Electrochemical Solutions for Advanced Life Support

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The Oxygen Generating Assembly (OGA) on-board the International Space Station (ISS) employs a polymer electrolyte membrane (PEM) water electrolysis cell stack to electrochemically dissociate water into its two components – oxygen and hydrogen. Oxygen is provided to the cabin atmosphere for crew respiration while the hydrogen is delivered to a carbon dioxide reduction system to recover oxygen as water. The design of the OGA evolved over a number of years to arrive at the system solution that is currently operational on ISS.

Future manned missions to space will require advanced technologies that eliminate the need for resupply from earth and feature in-situ resource utilization to sustain crew life and to provide useful materials to the crew. The architects planning such missions should consider all potential solutions at their disposal to arrive at an optimal vehicle solution that minimizes crew maintenance time, launch weight, installed volume and energy consumption demands. Skyre is developing new technologies through funding from NASA, the Department of Energy, and internal investment based on PEM technology that could become an integral part of these new vehicle solutions. At varying stages of Technology Readiness Level (TRL) are: an oxygen concentrator and compressor that can separate oxygen from an air stream and provide an enriched oxygen resource for crew medical use and space suit recharge without any moving parts in the pure oxygen stream; a regenerative carbon dioxide removal system featuring a PEM-based sorbent regenerator; a carbon dioxide reduction system that electrochemically produces organic compounds that could serve as fuels or as a useful intermediary to more beneficial compounds; and an electrochemical hydrogen separator and compressor for hydrogen recycle. The technical maturity of these projects is presented along with pertinent performance test data that could be beneficial in future study efforts.

Nomenclature

ARPA-E = Advanced Research Projects Agency – Energy
ARS = Air Revitalization System
BREATHE = Bifunctional Regenerative Electrochemical Air Transformation for Human Environments
CRES = corrosion resistant steel
DOE = Department of Energy
EHSC = Electrochemcial Hydrogen Separator and Compressor
HRS = Helium Recovery System
ISS = International Space Station

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M   = molar
N   = normal
NASA   = National Aeronautics and Space Administration
NUCRET = Northeastern University Center for Renewable Energy Technology
OGA   = Oxygen Generating Assembly
P&ID   = Piping & Instrumentation Diagram
PEM   = polymer electrolyte membrane
SSC   = Stennis Space Center
SSOCC   = Solid State Oxygen Concentrator and Compressor
TRL   = Technology Readiness Level
V   = volts
WPA   = Water Processor Assembly

I. Introduction

AS human beings reach out from their Mother Earth and seek to explore our solar system new technologies will be required to sustain life within a transport vehicle and extraterrestrial habitats. The International Space Station (ISS) has served as an excellent proving ground for advanced life support technologies, with a myriad of lessons-learned that can be applied to future manned space missions. The ISS, however, is in low-earth orbit, and is within relatively easy reach of earth for resupply of food, water, propellant and other supplies. The same will not be true for longer duration missions.

NASA is advancing life support technologies with a goal of enhanced capability and performance, reduced complexity, minimal maintenance and zero resupply to meet its mission of long-reaching exploration. Skyre is developing electrochemical products through various government-sponsored funding streams that recycle or produce valuable products from waste streams, and provide them at relevant throughputs and pressures. Similar to the Oxygen Generating Assembly, these new product offerings are based on polymer electrolyte membrane (PEM) technology to afford simplified system solutions with minimal moving parts. Relevant projects with potential applicability to future manned-space missions are presented.

II. Solid State Oxygen Concentrator and Compressor (SSOCC)

The International Space Station (ISS) requires high-pressure oxygen to support extravehicular activity (EVA) outside of the vehicle, provide an oxidizer for the Water Processor Assembly (WPA) catalytic reactor, and serve as contingency in the event of a prolonged failure of the Oxygen Generating Assembly (OGA). While the Space Shuttle was operational and making routine visits to the ISS the high-pressure oxygen gas tanks were recharged with a mechanical compressor using cryogenic boil-off from the LOX tanks on-board the orbiter. With the end of the Space Shuttle program oxygen resupply to the ISS has relied on resupply launches that carry oxygen tanks to the station. Alternate methods for providing high-pressure oxygen are desired for the ISS – but will be a necessity for future manned-space missions where resupply from earth is not viable. Long-duration missions will also require oxygen to address medical emergencies on-board a vehicle or within an extraterrestrial habitat.

No engineered systems exist that have met power, size and flow rate objectives for use in manned space flight. Viable system solutions must be lightweight, utilize minimal moving parts, require little to no
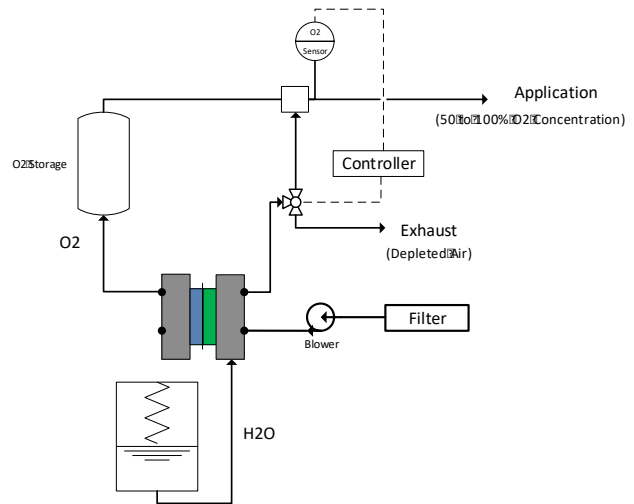

Figure 1. System block diagram for the Solid-State Oxygen Concentrator and Compressor (SSOCC).

maintenance, have little to no dependency on logistics and operate safely and efficiently in a high-pressure oxygen environment. NASA has funded Skyre to develop a Solid-State Oxygen Concentrator and Compressor (SSOCC) to meet future mission requirements. A system block diagram is shown in Figure 1. Filtered air from the cabin or habitat is fed to the oxygen concentrator and compressor electrochemical cell stack by means of a blower. Oxygen is removed from the stream and indirectly transported across the electrochemical membrane, where pressure is allowed to build to the product pressure required of the operation – governed by a pressure sensor. The oxygen production rate is roughly proportional to the current passed through the electrochemical cell stack. Waste gases are vented through an exhaust port.
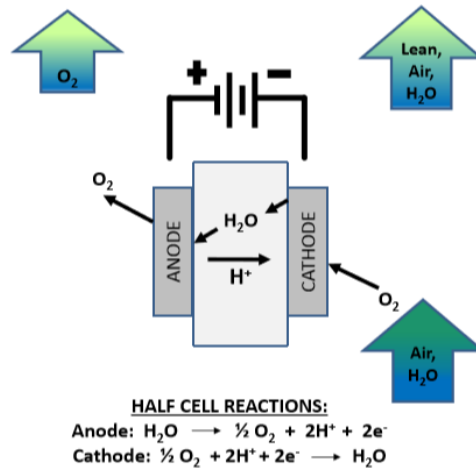

HALF CELL REACTIONS:
Anode: $H_2O \longrightarrow \frac{1}{2} O_2 + 2H^+ + 2e^-$
Cathode: $\frac{1}{2} O_2 + 2H^+ + 2e^- \longrightarrow H_2O$

Figure 2. Operation of an electrochemical oxygen concentrator and compressor cell.

At the core of the SSOCC is the electrochemical cell that is a combination of water electrolyzer and fuel cell. Referring to Figure 2, a humid air stream is delivered to the cathode chamber of the SSOCC. The water vapor permeates through the proton exchange membrane (PEM) to the dry anode side of the cell. The water is electrolyzed on the anode creating a pure oxygen product stream. The positively-charged protons that are generated from electrolysis permeate through the membrane to the negatively-charged cathode where they recombine with oxygen from the air and re-create water. Since oxygen is consumed and generated at equivalent rates, the partial pressure of oxygen in the habitable volume on average does not increase; rather the oxygen is concentrated and delivered to a specific location for application use. Similarly, water vapor from the ambient air is consumed and regenerated with no net change in the environmental humidity. A key aspect of this design is that management of water is achieved within the cell, such that performance is maximized and power is minimized. Skyre is developing the SSOCC in accordance with the enabling characteristics of Table 1.

