PLANETARY SCIENCE

Mars Oxygen ISRU Experiment (MOXIE)—Preparing for human Mars exploration

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MOXIE [Mars Oxygen In Situ Resource Utilization (ISRU) Experiment] is the first demonstration of ISRU on another planet, producing oxygen by solid oxide electrolysis of carbon dioxide in the martian atmosphere. A scaled-up MOXIE would contribute to sustainable human exploration of Mars by producing on-site the tens of tons of oxygen required for a rocket to transport astronauts off the surface of Mars, instead of having to launch hundreds of tons of material from Earth's surface to transport the required oxygen to Mars. MOXIE has produced oxygen seven times between landing in February 2021 and the end of 2021 and will continue to demonstrate oxygen production during night and day throughout all martian seasons. This paper reviews what MOXIE has accomplished and the implications for larger-scale oxygen-producing systems.

INTRODUCTION

What is the Mars Oxygen In Situ Resource Utilization Experiment?

In Situ Resource Utilization (ISRU) is the term commonly used to describe the harvesting and processing of native resources on other planetary bodies. MOXIE, the Mars Oxygen ISRU Experiment, represents the first demonstration of ISRU technology on another planetary body. An experiment inside NASA's Mars 2020 Perseverance rover, MOXIE has successfully produced oxygen from the carbon dioxide that comprises ~95% of the martian atmosphere.

Figure 1 shows a cutaway view of MOXIE, a full description of which is given by Hecht et al. (1). MOXIE takes in martian atmosphere through a dust-trapping HEPA filter, compresses the atmosphere via a scroll pump, heats it to 800°C, and sends it through a solid oxide electrolysis (SOXE) assembly, where CO_2 flows over a nickel-based catalyzed cathode and decomposes into oxygen ions and CO. The scandia-stabilized zirconia ceramic electrolyte selectively passes oxygen ions to the anode, where the ions recombine into O_2, which is measured for quantity and purity before being released to the Mars atmosphere. The cathode exhaust is a mixture of CO_2, CO, and inert atmospheric gases, primarily argon and nitrogen.

Why ISRU and why MOXIE?

Numerous analyses of Mars missions (2–5) have suggested using indigenous resources to manufacture rocket propellant for the ascent vehicle that will lift a crew off the surface of Mars. Of the estimated 50 tons of total mass of a six-person oxygen-methane propelled Mars ascent vehicle (MAV), ~31 tons will be oxygen and ~9 tons will be methane (5). While all MAV propellant could be brought from Earth to the surface of Mars, 12 to 13 tons are required in low Earth orbit for every ton landed on Mars using current technology (6, 7). Thus, ~500 tons would need to be launched to Earth orbit to transport the required MAV propellant from Earth for every Mars mission, a serious impediment to sustainable human exploration. Fortunately, oxygen can be produced in situ from the CO_2-rich martian atmosphere, which has a surface atmospheric pressure ranging from ~5 to 10 mbar.
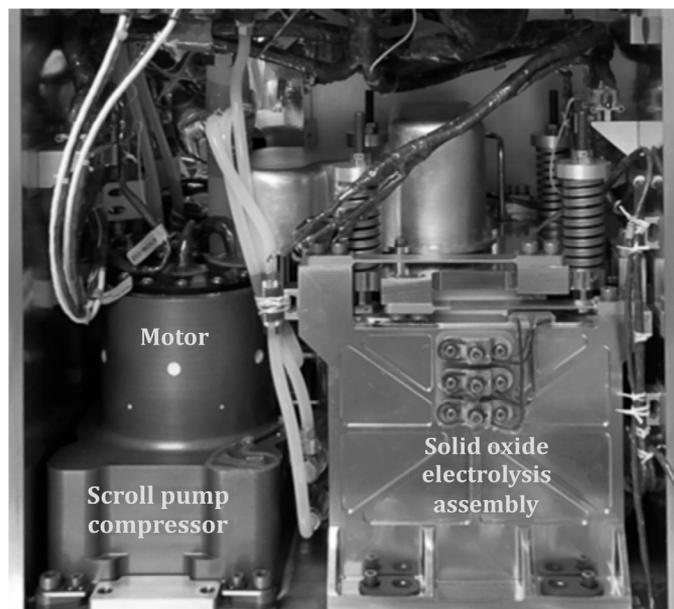
Fig. 1. MOXIE with the front cover removed, showing compressor and SOXE assemblies. The inlet filter, sensor and flow control panel, and electronics are not shown. The dimensions of the MOXIE chassis are 23.9 cm by 23.9 cm by 30.9 cm.

