

CO₂ Capture by Enzyme-Based Facilitated Transport

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ABSTRACT

Carbon dioxide (CO₂) control is crucial for crew inhabited space-flight. Existing systems suffer from high consumable usage rates (e.g., LiOH), high mass and/or volume, and/or high energy costs associated with regeneration of CO₂ adsorption capacity (e.g., metal oxide). Any new technology must be safe, reliable and have low EMS - small volume, low mass, low rate of energy use, minimal use of consumables, and little need for crew time for operation and maintenance.

Our enzyme catalyzed contained liquid membrane facilitated transport reactor/separator for the selective capture of carbon dioxide (CO₂) from mixed gas streams satisfies these requirements. The liquid membrane is held in place by hydrophobic microporous polypropylene membranes. This continuous process design is ideally suited to CO₂ concentrations ranging from 0.035% to 1% or even higher. The system is stable and can accept feed or sweep gases independent of relative humidity. This study explores the effect of electrodiffusion on CO₂ permeance and selectivity.

INTRODUCTION

CO₂ can be removed from dilute gas streams by a variety of physical and chemical methods. NASA has used and explored many of these since the start of the space program. The equipment that underlies these methods tends to be heavy, to require considerable power or the reactions are irreversible necessitating ever larger device volumes and masses or replacement consumables for longer missions. NASA is desirous of a smaller, lighter, regenerable systems to support more ambitious projects.

We have developed a novel, enzyme-based, contained liquid membrane (EBCLM) reactor to capture CO₂ from the respiratory gas stream and to enrich it for disposal,

distribution to a plant growth chamber or for delivery to a CO₂ reduction apparatus.

The enzyme carbonic anhydrase (CA – E.C. 4.2.1.1), used as the CO₂ facilitating agent, is the fastest CO₂ catalyst known. It accelerates the conversion of CO₂ to bicarbonate and the converse by about 2000-fold vs. the uncatalyzed condition. The membrane design is such that there are three steps to the extraction-transfer process. In the first CO₂ is converted to bicarbonate at the feed side gas-liquid interface. Second, the bicarbonate diffuses across the membrane. Third, at the sweep side gas-liquid interface the enzyme converts bicarbonate to CO₂ which then evolves into the sweep stream exiting the reactor as the permeate. With CA in excess bicarbonate diffusion is the key rate limiting step. At the same time non-CO₂ gases will dissolve into the liquid membrane, diffuse across the membrane and effuse into the sweep stream. In this case limited solubility and diffusivity are the rate limiting step.

Due to differences in diffusion rates of the various ions and other solutes there are inherent gradients across the membrane. Electrodiffusion (ED) has been suggested as a means of increasing bicarbonate diffusion while not improving the rate of diffusion of N₂ or O₂, thereby increasing CO₂ permeance. ED has been examined in relatively dilute (<100 mM) and relatively simple ionic solutions [Gallagher et al., 1986a; Athayde & Ivory, 1985; Selegny et al., 1983]. Ivory and colleagues used AC signals, Selegny and colleagues primarily DC. ED has also been examined in very simple but concentrated solutions (>3M) where it is used routinely for rapid recharging of modern batteries. However, the data regarding complex ionic solutions, at medium concentrations, where the object is gas permeance are not worked out.

Literature data suggest that the more complex the ionic mixture and the higher its concentration (in excess of 100mM) the more difficult and complicated the ED operation should become.

Our goal in these experiments was to examine ED as a means of increasing CO₂ diffusion thus increasing CO₂ permeance, selectivity of CO₂ vs. N₂ and O₂ and thus the concentration in the permeate.

