Materials and System Issues with Reversible SOFC

Dr. S. Elangovan, Ceramatec
Professor Prabhakar Singh, University of Connecticut

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Renaissance Arlington Capital View

Arlington, VA

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Reversible SOFC

- Balancing Energy, Environment, and Economy
- How does Reversible SOFC fit in Energy/Environment Picture
- Technical Challenges
  - Materials
  - System
- Conclusions

Reversible SOFC and Applications Options

- SOFC can be operated in two modes
  - Power Generation Mode – Fuel to Electricity
  - Electrolysis Mode – Electricity to Fuel (H_2)
- Options
  - One device optimized for fuel cell use (H_2, NG -> e)
  - Second device optimized for electrolysis use (Renewable e -> fuel: H_2, syngas etc.)
  - Under utilization of capital
  - A single device optimized for Reversible performance is desirable

- Fuel ⇔ Electricity
  - When excess power is available SOFC can be operated in Electrolysis Mode to generate Hydrogen
  - Stored hydrogen can be used later as fuel
- Renewable Electricity + Steam ➔ Fuel (H_2)
- Renewable Electricity + Steam + CO_2 ➔Fuel (synthetic methane, Liquid HC)

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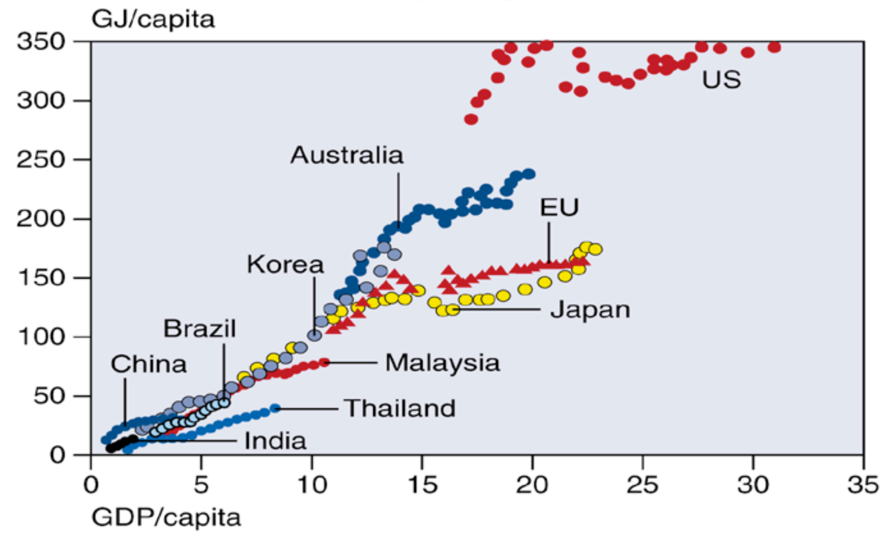
Broader Picture to Address Energy, Environment & Economy

- Environment
  - Climate Change
    - CO_2 mitigation
  - Habitat Impacts
  - Air pollution
- Limited Resources
  - Oil
    - National security
  - Gas
    - Heating vs. power generation
    - Transportation issues
  - Renewables
    - Intermittent
    - Dispersed
    - Biomass gasifier converts only 1/3 of carbon to syngas

GNP versus Energy Usage (*Source: Royal Dutch Shell*)



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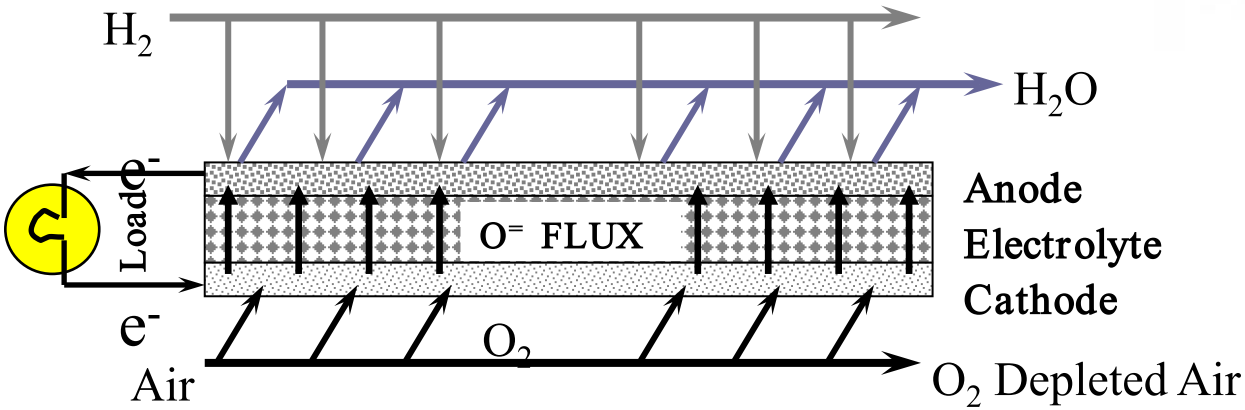
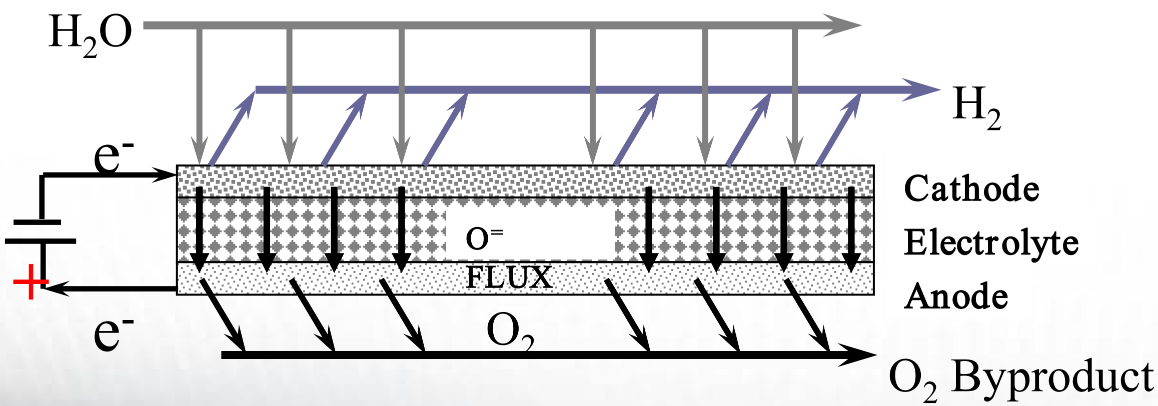
Steam Electrolysis Operating Principle



Solid Oxide Fuel Cell (SOFC) operation



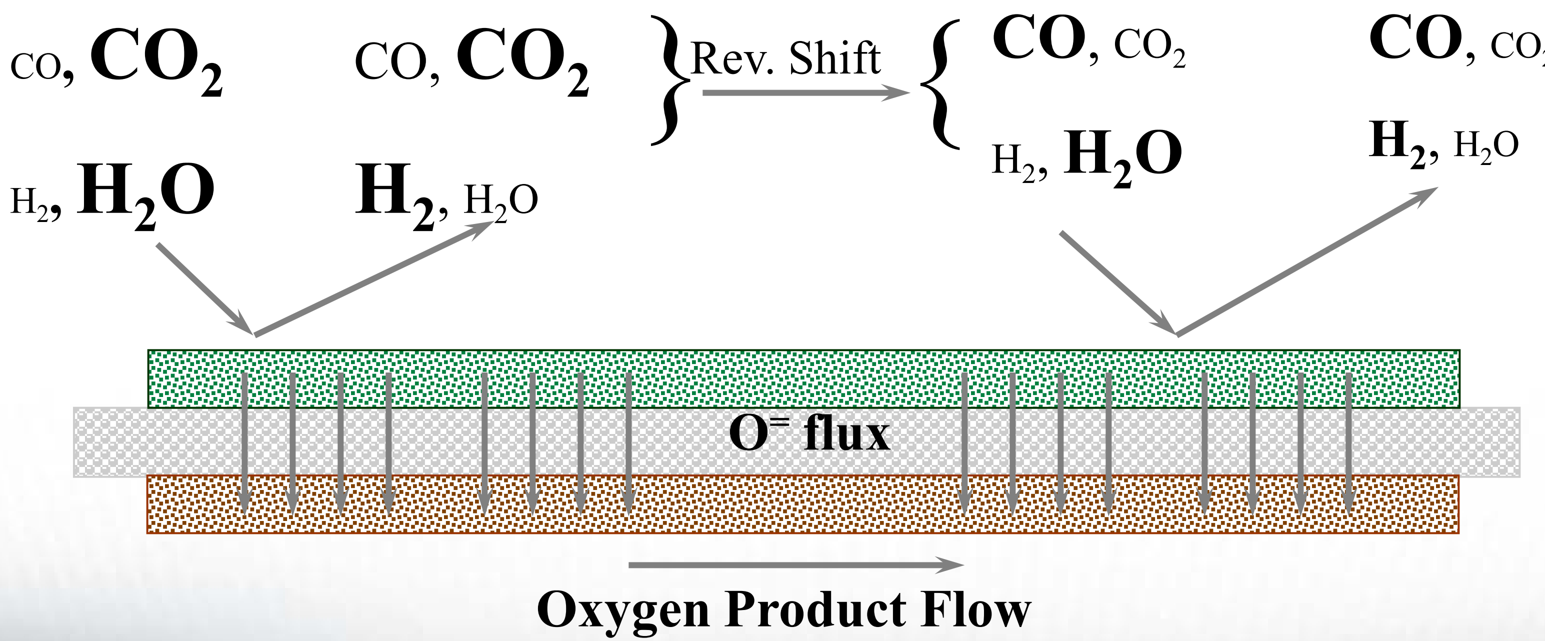
Same device in electrolysis operation

Reverse Shift & Electrolysis Of CO_2

Feed: H_2O, CO_2, (minor H_2, CO)

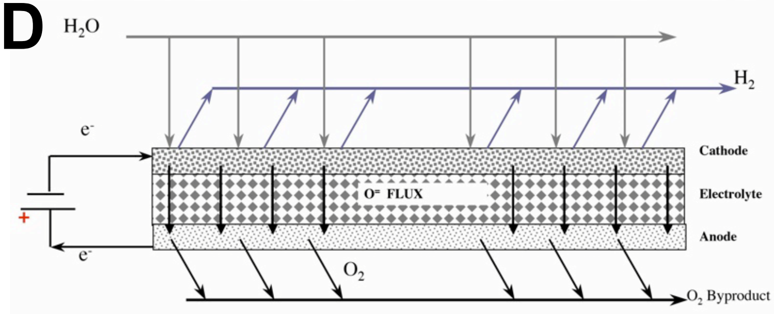
Reverse Shift Reaction: $CO_2 + \Uparrow H_2 \Longleftrightarrow CO + \Downarrow H_2O$