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Water ice is also a potential native resource for manufacturing fuel and oxidizer on Mars. In addition to the exposed polar layered deposits of water ice, permafrost is known to blanket most of Mars poleward of ~50° north or south latitude (8) and possibly as far equatorward as 40° (9). Vestigial pockets of ice may persist at lower latitudes (10), and water could also be extracted from hydrated soils even at equatorial latitudes (11). Water and carbon dioxide can serve as reactants to produce both methane and oxygen for a MAV. However, obtaining water requires an ice-mining operation, melting the ice, purifying the water, and transporting it near the MAV for propellant production. In contrast, atmospheric CO_2 can be acquired anywhere on Mars. Because oxygen makes up ~78% of the MAV propellant mass, carrying fuel from Earth while producing oxidizer on Mars still offers a substantial benefit until such time as a mining operation can be set up to obtain water (5).

A MOXIE-like system, scaled up several hundred times (2 to 3 kg/hour of oxygen production versus MOXIE's 6 to 8 g/hour), could produce sufficient oxygen to launch a MAV for a crew arriving one 26-month cycle later. Producing oxygen is such a critical function for human exploration that it demands prior validation in the actual Mars environment—NASA's Technology Readiness Level 9. This is the first purpose of MOXIE, to demonstrate successful operation of the system in the actual martian environment. The second, and equally important, purpose of MOXIE is to advance the scientific and operational knowledge of this type of ISRU system to inform the design of future, larger-scale systems.

MOXIE does not require mobility, but Perseverance was MOXIE's earliest mission opportunity. Being manifested inside the rover body led to volume, thermal, and power constraints that required compromises in MOXIE's design. The impact of these compromises and suggestions for future scaled-up MOXIE-type systems are discussed below.

RESULTS
MOXIE operations
Run history
McClean et al. (12) describe the architecture developed for planning, testing, and executing MOXIE runs. Between landing in Jezero Crater on Mars in February 2021 and the end of 2021, MOXIE produced oxygen seven times. These operational cycles (OCs) are summarized in Table 1. Note that the OC number increments every time MOXIE undergoes a heating cycle, whether or not oxygen is produced. The first seven cycles, flight model (FM) OC1 to OC7 were run in laboratories on Earth as part of preflight testing and qualification. FM OC8 was a heating cycle checkout with no oxygen production.

An important goal of MOXIE is to demonstrate successful operation during day and night throughout all martian seasons, showing robustness to variations in atmospheric pressure and temperature. Figure 2 shows predicted diurnal maximum (nighttime) and minimum (daytime) atmospheric densities throughout Mars year at the Perseverance landing site (13). Superimposed are MOXIE's seven oxygen-producing runs performed in 2021. A run will be scheduled during the annual maximum density period, shown as a star in Fig. 2. Other runs will be spaced out between the minimum and maximum extremes.

Operation on Mars
The Nernst potential (V_N) for an electrolysis reaction is the voltage above which the reaction can be initiated. To produce oxygen safely, MOXIE must operate at a voltage above V_N for the oxygen-producing reaction, $V_N(2CO_2 \rightarrow 2CO + O_2)$, and below V_N for carbon formation, $V_N(2CO \rightarrow 2C + O_2)$, both of which depend on the partial pressures and temperature of the reactants (1, 12). The latter process must be avoided to prevent coking (carbon deposition) in the SOXE cathode, which raises the resistance of cells by reducing their active area and may possibly fracture the cathode, causing an inability to produce oxygen. Experience in the laboratory and on Mars indicates that, with sufficient attention to these limits, MOXIE's electrolysis stack can be operated safely over many cycles.

