

2022-2023

# Improvements to ISRU for Rocket Fuel Generation

Justin Sharp

*James Madison University*

Follow this and other works at: <http://commons.lib.jmu.edu/jmurj>

---

## Recommended Vancouver Citation

Sharp J. Improvements to ISRU for rocket fuel generation. *James Madison Undergraduate Research Journal*. 2023;10(1):50-59. Available from: <http://commons.lib.jmu.edu/jmu/vol10/iss1/5/>

This full issue is brought to you for free and open access by JMU Scholarly Commons. It has been accepted for inclusion in *James Madison Undergraduate Research Journal* by an authorized administrator of JMU Scholarly Commons. For more information, please contact [dc\\_admin@jmu.edu](mailto:dc_admin@jmu.edu).



# Improvements to ISRU for Rocket Fuel Generation

Justin Sharp

## Abstract

The development of efficient in-situ resource utilization (ISRU) technologies is crucial for the establishment of an extraterrestrial, self-sustaining colony. The generation of rocket fuel at potential colony locations is necessary to provide the transportation of people and cargo to and from these locations. Three processes are discussed for the improvement of ISRU methods to generate rocket fuel: electrolysis and electrochemical improvements to the process of crude fuel production, physical and chemical methods for separation of gaseous  $H_2$  and  $O_2$ , and materials and cryogenics engineering for storage and transportation of liquid hydrogen (LH2) and liquid oxygen (LOX). Storage and transportation of cryogenics like LOX and LH2 is a highly researched field due to its applications in making clean and renewable energy widely available and similar methods can also be applied for the acquisition of rocket fuel. Storage methods such as the self-evaporating vapor cooled shield (VCS) or thermoacoustic refrigerator shield (TRS) have been shown to decrease the loss of evaporated cryogenics. Additional methods such as solid-state material engineering with materials such as cesium superoxide ( $CeO_2$ ) have also shown potential for long-term storage of LH2 and LOX.

*Keywords:* in-situ resource utilization, liquid oxygen, liquid hydrogen, pyrene-4,5,9,10-tetraone, thermoacoustic refrigerator shield, self-evaporating vapor cooled shield, cesium superoxide

## Introduction

The synthesis of hydrogen and oxygen gas can be broken down into four components: production, separation, transportation, and storage. Large-scale hydrogen production methods primarily use water electrolysis as water is an abundant resource on Earth.[1,2] While no liquid water is present on the Martian surface, subterranean lakes and ice caps contain substantial amounts of water necessary to synthesize rocket fuel from electrolysis.[3,4] Continuous improvement to producing hydrogen and oxygen will alleviate the resource and energy requirements necessary to produce rocket fuel for future colonists. Electrolysis operates through liquid water in a closed environment with a cathode and anode on opposite sides, and it separates oxygen from hydrogen with a working voltage between 1.8-2.4V.[2]

Equation 1 and Equation 2 represent the electrochemical equations for hydrogen and oxygen gas evolution in an alkaline environment:[1]

1.  $4\text{OH}^- (\text{aq}) \rightarrow 2\text{H}_2\text{O} (\text{l}) + 4\text{e}^- + 2\text{O}_2 (\text{g})$  (at the anode)
2.  $4\text{e}^- + 4\text{H}_2\text{O} (\text{l}) \rightarrow 4\text{OH}^- (\text{aq}) + 2\text{H}_2 (\text{g})$  (at the cathode)

A focus of electrolysis research is high-performance electrolysis in which alkaline and acidic environments are tested to improve reaction efficiency. Recent research has examined defect engineering in catalysts and using 3d transition-metals to improve electrolysis techniques.[1,5]

The development of effective separation techniques is necessary for the safe storage of evolved hydrogen and oxygen, as storing them together could lead to rather explosive consequences under numerous conditions due to their volatile nature. More efficient methods of separation are vital in ensuring the purity of stored hydrogen and oxygen, as high purity of both is necessary for fuel ratio calculations for interplanetary travel. Current separation methods of evolved hydrogen and oxygen gas utilize proton exchange membranes (PEMss), but recent studies have also used anion exchange membranes (AEMss) such as: pyrene-4,5,9,10-tetraone (PTO) to isolate hydrogen; size exclusion membranes; and other mixed ionic-electronic conducting (MIEC) permeable membranes such as one synthesized

from  $\text{Ba}_{0.98}\text{Ce}_{0.05}\text{Fe}_{0.95}\text{O}_{3-\delta}$  (BCF) to act as a two-way high-purity membrane.[2,5,6] Recent research has also shown that organic proton-buffer electrodes are a viable and self-sustaining option for separating evolved hydrogen and oxygen gas.[6]

