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Methane and Oxygen from Energy-efficient, Low Temperature *in-situ* Resource Utilization (ISRU) Enables Missions to Mars

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Abstract

NASA's mandate is a human mission to Mars in the 2030s and sustained exploration of Mars requires *in-situ* resource utilization (ISRU). Exploiting the Martian water cycle (alongside perchlorate salts that depress water's freezing point to < 213K) and the available 95 vol.% atmospheric CO₂, we detail an ultra-low temperature (255K) CO₂-H₂O electrolyzer to produce methane fuel and life-supporting oxygen on Mars. Our polarization model fit experimental Martian brine electrolyzer performance and predicted CO₂ electrolysis occurring at comparatively lower potentials (vs. water electrolysis) on Mars. A hypothetical 10-cell, 100cm² electrode-area-per-cell

electrolyzer produced 0.45gW⁻¹day⁻¹ of CH₄ and 3.55gW⁻¹day⁻¹ of O₂ at 2V/cell and 50% electrolyzer faradaic efficiency vs. a best-case production of 2.5gW⁻¹day⁻¹ of O₂ by the Mars Oxygen *in-situ* Resource Utilization Experiment (MOXIE) from NASA's Mars 2020 mission (MOXIE produces no fuel). Material performance requirements are presented to advance this technology as an energy-efficient complement to MOXIE.

Topical Heading

Separations: Materials, Devices, and Processes

Key Words

Mars, in-situ resource utilization (ISRU), Electrolysis, Life-support, CO2 valorization

Plain Language Summary

Future sustained human missions to Mars will require astronauts to "live off the land" through *insitu* Resource Utilization (ISRU). This is necessitated by the immense energetic cost of moving material out of Earth's gravity well – completely provisioning a Mars mission from Earth, including 35 metric tons of propellant needed for the return journey, is estimated to require *ca* 400 metric tons of propellant (fuel and oxidant) on 4-5 heavy lift launch vehicles. As a cost-effective alternative, NASA is considering deploying a high temperature solid oxide electrolyzer 26 months in advance of a human mission to produce 25-30 metric tons of oxidant (O₂) using atmospheric CO₂ abundantly present on Mars (based on technology demonstrated through the Mars Oxygen *insitu* Resource Utilization Experiment (MOXIE) from NASA's Mars 2020 mission). Remedying shortcomings of this system, we propose an integrated ultra-low temperature electrolyzer that produces both fuel and oxidant utilizing Martian atmospheric CO₂ in conjunction with liquid brines present on Mars. Thus, our system produces the same oxidant as MOXIE with the added benefit of producing the other propellant component, methane (CH₄), all at lower energy consumption. Given the geographic limitations on brine availability, we envision our system being an able complement to MOXIE to advance the goal of sustained human exploration of Mars.

Introduction

The United States National Aeronautics and Space Administration (NASA)'s current goal is to land humans on Mars in the 2030's. The exploration of Mars is also a priority for several national and private space entities with lander missions from the US and China and orbiters from the US, China, Europe, Russia, India, and the United Arab Emirates (UAE) presently active there¹. The duration of any mission to Mars is circumscribed by the constraints imposed by the mass that can be sent to Mars from Earth. For example, SpaceX's Falcon Heavy (weighing 1420 metric-tons fully loaded) is designed to deliver a 16.8 metric-ton payload to Mars (1.8% of total weight). The immense energetic cost of moving material out of Earth's gravity well is illustrated by the following example - completely provisioning a Mars mission from Earth, including 35 metric tons of propellant needed for the return journey, is estimated to require *ca* 400 metric tons of propellant (fuel and oxidant) on 4-5 heavy lift launch vehicles². Additionally, astronauts consume 0.8 to 1.2kg of oxygen a day depending on activity, sex, height, and weight³. Thus, any economical long-term (weeks to months) mission necessitates the exploitation of resources present on Mars for life-support and energy⁴.

Key inputs for *in-situ* resource utilization (ISRU) have been identified in the Martian atmosphere and surface. The Martian atmosphere significantly differs from that of Earth's with its predominant constituent being CO₂ and the atmospheric pressure on Mars (636 Pa) is significantly lower than that of Earth (101325 Pa) (detailed in **Table 1**). Critically, the relatively low diurnal temperature range on Mars also suggests a heating energy penalty for any ISRU process carried out there.

In addition to abundant CO_2 in the Martian atmosphere, the comprehensive elucidation of Martian regolithic geochemistry by a succession of robotic landers and orbiter missions has led to the identification of deliquescent perchlorate salts as outlined in our group's previous work⁵. This includes the notable discovery of significant quantities of perchlorate and sulfate salts of sodium and magnesium by NASA's Phoenix lander (through its wet chemistry instrument (WCI⁶)) and optically observed sublimation of water ice discovered under a few inches of regolith⁷. Multiple pathways allow for the existence of water on (or under) the surface of present-day Mars through premelting⁸, by adsorption of atmospheric vapor at grain-ice boundaries⁵ and by greenhouse melting creating three phases of water⁹, with one phase being a temporary liquid water at the top of the subsurface ice¹⁰. Perchlorate salts play an important role in any extant hydrological cycle on Mars by depressing the freezing point of water to *ca* 203K as shown in our group's previous work⁵, with Martian water phase thermodynamic analysis¹¹ and with solubility polytherms¹². This freezing point depression allows for the existence of liquid water, a key ISRU feedstock, which is further corroborated by the phoenix lander site's evidence for liquid water¹³ and saline water stability on Mars¹⁴. NASA's Spirit and Opportunity rovers found historic evidence of super-cold local acidic brines through observation of acidic aqueous activity, evaporation, and desiccation of the Martian regolith¹⁵. Contemporary liquid water flows are also indicated by the geological observations of the Mars Reconnaissance Orbiter (MRO¹⁶). Furthermore, 2x10¹⁸ kg of water on Mars is present in the form of polar ice caps¹⁷ as evidenced by the Mars Odyssey Gamma Ray Spectrometer (GRS¹⁸) and Mars Express spacecrafts. The Mars Advanced Radar for Subsurface and Ionosphere Sounding (MARSIS) instrument on-board the Mars Express spacecraft has also detected multiple sub-glacial water bodies underneath the Martian south pole at Ultimi Scopuli¹⁹. Thus, abundantly present CO₂ and H₂O have been chosen as ISRU feedstock.

State-of-the-art and Proposed New Direction in ISRU

NASA's Mars Oxygen *in-situ* Resource Utilization Experiment (MOXIE) on the Perseverance rover is the most advanced Martian ISRU demonstration till date. This high temperature (1073K) solid oxide electrolyzer testbed produces O₂ and CO from atmospheric CO₂ through the reaction shown below²⁰:

$$2CO_2(g) = 2CO(g) + O_2(g) \tag{1}$$

Presently, the 10-cell solid oxide electrolyzer (SOXE) stack (2x 5-cell stacks in series with electrode area = 22.7 cm²) in MOXIE has been reported to operate at 50 % Faradaic efficiency (F.E) with a total power requirement of ~300 W²¹. Of the 300W, *ca* 115 W is expended operating the stack with the rest powering the balance of plant. The stack operation in turn consumes *ca* 35 W^{21} (8.7 V stack operating voltage and maximum operating current of 4 A) for carrying out the electrolysis and *ca* 80 W for maintaining the stack temperature at 1037 K.

