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Technical Paper Session I-B - The Prospect of producing Breathing Oxygen, Pure Hydrogen and propellants from the Martian Atmosphere

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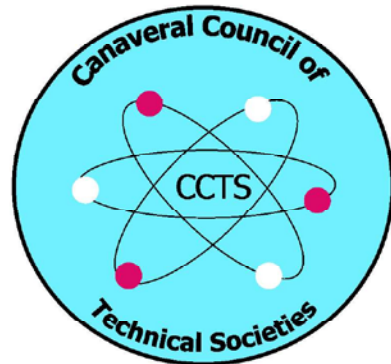
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SPACE VISIONS CONGRESS 2007

TECHNICAL PAPER
SESSION 1B

**“HIGH TEMPERATURE ELECTROLYTIC
CONVERSION OF CO₂ TO CO AND O₂: A STRATEGY
FOR IN SITU RESOURCE UTILIZATION ON MARS”
CLOVIS A. LINKOUS & MOHAMED M. ELBACCOUCH**



Biographical note

Clovis A. Linkous received his doctoral degree from Michigan State University in 1983. His thesis research involved photoelectrochemistry of organic semiconductor electrodes. He then worked at Brookhaven National Laboratory until 1989. Electrocatalysis of oxygen reduction in acidic media, solid oxide fuel cells, and steam electrolysis were among the topics investigated there. He then spent a year at Electron Transfer Technologies, an electrochemical engineering company near Princeton, New Jersey. In 1990 Dr. Linkous joined the staff at the Florida Solar Energy Center, a state research institute under auspices of the University of Central Florida near Kennedy Space Center. There he has studied advanced membrane technology for fuel cells, chemical hydrogen storage, and photocatalytic chemistry of semiconductor particulates.

INTRODUCTION

The prospect of producing Breathing Oxygen, Pure Hydrogen, and propellants from the Martian Atmosphere

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The cost of manned Mars missions could be significantly reduced if O₂, water, and propellant were to be extracted from the CO₂-rich Martian atmosphere. The objectives of this paper are to explore techniques of producing pure O₂ from the Martian atmosphere, and examine chemically stable reactors for H₂ production.

A method for obtaining O₂ on Mars is a high temperature solid oxide electrolysis of yttria-stabilized zirconia (YSZ) where CO₂ is electrochemically reduced to CO and pure O₂ is evolved from the opposite electrode compartment. An electrochemical cell will be demonstrated for CO₂ electrolysis with concomitant production of pure O₂ under partial pressures commensurate with the Martian atmosphere. Also, this paper investigates the impact of the In-Situ Resource Utilization for Mars mission by providing ultra pure H₂ and a chemically stable reactor in CO₂-rich mixtures needed to achieve long range mobility on Mars. The fabricated reactor is permeable to H₂ with infinite selectivity, chemically stable in CO₂, and does not require external electrical circuit. In addition, a system-level modeling will be presented to estimate cost, size, energy, power, weight, and volume equipment of a full-scale Mars mission.

High Temperature Electrolytic Conversion of CO₂ to CO and O₂: A strategy for In Situ Resource Utilization on Mars

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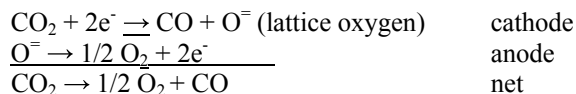
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Abstract

The cost of manned Mars missions could be significantly reduced if O₂, water, and propellant were to be obtained from the CO₂-rich Martian atmosphere. One method for obtaining O₂ on Mars is a high temperature solid oxide electrolysis using yttria-stabilized zirconia (YSZ) as an electrolyte, where CO₂ is electrochemically reduced to CO and pure O₂ is evolved from the opposite electrode compartment. Such an electrochemical cell could be employed for CO₂ electrolysis under partial pressures encountered in the Martian atmosphere. One method for utilizing the produced CO is to design a Fisher-Tropsch process where CO reacts with gaseous H₂ to produce hydrocarbons and H₂O. The hydrocarbon can be used as propellant while the water can be potentially purified.

1. Introduction

A tubular-type electrochemical cell can be constructed utilizing yttria-stabilized zirconia (YSZ) as a solid electrolyte, a Ni/Co/YSZ cermet as a cathode, and Sr-doped LaMnO₃ as an anode. This gas-solid electrochemical tubular cell is heated up to 1000 °C and aided with an external voltage to drive the electrochemical reactions. Measurement of CO₂/CO conversion from the cathode and O₂ from the anode compartment can be inexpensively confirmed via gas chromatographic apparatus with thermal conductivity detector. A high temperature zirconia-based electrochemistry can reduce the rich CO₂-environment in Martian atmosphere to CO and evolve pure O₂ from the opposite electrode compartment according to the following scheme of half-cell reactions:



In order to prevent the reverse Boudouard equilibrium ($2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$) that deposits carbon from CO decomposition, a background of recoverable water vapor could be maintained inside the reactor. Because of the positive entropy associated with the net CO₂ reduction reaction to CO,

the electrical energy requirement for the endothermic process goes down as the temperature increases. It is expected that the thermal energy requirement of the process can be met from the heat evolved from the electrochemical cell.

