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Electrolyzer Power Requirements for Oxidizer Production on Mars

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Proton-exchange-membrane electrolyzers and solid-oxide electrolyzers have both been proposed for propellant production on Mars. Past studies assume the latter requires more energy because solid-oxide electrolyzers have significantly higher operating temperature. However, heat-transfer needs of proton exchange membrane electrolyzers are often neglected. On Mars, where the atmosphere has a mean temperature of 215K, heat transfer must be considered. Notably, theoretical analyses show that the total energy requirements of both electrolyzers for a given oxygen production are equivalent. Also in opposition to common perception, calculations show heat-transfer direction is not dependent upon current but rather operating temperature and voltage. If either electrolyzer is operated above its thermal neutral voltage, excess power will be dissipated as heat. If either electrolyzer is operated below it, the electrolyzer will require additional energy in the form of heat to maintain its operating temperature. If the required thermal energy is available from another component within a propellant production plant, then operating the electrolyzer at its theoretical minimum voltage is more efficient. Calculations show that a solid-oxide electrolyzer minimum voltage is at least 20% less than a proton-exchange-membrane electrolyzer minimum voltage. Experimental observations and data are presented to corroborate calculations.

Nomenclature

$\Im$ = Faraday's constant
$\bar{h}$ = molar enthalpy
I = current
k_H = Henry's constant
M = molecular weight
$\dot{N}_i$ = molar flow rate of the ith constituent
P = total pressure
P_i = partial pressure of ith constituent
P_{v0} = saturated vapor pressure at 25°C
$\dot{Q}$ = heat transfer
R = universal gas constant
S_{O_2} = oxygen solubility
$\bar{s}$ = molar entropy
$\bar{s}^0_{i,\,T,\,P}$ = absolute molar entropy of the ith constituent at T and P
T = temperature
V = voltage
$\dot{W}$ = work transfer or power
X = molar fraction
Y = defined in Eq. (29)
Z = defined in Eq. (30)
$\Delta\bar{h}^0_{f,298}$ = molar enthalpy of formation at standard conditions
η = utilization of oxygen-providing gas
ν = specific volume
σ = standard deviation

Subscripts

applied = applied to the electrolyzer
ex = exhausting constituent
i = ith constituent
in = entering constituent
g = gas
ℓ = liquid
min = theoretical minimum
v = vapor

Superscript

- = (bar) molar variable

Introduction

ELECTROLYZERS are essential technology components for the production of propellant on Mars using the Martian resources. Two types of electrolyzers have been used extensively in various system designs.[1–6] These are the proton-exchange-membrane (PEM) electrolyzer and the solid-oxide electrolyzer (SOE). Regardless of the system design, the primary function of each is to provide oxygen (O_2) for propellant oxidizer. The PEM electrolyzer is used to electrolyze liquid water (H_2O) exclusively, whereas the SOE is capable of electrolyzing H_2O vapor and/or carbon dioxide (CO_2). Data from as early as Viking and as recent as Mars Odyssey and Mars Global Surveyor suggest near-surface H_2O ice exists and H_2O ice exists in the polar caps.[7–13] Regardless of H_2O availability on the planet, propellant systems usually produce H_2O as a byproduct of fuel production. CO_2 is obtained from the 95% CO_2 Martian atmosphere.[14]

There are pros and cons to either technology. For instance, the PEM electrolyzer has been used extensively in industry.[15] It also operates at relatively low temperatures, between 25 and 150°C (Ref. 16). However, as applied in Martian O_2/methane (CH_4) propellant production plants, it can only produce a 2:1 oxidizer-to-fuel ratio without wasting resources or relying on additional supplies brought from Earth. On the other hand, a SOE can produce an optimal 3.5:1 oxidizer-to-fuel ratio, but it has a lower technology maturity and operates at higher temperatures, at or above 750°C.

Performance data for PEM electrolyzer systems are not widely available because of the proprietary nature of the technology. In any case, an actual performance comparison between them and SOEs might not be fair because of the huge investment in PEM electrolyzer technology for submarine life support,[15] which inevitably increased the efficiency of the PEM system. As studies claim that the PEM electrolyzer operates "very near the theoretical minimum voltage,"[5] this paper quantifies what this minimum voltage is and

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how it compares to the theoretical minimum voltage of the SOE. Of importance to the system engineer is how this voltage influences 1) the overall power required for each system and 2) the thermal considerations for the systems. This paper will address both these issues for PEM electrolyzers and SOEs.

Background

A PEM electrolyzer uses a perfluorocarbon cation exchange membrane with metal electrodes.[15] When hydrated, the membrane is a good ionic conductor at ambient temperatures. Operating pressures and temperatures range between 1–200 atm and 25–150°C (Ref. 16), respectively. As shown in Fig. 1a, H_2O is supplied to the anode and, upon applying an electrical potential in the form of a voltage, broken up in the following reaction:

$$H_2O_{(\ell)} \rightarrow 2H^+ + \tfrac{1}{2}O_{2(g)} + 2e^- \tag{1}$$

The O_2 is carried out of the electrolyzer by the remaining H_2O that was not dissociated. The hydrogen ions (H^+) migrate across the membrane to the cathode and recombine with the electrons (e^-) to make hydrogen (H_2):

