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An Introduction to Mars ISPP Technologies

Research Needs in Fire Safety for the Human Exploration and Utilization of Space

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Background

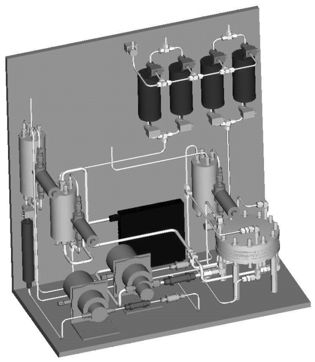
- ISPP is an enabling technologies for HEDS missions to Mars.
- $CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O \xrightarrow{\text{Electrolysis}} 2H_2 + O_2$

(Sabatier Reaction with Water Electrolysis)

- Supplemental oxygen production required
  - 2 CO2 $\rightarrow$ 2 CO + O2

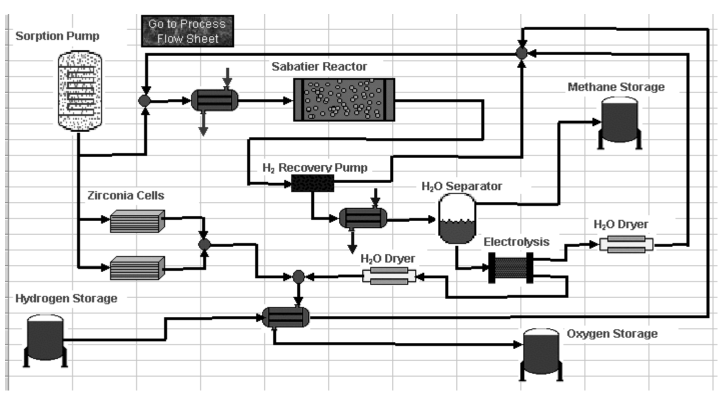
Sabatier Reactor / Water Electrolysis

2nd Generation SR/WE Test Bed



- Exothermic Reaction, must be cooled
- Operating Temp: 300°C
- Requires Hydrogen Transport and Storage
- CO2 Freezer
- Cryo-coolers and Storage for LCH4 & LOX (common bulkhead storage tank?)

Sabatier Reactor Flow Chart



Alternative Fuels?

- Methane requires 4 atoms of Hydrogen
- Lower hydrogen content improves ISPP weight savings ratio

	H/C	Tons H2
■ Methane	4	5.1
■ Ethane	3	4.7
■ Ethylene	2	3.4
■ Benzene	1	2.1

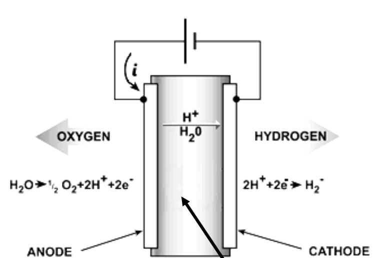
Fuels and Oxidizer

- ISPP saves weight by producing fuels on Mars (5 – 8 tons over H2 brought)
- Producing fuels other than methane is still in early development
- Producing oxygen saves 70+ tons for MAV oxidizer.
- Life support and mobile power further increases savings.

Oxygen Production

- All systems use electrolysis to produce oxygen
  - Electrolysis of water from a reactor
  - Direct electrolysis of CO2
- Electrolytes can be water, non-aqueous liquids or solids.
- 4 e- / O2 molecule establishes current
- Operating voltage and temperature establish efficiency and materials of construction.

PEM Cell Electrolyzer Schematic



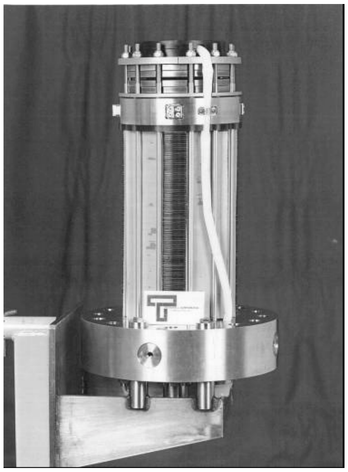
From Hamilton-Sundstrand Web site

•Nafion is preferred PEM

•Platinum group metals used for electrodes, deposited on PEM

• Uses Proton Exchange Membrane (PEM) to separate H2 and O2

Electrolyzer Stack for Seawolf Submarine



- 100Cells/Stack (7 Cells / Inch)
- 50-kW (360 SCFH-H_2)
- High Current Density (1000 A/Ft^2)
- Over 100,000 hours operation
- H_2 & O_2 at 3000 psi

Courtesy of J. Kosek, Giner, Inc.

Zirconia Solid Electrolyte Cell

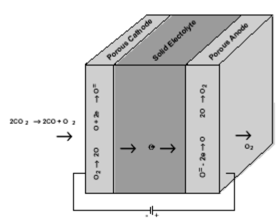


Figure 2. Principle of operation of a solid oxide electrolyzer.

