In-Situ Resource Utilization for Electrochemical Generation of Hydrogen Peroxide for Disinfection

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Disinfection needs to meet the personal hygiene requirements of interplanetary travel community in space vehicles is currently accomplished through the use of pre-packaged, disposable, wetted wipes, which represent an appreciable carry-along mass and disposal burden. There is a stated need to develop a system that could use onboard utilities to create on demand disinfectants thereby reducing the astronaut's dependence on earth-based supplies and further eliminating storage and disposal problems. Within this context, we are developing an in-situ approach to electrochemically generate hydrogen peroxide disinfectant utilizing onboard life support supplies (Oxygen/Water) to eliminate many of the surface contaminants present in closed living systems. As discussed within our 2019 paper we have demonstrated the potential to produce up to 1 w/w% peroxide with reverse osmosis (RO) treated and deionized (DI) water and oxygen utilizing our optimized system. This paper will build upon that work and discuss the results from our low-gravity flight test and system scale-up activities. The current operating target for the alpha scale system is set at 1 L of 1 w/w% peroxide per day. The peroxide generation system offers a more economical and practical alternative, with the disinfectant solution being generated on demand and in-situ; and applied to reusable cloths, reducing both the carried and disposed mass associated with the disinfection process. The peroxide generation system demonstrates a strong potential to address a critical need of disinfection within ISS and will also be able to address Earth-based needs in various settings such as hospitals, restaurants, movie theatres, among many others.

Nomenclature

AEM	=	Anion Exchange Membrane
CDC	=	Centers for Disease Control and Prevention
DI	=	Deionized
EML	=	Electrochemical Microgravity Laboratory
EEB	=	Environmental Enclosure Box
GDE	=	Gas Diffusion Electrode
ISS	=	International Space Station
MPL	=	MicroPorous Layer

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MMO = Mixed Metal Oxide
PGU = Peroxide Generation Unit
PEM = Proton Exchange Membrane
PEEK = Polyether Ether Ketone
RO = Reverse osmosis
SCC = Safety Containment Chambers
UPR = University of Puerto Rico
UV-Vis = Ultraviolet–visible

I. Introduction

Numerous technological advances are sought to facilitate human space travel. *Solutions and innovations are needed for technology that supports the mass- and energy-efficient maintenance of closed air, water, and waste systems in spacecraft habitats that operate on planetary surfaces, such as Mars, and that operate in the microgravity environment of space*. One such need is for disinfection to meet the personal hygiene requirements of interplanetary travel community in space vehicles. Currently, disinfection need is accomplished through the use of pre-packaged, wetted wipes, which is about 1 g wipe with about 5 g of 0.5% hydrogen peroxide solution. The disinfectant wipe usage rate on ISS is on average 3.8 wipes/person/day, which is equivalent to 8 kg of wetted wipes per person per year. This represents an appreciable carry-along mass and disposal burden. Accordingly, *"a mechanism for the in-situ generation of cleaning/sanitizing solutions is needed that will enable these solutions to be applied to reusable fiber-based wipes to remove particulate, food, and body oil soiling of surface."*[1] Such solutions must also serve an anti-microbial function, demonstrating efficacy against at least *food based bacteria, iodine resistant bacteria, and fecal coliform bacteria*.[1] Since the solutions will be used within closed crew compartments, it is also important that they are non-hazardous in the context of *direct crew contact with cleaning/sanitizing solutions and direct off-gassing and accumulation of solutions in cabin atmosphere*. Such an *in-situ* generation mechanism would replace the current consumables-intensive approach utilizing pre-moistened disposable wipes. In order to achieve that end, as initially introduced within our prior work[2] and 2019 ICES paper,[3] Faraday Technology Inc (Englewood, OH) and the University of Puerto Rico (UPR) are developing an on-demand system for the in situ electrochemical generation of hydrogen peroxide utilizing life support components of oxygen and water. As described within our previous publications,[2,3] hydrogen peroxide (H_2O_2) is readily synthesized by the electrochemical reduction of O_2 (Figure 1; $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) in presence of an aqueous working electrolyte (water), has non-toxic decomposition products (viz., O_2 and H_2O), is safe for direct skin contact at functionally active concentrations (~1-5% w/w), and has a demonstrated disinfection capability.[4] Hydrogen peroxide is thus an ideal active ingredient for a cleaning solution in the enclosed environment of a space vehicle crew quarters. Within the activity described herein, Faraday was tasked to: 1) demonstrate the potential to electrochemically generate peroxide in low-gravity using the bench scale peroxide generation unit from our prior work; 2) produce >1 w/w% H_2O_2 with available life support materials (oxygen and water), and; 3) design, build, and optimize an alpha scale system that can produce up to 1 L/day of >1 w/w% for either surface disinfection or laundry applications.

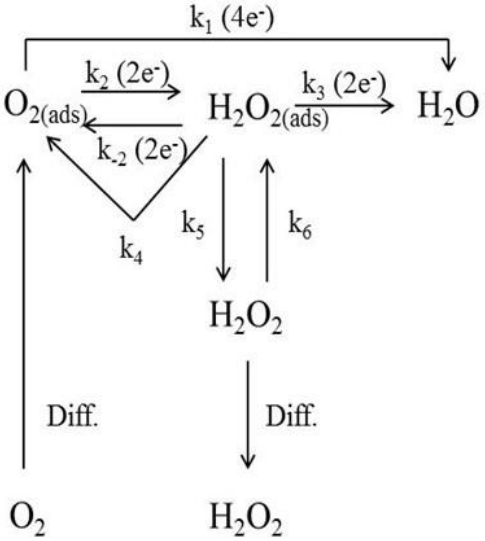

Figure 1. Potential reaction pathways for oxygen reduction to peroxide.