As steam is consumed and H_2 produced the RSR proceeds to the right

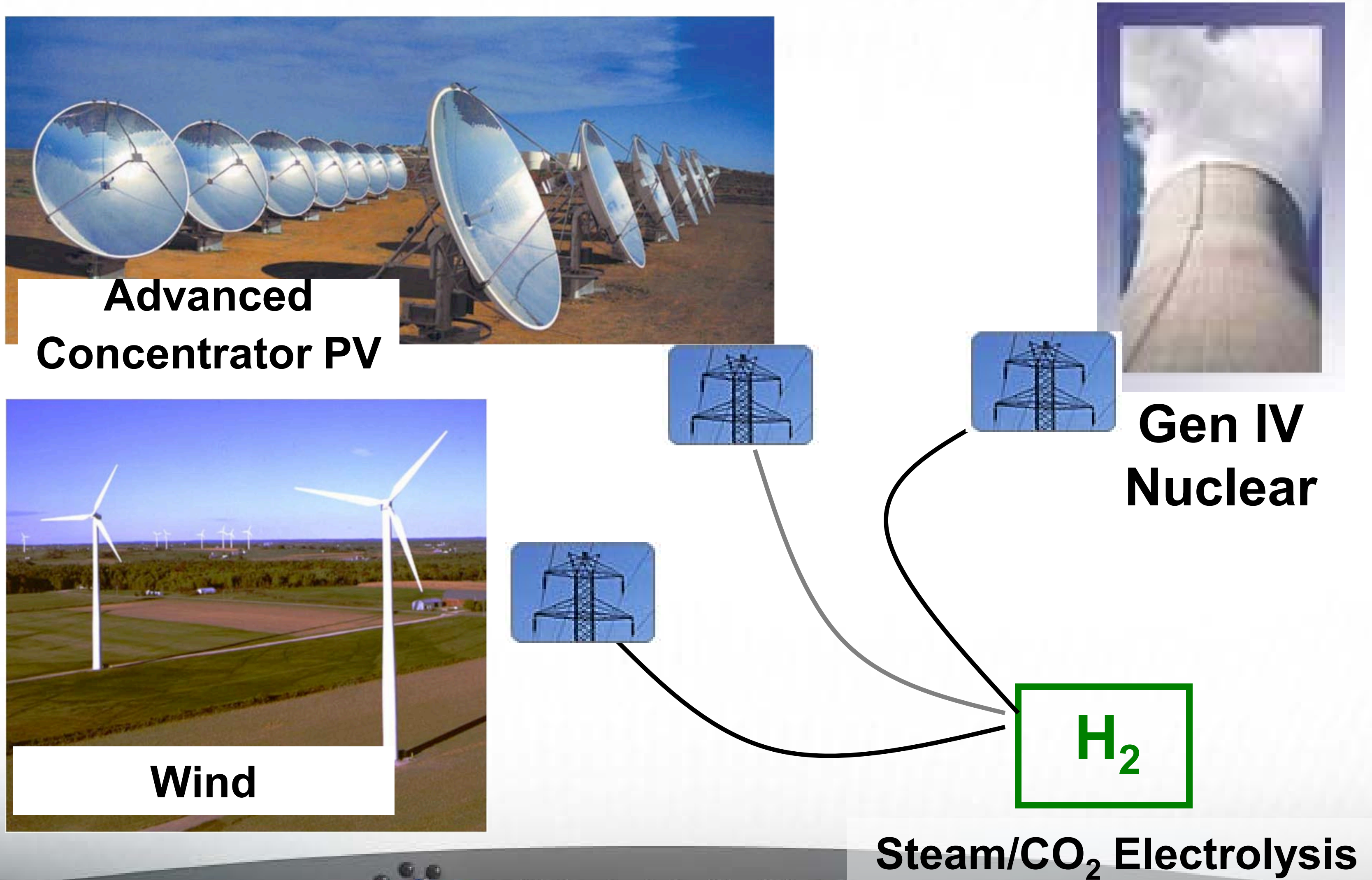


High Temperature Electrolysis

- Leverage decades of SOFC R&D
- Inputs
  - e^- (green electrons)
  - steam => hydrogen
  - co-electrolysis of H_2O + CO_2 => syngas
  - heat input optional, depends on operating point
- Most efficiency means of hydrogen production
  - e^- to hydrogen
    - η=100% at 1.285V (thermal neutral)
    - η= 95% at 1.35V (exothermic)
    - η=107% at 1.20V, (heat required)
- Hot O_2 and steam byproduct
  - Valuable for biomass gasification



Energy Mix Possibilities for Electrolysis



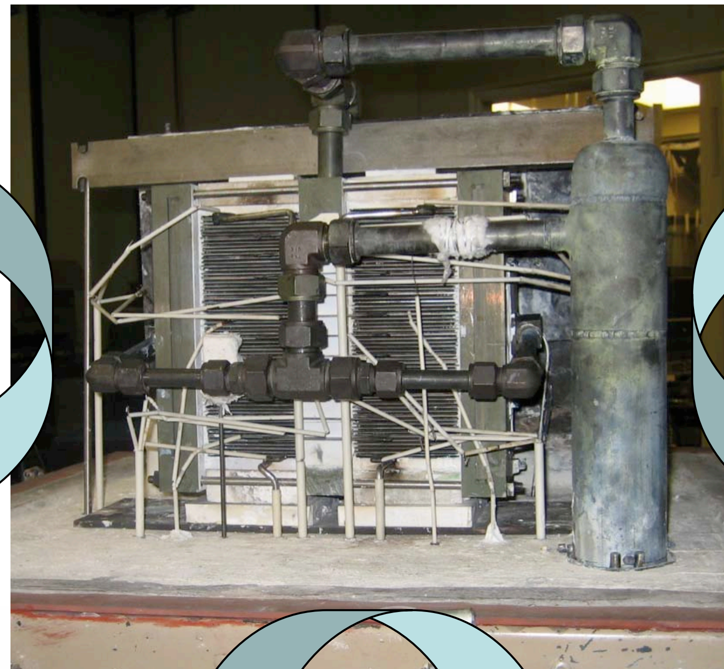
One Technology - Multiple Modes Of Operation

Solid Oxide Stack Module

NG
Biogas
Diesel
JP-8
Coal

Fuel

Electricity



Syngas

CO_2 & Steam
+ Electricity

Steam + Electricity

Hydrogen
(High Purity)

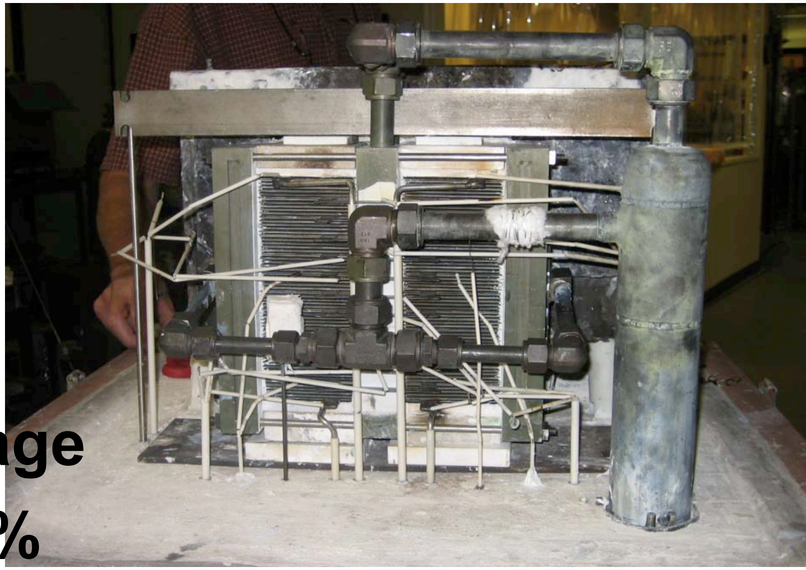
Benefits of R-SOFC

- Vastly expands applications
  - Potential to reduce manufacturing cost by using a common device for power generation, electrolysis, and reversible modes
- Environmental benefits
  - In SOFC mode (low emission) and in utilizing renewable energy in electrolysis mode
- Questions
  - Can current SOFC technology adequate to operate in electrolysis mode?
  - Cost implications
  - Manufacturing Challenges

Experimental Results

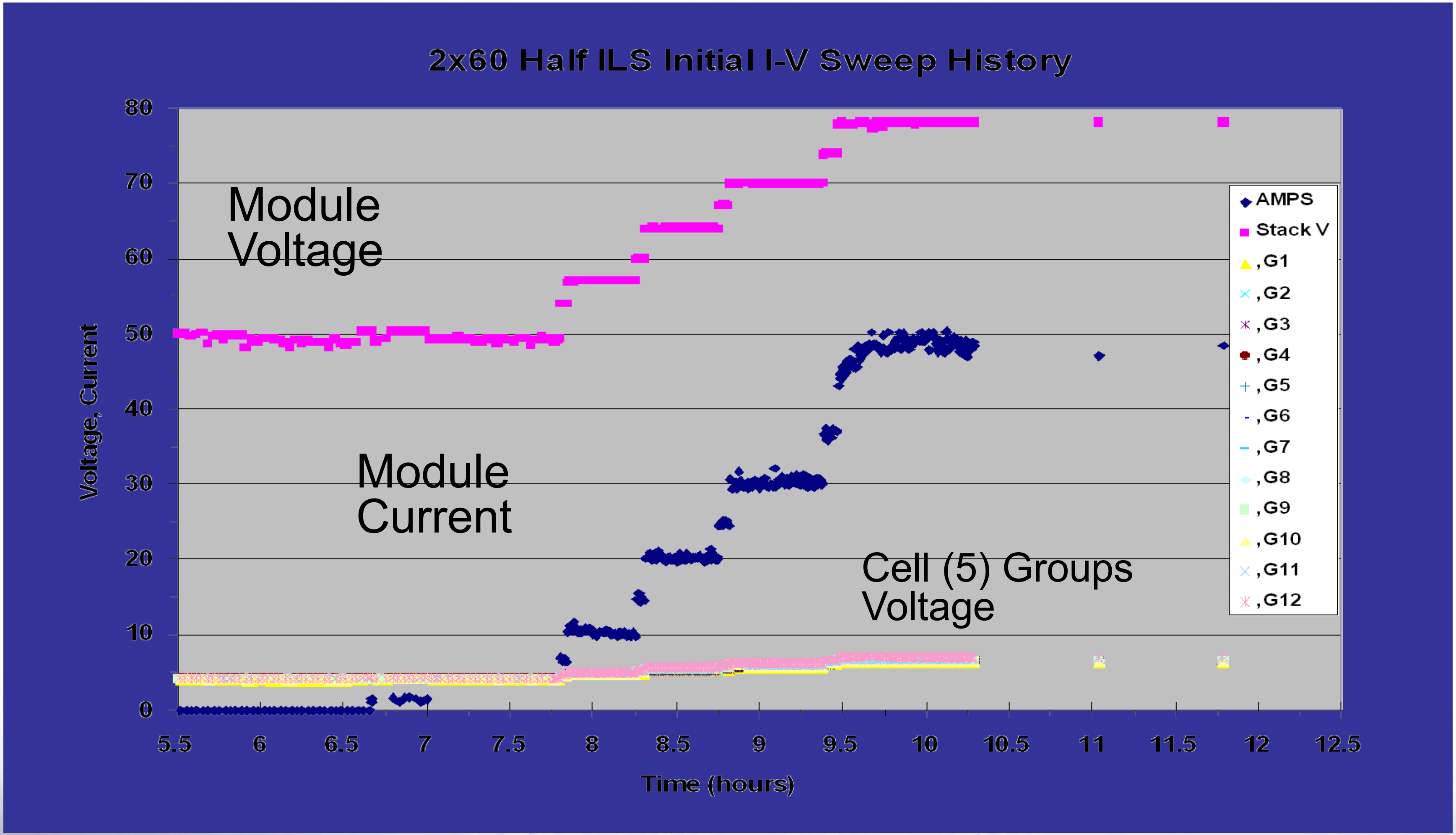
2x60 Cell Stack Module

Stack constructed with cell materials that showed good stability in SOFC



- **3.8 kW**
- **1,200 normal liters/hr. hydrogen production**
- **Operated at thermal neutral voltage**
- **Stack electrical efficiency = 96.4%**
- **System thermal distribution issues**
- **2,000 hrs. total operation**
- **1,000 hrs. on CO_2/H2O**
  - **Syngas production sufficient for 100 gallons of FT diesel**

Initial Load Steps of Half Module (4 kW)



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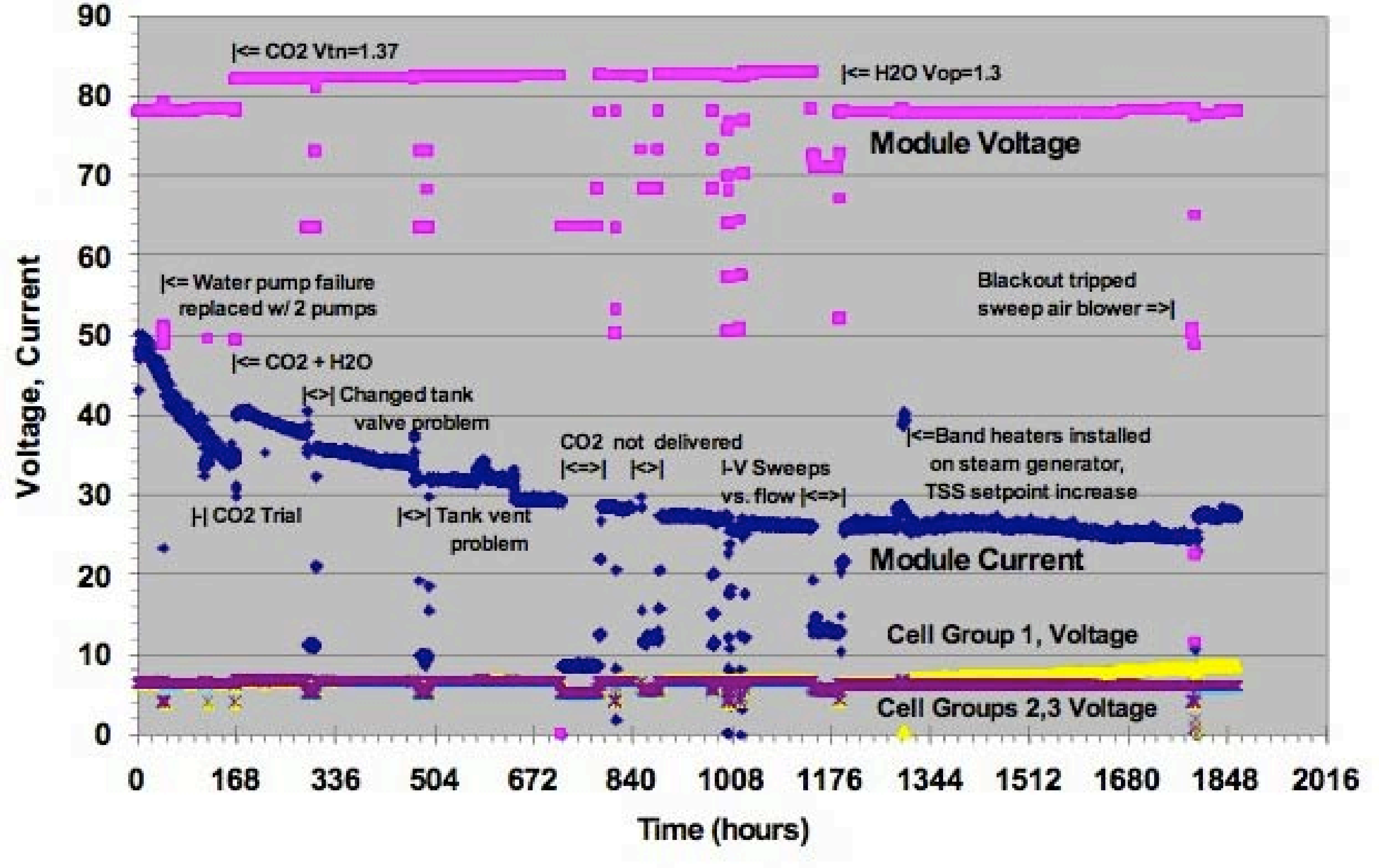
2 x 60 Cell Stack Module Load History



