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Review

Mars In Situ Resource Utilization (ISRU) with focus on atmospheric processing for near term application – a Historical Review and Appraisal)

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Abstract: The inspirational paper by Ash, Dowler and Varsi in 1978 proposing to utilize in situ resources on Mars (ISRU) rather than bringing them from Earth, originated the field of Mars ISRU that has been the subject of research ever since. In this paper we reviewed significant research reported on Mars ISRU since 1978 and reported briefly on accomplishments. We found that prior to 2014, progress on small tasks was sporadic and intermittent, always at low Technology Readiness Level (TRL). In 2014, the National Aeronautics and Space Administration (NASA) took a bold, imaginative, unprecedented step to fund a major project in Mars ISRU: the so-called "MOXIE" (Mars Oxygen In Situ Experiment) in which an oxygen production plant based on solid oxide electrolysis (SOEC) was developed, and finally demonstrated on Mars in 2022 and 2023. While MOXIE leaves behind it a wealth of accomplishments, there remains the need to close remaining gaps with additional laboratory and field work. Solid-oxide electrochemical cell (SOEC) technology has become a major area of worldwide investment for terrestrial energy and CO_2 control. There is a very strong overlap between this terrestrial technology and Mars ISRU. NASA has already leveraged the terrestrial development work via MOXIE. NASA can leverage further advances with a comparatively small investment beyond 2023. Because NASA is engaged in a major program to return humans to the Moon, NASA's focus is on lunar ISRU. Unfortunately, the mission impact and return on investment for lunar ISRU does not compare to that for Mars ISRU. NASA's concept for Mars ISRU is futuristic involving autonomous mining, transporting, and processing large amounts of Mars regolith. This might well occur long after initial human landings which could better profit in the near-term from MOXIE technology. By continuing further development of SOEC technology beyond MOXIE, while leveraging large investments in terrestrial applications, NASA can develop the Mars ISRU appropriate to nearer term human missions at modest investment. The goal of this paper is to place the relatively mature MOXIE technology advance and solid oxide electrolysis in general in perspective to the historical evolution of low TRL Mars ISRU technology.

Keywords: Mars; ISRU; solid oxide electrolysis; MOXIE; NASA

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1. Introduction

Exploration of Mars with a human crew is widely viewed as the ultimate culmination of planetary exploration [1]. Portree (2001) wrote a superb history of planning activities for missions to send humans to Mars [2]. In addition, Platoff (2001) wrote a history covering 1952 to 1970 [3].

According to Portree: "*More than 1,000 piloted Mars mission studies were conducted inside and outside NASA between about 1950 and 2000. Many were the product of NASA and industry study teams, while others were the work of committed individuals or private* *organizations. Due to space limitations, only 50 mission studies (one per year, or less than 5 percent of the total) are described in this monograph. The studies included are believed to be representative of most of the technologies and techniques associated with piloted Mars exploration."*

Rapp (2023) extended Portree's history another twenty years, from 2001 through 2022 [1]. As of about 2020, the consensus was that a long-stay human mission to Mars was the most feasible approach and provided by far, the greatest return on investment. Ash, Dowler and Varsi (1978) published a pivotal paper in which they pointed out the potential savings by producing rocket fuel in situ from Mars resources for ascent from Mars, rather than bringing the rocket fuel from Earth [4]. They coined the phrase "ISPP" (In Situ Propellant Production) that was commonly used until about 2000. In the late 1990s (and beyond) several technology tasks were carried out related to "ISPP" and Mars mission planners typically incorporated ISPP in their plans for long-stay Mars missions. [5] Starting somewhere around year 2000, Jerry Sanders at NASA JSC emerged as a leading NASA advocate for ISPP, and he produced a series of presentations over the years in which he broadened the concepts for utilization of in situ resources beyond propellant production, and he coined the now universally accepted phrase: "In Situ Resource Utilization" (ISRU). He and co-workers continue to advocate for a wide realm of ISRU activities on the Moon and Mars [6]. While Sanders continued to inform NASA on a wide array of potential ISRU opportunities, NASA did not develop Mars ISRU in a systematic way, and funding for specific tasks over the years was sporadic. That was, until a major new investment was decided upon in 2014, leading to the MOXIE project which reached completion September 30, 2023 [7]. Despite the change in reference to from ISPP to ISRU, the reality is that propellant production on Mars offers the most practical near-term advance in ISRU with significant demonstrable benefits, and essentially all the technical accomplishments in Mars ISRU (including MOXIE) since the original paper by Ash, Dowler and Varsi were aimed at propellant production on Mars. In the period 2020–2023, NASA revised its previous concepts for human exploration of Mars, substituting a speculative short-stay mission concept for accepted long-stay mission concepts. In the process, the Mars ISRU seems to have been sidestepped. It is not clear whether this mission concept will stand the test of time or be a temporary phase [8].

