

Perspective –Solid Oxide Cell Technology for Space Exploration

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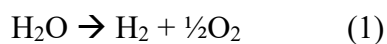
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Abstract: To enable long-term manned space exploration, there are critical needs in oxygen and water for life support, electrical power for on-board operation, and in situ generation of propellants for ascent vehicles. Low temperature electrochemical devices have been developed and utilized for on-board oxygen and power generation in several manned space programs. High temperature solid oxide cell technology offers unique advantages for future space missions. This perspective highlights recent advances in solid oxide cell technology that make it feasible for adoption in aerospace applications and outlines the projected needs in future research and development to better support space exploration.

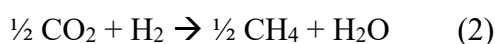
Introduction

Fuel cells and electrolyzers are electrochemical devices that have found aerospace application in the areas of power and life support. Fuel cell technology, in particular, has achieved early development and adoption in the space program, and low temperature fuel cells have been pivotal as lightweight and dependable power sources contributing to early successes in spaceflight[1]. The Gemini program pioneered the use of fuel cells in space with the first use of proton exchange membrane (PEM) fuel cells in the mid-1960s[2]. Subsequent Apollo manned flights (1968-72) utilized alkaline fuel cells due to their higher power density[3]. The alkaline fuel cell was continually refined and provided primary power in NASA's space shuttle program until retired in 2011. These fuel cells used liquid oxygen and liquid hydrogen to generate electricity and provided potable water as a byproduct for both drinking by the astronaut crew and humidification of the spacecraft's atmosphere.

In the area of life support, a PEM-based water electrolyzer was developed as part of the International Space Station's (ISS) Oxygen Generation System (OGS) and has been reliably producing oxygen from water (equation 1) for over a decade[4].



In addition, hydrogen produced via water electrolysis can be utilized by another ISS life support subsystem, the Carbon Dioxide Reduction Assembly (CRA), to recover oxygen from CO₂ (e.g., produced by crew metabolism and captured from the cabin atmosphere) through the Sabatier reaction (equation 2)[5]:



Through the combined reactions (1) and (2), O₂ is released into the cabin and the CH₄ vented overboard. Eqns. (1) and (2) are coupled and written such that the H₂O and H₂ are balanced. This is to illustrate that for a 1 mole basis of CO₂, only ½ (50%) can be processed. This

overall process recovers ~50% of O₂ from CO₂ due to H₂ loss in the vented CH₄[6]. For long-duration, crewed missions beyond Low Earth Orbit, alternative technologies to directly recover O₂ from CO₂ are desirable. Solid oxide electrolysis of CO₂ was suggested as a potential technique to recover O₂ from CO₂ in a spacecraft habitat as early as the mid-1960's[7]. In the late 1970's, it was further proposed as a means for generation of oxygen and propellant on the Mars surface via in-situ resource utilization* (ISRU)[8-10]. However, the early studies of CO₂ electrolysis in solid oxide cells used porous Pt as the electrode, showing slow electrode kinetics with low current densities [11]; work on mixed-conducting electrode materials[12] and improved electrocatalysts, primarily Ni, over the last 30 years has dramatically improved performance for the solid oxide fuel cell application and has been directly applied to more recent CO₂ electrolysis development[13].

More limited work has proceeded in the development of solid oxide fuel cells for aerospace application, focusing on improvements in volumetric and specific power density[14]. One example is NASA's development of a bi-electrode supported cell (BSC) that utilizes porous YSZ scaffolds, on either side of a thin electrolyte. The porous YSZ supports are produced with graded porosity as gas channels for fuel and oxidant flow, enabling thin LaCrO₃-based ceramic interconnects for the stack design and high temperature operation, with a goal to achieve specific power densities of 1.0 kW kg⁻¹. Furthermore, the NASA-BSC is symmetrical and thermally matched, providing balanced stresses and favorable mechanical properties for vibration and thermal cycling [15]. Unfortunately, issues related to reactant diffusion and distribution within the porous YSZ supports, sealing and mechanical integrity of the thin ceramic interconnect, as well as chemical reaction between YSZ and the ceramic interconnect would need to be addressed in order to make reliable high performance solid oxide stacks using this unique cell and stack architecture [16].