MOXIE has been reported to produce a maximum of 12 g/ hr of O_2^{22} which translates to a power normalized O₂ production of 8.27 grams.W⁻¹.day⁻¹ (considering only the power required for electrolysis, *ca* 35 W). But considering the total power requirements to run the stack (the SOXE will not run unless it is heated to or near its operating temperature of 1037 K)²¹ and normalizing the O₂ production rate using this value (*ca* 115W), the power normalized O₂ production rate was 2.5 grams.W⁻¹.day⁻¹ under MOXIE operating conditions on Mars. We will show that our electrolyzer modeled using a 10-cell stack (electrode active area = 100 cm²) can provide a higher (~1.4x) O₂ production operating at the same 50 % electrolyzer F.E.

ISRU systems could potentially be sent to the surface 26 months before a manned mission in order to produce the 30 metric tons of oxygen needed to support a human mission to Mars. Proposals

exist for a larger 1 metric ton MOXIE-like electrolyzer to produce 25-31 metric tons of oxygen for life support and oxidant²³. Despite MOXIE's successful production of O₂, the need for downstream processing to remove CO and the inherent risks of CO toxicity implies increased balance of plant (BOP) requirements and reduced overall energy efficiency. Furthermore, high operational temperatures introduce issues of thermal waste and, critically, safety. By running our system at (or close to) the Martian ambient temperature and producing O₂ from H₂O (and CH₄ from CO₂), we propose to avoid both these potential safety risks inherent in the MOXIE system.

Another critical design consideration is the nature of engines powering the descent stage landing on Mars. Methalox engines, utilizing cryogenic methane as fuel and cryogenic oxygen as oxidant, are the preferred power source (a listing, representative of global efforts towards developing methalox engines, is presented in **Table 2**). An issue for future missions is that MOXIE only produces one component used in methalox engines, O₂, leaving the need for the other propellant component, CH₄, unfulfilled. State-of-the-art methalox rocket engines require 12 to 13 metric tons of propellant (oxygen and methane) to transfer a metric ton of payload from low earth orbit²⁴. The economic value of the 35 metric tons of propellant needed for a return journey from Mars can be estimated from the Perseverance rover's cost of ~\$237,000 per kg of payload to the Martian Surface²⁵. Using this proven cost gives a potential savings of ~\$8.3 billion if propellant is created on the Martian surface, with ~\$1.66 billion of that cost being related to sending the methane needed for the methalox rocket engine propellant. The key aim of our electrolyzer is to model the production of both, methane (for methalox rockets) and oxygen (for life support and oxidizer) using ISRU of CO₂ at Martian conditions.

Sankarasubramanian and co-workers have previously demonstrated that electrolysis of Martian brines can be successfully carried out at the average Martian ambient temperature (237K) to

produce H₂ fuel and life-support O₂ with significantly improved energy efficiencies compared to $MOXIE^5$. Building on this work, the ultra-low temperature CO₂-brine electrolyzer (**Fig. 1**) can produce methane as fuel (in addition to O₂) through the following full cell reaction:

$$CO_2(g) + 2H_2O(l) = CH_4(g) + 2O_2(g)$$
⁽²⁾

We initially anticipated electrocatalysis being an impediment to realizing this electrolyzer. The average Martian diurnal temperature ranges between 184K to 242K. Thus, based on Arrhenius kinetics, it was anticipated that the rate of 8-electron CO₂ reduction to CH₄ would be significantly slower than at terrestrial conditions. Fortuitously, recent studies have demonstrated that Cu electrocatalysts exhibit anti-Arrhenius kinetics and, counterintuitively, improved CH4 selectivity going from 293K to 255K²⁶. This is attributed to the solubility of CO₂ increasing and the H₂evolution reaction (HER) kinetics decreasing as temperature decreases. At these lower temperatures, it was demonstrated that gas hydrate crystalline structures (clathrates) restrict rotation and translation of gas molecules²⁷ and influence carbon dioxide reduction reaction (CO_2RR) selectivity. Furthermore, at these lower temperatures, the competing HER pathway is shifted towards negative overpotentials, and is directly inhibited by adsorbed CO from the CO_2RR , leading to much higher selectivity and faradaic efficiency for CO₂ reduction on Cu electrodes²⁸. We anticipate the CH₄ and (unreacted) CO₂ exiting the electrolyzer being separated using cryogenic distillation and the lower Martian ambient temperature enabling down-stream cryogenic distillation (Figure 1) with a lower cooling energy penalty. However, the general electrolyzer design is the primary focus of this polarization model. We have already demonstrated O_2 production at acceptable rates and selectivity under Martian conditions in our previous work⁵. Ultimately, some of the conditions that make Mars uninhabitable for humans are anticipated to be

beneficial for the synthesis of methalox engine propellant using a liquid brine and CO₂ electrolysis system.

We evaluated the operational viability and materials requirements for the CO₂-H₂O electrolyzer by building thermodynamic and electrochemical polarization models of this system. The models were first validated against our experimental data for the operation of a Martian H₂-O₂ electrolyzer. For the proposed CO₂-H₂O electrolyzer, the Nernst potential, the choice of anode/cathode and overpotentials for the electrocatalyst at the anode/cathode were correspondingly calculated or parameterized from experiments in the literature to model the performance of these electrolyzers under Martian conditions. Finally, we modeled the fuel and oxidant generation capacity of a conservatively sized electrolyzer stack consisting of 10-cells of 100cm² active area each and show that this system is an energy-efficient method to provision long-term missions to Mars.

