

Materials Development for Solid Oxide Electrolysis Cells



CERAMATEC[®]

TOMORROW'S CERAMIC SYSTEMS

S. Elangovan, J. Hartvigsen, F. Zhao, I. Bay, D. Larsen



November 16-19, 2009 Palm Springs Convention Center, Palm Springs, CA, USA

Overview

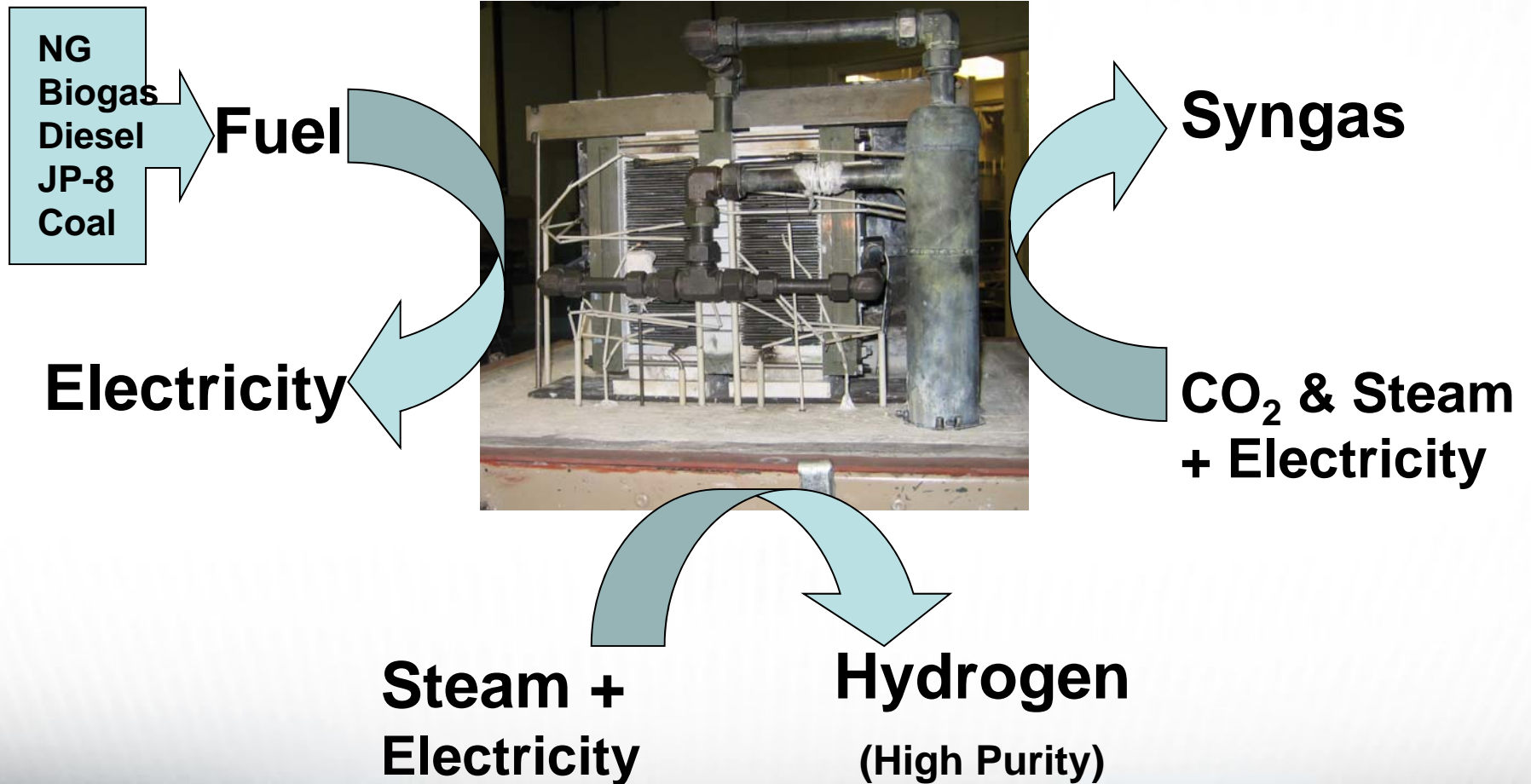
- Motivation & Opportunity
- Comparison of SOFC and SOEC
- SOEC Successes & Challenges
- Materials Investigations for increasing SOEC stack lifetime
- Results & Conclusions



