Improving the Recovery of Oxygen from Carbon Dioxide

Full Presentation *F0.1-0007-21*

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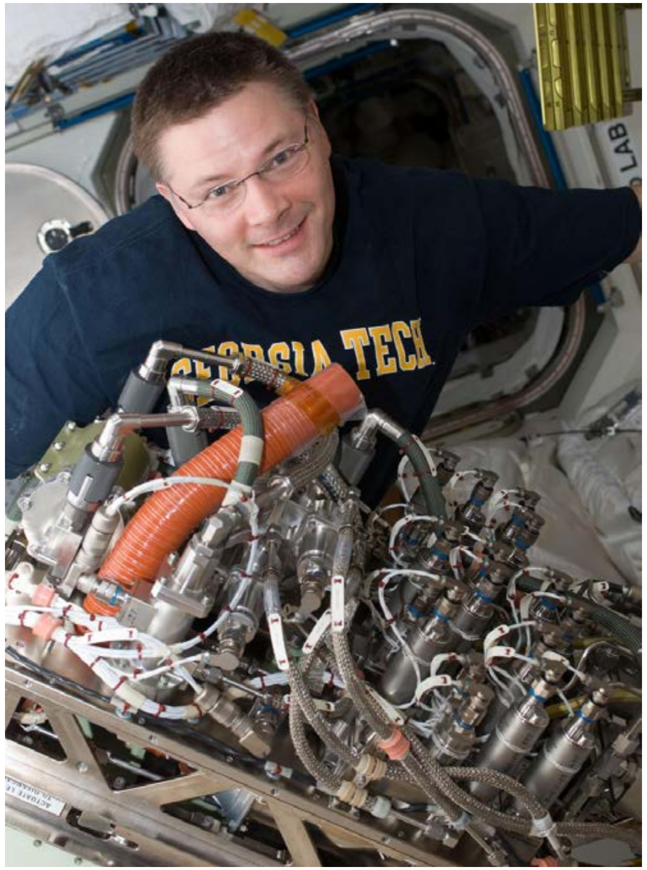
Background and Overview

- Oxygen is a critical life support system consumable for human spaceflight.
- On the International Space Station, oxygen is provided as compressed gas or by electrolysis of stored water.
- The mass of oxygen required for long duration human exploration missions can be prohibitive.
- Recovery of oxygen from metabolic carbon dioxide can reduce mission resupply requirements, providing benefit to long duration human exploration missions.
- This presentation will
  - o describe the state-of-the-art oxygen recovery technology used on the ISS.
  - o provide an overview of several alternative oxygen recovery technology investments by NASA to improve the percentage of oxygen recovered.
  - o summarize findings from trade studies comparing the equivalent systems mass estimates for life support system architectures using these alternative technologies.
- Please note: this presentation is limited to physicochemical technologies for use within pressurized spacecraft, and will not address in situ resource utilization (ISRU) nor biological systems.



Astronaut Doug Wheelock installs the Sabatier CO_2 Reduction Assembly (CRA) on ISS. The CRA was returned to Earth in 2018. ESA's Advanced Closed Loop System (ACLS) launched in 2018, contains a Sabatier reactor.

Sabatier: The ISS State of the Art for Oxygen Recovery from CO_2

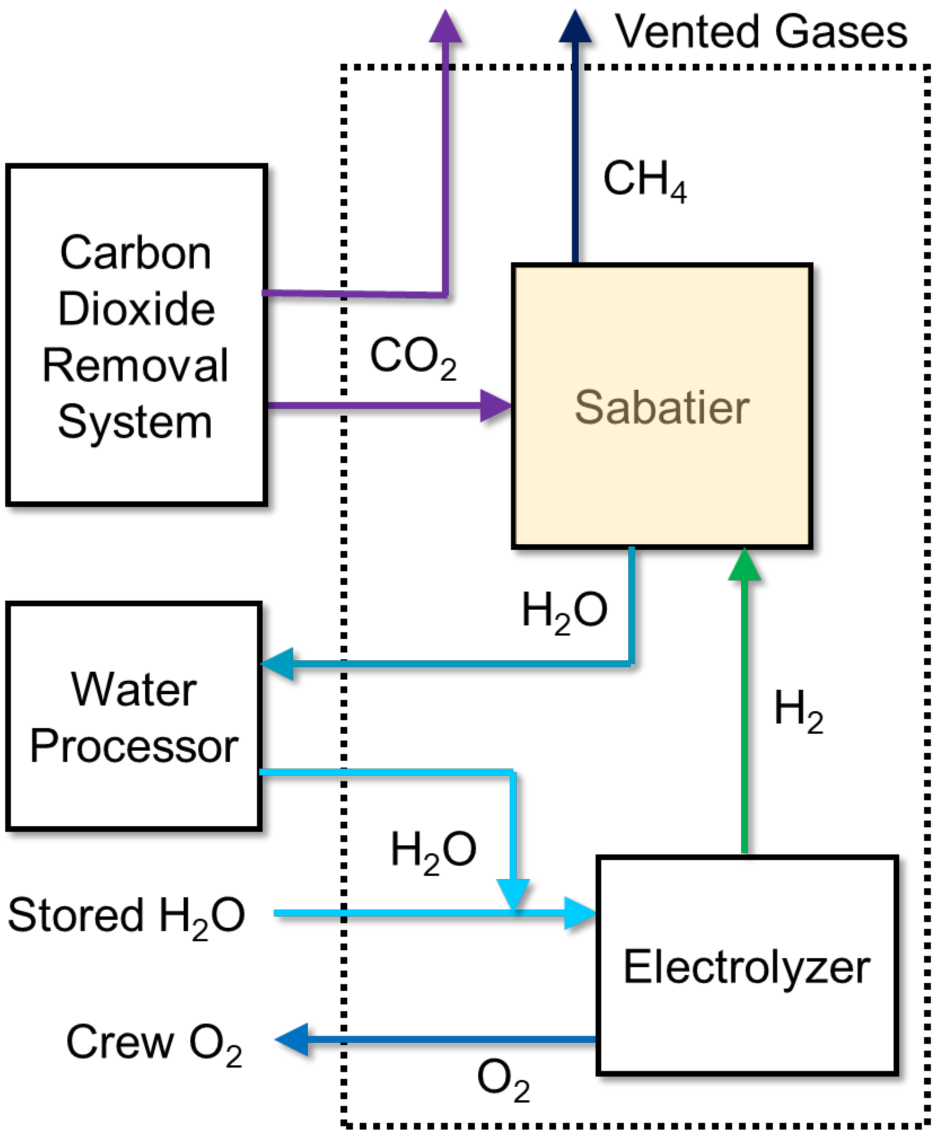
- **The state-of-the-art for oxygen recovery technology on the ISS is the Sabatier Reactor**
  - NASA's Carbon Dioxide Reduction Assembly (CRA)
  - ESA's Advanced Closed Loop System (ACLS)
- **Sabatier reactor operation**
  - Hydrogen (H_2) from an electrolyzer is combined with recovered Carbon Dioxide (CO_2) over catalysts at elevated temperature. Water (H_2O) and methane (CH_4) are produced as reaction products.