$$2H^+ + 2e^- \rightarrow H_{2(g)} \tag{2}$$

A SOE uses a ceramic-oxide electrolyte, for example, yttria-stabilized zirconia (YSZ), with metal electrodes. At elevated temperatures above 750°C, the YSZ acts as a good oxygen ion ($O^=$) conductor. As shown in Fig. 1b, H_2O vapor or CO_2 is supplied to the cathode and, upon applying a voltage, broken up in the following respective reactions:

$$H_2O_{(g)} + 2e^- \rightarrow H_{2(g)} + O^= \tag{3}$$

$$CO_2 + 2e^- \rightarrow CO + O^= \tag{4}$$

Each $O^=$ migrates across the electrolyte, where it gives up two electrons and recombines to form pure, dry O_2:

$$O^= + 2e^- \rightarrow \tfrac{1}{2}O_{2(g)} \tag{5}$$

For a PEM electrolyzer, use of the H_2O is low so that the H_2O can hydrate the membrane while carrying away O_2. During a single pass, typical values might be 2–3% and get as high as 10%. A SOE can be operated at use as high as 80% so the H_2O/H_2 or CO/CO_2 exhaust concentration will vary accordingly. Regardless of the electrolyzer, the overall reaction of electrolysis is a function of utilization:

$$H_2O \rightarrow \eta H_2 + (\eta/2)O_2 + (1-\eta)H_2O \tag{6}$$

$$CO_2 \rightarrow \eta CO + (\eta/2)O_2 + (1-\eta)CO_2 \tag{7}$$

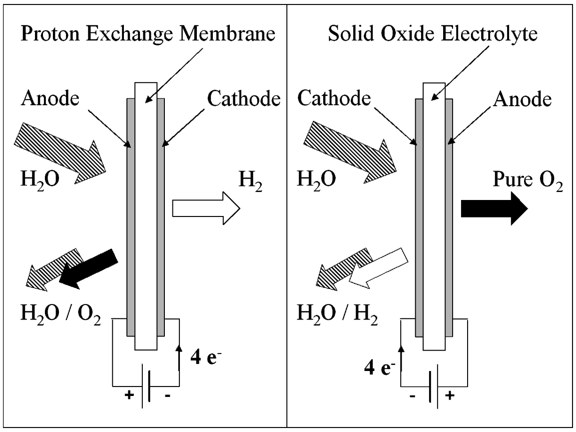

Fig. 1 Schematic of a) a PEM electrolyzer and b) a SOE.

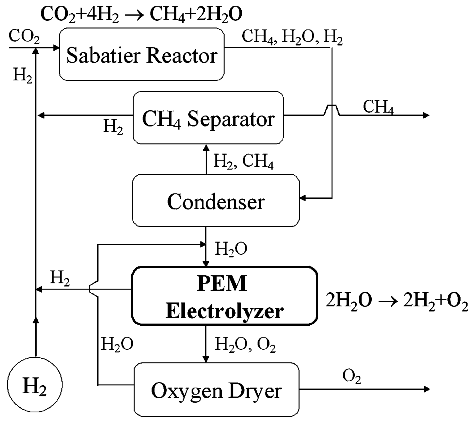

Fig. 2 Example application of a PEM electrolyzer for propellant production on Mars.

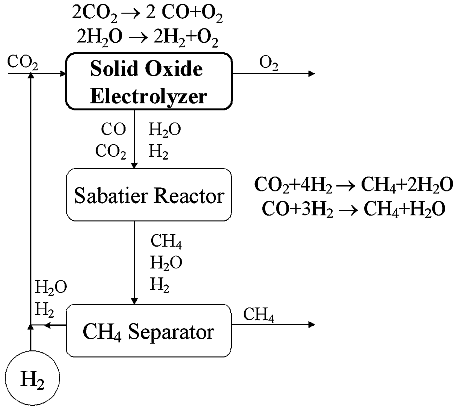

Fig. 3 Example application of a SOE for propellant production on Mars.

There are several ways to use both a PEM electrolyzer and a SOE for propellant production on Mars. As an illustration of their applications, Figs. 2 and 3 demonstrate how each could be used in conjunction with a Sabatier reactor to produce O_2 and CH_4 propellant.

In both systems, CO_2 is collected from the Martian atmosphere and compressed. For a PEM electrolyzer system,[5] the compressed CO_2 is delivered to a Sabatier reactor with excess H_2 to make CH_4 fuel and H_2O via the Sabatier reaction shown in Fig. 2. H_2O is condensed out of the Sabatier reactor's exhaust and sent to the PEM electrolyzer, while the CH_4/H_2 mixture is sent to a CH_4 separator and the excess H_2 is recycled. The electrolyzer produces hydrated H_2, which is recycled back to the Sabatier reactor as well. The O_2 from the electrolyzer is easily removed from the liquid H_2O and then dried to achieve a pure, dry O_2 product. All O_2 from a PEM system is produced from H_2O electrolysis.

For a SOE system,[6] compressed CO_2 goes directly to the electrolyzer along with recycled H_2O vapor. Pure dry O_2 is produced on the anode side. The SOE cathode exhaust is sent to the Sabatier reactor, where when run H_2 rich, consumes all of the carbon atoms to produce CH_4 and H_2O. A similar CH_4 separator to that used in the PEM system is then used to separate the CH_4 for fuel and recycle the H_2 and H_2O. Once enough CH_4 is produced through the combined electrolysis of CO_2 and H_2O, the Sabatier reactor is shut down. The remaining O_2 required to satisfy the 3.5:1 oxidizer-to-fuel ratio is then achieved by producing O_2 via CO_2 electrolysis.