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

One Technology - Multiple Modes Of Operation

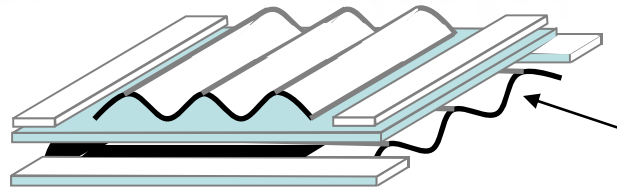
Solid Oxide Stack Module



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

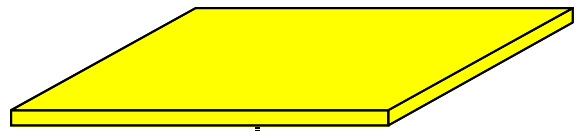
Repeat Unit Elements

Baseline Stack



Ferritic Stainless Steel Separator (Rare earth treated)

Corrugated Ferritic Stainless Steel or High Ni alloy



air
electrode

Cobaltite (oxygen electrode bond layer)

Manganite + Zirconia Composite



electrolyte

Sc – ZrO₂



H
electrode

Ni + ceria cermet

Ni (hydrogen electrode bond layer)

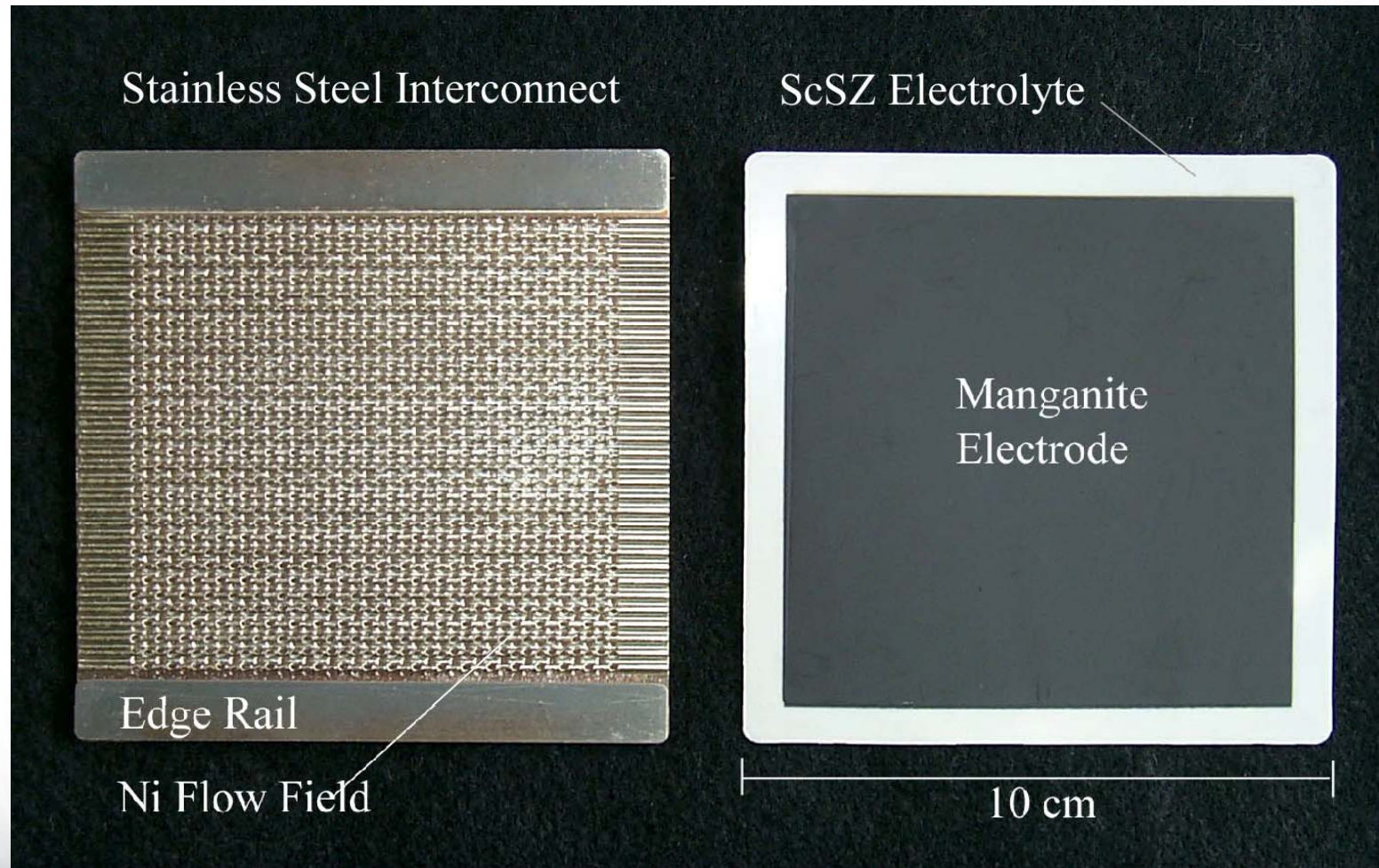


Corrugated Ni flow field on hydrogen side



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Stack Components



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

SOFC – SOEC differences

- SOEC relative to SOFC has
 - Higher performance (power, efficiency)
 - More uniform stack temperature
 - SOEC operating point determines heat needs
 - Very large area cells possible with SOEC



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

SOFC - SOEC Differences

- SOEC's tested before Q2-09 used SOFC component materials & design