Primary Reactions

Sabatier: $CO_2 + 4\,H_2 \rightarrow CH_4 + 2\,H_2O$

Electrolyzer (OGA): $2\,H_2O \rightarrow 2\,H_2 + O_2$

- **The supply of H_2 is limited to that produced by the electrolyzer, based on the crew's oxygen requirement.**
- **There is insufficient hydrogen to react all the CO_2.**
- **Only about ~50% of the O_2 from metabolic CO_2 can be recovered based on the H_2 limitation.**



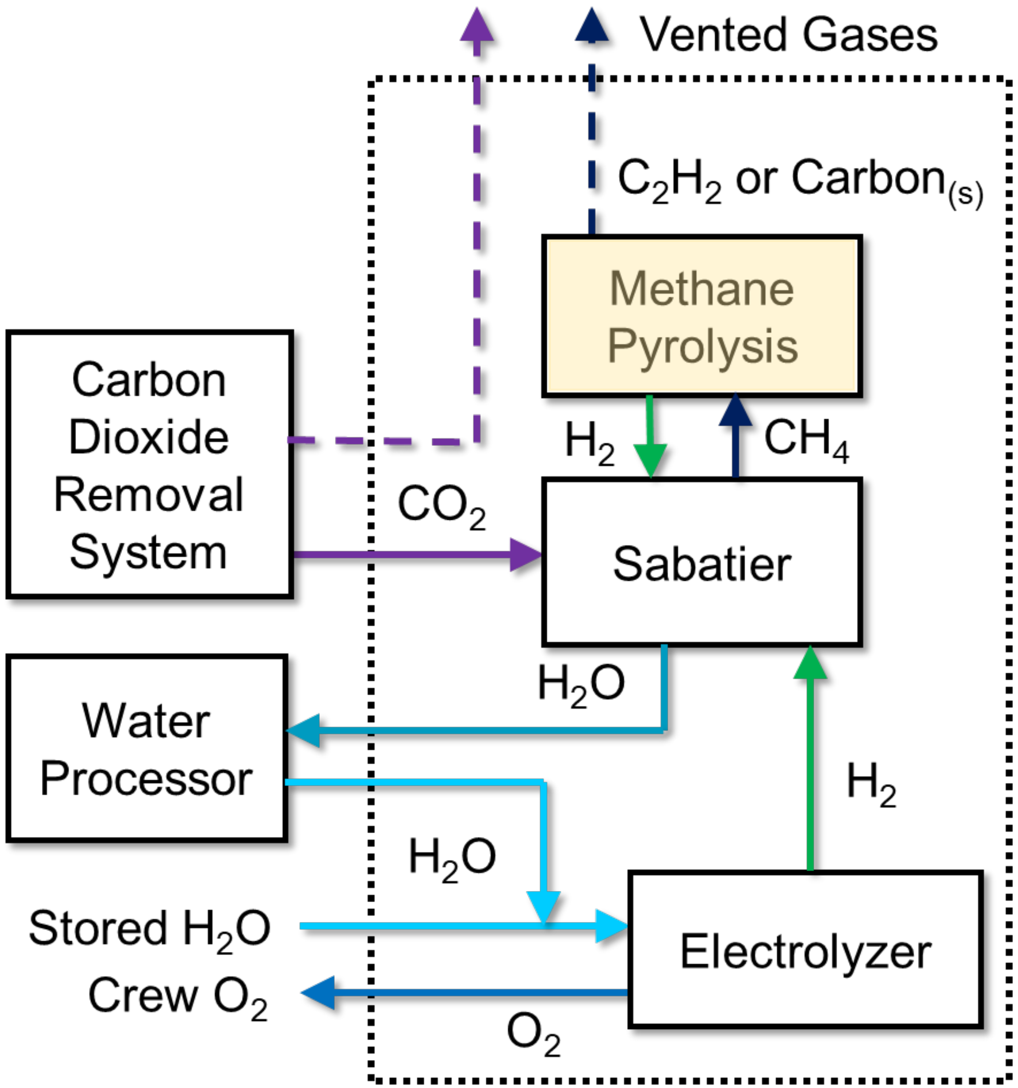
Methane Pyrolysis: Recovery of Hydrogen Lost as Methane

- The limitation of available hydrogen (H_2) for Sabatier can be overcome by recovery of H_2 by methane pyrolysis.
- Providing the additional hydrogen from resupplied compressed gas storage does not trade favorably.
- A separate processor is required, adding an additional element to the Environmental Control and Life Support System (ECLSS) architecture.
- Two methane pyrolysis technologies are under investigation by NASA:

1) Plasma Pyrolysis Assembly - PPA
   - ➢ Degrades methane (CH_4) into hydrogen and acetylene.

     Reaction: $2\ CH_4 \leftrightarrow 3\ H_2 + C_2H_2$
   - ➢ Can approach 75% hydrogen recovery efficiency
2) Hydrogen Recovery by Carbon Vapor Deposition (CVD)
   - ➢ Degrades methane into solid carbon and hydrogen.

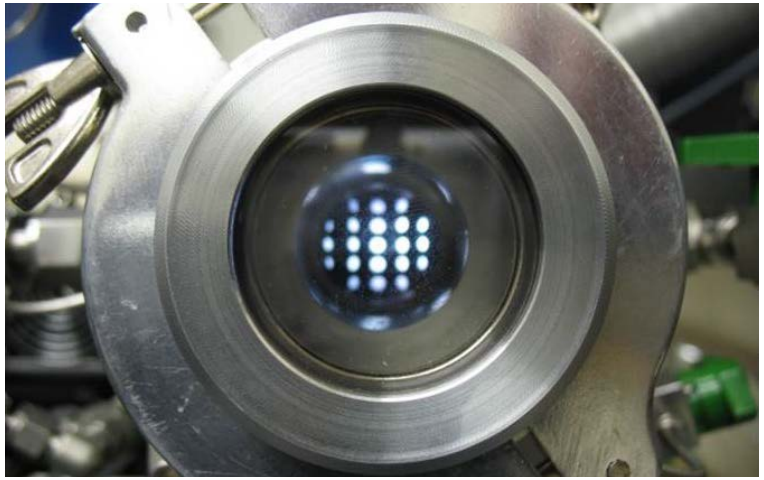
     Reaction: $CH_4 \leftrightarrow 2\ H_2 + C_{(s)}$
   - ➢ Can approach 100% hydrogen recovery efficiency.



Plasma Pyrolysis of Methane for Hydrogen Recovery (1 of 2)

PPA Operation

- The Plasma Pyrolysis Assembly (PPA) accepts methane from the Sabatier.
- The CH_4 is converted to H_2 and acetylene (C_2H_2) by partial pyrolysis in a microwave generated plasma.
- The H_2 is separated from the PPA product stream, composed of acetylene and other hydrocarbons and recycled back to the Sabatier.
- Acetylene is vented.
- Nuisance carbon soot is removed by a regenerable carbon trap.