Both electrolyzers drive the same amount of current for a given amount of O_2 produced. This is because four electrons must travel through each electrolyzer for every O_2 molecule generated. Therefore, each electrolyzer draws 3.35 A for every gram of O_2 produced per hour. However, the difference between the two electrolyzers resides in the amount of voltage that is needed to produce this current. This is a critical system design criterion because current multiplied by voltage dictates the power required to operate the electrolyzer.

The applied voltage is a function of operating temperature, pressure, and system irreversibility. Examples of irreversibility include over potentials caused by species concentration gradients, activation energies, and ohmic losses.[17] Irreversible effects are overcome by applying a voltage over the theoretical minimum voltage required for electrolysis.

In some cases, the irreversible effects can be used to the system's advantage. For example, electrolysis will require energy to satisfy the endothermic nature of the electrolysis reaction. However, should there be irreversibilities, the incurred losses can be dissipated in the form of heat. If there are enough losses, the heat generated can satisfy the endothermic energy needs. This could be used to an advantage in optimizing the overall energy requirements.

So the questions to be answered here are 1) what are the theoretical minimum voltages required by these two types of electrolyzers and 2) how do these minimum voltages affect electrical power and heat-transfer requirements.

Calculating Theoretical Minimum Voltages

General Procedure

A flow availability analysis was performed on each electrolyzer modeled as that shown in Fig. 4, where H_2O is used as an example. It is assumed that constituents entering and leaving the cell, as well as the environment in which the cell resides, are all at the desired operating temperature. Pressure drops across the system are also neglected such that the total pressure of each stream is P. For the PEM electrolyzer, gas 1 at the cathode is H_2, and gas 2 at the anode is O_2. For H_2O electrolysis in the SOE, gas 1 at the anode is O_2, and gas 2 at the cathode is H_2. [For CO_2 electrolysis, gas 2 at the cathode is carbon monoxide (CO).] This analysis uses the heat-engine sign convention[18] in which heat transfer *into* the system and work transfer *out of* the system are both positive.

Applying the first and second law of thermodynamics,[18,19] neglecting changes in potential and kinetic energies, and assuming a steady and completely reversible system (neglecting all losses), the theoretical minimum amount of power required to electrolyze an oxygen-providing molecule (i.e., H_2O) can be written as follows:

$$\dot{W}_{\min} = \sum_{\text{in}} \dot{N}_i(\bar{h}_{T,P} - T\bar{s}_{T,P})_i - \sum_{\text{out}} \dot{N}_i(\bar{h}_{T,P} - T\bar{s}_{T,P})_i \tag{8}$$

$$= \dot{N}_{\mathrm{H_2O,in}}(\bar{h}_{T,P} - T\bar{s}_{T,P})_{\mathrm{H_2O,in}} - \sum_{\text{out}} \dot{N}_i(\bar{h}_{T,P} - T\bar{s}_{T,P})_i \tag{9}$$

Because chemical reactions are occurring inside the cell, molar enthalpy evaluations use the enthalpy of formation [i.e., for $H_2O(\ell)$ $\Delta\bar{h}^0_{f,298K} = -285{,}830$ kJ/kgmol (Ref. 20)] to avoid difficulties of different reference states from different thermodynamic tables:

$$\bar{h}_{i,T,P} = \Delta\bar{h}^0_{f,298K,i} + \bar{h}_{T,P,i} - \bar{h}_{298K,1\mathrm{atm},i} \tag{10}$$

The minimum amount of work required to produce one mole of O_2 is calculated by dividing by the O_2 production rate. Finally, the application of Faraday's law[21] provides the theoretical minimum voltage required to produce O_2:

$$V_{\min} = \left(\dot{W}_{\min}\big/\dot{N}_{\mathrm{O_2}}\right)(1/4\Im) \tag{11}$$

Because all losses were neglected in calculating this theoretical minimum voltage, it can actually be observed experimentally at the onset of electrolysis when O_2 production just begins and the current is extremely small. A comparison of its calculation to data will be provided in a later section.

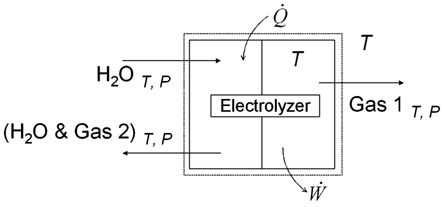

Fig. 4 Thermodynamic system for minimum work analysis of an electrolyzer.

Additional Assumptions for SOE Calculations

Recent advances in SOE technology for CO_2 electrolysis allow for performances up to 1 A/cm^2 at 850°C and 1 atm (Ref. 22). In the case of H_2O electrolysis, testing performed by Iacomini[23] has shown SOE cells to perform the same if not better than CO_2 electrolysis; therefore, this analysis will employ a SOE operating temperature of 850°C. The operating pressure will be treated as a variable in order to allow comparison to stated operating conditions of the PEM electrolyzer for Martian applications.