Electrolyzer operation on Mars

Thermodynamic and polarization models were built for the reactions depicted below. Brine electrolysis (eqn (3)) to produce H₂ and O₂ served as model validation against existing experimental data⁶.

$$H_{2}O(l) = H_{2}(g) + \frac{1}{2}O_{2}(g)$$
(Brine - electrolysis) (3)
$$CO_{2}(g) + 2H_{2}O(l) = CH_{4}(g) + 2O_{2}(g)$$
(CO₂ - Brine electrolysis) (4)

The corresponding half-cell reactions (and the standard electromotive force (emf) for the reaction (E^{θ}_{rxn})) for brine electrolysis to H₂ and O₂ are –

$$H_{2}O = \frac{1}{2}O_{2} + 2H^{+} + 2e^{-} (E^{0}_{rxn} = -1.23V)$$

$$(5)$$

$$2H^{+} + 2e^{-} = H_{2} (E^{0}_{rxn} = 0V)$$

$$(6)$$

$$H^{+} + 2e^{-} = H_2 \left(E^{0}_{rxn} = 0V \right) \tag{6}$$

And the corresponding half-cell reactions for CO₂-brine electrolysis to CH₄ and O₂ are ²⁹-

$$4H_2 O = 2O_2 + 8H^+ + 8e^- (E^{0}_{rxn} = -1.23V)$$
⁽⁷⁾

$$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O \left(E^{0}_{IXII} = -0.17V\right)$$
(8)

Thermodynamic model development

The thermodynamic property change (dS, dH and dG) over the course of the reactions depicted in **eqn (3)** and **eqn (4)** were obtained at Martian conditions. i.e., between 230K to 255K. The change in enthalpy (dH) was calculated using the following relationship –

$$dH = H_{298K} + c_p \times (T - T_{ref}) \tag{9}$$

The change in entropy (dS) was calculated using the following relation with the specific heat capacity (c_p) –

$$dS = S_{298K} + c_p \times ln\left(\frac{T}{T_{ref}}\right) \tag{10}$$

Having obtained dH and dS for the given reaction, the free energy change (dG) was calculated as shown below-

$$dG = dH - T \, dS \tag{11}$$

dG was in turn used to calculate the reversible electromotive force (E_{emf}) i.e., the minimum thermodynamic potential required for the reactions to occur, using the following equation -

$$\Delta G = -nF|E_{emf}| \tag{12}$$

where the number of electrons (*n*) is either 2 or 8 depending on whether brine electrolysis or CO₂brine electrolysis is carried out by the electrolyzer, and F is Faraday's constant (96,485 C mol⁻¹).

The c_p of supercooled water has been measured using various techniques like, differential scanning calorimetry³⁰, drift calorimetry³¹ and proton magnetic resonance chemical shift measurements³². These observations consistently point to an anomalous increase in c_p in inverse correlation to temperature.

For the case of brine electrolysis (**eqn** (3)), the thermodynamic properties (*dS* and *dH*) were calculated from the specific heat capacity (C_p , J mol⁻¹ K⁻¹) of supercooled water measured using an adiabatic calorimeter³³, between 235K to 285 K, with T_{ref} at 298K. The data from the literature was shown to accurately fit the following empirical expression³⁶ -

$$C_p^{H_20} = 0.44 \times \left(\frac{T - 222}{222}\right)^{-2.5} + 74.3 \tag{13}$$

The values of dH, dS and dG for H₂O (1) can be found in **Table S1** in the Supplementary Materials. Having obtained the thermodynamic values as detailed above, we calculated $|E_{emf}|$ and $E_{thermoneutral}$ across the temperature range of interest (230K to 500K) for brine electrolysis. The $|E_{emf}|$ and $E_{thermoneutral}$ can be found in **Table S2** in the Supplementary Materials. We also obtained the following general empirical correlation between $|E_{emf}|$ vs. temperature (*T*) between 230K to 1300K from these calculated values -

$$|E_{emf}| = (2e^{-7} \times T^2) - (6e^{-4} \times T) + 1.43$$
(14)

The thermoneutral voltage ($E_{thermoneutral}$) was calculated from the corresponding dH values using eqn. (15).

$$E_{thermoneutral} = \frac{dH}{2F} \tag{15}$$

For the case of CO₂-brine electrolysis, in addition to the thermodynamic properties of H₂O in liquid phase, the gas phase thermodynamic properties of CO₂ and CH₄ were required between 230K to 270K. The specific heat capacity (C_p , J mol⁻¹ K⁻¹) values for CO₂ and CH₄ were obtained from literature^{34,35}, respectively. The *dH*, *dS* and *dG* for CO₂ (g) and CH₄ (g) can be found in **Table S3** and **Table S4** in the Supplementary Materials. The thermodynamic properties (*dS* and *dH*) were calculated from C_p for temperatures between 220-300K and 120-500K with T_{ref} at 298 K. We also obtained the following empirical correlations for c_p vs. *T* from this data -

$$C_p^{CO_2} = 0.039 \times T + 25.74 \tag{16}$$

$$C_p^{CH_4} = 0.0001 \times T^2 - 0.038 \times T + 36.84 \tag{17}$$

Similar to the case of the brine electrolyzer, we obtained an empirical expression correlating $|E_{emf}|$ vs. temperature (T) between 230K to 1300K using these *dH* and *dS* values -

$$|E_{emf}| = (1e^{-7} \times T^2) - (2e^{-4} \times T) + 1.12$$
(18)

The thermoneutral voltage ($E_{thermoneutral}$) was calculated from the corresponding dH values using eqn. (19).

$$E_{thermoneutral} = \frac{dH}{8F} \tag{19}$$

The $|E_{emf}|$ and $E_{thermoneutral}$ can be found in **Table S5** in the Supplementary Material. These thermodynamic properties (d*G*, d*H*, E_{emf} and $E_{thermoneutral}$) for brine electrolysis and CO₂brine electrolysis from 230K to 500K are depicted in **Fig 2**. As a consequence of the anomalous c_p values, we saw that the dG and hence $|E_{emf}|$ and $E_{thermoneutral}$ increased in inverse proportion to the temperature. The effect of these anomalous c_p values at <273K was found to be more significant than any changes due to phase transitions.

Nernst Potentials for Electrolysis

The Nernst equation provides information about the equilibrium potential of the electrolyzer under open circuit conditions. The equilibrium potential is the sum of contributions from reversible electromotive force (minimum thermodynamic potential) and concentration (activity) of electroactive species in a reaction.

For example, in case of brine electrolyzers operating at terrestrial atmospheric pressure of 101325 Pa, the E_{Nernst} can be defined as,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{2F} ln\left(\frac{[y_{H_2}][y_{O_2}]^{\frac{1}{2}}}{[y_{H_2O}]}\right)$$
(20)

where the mole fractions of H₂, O₂ and H₂O are written as y_{H_2} , y_{O_2} and y_{H_2O} . Since the y_{H_2O} is ~1 in liquid phase, the expression reduced to,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{2F} ln\left([y_{H_2}] [y_{O_2}]^{\frac{1}{2}} \right)$$
(21)

We also corrected the Nernst potentials for brine electrolysis for Martian surface pressure (636 Pa) using the additional term, $\frac{P_{Mars}}{P_{Std}}$, as shown below,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{2F} ln\left([y_{H_2}] [y_{O_2}]^{\frac{1}{2}} \times \left[\frac{P_{Mars}}{P_{Std}} \right]^{\frac{3}{2}} \right)$$
(22)

Similarly, the Nernst potentials for CO_2 -brine electrolysis operating at terrestrial atmospheric pressure of 101325 Pa was calculated using the expression,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{8F} ln\left(\frac{[y_{CH_4}][y_{O_2}]^2}{[y_{CO_2}]}\right)$$
(23)

where the mole fractions of CH₄, O₂ and CO₂ were written as y_{CH_4} , y_{O_2} and y_{CO_2} . y_{H_2O} was ~1 as it was in the liquid phase.