ISRU has much greater leverage for ascent propellants than lunar ISRU [1]. The "gear ratio" (mass in LEO required to deliver one mass unit of payload to destination) for transport of mass from Earth LEO to the lunar surface is about 2.5; each mass unit saved on lunar surface saves 2.5 mass units in earth LEO. The gear ratio for transport of mass from earth LEO to Mars surface is about 8-10; each mass unit saved on lunar surface saves 8-10 mass units in earth LEO. Ascent from the Moon requires about 4-6 tons of O_2 propellant, while ascent from Mars requires about 30 tons of O_2 propellant. Combining gear ratios with propellant requirements for ascent, even if lunar ISRU and Mars ISRU were equally feasible, the total mass saving in earth LEO per ascent is about:

Lunar: (4 to 6)(2.5) = 10 to 14 tons
Mars: (30)(8 to 10) = 240 to 300 tons

In addition to leverage, Mars atmospheric processing is far simpler, reliable, and credible than lunar ISRU. Simply pull in atmosphere through a filter, compress it and pass it through electrolysis cells. On the Moon, you must dig tons of soil, heat to > 1650 C via solar concentrators in the carbothermal process, or mine tons of icy regolith in deep polar crevasses where there is no available power. Rapp [1] estimated zero return on investment for both lunar processes compared to launch from Earth.

Figure 1 provides a simplified timeline of highlights from the history of Mars ISRU, relevant NASA studies, and relevant events in relevant terrestrial technology. The modern era began with the landmark paper by Ash, Dowler and Varsi [4], lay dormant until the late 1990s, and then continued at low levels of funding thereafter until the advent of MOXIE in 2014, which completed in 2023. NASA DRA 5.0 [5] demonstrated the benefits of

Mars ISRU for long-stay missions, but NASA reverted to a short-stay concept without ISRU around 2020. Terrestrial developments that benefit Mars ISRU are also included.

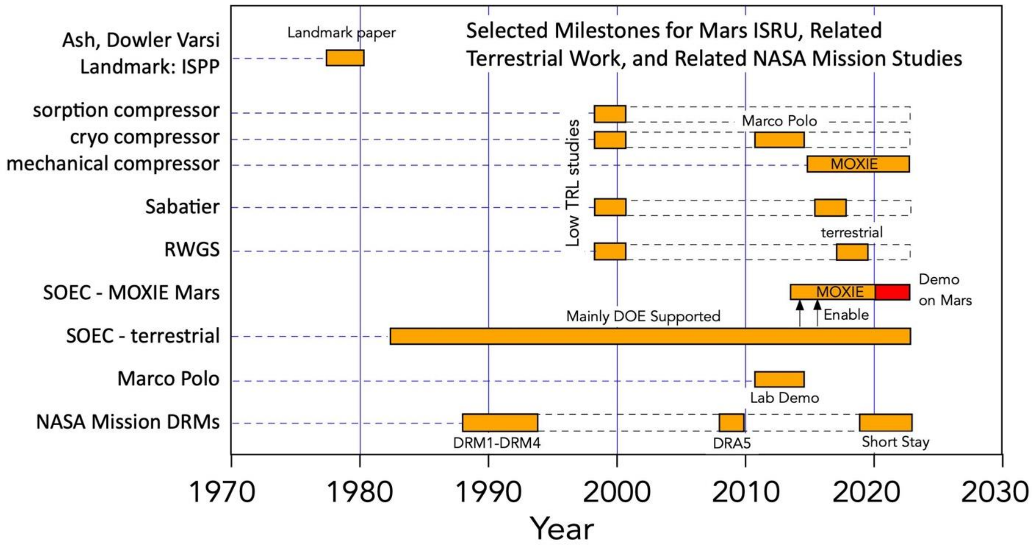

Figure 1. Simplified timeline of highlights from the history of Mars ISRU, relevant NASA studies, and relevant events in relevant terrestrial technology.

In this paper we will:

1. Place the relatively mature MOXIE technology advance and solid oxide electrolysis in general in perspective to the historical evolution of low TRL Mars ISRU technology.
2. Provide a summary of advances in Mars ISRU technology since the 1990s.
3. Develop a perspective of how the MOXIE Project relates to other advances in Mars ISRU technology.
4. Review the accomplishments of MOXIE and follow-on work, and identify technical issues left incomplete for Mars ISRU.
5. Suggest further work needed to fill the gaps left by MOXIE, as well as additional opportunities in solid-oxide electrochemical cell (SOEC) technology.

2. Materials and Methods

Because this is a review article, the methods were based mainly on literature review. However, one of the authors (DR) was an active participant in the field of ISRU for over 30 years. He provided funds to researchers from NASA Jet Propulsion Laboratory at Caltech (JPL) in the 1990s. His books provide analyses in depth of the technologies relevant to Mars ISRU [9]. He was a co-investigator of MOXIE for 9 years and wrote the documentation of that project. This experience provides additional insights beyond a literature search.

3. Results

3.1. Overview of Mars ISRU Technologies

The NASA Mars Architecture Team (MAT) describes the latest NASA concept for the first human mission to Mars, involving a very short round-trip duration, with only a 30-sol surface stay for two crew, minimal surface infrastructure, and ascent propellants brought from Earth [10]. This contrasts with previous architectures that showed benefits for a long stay with ISRU [5]. We believe that a long stay mission will be implemented using Mars ISRU, whether in the first landing, or possibly only in secondary landings. The main feedstocks for processing on Mars are the atmosphere, ice imbedded in the regolith at suitably high latitudes, and regolith containing hydrated minerals. The main component of the Martian atmosphere is CO_2, with smaller amounts of N_2 and Ar and traces of other gases (Table 1).

Table 1. The composition of Mars atmosphere [11].