Figure 3 shows the two Nernst potentials as a function of the gas intake and the amount of oxygen produced at an operating temperature of 800°C. The two circles and light vertical line indicate the "reference segment" condition of 55 g/hour of intake with 6 g/hour of oxygen production (see discussion of generic runs below). The safe operating zone is indicated in Fig. 3 by dark arrows, assuming nominal operating conditions. To ensure operation in this zone, parameters used to control MOXIE are validated using well-tested models and verified on the engineering model (EM) before each

Table 1. Seven oxygen-producing cycles successfully completed by MOXIE in 2021. Sols are martian days, counted from Perseverance landing on 18 February 2021 (sol 0). "FM" refers to the flight model of MOXIE, on Mars, to distinguish from Earth-based engineering model (EM), on which all runs are verified before being executed on the FM.

Run	Mission (sol)	Date	Time	Pressure (Pa)	Temperature (K)	Duration of O_2 production (min)	O_2 produced (g)	O_2 total (g)
FM OC9	60	20 April 2021	Night	751	201	59	5.4	5.4
FM OC10	81	12 May 2021	Night	768	199	74	6.9	12.3
FM OC11	100	1 June 2021	Day	757	256	71	6.9	19.2
FM OC12	155	27 July 2021	Night	737	201	96	8.9	28.1
FM OC13	176	17 August 2021	Night	720	199	82	8.1	36.2
FM OC14	241	24 October 2021	Night	651	206	73	6.9	43.1
FM OC15	276	29 November 2021	Day	631	253	74	6.8	49.9
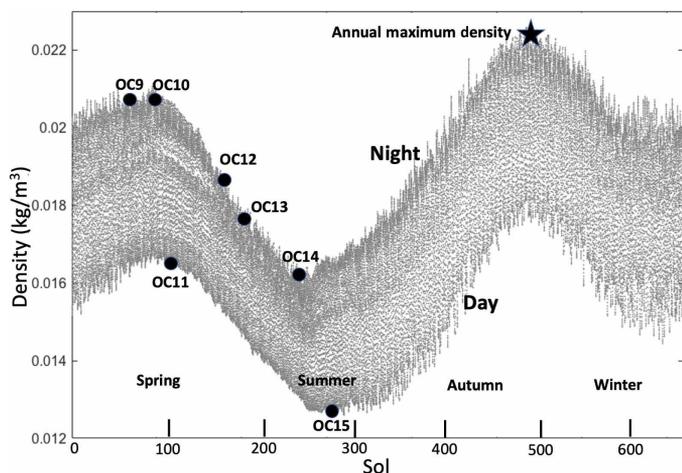
Fig. 2. Diurnal maximum (nighttime) and minimum (daytime) atmospheric density predicted (13) at the Perseverance landing site, Jezero crater, over one Mars year (668 sols). The circles show MOXIE runs completed in 2021, FM OC9 to OC15. The star shows the anticipated MOXIE run during the annual maximum atmospheric density.

Fig. 3. Nernst potentials for oxygen and carbon formation versus input mass flow for several rates of oxygen production at an operating temperature of 800°C. The two circles and the vertical line show reference segment conditions of 55 g/hour of intake and 6 g/hour of oxygen production. The dark arrows show the safe voltage zone for oxygen production, with no coking under these conditions. The vertical error bar reflects the effect of uncertainty in the lead resistance (see in the "Diagnostic runs" section) on the voltage applied to the cells. The horizontal error bar shows the uncertainty in determining the mass flow rate.

run on Mars. In addition to coking, governed by the Nernst potential, there is also a potential risk of oxidation of the nickel at the very entrance of the cathode, before CO production makes the overall gas mixture reducing. This has been mitigated, however, by a design that recirculates ~6% of the CO-rich cathode exhaust to the intake to prevent Ni oxidation.