- SOEC seals more challenging
 - Higher back pressure on seals due to product collection
 - Low molecular weight stream vs. reformatate
 - Diffusion mechanism more active relative to hydrodynamic mechanism
 - Hydrogen permeation in metal interconnect destabilizes air side scale



SOEC Open and Addressed Issues

- Thermodynamics
 - Operating Voltage/Efficiency
 - Steam Utilization
 - Co-electrolysis with CO₂
- High Temp Heat Duty
 - 0-15% of energy input
 - Wind/Solar/Low-Moderate Temperature Nuclear power
 - Biomass or Synfuel integration
- Energy Cost
 - \$50/MW-hr => \$1.72/kg H₂
- Amortized CAPEX
 - 24 month life => \$0.46/kg H₂
- Cell Size & Stack Height
 - Very large cells feasible
 - Porous metal support
- Degradation/Lifetime
 - Oxygen bond layer stability
 - Oxygen electrode delamination
 - Electrolyte stability
 - Chromium migration
 - Seals
 - Interconnect scale growth & resistance
 - Electrode microstructure
 - Electrode coarsening



Electrolysis Cells at 20x20 cm Scale



**500 liter/hr hydrogen production
(1.56 kW - 120A current, 1.3V/cell, 10 cells)**



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Half ILS 2x60 Cell Stack Module



