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Enzyme-Based Facilitated Transport: Use of Vacuum Induced Sweep for Enhanced CO_2 Capture

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ABSTRACT

The technologies for processing respiratory gases to support humans and plants and to provide material for regeneration of oxygen in Advanced Life Support applications remain far from optimal. Here we report on our ongoing efforts to develop an enzyme-based, hybrid, facilitated transport bioreactor for the efficient capture of CO_2 from dilute respiratory gas streams.

In this paper, we examine four different cases with respect to maintaining a driving force for removal of CO_2 from respiratory gas. These consist of employing each of the following on the sweep side of the reactor: 1) a relatively high flow rate of an inert sweep gas (in this case argon) at a nominal pressure of 101.3 kPa_{abs} (0 kPa gauge); 2) vacuum at a pressure of 16.3 kPa_{abs} (–85 kPa gauge); 3) a vacuum assisted flow of sweep gas (argon or air) flowing at a rate of 4 sccm (standard cubic centimeters per minute) and a pressure of 16.3 kPa_{abs} and, 4) a vacuum assisted flow of water vapor as the driving force for flow on the sweep side with or without the addition of argon or air as an added sweep gas.

Theoretical calculations show that the flow of an inert sweep gas, the application of a vacuum, and the combined application of vacuum with a small amount of sweep gas (fixed gas and/or water vapor) can result in effective removal of CO_2 from respiratory gas, provided the CO_2 driving force is maintained. The experimental data are in good agreement with the theoretical results. They show that any condition using a sweep gas can result in effective removal of CO_2. Theory also confirms that, as was observed, without an added sweep gas the sweep side pressure of 16.3 kPa_{abs} should not be effective. Furthermore, we calculate that with appropriate combinations of temperature and vacuum pressure it is possible to get effective CO_2 removal using water vapor alone as the sweep gas. This strategy results in a situation where it is possible to obtain a dry gas product from the permeate side that is extraordinarily enriched in CO_2. This work provides further evidence that our system will be suitable for all NASA applications in low Earth orbit (LEO - ISS, SS and EVA), as well as for long-term expeditions, e.g., to the moon or to Mars.

INTRODUCTION

Lab scale reactor systems based on the concept of an enzyme based contained liquid membrane (EBCLM) have shown good performance for the capture of CO_2 from respiratory gas [1-3]. However, as reported elsewhere [4], the driving force for separation is generally provided through use of an inert sweep gas (usually argon or helium). As a consequence the separation results in a dilution of the permeate gas (into the sweep gas). Under these conditions it is very difficult to get high purity CO_2. The use of a sweep gas would not be convenient in the case where a sweep gas is not readily available, e.g., spacecraft. Additionally, if the sweep gas used is dry or only partially humidified its use can lead to the evaporation of water from the liquid membrane. Unless appropriate water and buffer management steps are taken loss of water can lead to decreased performance and in the extreme to failure. The traditional approach to this problem is to humidify the feed and sweep gas. It has not succeeded in preventing all evaporation [1].

The EBCLM operates as follows to separate CO_2 from mixed gas streams: CO_2 in the feed stream is enzymatically hydrated to bicarbonate by means of carbonic anhydrase (CA – E.C.4.2.1.1), bicarbonate ions diffuse through the bulk phase which consists of a phosphate buffer solution and the CA at the permeate membrane surface dehydrates the bicarbonate ions which are then released as CO_2 [1-3,5].