The Nernst potentials also exhibit considerable significant sensitivity to temperature. For example, decreasing the operating temperature by 30°C lowers $V_N(2CO \rightarrow 2C + O_2)$ and raises $V_N(2CO_2 \rightarrow 2CO + O_2)$, effectively reducing the safe voltage zone by 0.027 V. A temperature increase similarly expands the safe voltage zone. Initial tests of the SOXE, performed in an oven, suggested that an operating temperature of 800°C is an optimal compromise between efficient operation and the risk of damaging heat-sensitive materials. Inside the Perseverance rover, however, volume and power constraints precluded an oven, so, instead, MOXIE's SOXE is heated by two heater plates at the top and bottom of the electrolysis stacks with insulation partially covering its sides. This configuration results in thermal gradients of up to 10°C between the cooler cells in the center of the stack and the warmer cells nearer the heaters. Cooler cells have both a higher resistance and a smaller safe voltage zone and are, thus, at greater risk of coking. MOXIE runs are operated conservatively, assuming worst-case (lowest) temperature in the middle cells and setting the voltages accordingly. The warmer cells, thus, will not produce as much oxygen as they potentially could.

Generic runs

Runs FM OC9 to OC13 were performed at a semiannual high-density season (northern hemisphere spring). FM OC14 was executed as the atmospheric density was decreasing, and OC15 took place near the annual minimum density. OC10, OC11, OC14, and OC15 were generic runs, essentially identical except for the time of sol they were run and the seasonal atmospheric density. Generic MOXIE runs start with a reference segment, described by McClean *et al.* (*12*), in which MOXIE's compressor is commanded to a revolution per minute calculated to input 55 g/hour of martian atmosphere into the system (55 g/hour is the maximum reliable intake during annual atmospheric

density minimum with MOXIE's compressor at its 3500 rpm maximum). The reference segment starts with a 16-min "equilibration" step with 2-A electrolysis current (6 g/hour of oxygen), during which time, the internal operating temperature stabilizes. This is followed by 3.5-min steps at 1.6 A and 1.2 A (4.8 and 3.6 g/hour of oxygen, respectively), providing a voltage-current (*V-I*) sweep to determine the internal resistance of the SOXE, an important instrument health parameter. The current returns to 2 A to end the reference segment. Running identical reference segments at the beginning of every MOXIE run allows for tracking changes in MOXIE performance. The intake of 55 g/hour and points of 6 g/hour are indicated in Fig. 3.

MOXIE software allows either specifying a desired current through the stack ("current-control mode," which effectively specifies the oxygen production rate) or specifying the desired voltage across the top and bottom parts of the stack ("voltage-control mode"). All runs described in this paper were run in current-control mode, where a feedback loop adjusts the stack voltage to obtain the desired current. Estimates of the internal resistance of the stack, obtained from the *V-I* sweeps described above, are used to predict the required voltages to ensure that the operation remains in the safe voltage zone. Voltage-controlled runs are planned for the future.

Following the reference segment, a generic MOXIE run steps the compressor up to its 3500 rpm maximum speed, implements another *V-I* sweep, and then sets the current to as high a value as possible for this maximum gas intake while keeping the estimated electrolysis voltage at least 0.1 V below the Nernst potential for carbon formation. At the end of a run, the compressor speed and electrolysis current are reset for 5 min to the values used in the reference segment to compare the system behavior at the beginning and at the end of the run.

Diagnostic runs

In addition to the generic runs just discussed, two diagnostic runs were carried out to shed light on uncertainties associated with determining the actual voltage across the cells and assessing the purity of the O_2 product. FM OC12 was designed to estimate the resistance (R_L) of the thin Inconel leads connecting the MOXIE voltage control circuitry to the stack of electrolysis cells that comprise the SOXE. R_L is only approximately known because of uncertainties in winding and installation, which results in an estimated uncertainty of ±15 mV in the voltage applied to each cell, shown as the vertical error in Fig. 3 and corresponding to >15% of the safe voltage zone of ~170 mV per cell in the reference segment.

The SOXE uses a stack of 10 electrolysis cells, electrically wired in series with a center tap such that they can be controlled as two five-cell stacks, referred to as top (T) and bottom (B). Analysis of early MOXIE runs showed higher voltages required to obtain the commanded current in B compared to T, which might indicate degradation of B. However, because voltage is measured directly at the power supply, the discrepancy could also be due to differences in R_L between T and B. The FM OC12 diagnostic run took advantage of the fact that the stack resistance is highly sensitive to small changes in stack temperature (T_S), while R_L is not. By varying T_S while holding other parameters held constant, it was possible to accurately estimate the difference between R_L(T) and R_L(B) and to confirm that most of the voltage difference between the stacks could be accounted for by a difference of ~50 milliohms between the two.