Operating at 850°C, it is assumed that all constituents entering and leaving the SOE cell behave as ideal gases. For ideal gases, enthalpy is independent of pressure. Values used here are taken from tables[20] at the operating temperature. Additionally, entropy is calculated by integrating one of the Gibbs equations[24] isothermally from a reference pressure of 1 atm to the partial pressure of the constituent:

$$\bar{s}_{T,P,i} = \bar{s}^0_{T,i} - R\ell\mathrm{n}(P_i) \tag{12}$$

Finally, all flow rates out of the SOE cell are dependent on use of the inlet stream (i.e., H_2O). As an example for H_2O electrolysis, partial pressures of H_2 and H_2O in the SOE exhaust are calculated by applying Dalton's law of partial pressures.

$$\dot{N}_{\mathrm{O_2}} = (\eta/2)\dot{N}_{\mathrm{H_2O,in}} \tag{13}$$

$$\dot{N}_{\mathrm{H_2}} = \eta\dot{N}_{\mathrm{H_2O,in}} \tag{14}$$

$$\dot{N}_{\mathrm{H_2O,ex}} = (1-\eta)\dot{N}_{\mathrm{H_2O,in}} \tag{15}$$

Additional Assumptions for PEM Electrolyzer Calculations

The calculations presented here will be made using suggested operating conditions for a Martian propellant production plant[4,5] of operating temperature 25°C and pressures of 1–35 atm. The stated operating pressure of the PEM electrolyzer is assumed to be universal in that both the anode and cathode operate at the same total pressure, as suggested by Takahashi.[16] H_2O entering the system at these conditions will be liquid and thus can be modeled as incompressible. Enthalpy then can be calculated at various pressures assuming a constant specific volume of 1.003 cm^3/kg (Ref. 20). Enthalpy can also be taken from tables. The difference between the two methods in evaluating enthalpy for the pressures and temperatures considered here is on the order of 0.001%. Enthalpy and entropy data at low pressures are taken from H_2O saturation tables at the operating temperature.[20] Enthalpy and entropy data at high pressures (35 atm) are taken from compressed H_2O tables at the given T and P (Ref. 20).

To simplify calculations, the H_2 gas produced at the cathode is assumed to be pure (no H_2O vapor present). Furthermore, the enthalpy only changes 0.4% as the pressure is increased from 1 to 35 atm. Therefore, the H_2 is assumed to act as an ideal gas, which allows for enthalpy and entropy calculations as just described for the SOE.

The evaluation of the H_2O/O_2 exhaust stream properties is a little trickier. Two phases exist: a gaseous O_2 and undissociated liquid H_2O. It is assumed that the two do not mix to form a homogenous mixture. However, it will be assumed that H_2O vapor exists in the O_2 and O_2 is soluble in H_2O.

The solubility (mol of O_2/L of H_2O) of O_2 in liquid H_2O is very small and thus can be calculated using Henry's law[25]:

$$S_{\mathrm{O_2}} = k_H P_{\mathrm{O_2}} \tag{16}$$

where k_H is 1.66E–06 mol O_2/(L of H_2O-mm Hg) at 25°C. For high O_2 partial pressures (near 35 atm in this study) and low utilization (<5%), over 3% of the O_2 produced will be absorbed by the H_2O. As utilization increases, the percentage of O_2 absorbed decreases.

The molar fraction of O_2 in H_2O can be calculated by using H_2O's specific volume at 25°C and P and its molecular weight:

$$X_{O_2} = \frac{S_{O_2} v_{H_2O} M_{H_2O}}{S_{O_2} v_{H_2O} M_{H_2O} + 1} \tag{17}$$

The liquid H_2O/O_2 mixture is then treated as an ideal solution, where it is assumed that the molecular forces between the unlike molecules (i.e., H_2O/O_2) are the same as those between the like molecules (i.e., H_2O/H_2O). More formally, an ideal solution assumption means that the chemical potential of each component is a linear function of the logarithm of its mole fraction.[24] From this formal definition, the enthalpy and entropy of each component can be calculated from values of the respective specific property in the pure state at the given T and P:

$$\bar{h}_{\text{mixture}} = X_{H_2O}\bar{h}_{T,P,H_2O} + X_{O_2}\bar{h}_{T,P,O_2} \tag{18}$$

$$\bar{s}_{\text{mixture}} = X_{H_2O}\left[\bar{s}^0_{T,H_2O} - R\ell n\left(1 - X_{O_2}\right)\right] + X_{O_2}\left[\bar{s}^0_{T,O_2} - R\ell n\left(X_{O_2}\right)\right] \tag{19}$$

The gaseous phase is assumed to behave as an ideal gas. Enthalpy and entropy for each the O_2 and H_2O vapor are calculated as described for the SOE. The absolute entropy used in Eq. (12) is obtained from ideal-gas H_2O tables.[20] Additionally, the H_2O vapor pressure is assumed to be that of saturated H_2O at 25°C. At higher pressures, the Poynting effect[24] is taken into account. At liquid O_2 mole fractions of less than 0.001, the liquid phase is essentially considered pure H_2O, and the following can be applied to solve for the corrected vapor pressure:

$$\ell n(P_v/P_{v0}) = \left[\bar{v}_{H_2O(\ell)}\big/RT\right](P - P_{v0}) \tag{20}$$