II. Experimental

A. Prototype Peroxide Generation Unit (PGU)

The continuous bench scale peroxide generation unit with 6.25 cm^2 active electrode area, optimized within our ICES 2019 manuscript is shown in Figure 2A and Figure 2B.[3] Based on results of the 2019 study, we down selected the following system variables: 1) ion exchange beads consisting of Amberlite IR120; 2) a gas diffusion electrode (GDE) cathode consisting of CeTech W1S1005; 3) catholyte consisting of water treated with reverse osmosis (RO) process; 4) a PEEK catholyte chamber with 0.37" thickness; 5) a titanium anode chamber; 6) an expanded mesh dimensionally stable anode welded into the Ti anode chamber; 7) a graphite cathode chamber; 8) an oxygen feed gas

in the cathode chamber; 9) a back pressure balance manifold (Equilibar LF Series Precision Back Pressure Regulator) around GDE to eliminate catholyte feed into the cathode chamber; and 10) a Nafion 117 ion exchange membrane.

The following discussion can also be found within our 2019 ICES manuscript[3] but due to its importance in understanding the operation of the PGU, this text has been included herein. During the operation of the bench scale PGU the RO water source will enter the liquid catholyte inlet port (within the catholyte chamber). Water from the solution diffuses across the proton exchange membrane (PEM; Nafion 117) to the catalyst-PEM interface at the anode. When an electrical overpotential is applied to the cell, water is converted to oxygen gas and hydrogen ions at the mixed metal oxide (MMO) anode ($2H_2O \rightarrow O_2 + 4H^+ + 4e^-$). These hydrogen ions are transported from the anode-PEM (such as NAFION 117) interface through the membrane and across the ion exchange media (Amberlite IR120) and catholyte (RO water) to the cathode gas diffusion electrode (GDE; CeTech W1S1005) where it reacts with the available oxygen gas to form hydrogen peroxide ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) at the cathode's catalyst-catholyte-gas (solid-liquid-gas) interface. Attraction of molecules to the positive charge of each proton exchange through the PEM results in a flux of previously-diffused liquid water transporting across the PEM from the anode to the catholyte, this behavior is called "protonic drag". A smaller fraction of the protonic drag is forced back at a rate determined by pressure, temperature and membrane conditions. At sufficiently low current density, the net flux of water is dominated by diffusion across the PEM to react at the cathode catalyst-PEM interface. Catholyte, oxygen, and hydrogen peroxide solution from each operating cell collects in each cell stack's internal manifold and exits each cell stack. The cell stack is powered via a dedicated power supply that is controlled by computer software and external shutdown signals from a programmable logic controller. The prototype PGU (Figure 2B) is currently being used for testing. Multiple catholyte channels have been constructed in order to understand the effect of conductivity gap and electrolyte volume on product generation and the potential to attain better control of the residence time. The catholyte process flow stream can be utilized via either a single pass or recycle loop orientation to reduce the size of the PGU or increase the concentration of the product collected.

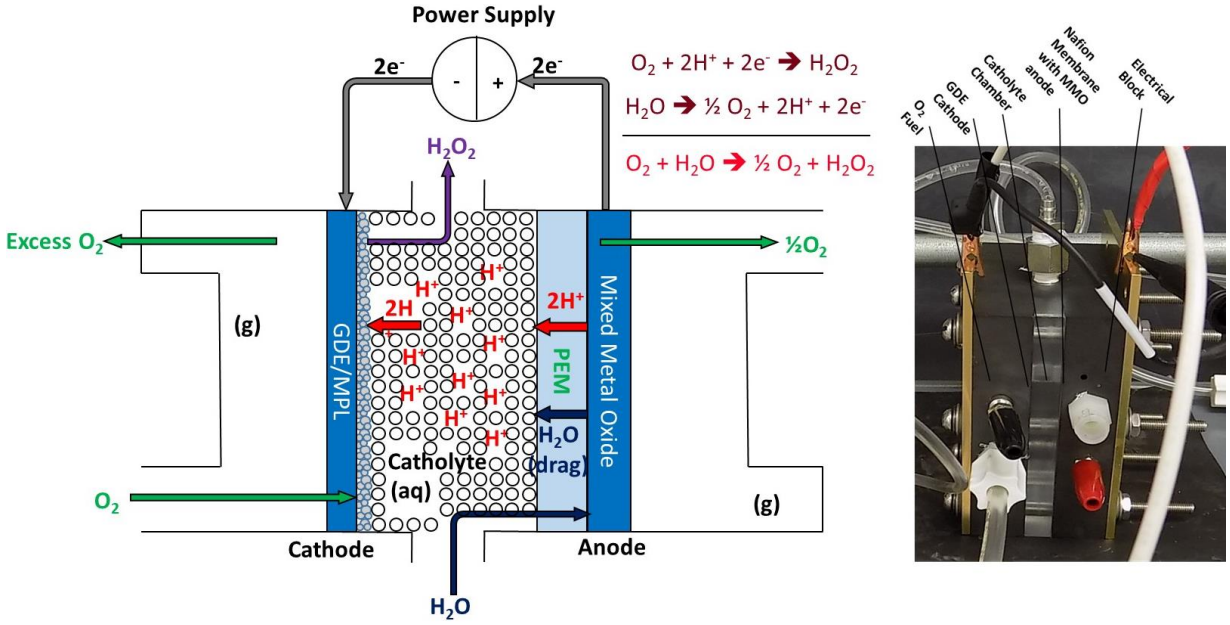

Figure 2. (A) Conceptual schematic of the Peroxide generation units with single-cell chemistry (left); (B) Modified PGU currently used for peroxide generation (right).

B. Characterization of Peroxide

In order to continuously measure the concentration of generated peroxide, we have developed a technique that utilizes UV absorption at about 240 nm [5,6] to quantitatively analyze H_2O_2 by using Beer-Lambert Law

$$A = \text{Log}\,(I_o/I) = \varepsilon bc \qquad (1)$$

where,

A is absorbance

I_o is the initial light intensity
I is the light intensity
ε is the molar excitation coefficient
b is the path length of the sample
c is the concentration of the samples

In order to facilitate *in-situ* measurements during the flight test, a portable FLAME-CHEM UV-Vis Spectrometer Systems (Part # FLMS05367) from Ocean Optics, Inc. and flow through cuvette (Part # 71B-Q-1) from Starna Cells were procured, as shown on the left in Figure 3. Using this system and a commercially procured unstabilized hydrogen peroxide (3% w/w) we prepared a calibration curve, as shown in Figure 4.