Component	**%**
CO_2	95
Ar	1.6
N_2	2.7
O_2	0.013
H_2O	~30 ppm

Our concept is that the initial human landing on Mars would be limited to the simple ISRU based on atmosphere only, which is immediately accessible without the challenge of remote, autonomous mining of regolith, transporting regolith, and processing regolith. In a second generation of missions, it might be possible to include processing regolith, either for hydrated minerals or for imbedded ice. There exist many Mars ISRU concepts, ranging from very likely practical, to likely second generation, to imaginative, futuristic ideas that might be pursued in the 22nd century or beyond. Here, we focus on ISRU processing for the first- and second-generation missions. It seems likely that the early application of Mars ISRU will be restricted to highly feasible atmospheric processing for production of ascent propellants and life support. The main product would be oxygen. Less likely, the inert gases in the atmosphere might be captured and the nitrogen might be used as a diluent or as a feedstock for processing. The second-generation missions in the campaign are likely to include processing atmosphere and water, obtained either from ice deposits, or hydrated minerals in the regolith. Several hydrated minerals on Mars have a high H_2O content (10%) and subsurface ice is abundant albeit at various depths at higher latitudes [11, 1]. Availability of water would enable a range of possible chemical engineering processes involving carbon, hydrogen, and oxygen leading to a variety of potential products (Figure 2).

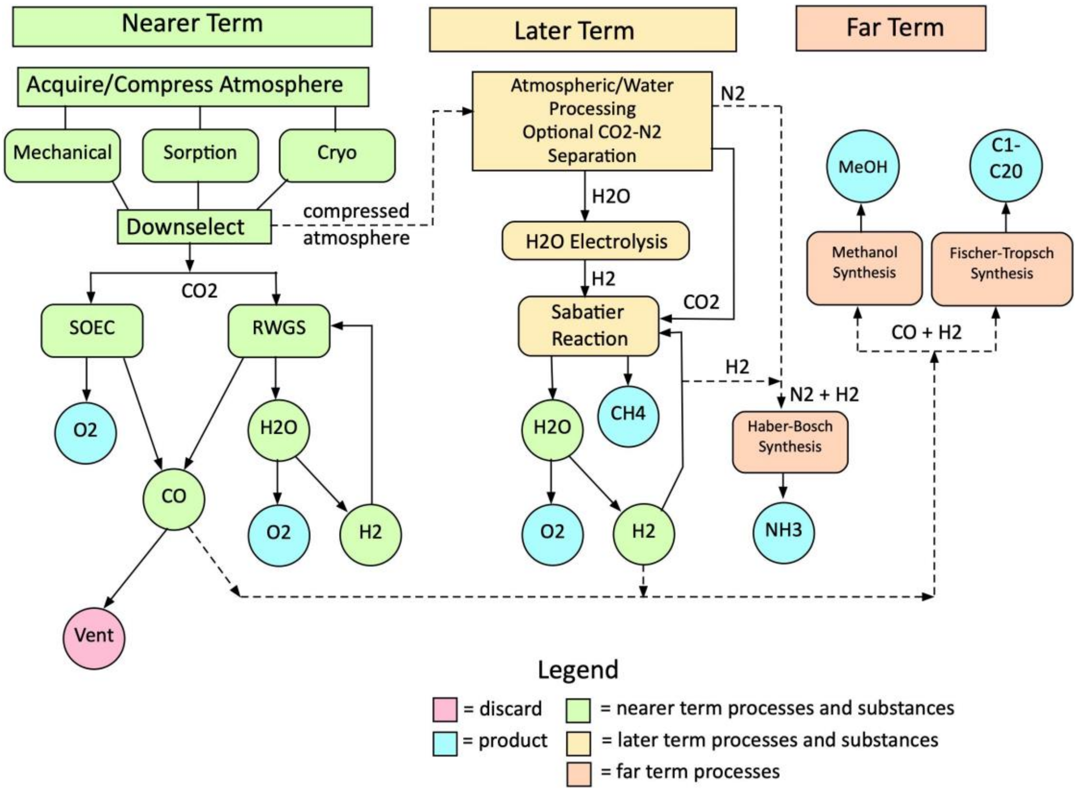

Figure 2. Potential Mars ISRU processes arranged by likely timing.

The abundant CO_2 can be converted into O_2 and CO by SOEC conversion or CO and H_2O by reverse water-gas shift reaction (RWGS). The use of H_2 in the RWGS process is internal. All the H_2 is recycled. The O_2 can then be used as an ascent propellant and for breathing, and if N_2 is recovered, it can be processed, or used as a buffer gas. A significant amount of CO is produced, and in the likely simplest case, vented. If the SOEC process is utilized, there is no need to separate trace components from the CO_2 in the Mars atmosphere since the inert gases simply pass through the electrolyzer. However, if cryogenic compression is used, separation is easily accomplished [11]. Studies of the RWGS process appear to have utilized pure CO_2 so it is not clear whether pure CO_2 is needed. Separation would be needed to acquire the N_2 in the Mars atmosphere. Processing of nitrogen is likely to be delayed until the second generation of landings [12].