The total molar flow rates of O_2 and H_2O are a function of utilization as shown in Eqs. (13) and (15). How these break up into gaseous and liquid contributions can be calculated from the O_2 solubility, Dalton's law of partial pressures and the ideal-gas law, and from the conservation of H_2O and O_2 molecules. The resulting four equations with four unknowns (the molar flow rates) are as follows:

$$X_{O_2} = \frac{\dot{N}_{O_2(\ell)}}{\dot{N}_{O_2(\ell)} + \dot{N}_{H_2O(\ell)}} \tag{21}$$

$$\frac{\dot{N}_{H_2O(g)}}{\dot{N}_{O_2(g)} + \dot{N}_{H_2O(g)}} = \frac{P_v}{P} \tag{22}$$

$$\dot{N}_{H_2O(\ell)} + \dot{N}_{H_2O(g)} = \dot{N}_{H_2O,\text{ex}} = (1 - \eta)\dot{N}_{H_2O,\text{in}} \tag{23}$$

$$\dot{N}_{O_2(\ell)} + \dot{N}_{O_2(g)} = \dot{N}_{O_2} = \frac{\eta}{2}\dot{N}_{H_2O,\text{in}} \tag{24}$$

The resulting molar flow rates of the H_2O and O_2 leaving the cell are

$$\dot{N}_{O_2(\ell)} = \frac{\dot{N}_{O_2} - Y\dot{N}_{H_2O,\text{ex}}}{1 - YZ} \tag{25}$$

$$\dot{N}_{H_2O(g)} = \frac{\dot{N}_{H_2O,\text{ex}} - Z\dot{N}_{O_2}}{1 - YZ} \tag{26}$$

$$\dot{N}_{O_2(g)} = \dot{N}_{H_2O(g)}Y \tag{27}$$

$$\dot{N}_{H_2O(\ell)} = \dot{N}_{O_2(\ell)}Z \tag{28}$$

where

$$Y = \frac{1 - X_{H_2O(g)}}{X_{H_2O(g)}} \tag{29}$$

$$Z = \frac{1 - X_{O_2(\ell)}}{X_{O_2(\ell)}} \tag{30}$$

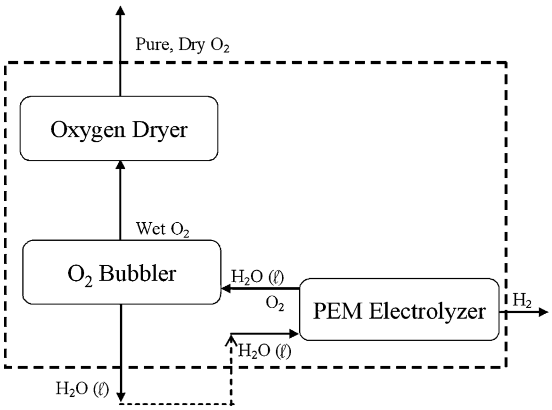

Fig. 5 PEM system for producing pure dry oxygen.

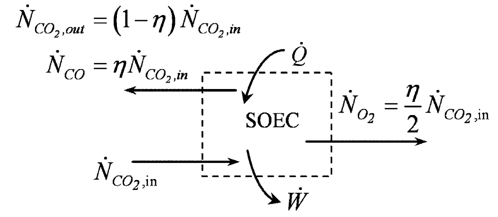

Fig. 6 System for SOE energy balance calculations.

Assumptions for the PEM System to Produce Pure Dry Oxygen

As just calculated, the O_2 retrieved from the PEM electrolyzer needs to be separated from H_2O and dried. If the desired product is pure dry O_2, it is useful to calculate the minimum amount of work required of a PEM system to produce this and compare it to the minimum work of a SOE system.

Figure 5 illustrates the new system for a PEM electrolyzer thermodynamic analysis. Inside the system, drying processes occur such that the H_2 and O_2 streams are both pure and act as ideal gases. The liquid H_2O is also pure and is treated as an incompressible substance.

Calculating Electrolyzer Power and Heat-Transfer Requirements

Power and heat-transfer requirements are calculated by applying the first law of thermodynamics only. When producing O_2 on Mars using a SOE, most of the O_2 will be produced by CO_2 electrolysis in order to satisfy the 3.5:1 optimal fuel ratio. Therefore, CO_2 electrolysis using a SOE is provided as an example in Fig. 6. As just stated, all streams enter and exit at the electrolyzer operating temperature.

Applying the first law, neglecting potential and kinetic energy contributions and changes, and assuming a steady-state system, the total heat transfer and work applied to the system is

$$\dot{Q} - \dot{W} = \sum_{\text{out}} \dot{N}_i\bar{h}_i - \sum_{\text{in}} \dot{N}_i\bar{h}_i \tag{31}$$

The work rate can be written as a function of the applied voltage and current (or O_2 production):

$$\dot{W} = -V_{\text{applied}}I = -V_{\text{applied}}4\Im\dot{N}_{O_2} = -V_{\text{applied}}4\Im(\eta/2)\dot{N}_{CO_2} \tag{32}$$