The H_2-CH_4 Plasma is visible through observation port of the reactor

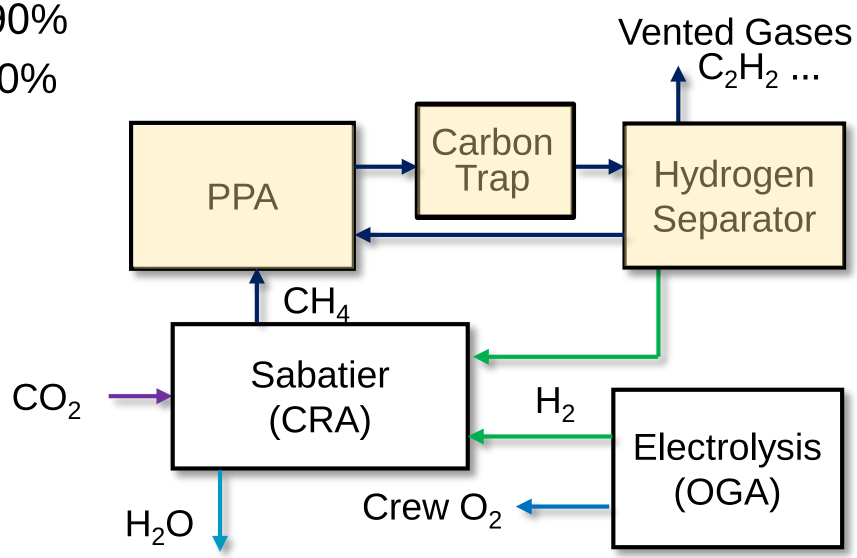
Selected Engineering Parameters:

- Operates at ~ 13.3 KPa (110 torr)
- Methane flow rate: 1400 SCCM
- Power: 750 W to 850 W
- Plasma Temperature: ~ 2000C
- Methane conversion (%): ≥ 90%
- Acetylene selectivity (%): ~90%

Targeted PPA Reaction $2CH_4 \leftrightarrow 3H_2 + C_2H_2$

Side Reactions

CH_4 Conversion to Ethane	$2CH_4 \leftrightarrow H_2 + C_2H_6$
CH_4 Conversion to Ethylene	$2CH_4 \leftrightarrow 2H_2 + C_2H_4$
CH_4 Conversion to Solid C	$CH_4 \leftrightarrow 2H_2 + C_{(s)}$
CO Production	$C_{(s)} + H_2O \leftrightarrow CO + H_2$
CO Production	$CH_4 + H_2O \leftrightarrow CO + 3H_2$



Plasma Pyrolysis of Methane for Hydrogen Recovery (2 of 2)

- NASA's investments in Plasma Pyrolysis were initiated in 2005, via a small business innovative research award to Umpqua Research Company.
- The technology has gone through several cycles of development.
- A "Third Generation" Plasma Pyrolysis Assembly (PPA) system was completed in 2013. NASA is currently testing and upgrading this system.

<u>Advantages</u>

- Gaseous byproducts are easily vented, making it microgravity compatible.
- Continuous operation.
- With a maximum hydrogen recovery rate of 75%, a theoretical oxygen recovery rate of 86% is possible when integrated with a Sabatier reactor.

<u>Challenges</u>

- Requires development of a hydrogen separator to purify H_2 from C_2H_2 and other hydrocarbons before sending it back to the Sabatier.
- Not all of the H_2 is recovered: some is lost as acetylene (C_2H_2).
- Production, management and removal of nuisance soot.
- Safety: High temperature reactor; use of microwave radiation.

<u>Maturity</u>

- The Technology Readiness Level (TRL) is approximately 5.
- Future work includes completion of development of a hydrogen separator and carbon trap before integration with a Sabatier reactor, to achieve a TRL 6.

Third Generation PPA

Hydrogen Recovery by Carbon Vapor Deposition

- NASA's second investment in methane pyrolysis is entitled "Hydrogen Recovery by Carbon Vapor Deposition (CVD)", under development by Honeywell Aerospace.
- NASA began sponsoring this work in 2017.
- Like the PPA, the CVD reactor accepts methane from the Sabatier.
- Under high reactor temperatures, methane decomposes into H_2 and solid carbon.
- Under this unique, controlled process, carbon infiltrates and deposits within preformed substrates, circumventing the formation of soot and particulate carbon.

<u>Advantages</u>

- Carbon management: Resultant densified carbon product is easily handled.
- Efficiency: The highest theoretical recovery of hydrogen from methane (100%). The carbon end product contains no residual hydrogen. An ECLSS architecture using this technology could theoretically achieve 100% recovery of O_2 from CO_2.
- Effluent gases can potentially be directly integrated with a Sabatier without gas separation. This is under evaluation.

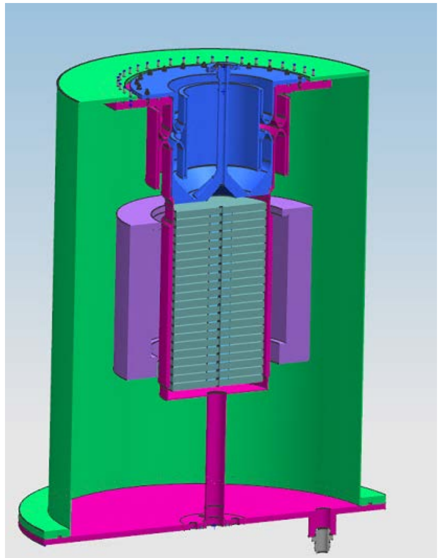
<u>Challenges</u>

- Mass and volume of consumable substrates
- Very high temperature reactor (~1200C)
- 2 reactor batch system requires crews intervention: while one reactor operates, spent substrates are removed from the second and fresh substrates are added.

<u>Maturity</u>

- A "TRL 5 ready" brassboard hardware will be delivered to NASA in 2021.