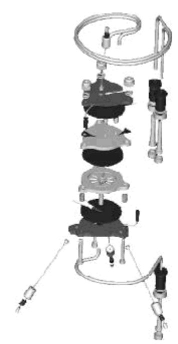


Figure 3. Exploded view of an electrolyzer assembly.

Sridar, Gottmann, and Baird, AIAA Publication

Zirconia Pros and Cons

- Direct electrolysis of CO2 with pure O2 separated.
- Good efficiency, about 1.5 V, similar to water electrolysis.
- Very high operating temperatures, 800 - 1000°C.
    - All ceramic construction in high temp zone.
    - Fragile, easily cracked.
- Membrane failure could threaten entire output.
- Has been proposed for water vapor electrolysis

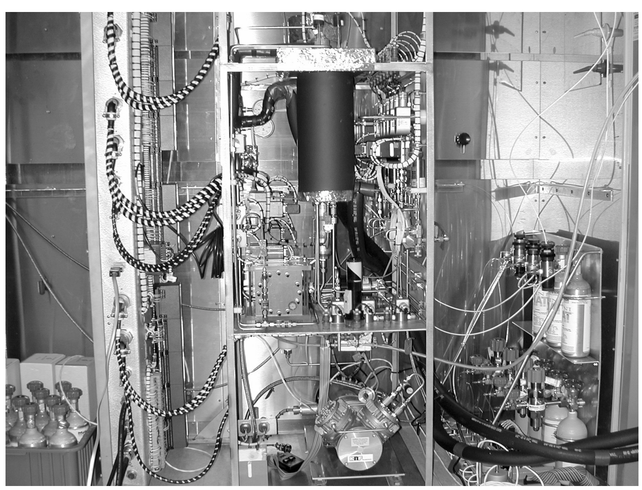
Possible Advantages for an Alternate System

- Lower temperatures
    - <700°C…use metals in construction
    - <270°C …use polymers and elastomers
    - < 31°C …liquid CO2 as co-solvent
- Lower operating voltage…better efficiency
- More rugged construction, a robust assembly

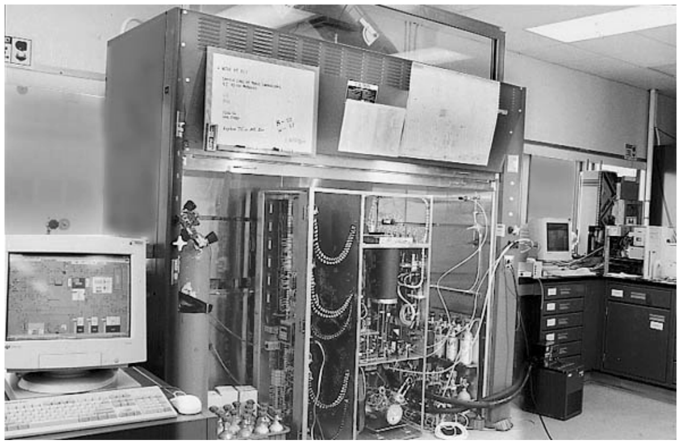
Reverse Water Gas Shift (RWGS)

- $CO_2 + H_2 \leftrightarrow CO + H_2O$ (RWGS Reaction)
- Equilibrium constant is only 0.1, must remove products to drive reaction to completion.
- Reactor requires pump, permeation filter and heat exchangers to run.
- Electrolysis of water requires as much energy as zirconia.
- Rugged and low temperature, but complex and heavy.