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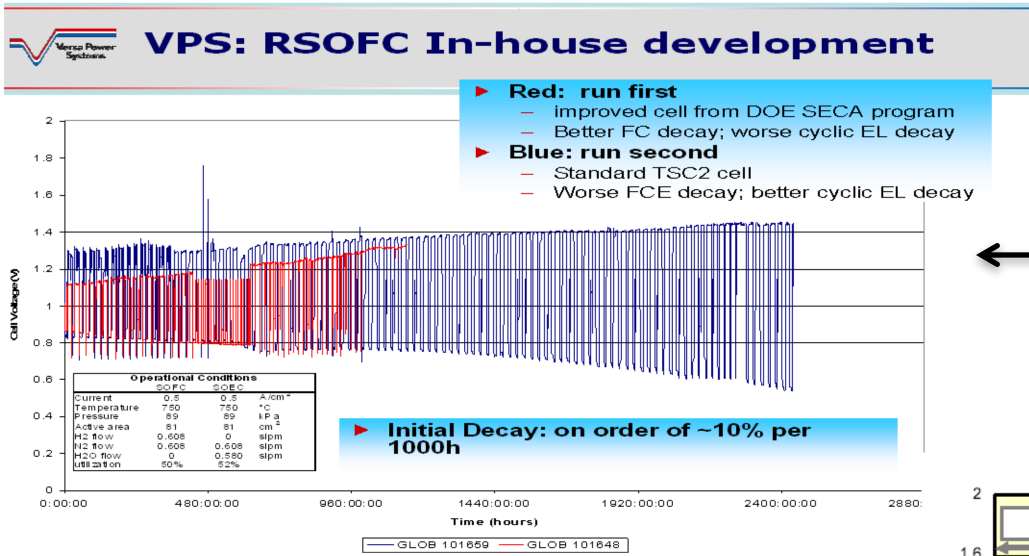
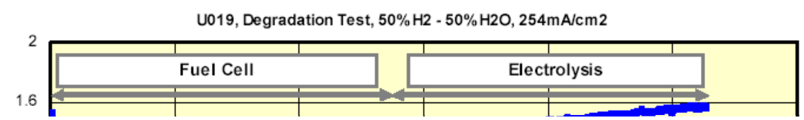
Literature Data



Versapower



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720 Cell Full-ILS System at INL
5.7 Nm^3/hr - 17.5kW H_2 Production

Idaho National Laboratory

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SOEC Open Issues

- Thermodynamics
  - Operating Voltage/Efficiency
  - Steam Utilization
  - Co-electrolysis of CO_2
- High Temp Heat Duty
  - 0-15% of energy input
  - Wind/Solar/Low-Moderate Temperature Nuclear power
  - Biomass or Synfuel integration

- Degradation/Lifetime
  - Oxygen bond layer stability
  - Oxygen electrode delamination
  - Electrolyte stability
  - Chromium migration
  - Seals
  - Interconnect scale growth & resistance
  - Electrode microstructure
    - Electrode coarsening

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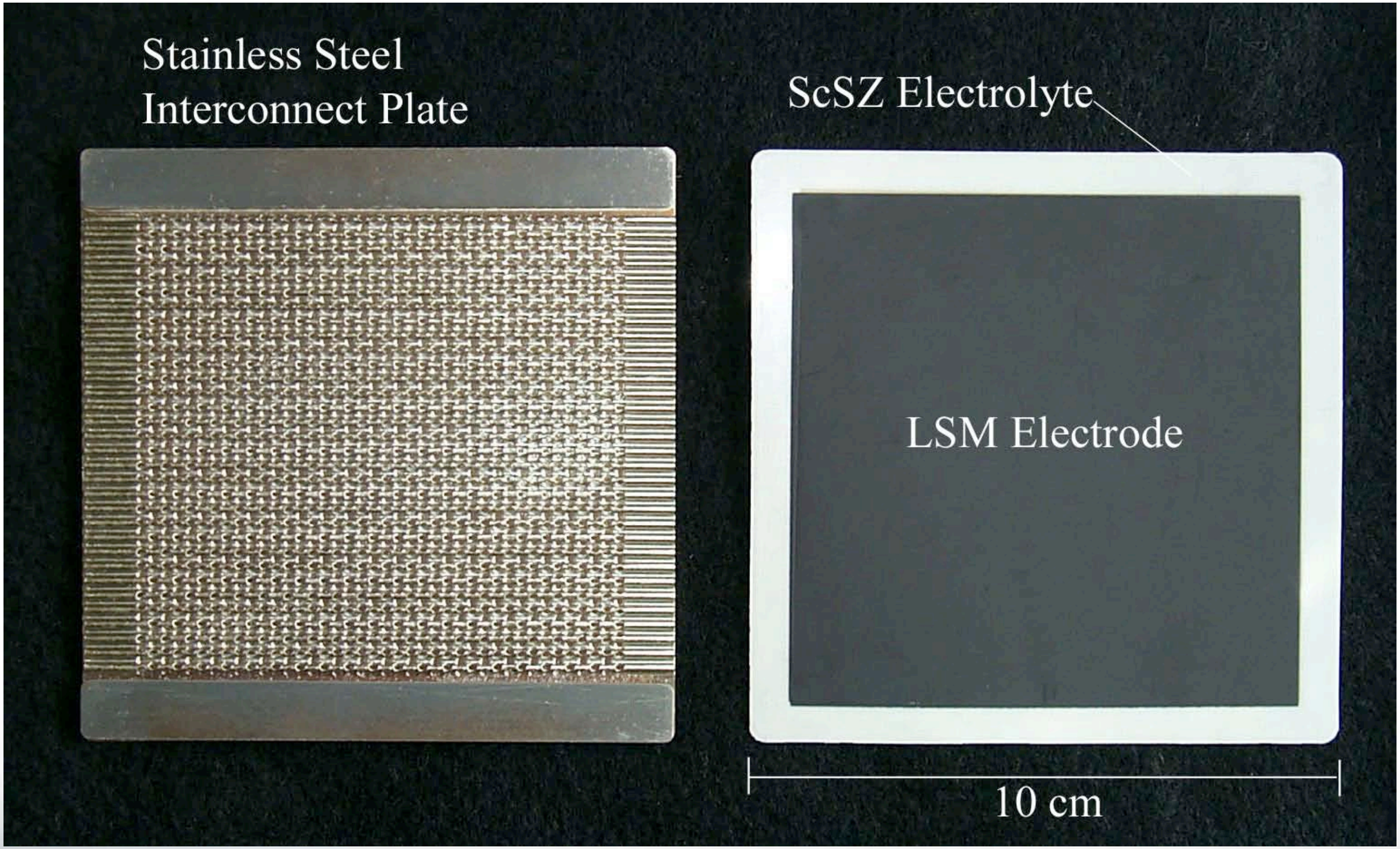
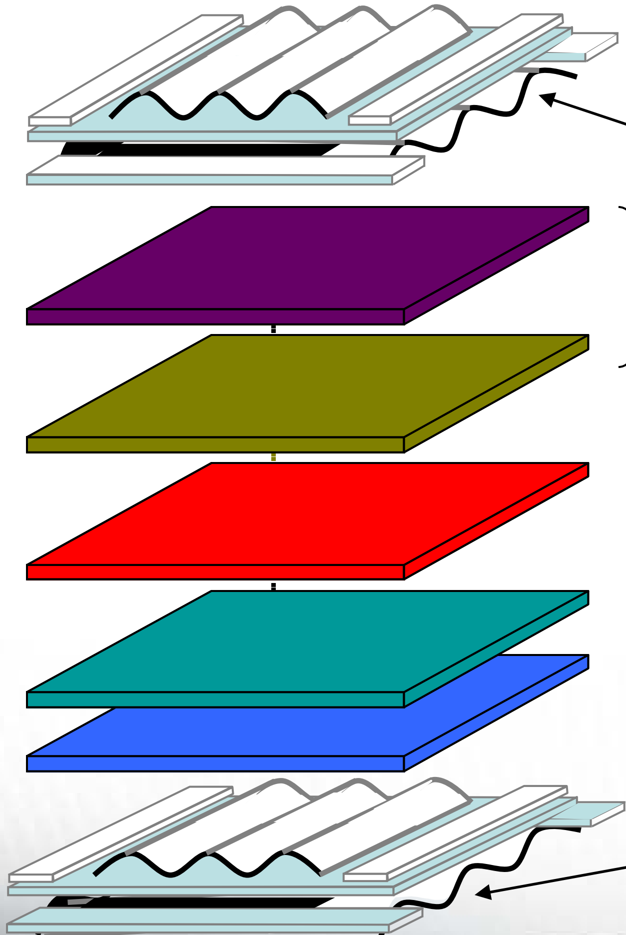
Stack Components



Repeat Unit Elements

Baseline Stack



Ferritic Stainless Steel Separator (Rare earth treated)

Corrugated Ferritic Stainless Steel or High Ni alloy

air electrode

Cobaltite (current distribution layer)

Manganite + Zirconia Composite

electrolyte

Sc - ZrO_2 (partially stabilized)

H electrode

Ni + ceria cermet

Ni (current distribution layer)

Corrugated Ni flow field on hydrogen side

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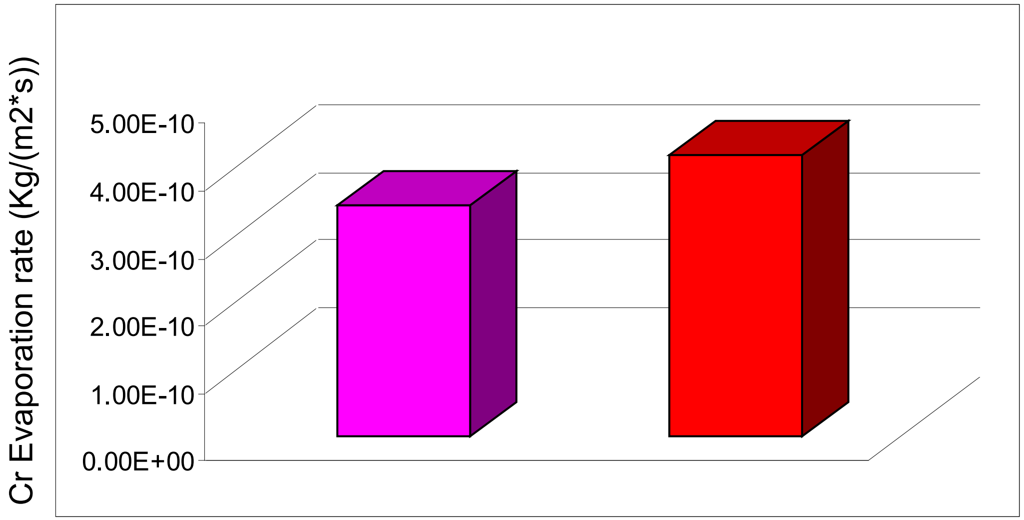
2X60 cell stack Key Observations

- Electrodes
  - Oxygen electrode delamination for 2,000 hr test
    - No delamination in short stacks tested for shorter periods (~300 hrs)
  - Hydrogen electrode & current distribution layer in good condition
- Metal Interconnect Edge Corrosion
  - Cr transport to oxygen electrode bond layer
  - Sr migration from oxygen electrode/bond layer
    - Gross changes in bond layer chemistry, phase assemblage, conductivity and performance
- Initial Performance Reproducible – short to tall stacks
- Unacceptably High Initial Degradation

Cr-evaporation

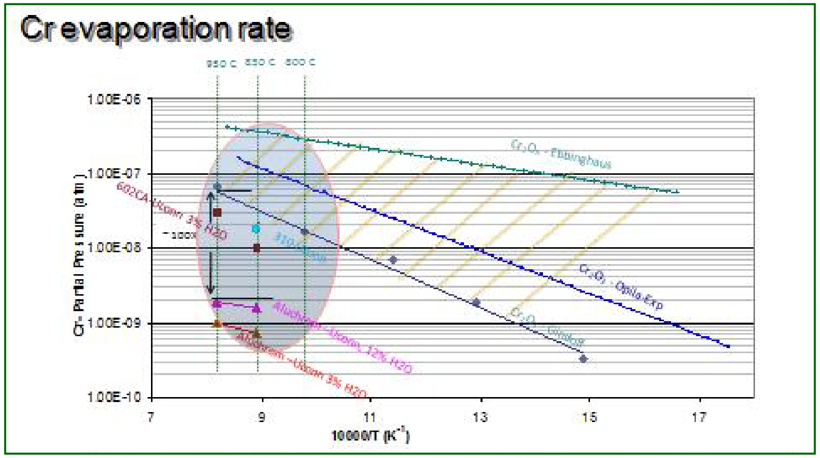


SOFC Mode

3%H2O+Air

SOEC Mode

3%H2O+50%O2+50%N2



$Cr_2O_3(s) + H_2O(g) + O_2(g) = CrO_2(OH)_2\,(g)$ (1)