Soot-free Carbon Infiltrated Substrate Product



Reactor Concept with Vacuum Shell

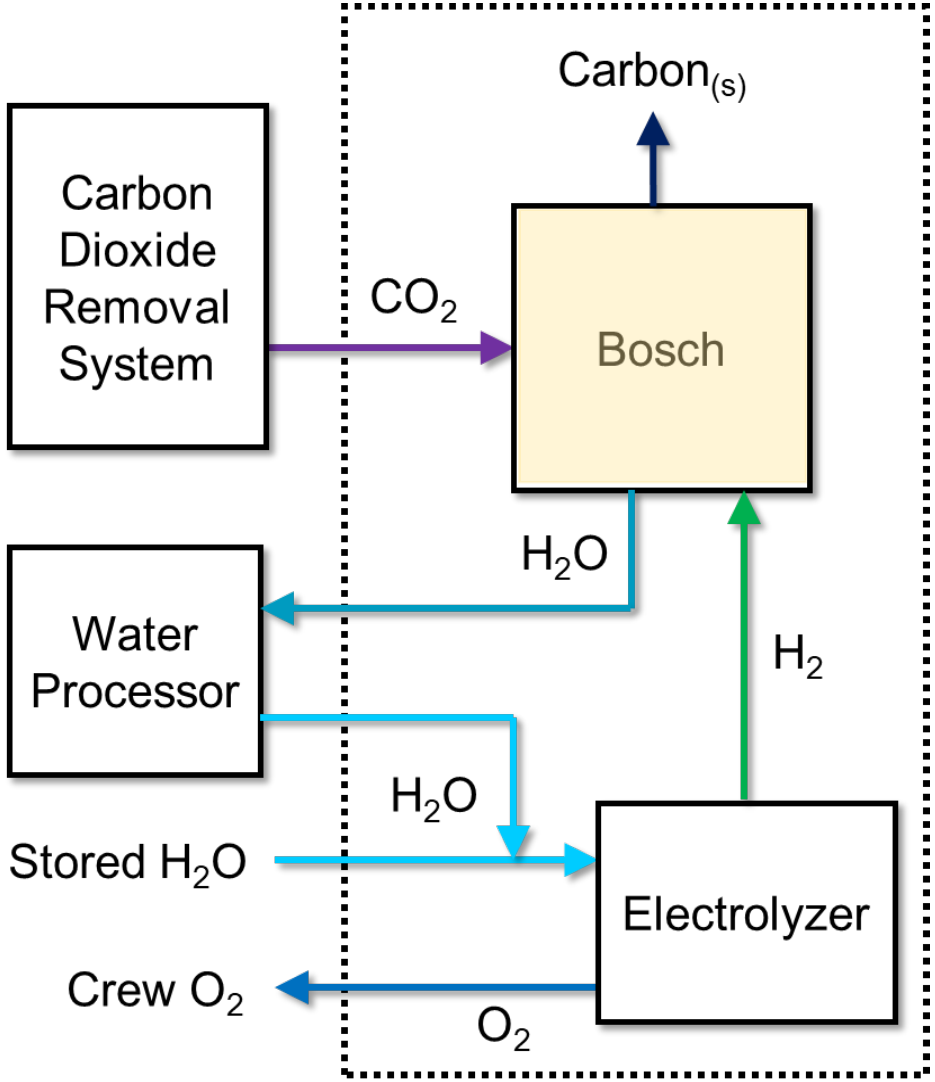
Bosch: A Replacement for the Sabatier

- **Replaces the Sabatier reactor in an ECLSS architecture**
  - o All H_2 in the reaction results in water production. Carbon is formed as a byproduct.
  - o Approaches 100% efficiency in recovery of O_2 from CO_2.
  - o Requires expendable catalyst as a consumable.

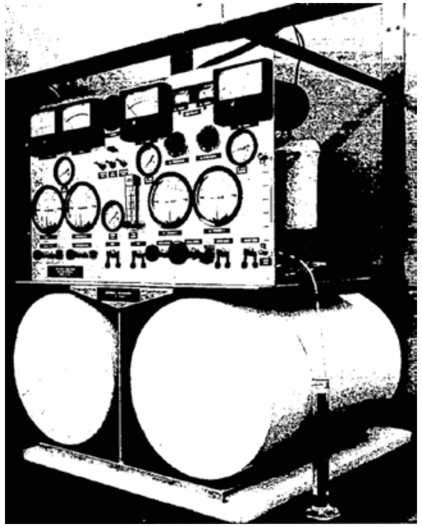
Bosch Reactions

RWGS:	$CO_2 + H_2 \leftrightarrow CO + H_2O$
CO Hydrogenation:	$CO + H_2 \leftrightarrow H_2O + C_{(s)}$
Boudouard:	$2CO \leftrightarrow CO_2 + C_{(s)}$
Net Bosch Reaction:	$CO_2 + 2H_2 \leftrightarrow C_{(s)} + 2H_2O$

- **Selected Bosch Technology Investments by NASA:**
  1) Horizontal Bosch and Vertical Bosch Systems
     - o 2 reactors in parallel: 1^{st} operating, 2^{nd} being serviced.
  2) Series Bosch Reactor
     - o Two reactors in series: 1st optimizes RWGS reaction, 2^{nd} reactor optimizes carbon formation reactions.
  3) Continuous Bosch Reactor
     - o Single continuously operating reactor.



Bosch History



General Dynamics Prototype

“Vertical” Bosch

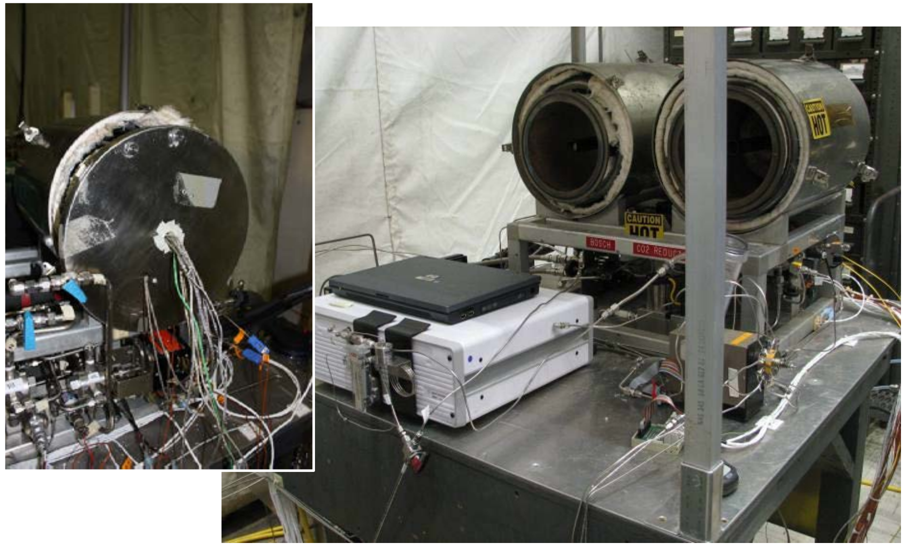
Early investments in Bosch technology by NASA started in the 1960’s.

Horizontal Bosch

- Initial prototype was built by General Dynamics in 1970. Life Systems produced an updated version in 1980’s.
- Dual reactor system.
- While one reactor was operating, the other reactor was in maintenance mode to remove carbon and replenish catalyst.
- Uses steel wool catalyst.
- 650°C to 688°C operating temperature.

Vertical Bosch

- Developed in the 1990’s by Life Systems.
- Dual reactor system.
- Nickel wool catalyst.
- Operates at about 565°C.
- The Vertical Bosch was tested against a Sabatier for use on Space Station, but ultimately the Sabatier was chosen.



Life Systems “Horizontal Bosch” Test Stand at MSFC

Challenges

- High use of catalyst & other consumables
- Low carbon packing density
- Low single pass efficiency
- Nuisance carbon & carbon management requiring regular maintenance
- Power/Thermal Management

Maturity

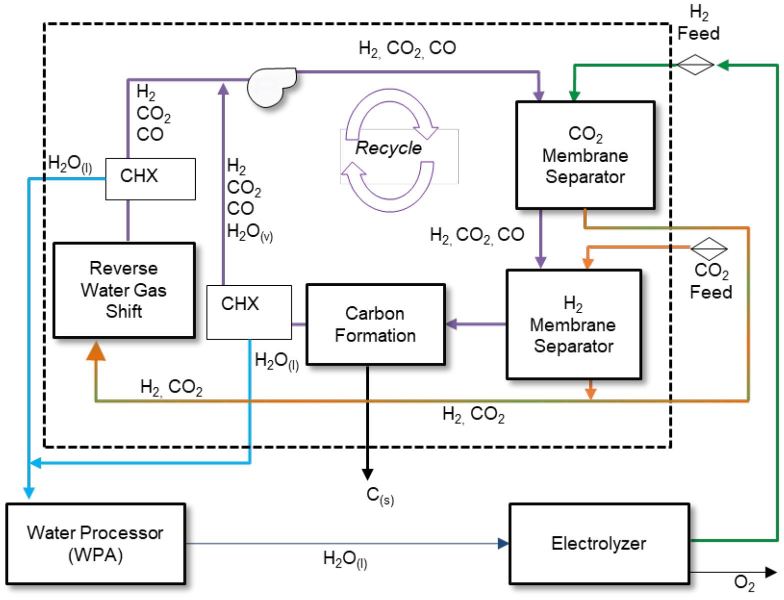
- TRL is 4 - 5

Series Bosch

- Development began around 2008.
- Two different reactors are in series to optimize the two types of reactions:
  - ➢ RWGS is optimized using a Nickel catalyst and is operated at ~650°C.
  - ➢ Carbon Formation is optimized using an Iron catalyst and is operated at ~550°C.
- Requires two gas separation membranes:
  - ➢ CO_2 separation & H_2 Separation.
  - ➢ A minimum of 34 kPa delta across membranes is required.
  - ➢ The RWGS is operated at 55 kPa and the CFR is operated at 93 kPa.
  - ➢ Sub-ambient pressures mitigate any leakage to the outside atmosphere.