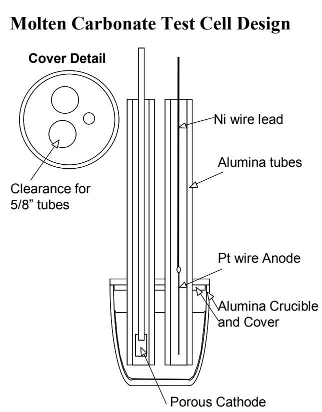
RWGS Reactor Assembly



RWGS Test Bed



Molten Carbonate Electrolysis



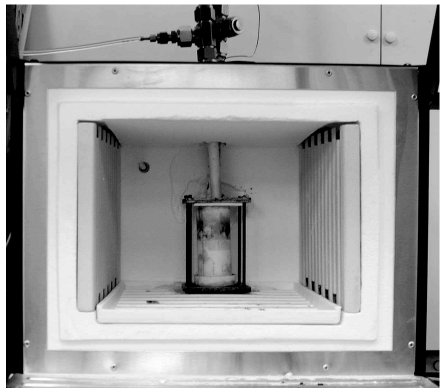
Anode Reaction

$2\ CO_3^{-2} \leftrightarrow 2\ CO_2 + O_2 + 4e^-$

Cathode Reaction

$2\ CO_2 \leftrightarrow CO + CO_3^{-2}$

Molten Carbonate Test Fixture



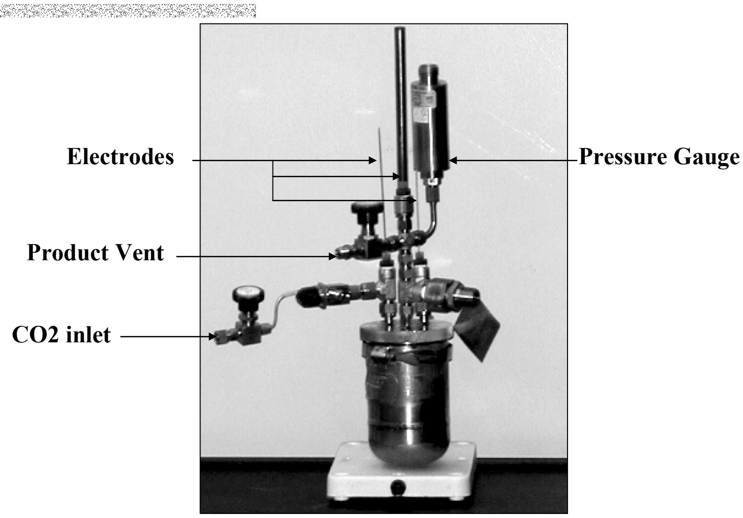
Molten Salt Results

- •Li_2O in Chloride melt $\longrightarrow$ Pure oxygen at anode
  - •Current decreased to zero over a few hours
  - •Carbonate formation at cathode is likely
- •Carbonate electrolysis at anode yields 2:1, CO_2/O_2
  - •Sustained reaction for 7 days
  - •Minimal loss of O_2 production
  - •Temperature of operation: 550°C
  - •Cell voltage: ~ 0.8 Volts
  - •Platinum anode and cathode

Non-Aqueous Solvents

- Potential Advantages
  - Wide electrochemical window
  - Low temperature operation
  - CO_2 a potential co-solvent
- Solvents Surveyed & Results
  - Acetonitrile, DMSO, Propylene Carbonate
  - C-V curves show CO_2 reduction
  - No evidence for oxide or carbonate solubility
  - No oxygen generation at anode

Liquid CO_2: Electrochemical Reaction Vessel



Pro and Cons of Liquid CO_2

- Advantages:
  - Very high electrode concentrations → High current density
  - No porous gas cathode required → Simplified Cathode
  - If carbon forms → Twice as much O2 out/ CO2 in

- Disadvantages:
  - CO2 at high pressure mixed with electrode products
  - If carbon forms → must remove carbon periodically
  - If CO forms, separation technology is critical for life support uses.
  - No known cell compartment separators that would transport carbonate, and simplify product separation.

Ionic Liquids

- What are they?
  - Low melting point ionic salts. By using large anions and cations, a low temperature melt with conductivity similar to molten salts can be obtained.
  - Examples include pyridinium and imidizolium cations with anions such as PF_6^-, BF_4^-, and many others.
- Desirable Properties
  - Low temperature (-100 - 300°C).
  - High conductivity (low I*R losses).
  - Wide electrochemical window.
  - Non-volatile.
  - Miscible with or high solubility for CO_2.

Hurdles for Ionic Liquids

. Find one that carbonate is soluble in, or carbonate is the anion.
(Working with Prof. R. Rogers @Univ. of Alabama)

•Confirm CO_2 reduction, preferably to CO.
•Confirm O_2 production at anode (2:1, CO_2/O_2).
•Confirm long term stability and balanced cell reactions.
•Minimize cell voltage.
  •Electrode materials
  •Minimize I*R drop → thin electrolyte film, highly conductive.
•Construct porous support for electrolyte (similar to carbonate).
•Construct cell manifolds and multi-cell assemblies.

Mobile Oxide Ceramic Membranes

•Similar to Zirconia, but lower temperature.
•Demonstrated on NO_x electrolysis.
•Oxide ion from CO_2 reduction stabilized by Ceramic Lattice structure.
•Operating temperatures 500 - 700°C allows use of metal manifolds and seals.

Working with Prof. E. Wachsman at Univ. of Florida to prove feasibility.

Oxygen Production Conclusions

- Oxide ions as an electrochemical intermediate are only viable in mobile oxide ceramics.
- Carbonate is formed from CO2 reduction in molten salts, and produces a 2:1 CO2/O2 mixture at the anode.
- Other products of CO2 reduction do not produce O2 at the anode.
- Carbonate melts and mobile oxide ceramics are probably useable below 700ºC for CO2 electrolysis.
- Ionic liquids may be able to operate below 200ºC if one compatible with carbonate can be found.

Acknowledgements

- KSC researchers involved in ISPP work presented here
  - Mike O'Neal Bill Larson Clyde Parrish
  - Bill Buttner Jan Surma Curtis Ihlefeld
- Approximately 50 workers have participated in ISRU related technologies at KSC, including biological research on plant growth chambers, Mars atmospheric test chamber, static charge experiments, ISPP and other technologies.