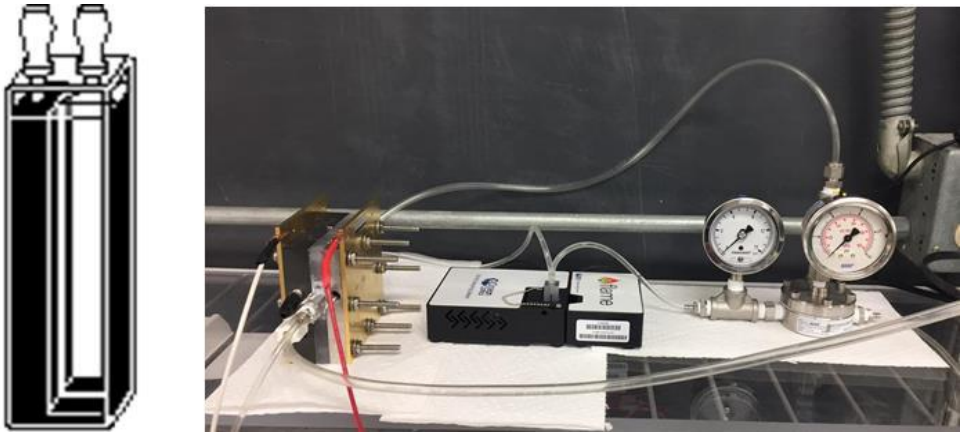

Figure 3. Flow through cuvette (Part # 71B-Q-1) from Starna Cells (Left); Peroxide generation unit with inline FLAME CHEM UV Vis unit and Equilibar back pressure regulator (Right).

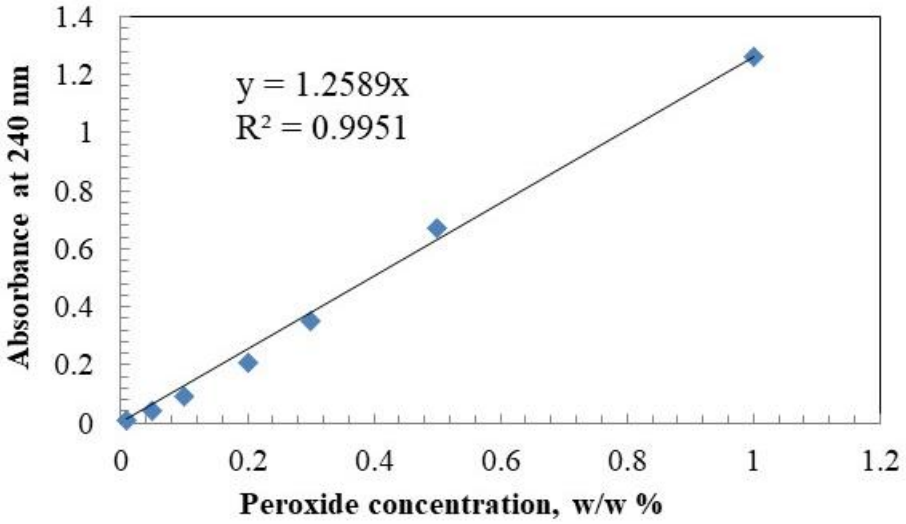

Figure 4. Concentration profile of hydrogen peroxide based on UV absorption spectra.

C. Electrochemical Microgravity Laboratory

A custom-made electrochemical microgravity laboratory (EML)[7] developed by the University of Puerto Rico was adapted for the in-situ peroxide generation *low-gravity* experiment. First, the system components for the low-gravity flight test were contained within three individual polycarbonate safety containment chambers (SCC), which are located within the environmental enclosure box (EEB) (47" x 14" x 12"; Figure 5). All boxes were bolted to an aluminum base plate with dimensions of 50" x 22" x ½". The base plate was bolted to the aircraft through AN-6 Steel

Bolts (3/8" diam.). Furthermore, the EEB is vented out of the aircraft ensuring any outgassing for the electrochemical process will not be exposed to the cabin or crew.

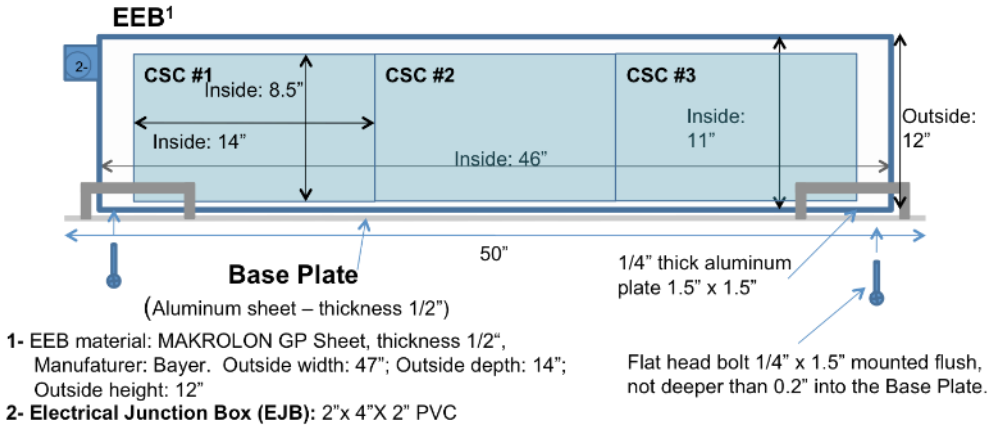

Figure 5. Detailed schematic front view of Experimental Equipment Box and base plate.

The EML, developed by UPR initially, had to be modified to meet the requirements for operation of the peroxide generation unit. Specifically, the EML's three SCC had to accommodate the pump, bench-scale PGU, the UV-Vis, the back pressure controller, the oxygen cylinder, and the oxygen pressure controller. Based upon these requirements, the EML's design drawing (Figure 6) was modified to accommodate all the components to perform the *in-situ* peroxide generation reaction. Figure 7 shows the location of each of these components within the EML; with the central containment holding the bench-scale PGU, UV-Vis, and pressure regulator; the left container holding the oxygen cylinder/controller; and the right containment holding the liquid flow pumps.