In second generation applications of Mars ISRU, where indigenous H_2O and CO_2 are both acquired, use of CO as a feedstock can be further pursued along several avenues. The Sabatier reaction will be important when hydrogen becomes available, converting H_2O and CO_2 to CH_4 and O_2 [11, 13, 14]. The Sabatier process was used in end-to-end lab demonstrations [15, 16]. The CO is also used in the Fischer-Tropsch synthesis to produce hydrocarbons and methanol. The produced CH_4, CO and O_2 can be used in a propellant mixture in rocket vehicles [15]. The N_2 can be converted to NH_3 by the Haber-Bosch synthesis [12]. These processes must be designed to work under Martian environmental and gravity conditions. An important aspect, sometimes overlooked, is that the above reactions produce mixtures that must be separated using processes such as distillation and membrane separation. Also, processing of Martian regolith challenging but might also provide Fe, Al and Si in future generations of landers. An early prototype of an integrated Mars atmosphere and soil processing system was developed during MARCO POLO project [15]. Table 2 provides a summary of potential Mars ISRU technologies.

Table 2. Chemical Based Processes for ISRU on Mars

Process	Description	Conditions	Common materials
	Reactions		
RWGS	$CO_2 + H_2 \rightarrow CO + H_2O$	700-900^{o}C 1 bar	*Fe_2O_3@ Al_2O_3
Sabatier	$CO_2 + 4H_2 \rightarrow CH_4 + H_2O$	200-500 ^{o}C 10-30 bar	*Ni@Al_2O_3
Fischer-Tropsch	$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$ $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$	300-350 ^{o}C 20-40 bar	*Fe_3O_4@ Al_2O_3
Methanol	$CO + 2H_2 \rightarrow CH_3OH$ $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$	200-300 ^{o}C 16-150 bar	*CuO@Al_2O_3
Haber-Bosch	$N_2 + 3H_2 \rightarrow 2NH_3$	400-650 ^{o}C 200-400 bar	*Fe_3O_4@ Al_2O_3
	Other		
SOEC	$CO_2 \rightarrow CO + 0.5O_2$ $H_2O \rightarrow 0.5O_2 + H_2$ Gas phase	800-1000^{o}C	Zr_2O Perovskite
Electrolysis	$H_2O \rightarrow O_2 + H_2$ Aqueous phase	25°C/1 bar	Polymers
Cryogenic separation	CO_2 (v) $\rightarrow$ CO_2 (s)	-78 ^{o}C - 1 bar	-

* A symbol such as Fe_2O_3@ Al_2O_3 means Fe_2O_3 supported on an alumina base.

In addition to all these chemical processes, other ISRU processes have proposed such as regolith usage for building and radiation shielding, crop production, etc. In this paper we are primarily concerned with the near-term ISRU processing of atmosphere to produce oxygen, which we think would be the only practical application for the first human landing.

3.2. Advances in Mars ISRU Technology 1996–2014

In the period from 1996 to 1998, Donald Rapp managed a small fund at JPL called the "Mars Technology Program". This fund provided seed money for low TRL tasks:

1. A small grant to test a cell for SOEC of CO_2 [17]. This device utilized Pt electrodes and produced oxygen at TRL 2. Funds were not available to continue the work.
2. An experimental study of a Sabatier reactor that achieved very high conversion [18]. This work was complete at TRL 4. Oddly, two NASA studies about 18 years later did not refer to this work.
3. Joint JPL-Lockheed-Martin Astronautics (LMA) development of a sorption compressor [19]. A large sorption compressor was built and tested but the results did demonstrate that this approach had great merit in terms of power efficiency.
4. Several JPL chemical engineers demonstrated methane reforming with excellent conversion at TRL 3 [20]. The Sabatier process produces excess methane.

In the period from 1996 to 2000, NASA JSC funded two important ISRU technology tasks, through leadership of Jerry Sanders. These included:

1. Demonstration of the reverse water gas shift process (RWGS) for Mars at TRL 3. [21, 22]. The work on the RWGS introduced an appealing possibility for Mars ISRU but funding was not available to continue the work (recent work on RWGS is discussed later in this paper).
2. CO_2 compression by freezing at TRL 3 [23]. Compression by freezing remains a possibility for the future.

These tasks in the late 1990s represented important initial work at low TRL on Mars ISRU. NASA provided the funding, but the decision to fund these tasks rested locally with Rapp and Sanders at their respective Centers. Adam Bruckner led a preliminary study of directly retrieving water from the atmosphere by adsorption in the 1990s at the University of Washington, but they appear to have relied on internal funding at the university [24]. This process appears to be very challenging. In the mid-2000s engineers at the Pacific Northwest National Laboratory (PNNL) under the Department of Energy (DOE) support developed micro reactor technology [25] and JSC provided NASA support via Jerry Sanders for adapting this technology relevant to ISPP [26] [27]. As of about 2013, advances in several aspects of Mars ISRU were made at TRL ~ 3 by intrepid researchers but Mars ISRU remained in an early evolutionary state.

3.3. Advances in Terrestrial Energy Technology by DOE and the International Community Relevant to Mars ISRU

It is a truism that NASA conducts space missions and DOE advances technology. Some of the energy technology supported by DOE over the years has important implications for Mars ISRU as well.