Table 1. System Requirements for NASA and the Commercial/Military Sectors

NASA Requirements	Commercial/Military System Requirements
- Adjustable positive pressure flow of 2-15 Lpm - Delivered O_2 concentration of 50% to 100% - Operates in microgravity and partial gravity - Atmospheres of 14.7 psia/21% O_2; 10.2 psia/26.5% O_2; 8.2 psia/34% O_2 - Operates on spacecraft power, (450W) - Operates below touch temperature of 45°C - Delivered O_2 pressure: ambient to 3600 psig - Quiet operation < 45dB - Volume 0.03m^3	- Quiet operation < 45dB - No moving parts/rotating machinery - Portable - Usable in contaminated atmosphere - Scalable to meet the needs of individual users or greater - Minimal energy requirements - Minimal maintenance

Initial development work at Skyre has focused on the electrochemical hardware illustrated in Figure 2. Skyre's existing gas separation electrochemical cell architecture, typically used for electrochemical hydrogen separation and compression, was the basis for creating an integrated assembly to support an electrochemically-facilitated oxygen concentrator with ambient air as the oxygen source. The cell embodiment uses electrically-conductive flow fields in the anode and cathode chambers, with a porous metal support structure inserted into the cathode to provide mechanical support of the membrane under high-differential pressure loads.

A. Preliminary Cell Performance
A laboratory breadboard system was developed during Phase I of the program to validate the SSOCC concept. A simplified Piping & Instrumentation Diagram (P&ID) of the test system is provided in Figure 3. In this design, regulated air is humidified and fed into the electrochemical cell. As air flows through the cathode, oxygen reduction

occurs with the protons generated from water oxidation on the anode. The water oxidation reaction on the anode electrochemically pumps protons to the cathode while producing pure oxygen. Oxygen is then separated within the cell and fed through a back-pressure regulator to a vent. For the preliminary system performance, the cell was run at 200 psid. In practice, the system is tested at a proof pressure of 6000 psi. Several polarization curves measuring cell performance were taken. The first set of polarization curves (voltage versus current density), shown in Figure 4, were taken at 25°C at varying inlet gas ratios while the second set of curves, shown in Figure 5, were taken at 35°C. Data for these cells show that operation with higher stoichiometric rates is preferred to achieve better mass transport on the cathode (air electrode). (Stoichiometric rate is

Figure 3. SSOCC test stand P&ID.

defined as the volume of oxygen fed to the cell to meet the operating current. A stoichiometric rate of 1 signifies that all of the oxygen is 'pumped' from cathode to anode; a stoichiometric rate of 2 signifies that half the oxygen is 'pumped' from cathode to anode, with the rest being swept out in the cathode exhaust). Furthermore, we see additional benefit to operating the cell at higher temperature. At the higher stoichiometric rate, the viable current density doubles from 150 mA/cm^2 to 300 mA/cm^2 by raising the operating temperature from 25°C to 35°C, as shown in Figure 5. Interestingly, the polarization curves exhibit an S-shaped pattern. This is due to the starvation of oxygen at the cathode.

When oxygen has been depleted due to mass transport limitations, the hydrogen evolution reaction takes over and the cell begins to operate as a traditional water electrolyzer. Increasing the operating temperature improved the mass transport characteristics in the cathode enabling greater oxygen pumping current densities. Limited durability testing was conducted on a cell at 35°C and a current density of 100 mA/cm^2. The cell ran at an average voltage of 0.8V for a total of 270 hours; cell voltage as a function of time is provided in Figure 6.
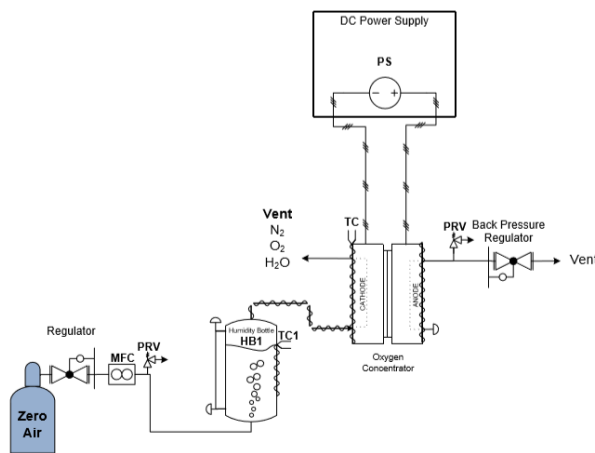
Skyre is currently under a Phase II program to advance the SSOCC to a five-cell prototype build. In the Phase II program three different cation exchange membranes will be evaluated through a characterization test program that includes oxygen permeability and water balance measurements. The ideal membrane candidate will have low oxygen permeability while supporting high water content at the anode electrode to facilitate operation at high current density.

An additional task in the Phase II effort is to assess the cell materials of construction. Cell materials must be selected for compatibility in a high-pressure oxygen environment while withstanding anodic potentials in an acidic environment imposed by the cation exchange membrane. Other factors to be considered in material selection include the
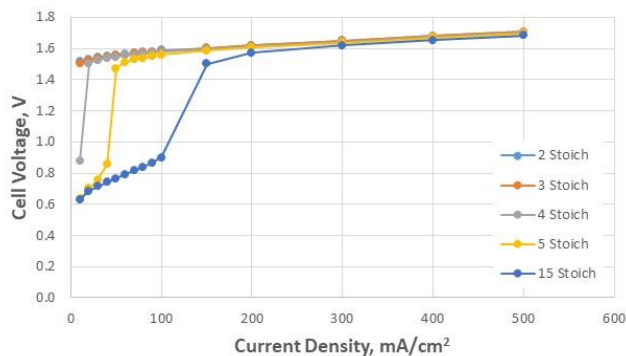

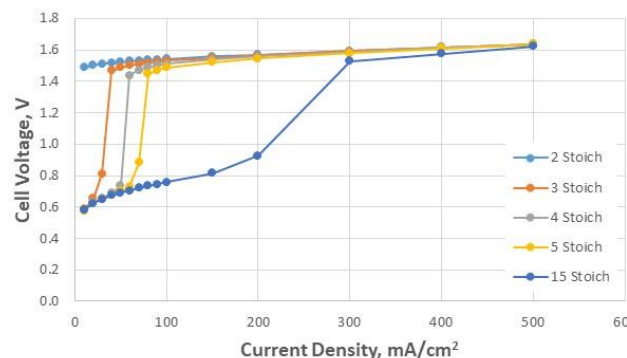**Figure 4. Polarization curve for 25°C operation, 200 psig.**

Figure 5. Polarization curve for 35°C operation, 200 psig.

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strength of material for high-pressure cell designs; compatibility with liquid water and water vapor; and compatibility under cathodic potential. Collins Aerospace has significant experience in the design of high-pressure oxygen equipment along with corrosion testing capabilities and has been issued a subcontract by Skyre to assist in materials selection.
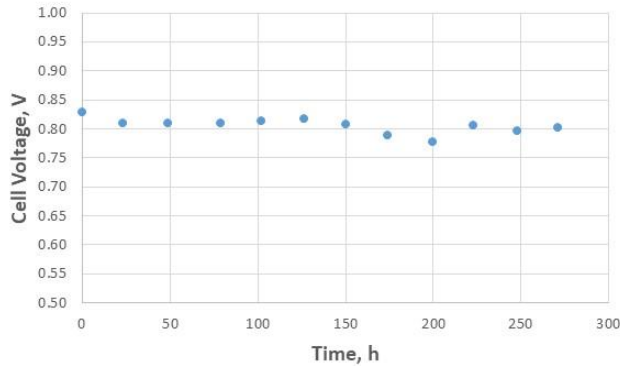

Figure 6. Extended durability testing of the SSOCC at 100 mA/cm2, 35°C.