The potential resources in space exploration can be solar energy, water and CO₂ from crew respiration, near-surface water or ice from the planet soil regolith, and CO₂ in the particular case of the Mars atmosphere. Solid oxide cells are fuel flexible and potentially more tolerant of reactant impurities compared to the low temperature electrochemical cells, can directly electrolyze CO₂, are reversible in fuel cell and electrolysis operation, and are potentially multifunctioning. Recent progress in solid oxide fuel cells (SOFCs) for power generation and solid oxide electrolysis cells (SOECs) for energy storage in terrestrial applications has paved the way for solid oxide cell technology for space exploration.

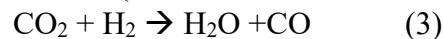
Current Status

Very recently, solid oxide cell technology has made the leap to a first flight application. A solid oxide electrolysis stack was developed and implemented in the Mars Oxygen In-Situ Resource Utilization (ISRU) Experiment (or MOXIE) on the Perseverance rover which landed on the surface of Mars in 2021. MOXIE is an exploration technology investigation that recently successfully produced a small amount of oxygen from Martian atmospheric carbon dioxide, the first flight demonstration of an ISRU technology[17]. This is a major accomplishment by the MOXIE team, but the work illuminates several hurdles that require

* ISRU is a term describing a suite of technologies for utilizing planetary resources to manufacture propellants or other products needed for survival on a planet or the return trip to Earth. Robert Ash, [author of Ref. 8](#), has informally been given credit by the ISRU community for inventing the concept of ISRU, with CO₂ electrolysis being the first proposed ISRU technology. Robert Zubrin, [author of Ref. 10](#), is probably the more well-known and influential advocate, who developed the key arguments and rationale for ISRU as a critical enabling concept for a manned mission to Mars.

solutions to pave the way for a full-scale manned Mars mission utilizing this technology. One of the technical challenges is the oxidation of the Ni-based cathode when directly exposed to CO₂, reducing the performance[17]. Furthermore, solid oxide cells used in the MOXIE demonstration adopted an electrolyte-supported cell design, mainly for durability and reliability considerations. Incorporating electrode-supported cell design with thinner electrolyte can potentially improve the oxygen generation rate for CO₂ electrolysis, lowering stack mass or power requirements and making a manned Mars mission more viable.

SOECs have recently made significant progress in terrestrial applications. CO₂ electrolysis has been sought to combat the environmental concerns through carbon capture and utilization to convert CO₂ to CO, which is needed in large quantities in the chemical industry with global demand at 80 million tons annually, providing economic and environmental incentives to develop the CO₂ electrolysis process. CO₂ utilization through solid oxide electrolysis has made significant progress and tests exceeding 1000 hours have been reported for direct electrochemical conversion of CO₂ to CO with negligible performance degradation[18]. Furthermore, water electrolysis in solid oxide cells have made significant development progress for hydrogen production, using renewable electricity[19]. Besides separate water and CO₂ electrolysis, co-electrolysis of H₂O and CO₂ has been extensively studied in solid oxide cells if both H₂O and CO₂ are available as resources[20]. Co-electrolysis is advantageous over dry CO₂ electrolysis since H₂O electrolysis has a lower thermo-neutral voltage than CO₂ electrolysis (~1.25V for H₂O vs ~1.46V for CO₂ @850 °C). The thermo-neutral voltage for co-electrolysis is between the values for CO₂ and H₂O electrolysis and is dependent on the ratio of CO₂ and H₂O in the feed and occurrence of the reverse water gas shift reaction below (also favorable at these temperatures) [21]:



Thus, the lower thermo-neutral voltage for co-electrolysis can result in lower electrical consumption compared to CO₂ electrolysis alone[22]. Experimental evidence, i.e. polarization data that tracks closely with the data for water electrolysis alone [23], indicates that a majority of the CO₂ may be converted to CO via Eqn. 3 vs. CO₂ electrolysis. The co-electrolysis of H₂O and CO₂ not only produces oxygen, but also syngas (H₂+CO) that can be used as feedstock to produce CH₄, an alternative propellant being considered for space applications (easier to liquify and store than H₂ due to CH₄'s higher boiling point), or a potential fuel for solid oxide fuel cells to power planetary landers or rovers.

