

Carbon Dioxide Collection and Pressurization Technology

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The Martian atmosphere is composed of about 95% carbon dioxide which can be processed to produce useful consumables such as oxygen and methane. Leading technologies for processing CO₂ are solid oxide electrolysis (SOE), reverse water gas shift (RWGS) and the Sabatier reaction. Typically, these processes require high purity, pressurized carbon dioxide to obtain a significant feed rate. Reactive Innovations has developed an electrochemically-driven technology platform which can be customized to fulfill the many individual separation requirements of ISRU technology processing streams. In recent NASA-funded programs, our technology was shown to be highly adaptable in performing selective separation of species from gas and liquid streams. Recent work has utilized this general approach to not only separate but pressurize carbon dioxide. In addition we applied this reactive chemistry to our tubular reactor platform for further advantages in reducing weight and volume for space-based applications. Specifically our results have shown that selective customization of the individual components of the supported ionic liquid membrane can maximize CO₂ separation from varying gas mixtures and demonstrate pressurization to greater than 15 psia. These results are discussed with respect to ISRU applications.

Nomenclature

ISRU	= In Situ Resource Utilization; using resources at the site of exploration
SOE	= solid oxide electrolysis
RWGS	= reverse water gas shift reaction
SILM	= supported ionic liquid membrane
MEA	= membrane electrode assembly
IL-PVDF	= ionic liquid polyvinylfluride composite membrane
mil	= unit of length equal to 0.001 inch
psia	= pressure measurement in pounds per square inch, absolute; includes atmospheric pressure

I. Introduction

Mars is the ultimate destination of NASA's human exploration program. In Situ Resource Utilization (ISRU) is a key technology required to enable such missions. The goals of using resources that are available at the site of exploration and pursuing the philosophy of "living off the land" instead of bringing it all the way from Earth are to achieve a reduction in launch and delivered mass for exploration missions, a reduction in mission risk and cost, enable new missions not possible without ISRU, and to expand the human presence in space. Past studies have shown making propellants and other mission critical consumables (life support and power) in situ can significantly reduce mission mass and cost,¹ and also enable new mission concepts.

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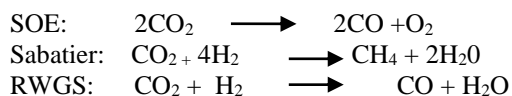
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Table 1. Mars atmosphere composition²

Viking atmospheric measurements		
Composition	95.32%	carbon dioxide
	2.7%	nitrogen
	1.6%	argon
	0.13%	oxygen
	0.07%	carbon monoxide
	0.03%	water vapor
	trace	neon, krypton, xenon, ozone, methane
Surface pressure	1-9 millibars, depending on altitude; average 7 mb	

While NASA's understanding of Mars' resources continues to evolve--significantly with the recent indication of the presence of water, a well-known resource is in the Martian atmosphere. The Martian atmosphere (Table 1) is composed of about 95% carbon dioxide which can be processed to produce useful consumables such as oxygen and methane. Leading technologies for processing CO₂ are solid oxide electrolysis (SOE), reverse water gas shift (RWGS) and the Sabatier reaction. The SOE process dissociates Martian CO₂ into O₂ and CO via a high temperature (~1000°C) electrochemical process through a thin zirconia membrane. The Sabatier and RWGS processes use a catalyst to react CO₂ with H₂ to produce

CH₄, and H₂O, and CO and H₂O respectively. The chemical processes are shown below:



Typically, these processes require high purity, pressurized carbon dioxide to obtain a significant feed rate. Currently the goal is to supply a Sabatier reactor with 88g CO₂/hr at 50 psia.³ To meet this goal, there have been a variety of methods studied to capture and pressurize carbon dioxide from the Martian atmosphere including: freezing at cryogenic temperature, mechanical compression, liquefaction at high pressures, adsorption pumping, separation using membranes, sorption by ionic liquids in both liquid form and supported membranes, acid-base reaction with amines, preparative chromatography, and molecular sieves. A recent study conducted by NASA³ concluded that freezing was the most advantageous of these when considering power usage, collection rate, and CO₂ purity. However, the freezing technology requires ancillary storage tanks adding to the mass and volume of the CO₂ collection system.⁴

Another important application for CO₂ separation technologies involves air revitalization where excess carbon dioxide must be removed from the cabin of spacecraft and spacesuits. Some separation technologies being considered for this application include physical, centrifugal processes, adsorption (pressure swing) techniques,⁵ and chemical absorption processes. These processes will have varying applicability depending on the reactant stream. Our approach relies on a self-regenerating supported ionic liquid membrane, where a redox carrier selectively binds and releases carbon dioxide into a pressurized gas stream which can be fed directly into the ISRU reactive processes.

II. Technical Approach

Reactive Innovations has developed an electrochemically-driven technology platform which can be customized to fulfill the many individual separation requirements of ISRU technology processing streams. The enabling component of our technology capitalizes on the unique customizable properties of ionic liquids in performing room temperature efficient separations. In recent NASA-funded programs, our technology was shown to be highly adaptable in performing selective separation of species from gas and liquid streams. In one program, we demonstrated carbon dioxide separation from a CO₂/N₂ stream at varying concentrations using a planar electrochemically modulated cell. Our recent work utilizes this general approach to not only separate but pressurize carbon dioxide. In addition, we are applying this reactive chemistry to our tubular reactor platform for further advantages in reducing weight and volume for space-based applications.