3.8 kW

10x10 cm cells

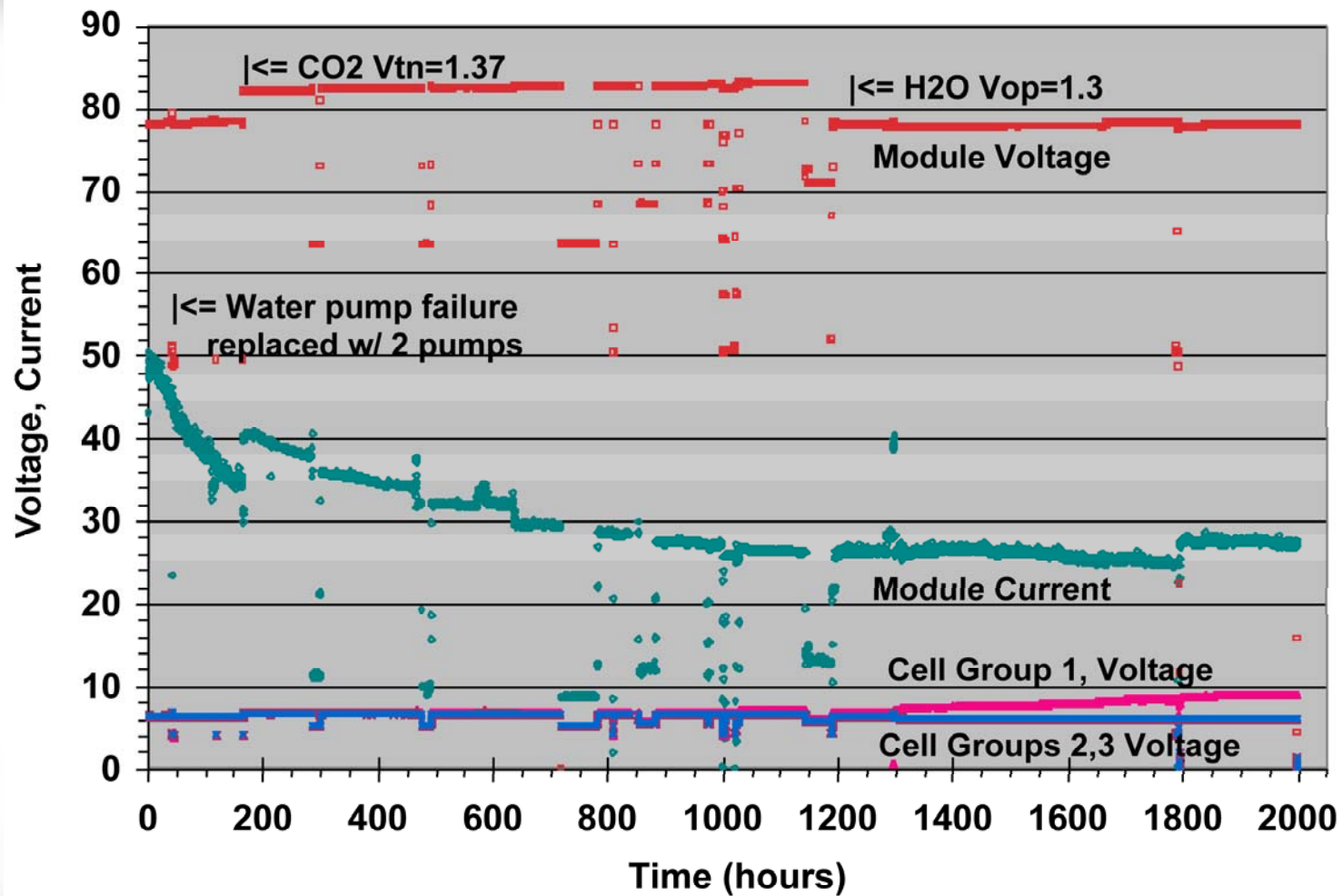
ILS Module: Integrated Laboratory Scale Module

- 1,200 normal liters/hr hydrogen production
- Stack electrical efficiency = 96.4%
- System thermal distribution issues
- 2,000 hrs total operation
- 1,000 hrs on CO₂/H₂O
 - Syngas production sufficient for 100 gallons of FT diesel



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Half ILS module load history



Module Tested at ~ Thermal Neutral Voltage at 800° C



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Half-ILS Post-Test Observations

- Electrodes
 - Oxygen electrode delamination for 2,000 hr test
 - No delamination in short stacks tested for shorter periods (~300 hrs)
 - Hydrogen electrode in good condition
- Metal Interconnects
 - Elimination of silica in seal eliminated the corrosion seen in early SOEC stacks
 - 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, tall stacks and modules
Unacceptably High Initial Degradation