Besides electrolysis, solid oxide cells have long been pursued for power generation for a broad spectrum of applications, to meet portable to stationary power needs. Unitized regenerative solid oxide cells, i.e. using the same stack for both power generation in the fuel cell mode and syngas (hydrogen and CO) and oxygen production in the electrolysis mode have also been demonstrated with excellent reversibility and stability[24]. Consequently, solid oxide cell may offer advantages over PEM electrochemical cells in a regenerative fuel cell application, since separate PEM stacks are likely necessary for optimal electrode reactions and liquid water management[25]. Furthermore, since the operating voltage for the electrolysis is lower in solid oxide cells than that in the PEM cells due to improved electrode kinetics, the round-trip efficiency for unitized regenerative solid oxide cells is significantly higher [26].

Future Needs and Prospects

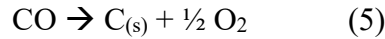
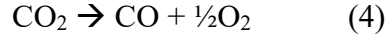
Significant progress has recently been made for terrestrial applications regarding H_2O electrolysis for hydrogen production, CO_2 electrolysis for CO production and co-electrolysis of H_2O and CO_2 for syngas production, as well as solid oxide fuel cells for power generation. This terrestrial-focused effort has made substantial progress in improvements in the cathode, anode, and electrolyte materials and processes along with the overall SOFC/SOEC cell architecture. A very recent review on solid oxide electrolysis materials[27] along with a recent status of a European Union (EU) funded project to address next generation improvements to the SOEC/SOFC cell architecture[28] provide a good overview of this extensive work. Since the adaption of solid oxide cells for space application offers additional challenges and constraints, this perspective will highlight these challenges and a few specific examples of past and on-going work to solve them.

Ideally, a solid oxide electrolyzer has the capability to produce oxygen from different resources available, either H_2O , CO_2 , or a combination of H_2O and CO_2 (co-electrolysis). The ability to operate at reactant pressures lower than the atmospheric pressure may be advantageous since these systems will be acquiring resources at near vacuum (Moon) or very low pressures (Mars atmosphere $\sim 1\%$ of Earth's atmosphere). Operating at lower pressures may have system savings in reducing power needed to pressurize captured CO_2 , or lower electrolyzer structure or sealing requirements by reducing the pressure difference between the pressurized stack vs. ambient pressure. Also, the capability to process less-than-high-purity feedstocks may lower the hardware requirements for clean-up of excavated water ice from regolith sources. For power generation, the ability to operate on H_2 , CO, CH_4 , or possibly solid carbon in the fuel cell mode is of interest.

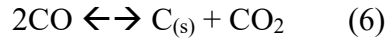
How to effectively utilize the available space resources is essential to achieve space exploration goals. Electrolysis has been a core technology focus for power-to-chemicals solutions, where the chemicals can be oxygen and fuels (or propellant), i.e. hydrogen or hydrocarbons such as methane[29]. Ideally, the same electrolysis stack can also be operated in the reverse mode to produce electricity if fuel and oxidant are supplied. Consequently, unitized regenerative solid oxide cells which have been demonstrated excellent reversibility may be well suited for space application. The CO_2/CO regenerative SOFC has been investigated and demonstrated good performance in fuel cell mode, but significant degradation on the CO/ CO_2 fuel along with soot formation in the fuel inlet tube was observed [30, 31]. Future research for unitized regenerative solid oxide cells should be directed towards the fuel electrode where fuel flexibility is of significance for fuel cell operation and oxidation-resistant for CO_2 electrolysis. A coking-resistant electrode is particularly important so that carbonaceous fuels can be directly fed without the need for external fuel reforming, along with avoiding carbon deposition during CO_2 electrolysis.