The storage and transportation of hydrogen and oxygen go together as both are needed in the handling and processing of both of these elements. Proper transportation techniques minimize the amount of material lost when initially storing hydrogen and oxygen after electrolysis and separation, as well as when rocket fuel tanks are loaded with propellant. Proper storage materials also improve storage capacity within a given volume and the safety of storage methods utilized.[6] While chemical storage offers a higher maximum energy density for a given volume, cryogenic storage of liquid hydrogen (LH2) and liquid oxygen (LOX) remain highly efficient methods of storage. This is due to the higher energy density of these elements as liquids compared to their gaseous states, along with the commercial availability, reduced cost, and increased structural stability.[7,8] Current technologies utilize vacuum jacketed transfer lines or an inert gas like helium to move cryogenic fluids.[9] New research discusses the efficiency of precooling LH2 and LOX at 300K, 200K, and 100K, along with the development of a 50 multilayer insulation pipe with a 3-channel coaxial liquid helium pipe, which reduced the overall energy loss to 0.2 W during the transfer of cryogenics.[10]

Current storage processes attempt to maximize the surface area within a vessel to increase the number of active sites available to uptake LH2 and LOX. Recent studies used nickel (Ni) nanoparticles to increase the surface area within a given volume and act as an oxygen storage reservoir.[11]  $\text{CeO}_2$  based materials in conjunction with various transition metal oxides have also been studied as a method for improving oxygen storage capacity (OSC).[12] Novel cryogenic and LH2 storage methods utilize an active cooling method to retain cryogenics in the liquid phase and use a self-evaporating vapor cooled shield (VCS) and thermoacoustic refrigerator shield (TRS) to minimize evaporated gas pressure in the containment vessel. A VCS and TRS decrease the loss of evaporated cryogenics up to 70.98% and 90.81%, respectively.[13]



## Current Research Electrolysis

Electrolysis operates with a cathode and anode at a working voltage between 1.8-2.4V to separate hydrogen and oxygen in liquid water.[4] Theoretically, water can be split into its components at 1.229V as this is the thermodynamic baseline to split water; however, overpotential, or excess voltage, is required to overcome losses in energy between the cathode and anode (Equations 1 & 2).[2,14,16,17] The electrolysis generator is constructed within a closed vessel where the cathode and anode are submerged in the electrolyte solution and separated by a diaphragm. The diaphragm separates generated OH<sup>-</sup> ions as well as evolved O<sub>2</sub> and H<sub>2</sub>. There is an inlet for the water supply and two different outlets, one for evolved H<sub>2</sub> and the other for evolved O<sub>2</sub>. Fine-tuning of the environmental conditions within the closed vessel is essential to optimizing the reaction and can be further optimized using catalysis to minimize the energy required for the continuous evolution of gaseous hydrogen (GH<sub>2</sub>) and gaseous oxygen (GO<sub>2</sub>). [2,4,13,16]

### Reaction condition improvements

Current electrolysis methods utilize three types of conditions: alkaline solutions, proton exchange membranes (PEMs), and anion exchange membranes (AEMs). Alkaline environments produce the GH<sub>2</sub> and GO<sub>2</sub> at 750 Nm<sup>3</sup>/h with 99.5% purity. PEMs and AEMs have a reaction rate of only 40 Nm<sup>3</sup> h<sup>-1</sup> and 1 Nm<sup>3</sup> h<sup>-1</sup>, respectively, but they also have purities of evolved gasses at 99.9999% and 99.99%, respectively. Both alkaline solutions and AEMs can operate between 1-30 bar while PEMs require higher pressures at 30-76 bar, while reaction temperatures are roughly similar among all conditions between 50-80°C. All conditions operate at the same working voltage, although PEMs require Pt group cathodes and precious metal anodes, while alkaline solutions and AEMs can widely available Ni and Ni-alloy cathodes and anodes.[2]

While PEMs and AEMs offer very high purity evolved gasses, alkaline solutions produce the most efficient results and at significantly lower costs.[2,16] Alkaline solutions also show the highest conductivity with 20-40 wt% KOH when compared to NaOH, CO<sub>3</sub><sup>-2</sup>, and HCO<sub>3</sub><sup>-</sup> anions. Higher conductivity is associated with higher efficiency as a result of increased current

density within a solution, which is a measure of the electrical activity across a given area.[2,4,14] KOH produces the highest current density within the electrochemical cell at 220 mA cm<sup>-2</sup> and (bi)carbonate solutions produces current densities of 95 mA cm<sup>-2</sup> and 160 mA cm<sup>-2</sup>, respectively.[2]

### Catalytic improvements

While a 20-40 wt% KOH solution is the most efficient electrolysis environment, the reaction efficiency of GH<sub>2</sub> and GO<sub>2</sub> evolution can be further improved through catalysis. Electrocatalysts are primarily evaluated by analyzing the current density and Tafel slope, which together are known as a Tafel analysis. The Tafel slope is calculated using Equation 3, where R is the universal gas constant, T is the absolute temperature in kelvin, α is the charge transfer coefficient (0.5 for nearly all cases), n is the number of transferred electrons when generating one molecule of H<sub>2</sub> (n = 2) or O<sub>2</sub> (n = 4), and F is the Faraday constant. [4] The Tafel slope can be determined by chronopotentiometry, electrochemical impedance spectroscopy (EIS), and voltammetry. The flatter the slope, the more efficient the energy transfer process.[5, 15]

