 19. Although the pump represents additional power consumption, it could be less than the power required for the Carbon Dioxide Removal Assembly (CDRA) on the International Space Station. Moreover, with the SLM, there is no potential for the sorbent to produce dust. An estimate of the pump power consumption is included in the following section.



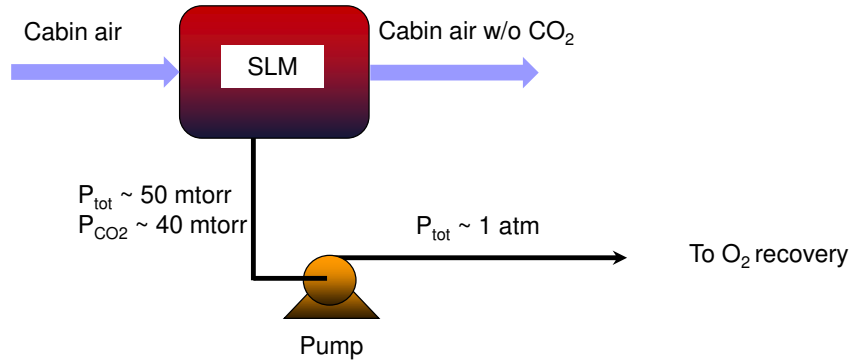
**Figure 17. CO<sub>2</sub> concentration and total pressure data in a mixed gas test with a skinned fiber module containing 0.854 g AP-Mim.**



**Figure 18. Predicted CO<sub>2</sub> concentrations exiting a skinned hollow fiber module at flow rates of 2.7, 3.5, and 4.4 cfm.**



The nominal value for generation of metabolic CO<sub>2</sub> in a cabin is 0.998 kg/CM-d or 41.5 grams per hour per crew member<sup>14</sup>. For a crew of six, the total CO<sub>2</sub> generation rate is 250 g/h. The CO<sub>2</sub> flow through the membrane must be equal to the total CO<sub>2</sub> generation rate of 250 g/h if the CO<sub>2</sub> is maintained at a constant value. Using the measured CO<sub>2</sub>/O<sub>2</sub> selectivity obtained in the flat sheet tests and relative O<sub>2</sub>/N<sub>2</sub> permeance of 2, we calculate that in addition to CO<sub>2</sub>, the O<sub>2</sub> flow will be 64 g/h and the N<sub>2</sub> flow will be 28 g/h, resulting in a total flow of 342 g/h.



Power required for product flow is on the order of 200 watts.

**Figure 19. Schematic of an SLM system used for control of cabin CO<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>, the mole fraction of CO<sub>2</sub> is 0.65 and therefore if the pressure on the low pressure side of the SLM is 50 mtorr or 6.58E-5 atm, then the CO<sub>2</sub> partial pressure on the low pressure side of the membrane is 4.31 E-5 atm. A CO<sub>2</sub> partial pressure of 2.8 mm Hg is equivalent to 3.68E-3 atm on the high pressure side of the membrane; therefore, the pressure differential is 3.64E-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. Initial calculations of pump power are based on mass flow rate and pressure differential as shown by:

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

Where P is power in kW, m is the mass flow,  $\gamma$  is the isentropic expansion factor for CO<sub>2</sub>, R is the gas constant, T is absolute temperature, P<sub>2</sub> is the pressure at the compressor outlet and P<sub>1</sub> is the pressure on the low pressure side of the compressor.<sup>15</sup> Using these results we obtained a power requirement of 190 watts. Although this value does not include additional power for less than 100% pump efficiency and it is only an estimate, it is still 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 savings of 118 kg using the factor of 237 kg/kW.<sup>16</sup> The flow exiting the pump can then be directed into the O<sub>2</sub> recovery system where it could be combined with H<sub>2</sub> and converted to methane and H<sub>2</sub>O in a Sabatier reactor or to carbon and H<sub>2</sub> in a Bosch system. While no data has been obtained using the module in this application, the results of these initial calculations justify additional module testing in a cabin configuration.

#### IV. Summary and Conclusions

Overall, the results reported here show that SLMs containing custom amine-functionalized ionic liquids have the potential to separate CO<sub>2</sub> from O<sub>2</sub> in EVA applications. We have prepared a new sorbent that has low viscosity and good reversible CO<sub>2</sub> 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<sup>3</sup>. Moreover, we achieved a CO<sub>2</sub>/O<sub>2</sub> selectivity of 1450 in the flat sheet configuration; therefore, the O<sub>2</sub> 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 those required to meet the size criteria. Although the CO<sub>2</sub>/O<sub>2</sub> selectivity is lower than needed, we demonstrated that the parameter is a strong function of methods used to impregnate the fiber. We made good progress in this area in a very limited amount of time and are continuing work to improve this important parameter. Finally, initial calculations indicate that SLM could be an effective technology to control CO<sub>2</sub> in the cabin.