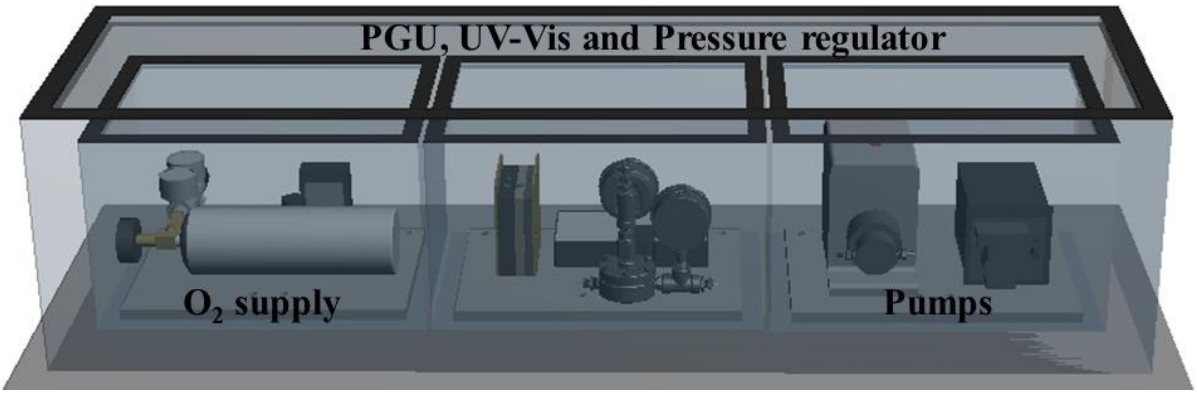

Figure 6. View of the full cell setup inside the *low-gravity* test rig.

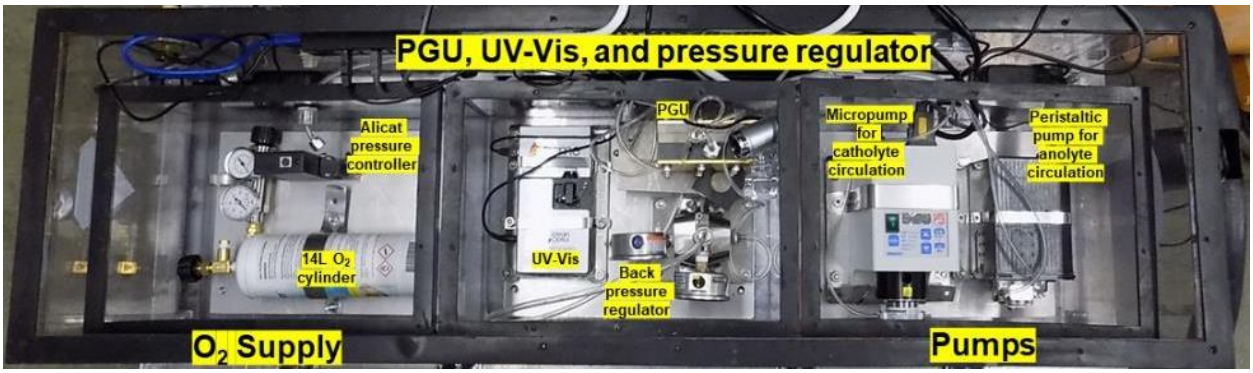

Figure 7. Top view of complete assembled PGU system in the EML

III. Results and Discussion

A. Ground Based Peroxide Generation Tests within the *EML*

Prior to initiating low-gravity trials, we performed a group of ground-based trials within the fully enclosed EML in order to down select operating conditions for the low-gravity flight test. Optimized conditions identified from our prior work were implemented for these trials.[3] The initial trial was performed using materials discussed above and with 50 mL of RO water continuously circulated through catholyte chamber at a feed rate of 15 mL/min. Additionally, RO water was circulated through the anode chamber at 10 mL/min at a constant voltage of 16 V and was operated for 2 h. Figure 8 shows the resulting current and voltage profile (Left) and the peroxide generated (Right) as a function of time within this bench-scale PGU system. This data further indicates the potential of generating 50 mL of ~1 w/w% peroxide within 2 h of PGU operation at 33% current efficiency and energy consumption of 77 kWh/kg_{H2O2}, within the fully enclosed EML. This trial along with a few others identified key issues with closed loop EML operation, specifically:

- We observed a large pressure build up in the anolyte and catholyte lines when operating at 16 V; therefore, during the low-gravity trial a lower potential of 12 V to 14 V was utilized.
- A 35 mL catholyte volume was recommended for peroxide generation and detection within the 3 h low-gravity flight test and ideally should generate up to 0.5 % H_2O_2.
- Running the PGU with and without water circulation in anode during the 3 h low-gravity flight test could enable characterization of the effects of bubble generation on the anode.

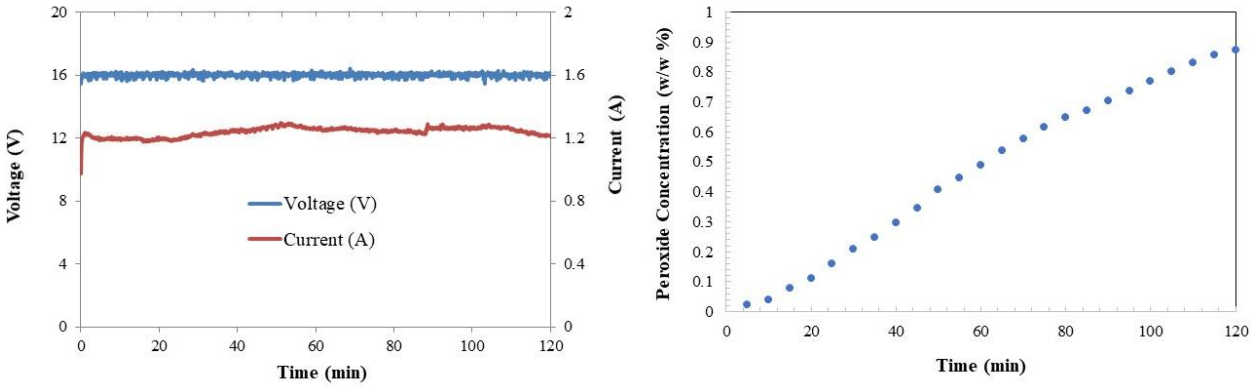

Figure 8. Performance of multi-pass polarization trials conducted within the EML

Based upon the above results, a trial was performed using the following processing conditions:

- Applied potential: 12 V
- Anolyte: off (no flow) for initial 100 min
- Anolyte: 20 mL/min flow of RO water for final 40 min
- Catholyte Electrolyte: 35 mL RO water at 20 mL/min
- Pressure balance around the GDE: 1 psi

Figure 9 shows the stable peroxide generation performance within the EML at nominally identical conditions to those planned for the low-gravity flight test discussed within the next section.