The Nernst potentials of CO₂-brine electrolysis was calculated after incorporating the corrections for surface pressure on Mars as³⁶,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{8F} ln \left(\frac{[y_{CH_4}][y_{O_2}]^2}{[y_{CO_2}]} \times \left[\frac{P_{Mars}}{P_{Std}} \right]^2 \right)$$
(24)

The E_{emf} for both the brine and CO_2 – brine electrolyzers was determined from the thermodynamic parameters as discussed in the thermodynamic model deveopment section. The contributions from concentration (activity) of electroactive species was calculated by varying the extent of the reaction (conversion) for the reactions from 5 % to 95 % as discussed below.

For example, the Nernst potentials of CO₂-brine electrolysis (eqn. (24)) was expressed in terms of conversion (ε) as,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{8F} ln \left(\frac{\left[\frac{\varepsilon}{3}\right] \left[\frac{2\varepsilon}{3}\right]^2}{\left[\frac{1-\varepsilon}{3}\right]} \times \left[\frac{P_{Mars}}{P_{Std}}\right]^2 \right)$$
(25)

Where the mole fractions of y_{CH_4} , y_{O_2} and y_{CO_2} and y_{H_2O} , are $\left[\frac{\varepsilon}{3}\right]$, $\left[\frac{2\varepsilon}{3}\right]$ and $\left[\frac{1-\varepsilon}{3}\right]$ respectively. The Nernst potential with 50 % conversion ($\varepsilon = 0.5$) at 298K and 636 Pa was calculated to be ~ 1.113 V as shown below,

$$E_{Nernst} = 1.07 - \frac{8.314 \times 298}{8 \times 96485} ln \left(\frac{\left[\frac{0.5}{3}\right] \left[\frac{1}{3}\right]^2}{\left[\frac{0.5}{3}\right]} \times \left[\frac{636}{101325}\right]^2 \right) = \sim 1.11 V$$
(26)

A 3-dimensional (3D) plot for the Nernst potentials at various reaction extents (conversion, ε) and temperatures ranging from 230K to 298K were calculated and plotted as surface plots as shown in **Fig. 3** for brine electrolysis (**Fig. 3(a)**) and CO₂-brine electrolysis (**Fig. 3(b)**) at 636Pa and 101325Pa. The various configurations of the electrolyzer, including balance of plant components, for operations at combinations of both terrestrial and Martian average surface pressures and temperatures are depicted in **Fig. S1-S3**. Based on these calculations, we conclude that temperature exhibits a greater impact on the Nernst potentials as compared to pressure and temperature effects will be emphasized going forward.

A comparison of Nernst potentials under Martian conditions (236K, 636 Pa) and terrestrial conditions (298K, 101325 Pa) at various ε values for brine electrolysis and CO₂-brine electrolysis is shown in **Fig. 4**. CO₂ electrolysis to carbon monoxide (CO) and O₂, (the MOXIE reaction) was also studied at low temperatures for comparison. The results clearly show the advantage (lower Nernst potential, hence a lower thermodynamic barrier) of operating a CO₂-brine electrolyzer to produce CH₄ + O₂ compared to a brine electrolyzer to produce H₂ + O₂ or MOXIE to produce CO + O₂ (at low temperatures) under both Martian and terrestrial conditions. It was observed that pressure variation between 636 Pa and 101325 Pa had minimal effect on the performance of the electrolyzer modeled at 236 K.

Polarization model development

The polarization model is built to capture the realistic operational voltage of the electrolyzer (E_{cell}) working under Martian conditions combining thermodynamic (electromotive force (E_{emf}) and Nernst potential (E_{Nernst}) for electrolysis along with activation overpotential for electrodes, anode (η_{act}^{anode}) and cathode ($\eta_{act}^{cathode}$) and transport losses ((Ohmic losses (E_{IR}) due to electronic and ionic resistances) . The polarization model is thus the sum of all these contributions as shown below-

$$E_{cell} = E_{Nernst} + |\eta_{act}^{anode}| + |\eta_{act}^{cathode}| + E_{IR}$$
(27)

 E_{Nernst} was calculated from E_{emf} and the reaction stoichiometry using the Nernst equation³⁶ as detailed in the previous section. Activation overpotential (η) was determined from linear sweep voltammetry (LSV) curves previously reported by Sankarasubramanian and co-workers.⁵

In addition to the electrode catalyst activation overpotentials η_{act}^{anode} and $\eta_{act}^{cathode}$, increases in faradaic (electrochemical reaction) current will also require an applied overpotential as described by the Butler-Volmer equation (**eqn 28**),

$$j = j_0 * \left(exp^{\left(\frac{\alpha_a n F \eta}{RT}\right)} - exp^{\left(\frac{\alpha_c n F \eta}{RT}\right)} \right)$$
(28)

Where, *j* is the current density (mA cm⁻²), j_0 is the exchange current density (mA cm⁻²) which is a common metric of electrocatalyst activity, *n* is the number of electrons, *F* is Faraday's constant (C mol⁻¹), *R* is the universal gas constant (J K⁻¹mol⁻¹), α_a and α_c are the dimensionless anodic and cathodic charge transfer coefficients respectively, η is the applied overpotential ($E - E_{eq}$), and *T* is temperature (K). Given that the faradaic current is proportional to the exponent of the overpotential, the overpotential contribution from pulling current is quite small. On the other hand, large overpotentials are needed to overcome the cell resistance (voltage and resistance are directly proportional) and hence the ohmic overpotential contributions are significantly larger. Thus, our model will accurately describe systems using most active catalysts with relatively high exchange current densities.

The polarization model was applied to a well-known water electrolysis reaction (**eqn. (3**)) as an initial validation exercise.

The corresponding Nernst equation for water electrolysis reaction is,

$$E_{Nernst} = |E_{emf}| - \frac{RT}{2F} ln\left(\frac{[H_2][O_2]^{\frac{1}{2}}}{[H_2O]}\right)$$
(29)

In the case of water electrolysis, the $|E_{emf}|$ is 1.23V at 298K and 101325 Pa³⁷ based on the difference between the equilibrium potentials for the oxygen evolution reaction (OER) (eqn. (5)) and the hydrogen evolution reaction (HER) (eqn. (6)). Accounting for 90% conversion, the E_{Nernst} was calculated to be 1.28V at 298K and 101325Pa. Activation overpotentials for the electrode, anode (η_{act}^{anode}) and cathode ($\eta_{act}^{cathode}$) at 298K and 101325Pa were obtained from the difference between the thermodynamic Nernst potentials for the anode (E_{ner}^{anode}) or cathode ($E_{ner}^{cathode}$) and the onset potential for the anode (E_{onset}^{anode}) or cathode ($E_{onset}^{cathode}$) as shown in eqn. (30). The onset potentials of the electrodes were measured using linear sweep voltammetry experiments performed at the respective electrodes.