The current presidential administration has declared that a manned space flight to Mars should be a major objective in NASA's mission. A long-term flight such as this requires that a great attention be paid to recycling of waste materials as well as exploitation of resources available on planetary bodies. A means of providing O₂ is of vital importance to a manned Mars mission, because of its use in regenerating a breathable atmosphere and in providing oxidant for the return trip to Earth.

The Martian atmosphere is quite thin compared to that of Earth, only 0.01 atm at ground level. However, some 95 % of it is comprised of CO₂, so that the partial pressure of CO₂ on Mars (9×10^{-3} atm) is actually greater than that on Earth ($\sim 3 \times 10^{-4}$ atm). It is perhaps the major resource on Mars that awaits the arrival of a manned mission. As Table 1 shows, only 0.03% of the Martian atmosphere is water vapor which can be found as water-ice clouds at high altitude (above 20 km). As a simple binary compound, CO₂ may serve as a source of carbon and a source of O₂ for human sustenance and mission objectives. CO₂ is a relatively inert, low energy

compound. Considerable energy input will be required to perform net chemistry on it.

The phenomenon of lattice oxygen conductivity through ceramic materials was first noticed by Nernst [1]. Its utility in functioning as a solid electrolyte material was soon realized. The first zirconia fuel cell was demonstrated by Bauer and Preis in 1937 [2]. Powdered coal was used as a fuel in this device, but the possibility of using H₂ in a gas-solid electrochemical interface came soon afterwards. Westinghouse Electric Company (now Siemens-Westinghouse) has pioneered zirconia-based electrochemical cells in the modern era [3,4]. Around 1970, they abandoned the traditional flat cell stack design, and instead produced a tubular module known as the "FBA cell" [4]. Nevertheless, the complexity involved in producing a multi-cell stack of tubes has motivated other research groups to continue to pursue flat cell designs [5,6].

Table 1. Chemical composition of Mars

Component	Percentage
Carbon dioxide	95.32%
Nitrogen	2.7%
Argon	1.6%
Oxygen	0.13%
Carbon monoxide	0.07%
Water vapor	0.03%
Neon, krypton, xenon, ozone, methane	trace

2. Water-Gas Shift Reaction

It is true that the same net chemistry could be accomplished by a reverse water gas shift (RWGS) reactor ($\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$) coupled to a conventional water electrolyzer. The electrolyzer would decompose water into O₂ and regenerate the H₂ that was used in the RWGS reactor. However, consider the following aspects of electrolyzer operation at high temperature:

- 1) A high temperature electrolyzer constitutes a single device for O₂ production, while the other approach involves two reactors, one high temperature and one low.
- 2) Because of the positive entropy associated with CO₂ reduction to CO, the electrical energy requirement for the endergonic process goes down as temperature increases, so that a larger proportion of the total enthalpy requirement can be met from the thermal reservoir surrounding the electrochemical cell.
- 3) Activation barriers for the various electrode surface chemical reactions and transport of mobile

ionic species within the solid electrolyte are more easily surmounted as temperature increases.

4) One may be able to substitute cheaper, less catalytic metals (i.e., nonnoble metals) with higher intrinsic activation energies into the electrochemical process.

5) There are engineering advantages associated with working with exclusively a gas-solid system, especially under a zero- or low-gravity situation.

This reasoning has stimulated interest in high temperature ceramic electrolytes based on YSZ. By doping the zirconia with the aliovalent metal, the cubic phase is stabilized, so that the material can be heated from ambient to high temperature without phase change. The Y-doping also generates oxygen lattice vacancies that serve as transfer sites for the mobile oxygen ions.

3. Electrochemical Cell Design

A schematic diagram of the electrochemical cell is illustrated in Figure 1. The YSZ can be obtained in the form of tubes that would be cut to a desired length, typically 25-50 cm in length. The anode is formulated by co-precipitating the hydroxides of the respective perovskite metals and dopant, in stoichiometric ratio, via neutralization of acidic chloride solutions, followed by calcination, regrinding, applying to the ceramic electrolyte tube as a slurry with an organic binder, and finally sintering. The cathode is a cermet formulated by obtaining powders of YSZ and the respective metal, blending them in an appropriate ratio (1: 1 metal to YSZ), slurring with organic binder (i.e. polyvinyl alcohol), and sintering. The anode will be applied to the inner wall of the YSZ tube, while the cathode is applied to the outer wall. CO₂ will then be passed over the outer surface of the electrolyte tube, and O₂ will be evolved on the inside. Platinum contact wires are sintered to each electrode in order to apply an external voltage.