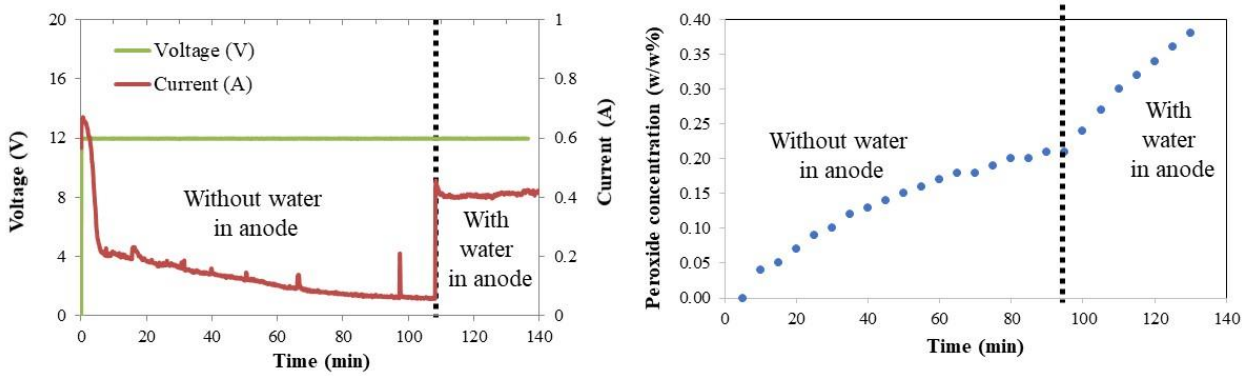

Figure 9. Performance of multi-pass polarization trials conducted within the EML

Based on these trials, the following conditions were down-selected to investigate peroxide generation performance in low-gravity environments.

- W/ and w/o anolyte RO water flow
  - ***first 15 low gravity simulations w/o water; final 15 low gravity simulations w/ water (at 20 mL/min)***
- How many catholyte cell passes per low-gravity moment?
  - ***Using a Catholyte Volume of 35 mL at 20 mL/min we anticipate that the 3 mL operating area of the PGU will observed ~2.5 passes per 17 sec low gravity moment.***
  - ***Additionally, we anticipate the full 35 mL volume to pass through the PGU at least every 2 min***
- Variables to be constant:
  - Applied voltage (***12 or 14 V***) with targeted current at ~0.2 A
  - Time between cell exit and U-Vis (***~10 mL or 30 sec***)

B. Low-Gravity Test

With the above UPR EML system and the simulated operating conditions, we contracted Zero G Corporation to take part in their parabolic research flight initiative. The flight test performed consisted of two Martian gravity simulation, three lunar gravity simulations, and twenty-five low-gravity simulations. The total time for each low gravity trial was ~17 seconds with two to three minutes between each low gravity event. During our flight, we were able to acquire accelerometer data with the help of Prof. Steven Collicott, (Purdue University). Figure 10 shows the overall flight profile while Figure 11 shows the profile broken down into segments of five low gravity moments.

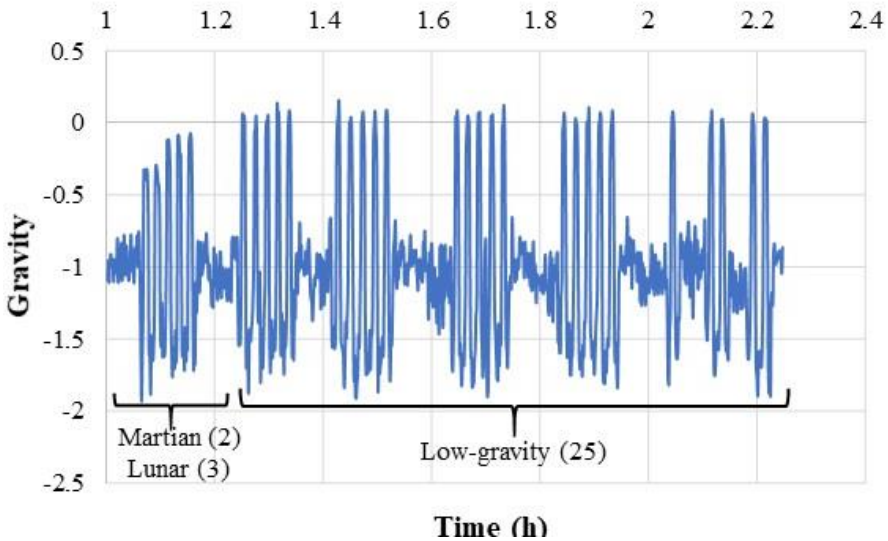

Figure 10. Accelerometer data from the low-gravity flight demonstrating the overall Martian, Lunar and low-gravity profile

