Oxygen Extraction from Regolith Using Ionic Liquids

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An important concern with long-duration manned space travel is the need to furnish enough materials to the vehicle, as well as the crew, for the duration of the mission. By extracting oxygen from the oxides present in regolith, propellant and life support could be supplied to the vehicle and the crew while in space, thereby limiting the amount of supplies needed prior to lift-off. Using a class of compounds known as ionic liquids, we have been able to lower the electrolysis operating temperature from 1600°C (molten oxide electrolysis) to less than 200°C, making this process much more feasible in terms of energy consumption and materials handling. To make this process ready for deployment into space, we have investigated what steps of the process would be affected by the low-gravity environment in space. In the lab, the solubilization of lunar regolith simulant in ionic liquid produces water vapor that is normally distilled out of solution and subsequently electrolyzed for oxygen production. This distillation is not possible in space, so we have tested a method known as pervaporation and have suggested a way this technique could be incorporated into a reactor design.

Nomenclature

aq. = aqueous
°C = degrees Celsius
e^- = electron
g/m^2h = flux; grams per meter squared per hour
H_2O = liquid water
$H_2O_{(v)}$ = water vapor
ISRU = In-Situ Resource Utilization
LEO = Low-Earth Orbit
MOE = Molten Oxide Electrolysis
mTorr = milli-Torr
NASA = National Aeronautics and Space Administration

I. Introduction

On July 12, 2011, NASA Administrator Charles Bolden, Jr. reported that the President's vision for human space exploration included a manned mission to an asteroid by 2025, followed by a manned mission to Mars in the mid-2030's. Research and development are currently underway for designing a suitable vehicle capable of transporting the crew to these far-out places (Fig.1). However, a reoccurring issue that must be addressed is the issue of how to supply the vehicle and the crew with enough supplies to last the duration of the mission. It would be prohibitively expensive to launch all of these supplies from Earth. Therefore, it has been suggested to learn how to utilize the materials already present in space in order to produce materials critical for the mission; a concept known as In-Situ Resource Utilization (ISRU).

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Figure 1. NASA's Multipurpose Crew Vehicle designed by Lockheed Martin

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Studies of lunar, Martian, and asteroid regolith have shown that these extraterrestrial regoliths are abundant in various forms of metal oxides. By extracting and isolating the oxygen (and in turn, the metals) that is present in the oxides of the regolith, fabrication of propellant and life support oxygen can be supplied to the crew and the vehicle while in space.

Over the years, multiple research efforts have gone into finding the most efficient way to extract this extraterrestrial oxygen. One such process is the method of hydrogen reduction. This process consists of a solid-gas reaction where the metal oxides would be exposed to gaseous hydrogen to produce metals and water. The water would then be electrolyzed to produce hydrogen and oxygen. However, this process has been proven to have a low oxygen yield of less than 1% per unit of regolith and is dependent upon the composition of the regolith being used. Another method known as Molten Oxide Electrolysis (MOE) has also been extensively studied in the past. In this process, regolith would enter a reactor that is maintained at very high temperatures (around 1600°C) where it would then melt and turn into a molten electrolyte. From here, electrolysis could be performed resulting in a final product of metals, gaseous oxygen, and expended regolith. This process is advantageous due to the fact that it eliminates any need for material beneficiation and Earth-supplied consumable reagents, as well as the fact that it is not highly selective of regolith composition. However, the big disadvantage to this process is the fact that it requires operation at such high temperatures. Operating any procedure at these temperatures poses significant issues in materials selection and general safety. One of the most recent research efforts suggests a process for oxygen extraction that corrects for these previous disadvantages.

This innovative process, explained in detail in the next section, makes use of traditional electrolysis procedures in conjunction with a unique class of materials known as ionic liquids.

II. The Innovative Oxygen Extraction Process

a. What are Ionic Liquids

Ionic liquids, while being discovered during the late 19th-century, have only recently come to the forefront of chemical research. With all the efforts towards becoming a "greener" nation, ionic liquids have presented themselves as a modest replacement for the traditional chemicals used in various everyday processes.