As shown in Figure 1, the finished tubular zirconia cell will be mounted concentrically inside a mullite or alumina tube using modified O-ring fittings outside the heating zone. This will allow independent control of gas flow inside and outside the YSZ tube. Current voltage performance will vary as a function of temperature, CO₂ partial pressure, and gas flow rate (utilization).

Another challenge is how to run the system in such a way as to keep the CO from disproportionating and depositing carbon (Boudouard equilibrium): If this reaction occurs inside the electrolysis cell, carbon build-up can poison the cathode. This can be prevented via a number of approaches. One would

be to keep the utilization of CO₂ to a minimum (high throughput) so as to force the Boudouard equilibrium to favor CO formation. Another approach is to recognize that the equilibrium has an inverse relationship with temperature; because of the negative entropy change associated with the reaction, the reactants are favored as temperature goes up. As long as electrolyzer temperature is held above 700 °C, carbon deposition is not anticipated to be a problem.

One could also maintain a background partial pressure of water vapor inside the reactor to remove any carbon via the water gas reaction: The source of the water and the recoverability of the H₂ can be obtained from the Fisher-Tropsch process (discussed next). Finally, it may turn out that carbon deposition is actually a useful reaction in terms of supplying raw material for other syntheses (e.g., methane production), so that the only consideration is to control the deposition zone where personnel can access and recover it.

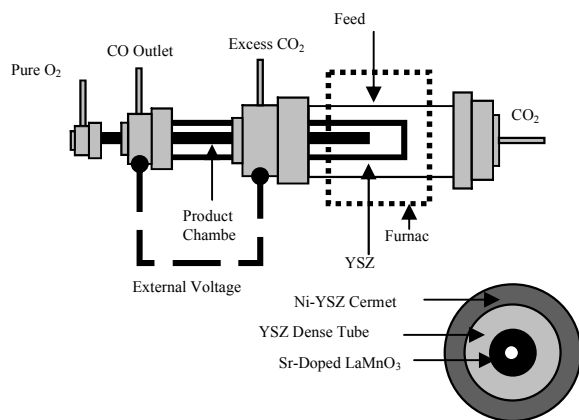


Figure 1. A Schematic diagram of a high temperature electrochemical cell.

4. Fisher-Tropsch Process

As shown in Figure 2, In Situ Resource Utilization (ISRU) for Mars mission can be applied by directing the CO produced from the electrochemical cell to a Fischer-Tropsch (FT) reactor. The Mars chemical plant consists of the electrochemical cell that produces pure gaseous O₂ and CO. The CO reacts with gaseous H₂ in the FT process to produce hydrocarbon and water. The hydrocarbon is separated and used as a fuel on Mars or a propellant for the return journey to Earth. The water can be potentially purified and converted via electrolysis to generate H₂ (recycled to the FT reactor) and O₂ for life support.

The FT synthesis was developed in Germany in World War II around 1925. The catalytic FT synthesis is a carbon chain building process according to the following reaction, $n\text{CO} + [n + m/2]\text{H}_2 \rightarrow \text{C}_n\text{H}_m + n\text{H}_2\text{O}$, [7]. The FT process reacts CO with H₂ to produce mainly aliphatic straight-chain hydrocarbons (C_nH_m). The distribution of the products depends on the catalyst and the process operating conditions. A typical FT processing conditions is iron-based or cobalt-based catalyst at 200-300 °C and 25-60 atmospheric pressure. The FT products have compatible autoignition characteristics and very low sulfur and aromatic content [8].

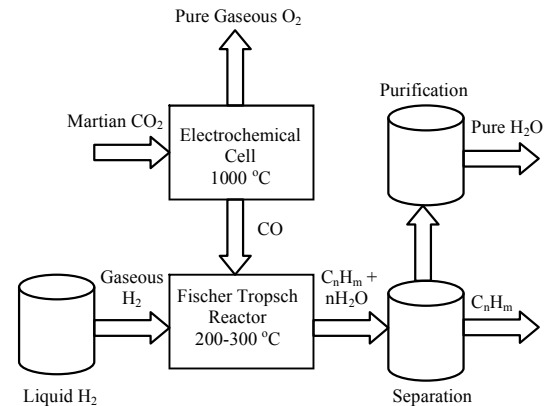


Figure 2. Schematic of Mars ISRU plant for O₂, fuel, and H₂O Production.

5. Energy and Economic Considerations

The Aspen Plus™ computer-aided design program can be utilized to perform a scale-up, economic analysis, costing, size, and electric and thermal power requirements to produce O₂ on the Martian planetary surface. The Aspen simulation will also aid in optimizing the configuration of the scaled up system in terms of maximizing energy efficiency and minimizing carbon deposition inside the reactor. Using experimental data, it will be possible to calculate the electrical energy requirement per unit volume of O₂. This value is subject to change, depending on the current density of the electrolyzer. In general, for electrochemical devices, there is an inverse relationship between energy efficiency and current density. Ultimately, systems engineers will have to strike a compromise between payload weight of electrolyzer and power generator versus the amount of time allowed to produce the O₂.