METHODS

A National Instruments model NI5411, Arbitrary waveform generator was used to provide DC or AC signals. In a first effort Pt-Ru electrodes contacted the gas sides of the Celgard PP2400 polypropylene membranes. The membrane impedance was measured. In a second effort the electrodes were placed at the membrane liquid interface. This was tested first by use of a crude but effective aluminum sheet electrode. Once proven to provide at least a minimal effect it was replaced by gold coating the polypropylene membranes. This was done by means of vapor deposition using a sputter coating apparatus. Electrodiffusion signal consisted of an offset square wave with duty cycle set to provide a net current of 0.0 amps. The frequency of the signal was varied in order to find the optimum value. The amplitude of the signal was varied to provide for a greater or lesser charge density. A functional limit on the acceptable amplitude occurs because applied voltages of +/- 1.23 V or more are sufficient to cause electrolysis of water with greater amounts of electrolysis expected at higher amplitudes (higher current densities).

Calculation of the optimal signal parameters was based on the concentration gradient and diffusivities of each of the ionic species present across the membrane. Using the equations provided by Athade and Ivory [1985] as modified based on the work of Selegny et al [1983] we designed the appropriate waveform and frequency profile.

RESULTS

GAS SIDE ELECTRODES

Initial calculations of waveshape and frequency indicated that the very high membrane impedance of the polypropylene film would not be too problematic at high frequencies (Fig. 1). Re-analysis of the situation revealed the need for low frequency signals (~1-10 Hz).

From direct measurement with the assembled liquid membrane and from the data in Figure 1 we found at these low frequencies the polymer membrane presents an effective resistance of >10MΩ. This high resistance and the need to maintain low voltage potentials so as to avoid or at least minimize water electrolysis severely limited the current available for ED enhanced ion transport. Therefore it is not surprising that the application of current under these conditions failed to yield any effect on separation performance. The applied current, on the orders of one microampere, would provide an ion flux orders of magnitude less that of the unassisted diffusive flux. In other words, with the electrodes placed on the gas side the electrical

resistance presented by the polymer membrane ensured the current density was insufficient to affect CO₂ permeance.

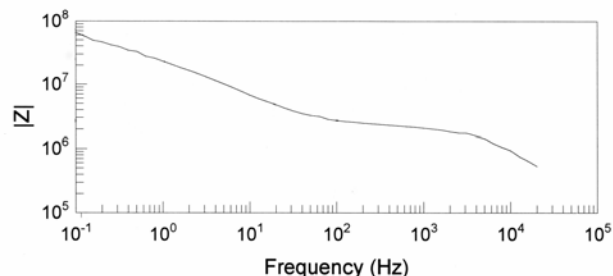


Figure 1. Impedance measurement of the polypropylene membrane. The high impedance prevented direct transmembrane electrodiffusion.

LIQUID SIDE ELECTRODES

Because it turned out to be infeasible to provide an ED derived benefit with gas side electrodes it was necessary to move to the use of liquid side electrodes. This work was initiated through use of a crude perforated aluminum foil electrode. This electrode was placed inside the liquid membrane reactor between the polymer membrane and the liquid phase. Figure 2 presents the data collected through the use of this assembly. The data show a clear, although small, benefit where the CO₂ permeance increased ~6%.

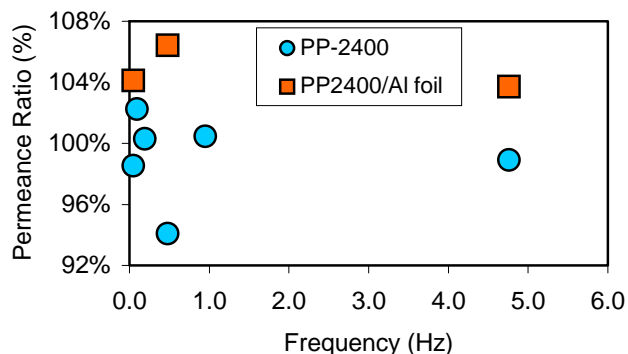


Figure 2. Influence of frequency on permeance (ratio to permeance without applied voltage) observed using a square wave having a magnitude of +2.2 and -1.5 volts. No current = 100%. Blue circles, current applied across the polypropylene membrane with gas side electrodes. Orange squares, current applied via perforated aluminum foil with liquid side electrodes.

