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Combined H_2O/CO_2 Solid Oxide Electrolysis for Mars In Situ Resource Utilization

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Mars sample return missions and eventual human missions will both benefit from using Martian resources to produce Earth-return propellant and life support consumables. A new architecture for an in situ propellant production plant is introduced that utilizes solid oxide electrolysis to perform the combined electrolysis of both water and carbon dioxide. The proposed system produces methane via a Sabatier reactor and oxygen via electrolysis in the optimal oxidizer-to-fuel mixture ratio with the capability to produce extra oxygen for life support needs. Each major component of the combined electrolysis/Sabatier architecture is modeled to assess the feasibility and size of such a propellant production plant. Sample return and human missions are analyzed with the models. Results demonstrate that combined electrolysis enables a competitive system for in situ resource utilization as well as an ease of scaling for sample return vs human missions. When compared to published data of other oxygen/methane-producing architectures, the proposed system is shown to be less massive while comparable in power. Other advantages of implementing combined electrolysis in a propellant production plant are discussed.

Introduction

MARS sample return missions have long been a much supported objective of NASA's Mars Exploration Program.[1,2] Additional goals within the program have been specifically set to lay the foundation for human exploration missions.[3] NASA has continued its pursuit of such missions in its current strategic plan[4]: not only are sample return missions being considered shortly after the turn of the decade,[5] but current NASA objectives also support preparing for safe and affordable human exploration of Mars.

To afford these highly anticipated missions in today's economy while guaranteeing their success, mission planners will need to rely on the ability to use the resources at Mars. If propellant required for the return to Earth can be produced with Martian resources, then sample return and human missions will not have the burden of transporting their return propellant from Earth. Therefore, launch mass and costs will be significantly reduced.

When humans travel to Mars, propellant and life support needs—such as oxygen and buffer gas—can also be produced from the local resources. Such production of consumables reduces mission cost and decreases mission risk through the ability to replenish supplies in the event of any unforeseen leaks or accidents.

NASA has recognized[2] that these reasons dictate the need for the development of an in situ life support and propellant production plant. With the possibility of a sample return mission in less than 10 years, simple, efficient, and proven technology will be required to bring in situ resource utilization (ISRU) to a reality in time.

Many in situ propellant production (ISPP) plant designs have been investigated over the years.[6–12] These studies have used various combinations of several technologies producing different propellant combinations. Not all plant designs address the capability to produce an optimal oxidizer-to-fuel (O/F) mixture ratio. Only one proposes the additional capability to provide extra oxygen for life support without wasting fuel. Most are relatively complicated.

One of the many propellant combinations that can be made on Mars is gaseous oxygen (O_2) and gaseous methane (CH_4). Methane's specific impulse at about 370 s is comparable or higher than alternatives, while still being relatively easy to produce on Mars.[13] The optimal O/F mixture ratio by mass for this propellant combination is around 3.5.

There are two architectures that produce O_2 and CH_4 that have been given much consideration in the past. These are a Sabatier reactor/liquid water electrolysis (SWE) system and a reverse water gas shift reactor/SWE (RWGS/SWE) system.

A flow chart of an SWE architecture is depicted in Fig. 1. The inlet process stream is composed of compressed carbon dioxide (CO_2) mixed with earth-sourced hydrogen (H_2). The mixture enters a Sabatier reactor, which is a well-proven, simple technology based on the following exothermic Sabatier reaction:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{1}$$

In the presence of excess H_2, the only constituents in the reactor's outlet are CH_4, H_2O, and unreacted H_2, which are sent to a condenser. The resulting CH_4/H_2 process stream is then sent to an H_2 separator. The separated hydrogen is recycled into the process stream. The water is electrolyzed to produce wet O_2 that needs to be dried.

The resulting O/F mixture ratio of the SWE architecture is 2:1. As previously noted, the optimal O/F ratio for oxygen and methane is near 3.5. Therefore, although the SWE system is designed around mature technology, it cannot achieve an optimal O/F mixture ratio or supplement life support consumables without producing excess methane. To boost the O/F ratio, an SWE system can be augmented with an RWGS reactor.

A flow chart of the RWGS/SWE system is shown in Fig. 2. An SWE system, as described earlier, generates oxygen along with the exact necessary amount of CH_4 as dictated by a specific mission. This modified system has the potential to supply oxygen for life support needs also.

The inlet process stream of the RWGS system contains compressed CO_2 mixed with recycled H_2 from a water source brought

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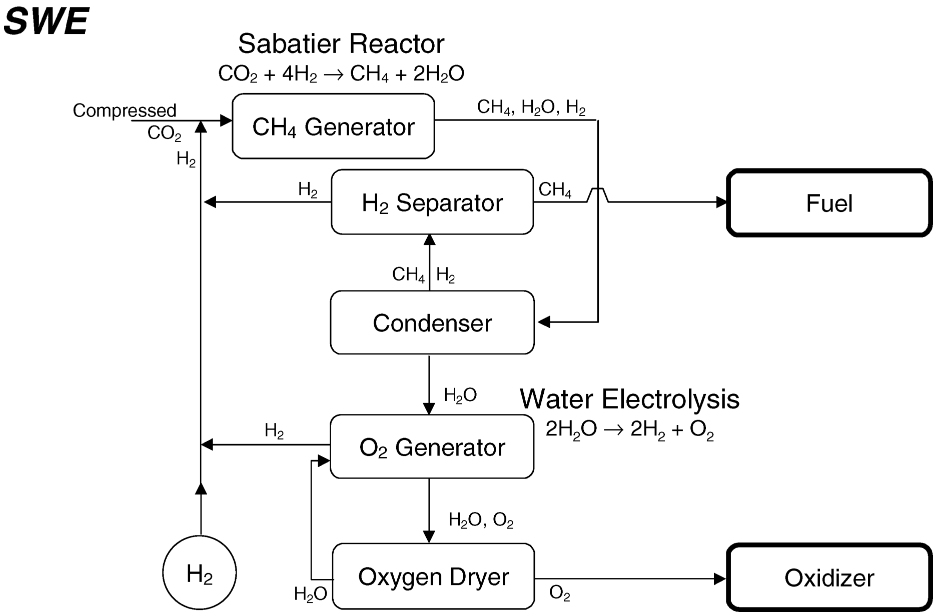

Fig. 1 SWE propellant production plant.