6. Conclusions

This paper outlines an approach for obtaining infinitely pure breathing O₂ from the Martin atmosphere via high temperature electrolysis on ceramic membranes. A tubular-type YSZ-based electrochemical cell is designed as means of extracting O₂ from the Martin atmosphere. YSZ is employed as the solid electrolyte, while porous layers of Ni/Co/YSZ cermet and Sr-doped LaMnO₃ are employed as cathode and anode respectively. The electrochemical cell operates at 1000 °C under voltage application, supplied by a stream of CO₂ at a potential pressure corresponding to Mars atmospheric conditions. Also, the produced CO from the electrochemical cell can be introduced in situ to a catalytic FT reactor where it reacts with gaseous H₂ producing hydrocarbon fuel and potentially purified water.

7. Acknowledgments

The authors acknowledge the support provided by the National Aeronautics and Space Administration through Glenn Research Center under contract No. NAG32751.

8. References

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High Temperature Electrolytic Conversion of CO₂ to CO and O₂: A Strategy for *In Situ* Resource Utilization on Mars



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Outline

- ISRU and rationale
- Importance of hydrogen
- Sources of O₂ and C
- Solid oxide-based CO₂ electrochemistry
- Sabatier reaction and syn-gas chemistry
- Systems considerations
- Conclusion

In Situ Resource Utilization (ISRU)

- Core component of Vision for Space Exploration
- Human life-support system replenishment
- Source materials (feedstock) for In Situ Fabrication and Repair (ISFR) technologies
- Source materials (composites, etc.) for radiation shielding and shelters
- Propellants—fuel and oxidant
- Source: Lunar and Martian regolith

Cost of Mars Mission

- All supplies brought from earth:

\$400-450 billion

- With integration of ISRU:

\$20-50 billion

ISRU displacements

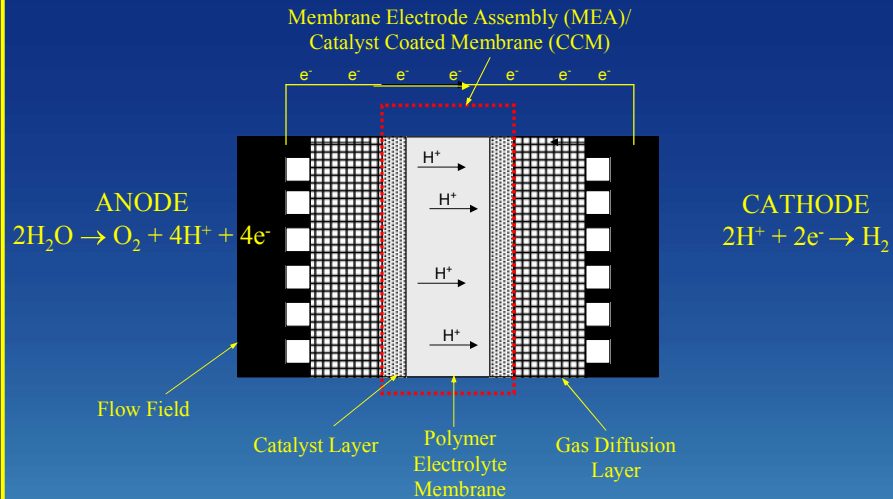
- Earth Return Vehicle
 - ▶ 6.3 metric tons LH₂ (CH₄ option to be discussed later)
 - ▶ ~50 metric tons LO₂
- Water: 30 kg/person/day
- Food: 1.5 kg/person/day
- Air replenishment: 1 kg O₂/person/day

Best scenario: find H₂O

Make H₂ and O₂ via electrolysis:



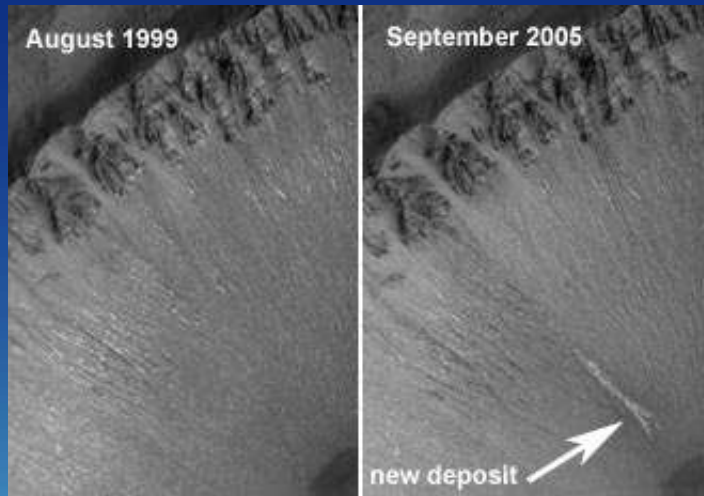
Polymer Electrolyte Membrane Electrolyzer



15 kW PEM Electrolyzer (Lynntech)



Is there water on Mars?