A number of alloys have been identified that demonstrate good compatibility characteristics in high-pressure oxygen environments. These alloys are being considered over our traditional materials of construction due to the fact that the anode will have oxygen, at pressures as high as 3,600 psi, in direct contact with high surface area porous materials. These high surface area porous materials are designed to place an even mechanical load on the membrane electrode assembly to minimize contact resistance through the cell while simultaneously providing a means of egress for the oxygen out of the cell cavity. It is necessary to include these porous materials for initial pressurization as well as providing mechanical compression in the event the cell is run at low differential pressure to achieve other mission goals. Due to their high surface area and small feature sizes, flammability of the cell is a major design concern. It should be noted that this list doesn't guarantee success in this particular application as oxygen compatibility is a complex topic that must consider ignition sources, gas velocity, particle impact potential, contamination, adiabatic compression and hardware configuration, among others. The flammability threshold of a 1/8" rod of a specific alloy or pure material is provided in Table 2. While none of the materials is completely non-flammable in high-pressure oxygen, the Haynes 25, Hastelloy C276, and Inconel 625 have the highest thresholds to be self-extinguishing of the alloys tested. The thresholds as a 1/8-inch diameter rod are 2,500 psi for Haynes 25 and 2,500 psi for Inconel 625 and C276. Both materials would be expected to be flammable at the anticipated use thicknesses; however, Haynes 25, C276, and Inconel 625 all have a heat of combustion that is low enough to significantly reduce the reaction effect in the event of an ignition.

Table 2. Oxygen compatibility of select metals (data taken from Ref. 1).

Alloy	Flammability Threshold, psia	Rationale
CRES 316	150	Establish as a baseline material
Ni-based alloys (Hastelloy® C276, Inconel 625)	2500	Nickel-based alloys typically exhibit good corrosion resistance; Inconel 625 has higher strength than Hastelloy C276
Co-based alloys (Elgiloy, Haynes® 25)	2500	Cobalt-based alloys are used in high-temperature applications; exhibit better oxygen flammability threshold compared to nickel-based alloys; Elgiloy has very high strength (250 ksi)
CP Titanium	5	Baseline for water electrolysis systems
Niobium	50	Baseline for water electrolysis systems; not evaluated in this program effort

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Materials compatibility in the operating cell environment can be determined using cyclic polarization in a 1M (2N) H_2SO_4 solution. This solution has historically been selected as it closely matches the local pH of the cell membrane. Cyclic polarization scans are used to evaluate a material's susceptibility to pitting corrosion as may be expected when operating under anodic potential (where oxidation occurs). The presence of hysteresis in the scan, and the size of the hysteresis loop, indicates the presence and magnitude of pitting corrosion occurring in the sample. Multiple scans for Haynes 25 is provided in Figure 7 with associated before, during, and after images of the tested material. As no single alloy provided 'clean' test results, composite structures are being investigated to m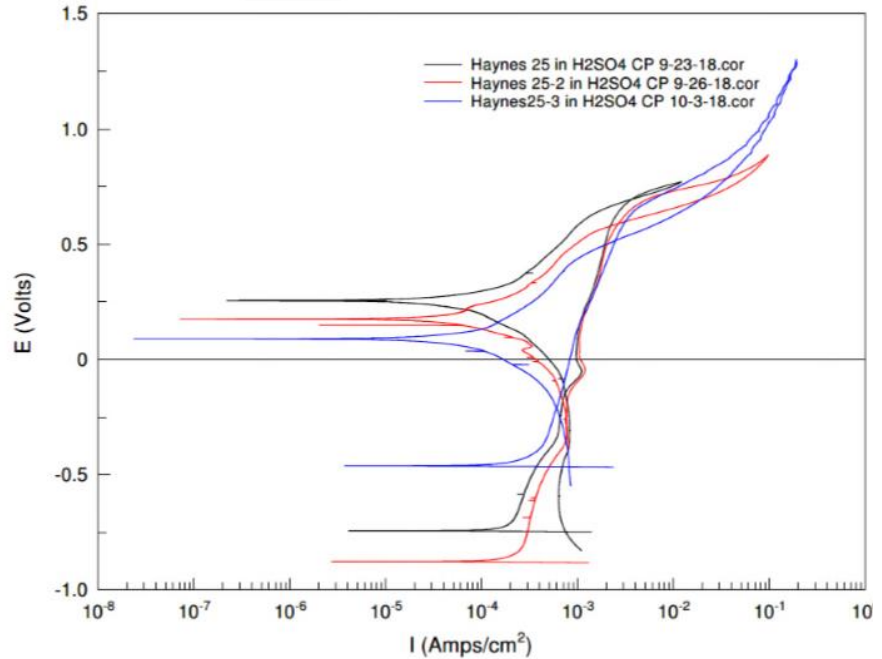eet the requirements of the harsh operating environment. Once a final material selection has been made, cell hardware will be constructed and the candidate membrane material from the prior characterization test program will be assembled into working single cell assemblies to conduct parametric testing. The results from this test program will direct the design and assembly of the five-cell prototype assembly to be completed in June 2020.

Figure 7. Polarization scans of Haynes 25 along with images showing the level of pitting from the test. (test results from Collins Aerospace).

III. Electrochemical Carbon Dioxide Absorption

Carbon dioxide removal, its compression and eventual reduction are integral processes of a manned, closed-environment atmosphere revitalization system (ARS). The current ARS on-board the International Space Station (ISS) utilizes a pressure swing adsorption system for CO_2 removal, a positive displacement mechanical compressor for its compression and a Sabatier CO_2 reduction system that reduces carbon dioxide to methane and water vapor in a catalytic reactor[2]. The removal and compression systems incorporate a number of moving parts that reduce the overall reliability of the ARS, require substantial crew time for maintenance, generate noise (blowers and compressor) and require significant power. NASA has funded Skyre to develop a Bifunctional Regenerative Electrochemical Air Transformation for Human Environments, or BREATHE, as part of the CO_2 removal system depicted in Figure 8. Cabin air is delivered to a caustic scrubber where an alkali hydroxide – such as potassium hydroxide –absorbs carbon dioxide and is converted to an alkali carbonate (potassium carbonate). Conditioned air is returned to the cabin. The carbonate solution is delivered to the electrochemical CO_2 concentrator. The technology is similar to an electrodialysis concentrator cell in which potassium carbonate solution is split into potassium and carbonate ions. The ions pass
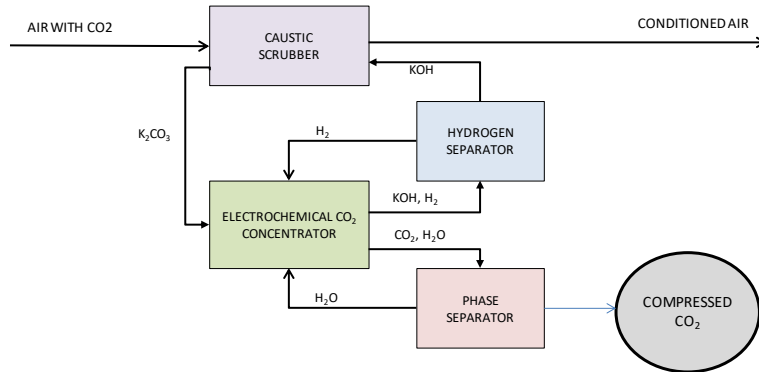

Figure 8. BREATHE – Carbon dioxide removal and compression featuring electrochemical CO₂ concentration and compression.

through their respective cation or anion exchange membranes. The carbonate reacts with hydrogen fed to the anode creating carbonic acid which dissociates into CO_2 and water. Since the carbonate ions are electrochemically pumped across the membrane, it can be compressed and produce high pressure CO_2. The regenerated potassium hydroxide is returned to the caustic scrubber via the hydrogen/caustic two-phase fluid separator.