FM OC13 explored the relationship between oxygen purity and relative anode and cathode pressures, a critical metric because a purity of >99.6% is recommended for both propellant and breathing oxygen. In principle, only oxygen ions should cross the electrolyte, and the oxygen flow rate depends on the current, as described above, regardless of any pressure differential between the cathode and anode. However, manifolds for the cathode inlet and exhaust and for the oxygen exhaust are common for all 10 electrolysis layers, requiring numerous joint seals, and a small amount of leakage between the cathode and anode has been observed under certain conditions in both the FM and the EM. This "crossover flow" can go in either direction and is dependent on the relative pressures in the cathode and anode. Oxygen purity is affected by CO_2 leakage into the anode, so determining the sensitivity of crossover flow to cathode-anode pressure differential is important.

The dominant cathode gases are CO_2 and CO. CO would rapidly be oxidized to CO_2 if it leaked into the anode at 800°C; thus, concern about impurities in the anode is limited to CO_2 contamination of the oxygen. Purity is determined by a commercial nondispersive infrared (NDIR) CO_2 sensor that monitors trace CO_2 (0 to 5%) in the anode exhaust. This is one of four gas-specific sensors. CO_2 and CO NDIR sensors monitor the utilization of CO_2 in the cathode gas, and a luminescence-type O_2 sensor monitors the anode gas. In addition to measuring the partial pressure of the target gas, NDIR sensors are extremely sensitive to total gas pressure because of pressure broadening of spectral lines. MOXIE's sensors are commercial products designed for operation at Earth-ambient conditions. Spectral broadening effects are poorly characterized, requiring extensive calibration. To reduce mass, volume, and complexity, the cathode and anode flow channels are equipped with passive viscous flow control devices rather than true pressure regulators. Accordingly, FM OC13 was designed to maintain a nearly constant total anode pressure by setting a fixed electrolysis current while stepping up the cathode pressure by increasing the compressor speed.

Figure 4 shows the derived O_2 purity as a function of the relative cathode over-/under-pressure, ΔP, as a fraction of the nominal anode pressure, P_{AEx}, where the x axis values are derived from pressure sensors at the anode and cathode exhausts, P_{AEx} and P_{CEx}, respectively. Because there are pressure drops in the system due to filters, heat exchangers, and the SOXE itself, the actual pressure at the cathode itself can be higher than P_{CEx} by as much as 10%, depending on the precise location of the leakage path(s). Moreover, the cathode pressure oscillates at the rotation frequency of the compressor with an amplitude that might represent an additional 5% of the pressure, again depending on leak location. This uncertainty explains why some impurity is seen even when the nominal value of $\Delta P = P_{CEx} - P_{AEx}$ is negative (anode exhaust pressure is greater than cathode exhaust pressure).

Compared to the difference in true cathode pressure and P_{CEx}, the true anode pressure is more closely represented by P_{AEx}, because the anode gas flow velocity is typically 10× less than in the cathode and is not subject to oscillations. As anticipated, Fig. 4 shows that the CO_2 impurity level is immeasurably small when anode pressure is maintained with sufficient margin above the cathode pressure. While a small amount of CO_2 crossover is seen when the cathode pressure exceeds the anode pressure, this has no other adverse effect on SOXE operation. The gray area represents the uncertainties in the calibration of the anode CO_2 sensor.