South Polar Cap on Mars



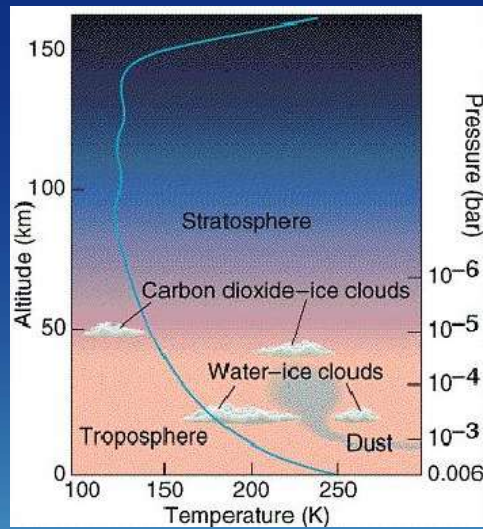
Mars Global Surveyor, 4/17/2000

Composition of Mars Atmosphere

95.7%	CO ₂
2.7%	N ₂
1.6%	Ar
0.13%	O ₂
0.07%	CO
0.03%	H ₂ O
trace	Ne, Kr, Xe, O ₃ , CH ₄

avg surface atmospheric pressure: 7 millibars
(< 1% of Earth's atmosphere)

Typical Atmospheric Conditions on Mars



Encyclopedia of Astrobiology, Astronomy, and Spaceflight

**So is there liquid
water on Mars?**

**Water ice in crater at Martian
north pole**



ESA Mars Express, 5/28/05

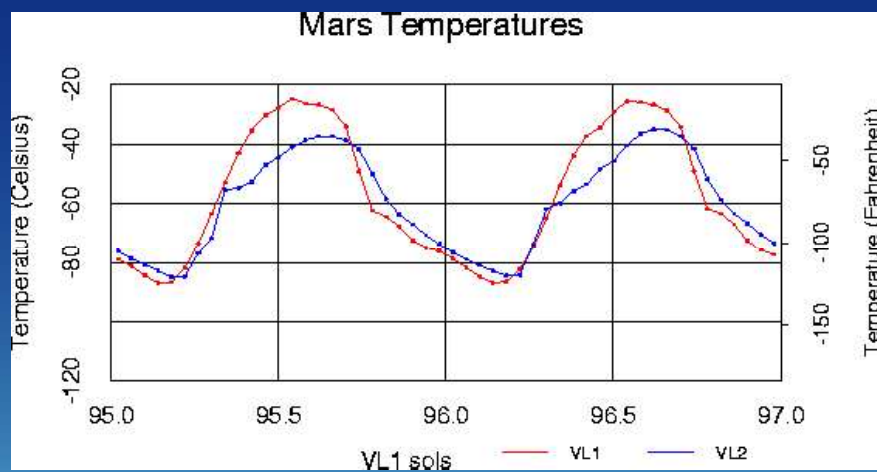
Surface temperatures vary widely

Average temperature on Mars ~218 K (-55 C, -67 F)

Winter pole extreme: 140 K (-133 C, -207 F)

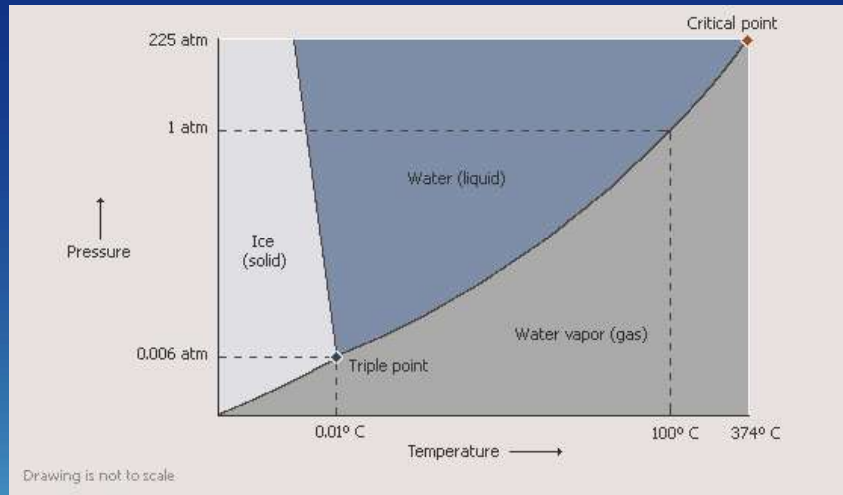
Summer equatorial extreme: 300 K (27 C, 80 F)