Our technology relies on a facilitated transport mechanism. The concept proceeds through the redox binding affinity of a carrier molecule. In the reduced state this molecule binds CO₂. By changing the potential, the carrier is oxidized and CO₂ is released. The redox carrier is carefully selected to maximize the "swing" in the redox potential to increase the effective binding and release of CO₂.

In our concept, an ionic liquid is used to dissolve the redox carrier molecule. The ionic liquid medium is an enabling component for demonstrating facilitated transport for this space application because of its many advantageous properties, which include near zero vapor pressure, wide liquidus range, thermal stability, non-explosive, and wide electrochemical window. In our approach, the ionic liquid/redox carrier in a membrane, such as Nafion, forming a supported ionic liquid membrane (SILM). Electrodes are pressed against the solid membrane and supply a potential to reduce and oxidize the redox carrier at the cathode and anode respectively forming an electrochemically modulated device as shown schematically in Figure 1. Gas mixtures containing carbon dioxide are introduced at the cathode. As a potential is applied, carbon dioxide is selectively bound to the reduced form of the redox carrier and is carried across the membrane to the anode where it can be released.

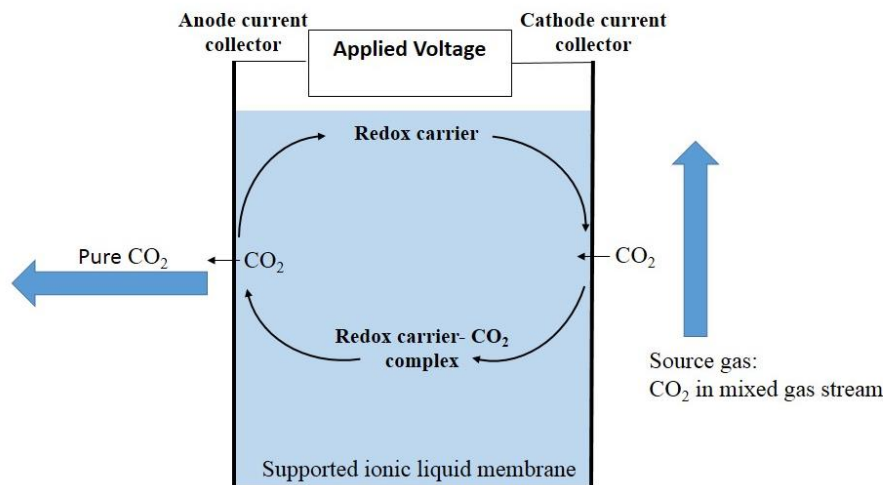


Figure 1. Facilitated Transport of CO₂

Unlike conventional membrane and absorption schemes, our approach selectively binds CO₂ via charge transfer mechanisms to redox carriers. This allows us to transfer the bound molecule through a membrane where it is subsequently released. With this approach, no regeneration step is required for this membrane allowing a continuous process to occur to separate and pressurize CO₂. This concept can be utilized in both a planar or tubular architecture. A schematic of the single tubular MEA is shown in Figure 2 along with the relevant reactive processes for CO₂ separation.

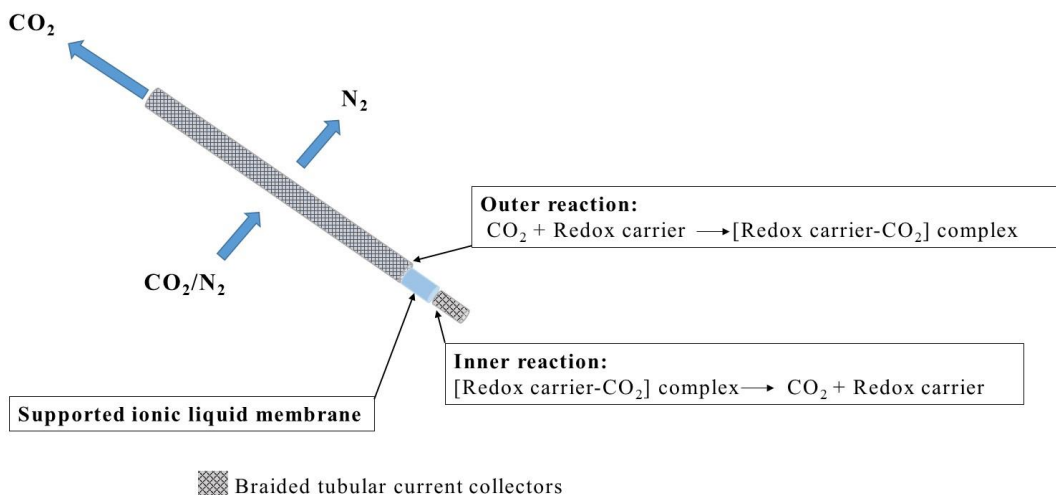


Figure 2. Tubular membrane-electrode assembly (MEA) Concept

An array of these tubular cells are then inserted into manifold covers that allow fluids to enter and leave through the interior flow tubes or through holes placed in the manifold as shown in Figure 3. Electrical connections are made from these manifold covers to either the interior porous metal flow through tubes or the external current collector wrapped around the outer electrode. The tubular cells are placed close together to allow sealing in the manifolds and for processing gases mixtures to flow over the tubes. Using the 0.1” Nafion based tubes, a multi-tubular assembly can be inserted into a cylindrical vessel with end-caps applied as shown in Figure 3. Similar hardware based on Reactive’s multi-tubular array technology has been previously delivered to NASA incorporating the reactive chemistry for a high-pressure (300 psia) water electrolyzer for lunar and Martian applications.⁶