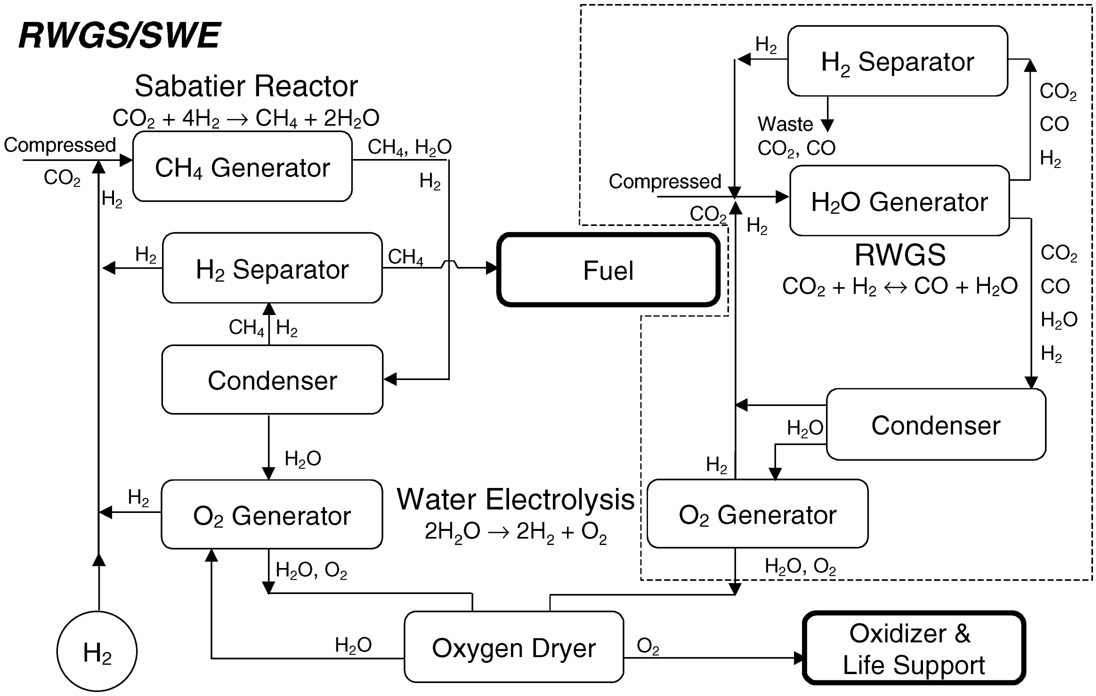

Fig. 2 RWGS/SWE life support and propellant production plant (dashed area[8]).

from Earth. The process stream enters a reactor that produces carbon monoxide (CO) and H_2O from CO_2 and H_2 in the presence of a catalyst in accordance with the RWGS reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \tag{2}$$

When the reaction is run at temperatures at 400°C and above, the reaction is slightly endothermic with a low equilibrium constant of values from 0.1 to around 1. Thus, it can be difficult to drive toward completion. However, conversions of 8–20% of the available CO_2 have been achieved with no undesired byproducts such as CH_4 (Ref. 8).

The RWGS/SWE system can produce an optimal O/F ratio and produce extra oxygen without wasting valuable hydrogen but is more complicated and less mature. The RWGS also operates at a pressure of about 10 bar.

With a Mars sample return mission on the horizon, the space program needs an ISPP architecture that is proven and simple yet still satisfies mission requirements. Such ISPP architecture is achievable through a novel application of solid oxide electrolysis. This application is the combined electrolysis of CO_2 and water vapor.

Solid oxide electrolysis has long been considered in ISPP plant designs to electrolyze the mostly CO_2 Martian atmosphere into pure O_2 and CO.[10–14] Solid oxide electrolysis of water has also been studied to aid life support systems.[15,16] Implementing combined CO_2/H_2O solid oxide electrolysis (CSOE) into ISPP plants is a new application.

"PROMISE: Production of Resources On Mars In Situ for Exploration" was a proposal submitted in response to a NASA Announcement of Opportunity (NASA AO 99-HEDS-01). It first proposed this new application of CSOE in conjunction with a Sabatier reaction. NASA recognized the merits of such an architecture and

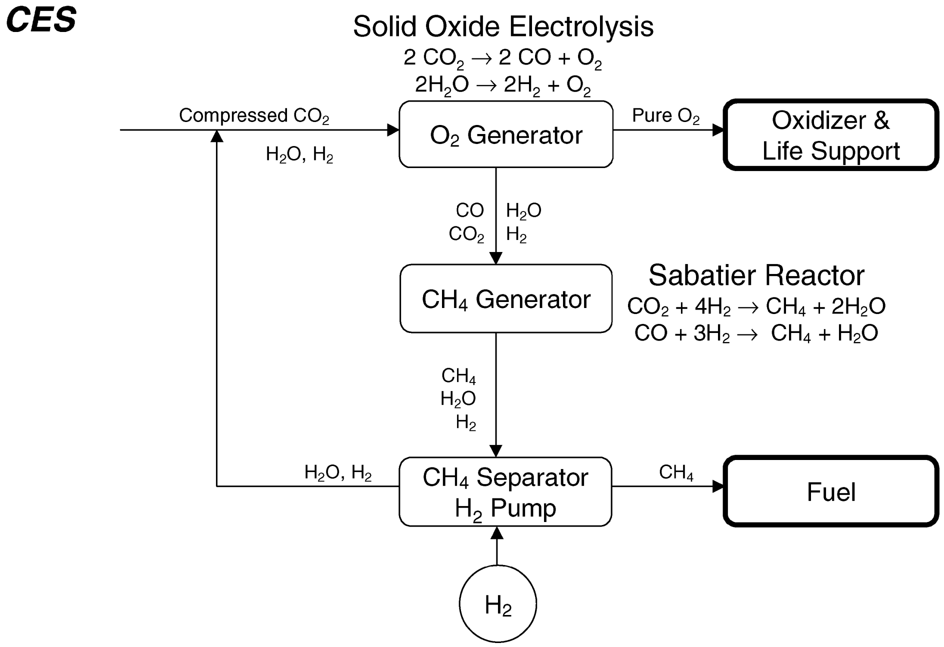

Fig. 3 CES life support and propellant production plant.

subsequently selected it to fly on the 2003 Mars Surveyor Lander. Later, the project was mothballed after the mission was canceled.

This paper introduces the application of CSOE to ISPP plant design. This application can reduce the complexity of an ISPP architecture using proven technology while providing the optimal mixture ratio plus additional oxygen for life support.

A combined electrolysis/Sabatier architecture will first be described in detail. To assess the viability of such an architecture, two mission scenarios, a sample return and human mission, are studied with mass and power models. The results are then compared to two other commonly investigated O_2/CH_4 architectures, SWE and RWGS/SWE. Finally, advantages of implementing CSOE are reviewed.

Combined Electrolysis/Sabatier Architecture

The combined electrolysis/Sabatier (CES) architecture is shown in Fig. 3. Compressed CO_2 combines with recycled H_2O vapor and H_2 before entering the CSOE unit. Solid oxide electrolysis uses a solid oxide electrolyte sandwiched between electrodes. At elevated temperatures, when a potential is applied across the cell, oxygen-bearing molecules at the cathode are electrolyzed. Oxygen ions are transported to the anode and recombine to produce pure, dry O_2. The overall reactions are

$$CO_2 \rightarrow CO + \tfrac{1}{2}O_2 \tag{3}$$

$$2H_2O \rightarrow 2H_2 + O_2 \tag{4}$$

The exhaust of the CSOE unit, which contains CO, H_2, and undissociated CO_2 and H_2O, is sent to a Sabatier reactor. When the system is run H_2 rich, the Sabatier reactor produces only CH_4, H_2O, and excess H_2. These products are sent to the separator side of an electrochemical pump and separator (EPS) which uses proton exchange membrane (PEM) technology.[17] On the separator side, when hydrogen protons are pumped through the membrane, water molecules are drawn along, providing water removal from the stream. The CH_4 is stored as fuel. On the pump side of the EPS, more H_2 is metered into the water/H_2 recycle stream to achieve the necessary amount of H_2 for the Sabatier reactor.