Maturity

- A TRL 4 breadboard has been built and tested.
- A TRL 5 brassboard design is complete.



Series Bosch Breadboard (above) & schematic (left)

Advantages

- Potentially lower catalyst use and higher single pass efficiency due to optimized reactors.

Disadvantages/Challenges

- High complexity
- Power Requirement/Thermal Management
- Carbon buildup causes pressure drop
- Nuisance carbon
- Reactor maintenance & crew time

Issues Common to All Bosch Systems

Continuous Bosch Reactor

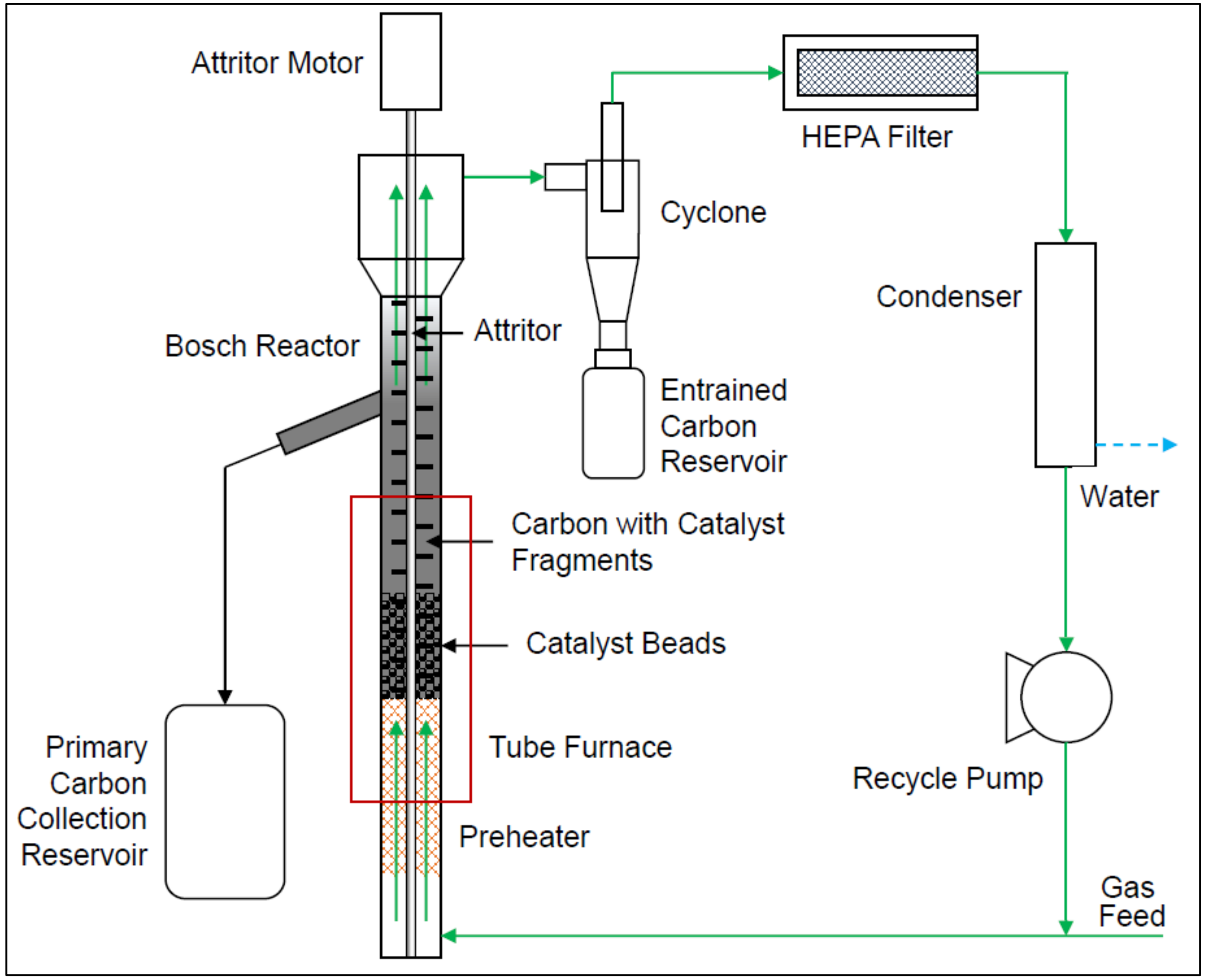
- Under development by Umpqua Research Company
  - Novel metallic catalysts were developed in 2011.
  - Reactor development was initiated in 2015.
- A novel design allows continuous operation.
  - Catalyst is fed into the reactor as needed.
  - Attritor stirs catalyst & prevents carbon clumping.
  - Carbon exits at port & collects in replaceable bag.
  - Cyclone separator removes suspended carbon from effluent gas stream.

<u>Advantages</u>
- Reduced catalyst consumption
- Improved carbon handling
- Less maintenance/crew time

<u>Challenges</u>
- Potential clogging of frits and filters
- Power Use/Thermal Management

<u>Maturity</u>
- TRL 4 breadboard was built and operated.
- High fidelity brassboard hardware has been designed.

Catalyst beads, particulate carbon & attritor are visible at base of subscale reactor

