Thermodynamic Constraints in Operating a Solid Oxide Electrolysis Stack on Dry Carbon Dioxide Gathered From the Mars Atmosphere

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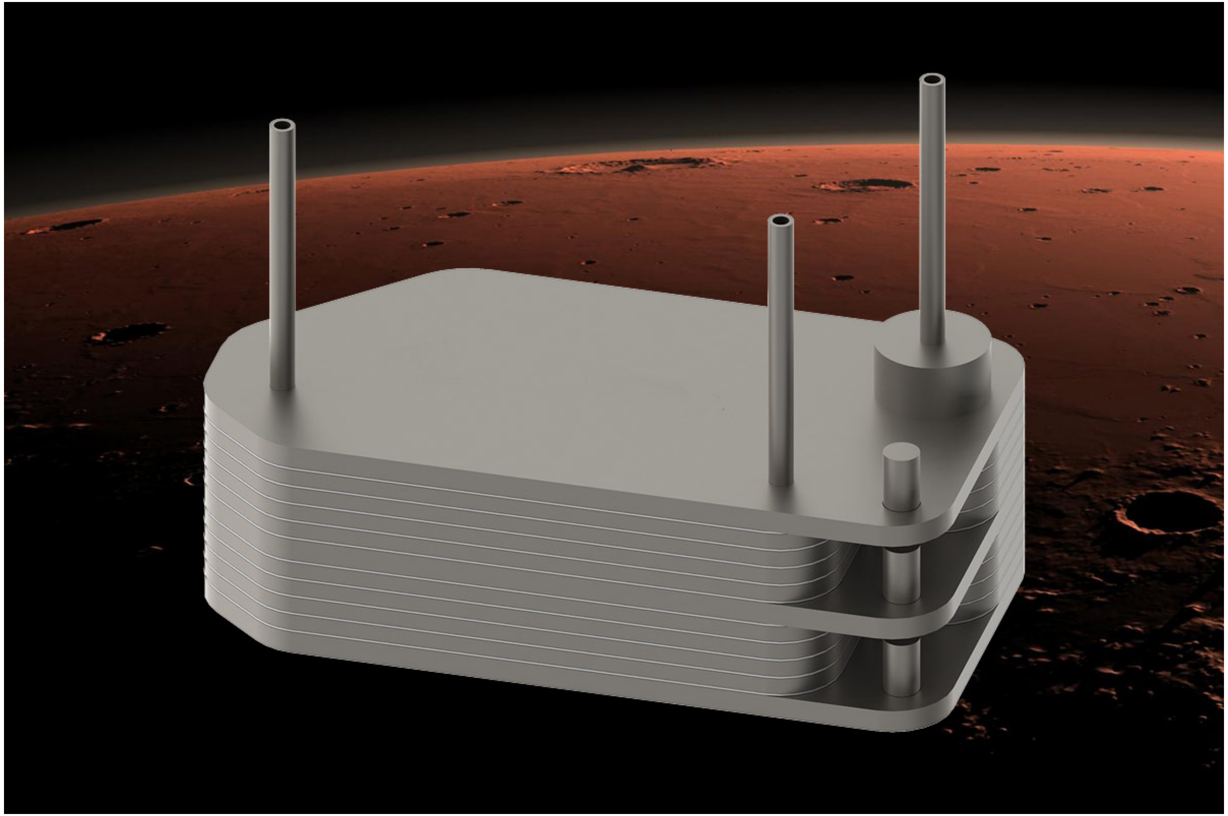
Why SOEC On Mars?



Mars Mission Architectural Decisions

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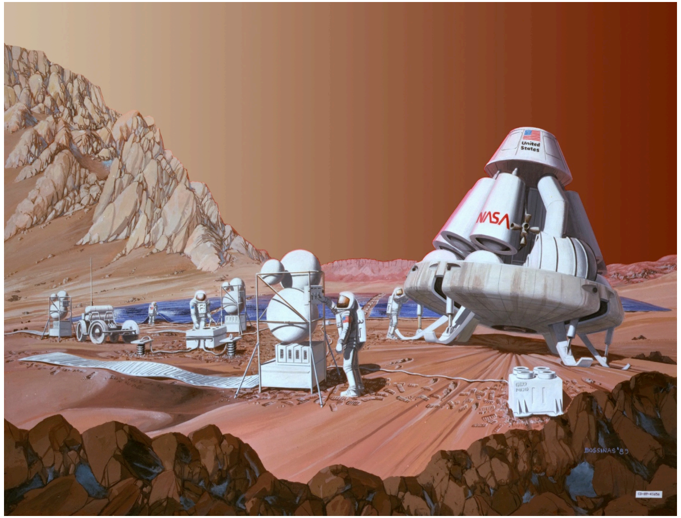
- Mars Design Reference Architecture (DRA 5.0)
  1. Mission type (orbital trajectory)
  2. All-up vs. Pre-deploy Cargo
  3. Aerocapture vs. Propulsive Mars Orbit Cargo Capture
  4. **In-Situ Resource Utilization for Mars Ascent (ISRU)**
  5. Mars Surface Power



DRA "Notable Advantages Of ISRU"

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- Production of O_2 from the atmosphere for ascent from Mars, as well as consumables (O_2, buffer gases, H_2O) for the crew, enables robust exploration.
- Atmospheric-based ISRU processes are less operationally complex than surface-based processes.
- Reduced total initial mass in Low Earth Orbit (LEO) and subsequent number of launches.
- Reduced lander vehicle size and volume.
- Greater surface exploration capability (Extravehicular Activity (EVA), roving, etc.).
- Life support functional redundancy via dissimilar means.
- Lower mission risk due to fewer launches.
- Lower life cycle cost through third mission (if same landing site).

More Advantages of CO_2 SOEC

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- Reversible operation for temporary power from stored gases
- Potential for electrochemical oxygen compression
  - 53mV/decade of pO_2, thermodynamic limit
  - Joule Thomson expansion for cryo-oxygen
- Estimate savings of 300-450 tons IM-LEO
  - Minimum savings of 3 heavy launches
- Cost savings > 10^9 USD