Thus, CO_2 is separated from N_2 and O_2 because it's hydration to HCO_3^- at the interface effectively increases its solubility many fold [6]. Although CA makes the hydration reaction and the dehydration reaction occur very fast it does not change the ultimate driving force for CO_2 transport. This driving force is the partial pressure difference across the membrane, i.e., the total pressure multiplied by the mole fraction of CO_2 in the gas phase on one side versus the total pressure times the mole fraction of CO_2 on the other side as is expressed in Equation 1.

$$\Delta P = P_1 - P_2 = P_{T1}[CO_2]_1 - P_{T2}[CO_2]_2 \tag{1}$$

P_1 is the feed side partial pressure, P_2 is the permeate side partial pressure, P_{Ti} is the total pressure on the appropriate side and $[CO_2]_i$ is the mole fraction of CO_2 (or $\%CO_2$) on the appropriate side. The rate of transport or flux per unit area (J) is then a function of the permeance, K, and the ΔP as expressed in Equation 2.

$$J = -K * \Delta P \tag{2}$$

Thus, if we take any given feed stream with a constant partial pressure of CO_2 as P_1 we see that P_2 (and the membrane area) must be manipulated to provide the necessary flux and that P_2 must be less than P_1 to favor transport to the permeate side. Furthermore, the greater the ΔP the larger the flux.

EXPERIMENTAL APPARATUS

TEST CELL CONFIGURATION - Figure 1 illustrates the test cell. It consists of a stainless steel body for delivery and recovery of gases. The housing is held at constant temperature. The liquid core is retained by hydrophobic, microporous, polypropylene membranes (Celgard PP-2400). These isolate the liquid membrane preventing leakage and minimizing evaporation. The polypropylene membranes are each supported by a perforated metal sheet. The liquid membrane, containing the sodium and potassium phosphate buffered CA solution(pH 8), was accessible to a fluid reservoir to replace any water that might be lost. A nylon mesh was used as the spacer to control the thickness of liquid phase and as the conductor to the reservoir.

Figure 2 is a schematic representation of the test stand. Air and argon (Matheson) were treated to remove all remaining traces of CO_2. A mass spectrometer (ABB Extrel) was used to provide real time online analysis of the composition of feed and sweep streams.

RESULT AND DISCUSSION

EFFECT OF SWEEP GAS - Figure 3 shows the effect of different flow rates of argon sweep gas on separation performance for the separation of CO_2 from air containing 1% CO_2. Under these conditions the partial pressure driving force across the membrane depends on the ratio of the flow rate of argon and the rate of CO_2 transport. As shown in figure 4 the observed driving force for the given conditions ranges from 0.83 to 0.90 kPa.

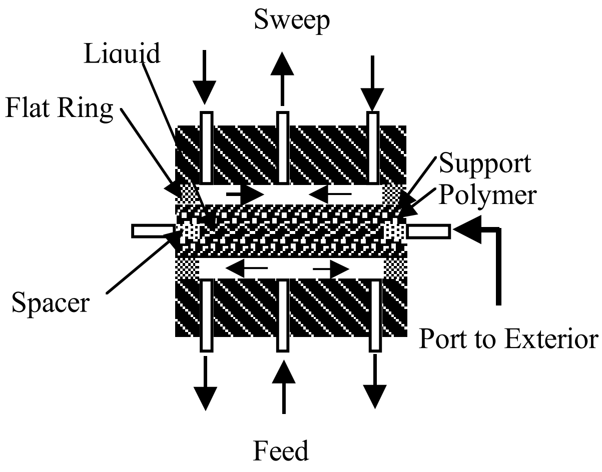
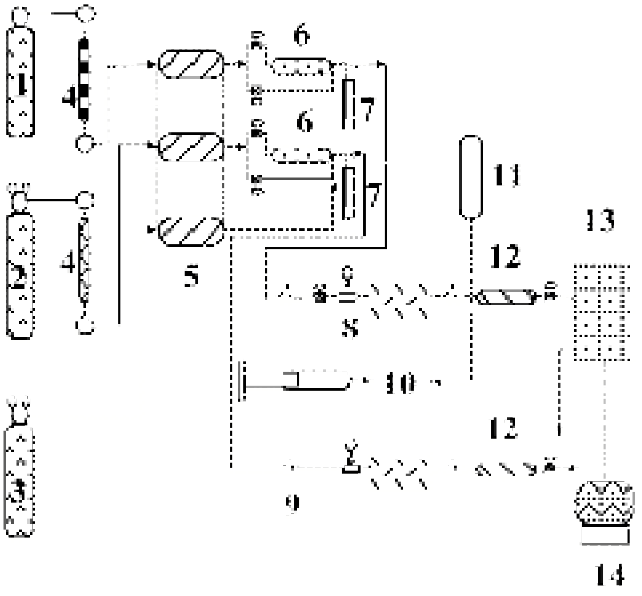


Figure 1 Schematic Representation of the Test Cell.