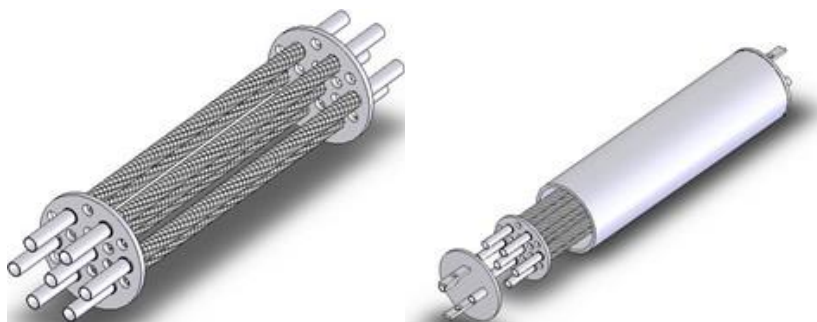


Figure 3. Reactive’s multitubular array hardware: Multi-tubular cell arrangement in manifold covers (left) and reactive-separator cells in a containment vessel (right)

III. Membrane Fabrication and Evaluation Methods

We have prepared and evaluated two types of membranes for this application: 1) Nafion-based ionic liquid imbibed membranes and 2) ionic liquid-poly-vinylidene fluoride (IL-PVDF) composite gel membranes. Commercial planar and tubular Nafion ion-exchange membranes (Nafion 115, Nafion 112) were purchased from Sigma Aldrich and Permapure and pretreated to result in an H⁺ form. Redox carriers (Alfa Aesar) were dissolved in 4-6 ml samples of commercially available ionic liquids (Aldrich) as received to result in saturated solutions. Nafion membranes were imbibed using a company proprietary method. A preparation method for IL-PVDF membranes has been reported by Jansen et al.⁷ This method was modified in the present work to include redox carrier species in the ionic liquid as well as to vary constituent concentrations and quantities to result in gel membranes of varying thickness and component ratios. In some instances, gel membranes were compressed in a heated hydraulic press to result in specific membrane thicknesses which range from 5– 12 mils.

Membranes were evaluated in planar and tubular forms. A schematic of the test apparatus is shown in Figure 4 incorporating the planar test hardware. A photograph is shown in Figure 5. The planar cell has a 25 cm² active area and Teflon flow fields on both the anode and cathode sides. Current collectors comprised of platinum mesh or carbon fiber were pressed against each side of the membrane inside the cell. MEAs were evaluated by flowing pure carbon dioxide (or a 1% carbon dioxide/nitrogen mixture) on one side of the single cell (cathode). Typical flow rates were 30 cc/min on both the anode and cathode. A DC power supply is used to apply a potential (0-4V) across the anode and the cathode and current is measured as reactive separation occurs. Outlet flow lines from the cell are directed to a commercial CO₂ analyzer (LiCOR) to give absolute concentration of CO₂ in the product stream and a gas chromatograph (SRI Multigas analyzer #2) to measure outlet composition ratios, thus confirming the reactive-separation process. As shown, helium (or nitrogen) is used to entrain the carbon dioxide in the anolyte to flow through the diagnostics and confirm CO₂ transport. The anolyte effluent stream has a pressure gauge and valving to allow CO₂ to build up pressure and confirm pressurization. A schematic of the single tubular membrane electrode assembly (MEA) was shown earlier in Figure 2 along with the relevant reactive processes for CO₂ separation. Photographs of a single tubular MEA and the tubular reactor are shown in Figures 6 and 7. Typical 6-inch tubular MEAs have electrode active areas of 12 cm².