Solid oxide technology for electrolysis and fuel cells has been under development worldwide for some fifty years for terrestrial applications [28]. Indeed, it was the terrestrial work prior to 2014 that enabled the MOXIE SOEC technology. NASA has already leveraged the terrestrial development work via MOXIE. Since then, the prospects for terrestrial SOEC technology have expanded greatly. A recent review [21] was downloaded 15,000 times from Science journal. A Scopus search with SOEC in the title returns about

1,000 papers; 45 were published in 2014 and 127 in 2023. In some cases, this technology directly overlaps with applications to Mars ISRU. For example, the Danish-funded work on SOEC of CO_2 is relevant [29]. Over the past thirty years, SOEC technology was widely supported across the world, and by DOE in the US. We will not attempt to cover the very wide range of research advances in this field but there are many, and this area of research deserves its own separate review. The foundation laid down at OxEon Energy LLC (nee Ceramatec) by DOE funding over the years prior to 2013 provided the technology background that enabled the implementation of SOEC of CO_2 on Mars in the MOXIE Project beginning in 2014. DOE-funded work on SOEC that developed the capability to build the MOXIE stacks for Mars is reported in [30] through [32].

Research on the RWGS process was supported by NASA about twenty years ago [21] [22] and was an option for a system to produce O_2 from CO_2 via recycled H_2O electrolysis. The RWGS recently became a topic of great international interest for terrestrial CO_2 removal. Support was provided by the DOE [33], by China [34], by the European Research Council [35] and by Japan [36]. A very impressive advance in RWGS development was made in 2017 [37]. A large scale RWGS system run at 70 L/min CO_2/H_2 feed was built and demonstrated and the CO exhaust from the RWGS was converted to storable methanol. This was quite an engineering achievement. It is noteworthy that funding for this important work was provided by a "private customer" with the intent of developing the process for terrestrial CO_2 removal. The needs for RWGS on Mars are somewhat different from terrestrial applications because on Mars, unlike Earth, there is a great shortage of hydrogen and recycling of hydrogen is a major challenge on Mars if indigenous water is not available. Nevertheless, the developments in terrestrial RWGS technology are very likely to enhance RWGS for Mars. NASA can leverage advances in SOEC and RWGS for Mars ISRU technology. Smaller NASA investments might lead to far greater advances than NASA funding could achieve alone.

3.4. The MOXIE project (2014-2023)

Prior to about 2014, technical advances in Mars ISRU were sporadic and intermittent, and always at low TRL. In late 2013, an unprecedented announcement of opportunity (AO) suddenly appeared for proposals for a (then) $30 million ISRU demonstration on Mars. This was a very bold, imaginative venture. It involved building an engineering payload and flying it "piggyback" on a Mars Science Rover, utilizing onboard electric power storage. It demonstrated Mars ISRU at a level not previously achieved. There was no solid basis for definition of requirements and budget because NASA was entering unchartered territory. The massive increase in Mars ISRU funding was unprecedented. How this project fitted into a long-term plan for Mars ISRU was not defined. We are not certain of the final runout budget for MOXIE. Our rough guess is that the total project runout cost was about $55 million, of which the amount spent on development of the SOEC stack was about $6 million. Another few million likely went into developing the mechanical compressor. The remaining roughly $45 million went into engineering the rest of the system to support design, development, test, and operation of a highly compressed system that was mounted on the Perseverance Rover for Mars. This AO was a stroke of genius because it saved all the costs of a mission to Mars by "piggybacking" a Mars ISRU system on a Rover, thus avoiding the need for a dedicated ISRU mission. It was also highly innovative because it involved putting an exploration device on a science rover and the several directorates of NASA fully cooperated. It changed Mars ISRU technology from a concept to a reality. A team from JPL and Massachusetts Institute of Technology (MIT) and a small contractor (Ceramatec, later changed to OxEon) wrote the winning proposal in response to the AO, and thus the MOXIE Project began in late 2014. The project ran until its close September 30, 2023.

MOXIE plans and results were documented in four publications [38] to [41]. The programmatic achievements of MOXIE included:

- Demonstrated production of oxygen on Mars up to ~12 g/h.

- Produced oxygen purity of ~ 100% with anode pressure > cathode pressure.
- Produced oxygen at low Mars temperature in early hours after midnight and warm Mars temperature in early afternoon in all seasons.
- Demonstrated low rate of degradation through more than 20 thermal cycles.
- Demonstrated a mechanical compressor to acquire Mars atmospheric gas.

The technical achievements of MOXIE included:

- Demonstrated sealed stacks of cells that could electrolyze essentially pure CO_2 without oxidation of the electrodes or reduction of product CO – a new first.
- Demonstrated that the Flight Model MOXIE on Mars was essentially identical in performance to the Engineering Model MOXIE in Lab – This was a major observation that showed that operation on Mars could be replicated in the lab on Earth.
- Explored the relationship between stack voltage and current (oxygen production rate was explored extensively).
- The intrinsic area-specific cell resistance (iASR) was evaluated over a wide range of operating settings and iASR was found to be small enough to allow efficient full-scale operation with such stacks.
- By comparing iASR from Mars run to Mars run, it was demonstrated that degradation due to thermal cycling was well within acceptable limits.
- Carried out extensive testing and analysis of filters for Martian dust and determined that dust removal in a full-scale Mars ISRU could be achieved with a reasonably sized filter system.