NASA has funded Skyre to develop and evaluate a low-power electrodialysis-based concept for BREATHE that can serve as an efficient, reliable building block in an advanced ARS for future manned-space missions. Skyre's BREATHE concept integrates the capture, separation and compression into a single electrochemical membrane-based device. Since electrochemical technology is solid state, compression is accomplished with no moving parts and a low noise emission. Low-temperature carbon dioxide separation and compression offers further system simplicity and a lower power requirement compared to traditional thermal regeneration of liquid or solid adsorbents. For this Phase I program effort Skyre has designed three different cell configurations for evaluation.
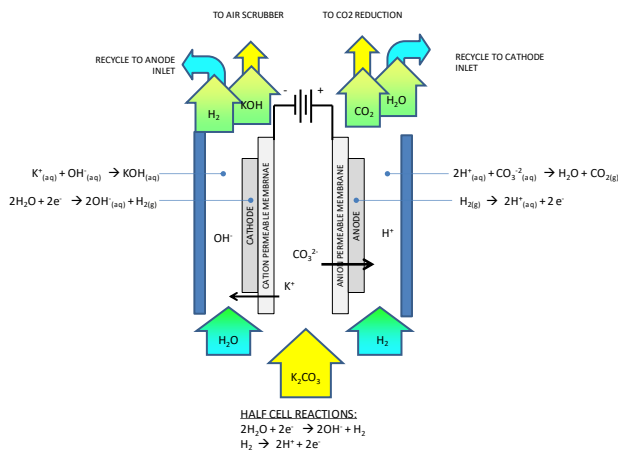

Figure 9. BREATHE – Three-chamber cell featuring an anion and cation exchange membranes for regenerating potassium carbonate to potassium hydroxide.

The first configuration shown in Figure 9 displays a three-chamber cell which utilizes both an anion and cation exchange membrane. Potassium carbonate is fed to the central chamber where it is split into potassium and carbonate ions. The ions are driven across their respective membranes due to an applied potential. The potassium reacts with water fed to the cathode to create potassium hydroxide and hydrogen. The potassium hydroxide can be sent to an air scrubber to form more potassium carbonate while the generated hydrogen can be used to supply the anode. At the anode the carbonate reacts with the supplied hydrogen to create carbonic acid which naturally dissociates into carbon dioxide and water. The carbon dioxide is separated from the water to be compressed and the generated water can be recycled to the cathode.

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The other two configurations, shown in Figure 10 and Figure 11, use either an anion exchange membrane or a cation exchange membrane, respectively. In each of these approaches, the carbonate solution may not be fully regenerated to the hydroxide form before being returned to the air scrubber. This inefficiency is traded against the simplification afforded in the design of the electrochemical cell hardware. The major difference in the dual-chamber design compared to the three-chamber design is the engineering problems associated with mixed flow on one side of the cell. In the cation exchange membrane configuration two-phase flow is necessary with hydrogen being bubbled through the potassium carbonate solution. This requires significant development to ensure proper contact of the reactants with the membrane. In the anion exchange membrane configuration, the concentration of the potassium
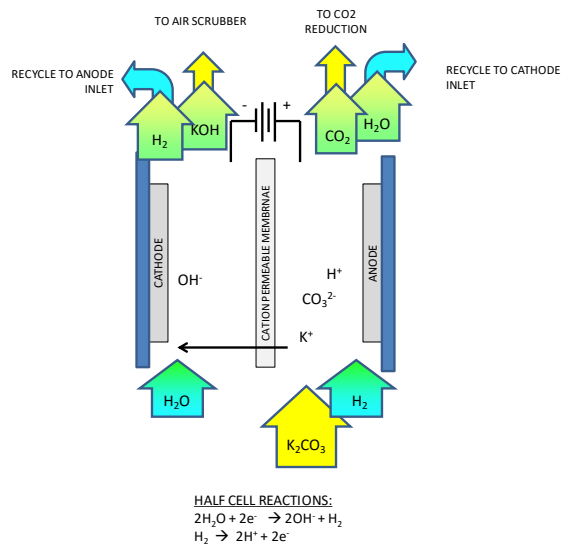

Figure 10. BREATHE – Two-chamber cell featuring an anion exchange membrane for regenerating potassium carbonate to potassium hydroxide.

carbonate is critical and will need to be adjusted to give the proper water balance.

In executing these designs, the two configurations using anion exchange membranes required development of catalyst application techniques. Bonding of catalyst materials to cation exchange membranes typically involves high-temperature and/or high-pressure, or the use of an ionomer material dissolved in a solvent that is compatible with the membrane. Anion exchange membranes are less robust than their cation counterparts, so processing conditions for attachment of electrodes needed to be carefully developed to ensure proper attachment without damage to the host membrane. Application methods were limited to temperatures below 60°C for thermal-based processes; the choice of solvent for 'painting' of electrodes required consideration of material compatibility with the membrane. The goal was to provide an evenly distributed catalyst layer on the membrane surface.

Figure 11. BREATHE – Two-chamber cell featuring a cation exchange membrane for regenerating potassium carbonate to potassium

The catalyst applied to the cathode was selected to promote the production of hydroxide from the electrolysis of water. The cathode was manufactured using Raney nickel, which has a significant amount of hydrogen gas trapped in the pores due to its fabrication method and is extremely pyrophoric. Therefore, it was passivated prior to being deposited onto the membrane to ensure safe handling. This was accomplished by adding the wet catalyst to an ice-cooled reactor containing 15 wt% hydrogen peroxide[3]. The hydrogen peroxide reacted with the Raney nickel, with the bath temperature reaching a maximum of 90°C during the passivation process. The Raney nickel was confirmed to be passivated by drying a sample on a hot plate above the boiling point of water and visually checking for pyrophoric activity. Once bound in the electrode, the inert catalyst was reactivated by running the cell for several hours at low current densities, ~5 mA/cm^2, and then monitoring to ensure the cathode is always wet. Cell voltage was tracked to determine when equilibrium had occurred, with the required voltage decaying over time due to the improved catalyst activity and electrical conductivity.
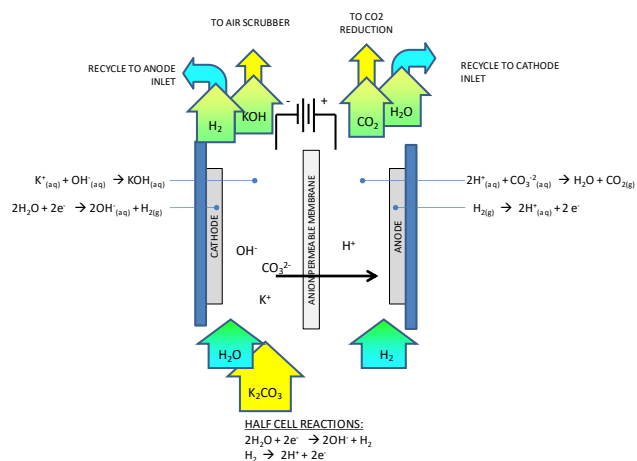
A. Preliminary Cell Performance

Each of the cell configurations depicted in FiguresFigure 9-Figure 11 was tested. The cells were tested at room temperature with 100 sccm of hydrogen and roughly 300 mL/min for the liquid solution flow rates. Potassium carbonate at a concentration of 1M was supplied to the cell in each case. The Faradaic efficiencies were calculated from gas chromatograph (GC) measurements of the carbon dioxide levels exiting the cell. The pH of the cell compartment containing the product potassium hydroxide was periodically measured to confirm the presence of the product solution. While the cation and anion membrane two-chamber cells did

Figure 12. Performance of the three-chamber cell.