So what exactly are ionic liquids? Ionic liquids are composed almost exclusively of oppositely charged ions and are generally composed of an organic salt or eutectic mixture of an organic and inorganic salt. Ionic liquids exhibit a low melting temperature at 100°C or below, making them capable of lowering the operating temperatures of various chemical processes. Also, these liquids exhibit negligible vapor pressures and very low flammabilities, meaning they are highly unlikely to produce pollution (like traditional chemicals and solvents) and that they are stable at relatively high temperatures. Finally, ionic liquids can be tailored towards a specific task and can be regenerated after one iteration of a chemical process has been completed.

b. Extracting Oxygen with Ionic Liquids

When compared to MOE, ionic liquids for oxygen extraction provide some very unique process advantages. One advantage is that the overall operating temperature is lowered from around 1600°C (for MOE) to approximately 200°C. This decreases the safety risks associated with handling molten materials and eliminates the material containment issues that arise when operating at such extreme temperatures. Another advantage to using ionic liquids is the elimination of the need to transport toxic chemicals and constantly resupply those chemicals to space. This is because ionic liquids have low-toxicity numbers and are able to be regenerated and then reused.

$$(a)\quad Regolith(Metal\ Oxides) + Ionic\ Liquid \rightarrow H_2O_{(v)} +$$

$$e^-$$

$$(b)\quad 2H_2O \xrightarrow[ionic\ liquid]{} 2H_2 + O_2$$

Figure 2. (a) Solubilization; (b) Electrolysis

When using an ionic liquid to extract

extraterrestrial oxygen from regolith, the following process would take place. Initially, the regolith would be ground to a fine, sandy consistency before entering the oxygen extraction process. Once ground to the desired consistency, the regolith would be introduced to an ionic liquid and a temperature of approximately 200°C. The regolith is then solubilized for approximately 24 hours, during which time a hydrogen atom from the ionic liquid bonds to the oxygen atoms of the metal oxides to form water vapor (Fig. 2.a). Once this has happened, a two phase mixture of water vapor and spent ionic liquid with metal ions resides inside the reaction chamber. The water vapor is distilled out of the ionic liquid mixture and is then condensed to form liquid water. The liquid water is introduced to an electrochemical cell where it will be electrolyzed into hydrogen and oxygen by using an ionic liquid electrolyte (Fig 2.b). The hydrogen produced will be recycled back to regenerate the spent ionic liquid and the oxygen will be collected in a cold trap for further use in the propellant or life support systems.

III. Working in a Low-Gravity Environment

Trying to perform this process in space present some very unique obstacles not normally encountered while working on Earth. Many natural phenomena, such as buoyancy and sedimentation, are simply not present in the low-gravity environment in space. In addition to the absence of these types of natural phenomena, there is the addition of the naturally occurring high vacuum atmosphere in space. These qualities of the space environment mean researchers must develop new ways of performing their Earth based experiments in order to overcome these obstacles. This is the case in the oxygen extraction process.

When evaluating the oxygen extraction process, the first issue that would be encountered in space would be the inability to dill off the water vapor produced from the solubilization of the regolith. The process of distillation relies heavily on the presence of buoyancy on Earth. It relies on one component of a mixture to vaporize (due to a difference in the boiling points of the various components) where those vapor bubbles, being less dense that the other liquid components, would rise to the top of the mixture and actually leave the system, therefore, separating the mixture. In space, due to the absence of buoyancy, the vapor bubbles would still form but they would not separate from the liquid components. The vapor bubbles would remain intermingled with the liquid. This is why an alternate separation method must be explored.

a. Pervaporation

To overcome the effects space has on the distillation of water vapor, a new separation method known as pervaporation has been proposed. Unlike distillation, pervaporation does not rely on the buoyancy of the components in order to perform the separations. Instead, pervaporation relies on a selective, porous membrane and an applied vacuum across the membrane. The vacuum is used to pull the selected component through the membrane, allowing the separation process to take place. An illustration of the basic pervaporation process can be seen in Fig.3.