$$3. \text{ Tafel slope} = 2.303RT/\alpha nF$$

While a Tafel analysis is used to determine the activity of electrocatalysts, the selectivity is determined by its Faradaic efficiency (FE) (Equation 4). Faradaic efficiency is defined as an electrocatalyst's ability to use the applied energy for electrochemical energy conversion processes. In these processes, every electrocatalyst is expected to have an FE of 100%.  $j_R$  and  $n_R$  is the current density and number of transferred electrons in the ring electrode, while  $j_D$  and  $n_D$  are the current densities and number of transferred electrons in the disk electrode, and  $N_{CL}$  is the collection efficiency. FE can be determined by gas chromatography (GC) or by a rotating ring disk electrode (RRDE).[3,5]

$$4. \text{ FE} = j_r \times (n_D/j_D) \times n_R \times N_{CL}$$

Transition metal-based catalysts from the 3d group in the periodic table, cobalt (Co), nickel (Ni), iron (Fe), manganese (Mn), and copper (Cu) show promise in improving the efficiency of neutral and slightly alkaline electrolysis. While alkaline conditions are shown to improve electrolysis efficiency over neutral conditions, primarily due to the dissolution of CO<sub>2</sub> in demineralized water hindering the current density of the electrochemical solution, several catalysts have

Tafel values low enough to be efficient in solutions at pH 7.[4] Several Ni-Pt doped and interfaced catalysts also showed decreased Tafel values as low as 24 mV dec<sup>-1</sup> in alkaline solution.[5] Similar Tafel value efficiencies were also observed at approximately pH 9.2 to those at pH 7.[2,4] However by pH 10.3 these catalysts became less efficient, with Tafel values starting at 30 mV dec<sup>-1</sup> at pH 9.2 while at pH 10.3 Tafel values start at 126 mV dec<sup>-1</sup>. [4] Because of this, these catalysts would currently be ineffective for use with alkaline electrolysis, as the pH range would be between pH 10-14. Future research could eventually produce a catalyst with similar efficiencies in the pH range of a KOH electrolyte solution, as Ni-based catalysts show significant promise from this experiment.[2,4,14] The primary benefit to these materials is that they are photo-catalysts, with the majority of materials absorbing light in the visible region.[18] Because of this, these catalysts could prove essential in conditions where initial energy production may be limited for water electrolysis, such as the start of a Martian colony before more efficient alkaline electrolysis can be utilized.

## Separation Methods

### Chemical

While alkaline water electrolysis produces high-purity hydrogen and 99.5%-purity oxygen, the evolved gasses still need to be separated from one another. PEMs and AEMs separate evolved hydrogen and oxygen automatically because of the molecular composition of the membranes in addition to performing electrolysis: an alkaline electrolyte would require a size-exclusion membrane in conjunction with it to achieve similar separation effects.[2,16,17] Pyrene-4,5,9,10-tetraone (PTO) has recently been synthesized and showcased as a regenerative organic proton buffer to separate evolved hydrogen and oxygen in situ with electrolysis. Characterization by in situ differential electrochemical mass spectrometry (DEMS) displayed the high purity separation achievable from this membrane. Evolved hydrogen is captured by PTO creating PTO-H, before being released again and regenerating PTO; oxygen is then released in a separate second step as it is in an AEMs electrolysis vessel.[16,17]

Organic buffers and membranes, such as PTO, that can operate within the electrolyte of the electrolysis apparatus have proven to be viable methods to achieve high purity hydrogen and oxygen separation. However, many of these organic complexes (including PTO) require an acidic environment to oper-

ate efficiently which was previously determined to be a less efficient environment for electrolysis and requires further research of complexes that can operate as efficiently in caustic environments.[2,4,16]

### Physical

Mixed ionic-electronic conducting (MIEC) permeable membranes have also been shown to separate evolved hydrogen and oxygen more efficiently than Pt/Pd-based membranes with greater structural stability while yielding high purity separation. [6,16] The membrane is composed of oxide ceramics which permit 100% oxygen permeation and provide electron conduction, and is encompassed by Ba<sub>0.98</sub>Ce<sub>0.05</sub>Fe<sub>0.95</sub>O<sub>3-δ</sub> (BCF) on its two faces. This allows the membrane to separate the two gasses: high-purity hydrogen is produced through one side, while high-purity oxygen is produced through the other side. The MIEC membrane can act as a diaphragm and it is positioned in the electrolyte solution between the cathode and anode similarly to a PEMs vessel. In a PEMs vessel, side one faces the cathode and produces high-purity hydrogen, while side two faces the anode and produces high-purity oxygen. [6,17] The MIEC membrane can also be utilized outside of the electrolysis apparatus where the evolved gasses are still in the same vessel as the electrolysis reactor but they flow toward the MIEC membrane for separation in a mixture of water and N<sub>2</sub>. This second method is crucial as a reaction temperature of 950°C is necessary for the membrane while 50-80°C is necessary for alkaline water electrolysis. Thus, the second method of operation would be necessary to create the most efficient apparatus for electrolysis and high-purity separation. This operation requires a flow rate of 180 mL min<sup>-1</sup> H<sub>2</sub>O with 20 mL min<sup>-1</sup> N<sub>2</sub> on side one and 50 mL min<sup>-1</sup> H<sub>2</sub> on side two and achieves a hydrogen separation rate of 13.5 mL cm<sup>-2</sup> min<sup>-1</sup>. [4,6]