function, there were various issues which will make implementing them a challenge. In the case of the two-chamber anion cell, the potassium carbonate and potassium hydroxide are mixed on the cathode of the cell. This led to low Faradaic efficiencies when attempting to drive the conversion higher. The reason for this was due to the competitive reactions taking place in the cathode. As the hydroxide concentration was driven higher, it was more likely that the cell would pump hydroxide across the membrane, forming water at the anode. In the case of the two-chamber cation cell, no carbon dioxide was initially emitted from the anode during operation. However, the cathode liquid was sampled and showed a pH of 14 indicating potassium hydroxide had been produced. This behavior was because of the well documented equilibrium conditions for carbon species in water[4]. The initial 1M potassium carbonate solution had a high pH of about 12. As solution was reacted in the cell, the pH slowly dropped. Equilibrium chemistry dictates the solution will shift from carbonate to bicarbonate as the pH drops to roughly 9. It isn't until the pH starts to approach a neutral value, when the initial salt is almost completely exhausted, that the equilibrium will shift towards carbonic acid, and as a result, gaseous carbon dioxide. This was confirmed by running the two-chamber cation cell for an extended period with a recirculating 0.1M potassium carbonate solution. As the potassium carbonate was depleted, carbon dioxide began to appear in the anode exhaust stream. Unfortunately, the high overpotentials and lack of reactant also caused cell corrosion to occur. Ultimately, it was determined that the three-chamber cell was the most viable design. Figure 12 gives the resulting cell polarization and Faradaic efficiency for the three-chamber cell assembled with Nafion 212 and Fumasep FAA-3-PK-75 selected as the membranes. The performance indicates a strong activation overpotential given that the equilibrium potential for the cell is only 0.83V at standard conditions. Optimization of the cathode will be necessary in the future to mitigate these losses as it is assumed the water electrolysis being performed with Raney nickel is the primary source of the activation overpotential. The Faradaic efficiency for the three-chamber cell decreases with increasing current density. This implies there are side reactions occurring due to the lack of reactants available locally. Water dissociation may be occurring in the central chamber, providing a proton and hydroxide, which then migrate to the anode and cathode to produce water[5]. The mass transport limitations most likely stem from the carbonate anion migration due to its poor ionic mobility. Future improvements can be made by improving the flow fields in the central chamber of the cell to minimize the development of concentration gradients.
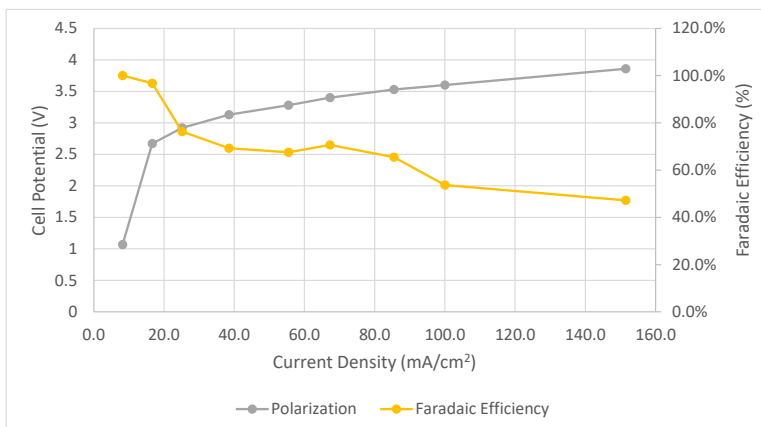
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IV. Electrochemical Reduction of Carbon Dioxide

Electrochemical conversion of CO_2 can generate a wide range of products including alcohols, alkanes, carboxylic acids and other hydrocarbons, turning a waste stream into a potential commodity on a pathway to higher value materials[6-8]. NASA currently employs a Sabatier carbon dioxide reduction system on-board the International Space Station to convert waste CO_2 from crew respiration along with the hydrogen byproduct from the water electrolyzer to produce methane and water vapor. The water vapor is condensed and delivered to the waste water bus for processing to potable water while the methane is currently vented overboard.

Half-Cell Reactions	E° (V)	n (#e⁻)
$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(l)}$	-0.10	2
$CO_{2(g)} + H_{2(g)} \rightleftharpoons HCOOH_{(l)}$	-0.17	2
$CO_{2(g)} + 2H_{2(g)} \rightleftharpoons HCHO_{(l)} + H_2O_{(l)}$	-0.11	4
$CO_{2(g)} + 3H_{2(g)} \rightleftharpoons CH_3OH_{(l)} + H_2O_{(l)}$	0.02	6
$CO_{2(g)} + 4H_{2(g)} \rightleftharpoons CH_{4(g)} + 2H_2O_{(l)}$	0.17	8

Full-Cell Reactions	E° (V)	n (#e⁻)
$2CO_{2(g)} \rightleftharpoons 2CO_{(g)} + O_{2(g)}$	-1.33	4
$2CO_{2(g)} + 2H_2O_{(l)} \rightleftharpoons 2HCOOH_{(l)} + O_{2(g)}$	-1.40	4
$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons HCHO_{(l)} + O_{2(g)}$	-1.34	4
$2CO_{2(g)} + 4H_2O_{(l)} \rightleftharpoons 2CH_3OH_{(l)} + 3O_{2(g)}$	-1.21	12
$CO_{2(g)} + 2H_2O_{(l)} \rightleftharpoons CH_{4(g)} + 2O_{2(g)}$	-1.06	8

Figure 13. Reversible electrochemical potentials of the CO_2 reduction reactions in half-cell (upper) and full-cell (lower) electrolyzer modes.

A number of alternate products are available through the electrochemical reduction of CO_2 as shown in Figure 13. Carbon dioxide can be reduced to such organic building blocks as carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH_3OH) and methane (CH_4). This electrochemical reduction to a liquid or gaseous organic produ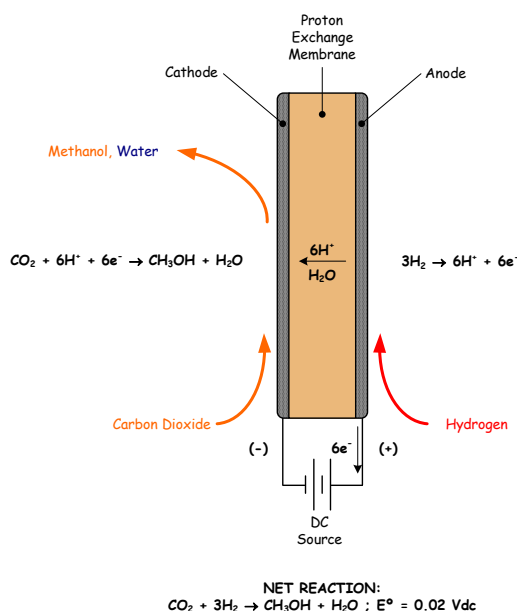ct requires the delivery of protons to the cell cathode and may be accomplished by operating the cell in either half-cell mode (where hydrogen is oxidized on the anode) or full-cell mode (where water is oxidized on the anode). The cell reactions, cell potential (at standard operating conditions), and number of electrons transferred per mole of carbon dioxide are defined in the table. Reactions with multiple electrons transfer are typically more difficult to execute.

Figure 14. Electrochemical reduction of carbon dioxide to methanol - half-cell mode of operation

In half-cell mode, hydrogen is delivered to the cell anode where it is oxidized to release protons and electrons as depicted in Figure 14. The protons migrate across the proton exchange membrane (PEM) under a voltage gradient imposed across the membrane. These protons are fully-hydrated as they transport across the membrane; hence, the hydrogen fed to the anode must be humidified to prevent membrane drying that would result in a decrease in the conductivity of the membrane. The electrons are conducted by a current collector within the anode cavity of the cell and are pumped to the cathode. Carbon dioxide is fed to the cathode side of the cell where it combines with the protons and electrons to produce methanol and water. The cathode electrode is produced to favor the formation of methanol over the evolution of hydrogen. Other organic products are possible depending on the cathode electrode and operating conditions of the cell.

In full-cell mode, water is delivered to the cell anode where it is oxidized to release oxygen gas, protons and electrons as depicted in Figure 15. As with the half-cell mode of operation, the protons migrate across the PEM to combine with the carbon dioxide on the cathode to produce methanol and water. The reversible cell potential for the full-cell mode

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of operation is lower than that of the half-cell mode by 1.23 Vdc – the reversible cell potential for the oxidation reaction of water in acid medium. In both cases it is apparent the role of the anode is to efficiently produce protons for the electrochemical reduction of carbon dioxide. Since water is fed directly to the anode there is no concern regarding membrane drying and its deleterious effect on membrane conductivity.