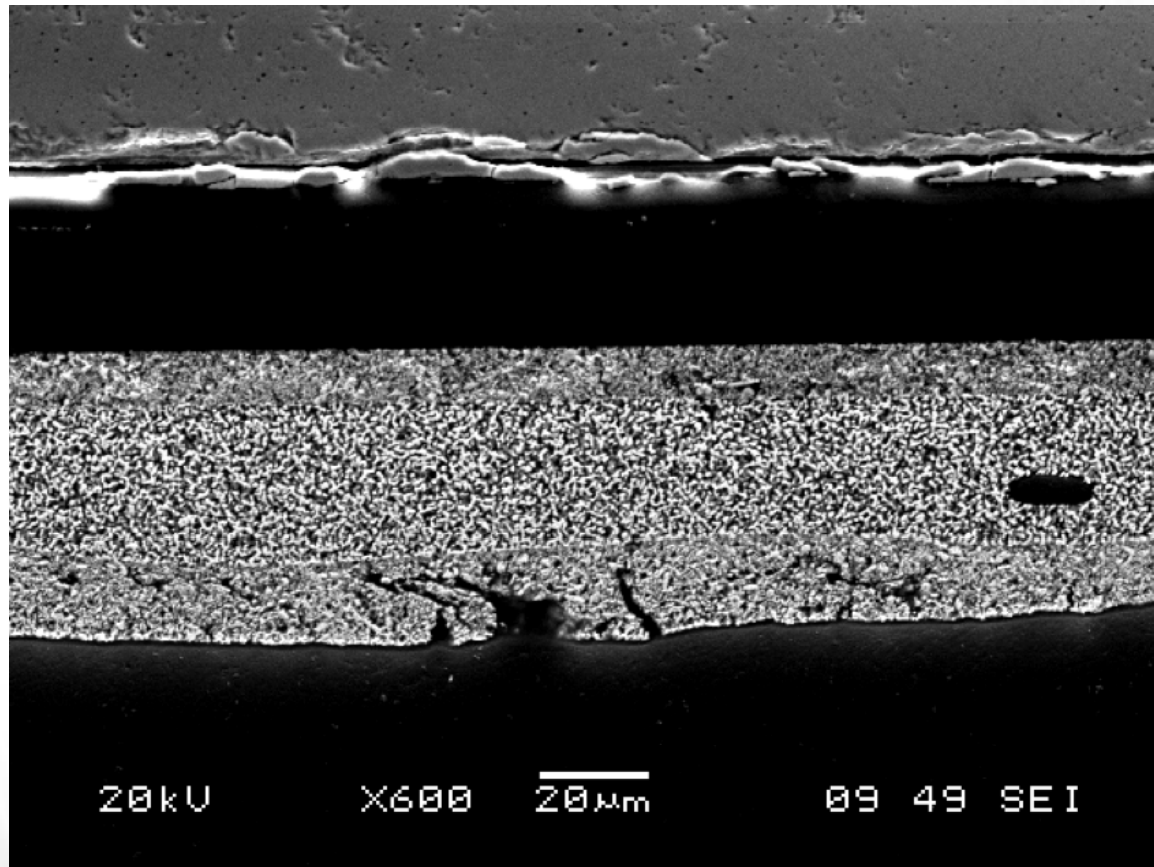
CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

720 Cell Full-ILS System at INL 5.7 Nm³/hr – 18kW H₂ Production



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

ILS Module #3 Post Test Examination



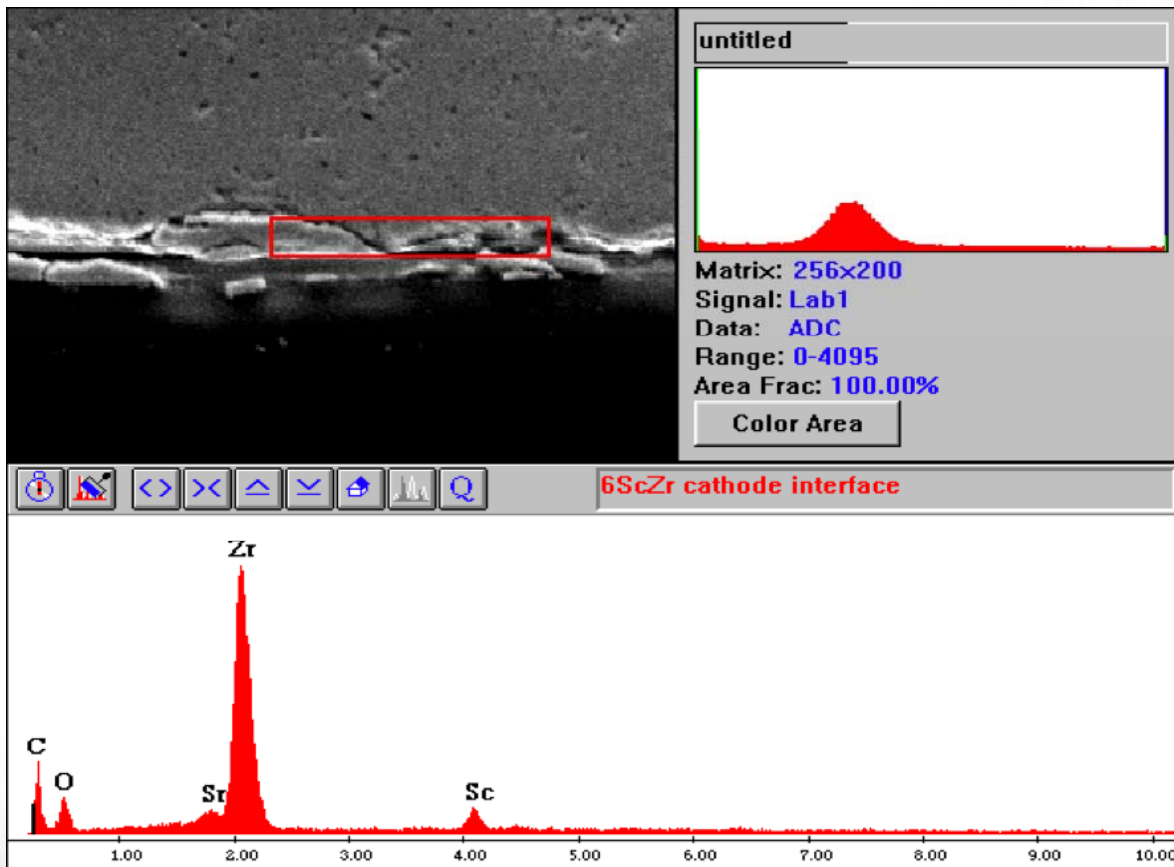
Delamination
More pronounced than half ILS
Phase change noted in half ILS