Models Used in Sizing a Combined Electrolysis/Sabatier Architecture

To assess the impact of using solid oxide electrolysis to produce O_2 from both H_2O and CO_2 in a more quantitative manner, the CES architecture was modeled. EXCEL spreadsheets and FORTRAN routines were developed to calculate performance characteristics and operational costs. The models for each of the subsystems are described as follows.

Combined Solid Oxide Electrolysis Model

The solid oxide electrolysis model is based on the oxygen generator system (OGS) developed by the Space Technologies Lab (STL) of the University of Arizona for NASA's 2001 Mars Surveyor Lander to demonstrate oxygen generation on Mars using the Martian atmosphere.[18] A single electrolysis cell is constructed of an yttria-stabilized zirconia electrolyte sandwiched between platinum-based electrodes and electrically conducting metal manifolds. Stacks of several cells can be assembled to increase the rate of oxygen generation. For packaging and thermal design considerations, the stacks of cells are sized to fit into a cube. Design parameters available to optimize the CSOE unit mass and reliability include active area of each cell and the number of cells per stack. Active areas of up to 80 cm^2 of this type of cell configuration have been successfully and extensively tested at STL.[19] Figure 4 exemplifies the tradeoff between reliability (increasing the number of stacks) and mass (not including insulation).

At 750–850°C, experiments at STL show that combined electrolysis of H_2O and CO_2 produces more oxygen than CO_2 electrolysis alone. However, to be conservative and given the fact that a portion of the oxygen produced in a CES system will be from pure CO_2 electrolysis, the model assumes oxygen generation rates as that achieved by CO_2 electrolysis testing. Example electrolysis performance used in the modeling is shown in Fig. 5 as a function of voltage. A substantial increase in performance is obtained by increasing the operating temperature from 750 to 850°C. Therefore, the model will assume an operating temperature of 850°C.

Solid oxide electrolysis' utilization of oxygen-bearing molecules has been reported up to 78.5%,[15] and demonstrated to over 90%, in testing at STL. Utilization depends on flow rate and active area of the unit's design, which can be dictated by mission requirements and is thus another variable to be optimized. The data presented in Fig. 5 achieve up to only 32% utilization because they were collected for scientific investigations at a fixed flow rate and low utilization to isolate electrochemical effects. Figure 6 shows an example of electrolysis performance used in modeling as a function of utilization for fixed voltage. It should be noted that the data being used in the CSOE model were collected with systems built for

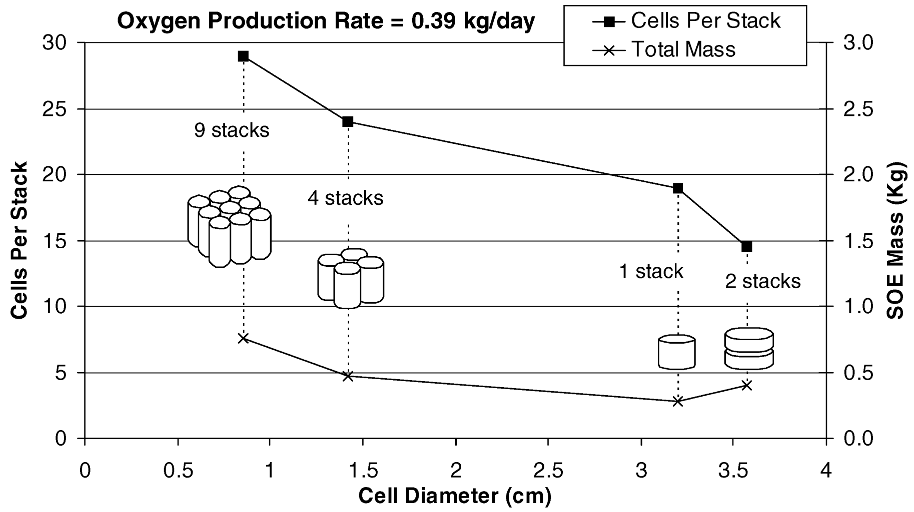

Fig. 4 CSOE stack design vs mass.

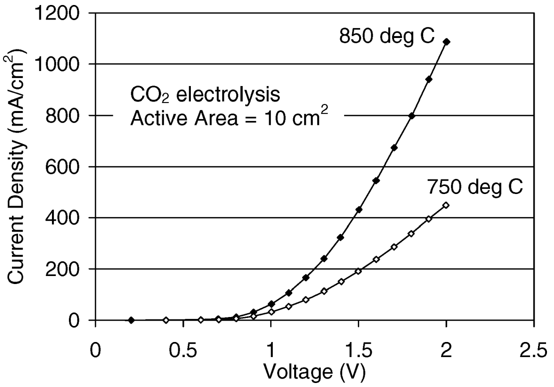

Fig. 5 Electrolysis performance assumed in the CSOE model[19] as a function of voltage.

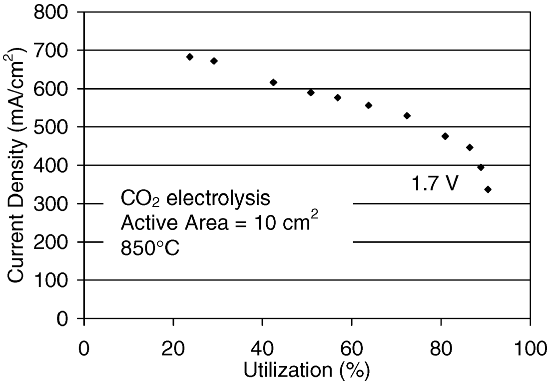

Fig. 6 Electrolysis performance assumed in the CSOE model as a function of utilization.

proof-of-concept purposes rather than systems specifically optimized for performance.

The reversible power required for oxygen production is equal to the cell's Nernst potential[20] multiplied by its current. However, the cell has losses due to phenomena such as cell resistance and other overpotentials.[21,22] To overcome these effects and initiate electrolysis, the cell requires an additional potential over the Nernst potential that in the end is converted to heat. The heat transfer $\dot{Q}$ to a cell can be calculated by applying a steady flow energy analysis[23]:

$$\dot{Q} = -V_{\text{applied}} I + \left(\sum_{\text{out}} \dot{N}_i \hat{h}_i - \sum_{\text{in}} \dot{N}_i \hat{h}_i \right) \qquad (5)$$

where V is the applied potential, I is the current, $\dot{N}_i$ is the molar flow rate of the ith constituent, and $\hat{h}_i$ is the molar enthalpy. Consequently, cells operating at low voltages require more insulation to minimize the power required to keep the cell at the desired operating temperature. Cells operating at higher voltages produce enough heat not to need additional power for temperature maintenance.