CO_2 in the feed is 1% in air at 101.3 kPa_{abs} yielding a P_{CO2} of 1.013 kPa; the sweep gas is CO_2-free argon at 101.3 kPa_{abs} The experiment was run at 20°C, with a membrane thickness of 330μm, a pH 6.94, sodium and potassium phosphate buffer at 20 mM, and a CA concentration of 1 mg/ml. The effective surface area for transfer is 62 mm^2. Therefore, the theoretical maximum driving force is 1.013 kPa. Combining the information in figures 3 and 4 , we find that the small change in driving force (~7%) that occurs with the change in flow rate from 3 to 12 sccm has little effect on selectivity (or permeance – not shown). Therefore it appears that, at least over this range, the driving force is not the limiting determinant of flux.

EFFECT OF SWEEP SIDE VACUUM - As our goal is to use this system in space where a hard vacuum is readily available we evaluated the use of a vacuum sweep effect on the separation performance of removing CO_2 from air. While space vacuum can theoretically provide a vacuum pressure of >100 kPa_{gauge} (1.3 kPa_{abs}) (maximum possible being 0kPa_{abs}) we used a laboratory vacuum pump that provided a moderate vacuum pressure of –85 kPa_{gauge} (16.3 kPa_{abs}).



1- Ar
2- Air
3- CO_2
4- CO_2 purified column
5- Mass flow controller system
6- Humidifier
7- Trap
8- Pressure gauge
9- Temperature/humidity Sample port
10- Test cell
11- Reservoir
12- Mass flow meter
13- Mass Spectrometer
14- Computer

Figure 2. Schematic representation of the test stand.

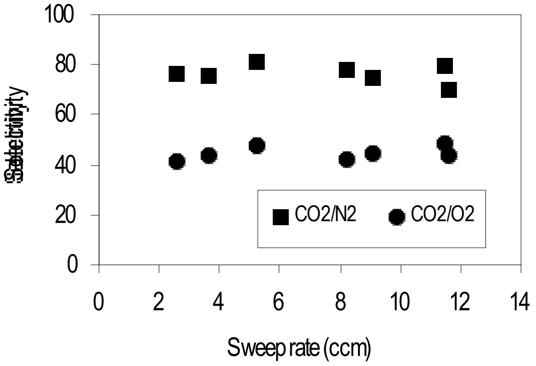


Figure 3. Effect of sweep rate on selectivity.

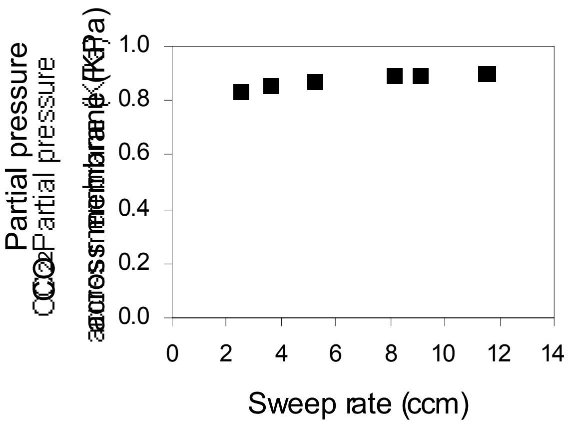


Figure 4. Effect of sweep rate on CO_2 driving force.