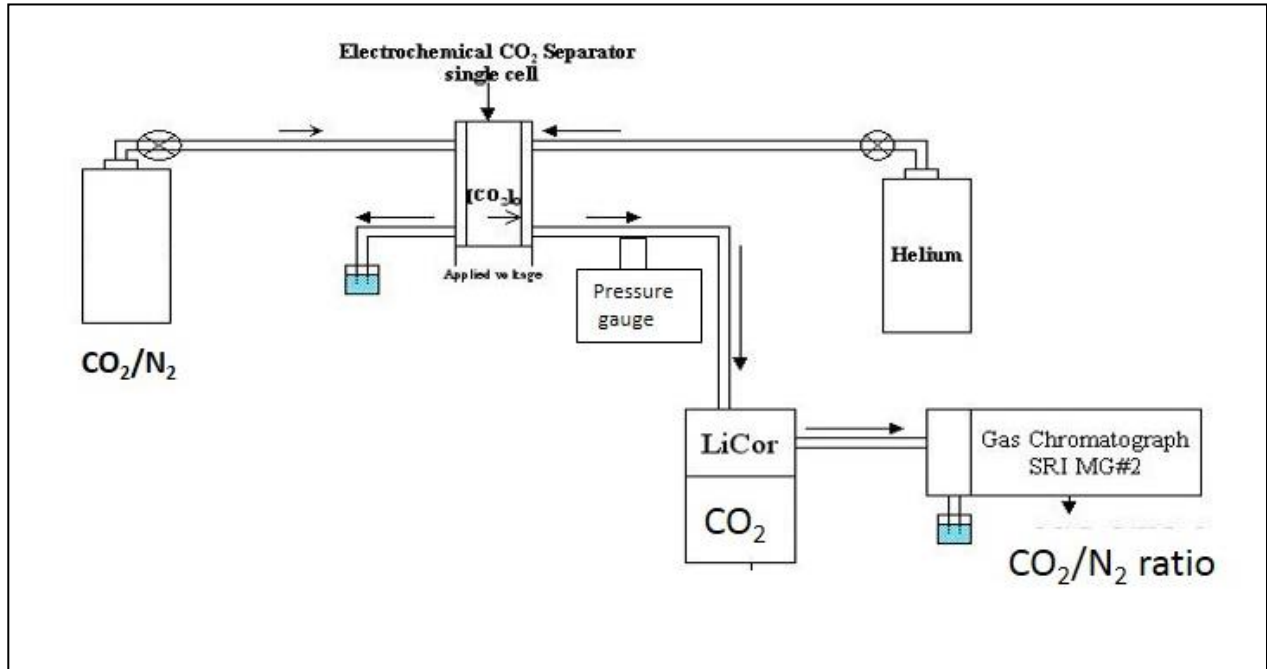


Figure 4. Single Cell Test Apparatus

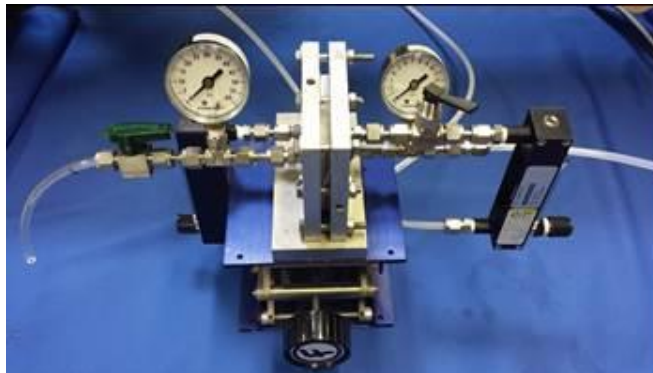


Figure 5. Photograph of Planar Membrane Test Apparatus



Figure 6. Photograph of Carbon Fiber Braided Tubular MEA



Figure 7. Photograph of a Single Tubular Reactor

We have evaluated both planar and tubular membranes using this hardware. The types of membranes are described in general in Table 2. Each category is representative of multiple experimental matrices designed to optimize the formulations.

Table 2. Membrane Categories under Development for CO₂ Collection and Pressurization

Redox Carrier/Ionic Liquid Formulation	Membrane support	Redox Carrier	Form
A	Nafion 115	1	planar
A	Nafion 115	1	tubular
A	Nafion 112	1	planar
A	PVDF	1	planar
B	PVDF	2	planar

A. Nafion-based Membrane Performance

Nafion-based membranes were evaluated for facilitated transport in the planar and tubular cell hardware. In our tests, the effluent of the permeate side of the single cell is monitored using LiCOR to measure the amount of CO₂ transported across the membrane and entrained in an inert gas as the voltage is turned on and off. Figure 8 is the data for a membrane with redox-IL formulation A. Pure carbon dioxide was used as the feed gas. As shown, the applied voltage across the cell results in an increase in the CO₂ gas concentration on the effluent side. In addition to the facilitated transport mechanism, transport is observed due to a dissolution/diffusion mechanism in the ionic liquid itself. This results in a constant background level of carbon dioxide. Applying the voltage to the cell increases the CO₂ concentration over that of the background. Based on the measured CO₂ concentration in the anode effluent and the carrier gas flow rate in these planar experiments, we calculate a range of transport rates between 1.04-2.67 x10⁻⁹ moles CO₂/min/cm² for the planar Nafion 115 membranes.

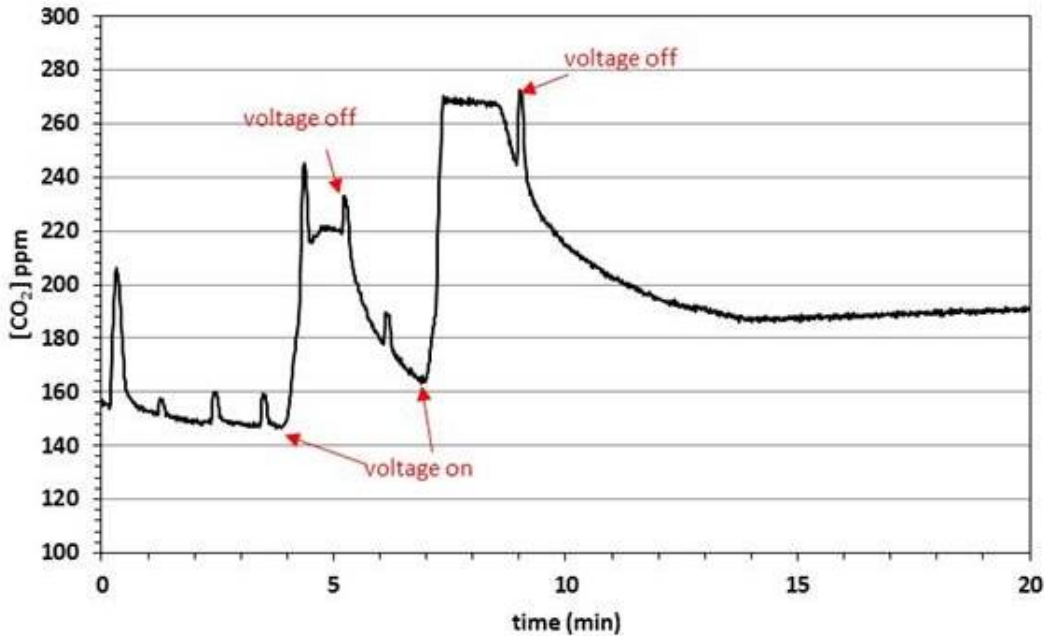


Figure 8. CO₂ transport data for Nafion membrane imbibed with Formulation A. LiCOR results as anode effluent gas stream is monitored. Feed gas is 100% CO₂