The insulation is modeled assuming the use of two substances to optimize weight: a layer of Thermal Ceramics TE-1400 and a layer of silica aerogel. This construction is chosen because in-house laboratory tests at STL provide data for such a configuration in simulated Martian conditions. Table 1 lists the assumed constant properties and parameters for modeling of both types of insulation.

The insulation is sized assuming a one-dimensional radial conduction model. The heat diffusion equation is applied[24] with temperature-specified boundary conditions. The outer layer of insulation is sized such that the outside temperature is the mean ambient temperature of Mars, 215 K.[25]

Sabatier Catalytic Reactor Model

The following two catalytic reactions are performed in the Sabatier catalytic reactor (SCR):

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (6)$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (7)$$

These reactions initiate and are self-sustaining above 200°C depending on the catalyst.[26] However, once initiated, cooler temperatures favor forward equilibrium. Thus, a reactor design with a higher inlet temperature and a lower downstream temperature is optimal. The desired negative temperature gradient along the reactor is achieved by placing the reactor within the insulation of the CSOE unit.

Due to the imposed temperature gradient, CO and CO_2 conversion occur at different temperatures along the length of the reactor. The heat given off from the reactions increases as the reaction temperature decreases. As a conservative estimate of the heat dissipated by the reactor during operation, it is assumed that all CH_4 is formed at the outlet temperature. A steady flow energy analysis of the reacting mixture leads to the following equation for heat transfer across the SCR,[23] $\dot{Q}$:

$$\dot{Q} = \sum_{i}^{\text{Products}} \dot{N}_i \left(\Delta \hat{h}^0_{f,298} + \hat{h}_{T,P} - \hat{h}_{298K,1\,\text{atm}} \right)_i - \sum_{i}^{\text{Reactants}} \dot{N}_i \left(\Delta \hat{h}^0_{f,298\text{K}} + \hat{h}_{T,P} - \hat{h}_{298\text{K},1\,\text{atm}} \right)_i \qquad (8)$$

Table 1 Parameters of mass and power models

Parameters	Values	
CSOE unit insulation properties	TE-1400	Aerogel
Density, g/cc	0.32	0.05
Thermal conductivity, W/m · K	0.03	0.02–0.43
Inner temperature, K	1073	Optimized
Outer temperature, K	Optimized	215
SCR modeling parameters		
Residence time, s	0.25	
H_2:C molar feed ratio	4.5	
Inlet temperature, °C	800	
Outlet temperature, °C	150	
Ruthenium catalyst density, kg/m^3 (Ref. 26)	21.6	
Aluminum density, kg/m^3 (Ref. 24)	2702	
Log[$K_p(6)$]	11.26	
Log[$K_p(7)$]	13.5	
EPS materials	Density or loading	
Nafion® solid polymer	1-2 g/cm^3	
Platinum catalyst	4 mg/cm^2	
Zirconium laminate	6.5 g/cm^3	
Titanium endplate and tie rods	4.5 g/cm^3	
CSC modeling parameters		
Number of units	2	
Number of cycles/unit	4	
Canister material	Al	
Sorbent material	NaX zeolite	
Sorbent C_p, kJ/kg · K	0.9	
Sorbent density, g/ml	0.7	
Sorbent heat of adsorption, kJ/mol	41	
CO_2 C_p, kJ/kg · K	0.737	
Inlet/outlet pressure, kPa	0.8/101	
Min/max operating temperature, K	200/348	
Output loading, wt %	13.6	

where $\Delta\hat{h}^0_{f,298}$ is the molar enthalpy of formation at 298 K and 1 atm. The heat transfer out of the Sabatier reactor is calculated knowing the molar flow rate of CO and CO_2 into the reactor. This heat can be used to condition the CO_2 from the carbon dioxide separator and compressor as it enters the CSOE unit.

To ensure that CO_2 and CO are depleted from the CH_4 product stream, the Sabatier reactor is run with excess H_2. For the methanation of CO_2 alone, the stoichiometric H_2:C ratio would be 4. Theoretical calculations and experimental results show that ratios of 3.5 and greater can encourage CO_2 depletion to >99%.[26–29] In this analysis, the addition of CO must also be considered. Depending on the CSOE conversion efficiency (utilization), there could be more CO than CO_2 entering the reactor. The amount of H_2 needed depends on both reactions shown in Eqs. (6) and (7). The equilibrium composition of a reacting ideal-gas mixture can be determined by simultaneously solving the following two equations[23]:

$$K_p(6) = \frac{N_{CH_4} N^2_{H_2O}}{N_{CO_2} N^4_{H_2}} \left(\frac{P_t}{N_t}\right)^{-2} = 10^{11.26} \tag{9}$$

$$K_p(7) = \frac{N_{CH_4} N_{H_2O}}{N_{CO} N^3_{H_2}} \left(\frac{P_t}{N_t}\right)^{-2} = 10^{13.5} \tag{10}$$

Note that N_i (N_{CH_4}, N_{H_2O}, N_{H_2}, N_{CO_2}, and N_{CO}) represent the number of moles of the ith constituent in the equilibrium mixture exiting the reactor and are thus the five unknowns to be solved. $K_p(6)$ and $K_p(7)$ are the equilibrium constants for Eqs. (6) and (7), respectively, and are calculated at the outlet mixture temperature of 150°C using tabulated data from JANAF.[30] N_t is the total number of moles; P_t is the total pressure (atm).

Two well-known catalysts for Sabatier reactions are ruthenium and nickel. However, the literature has reported that nickel experiences carbon deposition at 340–370°C.[27] Therefore, the catalyst modeled here is ruthenium on alumina in a 14- to 18-mesh-size granule. The ruthenium-based catalyst chosen for this model has been shown to work with inlet temperatures as high as 967°C and outlet temperatures from 35 to 400°C.[26]

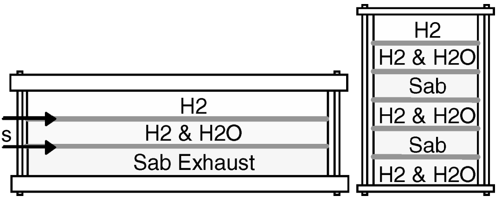

Fig. 7 Adding extra separation cells allows for smaller, lighter endplates.

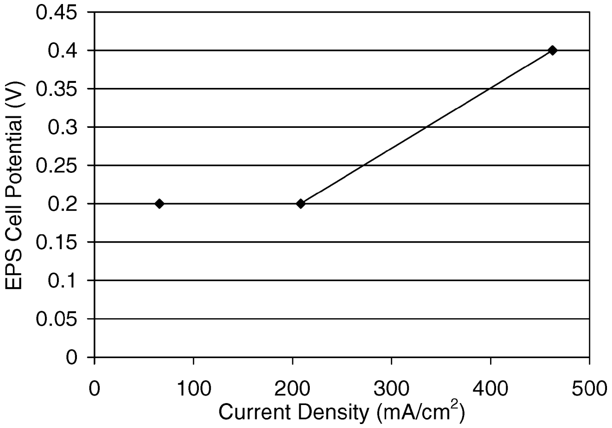

Fig. 8 Performance of EPS required to separate H_2 from CH_4.