Thermodynamic Boundaries

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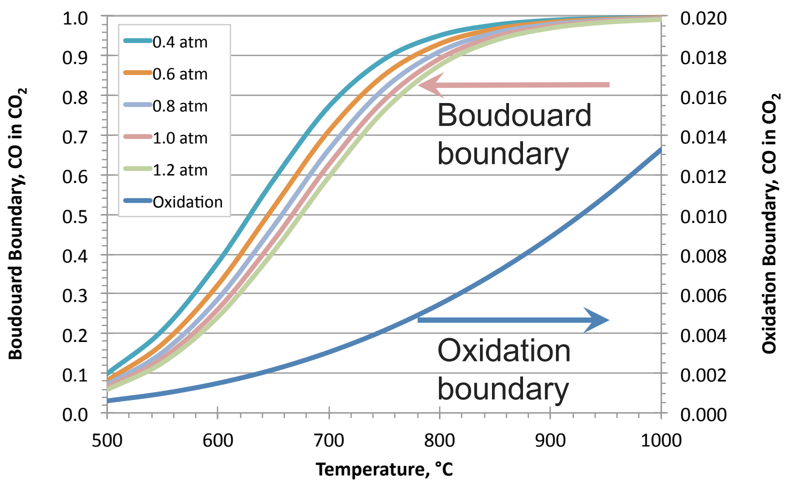
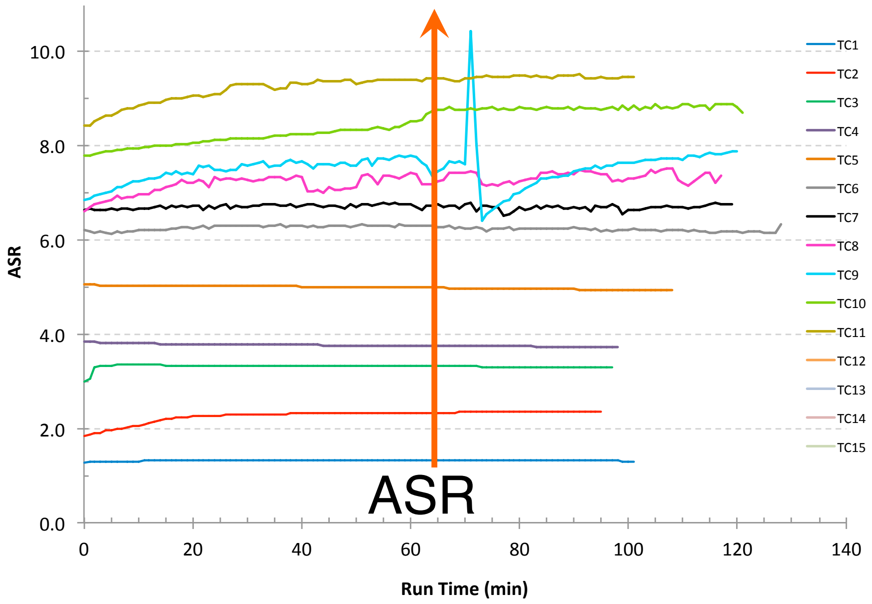
- High pO_2 boundary limited by Ni oxidation
  - Result of choice of nickel cermet cathode
- Low pO_2 boundary limited by Boudouard Rxn
  - Spontaneous disproportionation of CO to CO_2 and C_s
  - Independent of choice of cathode material
- Practical low pO_2 limit considers electrochemical factors:
  - Direct CO_2 reduction potential?
  - Electrochemical reduction of CO
  - Effectively an applied voltage limit



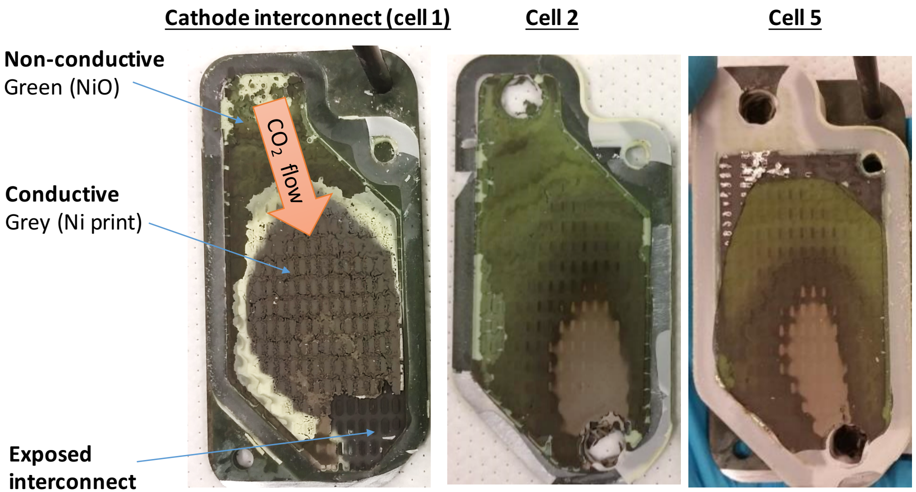
Governing Equilibrium	pO_2, atm	Vrev	CO in CO2, 1 atm
Ni-NiO	1.2e-14	0.741	0.55%
CO-CO_2, 2% CO in CO_2	8.9e-16	0.801	2%
CO-CO_2, 60% CO in CO_2	1.7e-19	1.000	60%
Boudouard	5.3e-21	1.079	89.3%

- $Ni + \frac{1}{2} O_2 \Leftrightarrow NiO, \quad \Delta G_f^\circ = -142.9$ kJ/mol
- $CO + \frac{1}{2} O_2 \Leftrightarrow CO_2, \quad \Delta G_f^\circ = -189.3$ kJ/mol
- $2CO \Leftrightarrow C_s + CO_2, \quad \Delta G_f^\circ = -2.506$ kJ/mol

Consequences of Oxidation



- STK-007 Operational History
  - 15 cycles, full thermal cycle with 120m operation on pure CO_2
  - Dramatic degradation suggestive of progressive oxidation front



- STK-007 Post Test Examination
  - Progressive oxidation front confirmed
  - Non-conductive cathode and current distribution layers

System Mitigation of Oxidation

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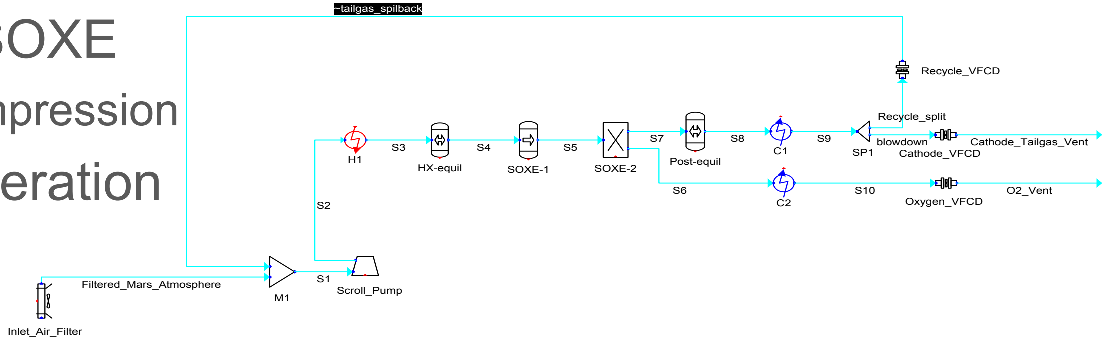
- "CAC" supplies pure CO_2 to SOXE
  - CAC = CO_2 Acquisition and Compression
- Pure CO_2 complications to operation
  - Not reducing at reactant inlet
    - Electrode oxidation possible
  - Thermodynamically indeterminate
    - Open circuit voltage undefined

$$E_{rev} = E_N^0(T) + \frac{RT}{2F}\ln\left(\frac{p_{CO2}}{p_{CO}\sqrt{p_{O2}}}\right)$$

  - No thermodynamic penalty for inert diluents
    - Reversible Driving Potential:
    - Ratio of p_{CO2} / p_{CO} unaffected by reactant diluents
    - Ratio of p_{CO2} / p_{CO} unaffected by total pressure
- Cathode tailgas recycle is needed



- VMGSim process simulation
  - Rigorous mass and energy balance
    - Full VLE and reaction thermodynamics
- One additional VFCD
  - Assumed 40% exit [CO]
  - 95:05 split gives 2% [CO] at inlet