We also evaluated these membranes using a feed gas with a much lower concentration of carbon dioxide. The LiCOR results of that test is shown in Figure 9. As this data shows, the reactor can successfully transport CO₂ from a dilute stream. We used a low concentration of carbon dioxide at atmospheric pressure in these experiments to demonstrate the process in a realm close to the true carbon dioxide number density in the Martian atmosphere. Specifically, operating at 1% carbon dioxide implies a partial pressure of 0.76 torr which is equivalent to a number density of 7.6×10^{15} molecules/cm³. On Mars, the number density of CO₂ based on an atmospheric pressure of 8 torr and a mole fraction of 95% CO₂ would be 7.6×10^{16} molecules/cm³. Thus this experiment was performed with at least an order of magnitude lower carbon dioxide number density than the actual Martian atmospheric conditions. Also shown in the data in Figure 9 is the effect of reducing the carrier gas flow rate to 10 cc/min in the effluent stream to result in a higher concentration of carbon dioxide.

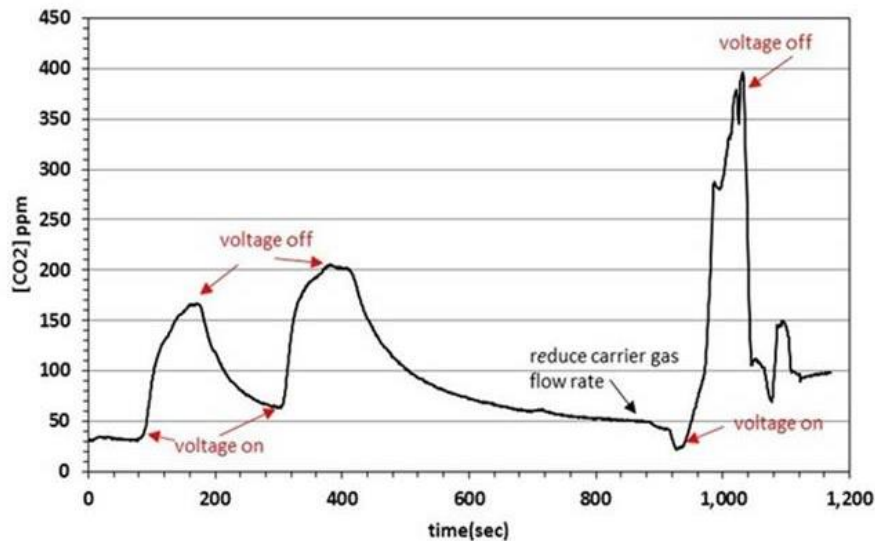


Figure 9. CO₂ transport data for Nafion membrane imbibed with Formulation A. LiCOR results as anode effluent gas stream is monitored. Feed gas is 1 % CO₂, balance N₂

We transitioned the reactive chemistry of formulation A to a tubular architecture. Figure 10 is an example of the LiCOR data, again monitoring the effluent of the permeate side as the voltage is turned on and off in the tubular reactor showing similar behavior to the planar cell.

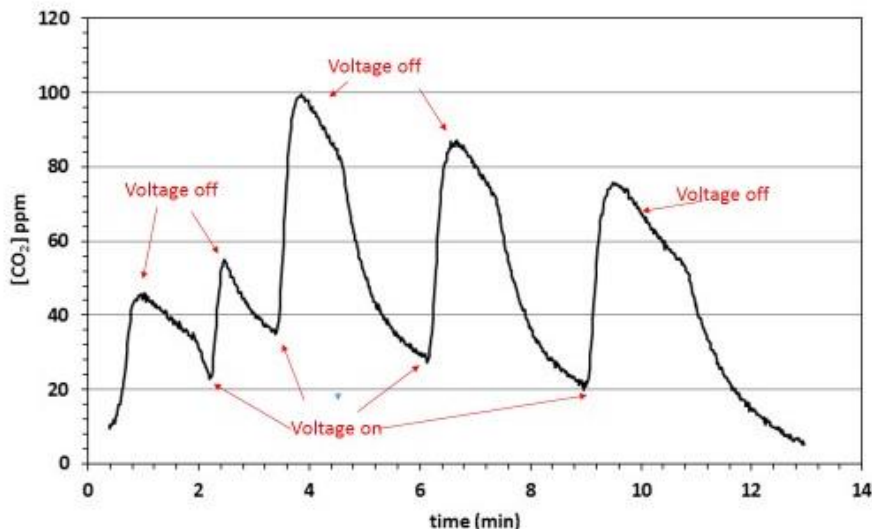


Figure 10. CO₂ transport data for tubular Nafion membrane imbibed with Formulation A. LiCOR results as anode effluent gas stream is monitored. Feed gas is 100% CO₂