$$\eta_{act}^{anode} = E_{onset}^{anode} - E_{ner}^{anode} \qquad \qquad \eta_{act}^{cathode} = E_{onset}^{cathode} - E_{ner}^{cathode} \qquad (30)$$

At standard temperature and pressure (STP) of 298K, 101325 Pa and pH =0, the activation overpotentials for the OER at anode (η_{act}^{anode}) and the HER at cathode ($\eta_{act}^{cathode}$) were calculated from their half-cell Nernst potentials as,

$$\eta_{act}^{anode} = E_{onset}^{anode} - 1.28 \qquad \qquad \eta_{act}^{cathode} = E_{onset}^{cathode} - 0 \qquad (31)$$

Having obtained the thermodynamic contributions to overall electrolyzer polarization, we turned to the Ohmic losses in the electrolyzer. The most resistive component (and hence the major contributor to Ohmic loses) is the resistance of the membrane, which was calculated using Ohm's law-

$$E_{IR} = jASR_{mem} \tag{32}$$

where, j is the current density (mA cm⁻²) and ASR_{mem} is the area specific resistance (ASR) of the membrane (Ω cm²).

The polarization model applied to both the Martian brine electrolyzer and the CO₂-H₂O electrolyzer and for both the cell and stack configurations has accounted for inefficiencies at several levels to provide realistic predictions of performance. First, a reactant conversion of 90% is assumed in the Nernst equation, reducing the operating potential of the electrolyzer. Secondly, the practically achievable open circuit potential (OCP) (which should ideally equal the Nernst potential) is assumed to be a mixed potential with a value equal to 70% of the calculated Nernst potential to account for potential contributions from unwanted side-reactions. These inefficiencies increase the electrolyzer power requirements for a desired production rate (which is proportional to current). Furthermore, catalyst faradaic efficiency (values assumed are a function of the catalyst and are listed for every cell configuration modeled) at each electrode reduces the desired product production rate for a given operating current. Finally, accounting for resistive losses at the electrolyzer cell and stack level, we have modeled the production rates at various electrolyzer efficiencies. Thus, the model conservatively builds in four different inefficiencies and this approach results in a very close model fit with our previously published Martian H₂O electrolysis data as detailed in the next section.

Model validation

The polarization model expression was validated against experimental data from our earlier studies on Martian brine H₂-O₂ electrolyzer before applying the model to the CO₂-brine electrolyzer.

Some key assumptions underlying the operation of the brine electrolyzer are -

- The brine solution is made up of 2.8M Mg(ClO₄)₂ dissolved in water and is assumed to be in liquid phase at 237K and 101325Pa
- The brine solution is acidic with pH = 3 as measured at standard atmospheric conditions
- Two configurations of the brine electrolyzer were considered -
 - Pb2Ru2O7 Configuration: OER is catalyzed at the anode by lead ruthenate pyrochlore (Pb2Ru2O7) and HER is catalyzed at the cathode by platinum on carbon (Pt-C)
 - **RuO₂ Configuration**: OER is catalyzed at the anode by ruthenium oxide (RuO₂) and HER is catalyzed at the cathode by platinum on carbon (Pt-C)
- The onset potentials for the Pb₂Ru₂O₇/RuO₂ anode (*E^{anode}*_{onset}) and Pt-C cathode (*E^{cathode}*_{onset}) were calculated from the experimental values from our previous work⁵.
- A commercial Fumasep[®] FAA-3-50 anion exchange membrane (AEM) separator was used in our previous work and its reported ASR was used in our electrolyzer validation calculations.

To develop this polarization model, first E_{Nernst} for brine electrolysis at various temperatures (~ 230-500K) and pressures (636Pa and 101325Pa) was calculated using the thermodynamic data and the Nernst equation. Second, the activation overpotentials at the anode and cathode were calculated

at the specific operating conditions of the brine electrolyzer. Finally, the Ohmic losses were calculated from the membrane resistance (R_{mem}) at varying *i* values.

The E_{Nernst} for a brine electrolyzer operating at 237K and 101325Pa with a conversion efficiency of 90% was calculated to be

$$E_{Nernst} = 1.34V \tag{33}$$

The activation losses differed based on the electrolyzer configuration (due to variations in electrocatalytic characteristics of the catalysts). The calculations are detailed below -

 Pb₂Ru₂O₇ anode and Pt-C cathode Configuration: The activation overpotential for OER on Pb₂Ru₂O₇ anode and HER on Pt-C cathode are calculated from half-cell Nernst potentials at pH = 0,

$$H_2 O = \frac{1}{2} O_2 + 2H^+ + 2e^- \qquad (E_{ner}^{anode,237k,101325Pa} = -1.3V) (34)$$
$$2H^+ + 2e^- = H_2 \qquad (E_{ner}^{cathode,237k,101325Pa} = 0V) (35)$$

Correcting it to electrolyzer operating conditions of 237 K, 101325 Pa with pH = 3 as,

$$H_{2}O = \frac{1}{2}O_{2} + 2H^{+} + 2e^{-} \qquad (E_{ner}^{anode,237k,101325Pa} = -1.16V) (36)$$

$$2H^{+} + 2e^{-} = H_{2} \qquad (E_{ner}^{cathode,237k,101325Pa} = -0.14V) (37)$$

$$/\eta_{act}^{Pb_{2}Ru_{2}O_{7}}| = E_{onset}^{Pb_{2}Ru_{2}O_{7}} - 1.16 \qquad |\eta_{act}^{Pt-C}| = E_{onset}^{Pt-C} - (-0.14) (38)$$

$$E_{enert}^{Pb_{2}Ru_{2}O_{7}} \text{ and } E_{enert}^{Pt-C} \text{ for the anode and cathode were calculated to be 1.35V and -0.55V from the$$

 $E_{onset}^{PD_2Ru_2O_7}$ and E_{onset}^{PT-C} for the anode and cathode were calculated to be 1.35V and -0.55V from the experiments performed on brine at 237K and 101325Pa. The calculated activation overpotential for the electrodes were,

$$|\eta_{act}^{Pb_2Ru_2O_7}| = 0.19V \text{ and } |\eta_{onset}^{Pt-C}| = 0.41V$$
(39)

The total activation overpotential was calculated to be

$$\eta_{act} = \left| \eta_{act}^{Pb_2 Ru_2 O_7} \right| + \left| \eta_{act}^{Pt-C} \right| = 0.6V \tag{40}$$

The R_{mem} for the Fumasep[®] FAA-3-50 membranes used were reported to vary between 0.2 - 0.7 Ω cm² ³⁸. We have conservatively used the maximum value of 0.7 Ω cm² for calculating E_{Ω} in our model. The predicted operating cell potentials of the brine electrolyzer (solid red line) at 237K and 101325Pa with Pb₂Ru₂O₇ anode and Pt-C cathode is shown in **Fig. 5**. The experimental values (brown squares) are compared with the calculated operating cell potentials (solid red line) as shown in **Fig. 5**. The experimental values lie close to the 70% efficiency (dotted red line) of the calculated values of the model. Given that the state-of-the-art electrolyzers operate at 70–80% electricity-to-hydrogen efficiency to produce high-purity (>99.9%) H₂ ³⁹, the close match with predicted performance at 70% efficiency serves as a powerful validator of our model. The model was also applied to configuration 2 as detailed below.