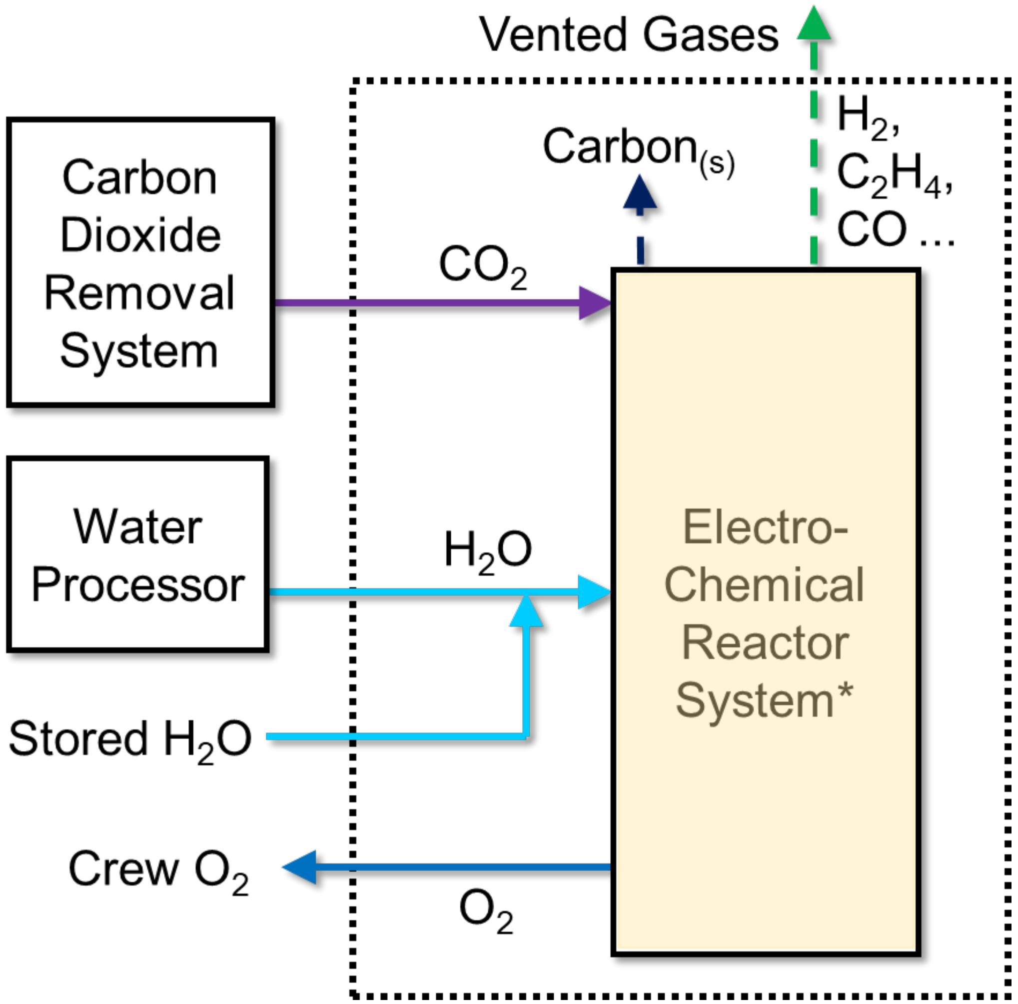


Schematic of Continuous Bosch Reactor & Gas Flow Loop

Electrochemical Reactors

- Direct generation of oxygen from CO_2.
- May eliminate need for a separate water electrolyzer (OGA), simplifying an ECLSS architecture.
- Can be coupled with carbon formation reactors* (CFR) to improve overall efficiency, at the expense of additional mass and complexity.
- Several technologies were investigated starting in 2015 in response to a NASA Solicitation.

1) Solid Oxide Co-Electrolysis (SOCE)
   - o Very high temperature ceramic electrochemical cells
   - o NASA Glenn (GRC) with pH Matter, Inc.
2) Microfluidic Electrochemical Reactor (MFECR)
   - o Ambient temperature electrochemical cell
   - o University of Texas at Arlington with NASA MSFC
3) Ion Exchange Membrane Electrolysis (IEME)
   - o Ambient temperature electrochemical cell
   - o University of Delaware, with NASA GRC



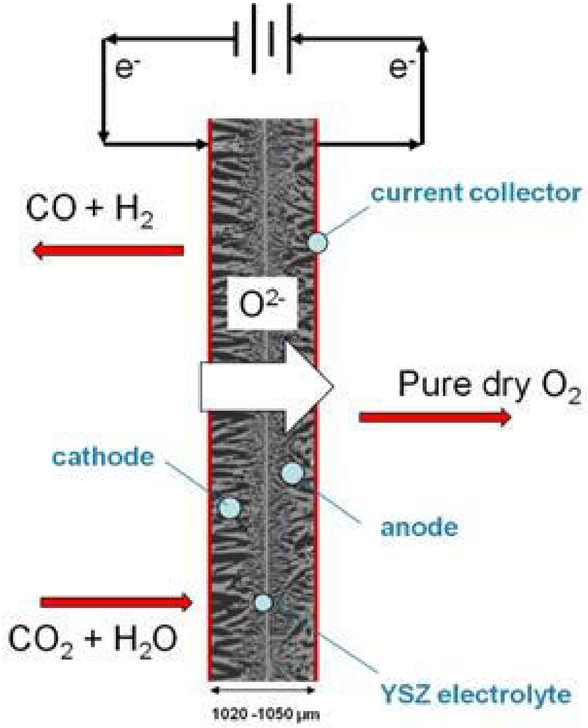
Solid Oxide Co-Electrolysis (SOCE)

Highlights
- Has heritage from solid oxide fuel cell development.
- Made of yttria-stabilized zirconia (YSZ) between electrode layers.
- Takes advantage of selective oxygen conduction through ceramics at high temperature.
- Theoretical oxygen recovery rate: 100% with a CFR; 50% without.

Advantages
- Pure, dry oxygen output
- Solid state reactor
- Water is conserved (SOCE + CFR)

Challenges
- Very high temperatures (800°C - 850°C)
- Differential thermal expansion
- Carbon management (CFR)
- Power Use/Thermal Management

Maturity
- TRL 4 breadboard was built & operated.



Schematic of Cell Operation

Primary Reactions

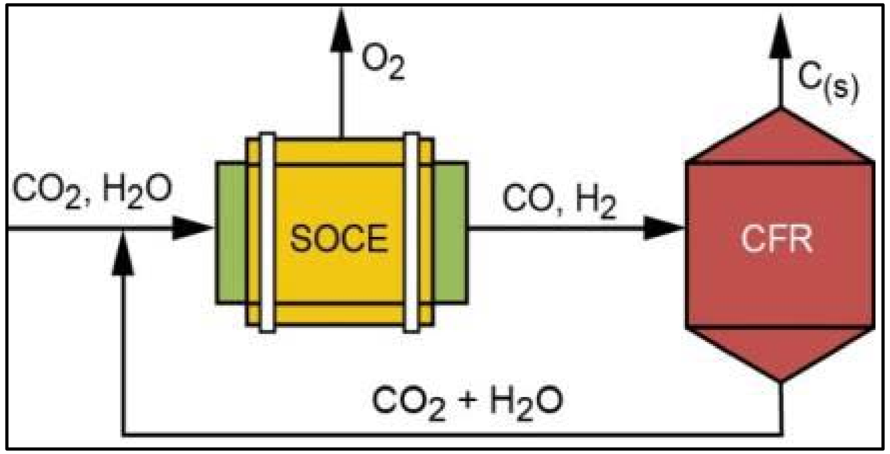
SOCE:
$2\ H_2O \rightarrow 2\ H_2 + O_2$
$2\ CO_2 \rightarrow 2\ CO + O_2$
$CO_2 + H_2 \leftrightarrow CO + H_2O$

CFR:
$CO + H_2 \leftrightarrow C(s) + H_2O$
$2\ CO \leftrightarrow C(s) + CO_2$

Net Reactions

SOCE+CFR: $CO_2 \rightarrow O_2 + C_{(s)}$

SOCE Only: $CO_2 + H_2O \rightarrow O_2 + CO + H_2$

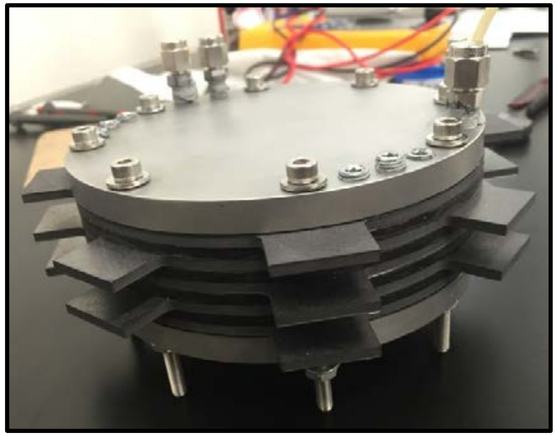


SOCE Integration with CFR

Microfluidic Electrochemical Reactor (MFECR)

Highlights

- Water and CO_2 react to form oxygen and ethylene.
- Novel design combines CO_2 conversion and water electrolysis into same electrochemical cell.
- Uses unique copper oxide–copper bromide electrochemical films.
- These electro catalytic films at electrodes serve as gas liquid contactors.
- Low temperatures enhance conversion of the intermediate CO to hydrocarbons.