$Cr2O3(s) + H_2O + O_2 = CrO(OH)_2\,(g)$ (2)

$Cr2O3 + O2 = CrO_3(g)$ (3)

Higher Cr vapor pressure possibly due to:

1. High PO_2 resulting in high CrO_3
2. Scale spallation and continued evaporation

oxygen and steam pressure dependence

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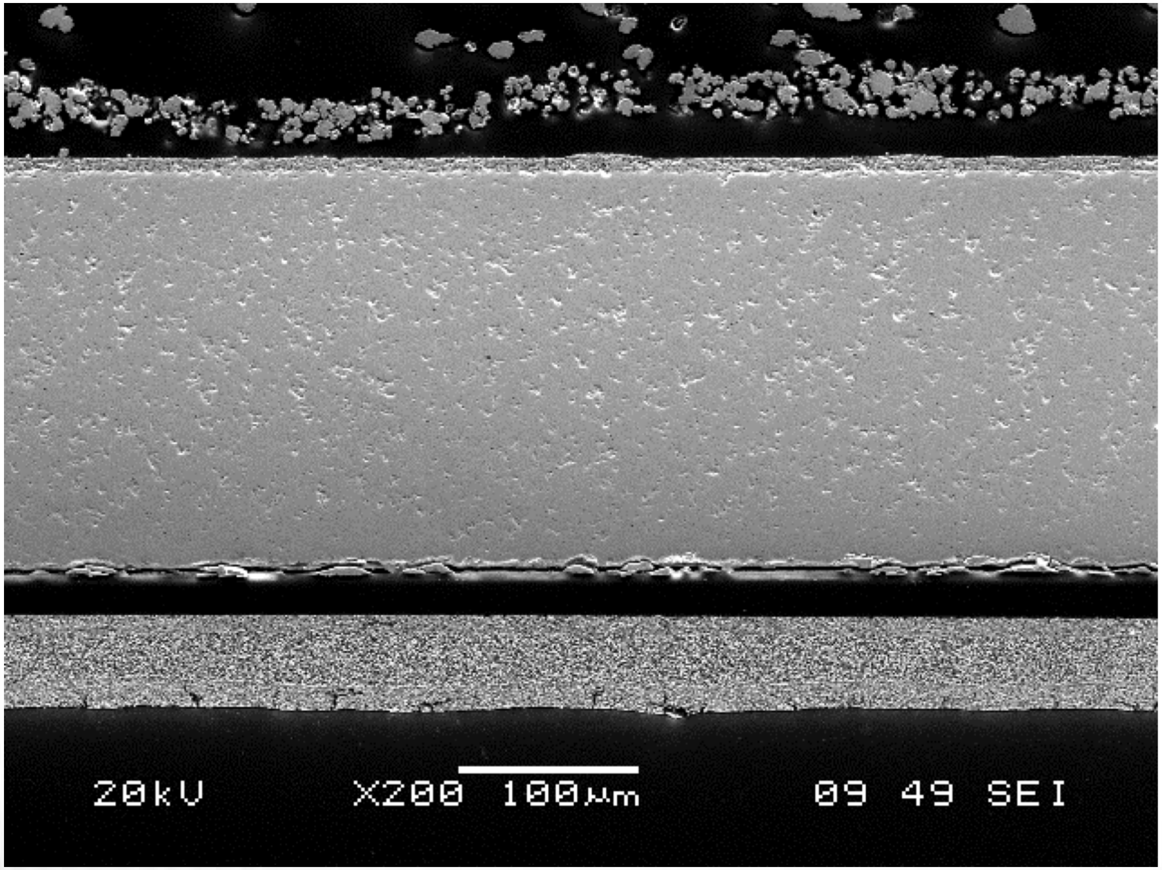
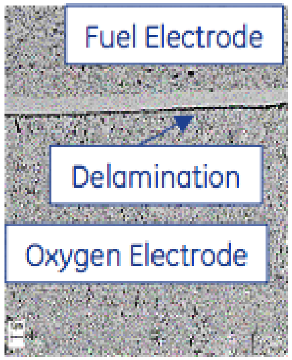
Full-ILS Module #3 Post Test Examination



Hydrogen electrode attached,
bond layer separated with interconnect

Oxygen electrode delamination
Similar effect as half ILS test

Literature Comparison



re 4-4 Cross section of a tested cell showing delamination between LSM/'
jen electrode and YSZ electrolyte

General Electric

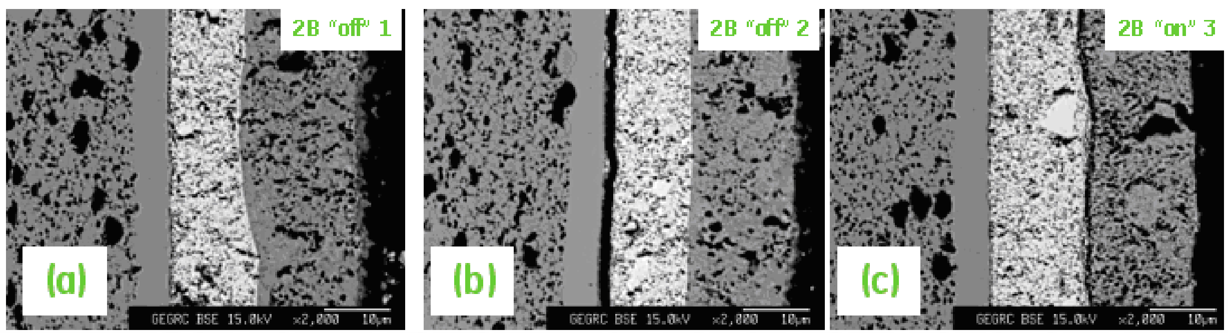
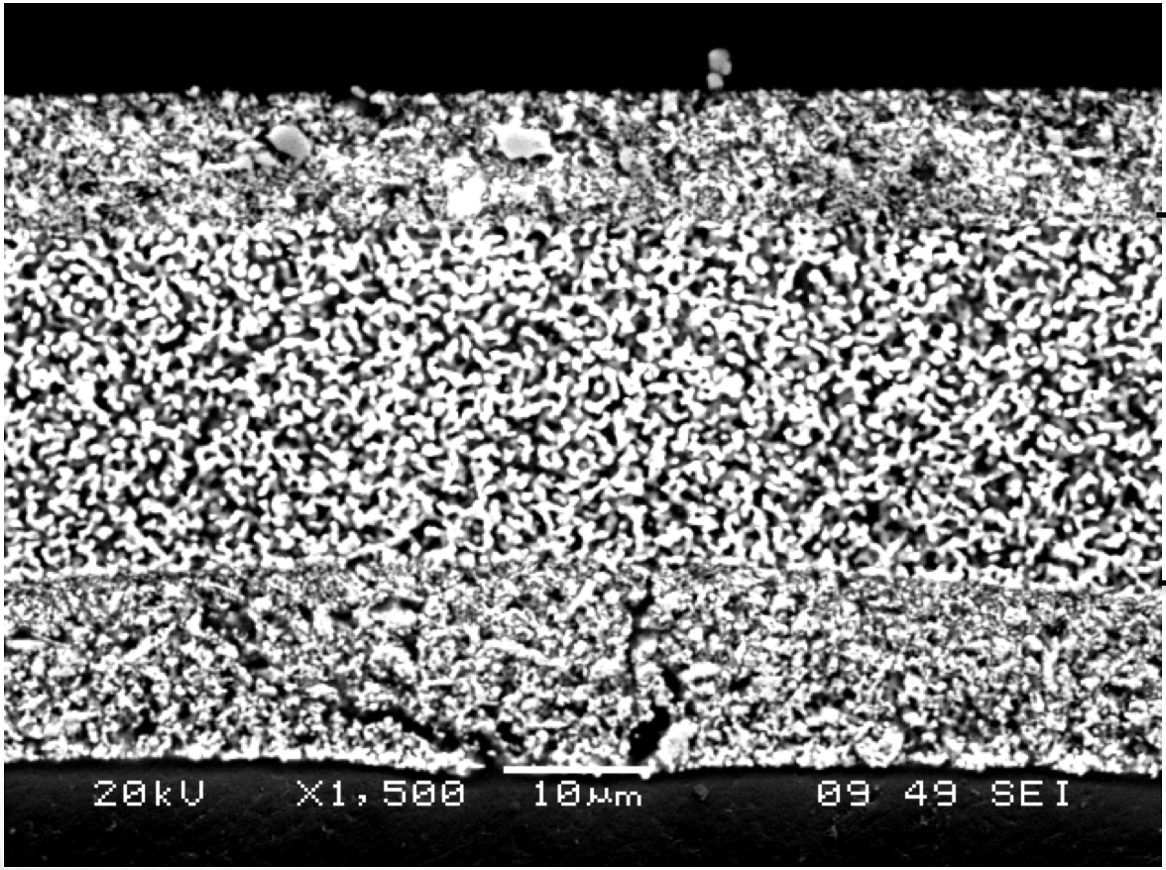


Figure 5-3 Microstructures of one cell in stack U047. (a) typical cross section, (b) cross section showing the delamination between YSZ electrolyte and barrier layer, (c) cross section showing delamination between SDC barrier layer and LSCF oxygen electrode.

720 cell Module #3 Post Test Examination

Electrode section in following EDS Maps



Manganite-Zirconia Composite

Manganite Electrode

Cobaltite (LSCo) contacting layer (bond layer)

No major change in air electrode microstructure

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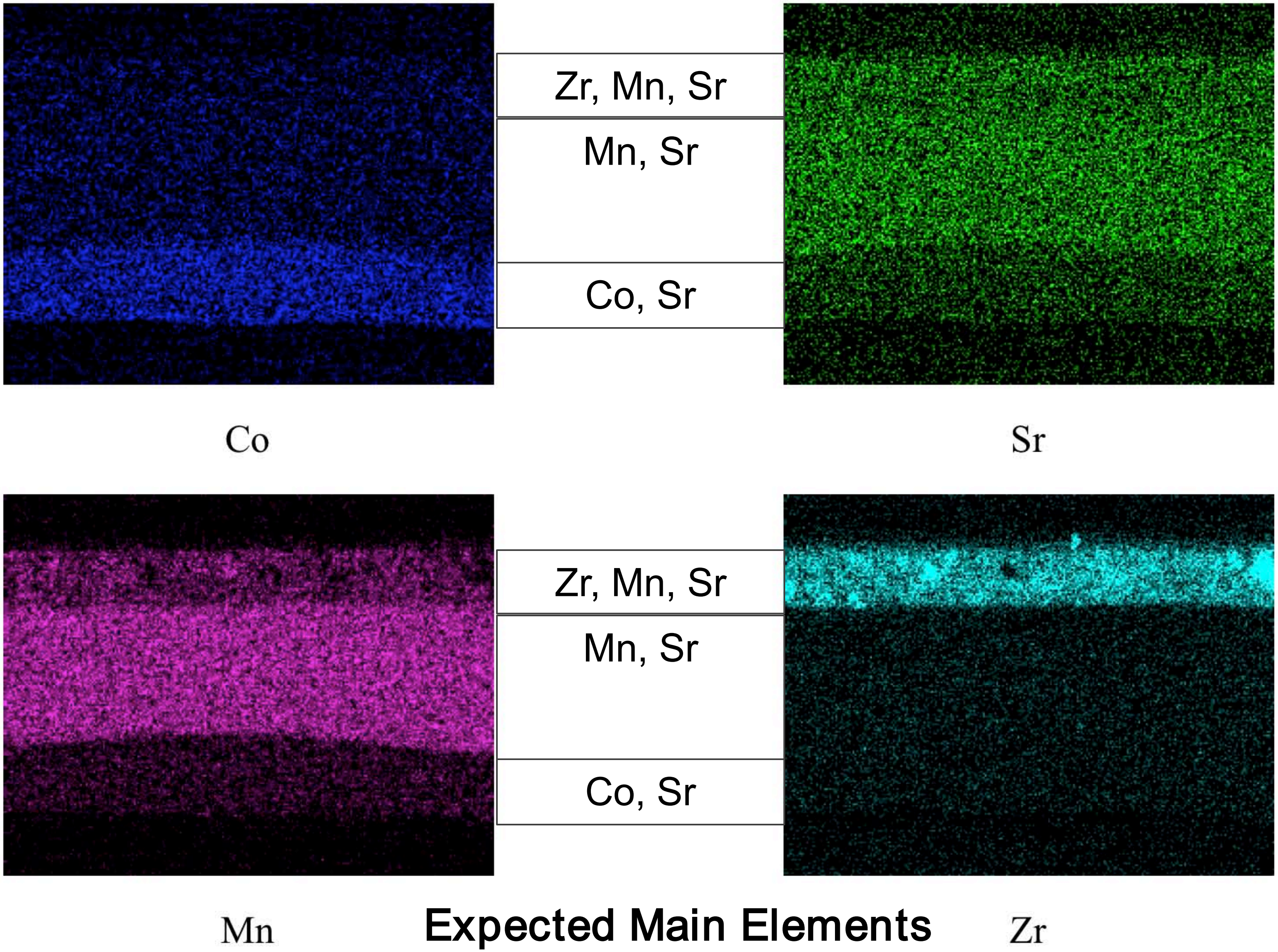
Co-Mn Inter-diffusion in Oxygen Electrode