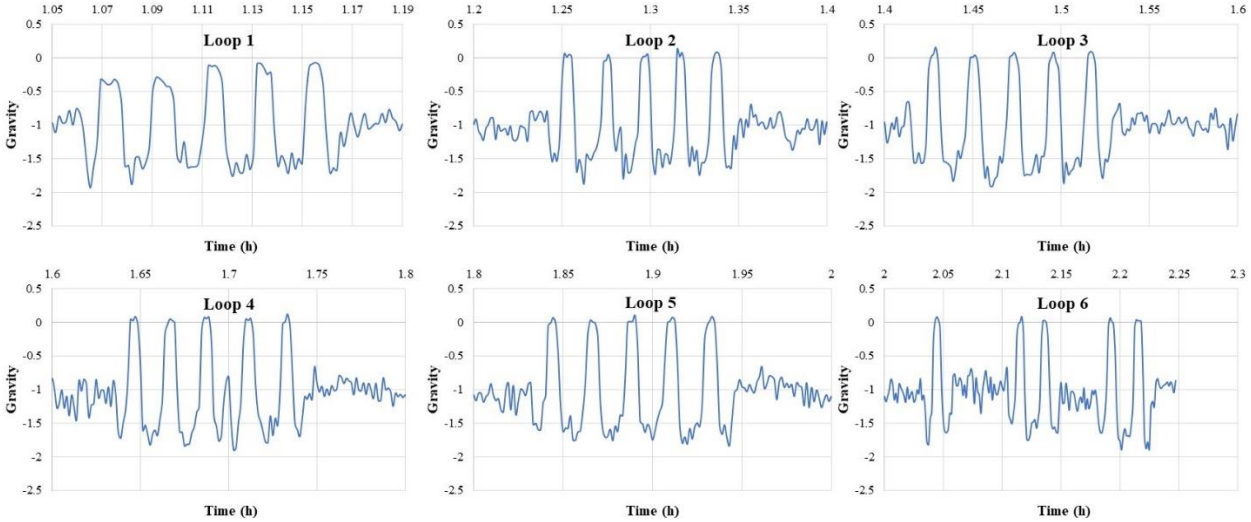

Figure 11. Accelerometer data from the low-gravity flight demonstrating the individual Martian and Lunar profile in loop 1 and low-gravity profile in loops 2 through 6.

The ground-based operating conditions discussed above were implemented during the low-gravity flight test to evaluate the feasibility of producing hydrogen peroxide in low-gravity environment. However, key issues experienced during the flight led us to modify some of these variables in order to acquire meaningful data. Issues identified during the flight test include:

- At the onset of the first low-gravity moment, we observed large positive pressure swing during the low gravity time and a reverse pressure swing during high gravity duration (Figure 12). In order to gain better control, we increased the back-pressure around the GDE to 3 psi to reduce liquid flow into the pressurized deadheaded oxygen chamber.
- At the onset of PGU operation, we observed a lower than anticipated current when the desired 12 V overpotential was applied. Therefore, the potential of the cell was increased to 16 V to increase the current and rate of peroxide generation during the anolyte water free trial.

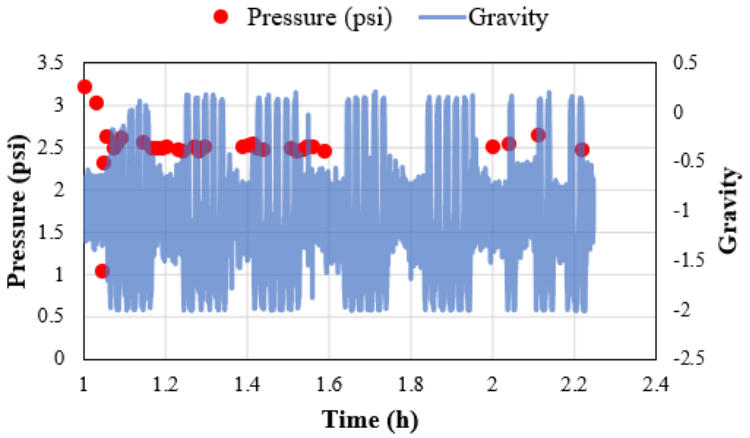

Figure 12. Pressure readings (represented by red dots) during the microgravity flight profile (represented by blue line)

- When the anolyte flow was initiated (after 15 low gravity simulations), we observed a pressure buildup in the system. Therefore, we reduced the potential from 16 to 8 V.

The hydrogen peroxide generated during the parabolic loop flight test is shown Figure 13. The data indicates that 0.08 w/w % hydrogen peroxide was observed by the end of the gravity modulation trials. This resultant concentration is much lower than anticipated from the ground-based simulations (Figure 8 and Figure 9); however, we did demonstrate the potential of continually generating peroxide over the course of gravity fluctuation and low gravity events, establishing the feasibility of the approach. The low peroxide concentration generated could have been due to the number of challenges discussed above which we believe are unrelated to the flight environment. In the future, we hope to conduct additional low-gravity flight demonstrations with our more stable anion membrane assisted PGU system discussed at the end of this article.

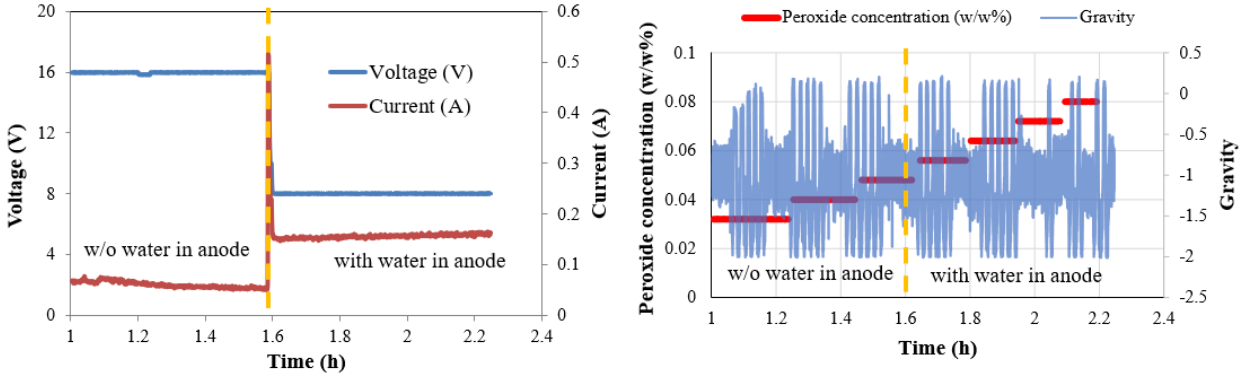

Figure 13. Process performance during low-gravity flight test with polarization profile (on the left) and plot with peroxide generation (represented by red dots) during the low-gravity profile (represented by blue lines) on the right.