The inlet temperature modeled here is 800°C. This eliminates the need to preheat the reactant gases exiting the CSOE unit before entering the Sabatier reactor. Only the excess hydrogen that is added to the reactant stream (to achieve the 4.5 H_2:C molar feed ratio) would need to be heated. To encourage the complete reduction of CO and CO_2, the outlet temperature is set at 150°C.

Sizing of the reactor depends on the chosen residence time. The residence time multiplied by the flow rate yields an estimate of the required volume for the reactor. In the 1970s, a typical value for residence time was 1 s. Reports from commercial developers suggest a 0.1-s residence may be adequate using current catalysts. This analysis conservatively assumes 0.25 s. The structure of the reactor is assumed to be aluminum. All parameters in modeling the Sabatier reactor are summarized in Table 1.

Electrochemical Pump and Separator Model

The EPS is composed of two electrolysis cells that share a common cathode cavity but have separate anode cavities. Adhering to proven technology, the EPS model used in this analysis assumes electrolytes are made of Nafion® solid polymer membranes with platinum electrodes.[31] Cell membrane support and sealing are constructed with a zirconium laminate.[32] Stacked between two endplates, the entire assembly is held in compression by high-strength tie rods. Table 1 lists the material properties assumed in the modeling. Figure 7 demonstrates how the EPS can be designed to optimize mass.

Sizing of the EPS is dependent on the amount of H_2 metering or separation required by the specific mission. The act of pumping protons across a membrane produces a current of 133 mA per standard cm^3/min (sccm) of H_2; thus, pumping a mission-specific amount of H_2 dictates the EPS current. To size the active area of the EPS, the amount of current to be consumed is compared to experimental data of cell voltage (V) vs current density (mA/cm^2). Cell voltage and active area of the electrode are the design parameters.

Testing of PEM-based H_2 separators and pumps have shown to separate over 99.9% of H_2 and produce H_2 flow rates of up to 140 sccm using only 0.25 V,[7] respectively. The EPS model presented here incorporates both functions into one unit and assumes H_2 separation performance of that shown in Fig. 8.[§]

[§] Personal communication, J. McElroy, McElroy PEM Technologies, Jan. 2002.

CO_2 Separator and Compressor Model

Carbon dioxide separation from the Martian atmosphere and its subsequent compression is accomplished via a temperature-swing adsorption process. A detailed description of the process is described elsewhere.[33] In essence, the unit consists of a canister containing a material that selectively adsorbs CO_2. Acquisition of CO_2 is achieved at a low, constant pressure by passing the atmosphere through the canister over the adsorbent. The canister is then closed and heated with waste heat from within the ISRU plant. During this heating, the CO_2 is released causing an increase in pressure inside the canister. Once a desired pressure is achieved, the canister is reopened while still being heated, releasing the CO_2 at a regulated pressure. Finally, the canister is closed, cooled, and ready to repeat another cycle.

Designing the CO_2 separator and compressor (CSC) to operate more than one cycle per day reduces the amount of sorbent required, thus reducing the unit's mass. In addition, having more than one unit and operating them out of phase allows for not only a continuous CO_2 supply, but also operation at a lower peak power. Therefore, this model assumes there are two units that each operate at four cycles.

The adsorbent material used in the modeling is NaX zeolite. NaX zeolite has been studied extensively for this type of application in the past.[34,35] With an adsorption cycle bounded by temperature extremes of 200 K (representing Mars nighttime ambient) and 348 K, and by pressures of 0.8 kPa (i.e., Mars atmospheric) and 101 kPa, a CO_2 loading of roughly 14 wt % per cycle, or 14 g CO_2 per 100 g adsorbent, is obtained.

The model assumes the canister is made out of aluminum. Its sizing is dependent on the amount of sorbent needed to obtain the desired CO_2 loading and is optimized to minimize canister mass. No mass estimates are made for heating elements because it is assumed that waste heat from the ISRU plant will be used. Mass required for transferring this waste heat is neglected, as well as a blower required to remove built-up N_2 and Ar gases.

Heat transfer to the unit is estimated by applying the first law of thermodynamics. Two contributions are important: the sensible heat required in raising the temperature of the unit and the heat of adsorption required in absorbing the CO_2 onto the sorbent. The heat of adsorption assumed in this model is 41 kJ/mol. Some parameters of the CO_2 separator and compression model are summarized in Table 1.

Other In Situ Propellant Production Plant Considerations

Handling of the fluid between major system components has been considered. For example, heat transfer to the fluid entering the CSOE unit is estimated with a steady flow energy analysis like those previously discussed. Similarly, the heat transfer capability from the CSOE exhaust is assessed. When methane is being produced, all the CSOE exhaust (at 1123 K) is diverted to the SCR (at 1073 K), generating little heat loss. When the desired amount of methane has been produced, the SCR and EPS are shut down and the heat of the CSOE exhaust can be fully exploited.

Components common to all architectures, such as sensors and flow/electronic controllers, have not been considered in this comparison study. Additionally, the condensing and storage of O_2 and CH_4 are not assessed because all plant architectures require it and the implementation of a CSOE does not affect this.

Modeling Results

The models were used to evaluate mass and power requirements for an ISPP system that incorporates CSOE. Two analyses were conducted: a sample return mission and a human mission. Propellant production requirements for these depend on the scope of the mission and technology used. For this study, to match other ISPP plant studies for comparison, the equivalent propellant production rates of 0.5 and 5 kg/day over 500 days were assumed for sample return and human missions, respectively.

Combined Solid Oxide Electrolysis Trades and Optimization

The data available for solid oxide electrolysis enables the systems engineer to optimize the ISPP plant mass as a function of CSOE utilization of oxygen-bearing molecules. Furthermore, system power can be optimized as a function of CSOE operating voltage. The following describes how each system component is affected, with an example illustrating those effects for a CSOE unit operated at 1.2 V in Figs. 9–11.

For a given operating voltage, the mass of the CSOE unit is directly proportional to its utilization of oxygen-bearing molecules. Utilization dictates the current density (mA/cm^2) at which a CSOE unit is operated. As was shown in Fig. 6, current density drops as utilization is increased. Therefore, mass of the CSOE unit will increase as more surface area is needed to produce the desired amount of oxygen per day.