Expected Main Elements

ILS Module 3 Post-test

- Air electrode delamination
- Potential for Mn & Sr diffusion into ScSZ playing a role in delamination
- Mn/Co interdiffusion changing electrode activity and conductivity
- No substantial change to air electrode microstructure
- Less Cr observed in electrode for module 3
  - Module 3 used spinel barrier coating on interconnect

Air Electrode is Key

- Evaluated more than 10 air electrode compositions
  - Manganite, Cobalt-ferrite, ferrite
  - Dopant variations
- One Cobalt-Ferrite was selected for stack test

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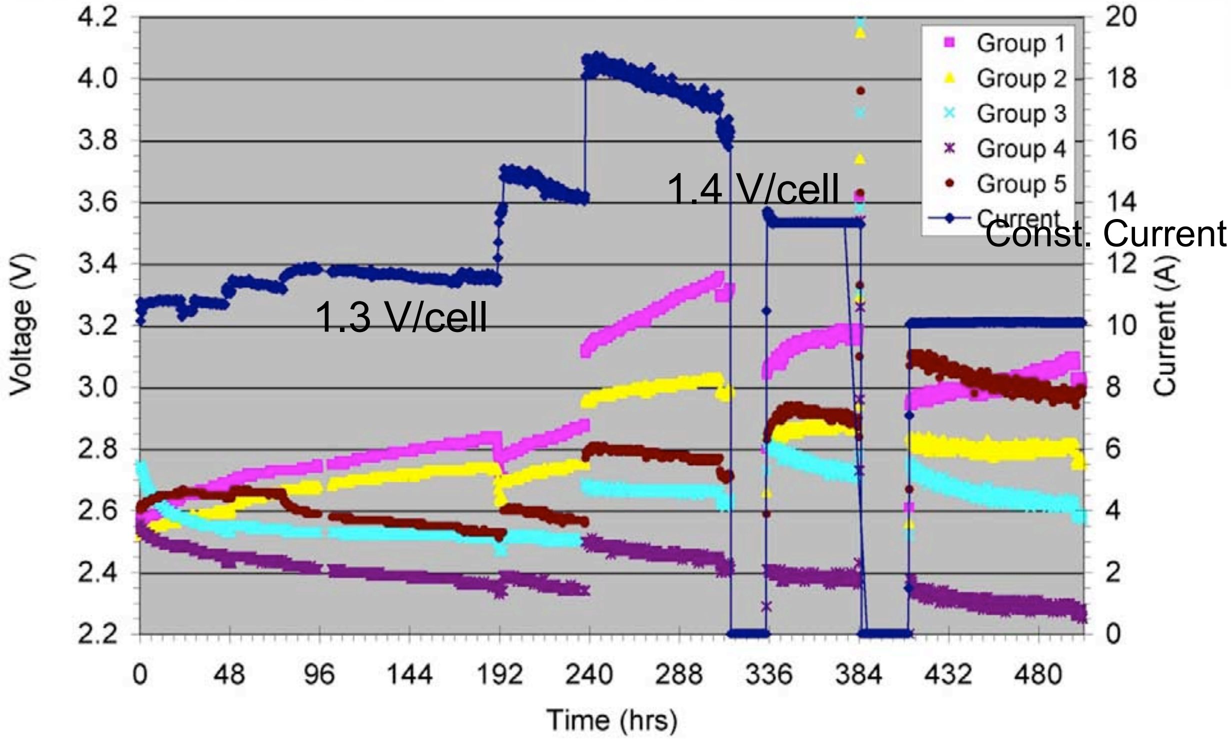
Air Electrode Comparison Stack

- 10-cell stack
  - 5 cells using baseline manganite electrode
  - 5 cells using new cobalt-ferrite electrode
  - All interconnect with air-side spinel coating
- Monitored voltage of 2-cell groups
  - Two 2-cell groups of manganite electrode
  - One 2-cell group of mixed electrodes
  - Two 2-cell groups of cobalt-ferrite electrode

O_2 Electrode Comparison Stack



- At fixed total stack voltage
  - Manganite groups: increase in voltage (ASR) with time
  - cobalt-ferrite groups: decrease in voltage with time
  - Mixed group: net decrease in voltage with time

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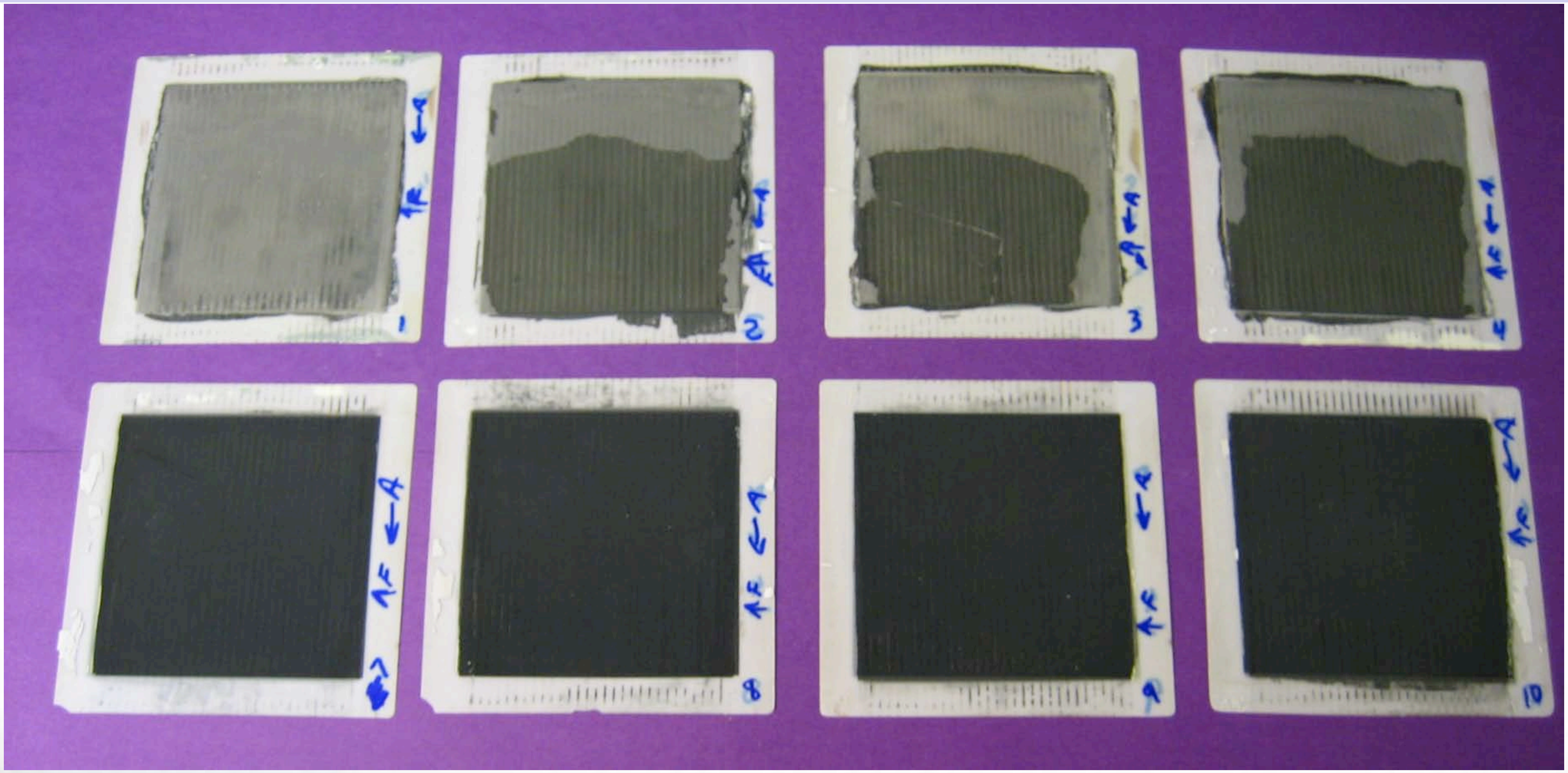
Post-test: Comparison Stack
Oxygen Electrode and Bond Layer

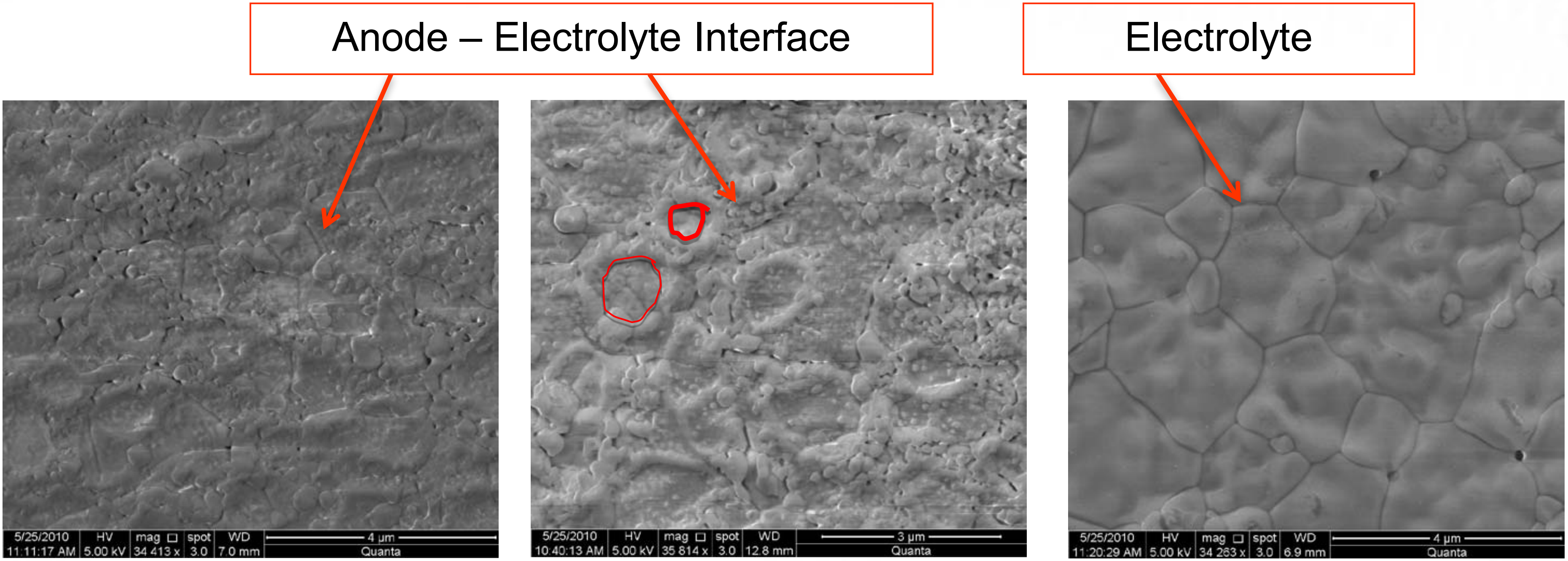
Extensive delamination of standard manganite Perovskite electrodes



No delamination of new cobalt-ferrite Perovskite electrodes (Ceria interlayer used)

Electrolyte/anode interface morphology

850C for 100 hrs



For 0.8 volt cell - Surface in contact with anode (after dissolving LSM in HCl)

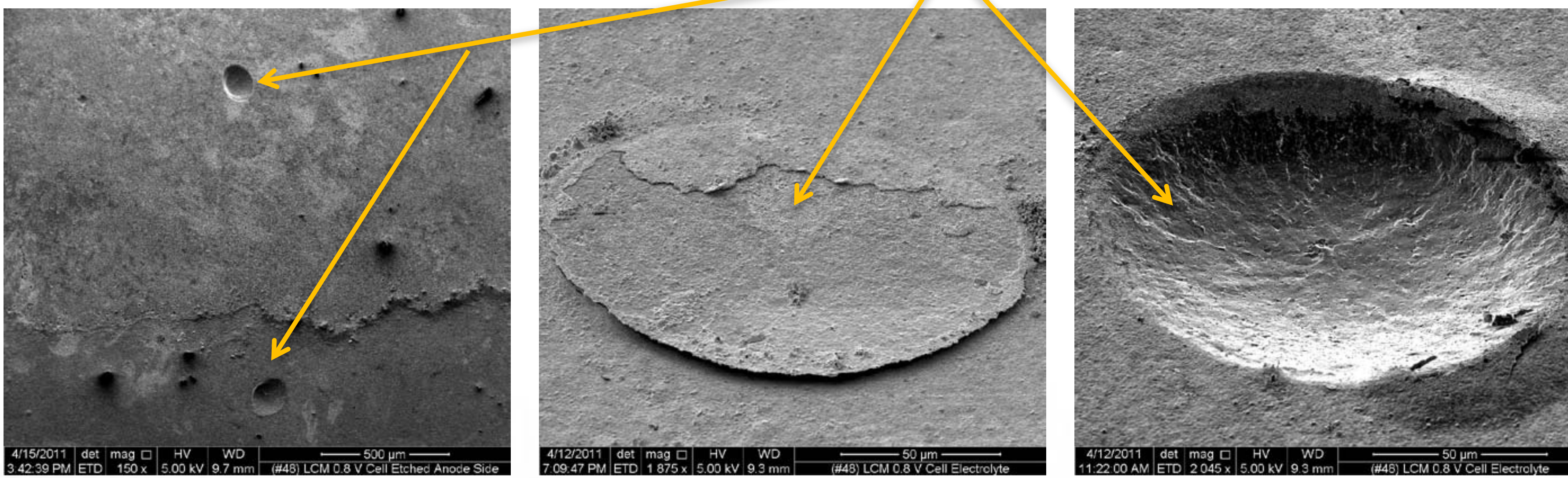
Anode imprint, Elevated ridge formation, Small particulate formation, YSZ grain boundary separation, Ellipsoidal porosity at GB

Electrolyte – Anode Electrode Interface

Accelerated tests were performed to understand the electrode – electrolyte interface delamination and interface compound formation. Large area delamination and crater formation was observed under a wide variety of electrolyte/ electrode contact.