Utilization Limit Sweeps, CSA-003R

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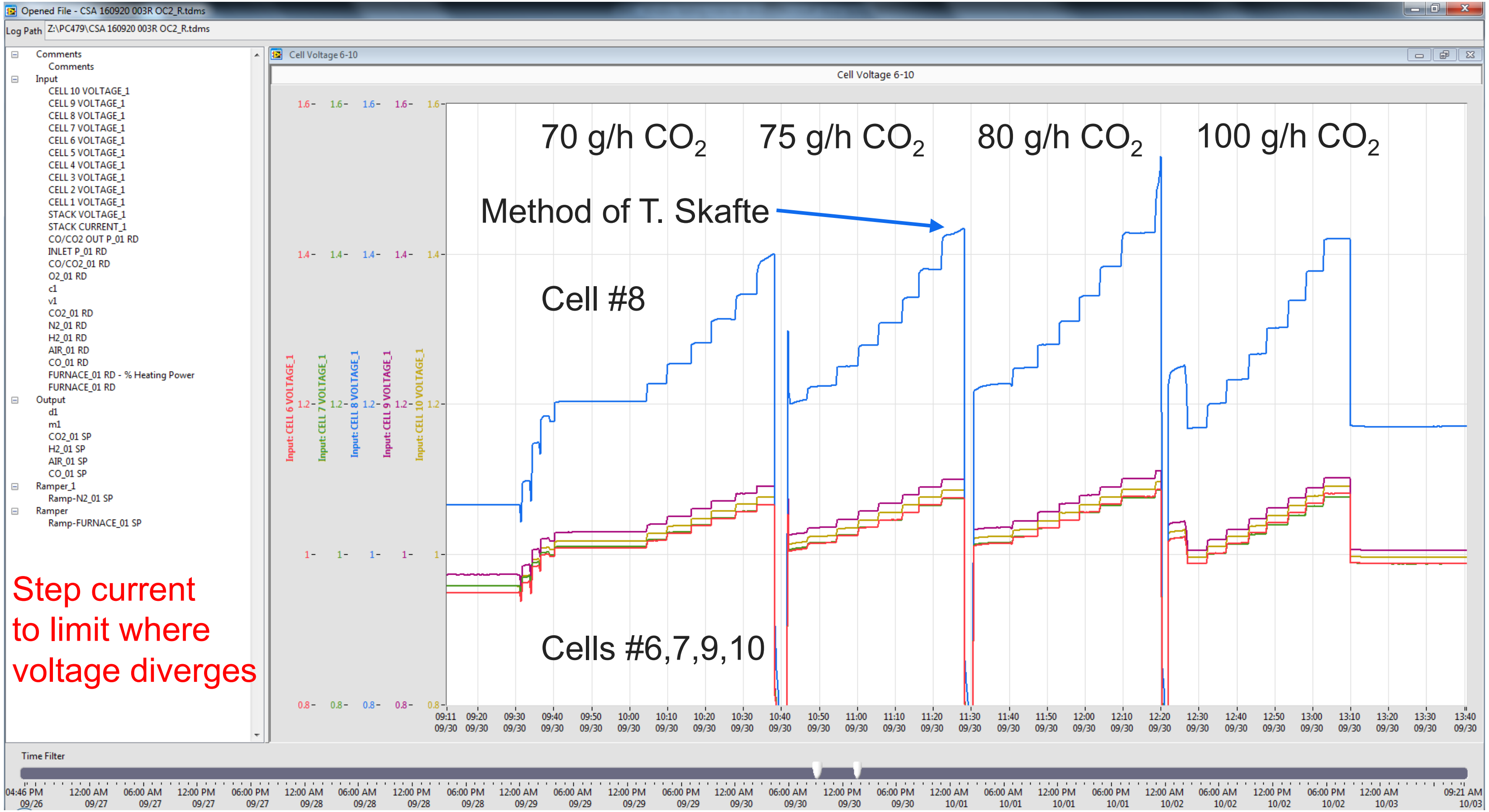

Step current to limit where voltage diverges

Consequences of C_s Deposition

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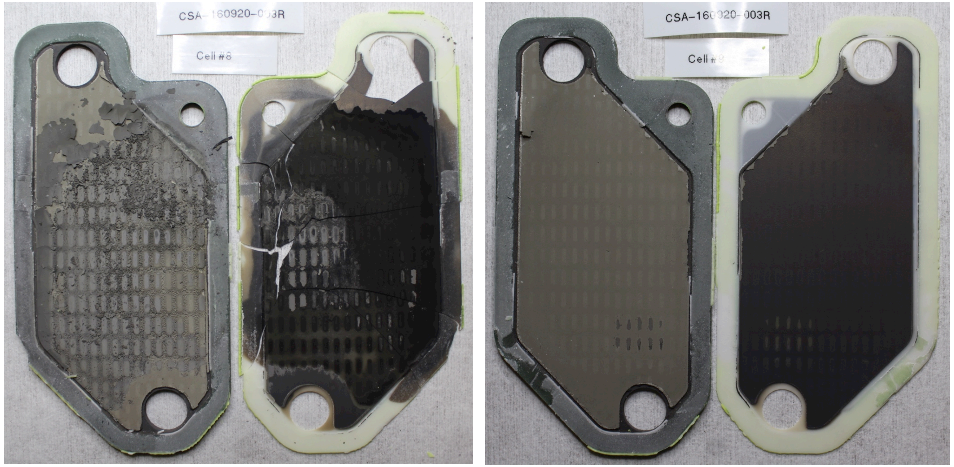
CSA-003R Cell #8 cathode channels



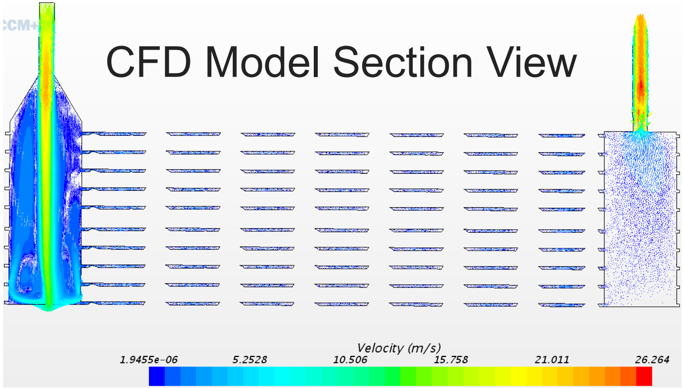
Cell #8 - CSA-003R – Cell #9

- Carbon deposition anticipated on cell #8
  - High cell voltage (cause or effect, or both?)
  - High open circuit voltage
    - Most cells ~0.8V
    - Cell #8, ~1.06V, C_s-CO equilibrium potential

- Electrode microstructure destroyed
- Electrode-electrolyte interface separated
- Flow channels blocked with solid carbon
- Electrolyte blackened, weakened, cracked
  - Partial reduction of zirconia?