Prototype Cell

Primary Reactions

$2\ H_2O \rightarrow 2\ H_2 + O_2$

$2\ CO_2 + 2\ H_2O \rightarrow C_2H_4 + 3\ O_2$

Maturity

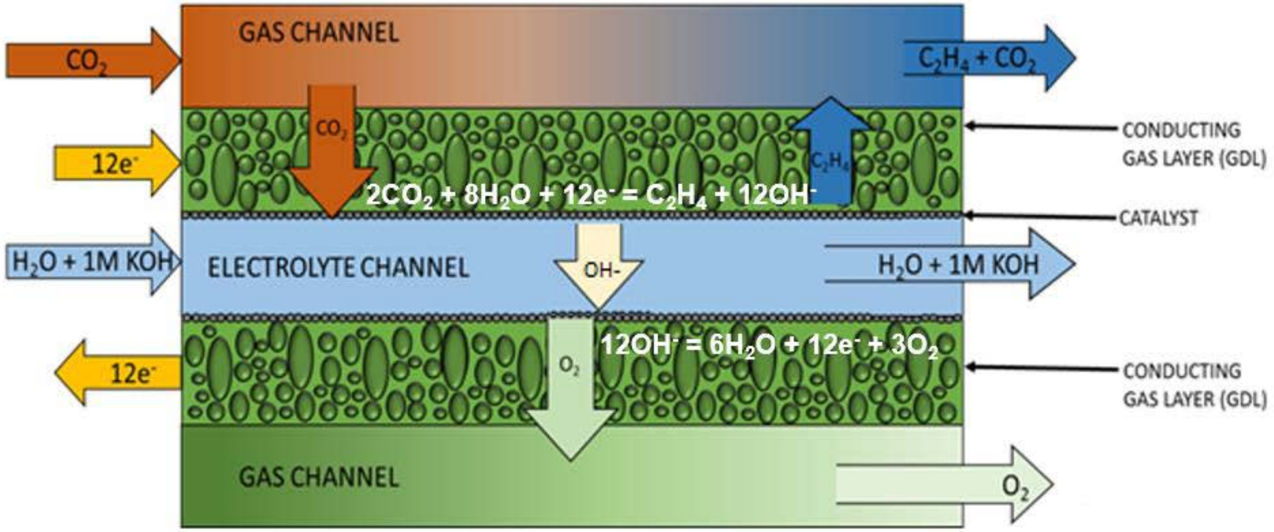
- A TRL 4 laboratory cell was evaluated.
- An Engineering Development Unit is under development.

Advantages

- Low temperature solid state reactor (3 - 5°C)
- High theoretical efficiency (up to 73%) for oxygen recovery from CO_2
- CFR and OGA not necessary

Challenges

- Selectivity for ethylene over other hydrocarbons (ethane, methane, propylene)
- Water electrolysis as a competitive reaction
- Electrode life



Schematic of electrochemical CO_2 reduction in the MFECR

Ion Exchange Membrane Electrolysis (IEME)

Highlights

- CO_2 is reduced to O_2 and CO at ambient temperature.
- Utilizes a novel polymer-electrolyte membrane electrolysis cell incorporating a nanoporous silver catalyst.
- CO can be re-converted to CO_2 & $C_{(s)}$ using a Catalytic Bed Reactor or CFM.
- A gas liquid contactor is necessary to dissolve gaseous CO_2 in electrolyte.
- Theoretical oxygen recovery rate: 100% with a CFR; 50% without.

Advantages

- Low temperature solid state reactor
- Directly produces O_2 (OGA not necessary)

Challenges

- Gas liquid contactors to achieve necessary concentrations of dissolved CO_2 in electrolyte
- Cell life and efficiency (to drop mass & volume)
- Integration and operation of a CFR

Maturity

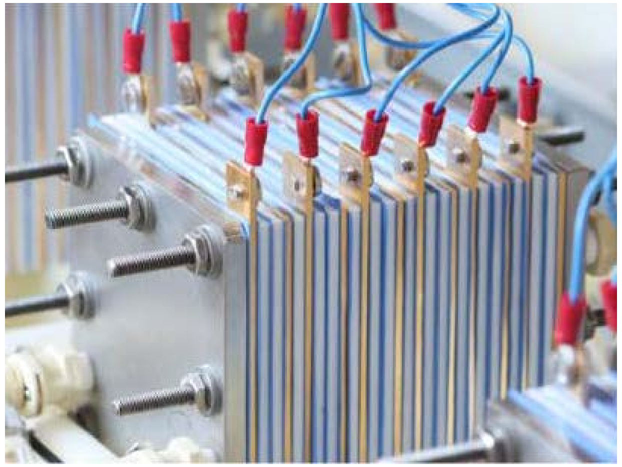
- TRL 4 breadboard components were evaluated
- Integration of IEME Cell Stack & CFR needed

Primary Reactions

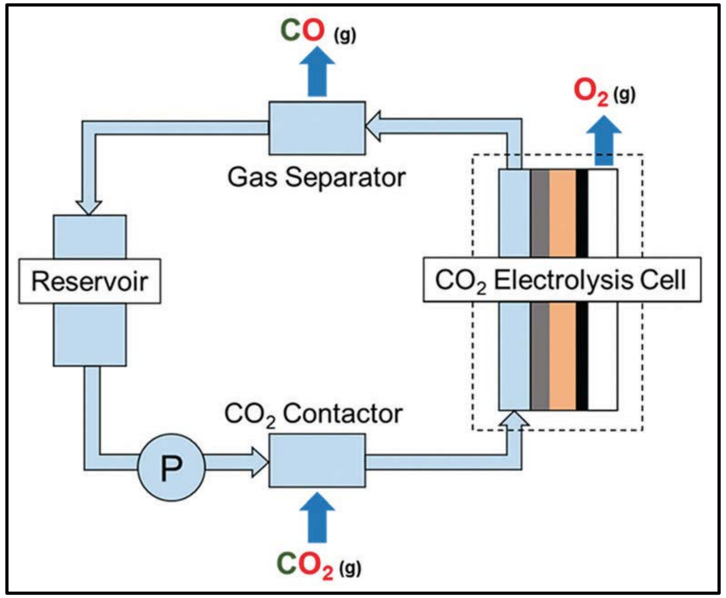
IEME:
$2\,H_2O \rightarrow 2\,H_2 + O_2$
$2\,CO_2 \rightarrow 2\,CO + O_2$