3.5. Advances in SOEC beyond MOXIE (2017-2023)

In its major role in MOXIE, OxEon Energy LLC delivered eleven final “flight equivalent” electrolysis stacks to JPL in 2017. After that, their role in MOXIE was advisory, playing a significant part in planning tests and analyzing data. In the post-2017 period, independent of MOXIE, OxEon Energy LLC continued work on several development tasks in SOEC with support from the DOE, Air Force Research Laboratory (AFRL) and NASA. Most of the terrestrial-oriented tasks overlapped to a considerable degree with Mars ISRU needs. While the stacks for MOXIE were devoted to electrolysis of pure CO_2 (with 2% CO recirculated to prevent oxidation of cathode electrodes), further research was successfully conducted in pure CO_2, co-electrolysis of CO_2 and H_2O, and electrolysis of H_2O, all with the same multi-cell stacks. The stacks developed for MOXIE and extended by OxEon Energy LLC are CO_2-conversion devices. The same SOXE stack can electrolyze dry CO_2, co-electrolyze CO_2-steam, or steam by itself. Higher current densities and operating voltages are possible with co-electrolysis, and higher still for straight steam electrolysis (it is necessary to limit voltages in pure CO_2 to avoid CO reduction to carbon when electrolyzing pure CO2). However, OxEon Energy LLC made progress in reducing the probability of carbon formation [42] to [45].

The advances made by OxEon Energy LLC from 2017 through 2023 were not incorporated in MOXIE. Some of these advances are summarized below:

- Scaled up the active area of cells from 22.7 cm^2 to 100 cm^2
- Assembled a 65-cell stack (MOXIE stacks were limited to 10 cells)
- Demonstrated use of the stack for electrolysis of CO_2, CO_2+H_2O or H_2O

OxEon Energy LLC tested advanced electrodes that better resist oxidation by CO_2, or carbon formation by dissociation of CO. They also carried out a long-term steady state test up to 1,000 hours.

The field of electrolysis via SOEC is far greater than Mars ISRU. Advances in electrode technology are being achieved continually. One example is exsolution that has emerged as a powerful new method for decorating oxide supports with uniformly dispersed nanoparticles leading to high-performance, versatile, and easily manufactured devices. This opens the possibility of simple, almost instantaneous production of highly active nanostructures for reinvigorating SOCs during operation [46][47].

3.6. Issues remaining after MOXIE

We cite six issues remaining after completion of the MOXIE Project.

(1) Lack of measurement of degradation due to long-term steady state operation. It is expected that a full-scale Mars ISRU would operate for about 10,000 hours in a steady state without interruption, except for rare shutdowns. MOXIE did not generate data on the degradation of the stack or the compressor for such long-term operation. MOXIE did acquire considerable data on stack degradation of efficiency due to thermal cycling after-short duration runs, but the connection between degradation from long-term operation and thermal cycling remains unclear. OxEon Energy LLC recently carried out some studies of degradation due to steady operation, but a significant gap remains regarding degradation from 10,000-hours of operation. The compressor for MOXIE was not designed for long life and no data is available on long duration testing.

(2) Uncertain quality control from stack to stack. MOXIE produced eleven approximately equivalent stacks. Stacks were characterized by (1) the absolute stack intrinsic area-specific resistance (iASR), (2) the variation in individual cell voltages after manufacture, and (3) leakage between the anode and cathode. The stack with lowest iASR and lowest range of cell voltages was chosen as the stack that was sent to Mars. The eleven stacks varied widely in the magnitude of the three basic attributes. After MOXIE, OxEon Energy LLC made a point of assembling a large stack of 65 cells, but it is not clear what the variation was from cell-to-cell voltages within that large stack, or how reproducible such stacks can be manufactured.

(3) Role of individual cells in creating the properties of stacks. While measurements on individual cells were made on the eleven MOXIE stacks as manufactured, only very limited measurements were made on stacks after cycling, and we lack data on how the cells contribute to the observed changes in stacks due to cycling (or long-term operation). Of particular interest is how the worst cell (with highest resistance) affects susceptibility to carbon formation. Within a stack, it is possible that non-uniformity in manifolding might contribute significantly to stack variability.

(4) Low cathode pressure operation. The side reaction that limits how high a voltage can be applied to cells for oxygen production involves reduction of CO to carbon. The voltage limit is determined by the Nernst voltage for carbon formation which increases at lower cathode pressures. It is therefore desirable to operate at lower cathode pressures, permitting higher cell voltage, and therefore higher current density. MOXIE was able to lower the cathode pressure to about 0.22 bar, but we have no data below that pressure. Lower cathode pressure also reduces the power required for compression of Mars gas. This parameter will be import in larger scale system design.

(5) Acquisition and compression of Mars atmosphere gas. Any Mars ISRU system requires acquisition and compression of Mars atmosphere gas. The simplest, most appealing approach is to use a mechanical compressor which runs continuously. While a prototype mechanical compressor was used successfully on MOXIE, it is not clear what the characteristics of a next generation compressor would be (mass, efficiency, lifetime). Two batch type systems for acquisition and compression of Mars atmosphere gas based on sorption and cryogenic freezing were studied briefly. In the sorption process, a sorbent at low temperature is open to the atmosphere where it absorbs CO2. Then it is closed off and heated to release CO_2 at comparatively very high pressure. In the cryogenic method, CO2 is frozen out using a cryocooler while exposed to the atmosphere and then warmed after closing off, to release CO_2 at comparatively very high pressure. [19][23][25][26][27][48][49]. These cannot yet be ruled out, pending further development.