The ceramic membrane can last for an extended period as it is highly stable and can resist the caustic conditions from alkaline electrolysis, although BCF still presents some issues in this area.[4,6] While extremely efficient, cost-effective, and more structurally stable compared to Pt/Pd catalysts that are used commercially, its ability to separate hydrogen will decay from structural degradation due to instability in the BCF catalyst. BCF requires reaction conditions of 950°C to efficiently operate while initial alkaline electrolysis requires temperatures between 50-80°C, and the transport of separated hydrogen and oxygen will need to be cooled to significantly

lower temperatures between 300-100K for eventual transport and storage.[2,4,6,7,10,13] Thus, the catalyst on side one exfoliates from the membrane when cooled closer to room temperatures, which decreases the rate of hydrogen separation. Side two encounters degradation to its surface morphology, as an enrichment of Ba atoms appears on side two, indicating a change in the molecular composition of the catalyst. While the rate of hydrogen production decreased minimally within a 100-hour test, by 310 hours of operation the MIEC morphology had exhibited the surface degradation previously entailed. Despite the structural degradation after several hundred hours of operation, MIEC membranes are a viable method for separating evolved hydrogen and oxygen from electrolysis. Future research can investigate improvements to structural stability in BCF or similar surface catalysts.[6]

## Storage and transportation

Once hydrogen and oxygen are separated appropriately, immediate storage will be necessary to maximize the amount of rocket fuel generated. Proper storage techniques are necessary to not only maximize the amount of fuel stored within a given volume but also to minimize the loss of these gasses over time. Consequently, adequate transportation methods are necessary to prevent excessive loss of the separated gasses into storage, along with transportation to rocket fuel tanks before transit from the Martian surface.[7,8,10]

### Storage

While the transportation of hydrogen and oxygen is primarily a mechanical problem, usually resolved through methods of chemical or materials science engineering, storage techniques can be divided into physical and chemical storage methods. Physical storage entails cryogenics and compression storage, while chemical storage encompasses adsorption through carbon allotropes and metal-organic frameworks (MOFs), and absorption through various metal hydrides. While it is necessary for rockets to utilize physical storage in their fuel tanks for immediate use of available hydrogen and oxygen, long-term storage vessels on the surface could utilize physical or chemical storage methods for later availability.[8]

### Chemical Storage

Chemical storage methods are up to twice as efficient as physical storage because of the maximum energy density available within a given volume,

where chemical storage with various hydride materials reaches  $4.95 \text{ kWh L}^{-1}$  while physical storage only reaches  $2.343 \text{ kWh L}^{-1}$ . Specifically for hydrogen storage, metal hydrides prove to be the most efficient method of storage with a maximum energy density of  $4.95 \text{ kWh L}^{-1}$ , while storage in water reaches  $3.663 \text{ kWh L}^{-1}$ , and other sorbents achieve  $2.31 \text{ kWh L}^{-1}$ , being outperformed by physical storage methods utilizing  $\text{LH}_2$ . Elemental hydrides like  $\text{MgH}_2$  display suitable applications as stationary, off-grid methods for hydrogen storage. When coated with three layers of Ni powder, hydrogen storage achieves a capacity of 6.1 wt% and can be reused for up to 600 cycles. Absorption and desorption of hydrogen by the fuel tank can be achieved at  $150^\circ\text{C}$  and  $200^\circ\text{C}$  at 10 bar and 0.2 bar, respectively.[8] Coupled with rapid kinetics by achieving full absorption and desorption within several minutes,  $\text{MgH}_2$  presents itself as an excellent chemical storage method for evolved and purified  $\text{GH}_2$  to be later used as rocket fuel, as it is also lower in cost compared to other metal hydride complexes that utilize more expensive intermetallic and complex hydrides.[2,8]

Storage of  $\text{GO}_2$  differs from storing hydrogen in that oxide-based materials present greater chemical storage efficiency as they have a greater affinity to uptake oxygen.[6,11,12] Similarly with hydrogen storage, maximizing the available surface area within a given volume increases the number of active sites available which can uptake oxygen for long-term storage. Recent research showcased the synthesis of a porous perovskite  $\text{La}_{0.5}\text{Ca}_{0.4}\text{Ni}_{0.2}\text{Ti}_{0.8}\text{O}_{3-\gamma}$  with exsolved Ni nanoparticles that acts as an oxygen storage reservoir. The exact kinetics for oxygen absorption and desorption remain unknown, as the material proved to be more efficient as a redox center for  $\text{CH}_4$  conversion to  $\text{GH}_2$ , which remains a less efficient electrolysis method than alkaline water electrolysis.[2,4,11,14]