The data in figure 5 illustrate the effect of three sweep side conditions on the removal of CO_2 from air. The three conditions tested are: a sweep side pressure of 16.3 kPa_{abs} with no added sweep gas; a sweep side pressure of 16.3 kPa_{abs} with 4 sccm of argon added as the sweep gas; and, a sweep side pressure of 16.3 kPa_{abs} with air added as the sweep gas. The influent air (feed side) containing 0.1056% CO_2 was delivered at a pressure of 101.3 kPa_{abs} at a nominal flow rate of 4 sccm. However, the flow rate was observed to vary over the range of 2.75-4.28 sccm. In these experiments the EBCLM was operated with an effective surface area for transfer of 62 mm^2, a CA concentration of 5 mg/ml, a pH 8.0 potassium and sodium phosphate buffer at 75 mM, and a membrane thickness of 330μm.

The data in figure 5 illustrate the CO_2 concentration in the treated (i.e., effluent) feed side air. From a quick look at the data it is easy to see there is a vast difference in the ability of the reactor to remove CO_2 from air when the vacuum is applied alone versus application of the vacuum with the addition of a sweep gas. Furthermore, there is very little difference between the amount of CO_2 removed from the feed side air when CO_2-free argon or air containing 0.035% CO_2 is used as the sweep gas added with the vacuum.

It is apparent from the data that it was not possible to maintain the removal of CO_2 from the feed stream when using a sweep side pressure of 16.3 kPa_{abs} with no added sweep gas. Instead there is a transient removal of CO_2 that appears to be decaying to a condition of no detectable removal. This transient condition is consistent with the removal of CO_2 from the feed stream that occurs as the buffer solution within the liquid membrane loads with dissolved CO_2 and bicarbonate (i.e., it comes into equilibrium with the feed stream). This occurs because under the given conditions only a very small amount of CO_2 will exit to the sweep side because the only mechanism available for movement of the CO_2 away from the membrane is molecular diffusion and the vacuum strength is insufficient to maintain an effective driving force. In other words, because the maximum feed side P_{CO2} is 0.1070 kPa the driving force for CO_2 transport will fall 0 kPa when the sweep side P_{CO2} becomes 0.1070 kPa. This is equivalent to a CO_2 concentration of 0.6563%. Because the conditions are such that, given the selectivity for CO_2 versus O_2 and N_2, the permeate should contain >50% CO_2, and no other sweep flow is being provided to dilute the permeate, the CO_2 accumulates. Thus the vacuum strength was insufficient to maintain the CO_2 driving force.

When 4 sccm of argon is used as an added sweep gas at a pressure of 16.3 kPa, the removal of CO_2 from the feed side was rapid and sustainable. Under these conditions the feed side concentration dropped to 0.0774% (0.0784 kPa). Assuming the feed flow rate is the target nominal value of 4 sccm during the period that this near steady state condition existed the effluent sweep side concentration is 0.0282% (0.00460 kPa). Therefore the maximum and steady state driving force under the conditions of 4 sccm argon sweep at 16.3 kPa are 0.1070 kPa and 0.0738 kPa, respectively. While the driving force is approximately 1/10th of that applicable for the conditions used for collecting the results shown in figures 3 and 4, it is more than adequate for driving the removal of CO_2 from air.

With the application of a sweep stream of 4 sccm of air containing 0.035% CO_2 at a pressure of 16.3 kPa the driving force for CO_2 transport is reduced from that applicable when argon is used under similar conditions. This reduction in driving force occurs due to the partial pressure of CO_2 contributed by that in with the air. This added P_{CO2} = 0.0057 kPa. From the data illustrated in figure 5 we estimate that the steady state feed side [CO_2] = 0.0805% (0.0815 kPa). Therefore at steady state the sweep side P_{CO2} = 0.0098 kPa. The maximum and steady state driving force under the conditions of 4 sccm air sweep at 16.3 kPa are 0.1013 kPa and 0.0707 kPa, respectively. As this steady state driving force is only 4.2% weaker than that for argon/vacuum it is not surprising that the steady state removal of CO_2 differs by less than 5%.