It is informative to write the heat-transfer rate per mol of CO_2 input as follows:

$$\dot{Q}\big/\dot{N}_{CO_2} = (\eta/2)\Big[-V_{\text{applied}}4\Im + \bar{h}_{T,P,O_2} - \bar{h}_{298K,\text{1atm},O_2} + 2\left(\Delta\bar{h}^0_{f298K,\text{CO}} + \bar{h}_{T,P,\text{CO}} - \bar{h}_{298K,\text{1atm,CO}}\right) - 2\left(\Delta\bar{h}^0_{f298K,CO_2} + \bar{h}_{T,P,CO_2} - \bar{h}_{298K,\text{1atm},CO_2}\right)\Big] \tag{33}$$

The quantity in the brackets determines the sign of the heat transfer. If it is positive, the system requires heat. If it is negative, the system will release heat. For a given operating temperature, this quantity inside the brackets is only a function of applied voltage. The sign of heat transfer is not a function of current or use. The applied voltage for a given temperature that results in zero heat transfer is called the "thermal neutral" voltage. A common misconception about electrolysis is that producing a lot of O_2 (current) will generate heat. However, Eq. (33) proves that, regardless of the amount of current, heat will not be produced if the system is operated under the thermal neutral voltage.

Discussion

Minimum Voltage Requirements

The minimum voltage required for electrolysis was calculated for both the "wet" and "dry" O_2 PEM systems. These results are plotted in Fig. 7. The extra work required to separate and dry the O_2 is practically nonexistent. When breaking up the individual contributions to the total minimum voltage, the contributions from each constituent were the same regardless of phase or mixture (i.e., dry O_2 vs wet O_2). This could be attributed to the ideal solution and ideal-gas assumptions, which can lower the required voltage. Regardless, the amounts of H_2O vapor and soluble O_2 in the wet O_2 model were extremely small (0.03 and 0.0008 molar ratios, respectively).

For the PEM electrolyzer, the minimum work required to produce O_2 from H_2O is directly proportional to the use of H_2O. However, the utilization is assumed to be small such that the exhaust of H_2O and O_2 is not a homogenous mixture. Therefore, dividing the minimum work by the O_2 production rate, as shown in Eq. (11), results in a minimum voltage that is independent of use. Therefore, there is only one curve in Fig. 7 for each PEM electrolyzer model (dry vs wet O_2) of low utilization. If a higher use is assumed and the mixture becomes homogenous, more work will be required to separate the oxygen. Subsequently, the required minimum voltage will increase with use.

For the SOE, the ideal-gas assumptions made in the calculations hold for any use. Therefore, the minimum work is a nonlinear function of use. The nonlinearity develops from H_2O/H_2 mixing entropy. The PEM dry O_2 calculations do not reflect any entropy mixing because the system is set up such that O_2 and H_2O cross the boundary separately. Because of the nonlinearity in use, the minimum voltage for a SOE increases with increasing use. These trends are demonstrated in Fig. 7.

In comparing the two electrolyzers, Fig. 7 shows that the minimum voltage needed to produce O_2 for both increases with operating pressure. For a SOE, the minimum voltage is a function also of use. The minimum voltage required for a SOE operating at 100% use is on the order of 20% less than that required by a PEM electrolyzer. The driving factor is that the formation of H_2O is enthalpy driven. Breaking up H_2O is endothermic, and in order to reduce this energy requirement higher temperatures are needed. Subsequently, increasing the temperature from 25 to 850°C decreases the Gibbs standard state energy of H_2O decomposition by 20%. The amount required for lower use is less; however, when targeting a required production rate, use will not come into play for electrolysis power. However, use *will* affect CO_2 acquisition and/or H_2O recycling power requirements.

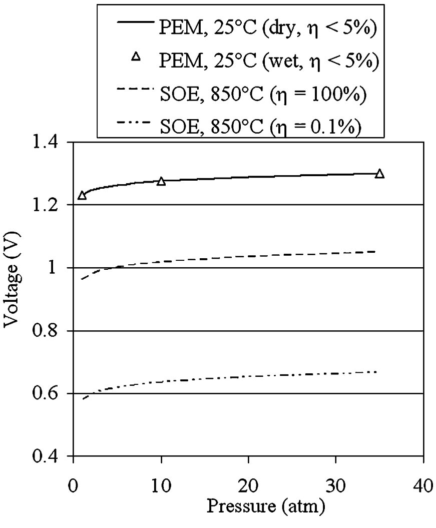

Fig. 7 Theoretical minimum voltage required to produce oxygen from water.

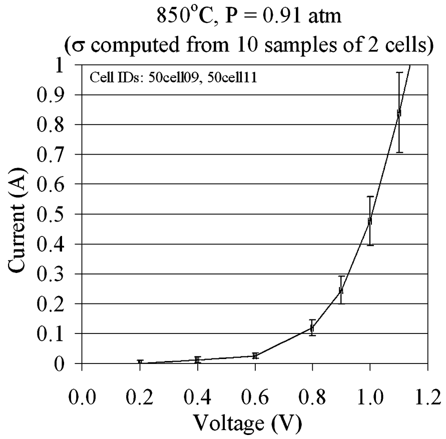

Fig. 8 SOE experimental data: CO_2 electrolysis.