CFR:
$CO + H_2 \leftrightarrow C(s) + H_2O$
$2\,CO \leftrightarrow C(s) + CO_2$

Net: $CO_2 \rightarrow C(s) + O_2$



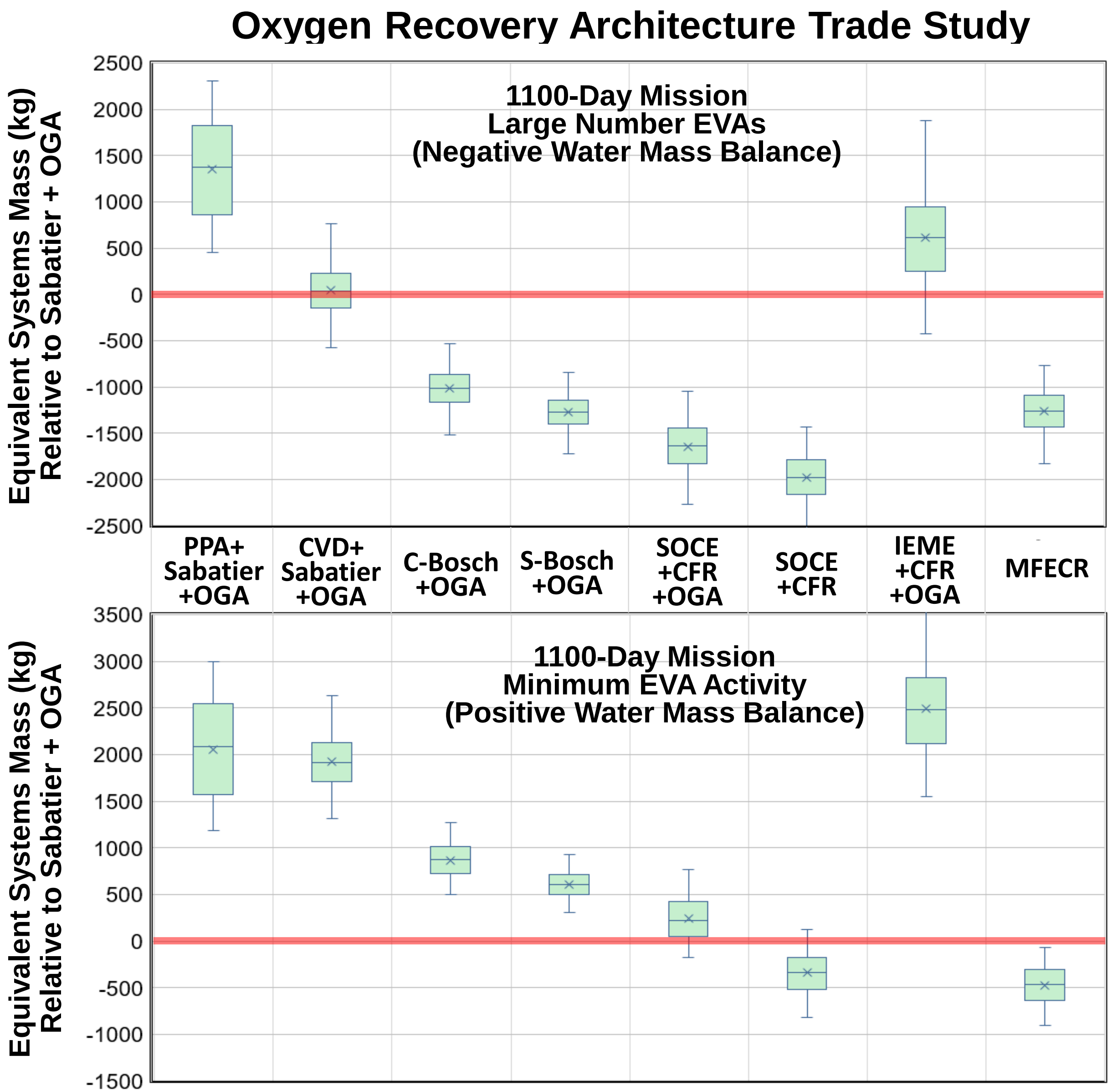
Breadboard IEME Cell Stack



Electrolysis Cell Fluid Loop

Trade Studies: General Findings and Conclusions

- **A trade study was performed that compared the Equivalent Systems Mass (ESM) of the Sabatier with an OGA against advanced technologies.**
  - o ESM combines hardware mass with mass penalties for volume, power and cooling.
  - o Mission duration: 1100 Days (Mars class)
  - o 2 EVA Cases: Large number vs minimal
  - o Does not consider ISRU
  - o Does not give credit for surplus water production.
- **Key Findings and Considerations**
  - o Advanced technologies are generally expected to trade better for missions with longer durations and higher water requirements.
  - o Example: extended duration planetary surface missions with regular EVA.
  - o Advanced technologies generally don't trade well for mission duration < 400-500 days or with high water system closure and little or no EVA losses.
  - o Consideration for other requirements for water or oxygen (e.g. radiation shielding) can affect trades.



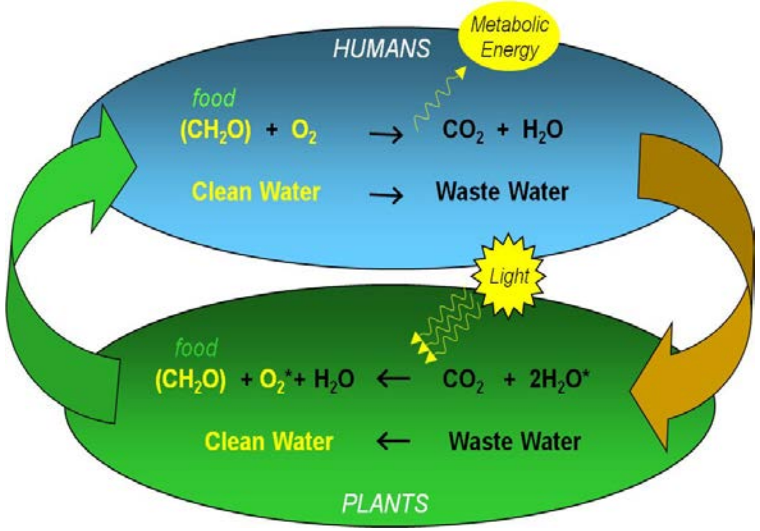
A Few Words on Biological Systems & ISRU

Bioregenerative Life Support

- Biological systems used on a mature planetary base can potentially provide 100% of the O_2 required for crew respiration, assimilating expired CO_2 via photosynthesis.
- In this context, physicochemical systems may be used during initial start up then held as secondary back up systems.

In Situ Resource Utilization (ISRU)

- Physicochemical systems for O_2 recovery may have dual use for ISRU on Mars to recover O_2 from CO_2 in the Mars Atmosphere.
- The MOXIE experiment on the Mars 2020 Rover, scheduled to land on Mars February 18, 2021, will demonstrate Solid Oxide Electrolysis of CO_2.
- The ISRU community is developing other alternative O_2 recovery technologies



Photosynthesis naturally recovers O_2 from CO_2

ISRU Systems on Mars

NASA's 15-day Human Bioregenerative Air Revitalization Test

Food Production Module with Mars Habitat

Image Credits: NASA, Ray Wheeler, Pat Rawlings

Acknowledgements

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