While the results at this stage demonstrate good potential for the membrane to control CO<sub>2</sub>, additional testing is needed to improve the scale up estimates, address lifetime of the sorbent, and examine the effects of contaminants.

### Acknowledgments

The authors gratefully acknowledge funding for this work, which was provided by the NASA Small Business Innovative Research office under Contract NNX12CA65C.

### References

- <sup>1</sup> Barta, D.J. and Ewert, M.K. "Development of Life Support System Technologies for Human Space Exploration," SAE Paper 2009-01-2483, *39th Int. Conf. on Environmental Systems*, Savannah GA, 2009.
- <sup>2</sup> Barta, D.J., Ewert, M.K., Anderson, M.S., and McQuillan, J. "Life Support System Technology Development Supporting Human Space Exploration," SAE Paper 2008-01-2185, *38th International Conference on Environmental Systems*, San Francisco CA, 2008.
- <sup>3</sup> Swickrath, M.J., Watts, C., Anderson, M., Vogel, M., Colunga, A., McMillin, S. and Broerman, C. "Performance Characterization and Simulation of Amine-Based Vacuum Swing Sorption Units for Spacesuit Carbon Dioxide and Humidity Control", AIAA Paper 2012-3461, *42nd International Conference on Environmental Systems*, San Diego CA, 2012.
- <sup>4</sup> Papale, W. and Paul, H.L. "Development Status of an EVA-sized Cycling Amine Bed System for Spacesuit Carbon Dioxide and Humidity Removal", SAE Paper 2007-01-3272, *37th International Conference on Environmental Systems*, Chicago IL, 2007.
- <sup>5</sup> Koscielniak, A.A. and Akin, D. "Development and Testing of a Metabolic Workload Measuring System for Space Suits", SAE Paper 2007-01-3212, *37th International Conference on Environmental Systems*, Chicago IL, 2007.
- <sup>6</sup> Wickham, D.T., Gleason, K.J., Engel, J.R., Cowley, S.W. and Chullen, C. "Advanced Supported Liquid Membranes for CO<sub>2</sub> Control in Extravehicular Activity Applications," AIAA Paper No. 2013-3307, *43rd International Conference on Environmental Systems*, Vail CO, 2013.
- <sup>7</sup> Wickham, D.T., Gleason, K.J., Engel, J.R., Cowley, S.W. and Chullen, C. "Advanced Supported Liquid Membranes for CO<sub>2</sub> Control in Extravehicular Activity Applications," ICES Paper No 231, *44th International Conference on Environmental Systems*, Tucson, AZ, 2014.
- <sup>8</sup> Seter, A.J. "Allowable exposure limits for carbon dioxide during extravehicular activity," NASA TM-103832, 1993.
- <sup>9</sup> James, J.T. and Zalesak, S.M. "Surprising effects of CO<sub>2</sub> exposure on decision making," AIAA Paper No. 2013-3463, *43rd International Conference on Environmental Systems*, Vail CO, 2013.
- <sup>10</sup> Watts, C., Campbell, C., Vogel, M., and Conger, B. "Space Suit Portable Life Support System Test Bed (PLSS 1.0) Development and Testing," AIAA Paper 2012-3458, *42nd International Conference on Environmental Systems*, San Diego CA, 2012.
- <sup>11</sup> Swickrath, M.J., Watts, C., Anderson, M., McMillin, S., Broerman, C., Colunga, A., and Vogel, M. "Performance Characterization and Simulation of Amine-based Vacuum Swing Sorption Units for Spacesuit Carbon Dioxide and Humidity Control," AIAA Paper No. 2012-3461, *42nd International Conference on Environmental Systems*, San Diego, CA, 2012.
- <sup>12</sup> Papale, W., O'Coin, J., Wichowski, R., Chullen, C., and Campbell, C. "Rapid Cycle Amine (RCA 2.0) System Development," AIAA Paper No. 2013-3309, *43rd International Conference on Environmental Systems*, Vail CO, 2013.
- <sup>13</sup> Morgan, P.W. and S. Kwolek. "Interfacial Polycondensation. II. Fundamentals of Polymer Formation at Liquid Interfaces, *Journal of Polymer Science: Part A: Polymer Chemistry*, **34**, ppg. 531-559, 1996.
- <sup>14</sup> Hanford, A.J. "Baseline Values and Assumptions Document", NASA/CR—2004–208941, 2004.
- <sup>15</sup> Peters, M.S, K.D Timmerhaus, and R.E. West. *Plant Design and Economics for Chemical Engineers*, Fifth Edition, McGraw Hill, New York 2003.
- <sup>16</sup> Levri, J., J. Fisher; H. Jones, A.E. D Drysdale, M. K. Ewert, J. Hanford, J.A. Hogan, J. A. Joshi, D. A. Vaccari. Advanced Life Support Equivalent System Mass Guidelines, NASA/TM-2003-212278.Document