• **RuO₂ anode and Pt-C cathode Configuration:** The activation overpotential for the OER at RuO₂ anode and the HER at Pt-C cathode are calculated from half-cell Nernst potentials which have the same values presented in the previous section. The activation overpotentials were calculated as -

$$|\eta_{act}^{RuO_2}| = E_{onset}^{RuO_2} - 1.16 \qquad \qquad |\eta_{act}^{Pt-C}| = E_{onset}^{Pt-C} - (-0.14) (41)$$

 $E_{onset}^{RuO_2}$ and E_{onset}^{Pt-C} for the anode and cathode were calculated to be 1.55V and -0.55V from the experiments performed with brine at 237K and 101325Pa. The calculated activation overpotential for the electrodes were,

$$|\eta_{act}^{RuO_2}| = 0.39V \qquad \qquad |\eta_{act}^{Pt-C}| = 0.41V \qquad (42)$$

The total activation overpotential was calculated to be

$$\eta_{act} = \left| \eta_{act}^{RuO_2} \right| + \left| \eta_{act}^{Pt-C} \right| = 0.80V \tag{43}$$

As the separator membrane did not change between the configurations, the Ohmic losses remained the same as in configuration 1. A model representing the operating cell potentials of the brine electrolyzer (red line) at 237K and 101325Pa with RuO₂ anode and Pt-C cathode is shown in **Fig. 6**. The polarization performance at 70% efficiency is depicted using a dotted red line and is expected to closely match the performance of an actual electrolyzer with this configuration. RuO₂ was used in the polarization calculations for electrolyzer modeling due to its degradation resistance and compatibility under acidic conditions as discussed in our previous study⁴⁰ and due to availability of overpotential data at operating conditions of the electrolyzer i.e. 255 K and in a Mg(ClO₄)₂ electrolyte. The CO₂-brine electrolyzer was also modeled using a RuO₂ anode as detailed in the next section.

CO₂-brine electrolysis to produce CH₄ and O₂ on Mars

The key assumptions underlying the operation of the CO₂-brine electrolyzer are -

- The brine solution is made up of 2.8 M Mg(ClO₄)₂ dissolved in water and is assumed to be in liquid phase at 255K and 101325Pa (see detailed discussions on the thermodynamic validity of this assumption in our previous work⁵)
- The brine solution is acidic with pH = 3 as measured at standard atmospheric conditions.

OER is carried out at the anode by ruthenium oxide (RuO₂) and carbon-dioxide reduction reaction (CO₂RR) is carried out at the cathode by copper (Cu(111)) and the activation overpotentials are calculated from the onset potentials of experiments with brine at 255K and 101325Pa. For CO₂-brine electrolysis, 255 K and 101325 Pa is considered for model instead of 236 K and 101325 Pa because, the Cu (111) cathode (*E^{cathode}*_{onset}) values are reported at 255 K in the literature²⁶.

We calculated E_{Nernst} for the CO₂-brine electrolysis at various temperatures (~ 230 - 500K) and pressures (636Pa and 101325Pa) using the thermodynamic data and the Nernst equation. The E_{Nernst} for the CO₂-brine electrolyzer operating at 255K and 101325Pa with a conversion efficiency of 90% is,

$$E_{\text{Nernst}} = 1.08 \text{V} \tag{44}$$

The half-cell Nernst potentials at 237 K, 101325 Pa and pH = 0 are -

$$4H_2 0 = 2O_2 + 8H^+ + 8e^- \qquad (E_{ner}^{anode,237k,101325Pa} = -1.30V)$$
(45)

$$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O \qquad (E_{ner}^{cathode, 237k, 101325Pa} = 0.22V)$$
(46)

Correcting to pH = 3, we obtained --

$$4H_2 0 = 2O_2 + 8H^+ + 8e^- \qquad (E_{ner}^{anode,237k,101325Pa} = -1.14V)$$
(47)

$$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O \qquad (E_{ner}^{cathode, 237k, 101325Pa} = 0.058V)$$
(48)

$$\left|\eta_{act}^{RuO_2}\right| = E_{onset}^{RuO_2} - 1.14 \qquad \left|\eta_{act}^{Cu(111)}\right| = E_{onset}^{Cu(111)} - (0.058) \tag{49}$$

 $E_{onset}^{RuO_2}$ and $E_{onset}^{Cu(111)}$ for the anode and cathode were calculated to be 1.49V and -0.25V from the experiments performed with brine at 255K and 101325Pa. The calculated activation overpotential for the electrodes are,

$$|\eta_{act}^{RuO_2}| = 0.34V \qquad |\eta_{act}^{Cu(111)}| = 0.32V \tag{50}$$

The total activation overpotential is thus-

$$\eta_{act} = |\eta_{act}^{RuO_2}| + |\eta_{act}^{Cu(111)}| = 0.66V$$
⁽⁵¹⁾

The Ohmic loss contributions were parameterized in our model of a CO₂-brine electrolyzer by assuming the conductivity of the separator membrane for the CO₂-brine electrolyzer to be equal to the conductivity of Nafion 117 at 303K. Thus, ASR_{mem} is estimated to be ~ 1.22 Ω cm^{2 41}. A higher conductivity separator membrane is thus a critical requirement for further improving the performance of these electrolyzer systems. The model predictions of the operating cell potentials of the CO₂-brine electrolyzer (red line) at 255K and 101325Pa with RuO₂ anode and Cu(111) cathode is shown in **Fig. 7**. Nafion 117 was selected for this polarization model due to the availability of data at lower temperatures and compatibility with the acidic conditions present in the electrolyzer. Further development of operational electrolyzers will utilize thinner and less resistive membranes to further increase performance.

Performance of a CO₂-brine electrolyzer stack

As shown in our model validation for the brine electrolyzer (**Fig. 6**), assuming a practical open circuit potential that is 70% of the calculated Nernst potential closely matches experimental data. Thus, this validated assumption was taken as the operational single-cell potential of the CO₂-brine electrolyzer and appropriately scaled-up (based on the assumed series- and parallel configuration of the cells in the stack) for our stack calculations. The electrolyzer stack was assumed to contain 10 cells of 100 cm² electrode surface area (each cell) and its performance is shown in **Fig. 8**. The operational cell potential of the stack along with the power requirements are shown in the primary Y-axis and the volume of CH₄ and O₂ generated by the stack is shown as secondary Y-axis with

the current density as the X-axis. The CH₄ generation rate (for a given electrolyzer operating power) was calculated assuming a cathode faradaic efficiency of 36% (matching the reported efficiency for the Cu catalyst²⁶) while the anode production rates of O₂ were calculated assuming a anodic faradaic efficiency of 70% (matching the reported efficiency for the RuO₂ catalyst).