These results invite the question as to what the maximum driving force might be if the only air available for CO_2 extraction were the 0.1% CO_2 feed side air. Under this condition with a sweep pressure of 16.3 kPa and 0.1% CO_2 in air the minimum sweep side P_{CO2} = 0.0163 kPa. Therefore the maximum driving force for CO_2 transport would be 0.1070 – 0.0163 = 0.0907 kPa. The data above show this to be sufficient.

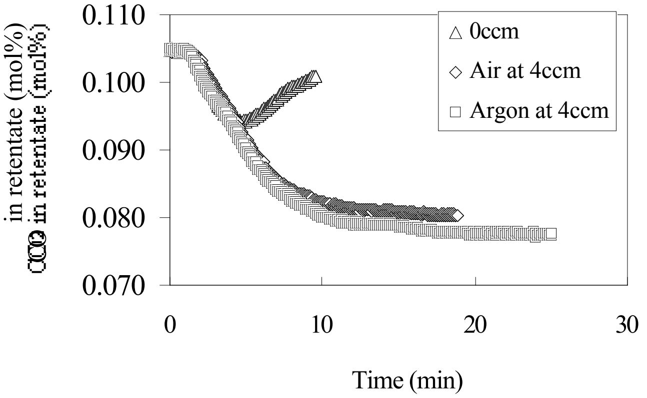


Figure 5. Effect of vacuum vs. vacuum plus sweep on CO_2 removal. These measurements are of the retentate, thus the curve inversion.

USE OF WATER VAPOR AS SWEEP GAS – Liquid water does not pass through the microporous polymer membrane used to contain the liquid membrane, but water vapor can. Therefore even if no sweep gas is provided or a dry sweep gas is used water vapor can exit the liquid membrane. The maximum extent to which this can occur is defined by the vapor pressure of water at the temperature of reactor operation. Experimentally we have observed that in all cases, even with a dry sweep gas delivered at higher flow rates (>10 sccm), the maximal degree of evaporative humidification occurs. This phenomenon presents several issues that are addressed in this section. The most important are the potential problems associated with water loss from the liquid membrane and the advantages that can be derived through the purposeful delivery of water vapor as a sweep gas.

The potential problems associated with loss of water from the liquid membrane include loss of liquid membrane integrity and changes in the concentration of the buffer and the CA. The potential for loss of liquid membrane integrity is eliminated by use of a contained liquid membrane supplied with an external solvent reservoir.

The potential advantages of the purposeful delivery of water vapor as the sweep gas (alone or in combination with a fixed gas like air or argon) derive from the fact that it can be readily separated from the permeate gases. Thus, the use of a vacuum induced flow of water vapor provides a regenerable sweep gas and a method for obtaining high concentrations of CO_2 as a product from the reactor.

This design, based on the use of water vapor as the sweep gas, works as follows: at an appropriate temperature and vacuum pressure are used to evaporate water from a sweep side reservoir (rather than from the liquid membrane). This evaporated water can make up either a portion of the sweep gas (e.g., with air or argon) or all of the sweep gas. All that is required is a vacuum pressure is low enough to make the water vapor a substantial portion of the sweep flow. Figures 6, 7 and 8 illustrate the potential for using this approach.

Figure 6 illustrates calculated values for CO_2 concentration versus permeate side vacuum pressure for the following conditions: feed side of air with 0.1% CO_2; sweep side at vacuum pressures and temperatures given on the plot. This feed side condition is illustrative of the conditions that might be used in a ALS system such as the ISS. The curve labeled with the filled diamond symbols shows the CO_2 concentration that can be achieved at a given vacuum pressure and any temperature when water vapor and any other sweep gas are included. The values given on that curve are the sweep side concentrations at which the partial pressure of CO_2 equals the feed side P_{CO2}. The other curves represent the CO_2 concentrations that can be achieved if all of the water vapor is removed, leaving CO_2, the other permeate gases, and any applied sweep gas. The difference between each of these other curves is the temperature of operation.