If only CO_2 is available, such as the unique Mars atmosphere which contains around 96% CO_2 , a CO_2 cathode that enables pure CO_2 electrolysis without the need of a protective (or reducing) gas is critical. The Ni catalyst in the current state-of-the-art nickel cermet CO_2 electrode is oxidized in high concentrations of CO_2 (or H_2O) causing subsequent degradation and structural damage. Recent work to develop a more oxidation-tolerant cathode for CO_2 and H_2O electrolysis has included electrode materials that possess redox stability such as the

perovskites $\text{SrFe}_{1.5}\text{Mo}_{0.5}\text{O}_{6-\delta}$ [32] and Ce-doped $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{O}_{3-\delta}$ [33] as well as enhancement of the oxidation tolerance for Ni-based cathodes using metal oxide dispersion additives[34, 35]. More fundamental computational chemistry work suggests that Co or Ru may be more electrocatalytically active for CO_2 reduction than Ni[36]. Although these catalysts may be cost prohibitive for terrestrial use, they could be considered for the less cost-sensitive low volume unit production needs of an aerospace application. In the case of the electrolysis operation, solid oxide cells can be used in the electrolysis mode to produce oxygen and CO through equation (4) or further reduction of the CO to solid carbon via equation (5)



Equation (4) is the desired oxygen-producing reaction, although only half of the oxygen available from CO_2 has been utilized. Although equation (5) extracts all the available oxygen from CO_2 but produces solid carbon (i.e. coking) that may passivate the CO_2 electrode, resulting in severe degradation of the solid oxide electrolysis cells. However, by adopting proper cell design and CO_2 electrode, unitized regenerative solid oxide cells could be developed to produce oxygen and solid carbon through equation (5) in the electrolysis mode and produce electricity using solid carbon as fuel in the fuel cell mode[37]. Furthermore, achieving high CO_2 utilization, i.e. high yield of Equation (4) is desirable to recover the most oxygen content. However, high CO_2 utilizations lead to an increase in the ratio of CO/CO_2 in the cathode, and carbon deposition may occur through Boudouard disproportionation (equation 6):



This coking phenomena has been observed under both CO_2 [38] and $\text{CO}_2/\text{H}_2\text{O}$ electrolysis conditions[39]. For pure CO_2 electrolysis, coking is thermodynamically favorable via equation (5) if the cell is operated above the Nernst potential for driving this reaction, which is lower than the thermoneutral voltage for CO_2 reduction (Eqn. 4); operating below this limit restricts the current density the electrolyzer can operate, and limits CO_2 utilization. The thermodynamics and cell voltage operating envelope to avoid coking for pure CO_2 electrolysis has been investigated[38], and operating at higher solid oxide cell operating temperatures may be desirable to minimize coking concerns and maximize CO_2 utilization. However, higher operating temperature will lead to coarsening of the catalyst, accelerate chemical interdiffusion among cell components, and increase thermal losses from the stack and the system. Given that Ni is an excellent coking catalyst, some investigation of alternative electro-catalysts that are not active for coking may also be a potential solution to increase CO_2 utilization.

If only H_2O is available, such as on the Moon from ice near the poles in permanently shadowed regions[40], solid oxide cells can be used in the electrolysis mode to produce oxygen and H_2 through equation (1). Solid oxide cells are preferred since they have more tolerance in the impurity from the available water extracted from the regolith in the moon or the Mars, does not involve two phase flow as that in low temperature electrolyzers, and better heat management and compatibility with the in-situ water extraction from surface soil on the moon or the Mars. In addition, solid oxide cells operate more efficiently in electrolysis compared with low temperature PEM or alkaline electrolysis cells due to a lower thermal-neutral voltage. The capability to operate at higher pressures has a potential advantage in

order to both produce and store the H_2 and O_2 products as high pressure gases, and an ESA project is developing a breadboard electrolyzer subsystem to demonstrate this[41].

If both water and CO_2 are available, co-electrolysis can produce oxygen in one electrode and H_2 and CO in the other electrode; this syngas product can be used to synthesize CH_4 via a methanation reactor. Instead of using separate components for electrolysis and methanation, it may be advantageous, from a system mass and volume viewpoint, to utilize a combined solid oxide cell stack for both electrolysis and methanation reactions[22]. However, integrating the electrolysis and methanation reactions, which are favored in different temperature ranges, in a single unit is challenging. For example, $650^\circ C$ has been reported as potential operating temperature for both co-electrolysis and methanation, but the resulting methane yield is low, (0.2% CH_4)[42]. Other work using tubular solid oxide cell configuration, as shown in Fig. 1, allows one section to be controlled at higher temperature for electrolysis while the downstream section is controlled at a reduced temperature for methanation, results in an improved yield of 11.84% CH_4 [43]. Further work is needed to achieve the high conversions demonstrated in conventional methanation packed bed reactors.