Our electrolyzer system operating with E_{stack} of 20 V (2.0V applied at each cell) has a theoretical power normalized production of ~ 0.45 g W⁻¹ day⁻¹ of CH₄ and 3.55 g W⁻¹day⁻¹ of O₂ (**Fig. 9**), assuming 50% system efficiency (same as MOXIE²¹). This translates to >1000L of both CH₄ and O₂ per day using this conservatively sized system^{42,43}. Thus, with the appropriate scaling, such an electrolyzer can produce sufficient fuel and oxidant for both payload return and life support for future missions to Mars. Notably, our CO₂-brine electrolyzer produces both propellant components for methalox engines anticipated to power future American and International missions to Mars. The critical next steps would be the down selection and experimental screening of efficient and selective catalysts for CO₂RR under Martian conditions.

Catalyst requirements for a Martian CO₂-brine electrolyzer

The model predicts the performance of a CO₂-brine electrolyzer employing well-known Cu catalyst for the cathodic CO₂RR with varying faradaic efficiencies. We anticipate the greatest improvements in performance to result from the use of alternate, high activity, high selectivity catalysts. Currently, the RuO₂ anode's predicted operational oxygen generation efficiency of 70% outperforms elemental copper cathode's operational methane generation efficiency of 36%²⁶, which would reduce the production rate of oxygen to match. To address this concern, a list of possible catalyst candidates is presented in **Table 3**. Replacing Cu with Cu-Bi or Cu-Zn alloys or single atom Zn is expected to significantly increase (potentially double) the production rate of CH₄ in our system given their much higher faradaic efficiency. Furthermore, the ultra-cold

temperatures and liquid brines present on the Martian surface have been shown to increase the methane selectivity of copper CO₂RR electrocatalysts²⁶. We anticipate this solvation effect to translate to these catalyst candidates as well and further increase their CH₄ selectivity and ultimately our electrolyzer.

Conclusion

A CO₂-brine electrolyzer operating at Martian ambient conditions has been found to be a viable and energy efficient solution for fuel and oxygen production on Mars through ISRU. Following successful validation of the model against experimental data, our model predicts our >1000L of CH₄ and O₂ production using a modestly sized 10-cell stack. The further development of this system incorporating more efficient CO₂RR catalysts and higher conductivity separators is expected to significantly improve performance and present a viable solution for fuel and oxygen production for sustained human exploration on Mars.

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Author contributions:

Dr. Mohamed Shahid: Data curation, formal analysis, investigation, methodology, resources, software, validation, visualization, writing – original draft, writing – review & editing.

Mr. Bradley Chambers: Investigation, resources, data curation, validation, visualization, writing – original draft, writing – review & editing.

Dr. Shrihari Sankarasubramanian: Conceptualization, funding acquisition, writing - review &

editing, supervision, validation, project administration, resources.

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Tables

Table 1. Comparison of conditions on Mars an	d or	Earth ⁴⁴ .
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	Earth	Mars	
Duration of revolution around the sun (days)	365.24	686.97	
Duration of rotation about its axis (h)	24	24.66	
Average diurnal surface temperature range (K)	283 to 293	184 to 242	
Average surface pressure (Pa)	101400	636 (seasonally variable from 400 – 870)	
Surface gravity (m.s ⁻²)	9.79	3.71	
Escape Velocity km/s	11.19	5.03	
Atmospheric composition	<u><i>Major (vol.%):</i></u> 78.08% N ₂ , 20.95% O ₂ , >1% H ₂ O (highly variable) <u><i>Minor:</i></u> 9340 ppm Ar, 410 ppm CO ₂ , 18.18 ppm Ne, 5.24 ppm He, 1.7 ppm CH ₄ , 1.14 ppm Kr, 0.55 ppm H ₂	<u>Major (vol.%):</u> 95.1% CO ₂ , 2.59% N ₂ , 1.94% Ar, 0.16% O ₂ , 0.06% CO <u>Minor:</u> 210 ppm H ₂ O, 100 ppm NO, 2.5 ppm Ne, 0.85 ppm H- D-O, 0.3 ppm Kr, 0.08 ppm Xe	

Engine	HD	MIRA	ACE-	BE-4	Raptor	LE-8	AEON-1	TQ-12
Name			42R					
Country	USA	Italy/EU	France	USA	USA	Japan	USA	China
Company	NASA	Avio	Airbus	Blue	SpaceX	JAXA	Relativity	Landspace
				Origin			Space	
Thrust	24	98	420	2400	2200	107	100	670
kN								
O ₂ /CH ₄	3.4-3.8	3.4	3.4-3.8	3.4-3.8	3.6	3.4-3.8	3.4-3.8	3.4-3.8
Ratio								

Table 2. Representative methalox engines in use or development around the World⁴⁵.

Catalyst	Products	Faradaic Efficiency	Temperature	Ref.
CoPc on Zn-N-C	CH4/CO	18.3% FE _{CH4}	298K	46
Cu with 15 µm of Nafion	CH4/CO	88% FE _{CH4}	RT	47
Pt	CH4/CO	1.19% FE _{CH4}	303K	48
	CH4/CO/			49
CuAl Ga doped	C_2H_4	54% FE _{CH4}	RT	
Single Atom Zn-MNC	CH4/CO	85% FE _{CH4}	RT	50
	CH4/CO/			51
Cu.7Bi.3 bimetallic	НСООН	70.6% FE _{CH4}	RT	
	CH4/C2H4/			52
Cu Oh-NC 75nm	HCOO-	55% FE _{CH4}	RT	
	CH4			52
	C2H4			
Copper (II) phthalocyanine	НСООН	66% FE _{CH4}	RT	
	CH4/CO/			53
Polycrystalline Cu	H_2	40.4% FE_{CH_4}	RT	
	CH4/CO/			54
CuS Nanosheets	H_2	73.5% FE _{CH4}	298K	
Pd decorated Cu	CH4/H2	50% FE _{CH4}	RT	55

Cu doped CuO2	CH ₄	58% FE _{CH4}	RT	56
Cu _{0.7} Zn _{0.3} Catalyst	CH ₄ /CO	70% FE _{CH4}	RT	57

Figures:



Figure 1: Schematic representation of a CO₂-brine electrolyzer for operation on Mars.



Figure 2: The calculated thermodynamic potential, E_{emf} , required for brine electrolysis and CO₂brine electrolysis between 230K and 500K.



Figure 3: Nernst potentials at 636Pa and 101325Pa for (a) brine electrolysis and (b) CO₂-brine electrolysis.