A. Test Results
Skyre has worked with the Northeastern University Center for Renewable Energy Technology (NUCRET) and Advent Technologies to develop and test different catalysts for the reduction of CO_2 to organic fuels such as formate and methanol. Skyre performed laboratory tests on low-temperature PEM-based laboratory cells having an active area of 82cm^2. These cells have a circular planform and are designed to safely contain a proof pressure of 6,000 psi. The cells were operated in a single-cell configuration; a total of 88 cells were built and tested as part of a program funded by the Advanced Research Projects Agency – Energy (ARPA-E). These cells were configured separately to evaluate:

- Cathode electrocatalyst material, preparation, and loading
- Effects of operating parameters on performance (pressure, temperature, supporting electrolyte)
- Manufacturing process control
- Flow field configuration
- Durability (limited testing)

A test system was built to run carbon dioxide cells in both half-cell and full-cell mode. The operating pressure ranged from 200 psig to 1200 psig; the operating temperature ranged from 25°C to 80°C; and the current density was varied between 0.1 to 0.5 A/cm^2. Samples were drawn from the cathode at specified times according to the test plan. Each sample was evaluated for methanol by using an SRI 8610C Gas Chromatograph with Flame Ionization Detector (FID) and for formate using a Dionex ICS-1500 Ion Chromatograph.
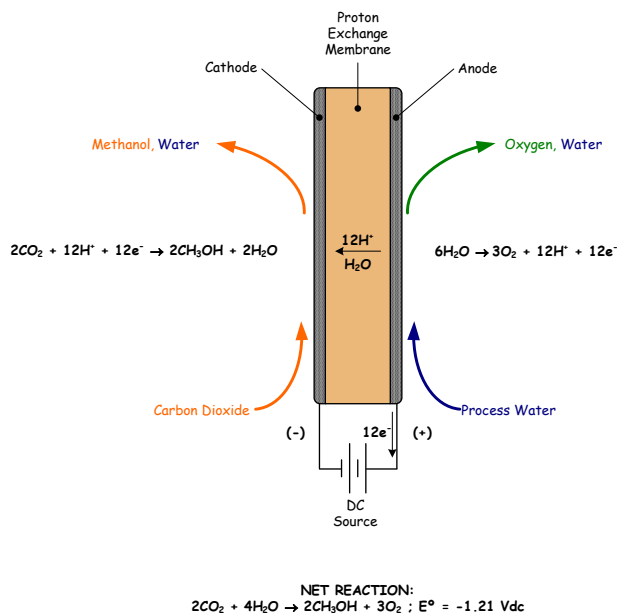

Figure 15. Electrochemical reduction of carbon dioxide to methanol - full-cell mode of operation
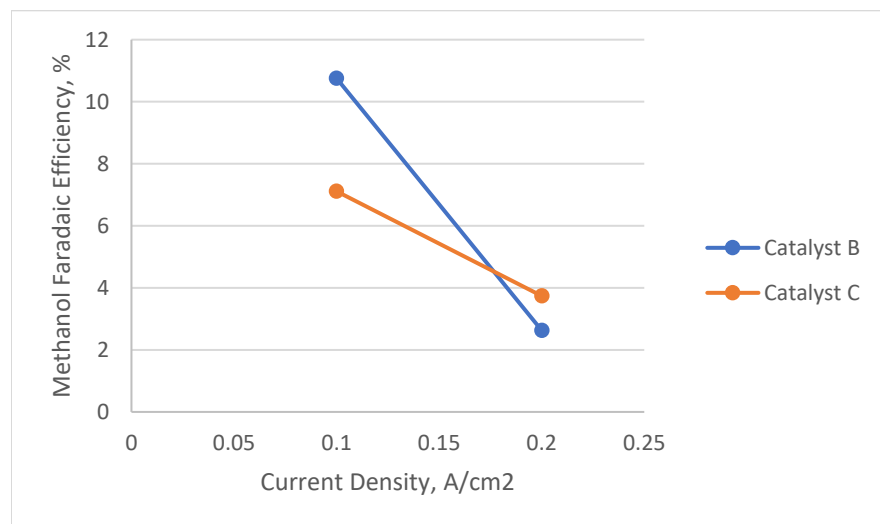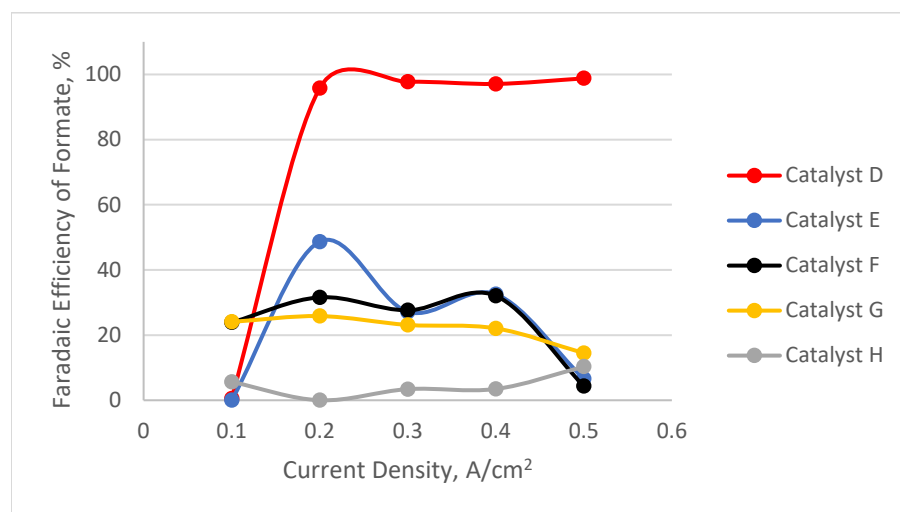

Figure 16. Catalysts B and C demonstrated the best performance for methanol production. Both catalysts were operated at 25°C, 200 psi in full-cell mode.

A total of 21 different catalysts were tested from 6 different catalyst families. For the production of methanol, Catalysts B and C seemed to exhibit the best performance compared to the other catalysts tested. Both catalysts achieved a reasonable Faradaic efficiency of 7.11% and 10.75% for methanol production as shown in Figure 16, but what is interesting is this efficiency is achieved at much higher current densities than other catalysts tested. For example, Catalyst A achieved a Faradaic efficiency of 8.64% for methanol at only 0.01 A/cm2 with a cell voltage

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of 2.58V. Catalyst B achieved a higher Faradaic efficiency operating at ten times the current density. The reason for this can be traced to operating voltage. Here it is important to keep in mind that in both cases the cell is operating in full-cell mode, meaning the equilibrium voltage shifts higher by at least 1.23V versus the half-cell mode. Both Catalysts B and C maintain a cell potential of only 2.45V and 2.32V at 0.1 A/cm², respectively, versus Catalyst A, which maintains 2.58V at 0.01 A/cm². This implies that there is far less cathodic overpotential associated with the catalyst family of B and C versus Catalyst A, highlighting the importance of selecting catalysts with low activation overpotentials to keep the cathode voltage as low as possible to improve methanol selectivity.

The formate results of one family of catalysts operating at 80˚C, 750 psig over varying current densities are presented in Figure 17. Interestingly all the catalysts produced formate in the range of conditions studied, with Catalyst D outperforming the rest with nearly 100% Faradaic efficiency obtained at up to 0.5 A/cm². None of the catalysts resulted in any measurable methanol production. This may be due to the higher current densities run, 0.1-0.2A/cm².

Figure 17. Faradaic Efficiency for Formate Production for Operating Conditions of 80 °C, 750 psi. All Cells Were Run as Half Cells.

The effect of cell operating conditions on selectivity and Faradaic efficiency was investigated with the use of multiple regression analysis for the full-cell reaction. The analysis confirmed that the cell voltage was an important parameter, with higher voltages favoring formate production and lower voltages favoring methanol. The effect of pressure and temperature were weaker, with increased pressure promoting the production of formate and increased temperature inhibiting methanol production. The first outcome relative to pressure is consistent with thermodynamic arguments but the temperature effect is not consistent with those arguments. The additional kinetic and solution equilibrium conditions, which were not considered in the preliminary analysis of the data, are most likely the cause.