We successfully demonstrated facilitated transport with nafion membranes in both the planar and tubular forms. However, some problems were encountered with the Nafion 115-based membranes involving performance decay over time. The ionic liquid-redox carrier interaction within an ionic exchange matrix is complex, with cationic exchange of the ionic liquid occurring with H⁺ groups in the membrane. The facilitated transport mechanism requires that dissolved redox carriers must electro-diffuse through potentially sterically-hindered pores to transport CO₂. In addition, operating at 4.0 volts resulted in higher currents through the cell, and initially higher transport rates. However, over time, this level voltage initiated side reactions that caused the CO₂ level in the effluent stream to decrease. Reducing the voltage to 2.0 volts has led to a more stable performance going forward in the development of Nafion-based approaches. In addition, reducing the thickness of the membrane to 2 mils has led to increased stability. Figure 11 is the LiCOR data for Nafion-112 imbibed with Formulation A tested at 2.0V.

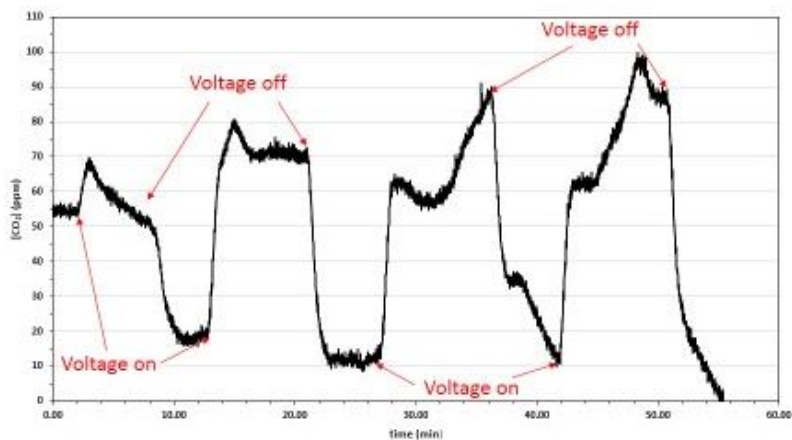


Figure 11. CO₂ transport data for planar Nafion 112 membrane imbibed with Formulation A. LiCOR results as anode effluent gas stream is monitored. Feed gas is 100% CO₂

B. PVDF-based Membrane Performance

A photograph of a IL-PVDF membrane is shown in Figure 12. IL-PVDF membranes were prepared using two different redox carriers. The performance of an IL-PVDF membrane imbibed with Formulation A is shown in Figure 13. Similar to the Nafion-based membranes we are again observing voltage dependent behavior of the transport mechanism for carbon dioxide through the membrane. The spikes in the data were typical of this type of membrane in early preparations, which is most likely related to non-uniform post-processing leading to pinholes in the membrane. These membranes have a spongy, somewhat sticky consistency which may allow pinholes to open and close with periodic ohmic heating.



Figure 12. Photograph of IL-PVDF membrane

We were able to improve the substrate uniformity for this type of membrane and further improve the performance by using a different redox carrier. Figure 14 is the LiCOR data for a PVDF type membrane incorporating Formulation B. As shown, the voltage on/off profile is more uniform and reproducible than the Nafion-based membranes. Current performance of these membranes indicate about a 3 times improvement in CO₂ transport rate compared to Nafion-based approaches. However, further evaluation is necessary to determine how this type of membrane will perform under CO₂ pressurization.

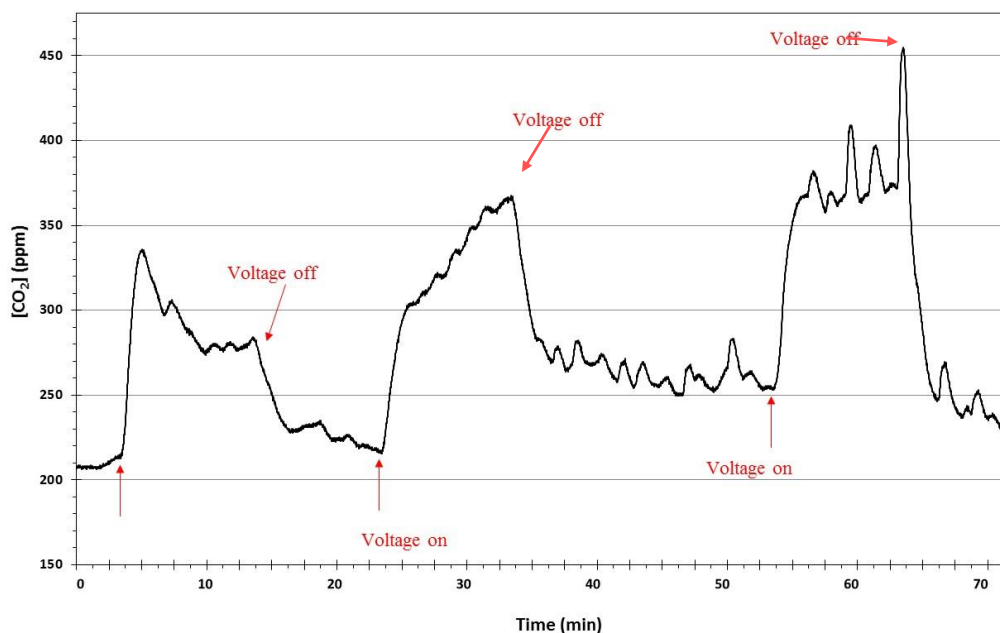


Figure 13. CO₂ transport data for IL-PVDF membrane imbibed with Formulation A. LiCOR results as anode effluent gas stream is monitored. Feed gas is 100% CO₂