Figure 4: Nernst potential for carrying out electrolysis at (a) 236K - 636Pa, (b) 298K - 636Pa,

(c) 236K-101325Pa and (d) 298K-636Pa.



Figure 5: Performance of the brine Electrolyzer operating with Pt-C cathode and Pb₂Ru₂O₇ anode at 237K and 101325Pa.



Figure 6: Performance of the brine Electrolyzer operating with Pt-C cathode and RuO₂ anode at 237K and 101325Pa.



Figure 7: Performance of the CO₂-brine electrolyzer operating with Cu(111) cathode and RuO₂ anode at 255K and 101325Pa.



Figure 8: Volume of CH₄ and O₂ produced and power requirements for a stack of CO₂-brine electrolyzer operating with 10 cells of 100 cm² each at 255K and 101325Pa.



Figure 9: Predicted power normalized production rates for (a) oxygen and (b) methane with varying overall system efficiencies (listed in the figure legend) in an CO₂-H₂O electrolyzer operating with a stack of 10 cells of 100 cm² each at 255K and 101325Pa. The best-case production rate for MOXIE is also depicted (red star) for comparison.

SUPPLEMENTARY INFORMATION

For brine-electrolysis

$H_2O = H_2 + 1/2O_2$

The dH, dS and dG values in table S1 are calculated from the¹

$$C_{\rm p} = 0.44 * \left(\frac{T - 222}{222}\right)^{-2.5} + 74.3 \tag{for - H_2O} \tag{1}$$

Table S1: Estimation of H₂O (l) thermodynamic properties for brine electrolysis

Temp	dH (kJ mol-1)	dS (kJ mol-1)	dG (kJ mol-1)
225	1804.31	6.019	450.09
230	412.25	0.645	263.72
235	323.92	0.307	251.73
240	303.77	0.230	248.47
250	293.13	0.190	245.61
260	290.03	0.178	243.64
270	288.47	0.173	241.85
298	285.53	0.163	237.14
400	242.29	0.047	223.95
500	243.83	0.049	219.05

Table S2: Estimation of Thermoneutral voltage and electromotive force from thethermodynamic properties for brine electrolysis.

Tama (C)	4.0	42	22	22	12	2	25	107	227
Temp (C)	-48	-43	-33	-23	-13	-3	25	127	227
Temp (K)	225	230	240	250	260	270	298	400	500
ΔG _{RXN-1} (KJ/mol)	450.09	263.72	248.47	245.6	243.64	241.85	237.14	223.95	219.05
ΔH _{RXN-1} (KJ/mol)	1804.3	412.25	303.77	293.13	290.03	288.48	285.83	242.85	243.83
ΔS _{RXN-1} (KJ/mol K)	6.02	0.65	0.23	0.19	0.18	0.17	0.16	0.05	0.05
TΔS _{RXN-1} (KJ/mol)	1354.2	148.53	55.29	47.53	46.39	46.63	48.69	18.89	24.77
E thermoneutral (V)	9.35	2.14	1.57	1.52	1.50	1.49	1.48	1.26	1.26

$E_{emf}(V)$	2.33	1.36	1.28	1.27	1.26	1.25	1.23	1.16	1.14

For CO₂-brine electrolysis

$\mathbf{CO}_2 + \mathbf{2H}_2\mathbf{O} = \mathbf{CH}_4 + \mathbf{2O}_2$

The dH, dS and dG values in table S3 and S4 are calculated from the below expressions^{2,3},

(2)

 $(for - CH_4)(3)$

$$C_p = 0.039 * T + 25.743$$
 (for - CO₂)

 $C_{\rm p} = 0.0001 * T^2 - 0.038 * T + 36.839$

Table S3: Estimation of CO₂ (g) thermodynamic properties for CO₂-brine electrolysis

Temp	dH (kJ mol-1)	dS (kJ mol-1)	dG (kJ mol-1)
225	-396.042	-0.00681	-394.51
230	-395.882	-0.00610	-394.479
235	-395.721	-0.00540	-394.452
240	-395.558	-0.00471	-394.428
250	-395.226	-0.00334	-394.39
260	-394.886	-0.00201	-394.364
270	-394.538	-0.000689	-394.351
280	-394.182	0.000605	-394.351

Table S4: Estimation of CH₄(g) thermodynamic properties for CO₂-brine electrolysis

Temp	dH (kJ mol-1)	dS (kJ mol-1 k-1)	dG (kJ mol-1)
225	-77.354	-0.090	-57.011
230	-77.188	-0.09	-56.561
235	-77.024	-0.089	-56.115
240	-76.858	-0.088	-55.672
250	-76.525	-0.087	-54.797
260	-76.189	-0.086	-53.936
270	-75.85	-0.084	-53.087
280	-75.506	-0.083	-52.25

Table S5: Estimation of Thermoneutral voltage and electromotive force from thethermodynamic properties for CO2-brine electrolysis.

Temp (C) -48 -43 -33 -23 -13 -3 25 127	227
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Temp (K)	225	230	240	250	260	270	298	400	500
ΔG _{RXN-3} (KJ/mol)	1237.69	865.36	835.69	830.81	827.70	824.97	817.88	800.49	800.26
ΔH _{RXN-3} (KJ/mol)	3927.31	1143.20	926.24	904.97	898.76	895.64	890.29	801.30	800.52
ΔS _{RXN-3} (KJ/mol K)	11.95	1.21	0.37	0.29	0.27	0.26	0.24	0.0020	0.0005
TΔS _{RXN-3} (KJ/mol)	2689.62	277.84	90.54	74.16	71.06	70.66	72.41	0.81	0.25
E thermoneutral (V)	5.09	1.48	1.19	1.17	1.16	1.16	1.15	1.04	1.04
E emf (V)	1.60	1.12	1.08	1.08	1.07	1.07	1.06	1.05	1.04

CO₂-brine electrolysis operating at different conditions



Figure S1: CO₂ – brine electrolyser operating at Earth atmospheric pressure and Martian

temperature.



Figure S2: CO_2 – brine electrolyser operating at Martian atmospheric pressure and standard Earth temperature.



Figure S3: CO₂ – brine electrolyser operating at Martian atmospheric pressure and temperature.



Figure S4: Thermodynamic properties for (a) brine electrolysis and (b) CO₂ - brine electrolysis between 230K and 500k.

References

1. Tombari EF, C.; Salvetti, G. Heat capacity anomaly in a large sample of super-cooled water. *Chemical physics letters*. 1999;(300):749-751.

Goodwin RD. *Thermophysical properties of methane, from 90 to 500 K at pressures to* 700 bar. 1974:Medium: X; Size: Pages: 280. <u>https://www.osti.gov/biblio/5043241</u>

3. Tables of thermal properties of gases; comprising tables of thermodynamic and transport properties of air, argon, carbon dioxide, carbon monoxide, hydrogen, nitrogen, oxygen, and steam (U.S. Dept. of Commerce, National Bureau of Standards) (1955).