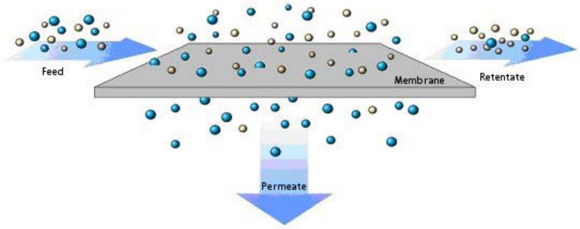

Figure 3. Basic Concept of Pervaporation

The research conducted for this study aimed to explore the possibility of utilizing and incorporating the method of pervaporation into the existing process for the oxygen extraction from regolith using ionic liquids. Before pervaporation testing could be performed in the presence of the actual solubilization product (spent ionic liquid, metal ions, water vapor), testing had to be performed on a simple ionic liquid and water mixture. This would allow the determination of the compatibility of the ionic liquid with the selected membrane as well as the performance of the designed test apparatus.

IV. Testing

a. The Membrane and Ionic Liquid Solution

The membrane chosen for the following series of testing was a sulfonated Teflon membrane with a thickness of 183µm. The ionic liquid chosen for testing was a 30% aqueous ionic liquid solution.

b. The Pervaporation Testing Apparatus

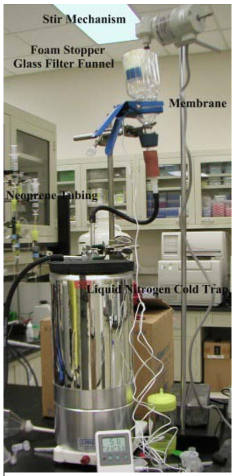

Figure 4. Testing Apparatus

The testing apparatus for this study was designed in lab by the researchers. Due to the fact that this apparatus was an in-house design, a verification study had to be completed prior to the start of testing with the ionic liquid. To verify the apparatus design, a 100mL sample of ordinary, distilled water was used and the process operated at 20°C for 4 hours. The water flux obtained was 1225.8g/m^{2}hr which verified that our apparatus worked nominally. However, the membrane itself absorbed 0.0646g of water during this 4 hour period which suggests that the membrane should be pre-saturated prior to testing with the ionic liquids. Figure 4 shows a picture of the apparatus used for testing. Below is a list of the testing apparatus parts:

- Stir mechanism
- Foam Stopper
- Liquid nitrogen cold trap
- Mechanical vacuum pump
- Neoprene tubing
- Helium purge
- Membrane contact area: 1017.88mm^2

c. Materials and Methods

To determine if the method of pervaporation was a suitable candidate for the extraterrestrial oxygen extraction process, a series of four tests were performed.

Test 1 and Test 2 were designed to determine if a stirring mechanism was needed for the process to operate efficiently. Both tests would use a 20mL sample of the 30% aq. ionic liquid and would run for 6.5 hours at a temperature of 20°C. Test 1 would be executed with no stirring mechanism in place, whereas, Test 2 would be executed with a stirring mechanism. The results would then be compared and taken into account before moving onto the next series of testing.

Test 3 was designed to determine if the membrane, in conjunction with the ionic liquid, could withstand a raise in operating temperature and still perform the pervaporation process. This test would also use a 20mL sample of the 30%aq. ionic liquid and would run for 6.5 hours at a temperature of 50°C.

Test 4 was designed to evaluate how the membrane and pervaporation process would withstand operating for extended periods of time. This test would use a 20mL sample of 30% aq. ionic liquid at a temperature of 20°C and would run for 78.5 hours (3 days, 6.5 hours).

d. Results

i. Test 1 and Test 2

After performing Test 1 and Test 2, it was verified that a stirring mechanism must be used in order to achieve appropriate results. Test 1 did not use any sort of stirring mechanism. After 6.5 hours of running, 1 mL of H_2O was collected and a water flux of only 150.90g/m^{2}h was achieved (Fig.5). This is significantly lower than the water flux of distilled water (1225.8g/m^{2}h). It was also noted that there was a significant pressure drop of 200 mTorr. These results suggest that there may have been a buildup of ionic liquids on one side of membrane due to the fact that the liquid just sat on the membrane without any agitation at all. Any sort of buildup could greatly decrease the water transport through the membrane, as was seen by the extreme decrease in water flux. When a stirring mechanism was added to the system (Test 2), 2mL of H_2O was collected and an increase in water flux was experienced (Fig.5). This