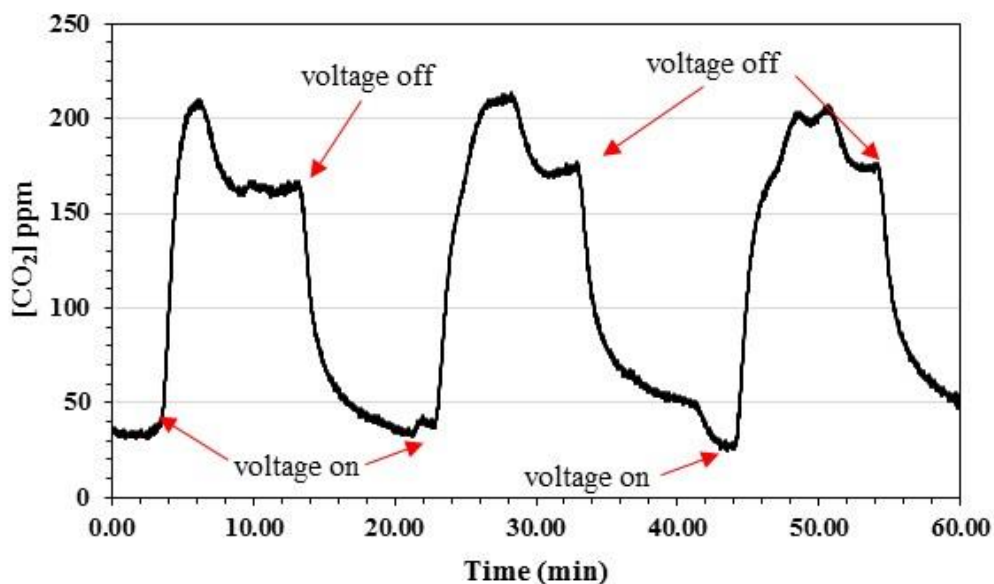


Figure 14. CO₂ transport data for IL-PVDF membrane imbibed with Formulation B. LiCOR results as anode effluent gas stream is monitored. Feed gas is 100% CO₂

IV. CO₂ Pressurization Studies

We evaluated a tubular cell using a Nafion membrane imbibed with formulation A for CO₂ pressurization in several trials. Pure CO₂ was introduced to the cathode at ambient pressure. With the anode sealed off (no gas flow) we applied 4 volts on the cell and monitored the pressure as well as the current. As shown in Figure 15, the pressure build-ups over time in two different trials. As shown, the rate of increase was about 0.26 psi/hr.

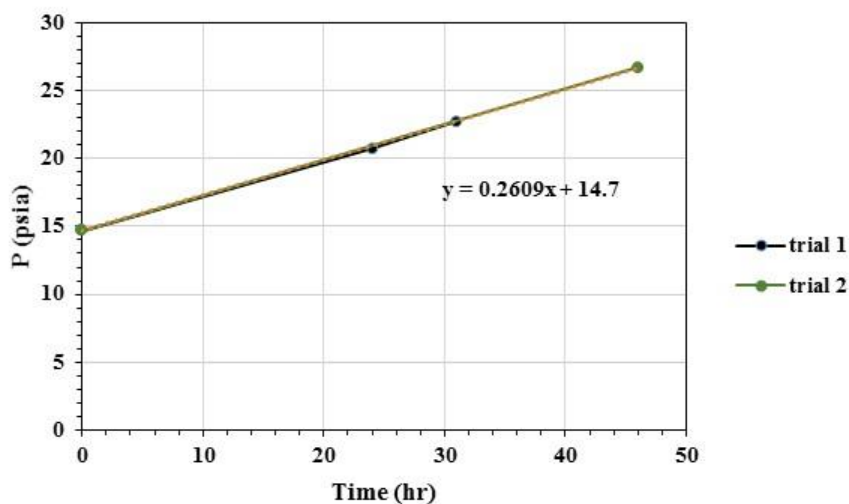


Figure 15. Single tubular reactor CO₂ collection and pressure build-up starting at atmospheric pressure

We also evaluated the cell performance to pressurize CO₂ starting at an elevated pressure. Figure 16 plots the pressure rise over time starting at a CO₂ gas pressure of about 58 psia. As Figure 16 shows, the initial rate of pressure rise was high (3.7 psi/hour) but decreased over time. Importantly, the fact that we observe a similar rate of pressurization starting at both low and high pressure in this experiment is very promising and implies that the rate is

independent of the final pressure. One concern that we had in implementing this technology to pressurize carbon dioxide was that back diffusion at higher pressures would result in a lower net transport rate. The pressure is asymptoting with time in Figure 16 because of performance loss in the MEA evidenced by a large drop in current. At the end of the test we allowed the cell to stay stagnant at differential pressure overnight and did not observe any back diffusion into the catholyte.