Further experimentation is planned whereby the cathode overpotential will be directly measured to more clearly define the relationship between voltage and selectivity and overall organic Faradaic efficiency. This activity is planned under a Department of Energy (DOE) program to produce formic acid from carbon dioxide emissions.

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V. Electrochemical Hydrogen Separator and Compressor (EHSC)

The production, transport, delivery and storage of hydrogen are costly processes, making hydrogen a valuable commodity. A significant portion of the cost of hydrogen to the end consumer is the cost associated with transportation. Various means are used to deliver hydrogen to the point of use, including cylinder delivery, gaseous tube trailers, cryogenic liquids and pipeline delivery methods[9]. The most economical mode of delivery for a given end user is dependent on both the amount of hydrogen consumed and the distance from a hydrogen production facility. NASA and many others often rely on delivery of cryogenic hydrogen to meet their facility needs. NASA's Stennis Space Center (SSC) is one of the largest users of hydrogen, where the liquid hydrogen (LH$_2$) is used as a fuel for rocket engine testing. Other NASA centers, including the Kennedy Space Center, historically utilized hydrogen to support space shuttle launches, and many industrial locations also use significant amounts of hydrogen. Unfortunately, extremely large amounts of hydrogen are lost during transfers and test operations due to boil-off resulting from heat transferred into the equipment, or by other means. Additionally, either through test operations or industrial processes, hydrogen becomes mixed with other gases; this gaseous hydrogen "waste" is typically flared as a safety measure with little to no economic value or energy recovery realized from the process.
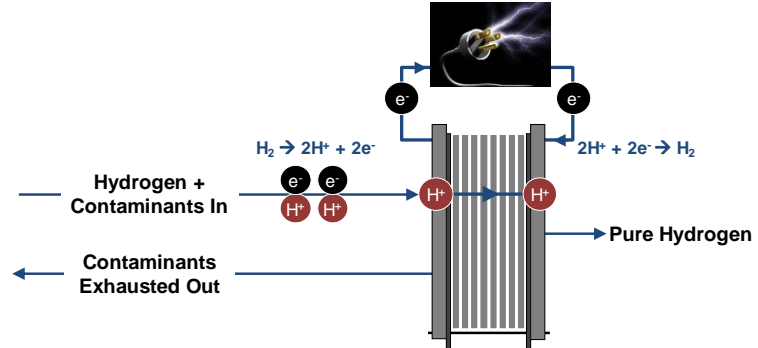

Figure 18. Electrochemical hydrogn pumping – cell schematic.

Skyre has developed an electrochemical hydrogen separator and compressor (EHSC) to safely capture, process and store/deliver high-purity hydrogen (>99.99%) from the large amounts of gaseous hydrogen released during NASA test operations, or in industrial application where hydrogen is used. The process is depicted in Figure 18. A stream rich in hydrogen is fed to the anode of an EHSC cell stack where the hydrogen is broken down into protons and electrons. The protons are transported across a proton exchange membrane from the anode to the cathode due to the imposed electrical field across the cell. The electrons are pumped by a DC power supply to the cathode where they recombine to form pure hydrogen gas. Any contaminants present in the feed stream are exhausted along with a small amount of hydrogen gas that purges the anode cavity of the cell. Most of the time these contaminants include various inerts such as nitrogen. However, additional consideration must be given to certain components such as carbon monoxide or sulfur compounds which may poison the stack. Depending on the levels present, additional filtering or processing upstream of the stack may be deployed. The hydrogen pressure on the cathode is only limited to the design pressure of the cell hardware and its ability to effectively seal the membrane overboard (internal pressure to ambient) and cross-cell (cathode to anode). Individual cells are stacked in a filter press arrangement such that they are electrically in series but with the fluid paths in parallel. A photograph of four 30-cell EHSC stack assemblies is included as Figure 19 Polarization curves (voltage versus current) and a life curve for a 16-cell stack assembly are included in Figure 20 and Figure 21, respectively.

Figure 19. Four 30-cell HHSC stack assemblies.

1. System Applications and Results

Skyre has built and tested a number of electrochemical hydrogen separation and compression (EHSC) cell stacks and systems for both NASA and industry to safely and efficiently separate hydrogen gas from a variety of feedstocks rich in hydrogen. While each application is unique – varying composition or gas quality, different output pressures, or
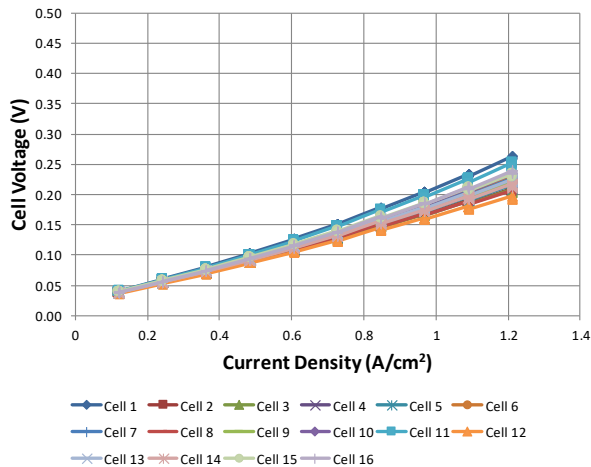
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Figure 20. Initial polarization curves for a 16-cell hydrogen pump stack assembly operating on pure hydrogen.

hydrogen recovery rates – the basic cell architecture depicted in Figure 8 is the same. Specific examples including relevant performance information are provided in the following paragraphs.

• *Recovery of hydrogen from cryogenic boil-off.* The NASA Stennis Space Center (SSC) requires hydrogen gas for test firing of rocket engines. Given the volume of hydrogen required for these test firings Stennis has significant inventory of liquid hydrogen on-site in vacuum-jacketed storage tanks, or dewars. Hydrogen gas from the boil-off of the cryogenic liquid is required to pressurize the liquid hydrogen storage tanks and purge helium from the liquid hydrogen supply lines. This hydrogen supply line operates between 2500 psig and 3200 psig. The EHSC system was designed to take hydrogen from between ambient and 185 psig and compress it to up to 4500 psig. Four 30-cell stacks in the EHSC system can replace (2) 10-gpm liquid hydrogen pumps that operate a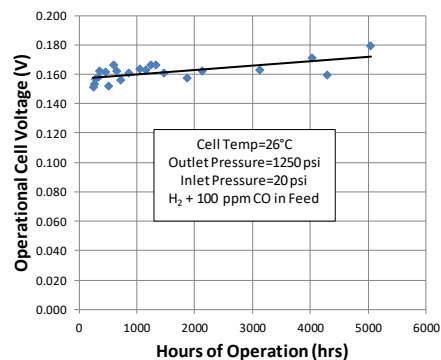n estimated 2-4 hours per week (plus additional hour of parasitic run time to cool the pumps) to maintain this pressurized hydrogen system. The performance curve for one of the four cell stack assemblies is included as Figure 22. The cathode pressure is the hydrogen delivery pressure at the outlet of the electrochemical hydrogen compressor. At the maximum design pressure of 4500 psig, the average cell voltage is just under 150 mV, representing a specific energy of about 4 kW-hr/kg for the EHSC cell stack assembly. The Nernst+IR curve represents performance predictions based on the Nernst equation (defines cell overpotential due to operating pressure) with IR overpotential (product of cell resistance and cell current). Isothermal performance is based strictly on predictions from the Nernst equation and can be used as a baseline for cell performance.

• *Recovery of helium (and hydrogen) from test engine firing.* The NASA SSC has an additional need for hydrogen separation from helium purge gas after cleaning of the hydrogen lines after engine testing events. Large amounts of hydrogen are currently flared along with valuable helium gas following system purges. Using an EHSC system, the hydrogen and helium can be captured and separated; the hydrogen is compressed without

Figure 21. Average cell voltage over 5000 hours of operation. Feed: hydrogen with 100 ppm carbon monoxide operating for 5000 hours.

additional capital equipment and for low incremental electricity consumption, for energy uses such as fueling vehicles or power generation; the helium can be compressed and stored in high-pressure cylinders via a mechanical compressor for subsequent rocket engine firing test programs.