The amount of crossover flow varies with each unit; in the FM, it is several times greater than in the EM. Figure 4 shows that as the cathode-to-anode overpressure increases, the oxygen purity falls off rapidly. However, if the system is operated at a sufficiently high oxygen production rate, then the anode pressure will be sufficiently high to avoid CO_2 contamination. Because scaled-up operational MOXIE-type systems will produce the maximum amount of oxygen for the available CO_2 intake, anode pressure will always exceed cathode pressure, producing pure oxygen. Note that there are additional advantages to operation with a relatively low cathode pressure, including considerable savings in compressor power and greater separation between the threshold voltages for oxygen production and deleterious carbon generation.
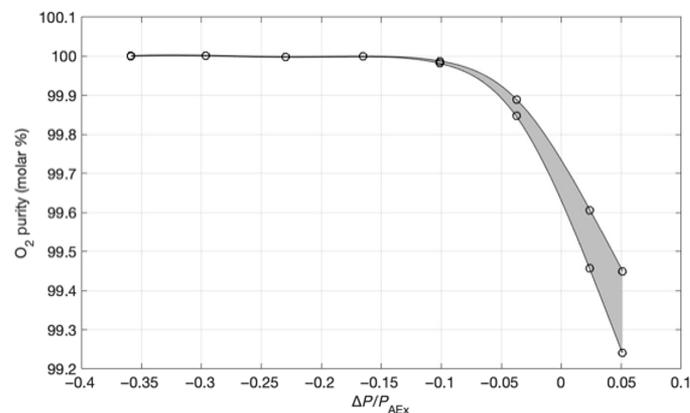
Fig. 4. Measured oxygen purity as a function of the nominal pressure difference between cathode and anode, normalized by the anode pressure (FM OC13). The x axis is determined by the measured differential exhaust pressure, which is smaller than the actual SOXE pressure. The gray area represents the range between the best fit to the composition data (higher purity) and a more physically reasonable model (lower purity). Note that other MOXIE runs were operated at even higher values of $\Delta P/P_{AEx}$ but were not part of this focused diagnostic.

Run-to-run degradation of MOXIE

The primary metric of cell performance is the cell resistance, here designated as iASR [intrinsic area-specific resistance (in $ohm \cdot cm^2$)], which is determined from the I-V relationship. Because the current is proportional to the oxygen-production rate and the voltage needs to stay within a range dictated by V_N, iASR determines the amount of oxygen that can safely be produced at any time.

Figure 5 shows the evolution of the measured iASR of the top and bottom FM MOXIE stacks during runs on Mars. In the seven oxygen-producing runs conducted on Earth, iASR rose relatively quickly from an initial value of less than 0.75 $ohm \cdot cm^2$ to the observed plateau at ~0.9 $ohm \cdot cm^2$. This behavior is typical of all MOXIE stacks and can be thought of as a "burn-in" period. FM OC8 was a test of the heating cycle after landing on Mars, during which no oxygen was produced. As seen in prototype stacks, after the burn-in period, iASR increases slightly with every cycle. In selecting electrolysis stacks for future missions, MOXIE experience has shown that stacks should be run for at least seven cycles to get past the burn-in period before selecting units for flight.

At the observed rate of increase, MOXIE is expected to meet nominal requirements (6 g/hour with 55 g/hour of CO_2 intake) for more than 60 cycles. Previous laboratory tests have demonstrated that it is the cooling and heating between cycles rather than the start-up and shutdown of the oxygen production process that causes this degradation, suggesting that it is likely associated with differential thermal stress. While further determining the cause of cycle-to-cycle degradation is of interest, a full-scale, continuously operating MOXIE-type system is not expected to be subjected to more than a few such thermal cycles. To support the design of such a system, it is more important to determine to what extent long-term continuous operation may also cause degradation. Because of energy constraints on the Perseverance rover, this investigation will need to be conducted in the laboratory.

DISCUSSION
Implications for future atmospheric ISRU systems

MOXIE is the first step leading to a system hundreds of times larger to support human exploration. Operations described in this paper show that MOXIE is well on the way to fulfilling its first goal—demonstrating daytime and nighttime oxygen production during all martian seasons without any detectable difference in performance beyond that expected from the changing atmospheric density. The second, and equally important, goal, to inform the design of future scaled-up systems, will be met by a combination of laboratory experiments on Earth and analysis of the long-term behavior of MOXIE on Mars. Problems may arise in scaled-up systems that are not faced by MOXIE, but much of relevance to future systems has been learned from building and operating MOXIE. In seven oxygen production runs through 2021, MOXIE successfully produced ~50 g of oxygen and definitively demonstrated that it meets requirements for oxygen generation rate and purity despite design compromises demanded by severe constraints on mass, power, volume, and cost. A strong start has been made at testing performance over the full range of Mars' diurnal and seasonal environments. Diagnostic baselines have been established (including the use of a microphone to characterize the mechanical compressor), and new techniques have been developed and validated for in situ diagnostics and calibration.