From the data given in figure 6 it is apparent that higher temperatures enable one to obtain higher dry sweep gas CO_2 concentrations at lesser vacuum strengths. This follows from the increased vapor pressure of water as a function of temperature. While these calculations define the conditions under which 100% CO_2 sweep could be obtained, in reality this is cannot be attained as other gases will permeate the liquid membrane as determined by the membrane selectivity.

For selectivity values of CO_2:O_2 of 3000 and CO_2:N_2 of 5000 given a feed of 79% N_2, 20.9% O_2, 0.1% CO_2 we calculate that the dry permeate, undiluted with any sweep gas (i.e., water vapor sweep gas), would contain: 81% CO_2, 13% N_2 and 6% O_2. For all values lower than maximum CO_2 concentration (ca. 80%) this, at any temperature, indicate that another sweep gas is being used in addition to water vapor.

Figure 7 shows the case for EMU-EVA application where the feed pressure is 29.6 kPa and CO_2 concentration is 0.5% in O_2. The results obtained here are similar to those for the ISS or SS case (above). The small difference in the feed side P_{CO2} changes the theoretically obtainable sweep side P_{CO2}. In this case the maximum dry permeate CO_2 concentration at a CO_2:O_2 selectivity of 3000 is 94% CO_2 and 6% O_2.

Figure 8 plots vacuum pressure against temperature to attain 50% pCO_2 in the permeate stream for each of the three test conditions with water vapor as the sweep gas. The curves for the several cases are very similar. This shows that ours is an effective means of capturing CO_2 from respiratory gas feed streams using the EBCLM design.

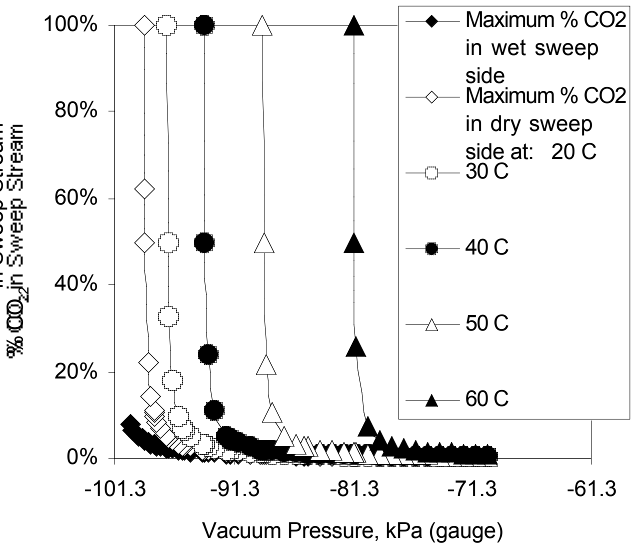


Figure 6. Calculated CO_2 concentration in the dry sweep gas versus the vacuum pressure when the feed is with CO_2 of 0.1% and at 1atm.

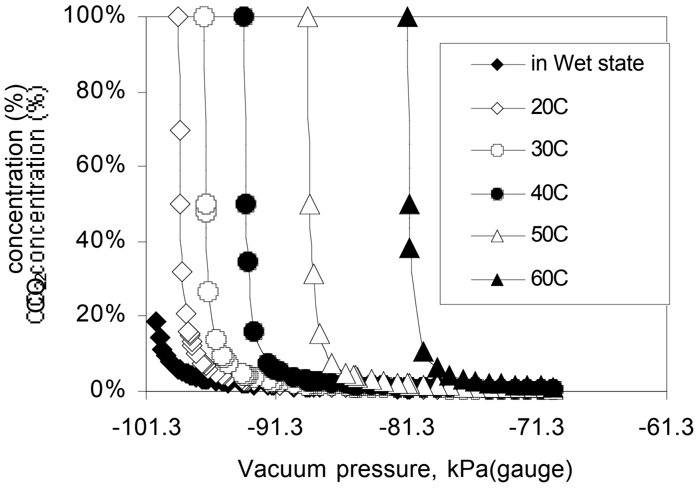


Figure 7. The estimated CO_2 concentration in the dry sweep gas versus the vacuum pressure when the feed is with CO_2 of 0.5% and at 29.6 kPa (EMU).