(6) How will NASA deal with the legacy of MOXIE? The field of SOEC technology for terrestrial applications is worldwide and funded at much higher levels than NASA could consider. MOXIE demonstrated that this technology is also applicable to Mars ISRU

technology. Post-MOXIE activities by OxEon Energy LLC showed that this technology might be applied to lunar ISRU as well via electrolysis of water. MOXIE left behind it a well-equipped state of the art laboratory for testing SOEC devices and systems. It seems likely that NASA could leverage the field of SOEC technology with a relatively small investment, by continuing to adapt advances in terrestrial SOEC technology to space applications. While MOXIE was a small scale demonstration, Hinterman (2022) developed a detailed model of a full-scale version of MOXIE including a very detailed analysis of requirements and expected performance of all subsystems. He optimized the design based on mass, power, risk and ancillary factors [50]. Rapp and Hinterman (2023) tested how Hinterman's design would perform with several alternative control schemes of against 10,000 hours of Mars atmospheric data at half-hourly intervals [51]. They evaluated power requirements and determined the most efficient control scheme based on power and avoidance of carbon formation. These results provided further evidence that an extension of MOXIE technology would prove effective on Mars.

3.7. Advances in other Mars ISRU Technology (2014-2023)

Dust is a perennial problem on Mars, especially when a process must intake large volumes of Martian atmosphere. NASA funded some early work on dust mitigation [32]. MOXIE later performed far more extensive testing and modeling of dust mitigation in 2019-2022 [33] to [36]. These results indicated that a suitable filter and inlet system can adequately protect a Mars ISRU system. The method of compressing the Mars atmosphere via freezing the CO_2 and then warming in a closed volume was further advanced [52] after being originally investigated by [23]. Lee (2016) reported on electrolysis of water in a NASA report [53]. Meier, et al. (2017), Hintze, et al. (2018) and Franco, et al. (2019) reported further results on the Sabatier process with NASA funding [54][55][56]. Oddly enough, none of these papers referenced [11] that had already demonstrated a Sabatier Mars ISRU system with high conversion twenty years earlier. The Sabatier process is well advanced. But it requires hydrogen, and hydrogen is scarce on Mars. Berg and Ianetti (2019) worked on a sorption compressor for Mars using rapid cycling, but progress was slow, and further work is needed [57]. There is a small amount of oxygen (about 0.13%) in the Mars atmosphere. Some concepts were developed to directly separate this oxygen from the other 98.87% of gases. We have already mentioned [24]. Recently, a new concept for selectively absorbing oxygen on Mars was proposed and is under study [58]. An alternative approach for Mars ISRU involving plasmas to dissociate CO_2 to O_2 is now under study, but O_2 separation and purification from product CO introduces a significant challenge. [59] In comparison, MOXIE always produces pure O_2 directly.

Starr and Muscatello (2020) presented a review of Mars ISRU. [60] This publication provides a good overview of various technologies relevant to Mars ISRU. However, this paper was written before MOXIE carried out its major experiments and made important findings. For example, the review describes complex approaches to dust filtration, but MOXIE demonstrated that a simple HEPA filter is adequate [38][39]. Under "atmospheric capture" the review provides an excellent discussion of the cryogenic approach. Under adsorption pumps, it did not report Reference [19]. It was perhaps overly optimistic about the possibility of accessible water at moderate latitudes and might benefit from Appendix C in Reference [1]. After this review was published, MOXIE demonstrated successful use of a scroll compressor and CO_2 electrolysis on Mars.

Muscatello, Devor and Captain (2014) described a laboratory demonstration of an end-to-end Mars ISRU system at a significant scale (MARCO POLO project). [61] This system:

- Did not include dust filtering.
- Utilized the cryogenic method for CO_2 acquisition and compression developed by Muscatello and co-workers in References [48] and [52].
- Utilized the Sabatier process for CH_4 and O_2 production with water and CO_2 as feedstocks.

- Assumed that water-laden soil was available as a source of water.

It was not clear how the "Soil Hopper" operates autonomously to deliver soil to the processor, what the "soil" actually is, how the water is distributed in the "soil" or whether the whole process is autonomous or managed.

One oddity of the system is that the CO_2 collection system ran during the day and was dormant overnight, probably because it would run on solar power. But the freezing system is more efficient at night when it is colder, and the radiators can radiate to a much lower sink temperature. Any real system on Mars would collect CO_2 at night.

4. Discussion

Werkheiser and Sanders (2023) presented NASA's overview of ISRU [62] and Sanders and Kleinhenz (2023) presented an update on NASA ISRU plans, priorities, and activities at the same meeting [63]. Because NASA is currently in the process of a major program to send humans to the Moon, the main NASA focus is presently on lunar ISRU as opposed to Mars ISRU. At first glance, this makes sense. NASA is engaged in a major undertaking to exploit the Moon, while a human mission to Mars seems likely to be at least several decades in the future. If lunar ISRU were equally feasible to Mars ISRU, and if lunar ISRU produced comparable return on investment as Mars ISRU, then NASA's focus on lunar ISRU would be fully justified. However, ascent from the Moon requires considerably less propellant than ascent from Mars, delivery of propellants to the Moon from Earth is far simpler and less demanding of resources than delivery to Mars, and most important of all, resources on the Moon are far more difficult to access than resources on Mars.