Utilization Limiting Cell

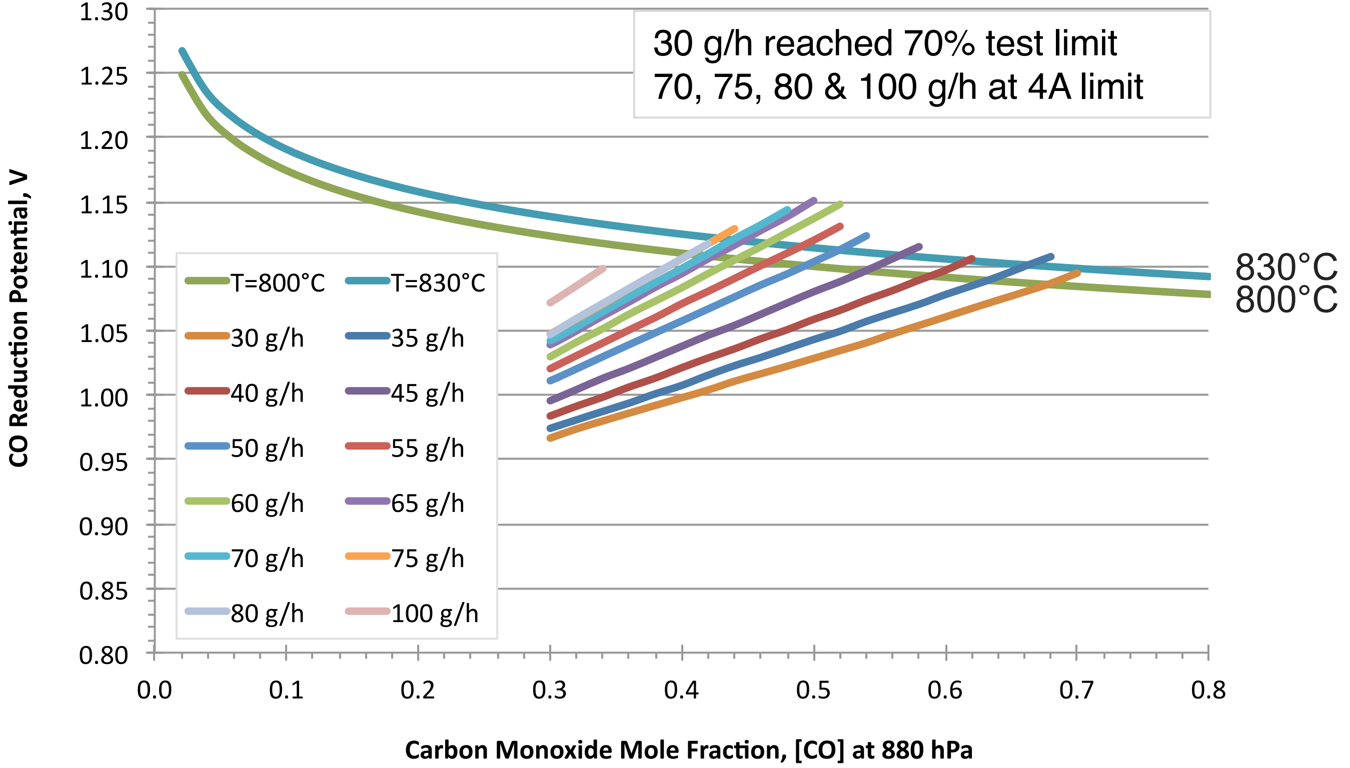
- Minimum CO_2 flow rate cell
  - One cell must have lowest flow in stack
  - Position in stack
    - Entrance jet plenum flow circulation
    - Cell outflow effect on local pressure
  - Entrance/Exit obstructions
    - Glass overflow into channels
  - Channel height variation
    - Flow ~ channel height as h^3
      - Pressing variation
      - Sanding
      - Coating



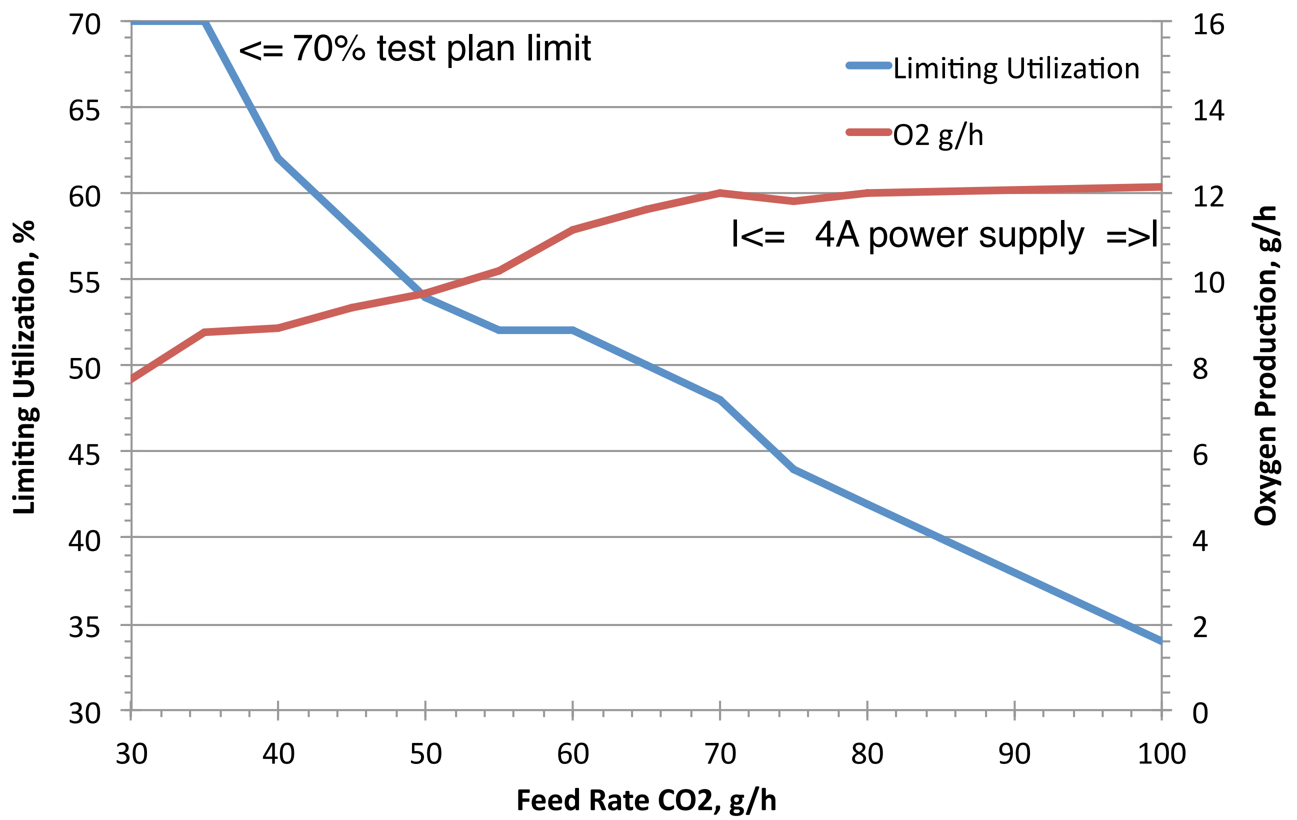
	AVG_CELL1	AVG_CELL2	AVG_CELL3	AVG_CELL4	AVG_CELL5	AVG_CELL6	AVG_CELL7	AVG_CELL8	AVG_CELL9	AVG_CELL10	AVG_ASR
CSA-007	1.032	1.039	1.043	1.052	1.043	1.034	1.035	1.044	1.059	1.045	1.378
CSA-008	1.047	1.040	1.048	1.039	1.054	1.042	1.034	1.033	1.035	1.050	1.378
CSA-006R	1.033	1.031	1.039	1.032	1.041	1.037	1.048	1.044	1.046	1.034	1.365
CSA-009	1.059	1.045	1.036	1.042	1.044	1.079	1.043	1.043	1.036	1.065	1.411
JSA-004	0.925	1.006	1.027	1.043	1.034	1.033	1.035	1.041	1.033	1.037	1.338
JSA-005	1.074	1.071	1.067	1.065	1.044	1.133	1.151	1.080	1.070	1.074	1.609
JSA-006	1.024	1.035	1.018	1.040	1.040	1.020	1.030	1.037	1.045	1.031	1.312
JSA-007	1.143	1.059	1.088	1.092	1.092	1.067	1.058	1.052	1.045	1.070	1.549
JSA-008	1.060	1.053	1.038	1.038	1.038	1.040	1.042	1.038	1.045	1.027	1.378
JSA-009	1.046	1.115	1.091	1.080	1.068	1.038	1.056	1.067	1.069	1.057	1.529
CSA-010	1.122	1.080	1.090	1.107	1.086	1.053	1.056	1.051	1.090	1.055	1.601
JSA-010	1.042	1.040	1.063	1.074	1.046	1.038	1.041	1.066	1.072	1.042	1.437
JSA-011	1.070	1.077	1.067	1.081	1.052	1.045	1.060	1.094	1.053	1.046	1.518
JSA-012	1.020	1.029	1.031	1.028	1.050	1.025	1.030	1.050	1.045	1.058	1.417
JSA-013	1.018	1.092	1.054	1.054	1.065	1.038	1.053	1.047	1.069	1.044	1.515
JSA-014	1.066	1.028	1.052	1.051	1.021	1.035	1.025	1.039	1.032	1.020	1.422
JSA-015	1.036	1.025	1.066	1.063	1.046	1.037	1.037	1.068	1.041	1.040	1.470
JSA-016	1.038	1.030	1.031	1.020	1.063	1.055	1.079	1.048	1.043	1.064	1.479
JSA-017	1.042	1.054	1.011	1.023	1.018	1.065	1.025	1.037	1.028	1.023	1.395
JSA-018	1.033	1.022	1.048	1.033	1.043	1.030	1.061	1.052	1.049	1.057	1.457
Averages	1.047	1.049	1.050	1.053	1.049	1.047	1.050	1.051	1.050	1.047	1.448