To move to a more sophisticated design we utilized metal sputter coating methods to surface coat the polypropylene with a gold film (Figure 3) to serve as the electrode. In view of the very high resistance of polypropylene (~10MΩ) it was necessary to create electrodes at the gas-liquid interface. The gold layer did not greatly decrease the gas transport as shown in

Figure 4. The electrical resistance of the assembled liquid membrane with the gold coated polypropylene electrodes was approximately 300-500Ω. Using the gold electrode we delivered sufficient current to effect changes in bicarbonate flux. With this approach we have demonstrated very much more substantial improvements in CO₂ permeance and selectivity. As shown in Figure 5 imposition of a signal of +3.25V to -1.17V now results in a 19.1% increase in CO₂ permeance.

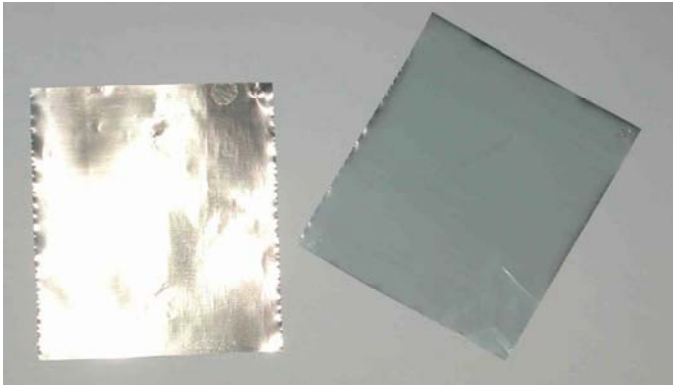


Figure 3. Photograph of gold coated polypropylene membrane. Membrane on left is gold coated, membrane on right is uncoated.

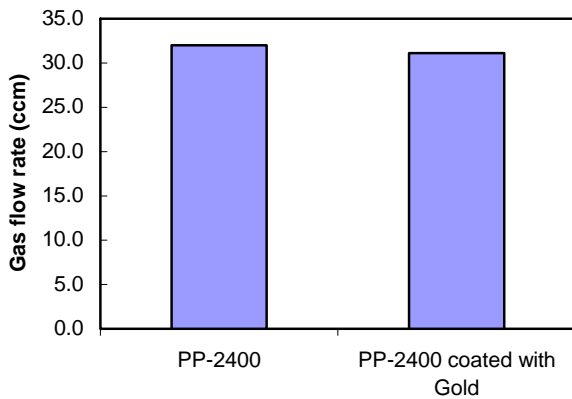


Figure 4. Comparison of transmembrane gas flow rate of the native membrane (left) and the gold coated membrane (right).

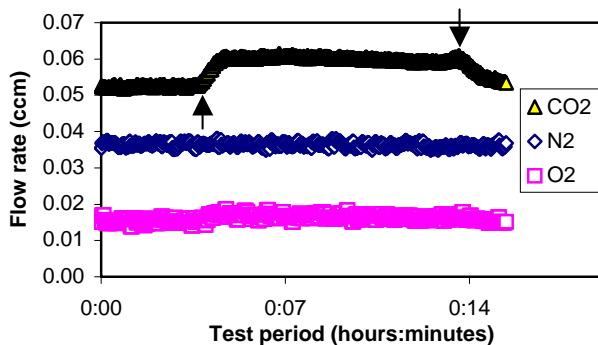


Figure 5. Increase in CO₂ flux due to application of electrodiffusion (voltage +3.25 to -1.17 volts; PO₄ buffer, 0.5% CO₂ in air). Arrows indicate time at which current was turned on (up) and off (down).