Local temperatures on Mars can fluctuate 80-100 °F/day



Viking Landers 1 & 2, 1976

Phase Diagram for Water



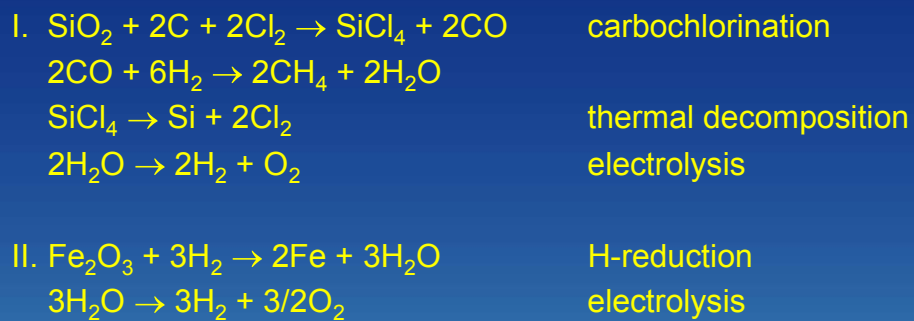
South Polar Cap of Mars



Mars Global Surveyor, 4/17/2000

**ISRU without water: bring
extra H₂ and do chemistry!**

**Martian Regolith: Another
Possible Source of O₂**



Both involve 1000 °C processes

Composition of Mars atmosphere is mostly CO₂

95.7%	CO ₂ ; molecular density actually 30x greater than Earth's
2.7%	N ₂
1.6%	Ar
0.13%	O ₂
0.07%	CO
0.03%	H ₂ O
trace	Ne, Kr, Xe, O ₃ , CH ₄

avg surface atmospheric pressure: 7 millibars
(< 1% of Earth's atmosphere)

Electrochemical reduction of CO₂ over doped solid oxide electrolytes



Tubular Ceramic Electrolytes

Most common example:

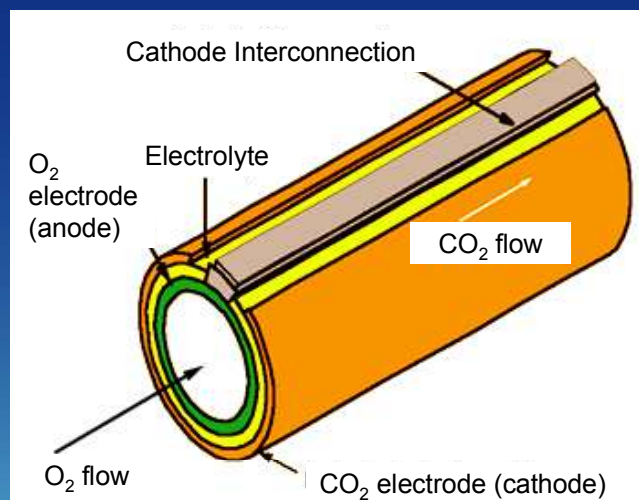
ZrO_2 doped with Y^{+3}

ion conductivity at $1000\text{ }^\circ\text{C}$

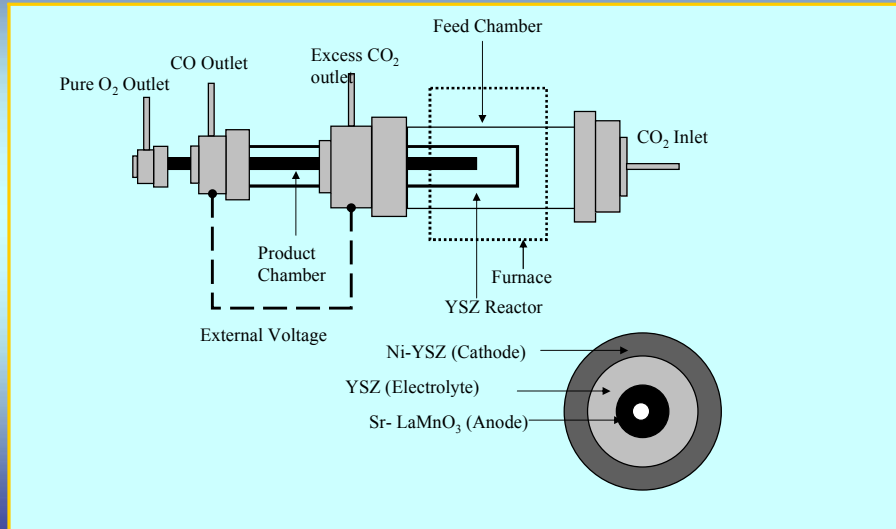
$= 0.1\ (\Omega\text{-cm})^{-1}$



Tubular CO_2 Electrolysis Cell



Schematic of Individual YSZ Electrolysis Cell



Synthesize CH₄ propellant from H₂ and CO₂

Sabatier reaction



Get O₂ via electrolysis

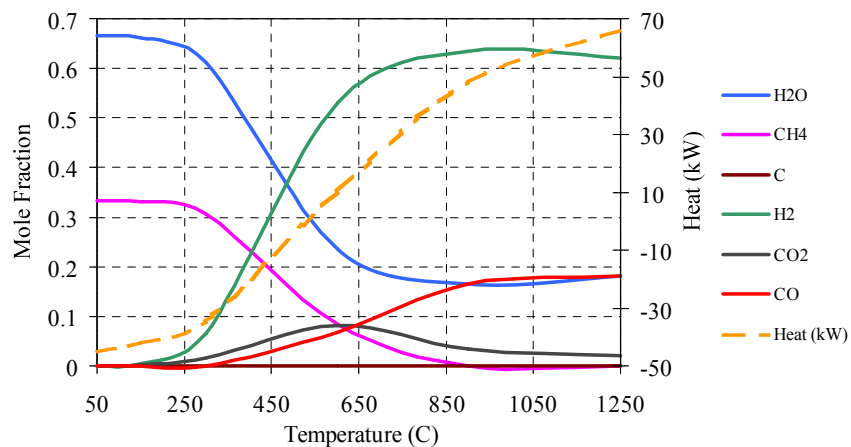
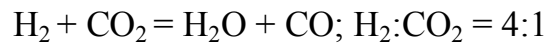


Effectively doubles energy content of available fuel

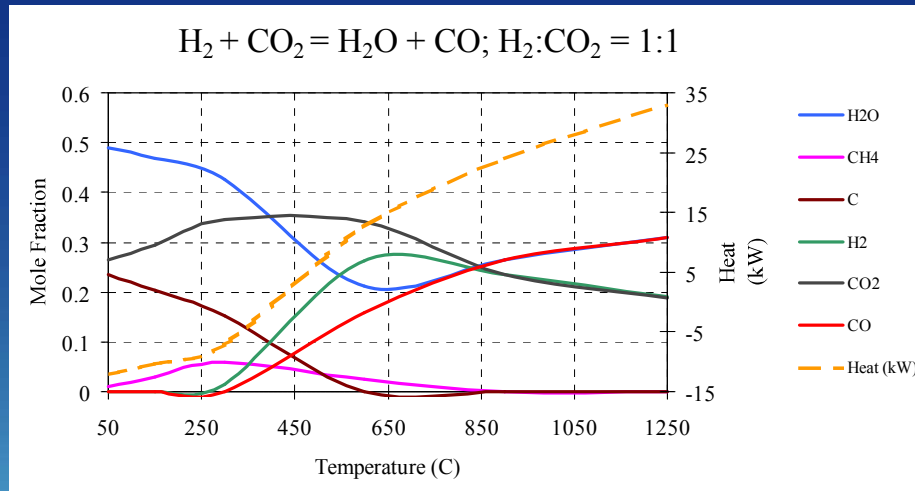
Cautionary Notes on Sabatier

- Still need H-independent O₂ production to fulfill combustion stoichiometry:
 - $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$
- Still have to use cryocooler (b.p. -164 °C)
- Inverse relationship between yield and kinetics