Baseline High / Low Voltage Cell Position

CSA-004 800°C Utilization Sweeps



CSA-004 800C Flow-Utilization Limit



CSA-004 Activation Polarization

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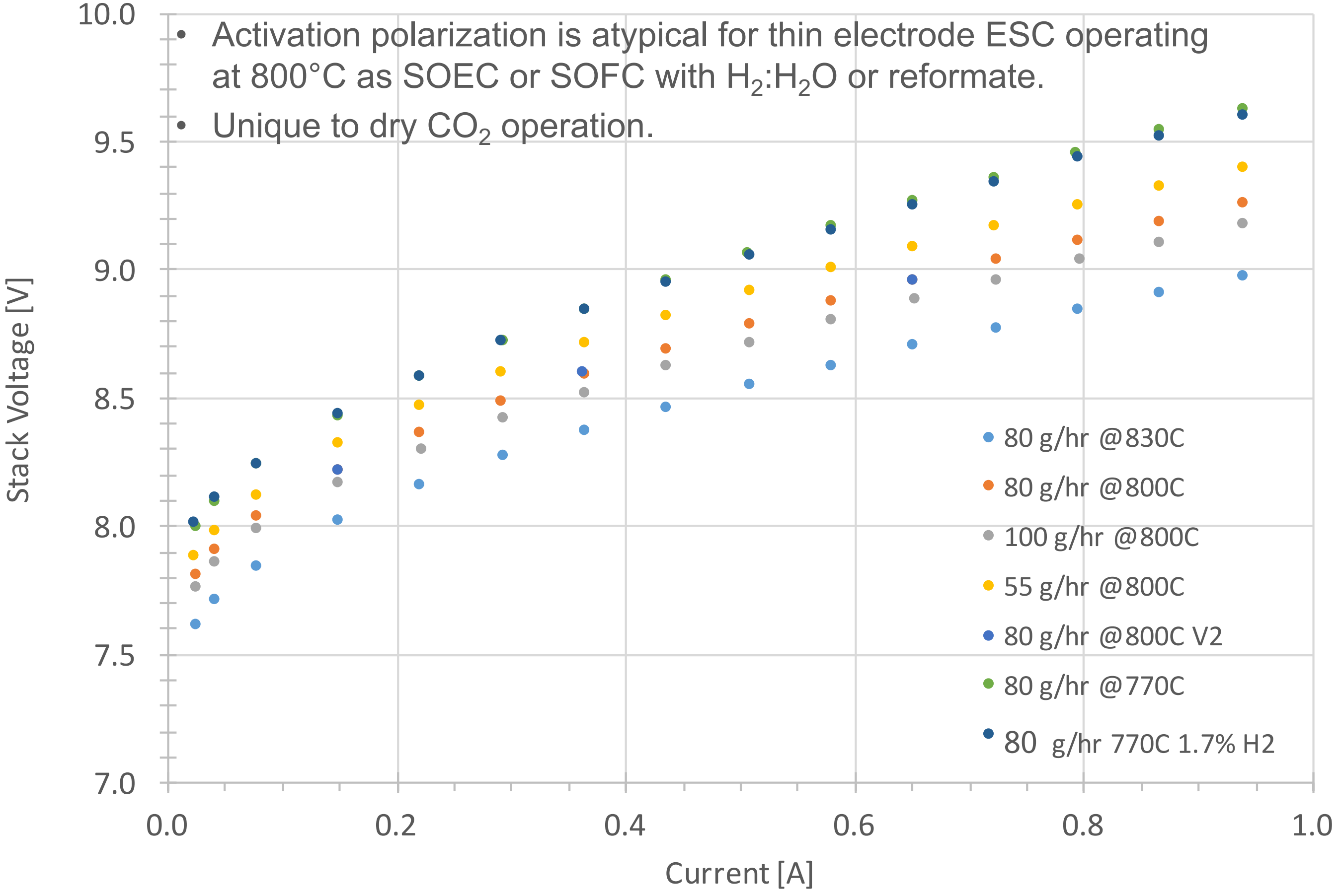
- Activation polarization is atypical for thin electrode ESC operating at 800°C as SOEC or SOFC with H_2:H_2O or reformate.
- Unique to dry CO_2 operation.