From a long-term point of view, lunar resources might be viewed as a large-scale source of propellants and oxygen in cis-lunar space to fuel all deep space missions in the future. But for the short term, producing propellants for ascent from the Moon in relatively small quantity may require more effort than it is worth. Rapp (2018) analyzed various options for short-term lunar ISRU, and he concluded that they did not provide adequate return on investment, while Mars ISRU produced a substantial return on investment [9]. NASA's plan for lunar ISRU appears to look beyond the early human landings on Mars to a futuristic scenario where large-scale mining, moving, and processing of regolith play a major role in supplying propellants to cis-lunar space [64]. This encompasses processing equatorial regolith to extract oxygen from oxide, as well as processing polar ice to obtain H_2O from which H_2 and O_2 can be produced by electrolysis. There are some problems with this. First, the lunar ice lies in deep crevices in lunar polar areas where mining would be energy intensive and technically difficult. There is no plausible power source available. The ice, once mined, must be transported a considerable distance upward to a plateau where horizontal solar power is available.

The NASA ISRU plan conceives that if lunar ISRU is fully developed, it will provide an important starting point for Mars ISRU as provided by the slogan: "Moon to Mars Forward ISRU". Therefore, recent activity in Mars ISRU has assumed that indigenous water will be available on Mars. Hoffman et al. (2016) presented options for mining presumed Martian ice with NASA funds [65]. It seems likely that early human missions to Mars will land at an equatorial site where prospects for available near-surface water are very poor. Although the possibility of ice down to 30 degrees north latitude has been raised [66], this remains very unlikely. This study combined data from several sources of direct and indirect evidence of near-surface water into a suggestive map of where such deposits might lie, and there is no direct data. Susante et al. (2021) considered options for acquiring and processing regolith of various types on Mars [65]. Hoffman et al. (2016) [66] and Putzig et al. (2019) [67] also investigated access to water on Mars. Barmatz et al. (2016) investigated the effectiveness of using microwaves to release hydrated H_2O from minerals at low temperature. Favorable results were obtained [68]. But large-scale mining of regolith, delivering regolith to solid processors, and carrying out input and output of regolith to processors autonomously seems likely to be relegated to later missions to Mars, well after the first human landings.

Alternatively, if a futuristic human mission were to land at a high latitude on Mars were near-surface water is available, the processes for collecting water would be quite different than in the dark crevices on the Moon. The reality seems to be that initial human landings on Mars would be equatorial, and processing the atmosphere, as demonstrated by MOXIE, would be the only practical approach to Mars ISRU for early landings. The recent NASA emphasis on utilizing indigenous water on Mars appears to be "putting the cart before the horse". Mars ISRU has already been demonstrated on Mars by MOXIE. Yet a NASA presentation: "In-Situ Resource Utilization (ISRU) Overview" in 2023 did not even mention MOXIE at all [62], NASA's only significant achievement in ISRU.

5. Conclusions

ISRU has the instant appeal that it appears to be more efficient to produce resources on the Moon or Mars than to bring them from Earth. In both cases, the predominant initial target would be to produce ascent propellants in situ, particularly oxygen. The return on investment for any ISRU process depends on the amount of oxygen produced, the availability of feedstock, the practicality of the proposed process, and the relative cost of transporting the resources from Earth. Prior to the advent of MOXIE in 2014, the history of Mars ISRU development was sporadic and intermittent, and always at low TRL. In 2014, NASA took a bold, imaginative, unprecedented step to fund a major project in Mars ISRU: ("MOXIE") in which an oxygen production plant based on SOEC was developed, and finally demonstrated on Mars in 2022 and 2023. While MOXIE leaves behind it a wealth of accomplishments, there remains the need to close remaining gaps with additional laboratory work. The MOXIE Team has unique capability in electrolysis of CO_2 and created a world-class laboratory for testing devices. NASA is currently focused on lunar ISRU because NASA is embarked on a major program to exploit the Moon. There is less interest in supporting Mars ISRU since a human mission to Mars seems to be decades away.

The current NASA interest in Mars ISRU is focused on distantly future missions when indigenous H_2O might be available. The first human landed missions on Mars will most likely process atmosphere only for ISRU. Mars ISRU based on processing the atmosphere has an excellent return on investment and has already been demonstrated on Mars, whereas lunar ISRU has at best, dubious return on investment, and has yet to be demonstrated to be feasible. Solid oxide technology for electrolysis and fuel cells has been under development worldwide for some thirty years for terrestrial applications [28]. Over the past thirty years, SOEC technology was widely supported across the world, and by DOE in the US. The foundation laid down at Oxeon Energy LLC by DOE funding over the years prior to 2014 provided the technology background that enabled the implementation of SOEC of CO_2 on Mars in the MOXIE Project beginning in 2014. It makes a great deal of sense for NASA to continue to fund solid oxide electrolysis relevant to Mars ISRU because the NASA work would be highly leveraged by relevant technology advances from the far greater investment outside NASA in solid oxide technology for terrestrial applications. In this paper, we have placed the relatively mature MOXIE technology advance and solid oxide electrolysis in general in perspective to the historical evolution of low TRL Mars ISRU technology. While visionaries imagine futuristic applications of Mars ISRU, extension of MOXIE appears to be the most practical near-term application of Mars ISRU. Section 3.6 provides six steps for advancing the solid-oxide technology of MOXIE to a state of readiness for mission application.

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