CONCLUSION

This report shows that a partial vacuum, used in conjunction with a modest sweep stream in our enzyme-based contained liquid membrane (EBCLM) separator/reactor, can provide the driving force necessary to capture CO_2 from respiratory gas stream. The separation under these conditions is quite similar when using an inert sweep gas or room air. In addition we show that water vapor can be an effective sweep gas. This converts a potential problem, viz. vacuum aided evaporative loss, into a substantial benefit. We also show that with the correct selection of operating parameters – vacuum force, temperature (and selectivity) the EBCLM

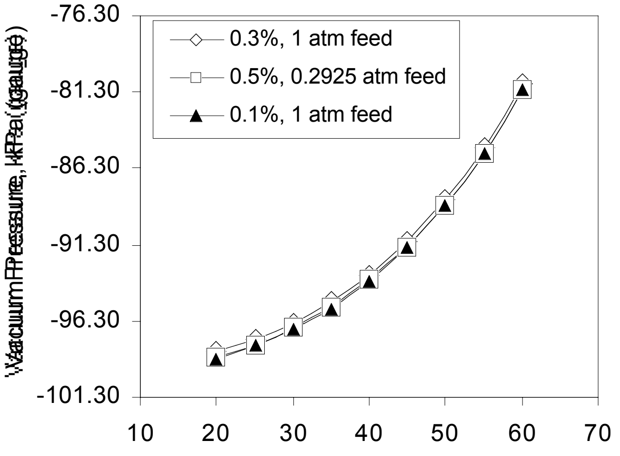


Figure. 8. Calculated experimental condition: Temperature of bypassing gas (water vapor) versus vacuum.

is capable of generating a gas stream that is significantly enriched after only a single pass across a single membrane.

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REFERENCES

1. Trachtenberg MC, Tu CK, Landers RA, Willson RC, McGregor ML, Laipis PJ, Kennedy JF, Paterson M, Silverman DN, Thomas D, Smith RL, Rudolph FB. Carbon dioxide transport by proteic and facilitated transport membranes. *Life Support & Biosphere Sciences*, **6**:293-302.1999.
2. Trachtenberg MC, McGregor ML, Tu CK, Laipis PJ, Willson RC, Kennedy, JF, Paterson M, Rudolph FB. Enzyme-enhanced membranes for gas separation. *29th Intl. Conf. Environ. Sys.,* Denver, CO, July 1999. SAE 99ES-72
3. M.C. Trachtenberg, J.-J. Ge, Biomimetic strategy for carbon dioxide capture, Bioastronautics Investigators' Workshop, January 17-19, 2001, Galveston, Taxas, p218-219
4. A.K. Guha, S. Majumdar and K. K. Sirkar, Facilitated transport of CO_2 through an immobilized liquid membrane of aqueous diethanolamine, *Ind. Eng. Chem. Res.*, **29**(10)(1990)2093-2100
5. N.C. Otto and J.A. Quinn, The facilitated transport of carbon dioxide through bicarbonate solutions. *Chem. Eng. Sci.*, **26**(1971)949-961
6. C.K. Tu, D. N. Silverman, C. Forsman, Role of histidine 64 in the catalytic mechanism of human carbonic anhydrase II studied with a site-specific mutant. *Biochemistry*, **28**(1989) 7913-18.

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

LEO – low Earth orbit

ISS – international space station

SS – space shuttle

EMU – extravehicular mobility unit

EBCLM – enzyme-based contained liquid membrane

SLM – supported liquid membrane

CLM – contained liquid membrane

CA – carbonic anhydrase

sccm – standard cubic centimeters per minute

EVA – extravehicular activity

RH – relative humidity