The SCR mass is inversely proportional to CSOE utilization. During the generation of methane, the *system* utilization of CO_2

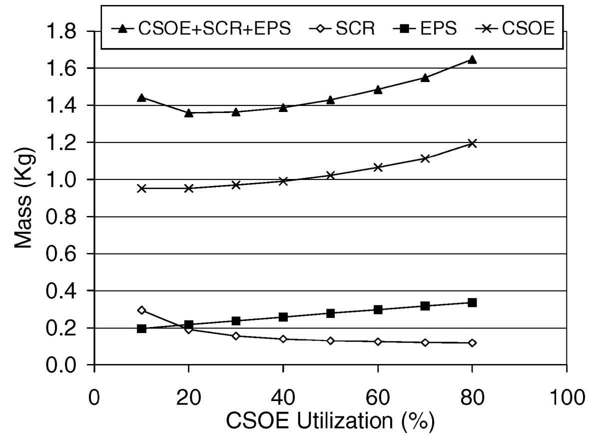

Fig. 9 **System masses as a function of CSOE utilization to produce 0.39 kg of O_2/day.**

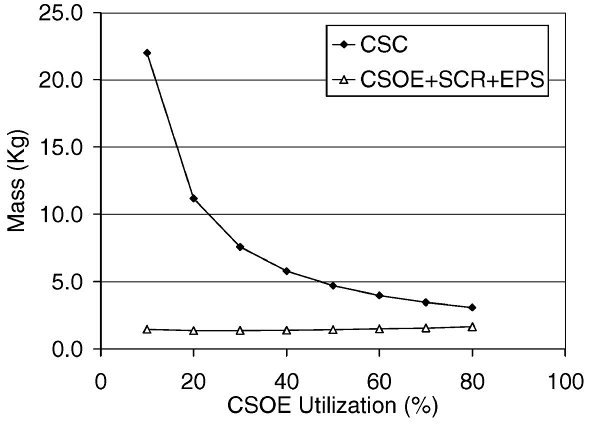

Fig. 10 **CSC mass compared to the rest of the system mass as a function of utilization to produce 0.39 kg of O_2/day.**

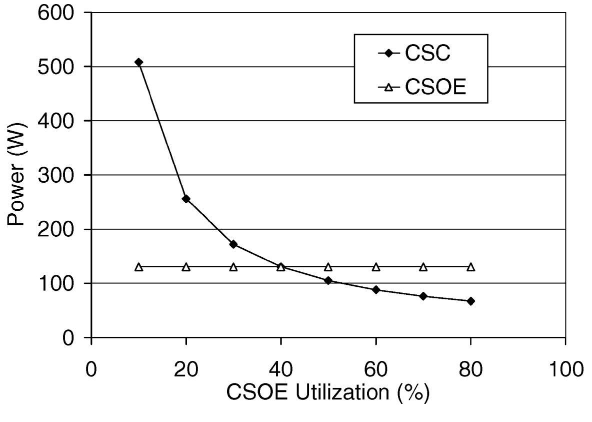

Fig. 11 **CSC power compared to CSOE power as a function of utilization to produce 0.39 kg of O_2/day.**

actually achieves 100%. This is because CO and unreacted CO_2 from the CSOE exhaust are completely converted to water and methane. Because the water is recycled back to the electrolysis unit, all oxygen in the acquired CO_2 is eventually converted to pure dry oxygen.

However, depending on the *CSOE* utilization, the amount of water electrolyzed will vary proportionally. Thus, the amount of water being passed to the SCR decreases as the utilization increases. This decrease in flow rate to the SCR enables a smaller reactor.

In contrast to this, the EPS mass is directly proportional to CSOE utilization. Looking at Eqs. (6) and (7), converting CO_2 to methane requires more H_2 than converting CO. Therefore, because the EPS receives the SCR exhaust, the amount of H_2 passed on to the EPS will decrease as utilization is decreased.

Figure 9 exemplifies how, when combining the components, CSOE utilization can be used to minimize mass. During methane production, the optimal utilization appears to be between 20 and 30% for a sample return mission requiring 0.39 kg of O_2/day.

However, the CSC mass (and power) is inversely proportional to CO_2 utilization. Because the system utilization of CO_2 is 100% during methane production, the size of the CSC required during this phase of propellant production is actually independent of CSOE utilization. But once the required amount of methane is produced, water is no longer recycled (because it is not being created) and system utilization of CO_2 affects CSC sizing. The less CO_2 the CSOE unit utilizes, the more CO_2 the CSC will have to acquire. The dependence is strong as shown in Figs. 10 and 11 and, for the two missions in consideration here, outweighs the mass optimization as exemplified in Fig. 9.

The system mass and CSC power dictate that the CSOE unit should be operated at the highest possible utilization that is safe for the CSOE. Ultrahigh utilization (90–100%) threatens the stability of the cell and health of the electrolyte. This is because, at high utilization, oxygen can be stripped away from the electrolyte itself. For this reason, the final results of the modeling assume that both the human and sample return missions will operate the CSOE unit at 80% utilization.

For any electrolyzer, a given amount of oxygen production requires a fixed amount of power, which can be broken up into heat and dc power. The dc power is simply the voltage multiplied by the current (or oxygen) produced. Because the electrolyzer produces a fixed amount of oxygen per day regardless of utilization, dc power is independent of utilization. Instead, the division of electrolysis power between dc power and heater power can be designed to optimize the total system power as a function of CSOE voltage. For CO_2 solid oxide electrolysis, Fig. 12a shows that the break-even point where no heat transfer is required is 1.46 V. If waste heat is readily available, the electrolyzer could save power by using it and operating at lower voltages. If waste heat is not available, the electrolyzer could be operated at higher voltages where it can generate its own heat (plus excess for the system if desired).

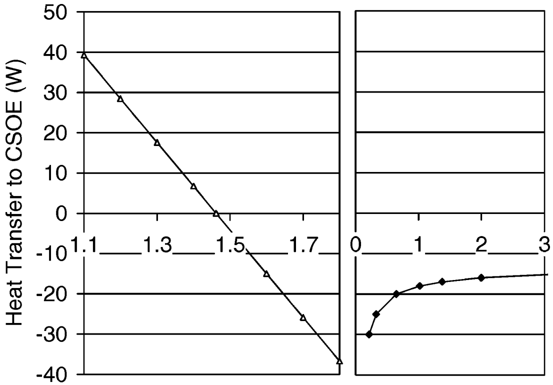

Fig. 12 CSOE heat transfer requirements as a function of a) voltage and b) corresponding CSOE insulation masses (for an O_2 production rate of 0.39 kg/day).

Another consideration in designing the operating voltage of any electrolyzer unit is its insulation mass. If no heat transfer is allowed out of the unit then an infinite amount of insulation will be required, which is prohibitive on a mass basis. Thus some heat transfer out of the unit must be designed into the system. Figure 12b shows how insulation mass varies with allowed heat transfer out of the system (or negative heat transfer to the system). Comparing the two figures, an operating voltage of 1.7 V was chosen for this study; this voltage allows all power to the unit to be in the form of dc power (more efficient than heating power) yet keeps insulation to a minimum, which, for example, is under 300 g for a sample return.