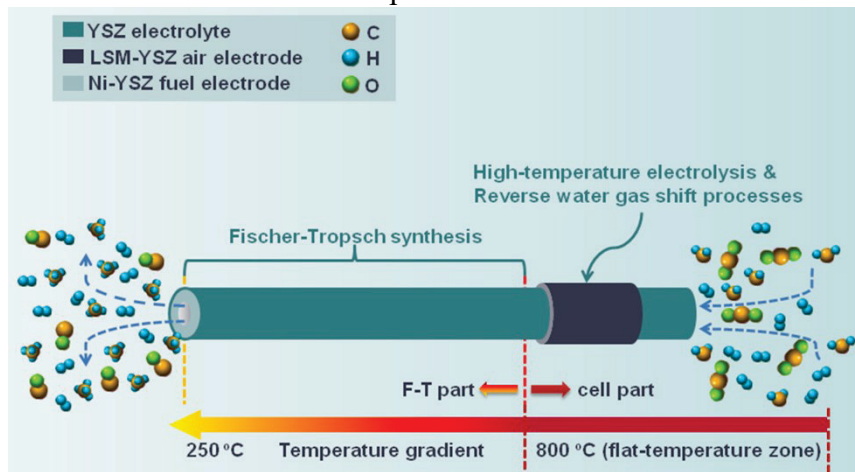


Fig. 1 Schematic illustration for direct methane synthesis from CO_2 - H_2O co-electrolysis in a tubular solid oxide cell combining a high-temperature electrolysis and a reduced temperature methanation reactor[43].

An alternative to the above tubular cell configuration would be feeding H_2O to the cathode side and CO_2 to the anode side of a planar cell with either a protonic-conducting or mixed-conducting electrolyte operated at reduced temperatures. Water electrolysis (only) takes place to produce oxygen on the cathode, while H_2 can react with CO_2 via the Sabatier reaction to synthesize CH_4 on the anode, as schematically shown in Fig. 2. Proton-conducting[44] and oxide-ion conducting[45] solid oxide cells have showed improved performance at reduced temperatures of $<500^\circ C$, making the scenarios in Fig. 2 feasible. The examples presented in Fig. 1 and 2 illustrate the potential of adopting solid oxide cell technology for both oxygen and methane production directly using water and CO_2 .

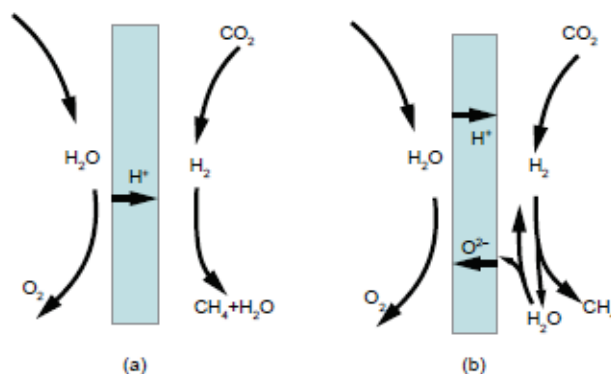


Fig. 2 Schematic illustration of solid oxide electrolysis cells using (a) proton-conducting electrolyte, and (b) mixed ionic conducting electrolyte. Note that in both configurations, CO_2 and H_2O are fed to separate electrodes.

In order to minimize energy requirements, it is desirable that electrolysis can be operated near thermal neutral conditions, simplifying thermal management, and hence the overall system. This will require the electrolysis to be conducted in a potentiostatic mode by operating the cell at thermal neutral voltage. However, when operated in a potentiostatic mode, fuel electrode supported solid oxide cells are observed to exhibit a larger degradation in long-term performance than galvanostatic, likely due to the larger overpotentials applied to the cathode during initial operating conditions [46]. Consequently, reducing the fuel electrode overpotential by developing new fuel electrode composition or novel fuel electrode microstructure with facile mass transport may ensure acceptable long-term performance.