C. PGU Scaling

Utilizing the bench-scale PGU platform, we performed scaling analysis in order to design an alpha scale PGU that can produce 1 - 6 L of >1 w/w% H_2O_2 in RO or DI water. For this analysis, we started with the results from Figure 8 which showed 50 mL of ~1 w/w% peroxide generation in about 2 h of operation. We then assumed that the electrode scales linearly and leaves some scaling room to enable the system to produce high quantities of peroxide in the future. Based on these estimates, the alpha scale PGU system was determined to have a planar working area of about 30 cm^2 to 160 cm^2 to produce 1 to 6 L of >1 w/w% H_2O_2 in RO or DI water per day. Additionally, the alpha scale PGU system (Figure 14) components consisted of:

- Oxygen chamber formed from SS316 with a central 5" x 5" flow field and was gold plated in order to inhibit oxidation.
- Catholyte chamber that was additively manufactured to incorporate a fluted flow design (Figure 15), which should improve the flow distribution as it passes through the cell.
- Anode chamber that was constructed of a titanium block with a central 5" x 5" MMO mesh

Images of these components as constructed are shown in Figure 16.

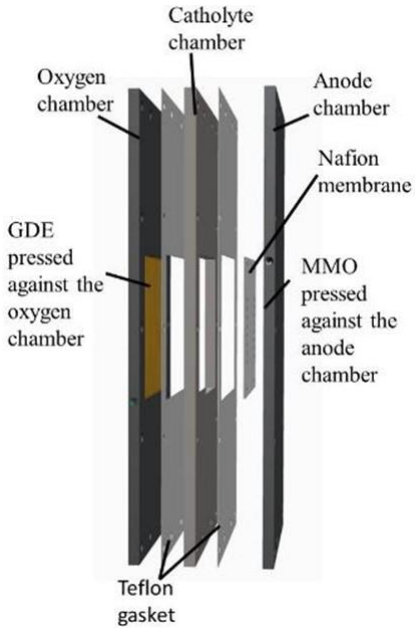

Figure 14. Exploded view of the alpha-scale PGU system

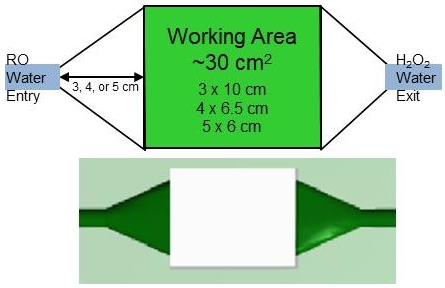

Figure 15. Alpha scale design target for the catholyte chamber

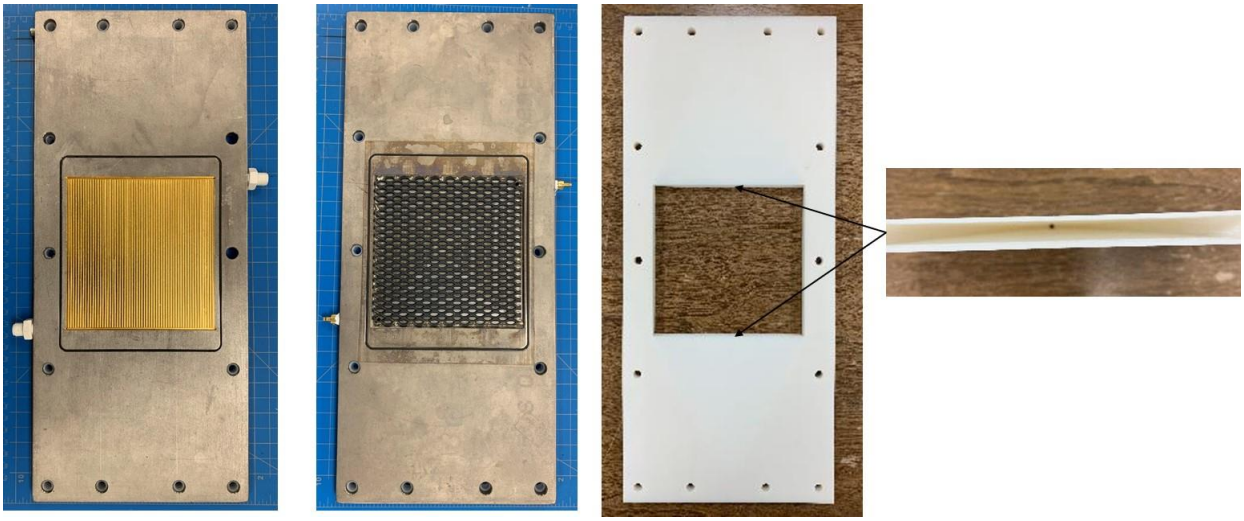

Figure 16. Oxygen chamber gold plated SS316 with a central 5” x 5” flow field (left); anode chamber titanium block with a central 5” x 5” MMO mesh (center); and catholyte chamber additively manufactured to incorporate the fluted flow design (right)

Initial trials with the alpha scale PGU design indicated electrolyte leaking around the gasketing due to insufficient flatness of the additively manufactured catholyte chamber. Therefore, we redesigned the construction of the central chamber to consist of flat machined PVC pieces that can be pressed together, as shown in Figure 17. Initial trials with this orientation demonstrate the potential to produce peroxide however at a much slower rate than was observed with the bench-scale PGU. Additionally, we generally observed liquid formation within the cathode chamber due to the high head pressure associated with flowing the catholyte up the 18” head. This result led us to modify the PGU and incorporate an anion exchange membrane (AEM; Sustainion® Alkaline Anion Exchange Membrane X37-50 grade T)[8] between the GDE and the catholyte chamber, as shown in Figure 18. This modification enabled an enhanced pressure balance between the cathode gas chamber and the catholyte chamber.