A past concern of using solid oxide electrolysis for large missions has been the fear of needing "tens of thousands"[8] of cells. Using current technology developed during the OGS program, modeling results conclude that the number of cells needed to accomplish a given oxygen production rate has gone down significantly. For a Mars sample return mission requiring 0.39 kg of O_2 per day, assuming a cell diameter of 5.4 cm, there are two stacks at a total of only 17 cells. Scaling the CSOE unit up is not linear when the cell diameter is optimized as a function of reliability vs weight and the tradeoff between power and mass is assessed. The number of cells for a human mission requiring 3.9 kg of O_2 per day, assuming a cell diameter of 9.6 cm, only increases to 41 cells total.

Other In Situ Propellant Production Components

The size of the Sabatier reactor turns out to be relatively small. This is because the reactor sits inside the CSOE unit's insulation and a heating element for cycle startup and the reactor's own separate insulation package are not required. The resulting sizes of the reactors are 0.12 and 0.68 kg for sample return and human missions, respectively. Both reactors assume a diameter of 2 cm in accordance with proven designs.[26]

The sizing tradeoffs of the EPS are demonstrated in Fig. 13 for a sample return mission. Adding other separation cells allows for the radius (and thus mass) of the endplates, as well as the radius of the support structure, to decrease. However, as more cells are added, more levels of support structure are needed. Initially, the supporting structure decreases in mass as well, but as more levels of structure are added, the design hits the point of diminishing returns. Therefore, the resulting EPS design for each mission used three PEMs.

Finally, the energy interactions between components are summarized in Table 2. Utilizing a CSOE unit requires heating the acquired CO_2 to temperatures of 850°C (1123 K). Assuming 90% recuperation of heat loss from components in the plant, the heat transfer needed for this task is easily available. In fact, there is additional heat transfer available to be applied to the CSC.

Summary of Modeling Results

Using the models and tradeoffs described previously, a preliminary analysis of a CES architecture was completed. The results are summarized in Table 3 for a sample return and human mission.

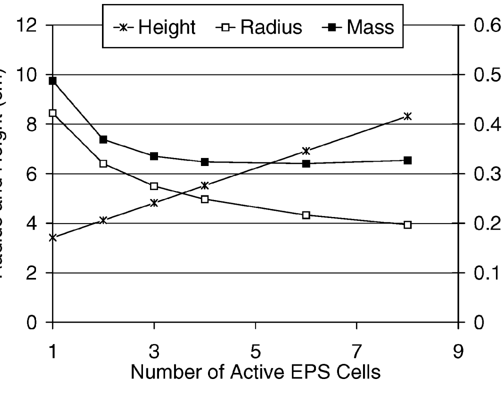

Fig. 13 Example EPS sizing (for an O_2 production rate of 0.39 kg/day).

Table 2 Energy interactions between system components

Heat transfer calculations (W)	During CH_4 and O_2 production		Finishing O_2 production	
	Sample return	Human	Sample return	Human
CSOE	−25.8	−258.3	−25.8	−258.3
Available heat recovery from CSOE exhaust (1123 to 220 K)	——	——	−21.7	−217.0
Available heat recovery from CSOE exhaust prior to SCR entry (1123 to 1073 K)	−1.2	−11.9	——	——
Sabatier reactor	−91.1	−910.6	——	——
Total heat available	−118.1	−1180.8	−47.5	−475.3
Total heat available assuming 90% recuperation	−106.3	−1062.7	−42.8	−427.8
CO_2 heating required prior to CSOE entry (348 to 1123 K)	10.8	107.7	26.9	269.4
Remaining heat transfer available for CSC application	−95.5	−955	−15.9	−158.4
Required CSC average power	29.5	256.1	67.3	633.6

Table 3 First assessment of a CES ISPP plant for a sample return and a human mission

Mission	Sample return	Human
Propellant	0.5 kg	5 kg per
Production rate	per 12 hr	12 hr
O/F ratio	3.5	3.5
Power, W	251.9	2479.3
CSC	67.3	633.6
CSOE	184.6	1845.7
Sabatier reactor	N/A	N/A
EPS	N/A	N/A
Mass, kg	4.34	33.35
CSC	3.07	27.40
CSOE	0.80	3.05
Sabatier reactor	0.12	.68
EPS	0.35	2.22
Volume, L	6.65	45.99
CSC	4.42	40.8
CSOE	1.75	1.68
Sabatier reactor	0.05	.46
EPS	0.43	3.05

ISPP Plant Comparison

The results of the modeling are compared to those published for two much-investigated ISPP plant designs that produce O_2 and CH_4, namely SWE and RWGS/SWE. Tables 4 and 5 list a comparison of mass, power, and production rates of the major defining pieces of technology for a sample return and human missions, respectively, using the different ISPP architectures. The overall specific energy and system specific mass are also listed per kilogram of O_2 produced.

The three sources used for comparison derive their numbers differently. The first source, Zubrin et al.,[8] presents numbers for the sample return mission that are mostly based on experimental data and then linearly scaled to size the larger human missions. The second source, Reddig et al.,[6] uses a chemical engineering process-modeling program to estimate power requirements. The method of mass modeling is not discussed. The third source, Green et al.,[10] uses commercial chemical plant software to estimate thermal and chemical performances. The method of mass modeling is not explicitly outlined in their work either.

It has been suggested that solid oxide electrolysis-based systems require up to ten times the amount of power of other ISPP options.[8] However, this is not true when using the current level of solid oxide electrolysis technology and taking into account heat transfer. Because PEM electrolyzers have been tested at room temperature,[7] it is easy to neglect their heat transfer needs. But for a Martian application, the electrolyzer will be operating in much lower temperatures. Assuming the PEM electrolyzer operates at an optimum temperature around 43°C,[¶] the minimum amount of heat transfer required for electrolysis was calculated. An amount needed to minimize electrolyzer insulation was added and assumed to be the same as that used for the CES system (25 and 250 W for the sample return and human missions, respectively). The results are presented in Tables 4 and 5 and show that the CES specific energy is the same as the other proposed systems.

The system specific mass of CES is significantly lighter than for the other two alternatives. For a sample return mission, the CES system specific mass is over three times lighter. For a human mission, the CES system specific mass is over two times lighter. Mass savings are derived from the synergy between the CSOE and the Sabatier reactor heat transfer requirements and the CSOE being a compact and light technology.

All three sources suggest using a temperature-swing adsorption unit for CO_2 acquisition and compression. The amount of CO_2 needed for the production of CH_4 will be the same for all plants because they all use the Sabatier reactor. However, the amount of CO_2 required to produce oxygen beyond a 2:1 ratio to reach the desired 3.5:1 ratio will vary. The SWE system will have to make up the extra oxygen by producing one O_2 for every CO_2 obtained while storing away the excess CH_4.

The RWGS reactor, with an optimistic utilization of 20%, will only get one O_2 molecule for every 10 CO_2 processed. In addition, the higher operating pressure of the RWGS reaction would put a higher load on the CSC. For the CES system, 100% utilization is achieved during the production of methane (which is achieved during more than half the production time, in this case, 285 of the 500 days). Assuming a conservative 30% utilization for the duration of the oxygen production, the CES system produces 1.5 O_2 for every 10 CO_2 processed and only operates at 1 bar. Operating at the optimal 80% utilization produces 4 O_2 for every 10 CO_2 processed. Thus, it is sufficient to say that the load on the CO_2 acquisition and compression unit for a CES system would be smaller than that for a RWSG/SWE system.