Figures 6 and 7 further illustrate the results achieved through use of ED with the gold coated polymer electrodes. While Figure 5 illustrates the raw data from one experiment Figure 6 and 7 present a summary of data from several experiments. In Figure 5 the up arrow indicated the time at which the ED signal was turned on, the down arrow the time the current was turned off. It is clear from the data that the applied current provided a significant increase in CO₂ flux. The data also show a small increase in the flow rate of O₂ in the permeate during the ED period. This increased oxygen flow rate was due not to increased O₂ flux across the liquid membrane, but to O₂ production from hydrolysis of water. Figure 6 shows the effect of using different frequencies of the same waveform shape and voltage on the performance improvement achieved through use of ED. The data show increasing benefit with increasing frequency over the range of 0.00588 to 0.588Hz. Further increases in frequency led to decreases in the benefit of ED as is illustrated for 5.88Hz. This behavior is consistent with the generalized behavior of AC driven ED theoretically predicted by [Athayde and Ivory \(1985\)](#). Figure 7 displays the effect of increasing driving force (voltage) at the optimal frequency of 0.8Hz. The data are shown in terms of current density. They illustrate that increased current density can provide much higher benefits. Unfortunately the benefit derived at the highest current density given was short lived due to increased electrolysis of water.

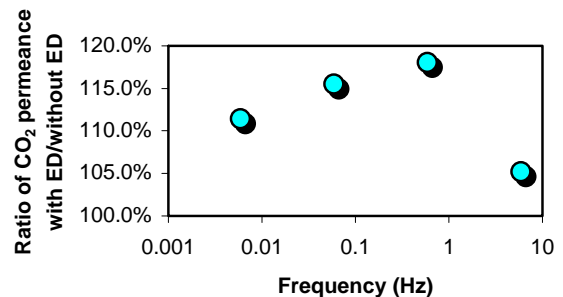


Figure 6. Influence of electrodiffusion pulse frequency on permeance.

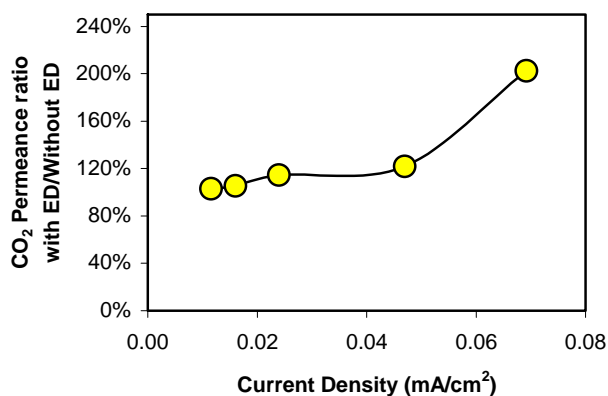


Figure 7. Effect of current density on CO₂ permeance at “optimal” frequency. Note: for these conditions (50 mM PO₄ buffer) a current density of > 0.016 mA/cm² can only be obtained for voltages that cause electrolysis of water.

CONCLUSION

The data clearly support the hypothesis, that ED can drive and enhance CO₂ permeance while not affecting that of nitrogen from the feed gas stream. However, if water is electrolyzed then the apparent oxygen flux increases as a by-product. In the current experiments the magnitude of the improvement at acceptable current densities is too small, <20%, for effective use of this approach in other than a laboratory sized demonstration reactor. It is possible that other pulse profiles or the use of other liquid membrane chemistry may yield greater benefits. Research is ongoing to examine this issue.

ACKNOWLEDGMENTS

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Dr. Trachtenberg received his doctorate at UCLA. He has held academic positions at Harvard Medical School, Boston University School of Medicine and the University of Texas Medical Branch. He co-founded a biotechnology company and is presently Director of the Sapient’s Institute, 20 Ag Extension Way, New Brunswick, NJ 08901, Ph. 732.932-8878, e-mail miket@aesop.rutgers.edu.

DEFINITIONS, ACRONYMS, ABBREVIATIONS

EBCLM: Enzyme-based contained liquid membrane

ED: electrodiffusion