Accordingly, we initiated trials for evaluating the performance of alpha scale PGU with fluted channel catholyte chamber, as shown in Figure 17, and an AEM with the following processing conditions:

- Pass: Multi pass
- Ion exchange beads: Amberlite IR 120 Hydrogen form
- Electrolyte: 1 L DI water

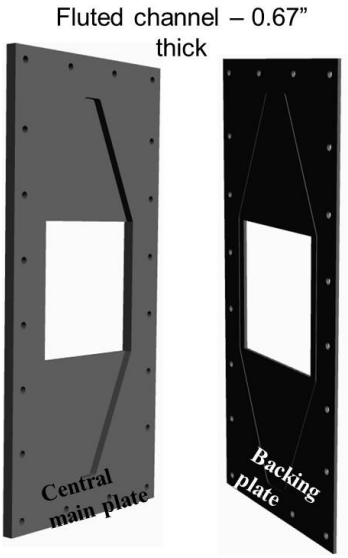

Figure 17. Fluted flow channel flow field catholyte chamber

- Flow rate: 20 mL/min
- Feed source: Oxygen UHP300
- Pressure balance: 0.5 psi
- Cathode: CeTech W1S 1005 GDE
- Anode: Ti plate with MMO DSA
- Catholtye chamber: Fluted channel
- AEM: Sustainion® Grade 37-50 anion exchange membrane
- PEM: Nafion 117 cation exchange membrane
- Volume of Catholyte with beads: 80-100 mL
- Applied current: 0.5 A for 2h then 2 A
- Threshold Voltage: 26V
- Water Circulation in Anode: No

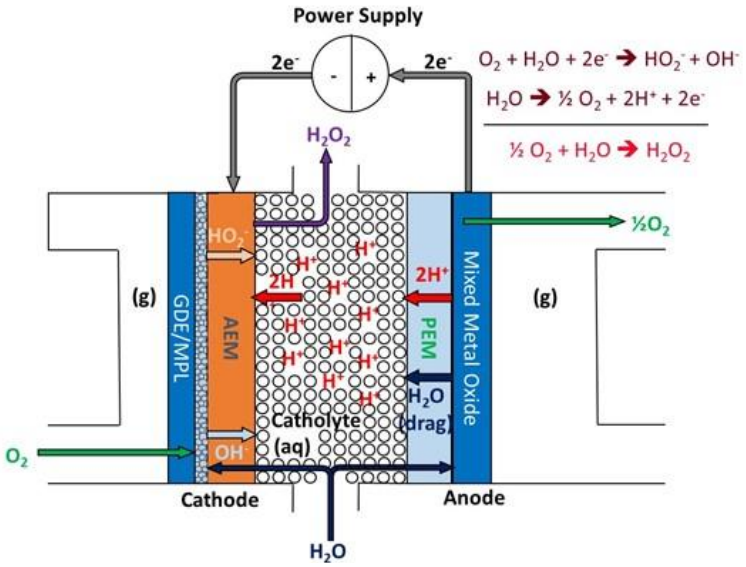

Figure 18. Conceptual schematic of the PGU with the incorporation of an anion exchange membrane.

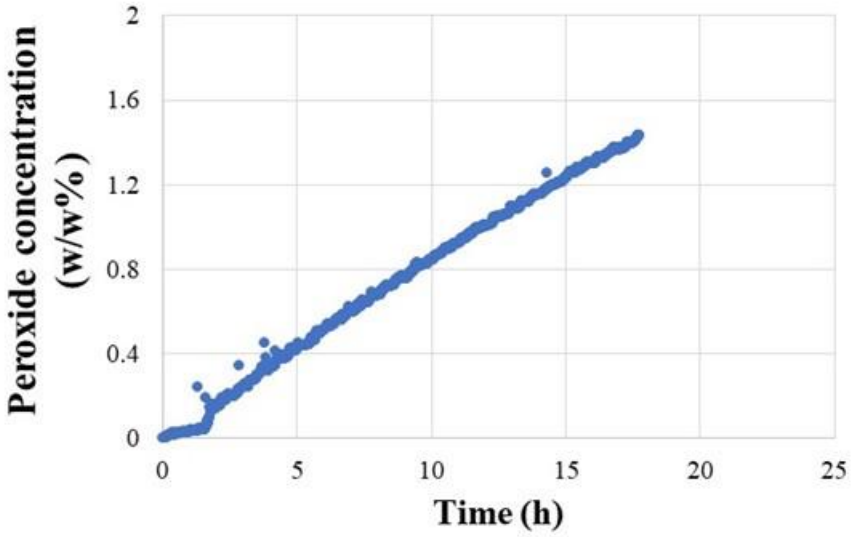

Figure 19. Peroxide generation from multipass polarization trials using 1L DI water in alpha scale PGU

Figure 19 shows that the alpha scale PGU with an AEM has the potential to produce at least 2 L of 1 w/w% H_2O_2 per day with deionized water as the catholyte. Furthermore, the generation efficiency of the alpha scale PGU (Figure 19) using 1 L of catholyte is significantly higher than the 6.25 cm^2 bench-scale PGU (Figure 8) using 50 mL of catholyte, with enhanced current efficiency [74%, a 41% increase] and reduced energy consumption [11 kWh/kg_{H2O2}, an 86% reduction], when using the ultra-low conductivity DI water catholyte. Moreover, the oxygen supplied to the system was pure and the flow was a pressurized deadhead so all the oxygen that enter the chamber was utilized for the reaction. This data also indicates the potential for high output concentration through better tuning of the operation conditions and reactor design.

IV. Conclusion

A peroxide generation system was designed, fabricated, optimized, and evaluated during a low gravity flight test to demonstrate the potential of *in-situ* on demand generation of a peroxide disinfecting solution utilizing life support components during space missions. The data included herein demonstrated that the PGU was able to maintain operation through a low-gravity and was scalable to generate at least 1.5 w/w% H_2O_2 in a day using life support DI water supplies and pure oxygen.

In future studies, we plan on to continue utilizing available water stream on-board the ISS to generate peroxide in the PGU and assess the sensitivity of the system to air being a feed source for the oxygen and common contaminates like Ag or I in the catholyte water supply. Additionally, we will continue to optimize the system to improve its rate of peroxide production and improve its durability and lifetime.

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