Oxygen electrode and ion
contacting layer (bond layer)



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

ILS Module #3 Post Test Examination

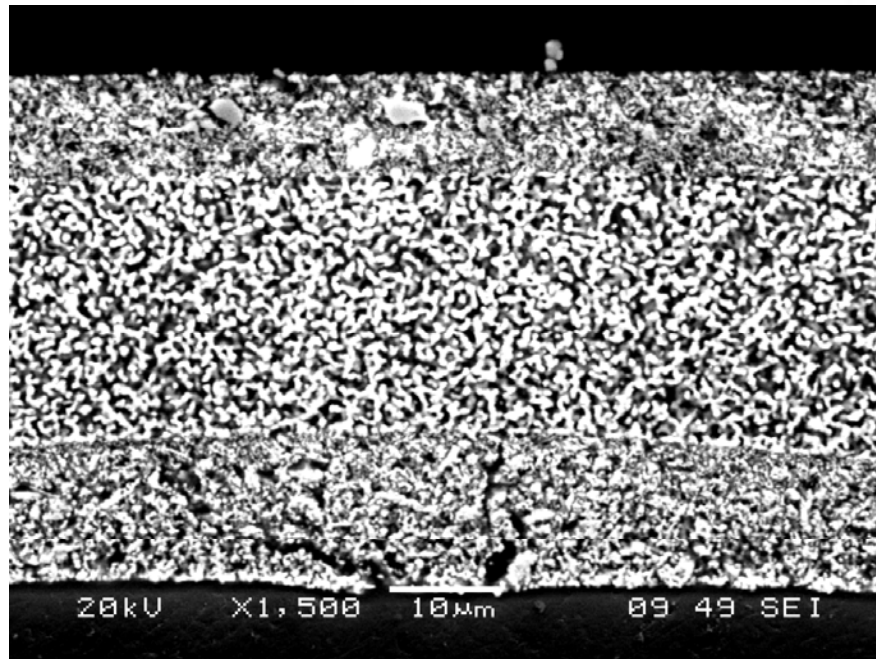


- EDS Indicates only ScSZ at the interface.
- The apparent deposition layer is a layer of zirconia that has spalled off.
- Hypothesis:
 - Sr or Mn diffusion from manganite electrode introduces electronic conductivity in ScSZ
 - Promotes oxygen to evolve inside the electrolyte, build up pressure and split off a layer near the electrode.



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

ILS Module #3 Post Test Examination



Manganite-Zirconia Composite

Manganite Electrode

Cobaltite (LSCo)
contacting layer (bond layer)

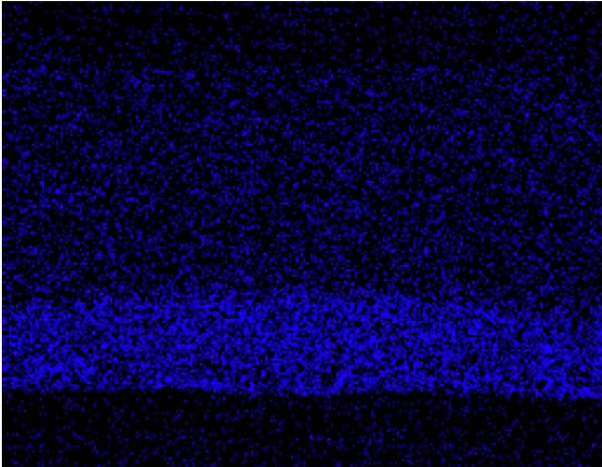
No major change in air electrode microstructure