CSA-005: Mapping Test Plan

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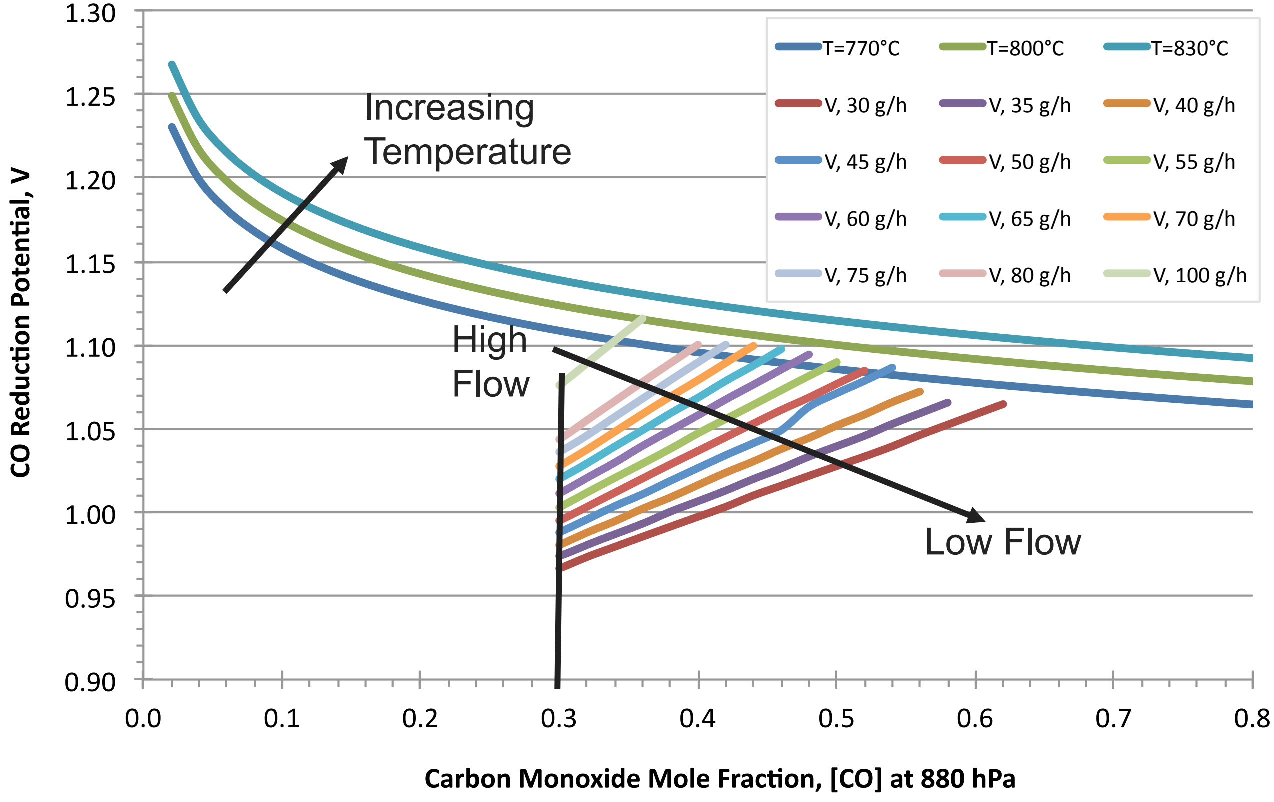
Build: 17Oct16 **End Test:** 11Nov16

Operational Testing started October 24

- Explore going from high to low temperatures
  - 830°C, 810°C, 800°C, 790°C, 770°C
  - High temperature has lower ASR, higher CO reduction V_{Nernst}
  - **Stop based on V_{op} < V_{Nernst} to avoid crossing threshold**
  - **Map becomes bounded by performance (ASR) and safe thermodynamic space rather than detecting unsafe state.**
  - <u>Try to run test without reaching any carbon deposition state</u>

CSA-005 800C Operating Lines at Varying CO_2 Flow Rates



CO reduction Nernst is a function of cathode gas composition and temperature – staying below this minimizes risk of coking

Graph based on overall average exit [CO], local [CO] may be higher.

Effect of Flow Rate on Stack Performance

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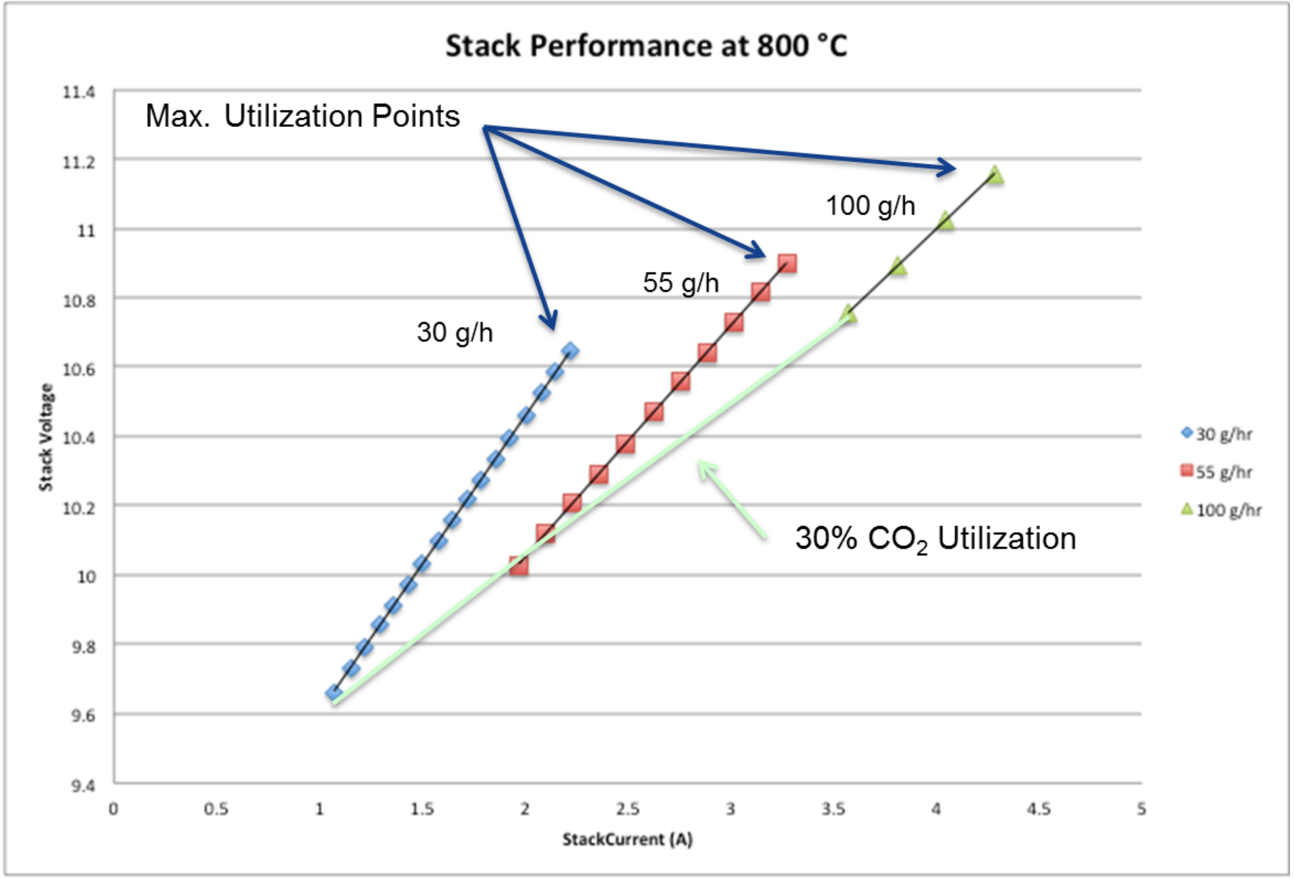