Additionally,  $\text{CeO}_2$  materials have been extensively studied specifically for oxygen storage by investigating their oxygen storage capacity (OSC). This property allows  $\text{CeO}_{2-x}$  complexes to readily uptake and release large quantities of oxygen regeneratively due to the redox couple formed by  $\text{Ce}^{+3}/\text{Ce}^{+4}$  in the structure while remaining structurally stable. Total OSC for  $\text{CeO}_2$  was determined to be up to  $0.051 \mu\text{mol O}_2/\mu\text{mol CeO}_2$  with  $\text{H}_2$  used as a reducing agent. When doped with Zirconium (Zr) to produce  $\text{CeO}_2\text{-ZrO}_2$  or  $\text{CeZrO}_2$  (CZO) complexes, total OSC values increased between  $390\text{-}406 \mu\text{mol g}^{-1}$



during the first oxygen uptake cycle and increased in the second cycle to be between 400-410  $\mu\text{mol g}^{-1}$ . Additionally, with  $\text{H}_2$  used as a reducing agent, when Rh was used as a catalyst specifically with  $\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$ , further increased to 9.0 mL  $\text{O}_2 \text{ g}^{-1}$  of catalyst when heated to 500°C, producing the highest OSC of the investigated  $\text{CeO}_2$  materials.[12] These findings quantitatively identify the high efficiency of Rh/CZO-based materials, which presents itself as a suitable candidate for solid-state storage of evolved and purified  $\text{GO}_2$ .[11,12]

### Physical Storage

While chemical storage is up to twice as efficient as physical storage methods in terms of storage capacity and surface area to uptake hydrogen and oxygen within a given volume, improvements to physical storage are still necessary for improving the fuel vessels within rockets, and other temporary storage systems intermittently needed between long-term solid-state storage and temporary storage within the rocket. Cryogenic storage of liquid hydrogen (LH2) and liquid oxygen (LOX) is more efficient than compressed gas storage as the liquid state contains a higher energy density than their gaseous counterparts and is safer because of the reduction of pressure from the gasses. The primary issue with cryogenic storage is the evaporation of LH2 and LOX in storage, leading to an increase in container pressure which needs to be relieved and consequently leads to the loss of material.[8,13]

Novel cryogenic storage methods utilize an active cooling method to retain cryogenics in the liquid phase and reduce pressure in the containment vessel by minimizing evaporated gas pressure using a self-evaporating vapor cooled shield (VCS) and thermoacoustic refrigerator shield (TRS). VCS corresponds to the active cooling of the cryogenics at their sensible heat level, while TRS actively cools the cryogenics at their combustible heat level, which is the critical point that evaporated cryogenics need to be vented to relieve pressure on the containment vessel.[8,13] These methods decrease the loss of evaporated cryogenics by 70.98% and 90.81% respectively compared to commercial storage vessels. VCS and TRS are also both energy independent and are more efficient than commercial 20K refrigerator systems by 26-46%, respectively.

Both insulation systems operate by surrounding a cryogenic vessel, and when hydrogen or oxygen evaporates and reaches combustion heat tempera-

tures, the insulation systems actively recover thermal energy from  $\text{GH}_2$  or  $\text{GO}_2$  at their respective sensible or combustible heat levels to then condense the gasses back into their liquid state. This improvement to cryogenic storage is instrumental in reducing the amount of fuel lost when fueling rockets for transit. It is also influential in any intermittent physical storage vessel used between long-term and temporary storage for hydrogen and oxygen.[13]

### Transportation

As with physical storage, mitigating the loss of material from escaping  $\text{GH}_2$  and  $\text{GO}_2$  is essential to improving transportation methods for both evolved gasses.[7,8,10,13] Current gas transfer lines are well documented and utilized in commercial and private industry, which can be used for  $\text{GH}_2$  and  $\text{GO}_2$  transportation between electrolysis and long-term solid-state storage, and between long-term and temporary storage. Current cryogenic transportation technologies utilize vacuum jacketed transfer lines. They can also use an inert gas (such as helium) in a 3-channel coaxial pipe, with liquid helium (LHe2) through the major line and gaseous helium (GHe2) in the two secondary lines.[7,9,10]

For physical storage of LH2 and LOX, the efficiency of pre-cooling methods was investigated at temperatures between 300-100K within a transfer line of 15mm in diameter, and was shown to significantly reduce the amount of  $\text{GH}_2$  and  $\text{GO}_2$  lost during transport.[7] Notably, the development of a multilayer insulation (MLI) transfer line was reported. A 50-layer insulation pipe was developed to encase a commercially available 3-channel coaxial LHe pipe. The insulation pipe is constructed by utilizing two main components: a reflector and spacer. The reflector reflects thermal energy within the insulation into the system, while the spacer helps to dissipate external heat, and prevent the transfer of thermal energy into the system. The 50-layer MLI was constructed using 0.012 mm thick double-aluminized Mylar for the reflector while the spacer was constructed from 0.07 mm thick fiberglass paper. An overall minimal heat leakage of 0.2 W was reported for the system during the transfer of LH2 and LOX, displaying a significant decrease in thermal energy waste and lost product.[10] Both a pre-cooling system from long-term storage, as well as the use of the MLI transfer line, are essential to prevent the significant loss of material when loading propellant into a rocket for transit from the Martian surface.[7,10]