Half cell test- 850C, 100Hrs.

Delamination and crater formation



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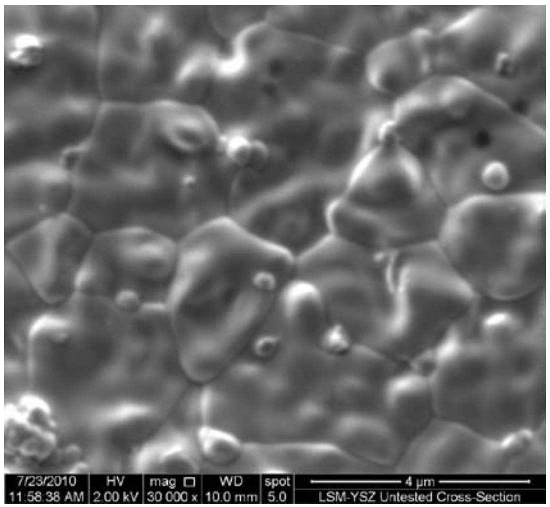
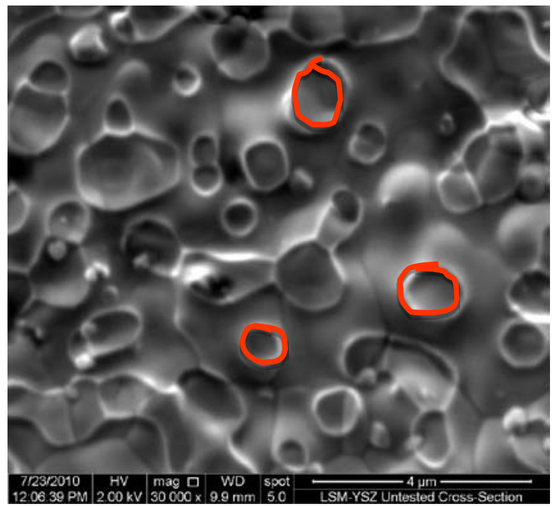
Electrolyte/Electrode interface examination

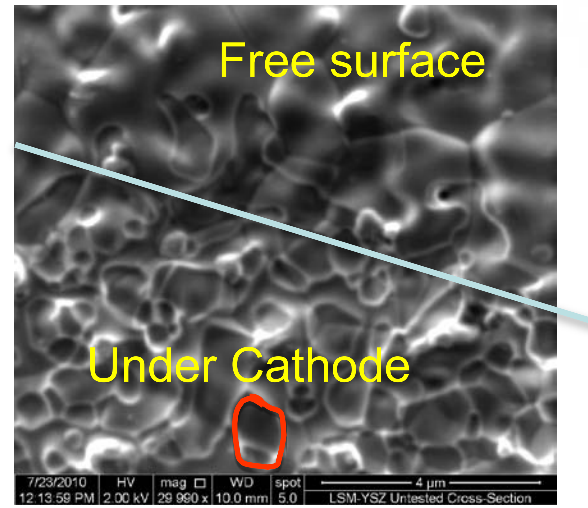
No voltage applied



Free Electrolyte surface



Electrolyte surface under cathode



Electrolyte surface under cathode

For “No –Volt Apllied” cell - Surface in contact with electrode (after dissolving LSM in HCl)

A. Mittledorfer, L.J. Gauckler, Solid State Ionics, 111, 185-218, 1998

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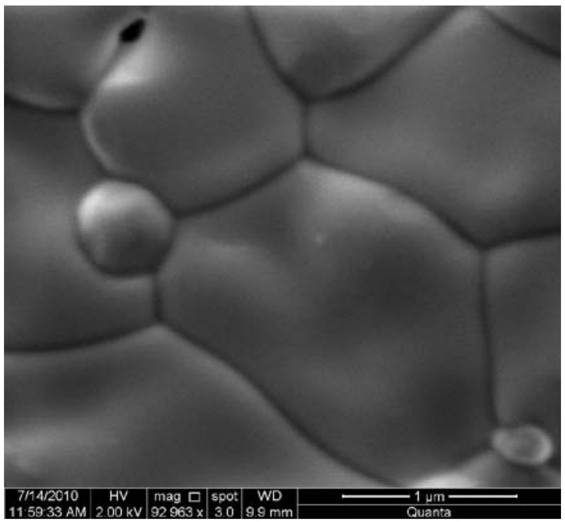
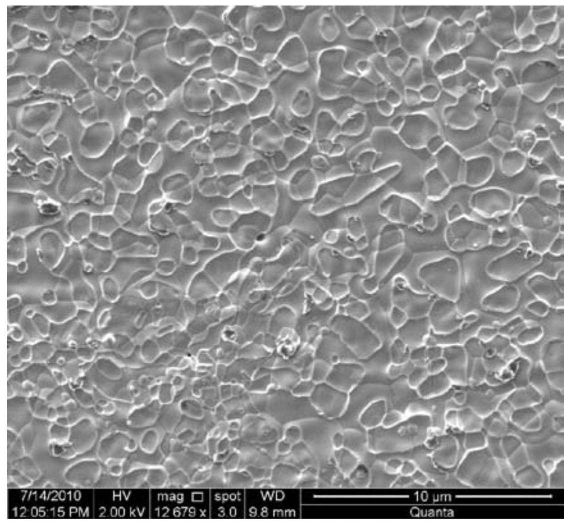
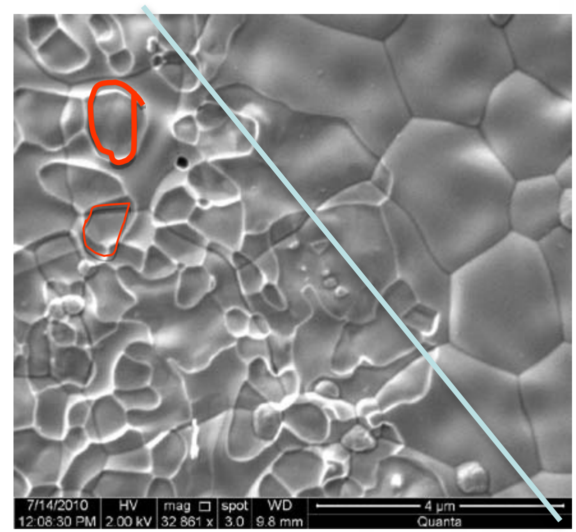
Electrolyte – Cathode Interface

Free electrolyte surface

Cathode impression



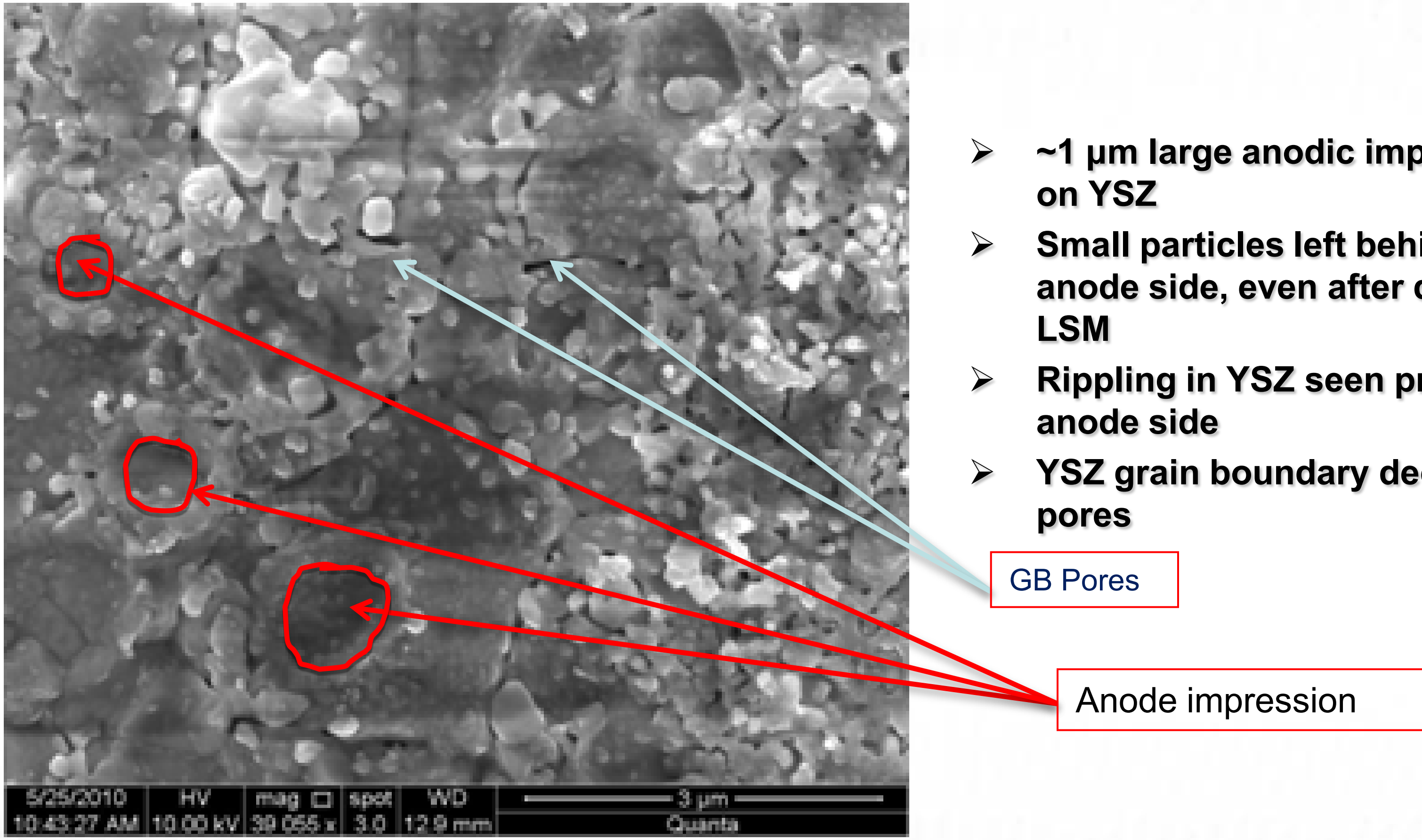




For 0.8 volt cell - Surface in contact with cathode (after dissolving LSM in HCl)

Fred van Heuveln. Characterization of Porous Cathodes for Application in Solid Oxide Fuel cells, Ph. D dissertation, Technische Universiteit Twente, 1997.