Another aspect of the architectures to compare is the H_2 metering systems. It is felt that the CES will compare well. Because the SWE system will have to make more CH_4 to produce the 3.5:1 O/F ratio, there is a higher load on the H_2 metering system. Furthermore, the RWGS/SWE system uses two, one for the SWE process and another for the RWGS process.

Finally, system components such as valves, plumbing, and so forth will probably compare well or lighter for the CES architecture. The SWE system is comparable in complexity whereas the RWGS/SWE system is more complicated. Table 6 summarizes how other aspects of the systems could generally compare to a CES

[¶] Personal communication, J. McElroy, McElroy PEM Technologies, Jan. 2002.

Table 4 Comparison of SWE and RWGS/SWE components to CES for a sample return mission

	Zubrin et al.[8]		Reddig et al.[6]	Authors
Source	SWE	RWGS/SWE	SWE	CES
Plant				
Propellant production rate, g/h	41.7	41.7	58.3[a]	41.7
O/F ratio	2	3.5	2	3.5
Specific energy (kWh/kg O_2 produced)	5.9	5.7	5.6[a]	5.7
RWGS, W	——	150[c]	——	——
Electrolysis, W	120		120	184.6
Electrolysis heater, W[b]	43	36	98	0
System specific mass (kg/kg O_2 produced/hr)	108	123	309[a]	28
RWGS, kg	——		——	——
Sabatier, kg	3[c]	4[c]	9	0.12
Electrolysis, kg			3	0.8

[a] Assume production "day" is 12 h.
[b] Calculated by authors assuming PEM electrolyzer operated at 55°C and same heat losses as CES.
[c] Value listed for more than one component (i.e., RWGS and electrolysis).

Table 5 Comparison of SWE and RWGS/SWE components to CES for a human mission

	Zubrin et al.[8]		Green et al.[10]		Authors
Source	SWE	RWGS/SWE	SWE	RWGS/SWE	CES
Plant					
Production rate, kg/h	416.7	416.7	375[a]	317.5[a]	416.7
O/F ratio	2	3.5	1.86	3.7	3.5
Specific energy (kWh/kg O_2 produced)	5.9	5.7	6.0	8.9[a]	5.7
RWGS, W	——	1500[c]	——	731	——
Electrolysis, W	1200		1313	1308	1846
Electrolysis heater, W[b]	430	360	175	160	0
System specific mass (kg/kg O_2 produced/h)	21.6	24.7	61.2	79.4[a]	11.7
RWGS, kg	——		——	4.3	——
Sabatier, kg	6[c]	8[c]	4.3	4.3	0.7
Electrolysis, kg			11	11	3.1

[a] Assume production "day" is 8 h.
[b] Calculated by authors assuming same losses as CES.
[c] Value listed for more than one component (i.e., RWGS and electrolysis).

Table 6 General comparison of other system component masses to that of a CES system

System	SWE	RWGS/SWE
CSC mass	Smaller	Higher
H_2 metering mass	Higher	Higher
Plumbing hardware mass	Similar	Higher

system. Because of these and the results presented in Tables 4 and 5, it is concluded that the CES overall system weight is very attractive.

Advantages of Implementing Combined Solid Oxide Electrolysis

The SWE architecture is fairly reliable, comprising only a few components that are well-proven, simple technologies. However, the SWE system is only capable of producing an O/F mixture ratio of 2:1. For this system to achieve 3.5:1, CH_4 (and thus the valuable H_2 brought from Earth contained within it) would have to be discarded. A solid oxide electrolysis unit could be added to electrolyze additional CO_2 into waste CO and pure O_2, but then the plant would have two electrolyzers. Instead, it is much more efficient to replace SWE's water electrolysis with CSOE. When extra O_2 is needed, one simply turns off the H_2/H_2O recycle loop.

Like the CES system, the RWGS/SWE architecture can theoretically achieve any O/F mixture ratio plus make additional oxygen for life support needs. However, to be able to accomplish this endless supply of oxygen, it must be kept in mind that the RWGS/SWE system must have a source of H_2. If the H_2 source is depleted for some unforeseen reason, no additional oxygen can be produced. A CES system does not rely on any H_2 to produce oxygen. All it needs is CO_2, which is readily available no matter where on Mars the plant is located.

Reviewing the CES schematic in Fig. 3, it is obvious that a flow diagram that implements CSOE is refreshingly simple. But what can be said about the maturity and reliability of the technology? Solid oxide electrolysis is a well-proven technology that has long been investigated since the idea of electrolyzing the mostly CO_2 Martian atmosphere was first introduced in 1978.[13] Over time, successful long-duration experiments have been demonstrated, with cells being tested for months.[36]

In more recent years, solid oxide electrolysis of H_2O has been demonstrated successfully as well.[37] Results within STL have confirmed that not only is the solid oxide electrolysis of H_2O safe and doable, but that the combined electrolysis of H_2O and CO_2 is very effective. Finally, solid oxide electrolysis technology has already been proven to meet space flight hardware requirements. As previously mentioned, this technology was applied to the OGS that was to be flown onboard the Mars 2001 Lander.[18,38] Though the mission was canceled, OGS was delivered and passed all certification testing.

Finally, one capability that CSOE has to offer that no other system can is nighttime power. Solid oxide electrolysis run in reverse is simply a fuel cell. Successful testing of such a device has already been accomplished.[19] Using some of the CH_4 and O_2 generated during the day, the system could generate heat at night to maintain the system at operating temperatures so that startup power for the next day could be substantially reduced.

Conclusions

The concept of applying CSOE to ISPP plant design has been introduced. The resulting architecture is a CES system that produces oxygen and methane in the optimal O/F mixture ratio. An additional capability of the system includes the ability to produce extra oxygen for life support, irrespective of the resources brought from Earth.

The CES system was modeled to assess the feasibility of implementing CSOE into ISPP plant design. Modeling results suggest impressive mass savings, even when using data collected from a CSOE unit not optimized for performance. Results also indicate that a CES system scales easily for either a sample return or human mission. This means systems engineers can use CSOE technology now for sample return missions and not have to develop something entirely new for human missions later.

The CES architecture compared well to published sizing of its O_2/CH_4-producing predecessors. Taking advantage of recent developments in solid oxide electrolysis, the mass of a CES system is 50–75% less than the other alternatives for human and sample return missions, respectively. Power requirements of a CES system are the same.

Mars exploration is active right now, and a sample return mission is a realistic consideration for the next phase of missions. To accomplish such a goal in today's economy and to make human missions more plausible, the resources at Mars must be used. This paper has shown that these goals can be reasonably achieved through the application of combined CO_2/H_2O solid oxide electrolysis to an ISPP plant. The resulting simple CES architecture is of attractive mass and power requirements using established technologies that can be scaled for future human exploration.

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