## Future Research

The most efficient methods of electrolysis,  $\text{GH}_2$  and  $\text{GO}_2$  separation, storage, and transfer methods were discussed, although there are still several areas to revisit for future improvement. While alkaline water electrolysis is the most efficient method, the presented photo-catalysts are most efficient in neutral or slightly alkaline conditions below the necessary pH for alkaline electrolysis, which inhibits the potential efficiency of the electrolysis process. Additionally, separation membranes and organic buffers offer high efficiency for purifying evolved  $\text{GH}_2$  and  $\text{GO}_2$ , but primarily operate in acidic electrolysis, and still encounter issues with structural stability. Future research could aim to investigate photo-catalysts with similar efficiencies in alkaline electrolysis to those in neutral conditions, along with separation membranes with increased stability or similar regenerative buffers that could operate in alkaline conditions. As for storage methods, solid-state storage using metal hydrides for hydrogen storage and  $\text{CeO}_2$  materials for oxygen storage presents intriguing results compared to current storage methods. Further research into metal-hydride hydrogen storage could present even further improvements to the presented storage methods. Similar research with CZO complexes could provide potentially useful insight to further improve oxygen storage and reduce costs from using precious metal catalysts such as Rh. VCS and TRS provided significant advancements to cryogenic storage of LH2 and LOX compared to prior methods using primarily MLI. Future research in this field could help to reduce thermal energy waste even further, as TRS reduced cryogenic fluid loss by approximately 90%, still leaving room for improvement. Transportation methods for cryogenics in temporary storage were also significantly improved; however, the exact efficiencies of pre-cooling during transfer requires further investigation.

## Conclusion

The synthesis of  $\text{GH}_2$  and  $\text{GO}_2$  was assessed by its four components: electrolysis, separation, storage, and transportation. Several electrolysis techniques were identified, with alkaline water electrolysis identified as the most efficient method with a production rate of  $750 \text{ Nm}^3/\text{h}$  at 99.5% purity. While several photo-catalysts were identified to further improve electrolysis efficiency, primarily with Ni/Ni-Pt-based materials due to their low Tafel slope values, future research was also identified to improve their affinity in alkaline conditions. Several chemical and physical separation methods were identified to purify

evolved  $\text{GH}_2$  and  $\text{GO}_2$  from electrolysis, with promising results occurring from the cost-efficient organic buffer PTO, which is submerged in the electrolyte, and a separate MIEC permeable membrane with the BCF catalyst on either membrane surface. Improvements to both of these separation techniques were also identified to better suit alkaline conditions for electrolysis. Physical and chemical techniques were introduced for hydrogen and oxygen storage, with long-term solid-state storage techniques discussed with elemental metal-hydrides for hydrogen storage and  $\text{CeO}_2$  materials for oxygen storage. Solid-state chemical storage techniques were found to be approximately twice as efficient as physical storage methods, where chemical storage with various hydride materials reaches  $4.95 \text{ kWh L}^{-1}$  while physical storage only reaches  $2.343 \text{ kWh}$ . Temporary storage techniques in the form of cryogenics were also discussed as it is still a necessary method for rocket fuel tanks and any intermittent storage vessels which are necessary between long-term and temporary storage. Significant improvements were identified for cryogenics storage to retain cryogenic fluids and improve container vessel safety, where VCS and TRS decreased the loss of evaporated cryogenics by 70.98% and 90.81%, respectively, which is a 26-46% improvement over commercial 20K refrigerator systems currently used. Transportation methods for  $\text{GH}_2$ ,  $\text{GO}_2$ ,  $\text{LH}_2$ , and LOX were also introduced, and MLI materials using double-aluminized Mylar and Fiberglass paper were discussed; pre-cooling methods were identified to minimize the loss of material during transportation and reduce the effects of thermal radiation contamination.

## Glossary

AEM electrolysis vessel: a type of electrolysis cell used for the production of hydrogen gas by the electrolysis of water. It consists of an anode and a cathode separated by an anion exchange membrane, which conducts negatively charged ions (anions) while preventing the mixing of the anolyte and catholyte solutions.

Alkaline electrolysis: a process in which an electrical current is used to split water molecules ( $\text{H}_2\text{O}$ ) into their constituent elements of hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ) using an alkaline electrolyte solution. The process involves passing an electrical current through two electrodes placed in an electrolyte solution which serves as a conductive medium.

Anion exchange membranes (AEMs): a semiperme-



able membrane made from ionomers and designed to conduct anions.

**Chronopotentiometry:** galvanostatic method in which the current at the working electrode is held at a constant level for a given period of time.

**Differential electrochemical mass spectrometry (DEMS):** a technique used to study the electrochemical reactions that occur at an electrode surface. It combines electrochemistry with mass spectrometry to provide real-time monitoring of the products and intermediates of electrochemical reactions.

**Doped and interfaced catalysts:** Doped catalysts involve the incorporation of small amounts of foreign elements or compounds into the catalytic material. These dopants can improve the catalytic performance by modifying the electronic structure, the surface chemistry, and the morphology of the catalyst. Interfaced catalysts involve the creation of a boundary or interface between two or more different materials with different catalytic properties. The interface can facilitate the transfer of charge, mass, or energy between the different materials, leading to synergistic effects that enhance catalytic performance.