Degradation at YSZ/LSM anode under load



- ~1 µm large anodic impression on YSZ
- Small particles left behind on YSZ anode side, even after dissolving LSM
- Rippling in YSZ seen primarily on anode side
- YSZ grain boundary decorated by pores

Surface in contact with anode after applying 0.8 volts for 100 hours – anode delaminated

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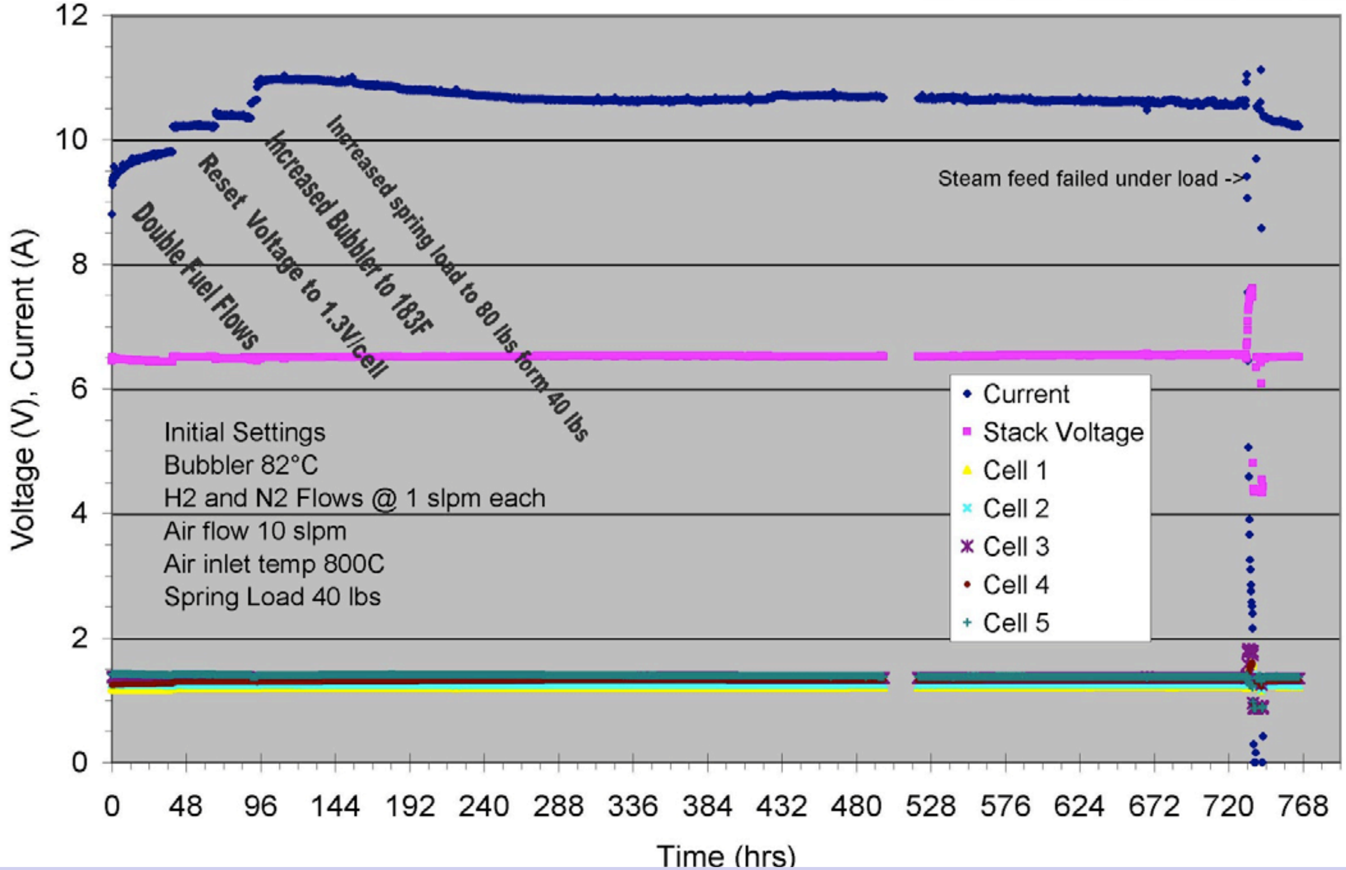
New O_2 Electrode Improves Stack Stability

5-cell stack with cobalt-ferrite electrode and Current Collection Layer
Ceria interlayer between ScSZ and electrode



Excellent Stability, but lower initial performance

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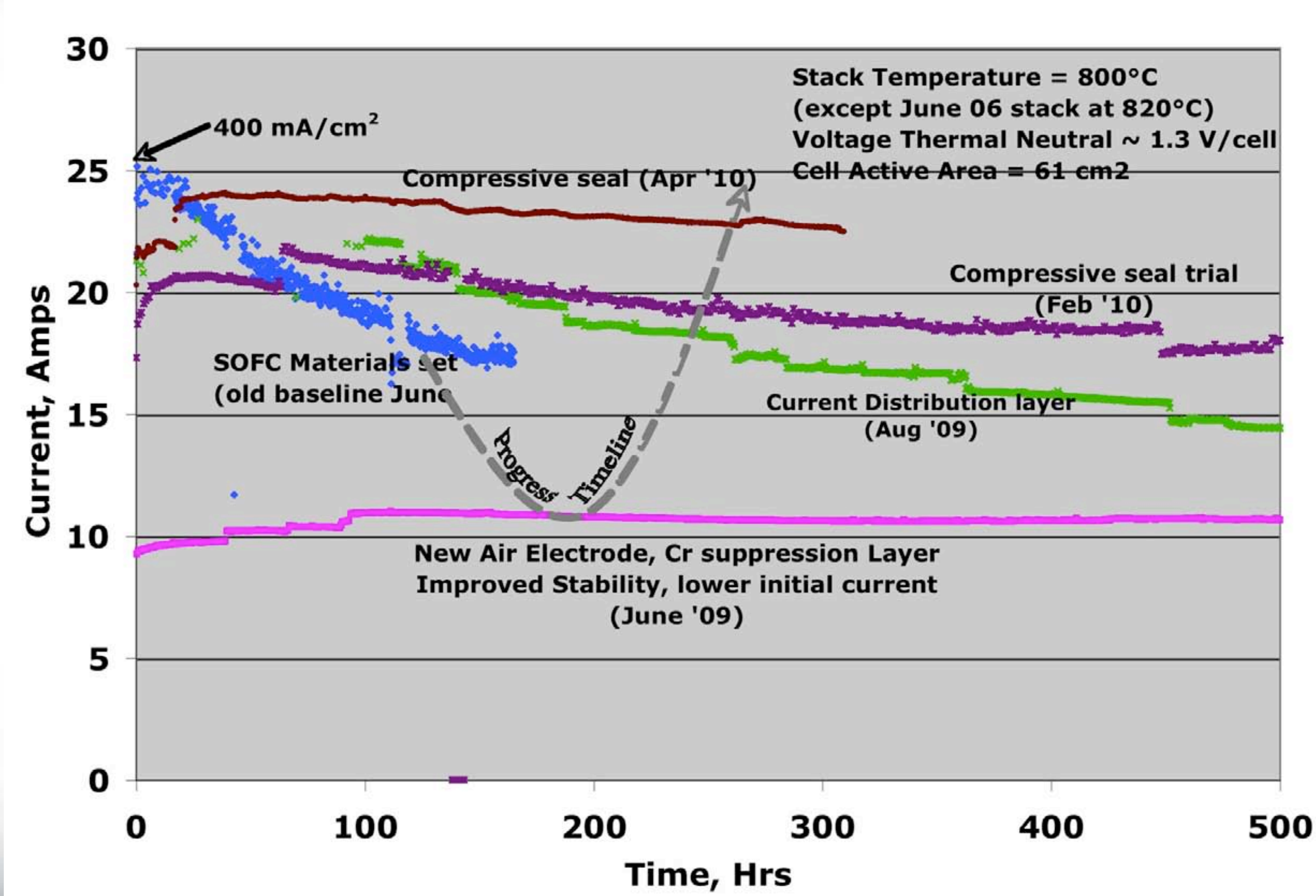
Electrolysis Stack Stability Progress



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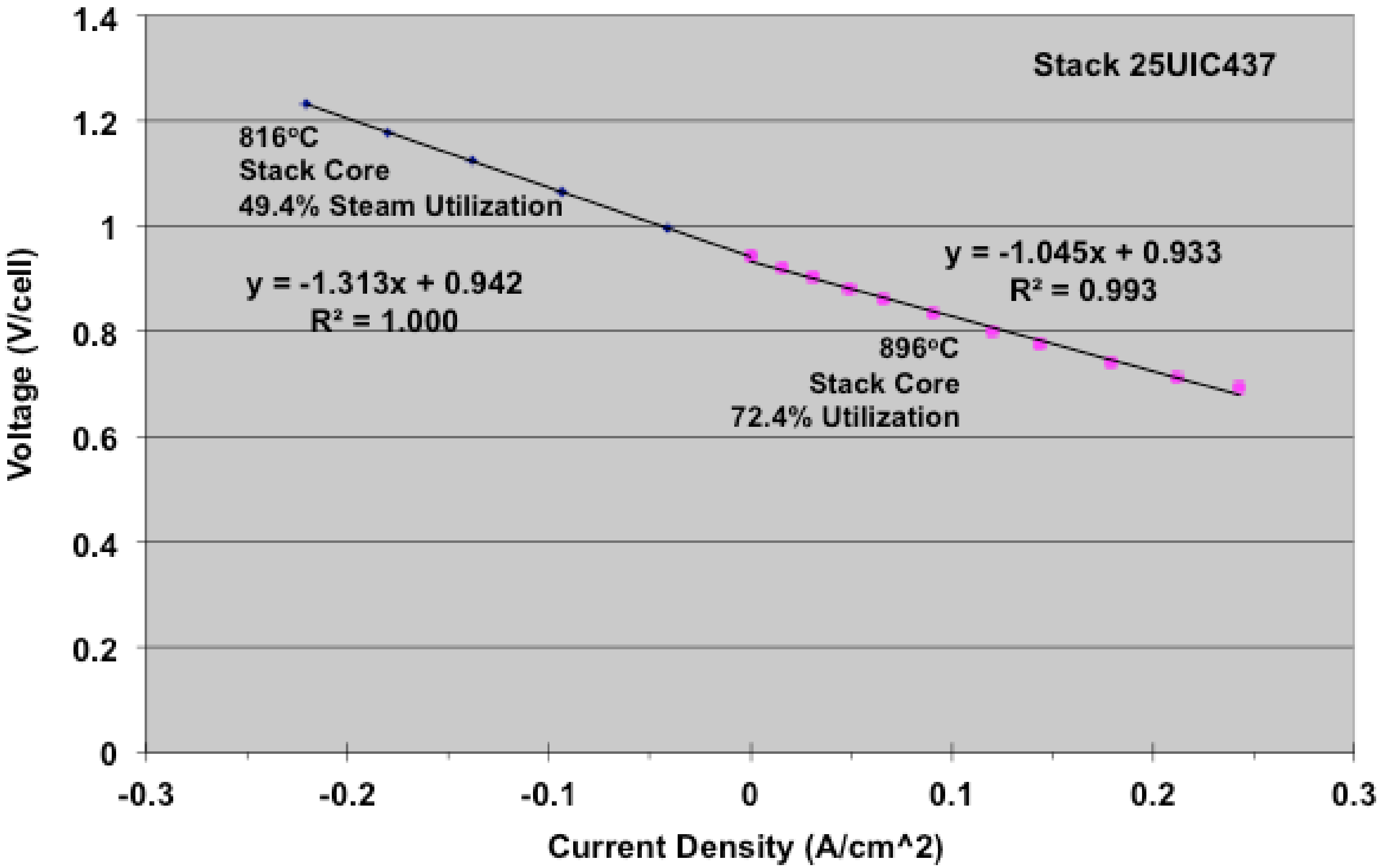
System Issues

Reversible Operation – 25 cell Stack



Typical button cell performance 0.6 to 0.7 ohm-cm^2 at 800°C

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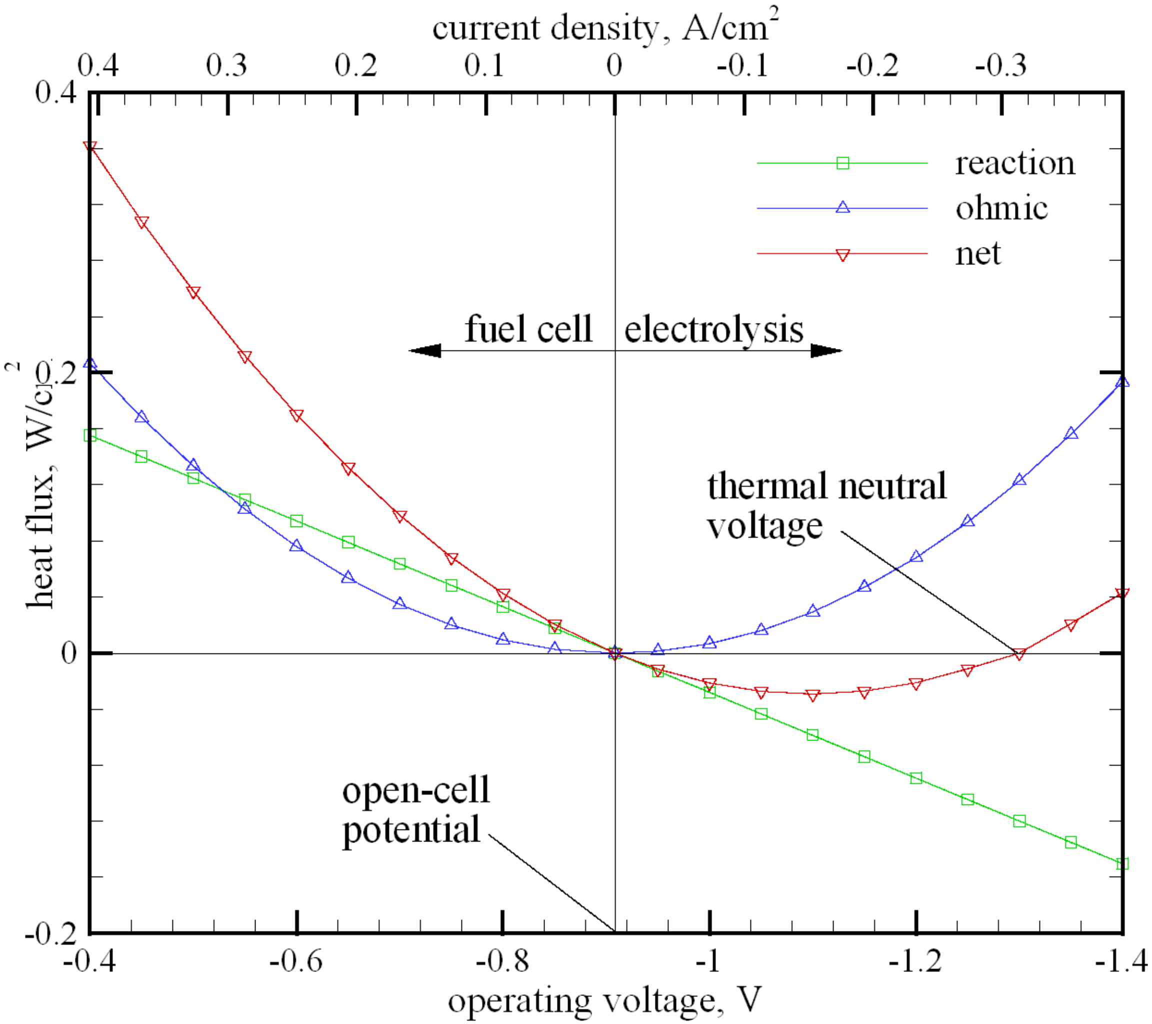
Energy of fuel-cell vs. electrolysis mode