Slope of I-V curve reduces as flow rate increases

Extrapolated intercept is near constant and ≠ OCV

Effect of Temperature on Performance

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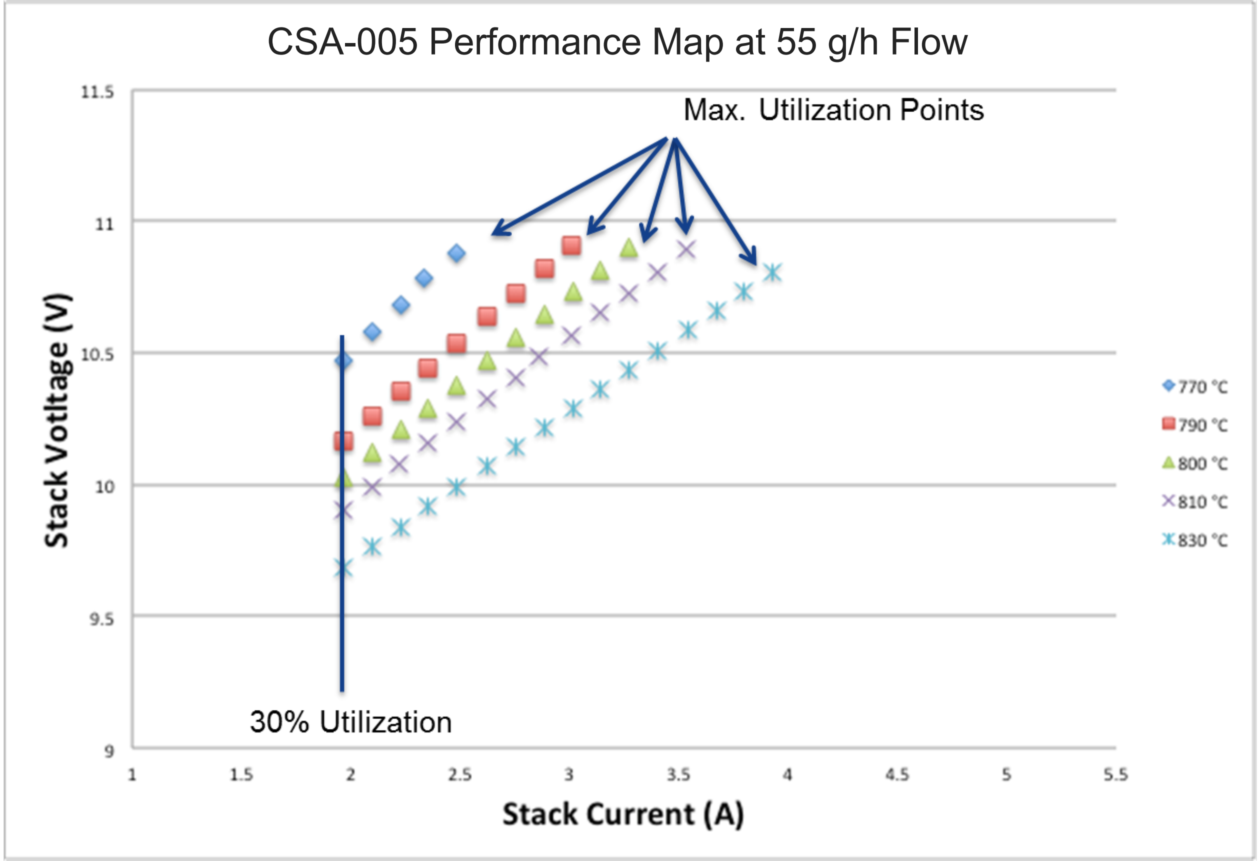
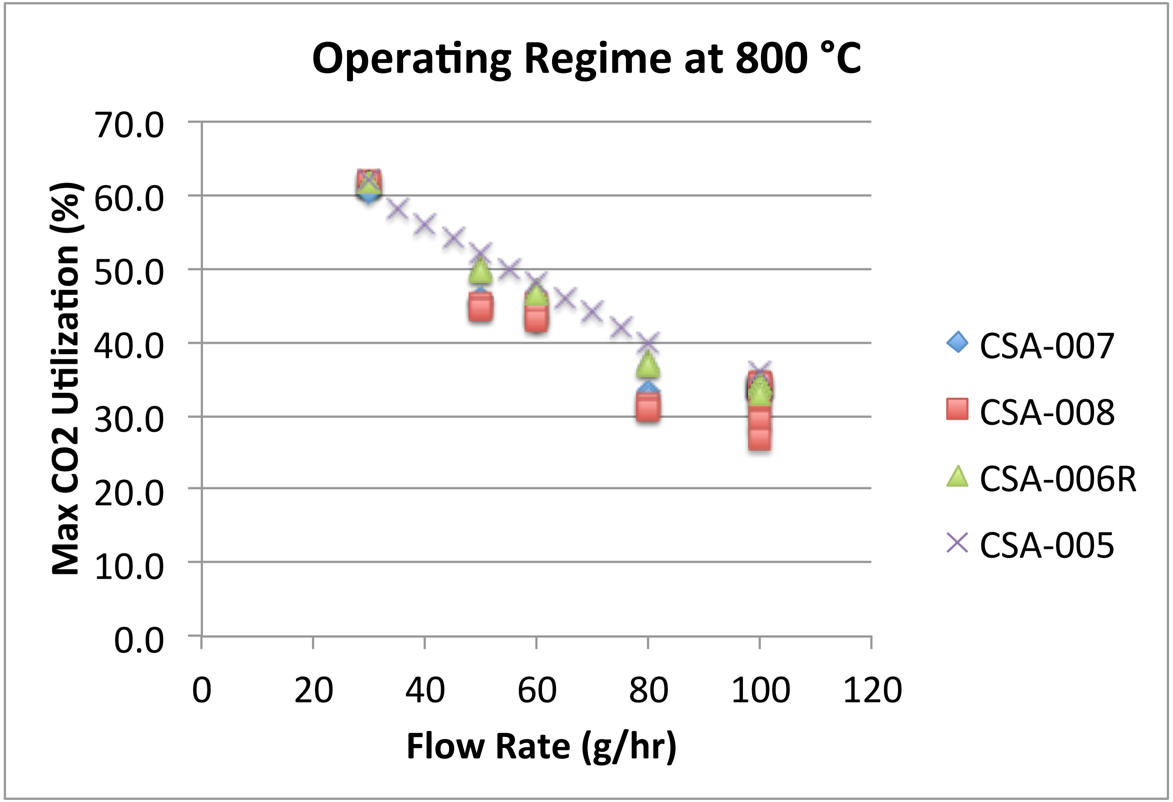


Slope (and ASR) decreases with increasing temperature at fixed flow rate

Safe Operating Regime at 800°C



Cycles and additional stacks don't change limits much at low flows

Mid-range flows appear to challenge stability

Safe operating boundary less certain at mid-range flows and higher flows with accumulation of cycles

Stacks CSA-007, CSA-008 and CSA-006R were run to 21 cycles with a limit as used for CSA-005