**Disk electrode:** a type of electrode used in electrochemistry, specifically in techniques such as cyclic voltammetry and rotating disk electrode experiments. It consists of a disk-shaped working electrode that is typically made of a conductive material such as platinum, gold, or glassy carbon.

**Electrochemical impedance spectroscopy (EIS):** a non-destructive technique used to study the electrical behavior of electrochemical systems, such as batteries, fuel cells, and corrosion protection coatings. It is based on the measurement of the impedance of the system over a range of frequencies.

**Faradaic efficiency (FE):** describes the overall selectivity of an electrochemical process and a measure of the effectiveness of an electrochemical reaction. It is defined as the ratio of the number of electrons involved in the desired reaction to the total number of electrons transferred during the reaction, expressed as a percentage.

**Faraday constant:** the electric charge per mole of elementary charges.

**In-situ resource utilization (ISRU):** term used to refer to the generation of consumables for autonomous or human activities from raw materials found in situ (in the original place) on planetary bodies.

**Metal-hydride hydrogen storage:** A type of storage for hydrogen, most effective and usable technology developed to store hydrogen.

**Metal-organic frameworks (MOFs):** a class of materials made up of metal ions or clusters connected by organic molecules to form porous three-dimensional structures with a high surface area and tunable pore size.

**Mixed ionic-electronic conducting (MIEC):** materials that conduct both ions and electronic charge carriers (electrons and/or holes).

**Oxide ceramics:** oxidized inorganic compounds of metallic elements.

**Oxygen storage capacity (OSC):** the amount of oxygen that can be exchanged by a reducible oxide with the gas phase or with an active metal component.

**Proton-buffer electrodes:** a type of electrochemical cell electrode that is designed to maintain a constant pH during an electrochemical reaction.

**Proton exchange membranes (PEMs):** a semipermeable membrane made from ionomers designed to conduct protons while acting as an electronic insulator and a reactant barrier.

**Pyrene-4, 5, 9, 10 tetraone (PTO):** a chemical compound with the molecular formula  $C_{16}H_6O_4$ . It is a polycyclic aromatic ketone with four carbonyl groups located on the pyrene ring and is a yellow to orange crystalline solid used as a synthetic intermediate in organic synthesis.

**Redox center:** a specific location within a molecule or a complex where a redox reaction occurs. Redox centers are typically composed of atoms or functional groups that can undergo reversible oxidation or reduction.

**Regenerative organic proton buffer:** a type of material that can act as a reversible proton donor or acceptor in aqueous solutions. It is a type of buffer system that can maintain the pH of a solution within a certain range by absorbing or releasing protons,

depending on the pH of the solution.

**Ring electrode:** a type of electrode used in electrochemistry, specifically in cyclic voltammetry experiments. It consists of a central working electrode, a reference electrode, and an auxiliary electrode, all arranged in a ring-shaped geometry.

**Rotating ring disk electrode (RRDE):** a double-working electrode used in hydrodynamic voltammetry.

**Size-exclusion membranes:** a type of filtration membrane that allows molecules to pass through based on their size. This membrane contains pores of a specific size range, and only molecules smaller than the pore size can pass through while larger molecules are excluded or retained.

**Surface morphology:** high spatial resolution imaging of microscopic objects. It refers to the physical characteristics of the surface of a material, such as its shape, texture, roughness, and topography.

**Tafel slope:** The Tafel equation is an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential. The Tafel slope is part of the equation.

**Thermoacoustic refrigerator shield (TRS):** a novel insulative material for cryogenic liquid hydrogen storage.

**Transition metal-based catalysts:** Catalysts with incomplete d-orbitals, are able to gain and lose electrons easily.

**Vacuum jacketed transfer lines:** a type of insulated pipe used for the transfer of cryogenic fluids such as liquid nitrogen, liquid helium, or liquid oxygen. These transfer lines consist of an inner pipe that carries the cryogenic fluid, and an outer pipe that forms a vacuum space between the inner and outer pipes. The vacuum space acts as an insulator, reducing heat transfer and minimizing the loss of cryogenic fluid due to evaporation.

**Vapor-cooled shield (VCS):** a type of thermal shield used in cryogenic systems to reduce heat transfer from the environment to the cryogenic vessel or component.

**Voltammetry:** the study of a current response of a chemical under an applied potential difference.



## Author's Note Justin Sharp

Justin Sharp ('22), from Winchester, Virginia, completed his undergraduate degree in Chemistry at James Madison University with a minor in mathematics. He recently finished a year-long internship as a graduate researcher with NASA at the Johnson Space Center. Justin is pursuing his master's in chemical engineering at Rice University in Houston, Texas, and he will graduate in May 2024. After that, he intends to work in R&D in the private aerospace industry, particularly in areas of materials science, synthesis processes, life support technologies, and rocket propulsion. In his free time, he loves to be outside and hike, run, bike, and be out on the water. He enjoys listening to music and hanging out with friends, along with meeting new people on different adventures.