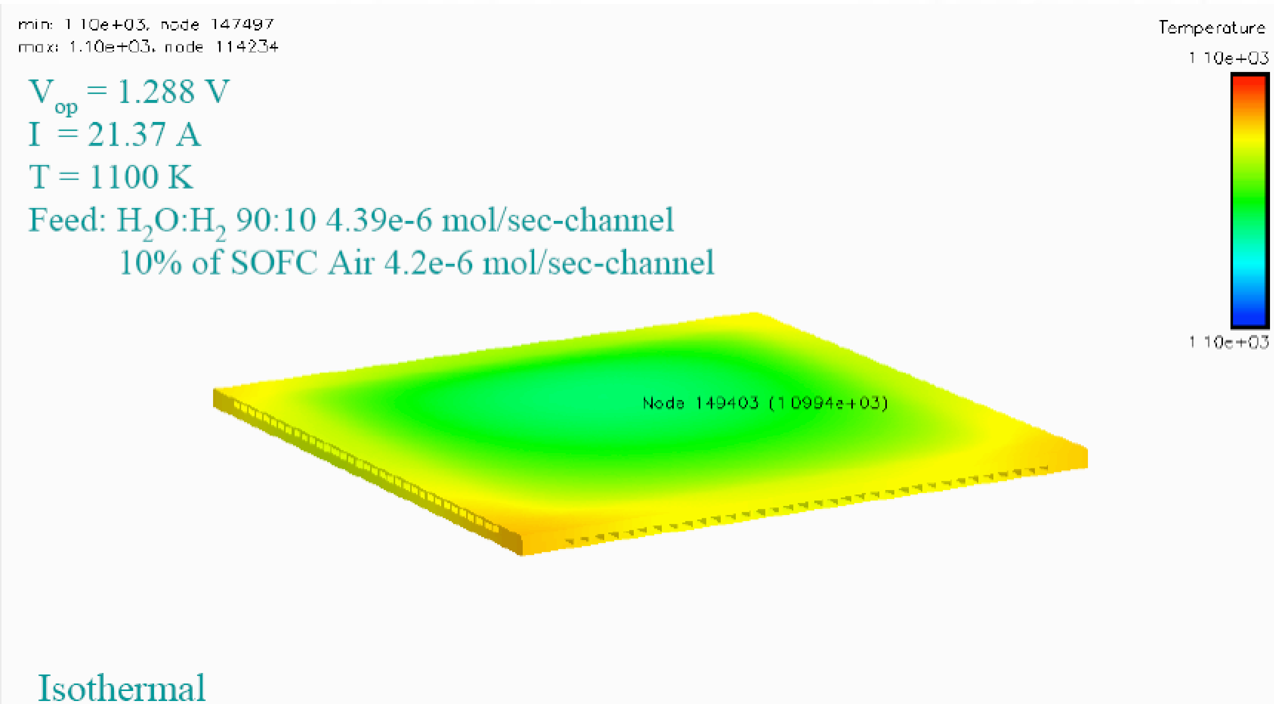


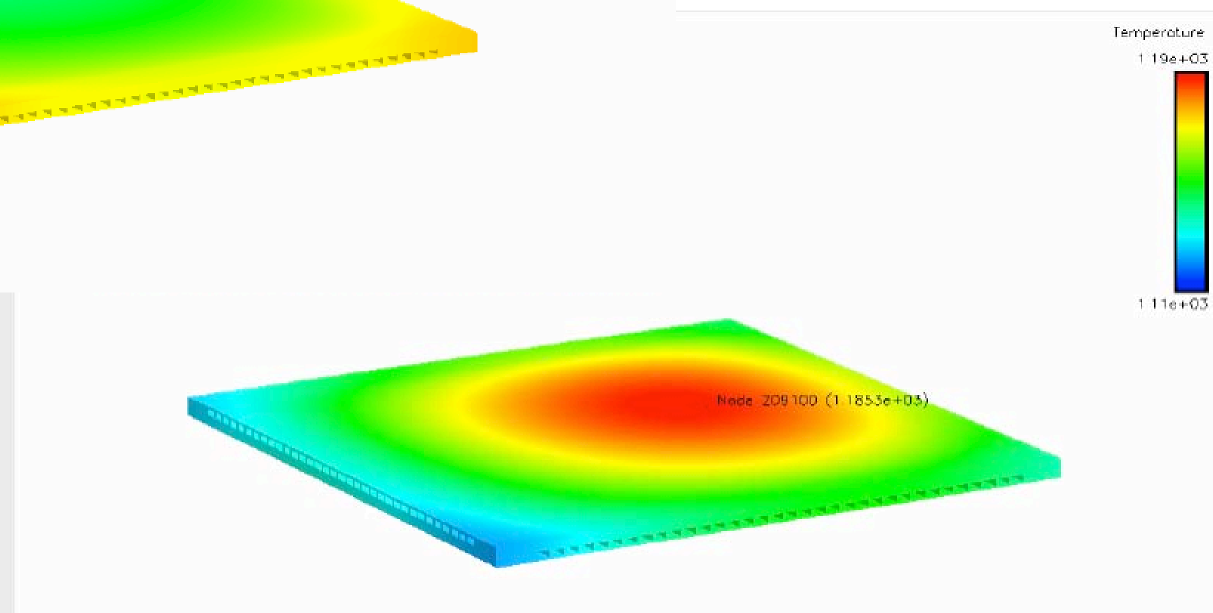
Stack ASR = 1.25,
T = 927 C,
$y_{H2,i} = 0.1$,
$y_{H2,o} = 0.95$

$$V_{tn} = \frac{-\Delta h_R}{2F}$$

(1.291 V at 1200 K)

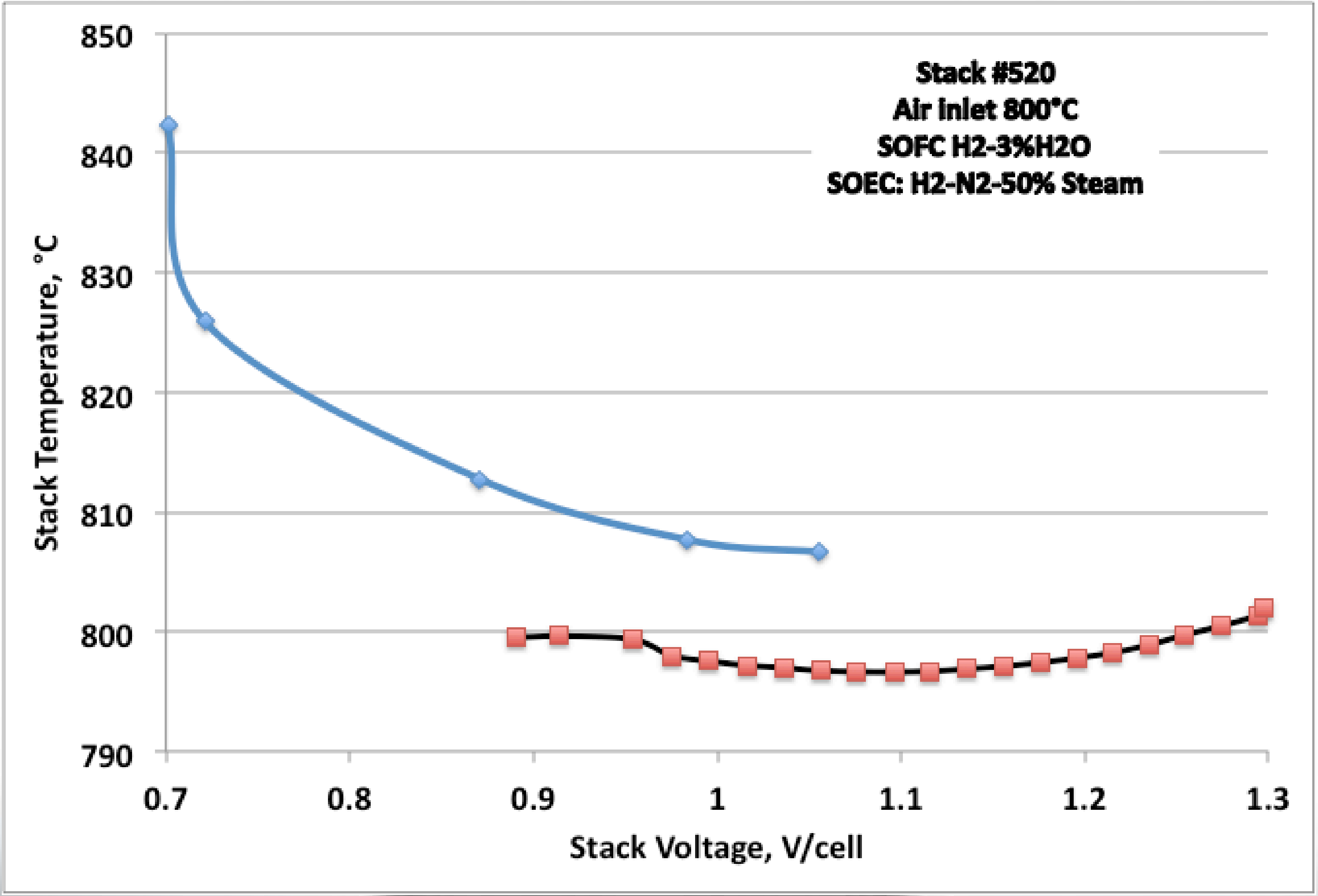
Typical SOEC and SOFC Temperature Maps





SOFC ΔT > 90°C
Resistance doubling ~ 67 °C
Thermal expansion issues

SOFC vs SOEC Operation



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System Issues Controlled by SOFC Mode

- SOFC mode dominates
  - Cell foot print (heat removal issues)
  - CTE issues
- SOEC mode
  - Materials issues
  - Capable of solar (in endothermic mode) and wind (exothermic mode) integration

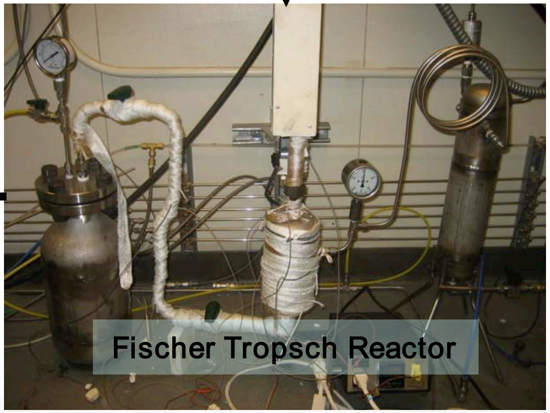
Current Project on CO_2 Beneficiation

Steam+ CO_2

Renewable Electricity

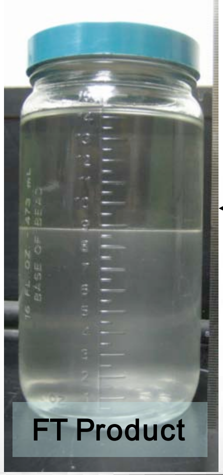
Other Option
Reformed Biogas

Syngas



Synthetic Diesel Fraction

Water Fraction



Summary

- Single SOFC device capable of reversible operation expands applications potential
  - Allows greater use of renewable resources
  - Opportunity for CO_2 re-use to store renewable as liquid transportation fuel
  - High efficiency hydrogen generation
- Significant differences in degradation mechanism between SOFC and SOEC
  - Promising composition identified
  - Good stability in SOFC mode with new materials
  - Requires additional research to study cyclic behavior between modes of operation
- Thermal issues more severe in SOFC mode

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the Department of Energy through
Idaho National Laboratory

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