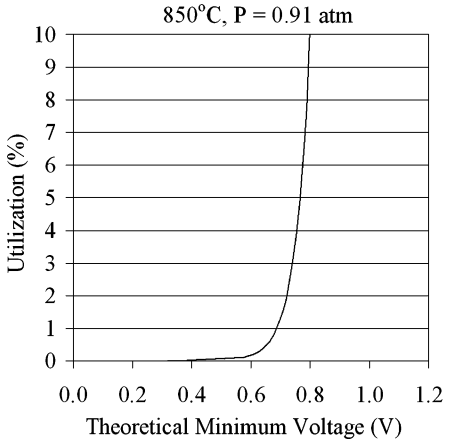

Fig. 9 SOE calculations: CO_2 electrolysis.

Theoretical results can be compared to the minimum voltage required to initiate electrolysis in experiments. At the onset of electrolysis, when O_2 production is just begun, there are very little irreversibilities or losses because the current is extremely small. Such a condition matches the assumptions made in these calculations. For a SOE operating at 850°C and 0.91 atm, experiments conducted by Iacomini[23] show CO_2 electrolysis initiates around 0.6 V (see Fig. 8). Figure 9 calculations show that electrolysis initiates for voltages above 0.6 V.

To date, the authors have not yet found published performance curves for a PEM electrolyzer. However, PEM electrolyzer application papers have suggested increasing performances. In 1991, McElroy[15] reported operation at 1.8 V. In 1995, Murphy et al.[26] reported 1.5 V. In 1997, Clark[5] reported operating at "very near the theoretical minimum voltage," producing about 28.7 g/h of O_2 for 120 W over about six hours. This equates to approximately 1.25 V, whereas the theoretical minimum calculated here ranges from 1.23–1.3 V depending upon operating pressure.

Power and Heat-Transfer Requirements

A typical sample return from Mars might require a propellant production plant to produce 500 g of propellant per day.[4] Calculations

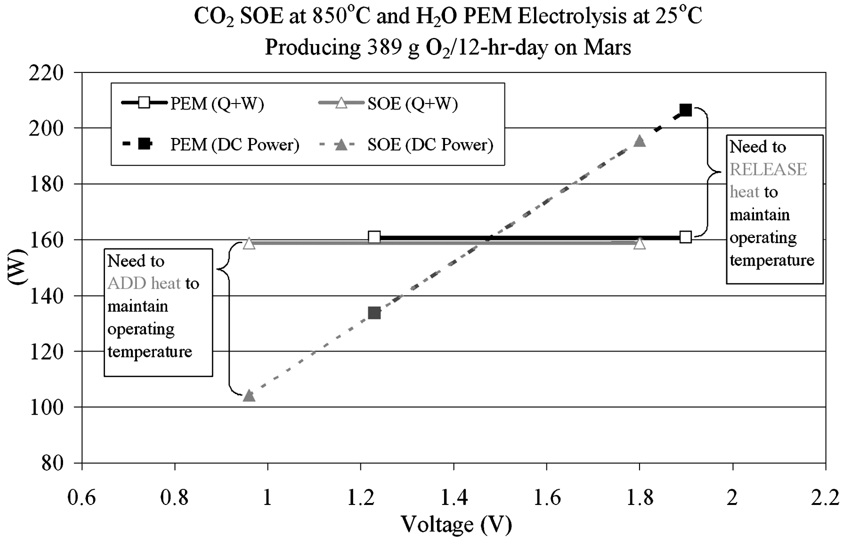

Fig. 10 Power and heating requirements vs operating voltage.

show that the total power and heating requirements for a CO_2 SOE at 850°C and 1 atm to produce 388.89 g of O_2 per 12-hour day (3.5:1 oxidizer-to-fuel ratio) is 159 W. The total power and heating requirements for a H_2O PEM electrolyzer at 25°C at 1 atm to produce the same amount of O_2 is 161 W. The thermal neutral voltages are 1.46 and 1.48 V for the SOE and the PEM electrolyzer, respectively.

Figure 10 compares the total power and heating requirements as a function of voltage for each electrolyzer. The total amount of power required by both is practically the same. H_2O electrolysis using the PEM electrolyzer costs negligibly more. When either electrolyzer is operated below its thermal neutral voltage, Fig. 10 shows that the electrolyzer will require additional power in the form of heat. If either is operated at voltages above the thermal neutral voltage, the extra dc power will be converted to heat. This heat in turn would be available for other processes within a plant. Operating at the thermal neutral voltage implies the electrolyzers can be operated at pure dc power with no additional heating requirements. If no alternative heating source is available, this scenario is most effective because dc power can be generated more efficiently than heating.

SOE experimental data support the thermal neutral voltage results just calculated. Figure 11 show temperature and current measurements for a span of voltage settings vs time for a SOE experiment. A SOE was placed in a furnace, where the environment was controlled to 847.6 ± 0.83°C with a Watlow Series 942 controller and K-type thermocouple. The temperature measurements shown are from a second K-type thermocouple (±0.83°C) that was placed against the SOE and shielded from the furnace's heating elements. At voltages below 1.5 V, the second thermocouple indicates the cell temperature appears to lower below the furnace temperature (indicating energy is being consumed to support the endothermic reaction of breaking up CO_2). Above 1.5 V, the cell temperature increases correlating to the cell's need to give off heat. Thus Fig. 11 shows that for a SOE temperature observations suggest the thermal neutral voltage to be around 1.5 V. Furthermore, the magnitude and slope of the temperature measurements correlate to the current. This implies current influences the magnitude (not direction) of the heat transfer as suggested in Eq. (33).