Among MOXIE's design compromises mentioned above are the following: the use of fixed apertures in lieu of pressure regulators, compromises in stack thermal control resulting in substantial thermal gradients and lags, a greatly simplified command and control system with limited sensor measurement and self-calibration capability, and the need for intermittent operation with full heat/cool cycles on each run. All of these liabilities would be addressed in a future scaled-up system.

It is possible that some of the technologies appropriate for this small-scale demonstration would be less efficient and effective in a full-scale implementation. For example, while a mechanical scroll compressor was an effective solution for MOXIE's small size and intermittent run opportunities, a full axial, lobe, or centrifugal compressor may be better suited for a full-scale system. Alternatively, cryogenic pumping systems that cycle between gas, liquid, and solid phases may have synergy with the liquefaction process that would be the final propellant production stage. Modifications of the cathode microstructure or material choices should be investigated to increase resistance to oxidation.

An important but unavoidable difference between MOXIE and future systems is the occasional and intermittent nature of MOXIE operation, which imposes substantial thermal stress on materials with each heating cycle. Reduction in cycle-to-cycle SOXE degradation was a primary development focus, and operation so far on Mars indicates
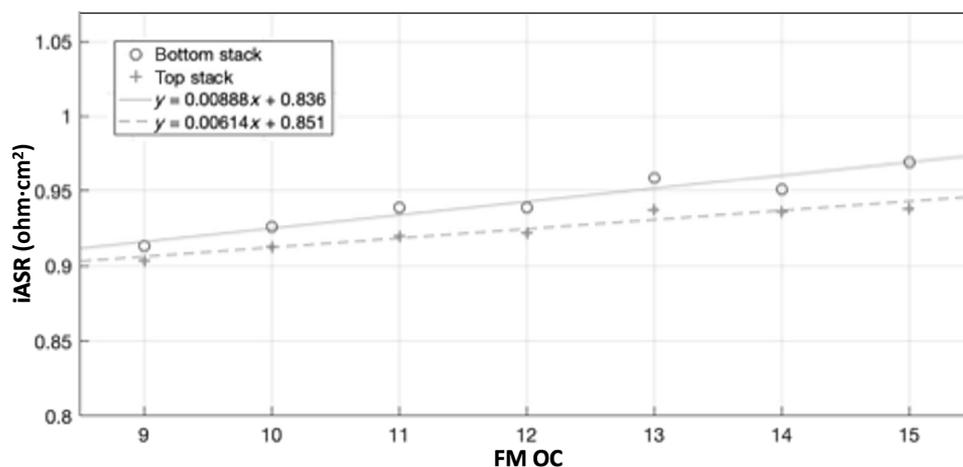
Fig. 5. MOXIE's iASR is seen to increase slowly with operating cycles.

that the outcome was highly successful. At the same time, the energy constraints of Perseverance do not allow testing of longevity over the thousands of hours of continuous operation that will be required in support of a human mission, both at the system and component level—these tests are planned as part of an ongoing laboratory program. An additional, subtle consequence of occasional operation is that it is less dependent on autonomous control than continuous operation. Ample time is available between runs to, for example, estimate atmospheric conditions and tune the compressor speed accordingly. A full-scale oxygen production plant will need a sophisticated monitor and control system to respond to daily and seasonal variations in the Mars atmosphere as well as changes in the performance of the plant itself. This will require not only advanced, adaptive software but also more capable processors and more extensive and robust self-calibrating sensors of gas flow, reactant concentrations, individual cell voltages, pressure, and temperature.

MOXIE has shown that a SOXE technology for producing oxygen on Mars from the atmosphere is viable, is scalable, and meets expectations for efficiency and quality, although long-term durability and resilience remain to be demonstrated during the balance of the Perseverance mission. Future work needs to emphasize enhancement of monitor and control capability coupled with increased SOXE robustness against carbon formation, but all indications are that a scaled-up version of MOXIE could produce oxygen in sufficient quantity and with acceptable reliability to support future human exploration.

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