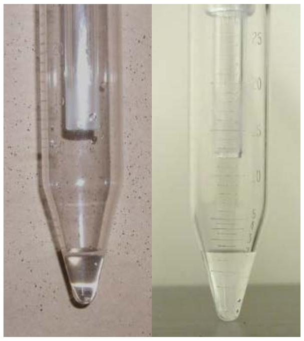

Figure 5. (left) Test 1: 1mL H2O collected, no stirring; (right) Test 2: 2mL H2O collected, stirring

increase was approximately three times higher than seen in Test 1 (water flux=301.71 vs. 150.9 g/m^{2}h). Also noted was the significant reduction in the pressure change from -200 mTorr (Test 1) to +33 mTorr (Test 2). These results conclude that a stirring mechanism is necessary in order to achieve the desired results.

ii. Test 3

Raising the temperature of the pervaporation process actually increased the water flux through the membrane. 3 mL of H_2O was collected and the water flux was measured to be 452.52 g/m^{2}h for this 50°C test (Fig.6). This is a good result; however, further modifications of high temperature operation must be made due to the fact that approximately 2.5 mL of water was lost, most likely due to evaporation. It is suggested that a tighter seal placed around the stirring mechanism may prevent the loss of water due to evaporation.

Figure 6. Test 3: 3mL H2O collected

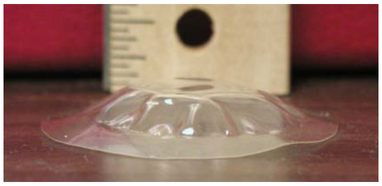

Figure 7. Pre-saturated membrane

iii. Test 4

Test 4 successfully demonstrated that the sulfonated Teflon membrane and the aqueous ionic liquid could be in contact with each other for extended periods of time without degradation of either material. At the end of the 78.5 hour test period, the once swollen, pre-saturated membrane (Fig. 7) was completely flat (Fig. 8) and the remaining 10mL of liquid not pulled through the membrane became quite viscous. The fact that the swollen, pre-saturated membrane became flat during this time period suggests that at some point throughout the test period, water stopped being drawn from the aqueous ionic liquid and began to be drawn out of the membrane itself. It is for this reason that a water flux could not be calculated for this process. The highly viscous liquid remaining on top of the membrane is the ionic liquid as ionic liquids are more viscous than water and therefore, more viscous than an aqueous ionic liquid solution.

Figure 8. Membrane after long run (Test 4)

V. Conclusion

This study confirmed that a sulfonated Teflon membrane could successfully separate water from an ionic liquid. A stirring mechanism must be used for this process in order to avoid any potential buildup of a substance on the membrane as this could prohibit water transport through the membrane. This study has also shown that the membrane can withstand exposure to ionic liquids at elevated temperature and for extended periods of time – two conditions that would be experienced if deployed in space. All of these results suggest that the method of pervaporation could be a highly successful replacement for the distillation of water in the oxygen extraction process. Due to the fact that pervaporation relies on diffusion rates as opposed to buoyancy, this process could be highly successful in the low-gravity space environment, but further testing would need to be completed in order to verify this assumption.

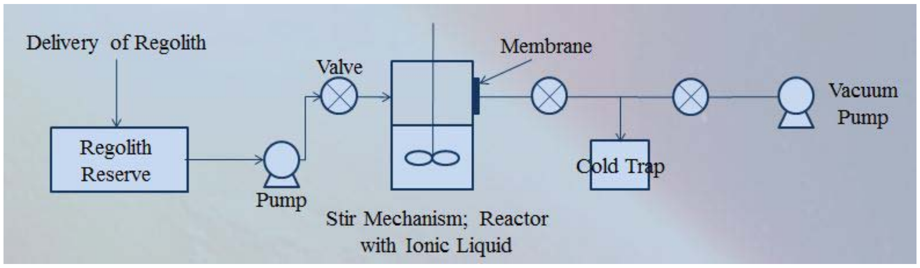

Figure 9. Schematic of Pervaporation Incorporation

A basic schematic of how the method of pervaporation could be incorporated into a process system is presented in Fig. 9. The regolith would be ground up to the desired consistency and deposited into a regolith reserve container. A controlled amount of regolith would then be transported from the reserve to the reactor that contains the ionic liquid at 200°C. The reactor would be constantly stirred for a set period of time that would allow the solubilization of the regolith to take place. Once solubilization is complete, a door would open exposing the mixture to a pervaporation membrane and a pressure differential. From here, the method of pervaporation would take place and the water vapor would be condensed and collected into a cold trap.

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