The data presented in Fig. 11 merely support the theory that operating above the thermal neutral voltage induces the cell to give off heat. It does not imply that operating above the thermal neutral voltage will always raise cell temperature. Higher cathode flow rates and/or higher anode flush rates could carry away any excess heat. Or, low current density might not produce enough heat to induce a measurable temperature change. So in other words, the operating voltage only dictates the direction of heat transfer, not its magnitude.

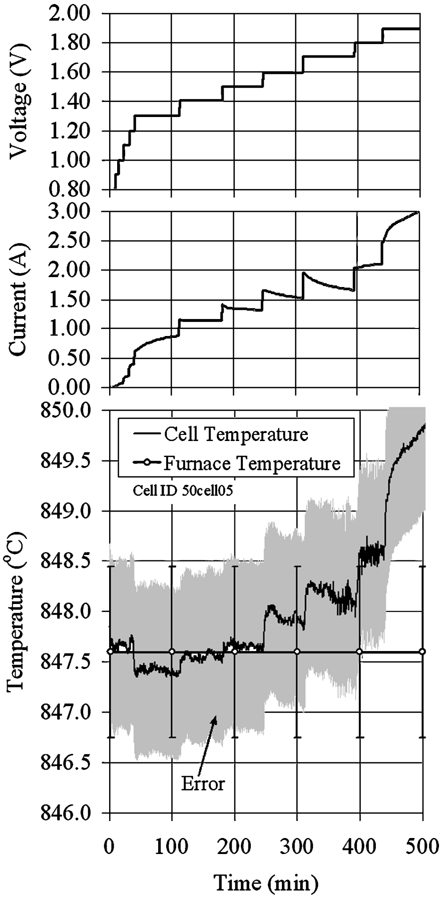

Fig. 11 SOE temperature data (±0.83°C) indicate voltage (±10 mV) above 1.5 V cause the cell to heat up while current (±0.05%) influences the magnitude.

Conclusions

The theoretical minimum voltage required for H_2O electrolysis has been calculated for both a PEM electrolyzer and a SOE. In general, the minimum voltage increases with operating pressure. Because a SOE can be operated at a wide range of use, this minimum voltage increases as more H_2O is electrolyzed. Regardless, the SOE operating at 100% use requires 20% less voltage than does the PEM electrolyzer operating at low use. Thus, the minimum voltage required for H_2O electrolysis is less for a SOE than for a PEM electrolyzer. These calculations compare reasonably with the limited amount of experimental data available.

Total power requirements for producing O_2 using a CO_2 SOE and a H_2O PEM electrolyzer are essentially the same. This conclusion contradicts a common conception of PEM electrolyzers vs SOE. Literature has reported that a PEM electrolyzer requires less power than a SOE.[4] What has been overlooked is the heat transfer to PEM electrolyzers. When tested on Earth, the ambient functions as an unlimited source of heat. Thus the heat required by PEM electrolysis to sustain the electrolysis reactions goes unnoticed. On Mars, the ambient temperature varies from −143 to 27°C (130 to 300 K), with a mean temperature of −58°C (215 K) (Ref. 14). Thus, for low-temperature environments heat-transfer requirements need to be accounted for in power calculations.

In low-temperature environments, heat loss from the electrolyzer is inevitable regardless of the operating voltage. Both will require insulation packages to minimize the heat loss. Because SOEs operate at such greater temperatures, a SOE will require more insulation mass as compared to a PEM electrolyzer for a given amount of heat loss. However, such a penalty has been shown to not have a significant effect on system mass for Mars propellant production plants. Sridhar et al.[6] show in fact that a system employing a SOE can cut the overall mass savings by more than half. Of course, should an exothermal process in the system or a radioisotope thermoelectric generator be available, as opposed to relying solely on solar cells, this becomes even less of an issue.

Therefore, it should also be emphasized that power assessments presented here are solely for the electrolyzers. Other factors of the propellant production system design will influence the total power needs. For example, at low use the PEM electrolyzer will require a high accumulation and circulation rate of H_2O to meet the desired O_2 production rate dictated by a given Mars mission. For a SOE, as use is decreased, the burden on a CO_2 collection and compression system will be increased. Both of these situations increase the power requirements of other components in a propellant production plant.

Regardless, both have flexibility when being incorporated into a plant design because of their capability to use or produce heat, depending upon their operating voltage. This is because the direction of heat transfer in electrolysis units is dictated solely by operating voltage and temperature. For a given operating temperature, if operated above the thermal neutral voltage, the electrolysis unit gives off heat. If operated below the thermal neutral voltage, the electrolysis unit requires heat. The thermal neutral voltage for both types of electrolysis units was shown to be practically the same (just under 1.5 V) when the PEM electrolyzer is operated at 25°C and the SOE is operated at 850°C.

If, for a given system, excess heat is available for the electrolyzer to use, the minimum voltage calculations suggest that much can be gained from operating a SOE at near theoretical voltages. For instance, at 80% use and 1 atm the theoretical SOE voltage is 0.93 V compared to 1.23 V for the PEM at low utilization. To produce the oxidizer required by a spacecraft to return to Earth, 25% less electrolyzer power would be needed on Mars when using a SOE. These savings are powerful motivation for further research into SOEs.

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