Justin is incredibly humbled to see his paper published in *JMURJ*, as this is not only his first ever publication, but he is also the sole author. He wrote this review article in his senior chemistry literature and seminar class with Dr. Foust. Dr. Foust commended him on his report and encouraged him to go further with it, leading Justin to submit to *JMURJ*. Justin would also like to thank the *JMURJ* Editorial Board for their help with making the publication process smooth, concise, and clear with consistent communication along the way.

## References

1. Orosei R, Lauro SE, Pettinelli E, et al. Radar evidence of subglacial liquid water on Mars. *Science*. 2018;361(6401):490-493. doi:10.1126/science.aar7268
2. Miller HA, Bouzek K, Hnat J, et al. Green hydrogen from anion exchange membrane water electrolysis: a review of recent developments in critical materials and operating conditions. *Sustain Energy Fuels*. 2020;(5):2114-2133. doi:10.1039/c9se01240k
3. Roberto O, Ding C, Fa W, et al. The global search for liquid water on mars from orbit: Current and Future Perspectives. *Life*. 2020;10(8):120.

- doi:10.3390/life10080120
- Anantharaj S, Aravindan V. Developments and perspectives in 3d transition-metal-based electrocatalysts for neutral and near-neutral water electrolysis. *Adv Energy Mater.* 2019;10(1). doi:10.1002/aenm.201902666
  - Jiao S, Fu X, Wang S, Zhao Y. Perfecting electrocatalysts via imperfections: towards the large-scale deployment of water electrolysis technology. *Energy Environ Sci.* 2021;(4):1722-1770. doi:10.1039/d0ee03635h
  - Li W, Cao Z, Zhu X, Yang W. High-rate hydrogen separation using an MIEC oxygen permeable membrane reactor. *AIChE J.* 2016;63(4):1278-1286. doi:10.1002/aic.15502
  - He M, Lv C, Gong L, et al. The design and optimization of a cryogenic compressed hydrogen refueling process. *Int J Hydrogen Energy.* 2021;46(57):29391-29399. doi:10.1016/j.ijhydene.2020.11.061
  - Hassan IA, Ramadan HS, Saleh MA, Hissel D. Hydrogen storage technologies for stationary and mobile applications: review, analysis, and perspectives. *Renew Sustain Energy Rev.* 2021;(149). doi:10.1016/j.rser.2021.111311
  - Fydrych J. Cryogenic Transfer Lines. In: Weisend II JG, ed. *Cryostat Design*. Springer; 2016:241-274. doi:10.1007/978-3-319-31150-0
  - Deng BC, Yang SQ, Xie XJ, et al. Thermal performance assessment of cryogenic transfer line with support and multilayer insulation for cryogenic fluid. *App Energy.* 2019;(250):895-903. doi:10.1016/j.apenergy.2019.05.025
  - Otto SK, Kousi K, Neagu D, Bekris L, Janek J, Metcalfe IS. Exsolved nickel nanoparticles acting as oxygen storage reservoirs and active sites for Redox CH<sub>4</sub> Conversion. *ACS Appl Energy Mater.* 2019;(2)10:7288-7298. doi:10.1021/acsaem.9b01267
  - Li P, Chen X, Li Y, Schwank JW. A review on oxygen storage capacity of CeO<sub>2</sub>-based materials: Influence factors, measurement techniques, and applications in reactions related to catalytic automotive emissions control. *Catal Today.* 2019;(327):90-115. doi:10.1016/j.cattod.2018.05.059
  - Zheng J, Chen L, Xu X, Guo L, Zhou Y, Wang J. A novel insulation system based on active cooling without power input for liquid hydrogen storage. *Energy.* 2019;(182):1-10. doi:10.1016/j.energy.2019.06.050
  - Fortin P, Khoza T, Cao X, Martinsen SY, Barnett AO, Holdcroft S. High-performance alkaline water electrolysis using Aemion™ anion exchange membranes. *J Power Sources.* 2020;(451). doi:10.1016/j.jpowsour.2020.227814
  - Anantharaj S, Ede SR, Karthick K, et al. Precision and correctness in the evaluation of electrocatalytic water splitting: revisiting activity parameters with a critical assessment. *Energy Environ Sci.* 2018;(11)4:744-771. doi:10.1039/C7EE03457A
  - Ma Y, Guo Z, Dong X, Wang Y, Xia Y. Organic proton-buffer electrode to separate hydrogen and oxygen evolution in acid water electrolysis. *A Journal of the German Chemical Society.* 2019;(58)14:4622-4626. doi:10.1002/anie.201814625
  - Keçebaş A, Kayfeci M, Bayat M. Electrochemical hydrogen generation. In: Calise F, D'Accadia MD, Santarelli M, Lanzini A, Ferrero D, ed. *Solar Hydrogen Production*. Elsevier; 2019:299-317. doi:10.1016/B978-0-12-814853-2.00009-6
  - Ashitha S, George SC. Splitting of water: biological and non-biological approach. In: Sahay S, ed. *Handbook of Biofuels*. Elsevier; 2021:453-369. doi:10.1016/B978-0-12-822810-4.00023-3