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

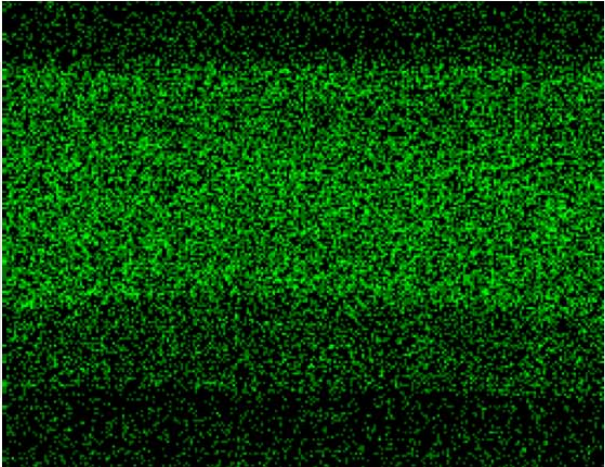
Co-Mn Inter-diffusion in Oxygen Electrode

Expected Main Elements

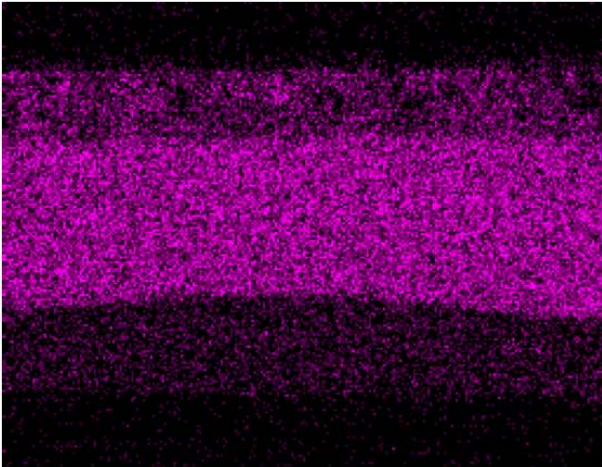


Co

Zr, Mn, Sr
Mn, Sr
Co, Sr

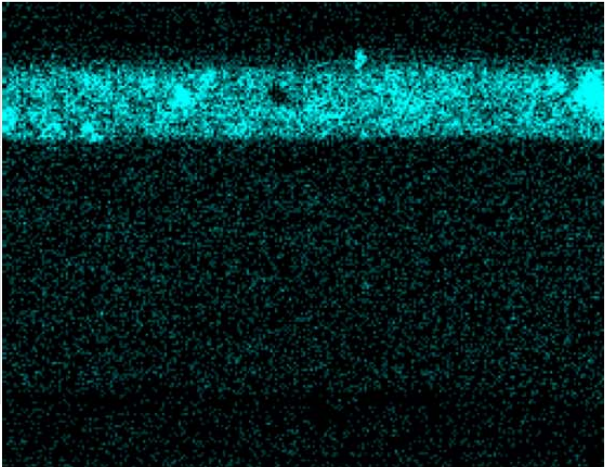


Sr



Mn

Zr, Mn, Sr
Mn, Sr
Co, Sr



Zr

ILS Module 3 Post-test

Preliminary analysis results and approach to improve stability

- Air electrode delamination
- Potential for Mn & Sr diffusion into ScSZ playing a role in delamination
 - Improve interface stability: Interlayer option
- Mn/Co interdiffusion changing electrode activity
 - Chemistry change in electrode/bond layer
 - Lower driving force for interdiffusion
- No substantial change to air electrode microstructure
 - Achieve similar microstructure & stability
- No Cr observed in electrode? Confirmation pending
 - Module 3 used spinel barrier coating on interconnect