A thorough understanding of the durability and reliability of the power, life support, and ISRU systems is of key importance so that redundancy can be designed to avoid system failures. As a specific example, a recent trade study for a Mars ISRU plant to generate liquid methane and oxygen propellants estimates a required operational time of 480 days (~11,000 hours)[47]. Limited testing of water electrolysis on single solid oxide cells has been performed that demonstrates these lifetimes[48], but CO_2 electrolysis long-term testing has not been investigated. Long term durability testing will need to be performed at the single cell as well as stack levels and the degradation mechanisms need to be well understood in order to accurately predict the degradation behavior and properly size the solid oxide cell stack and system for the intended mission length.

Up to this point, this paper has focused on research and development improvements at the cell level, but additional work is needed on overall stack and system design. Volumetric and specific power goals for a particular solid oxide cell stack design often consist of just the “bare” stack, i.e. the cells and interconnects, and gas manifolds. But other elements including high temperature insulation, clamping mechanisms for stack sealing, gas tubing, and heating/cooling elements may increase the mass/volume by 80-200% in terrestrial designs. For aerospace applications, these extra stack components and design considerations are candidates for novel solutions that significantly lower mass/volume characteristics. One example, newly developed high-temperature aerogels offer an order of magnitude reduction in mass density compared to conventional high temperature insulation. Development of stack structure and packaging designs that incorporate features that isolate the stack and thin

ceramic components (cells and glass seals) from acoustic, launch, and planetary landing loads are an additional challenge that stationary terrestrial applications do not require (although mobile applications do).

Looking at the integration of fuel cell or electrolyzer stack into the larger scale system, the “Balance-of-Plant” (BoP) design becomes important, also from a mass/volume, and in addition, power perspective. This paper has suggested a direct methanation synthesis (Figure 1) as a simple example to synergistic design, but any design will have multiple subsystems or unit operations that require integration with the SOEC or SOFC in a way that minimizes complexity, mass, and power requirements. Examples of approaches to integrate the “unique” high temperature SOEC into total synthesis process routes that are being pursued for terrestrial applications[29] take advantage of high temperature waste heat for energy savings, and the ability of the SOEC to produce syngas, H_2 , and O_2 that do not require further processing steps before being fed to methanation or ammonia synthesis reactors. The reliability and redundancy of these SOEC/SOFC aerospace systems is another challenge. For the Mars ISRU plant example [39] the redundancy approach suggested is to build 3 complete ISRU plant “modules” operating in parallel and sized to produce 40% of the required production rate of CH_4 and O_2 , which would provide a margin of 20% on the total production rate. For a more conservative design, these modules could be sized to 50% of the production rate and if any component in one of these plant fails, the remaining 2 operational plants could still provide the full production rate required. Alternatively, improving the reliability and redundancy of each individual component, e.g. by adding redundant electrolyzer stacks to improve the electrolyzer subsystem reliability, may offer a more optimum mass/volume approach.

Finally, although aeronautics is not in scope for this paper, this application area also has strict mass/power/volume limitations somewhat analogous to space applications. There is recent interest in development of all-electric aircraft, such as NASA’s X-57[49] to reduce or eliminate greenhouse gas emissions for the airline transportation sector. Solid oxide fuel cell technology coupled with batteries in a hybrid electric system, analogous to terrestrial hybrid automobiles, can offer a reduction in emissions and improve fuel efficiency if a high energy density fuel is utilized, potentially CO and H_2 , reformat from a conventional aviation fuel or other carbon-neutral produced biofuels, and possibly ammonia (NH_3).

Conclusions

Solid oxide cell technology has matured from past development for terrestrial applications and now should be considered for aerospace application. CO_2 and CO_2/H_2O co-electrolysis utilizing solid oxide technology has the potential to provide efficient production of oxygen, syngas, or methane and a recent flight experiment (MOXIE) has demonstrated the feasibility. Advanced fuel electrode catalyst composition and architecture will be needed to achieve enhanced CO_2 utilization and minimize the performance degradation for long-term operation. Solid oxide fuel cell technology can also provide power for aerospace application where methane or other hydrocarbon fuels are readily available. Unitized regenerative solid oxide cells could provide a broad range of energy storage needs for aerospace application.

Acknowledgments

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