Mars Operations Challenges

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- No possibility of man-in-loop operation
  - Twice daily communication windows
- Daily variation of CO_2 flow rate anticipated
  - CO_2 flows vary with ambient pressure & temperature
- Primitive data acquisition and control
  - "Flight Heritage" hardware
  - Software qualification standards
  - Simple run table control
- Sensor uncertainty
  - Flow, Temperature, power supply
  - No stack voltage leads
    - High lead loss to minimize heat leak through leads
- High number of thermal cycles
  - Degradation must be well characterized
- No process utilities for stack recovery
  - Cathode oxidation – ends mission
  - Carbon deposition – ends mission
- Need to plan safe conditions as a function of:
  - Projected CO_2 flow rate (Mars ambient T, P)
  - Inferred temperature deviations (overall, end to mid)
  - Cycle to cycle performance decay
- As simple as possible

Operating Window - Driving Performance

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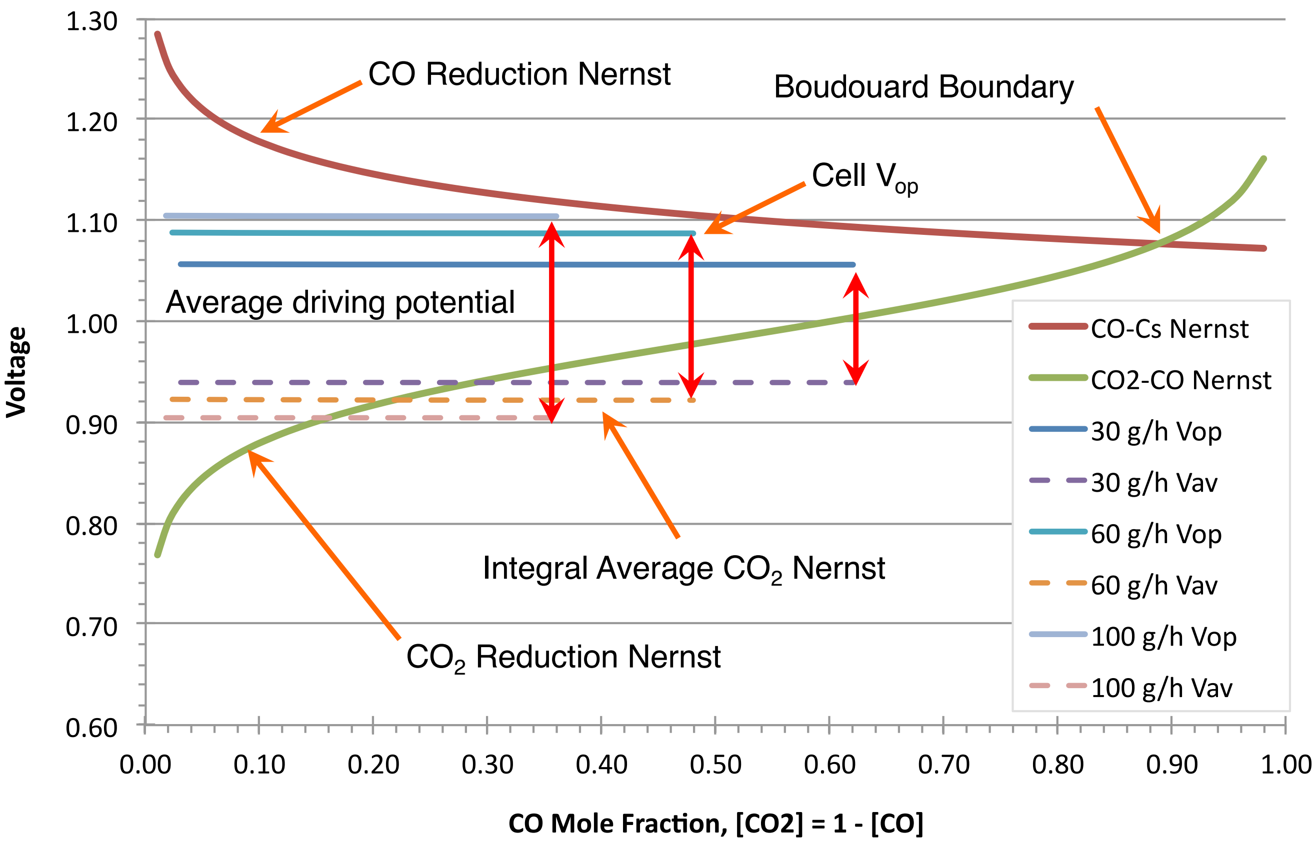

Basic Operating Model

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- "Apparent" ASR doesn't address flow variations, $R_a'' = \left(\frac{V_{op} - V_{OC}}{j_i}\right)$
- or observed activation polarization,
- so define an "Intrinsic" ASR as, $R_i'' = \left(\frac{V_{op} - \overline{E_N} - V_{act}}{j_i}\right)$
- with fixed activation polarization V_{act},
- and the integral average CO_2 reduction
- Nernst potential as:

$$[CO_2] = 1 - [CO]$$

$$\Delta G_{CO_2}([CO]) = \Delta G^{\circ}(T) + RT \ln\left(\frac{[CO]\sqrt{[O_2]}}{(1 - [CO])}\right)$$

$$\overline{E_N} = \frac{\int_{[CO]_{inlet}}^{[CO]_{exit}} \Delta G_{CO_2}\, d[CO]}{2\mathcal{F}([CO]_{exit} - [CO]_{inlet})}$$

- which evaluates and simplifies as:

$$\overline{E_N} = \frac{\left([CO]_{exit}\Delta G_{CO_2}([CO]_{exit}) - [CO]_{inlet}\Delta G_{CO_2}([CO]_{inlet}) + RT \ln\frac{([CO]_{exit} - 1)}{([CO]_{inlet} - 1)}\right)}{2\mathcal{F}([CO]_{exit} - [CO]_{inlet})}$$

- Fit *iASR* temperature variation $f(T) = Ae^{\left(\frac{-E_{act}}{RT}\right)}$, such that $f(1073°K) = 1$

Cycle Life Model

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- Assume power law in intrinsic ASR
- Similar to long term operation increase in ASR using a parabolic rate law where $\gamma = 0.5$ and tau, is the time to double initial ASR

$\tau \sim 40e3\ hours$

- Time replaces (n-1)

$$R''_{i_n} = R''_{i_0}\left(1 + \left(\frac{(n-1)}{\tau}\right)^{\gamma}\right)$$

$$R''_{i_0} = 0.68\ \Omega - cm^2$$

$$\tau = 70\ cycles$$

$$\gamma = 0.89$$

Ceramatec Fuel Cells Moving Forward

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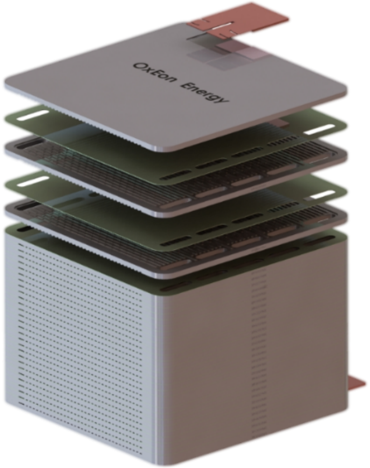

OxEon energy

Beyond Current Potential

www.OxEonEnergy.com

Flight qualification completed,
MOXIE flight builds completed June 2017,
System integration underway at JPL

Scale-Up and Manufacturing

- Formation of OxEon Energy
- Focus on Scale-up and commercialization of the ruggedized hermetic stack for hydrogen/syngas production, or fuel cell operation

Thank You

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