H₂/CO₂ equilibria vs T

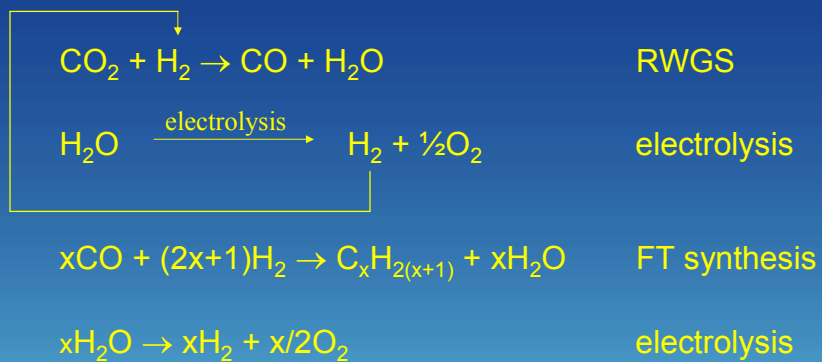


H₂/CO₂ equilibria under H₂-starved condition



Use H₂ for CO₂ partial reduction and FT synthesis

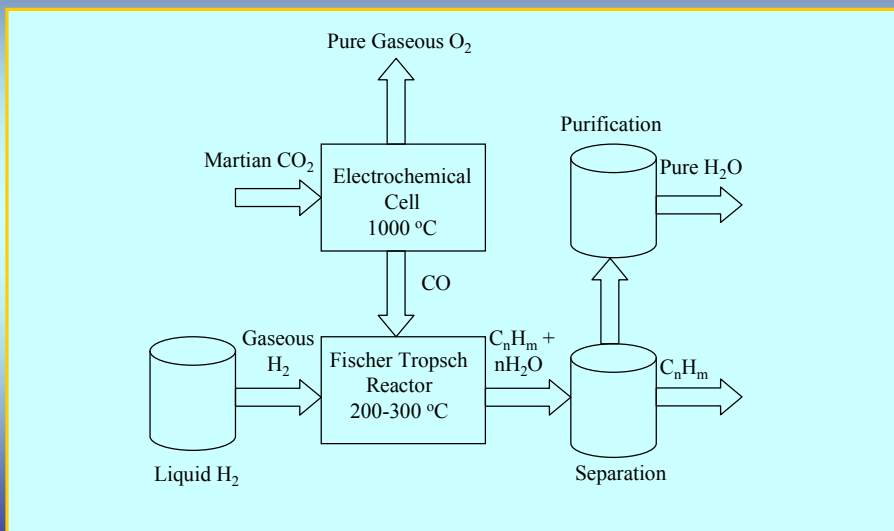
Reverse water gas shift followed by Fischer-Tropsch synthesis and water electrolysis:



Physical properties of low MW alkanes

Fuel	Mp	Bp	Btu/lb	Btu/gal
Methane	-182	-164	23,825	92,862
Butane	-138.4	-0.5	21,085	106,027
Pentane	-130	36.1	20,864	109,279
Hexane	-95	69	20,724	114,456

Schematic of Mars ISRU plant for O₂, fuel, and H₂O Production



Advantages of High Temp Electrolytic Process

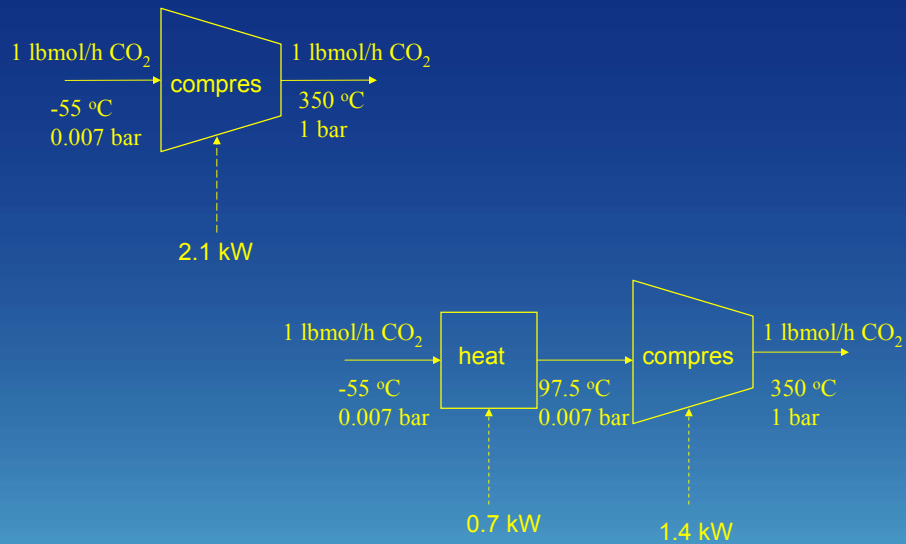
- Excellent separation of oxygen from the other gases.
- Solid electrolyte is noncorrosive (as opposed to molten salt electrolysis).
- The continuous electrolysis of CO₂ or H₂O, or a mixture of CO, CO₂, and H₂O, is possible.
- Less sensitive to impurities than lower temperature electrochemical processes.

Disadvantages of High Temp Electrolytic Process

- Thin ceramic layers are brittle, easily cracked or broken.
- Coefficients of thermal expansion of all components (electrodes, electrolyte, interconnect) must be closely matched.
- Gas-tight seals difficult to maintain.
- Interdiffusion of adjacent layers.
- Precipitation of carbon if P_{CO} becomes too large at intermediate T (Boudouard equilibrium).



Compression and Heating Requirements on Mars



Energy Sources

Need 100 kW continuously for ~ one year

Nuclear

Cassini: 32.8 kg ²³⁸PuO₂ delivering 628 W for 11 years

Wind energy: generally between 2-10 m/s at 0.007 atm
(up to 50 m/s during global dust storms)

Solar: would require 1.2 acres of PV panels

- average irradiance at the Martian surface: 345-575 W/m²
- 25% PV panel efficiency → 85-140 W/m²
- 24 hour, 37 min/ day; 6 h direct irradiance/day
- battery storage with 60% RT efficiency

Conclusion

- Locating and decomposing water via electrolysis would be the best application of ISRU on Mars.
- Liquid water may well be found at the receding edge of the polar ice caps; bring ice pick just in case.
- Direct CO₂ electrolysis at 1000 °C may be best nonaqueous method for deriving O₂.
- Syn-gas chemistry to produce C₄-C₆ alkanes can be stored and used at ambient temperatures.
- Would need ~1.2 acres of PV to power a propellant production plant.

Acknowledgement

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