An advanced prototype system called the Helium Recovery System, or HRS, was built and delivered to NASA SSC to demonstrate the viability of hydrogen/helium separation, with testing and system commissioning completed in March 2018. A photograph of the unit is included as Figure 23; the smaller container in the foreground housed the HRS while the large container housed the capture module (capable of collecting up to three hundred cubic feet of gas in under five minutes at up to 50 psig). Photographs of the HRS cell stack assemblies are included in Figure 24. The HRS was dormant at NASA SSC for over a year prior to its commissioning.

The HRS incorporates four eight-cell stack assemblies that perform the bulk separation of hydrogen from helium. The gas mixture flowed through the anode side of each of the stacks sequentially such that each subsequent stack in the series saw reduced hydrogen/enriched helium content. Hydrogen is pumped across the membrane to the cathode leaving an enriched helium gas stream on the anode. The enriched helium stream at the exit of the fourth stack (>97%
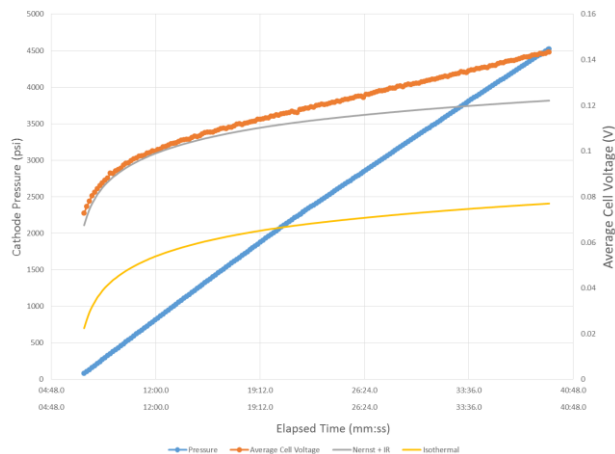
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Figure 22. Average cell performance of a 30-cell EHSC cell stack assembly. The cathode pressure is the hydrogen discharge pressure from the cell stack assembly.

by volume) is pressurized via a mechanical compressor (up to 850 psig) and delivered to the anode of a five-cell polishing stack (five electrochemical hydrogen pump cells flowing in a series configuration) where almost all of the remaining hydrogen is pumped and delivered to the cathode.

During the commissioning test the capture tank was filled with 36% hydrogen, 4% nitrogen, balance helium at 44 psig. The current for each of the four eight-cell stack assemblies was monitored; the results depicted in Figure 25 show decreased current for each subsequent stack in series indicating reduced hydrogen content in the inlet mixture to each stack. The commissioning test was run for seven hours, with the helium storage tank pressurized to about 500 psig; for this test program the hydrogen was not recovered. The purity of the helium was measured by the NASA SSC lab and found to be 99.659%, with the primary contaminants being hydrogen and nitrogen (the dew point of the product helium was -72°C (-97°F)). A plot of the helium pressure versus test time is included as Figure 26.

Figure 23. Helium Recovery System (HRS) being readied for commissioning at NASA Stennis Space Center.

Skyre is currently constructing another unit for NASA SSC having a higher processing throughput capability and a 3000 psig helium compressor to enable higher pressure charging of their helium storage system. This unit is scheduled to ship to NASA SSC in April 2019.
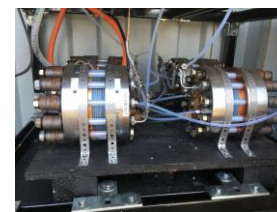
• *Hydrogen recovery from heat treat furnaces.* The metals heat treat industry use hydrogen to inert their furnaces. The

Figure 24. Four eight-cell EHSC cell stacks for the HRS at NASA SSC.

hydrogen from the process is typically vented or flared, representing significant operating cost. Skyre has adopted the EHSC technology to a commercial product called H2RENEW™ that takes hydrogen-rich furnace exhaust gases, purifies and pressurizes the hydrogen for return to the furnace. Impurities such as carbon monoxide, ammonia, oil and metal dust are removed from the exhaust in a multi-step process; up to 95% of the available hydrogen can be recycled depending on the degree and type of initial contamination (75% to 85% is typical). The current H2RENEW can process up to 100 kg of hydrogen per day and return it at 100 psig at >99.99% purity. Plans are underway to increase the pressure rating to 1000 psig.
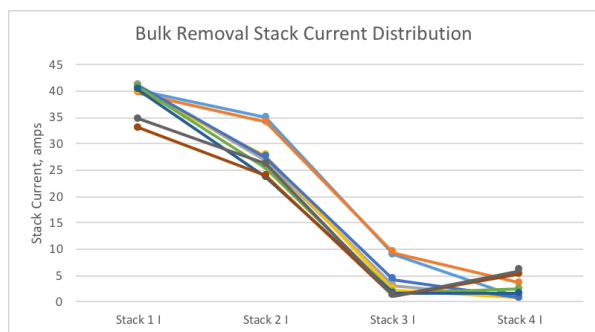
• *Recovery of hydrogen from a gas stream containing acetylene, carbon monoxide and other hydrocarbon species for recycle to the Sabatier carbon dioxide reduction system.* NASA is examining methods to 'crack' the methane produced from the Sabatier reaction to recover the hydrogen for increased oxygen recovery. A plasma pyrolysis assembly is being developed which cracks methane producing a gas stream that contains hydrogen, carbon monoxide and a variety of hydrocarbons including unreacted methane, acetylene, ethane, and ethylene, among others, in a
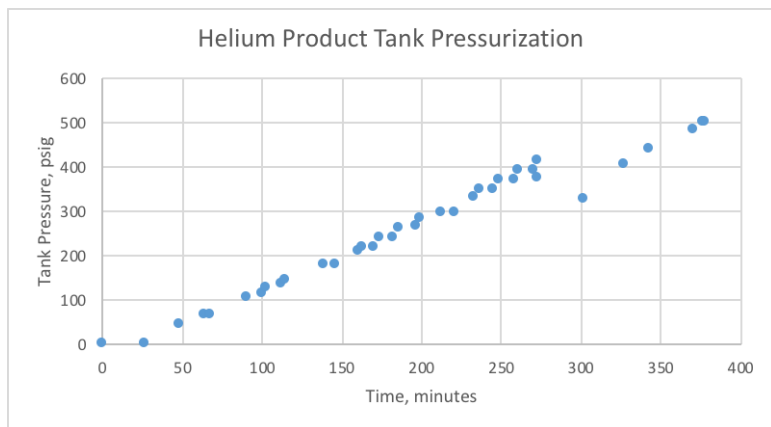

Figure 25. Bulk hydrogen removal cell stack current distribution.

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Figure 26. Helium product tank pressure versus operating time of HRS.

saturated gas stream. The cell design utilizes a unique anode catalyst that effectively manages the carbon monoxide contaminant and limits the hydrogenation of acetylene. This application is further described in a separate ICES 2019 paper (ICES-2019-150).

VI. Conclusion

Future manned space missions will require new approaches to life support systems that finally break the supply chain back to earth. Technologies that improve recycling efficiency of oxygen and water, and can make use of available resources on extraterrestrial bodies to provide for the crew are important steps in breaking this dependency. Electrochemical solutions based on the same PEM technology currently operational on-board the ISS can help to resolve pressing issues of: oxygen purification and compression for medical use and recharge for EVA; carbon dioxide and compression in a single cell embodiment without the noise and maintenance requirement of a mechanical compressor; carbon dioxide reduction to useful fuels and starting chemicals that could facilitate production of other chemicals, building materials or foodstuffs; and hydrogen separation, its purification and compression in chemical processes such as propellant manufacture. Skyre continues to advance the electrical performance and efficiency of their electrochemical conversion devices with improvements in membrane transport processes, catalysis and mechanical and electrical cell design through self-investment as well as investments made by key government agency stakeholders. These improvements not only benefit those who bravely enter our final frontier, but also those of us on Mother Earth as these new technologies can reduce our waste streams by recycling valuable hydrogen or upcycling waste carbon dioxide to useful organic materials.

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