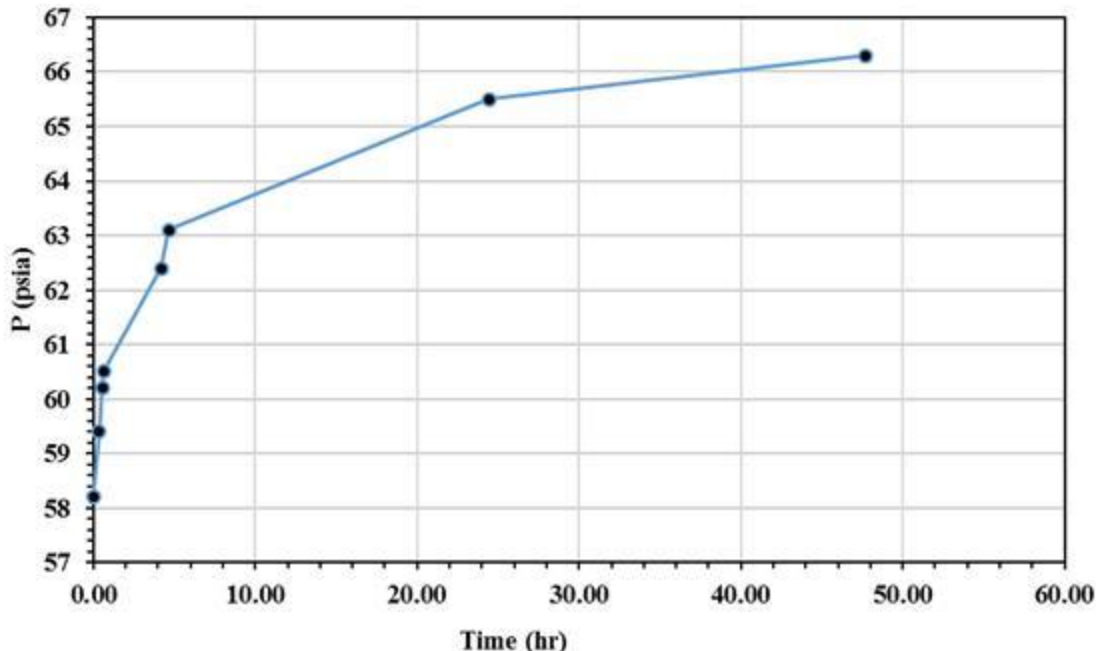


Figure 16. Single tubular reactor CO₂ collection and pressure build-up starting at 58 psia

V. Conclusions

In this work we evaluated Nafion-based and PVDF-based membranes incorporating different redox carriers to transport and pressurize carbon dioxide. Both types demonstrated successful transport; however, we have observed significant differences in stability and performance with component and membrane choice. Current planar data suggests that a PVDF-membrane may have advantages in improving the rate and stability of the process. These membranes have not been thoroughly tested, particularly with respect to pressurization. A Nafion-based tubular reactor has been shown to collect carbon dioxide from both pure and dilute sources and pressurize it to within the range required for ISRU processing (15-75psia) to support various technologies including supplying a Sabatier reactor to produce methane. If we consider the tubular performance as a unit cell, with a baseline pressurization rate of 0.17 g CO₂/hr, then one option is to increase the length of this cell and duplicate it the appropriate number of times to result in a projected CO₂ collection rate of 88 g/hr to meet NASA's specification for supply to a Sabatier reactor. With our present tubular performance this would be 244, 8 inch tubes. An artist's rendition of this design is shown in Figure 17. We expect additional improvements, such as adopting the PVDF formulation will result in a design with fewer tubes to meet NASA's goals for CO₂ collection and pressurization.

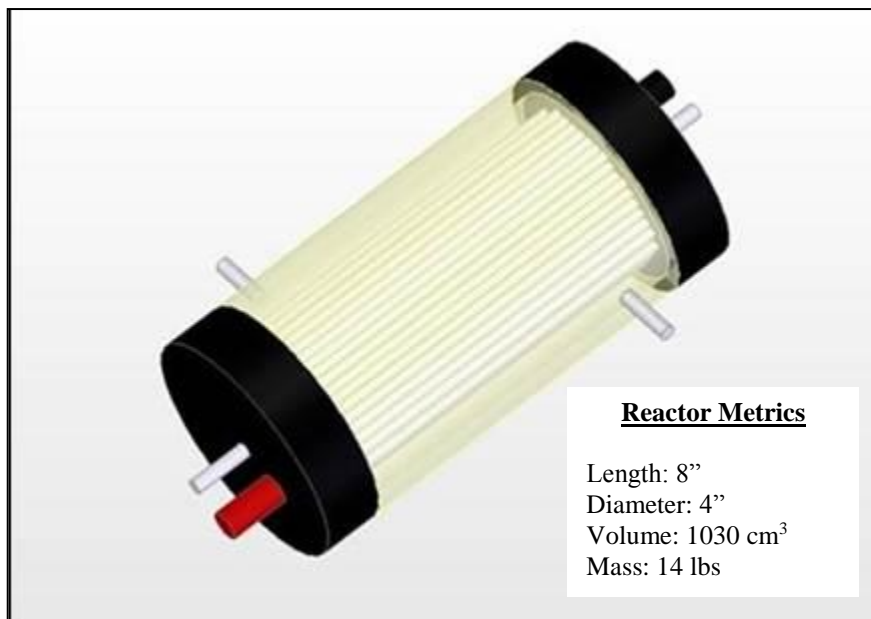


Figure 17. Conceptual Design of Scaled-up Reactor

Acknowledgments

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