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Prioritized Areas of Focus

- O₂ Electrode Delamination – inherent to SOEC operation?
 - Electronic conductivity due to Mn & Sr diffusion into electrolyte
 - Barrier layer & alternative compositions
- O₂ Electrode Bond Layer Stability
 - **Stoichiometry changes**, phase change
- O₂ Electrode Chromium Poisoning
 - Solid state diffusion by interconnect contact
 - CrMn & CuMn spinel coatings
 - Evaporation/Condensation from interconnect, manifold, piping
- Electrolyte Stability
 - Minimum dopant level (strength trade-off)
- System BOP Reliability
- Seal Stability

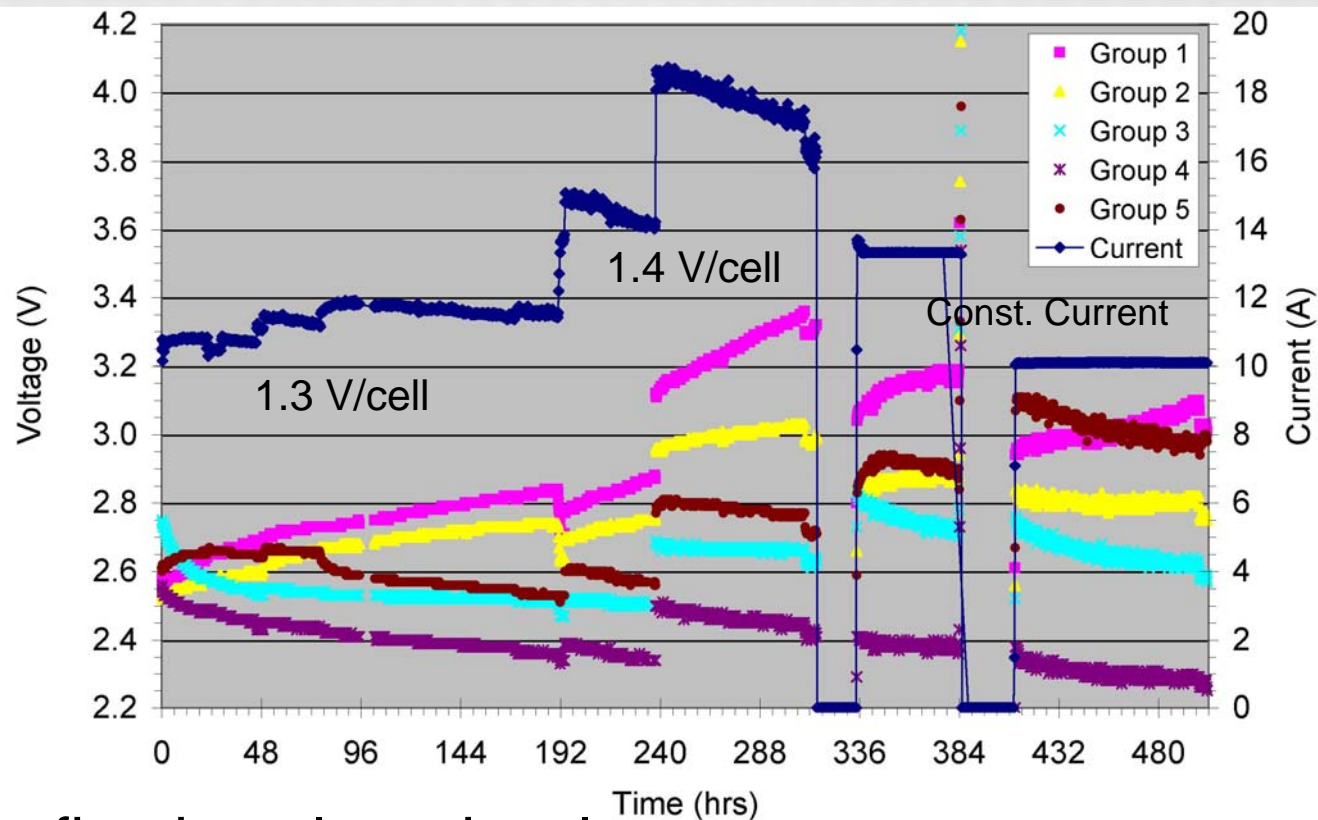


Air Electrode Comparison Stack

- 10-cell stack
 - 5 cells using baseline manganite electrode
 - 5 cells using cobalt-ferrite electrode
 - All interconnects 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



O₂ Electrode Comparison Stack

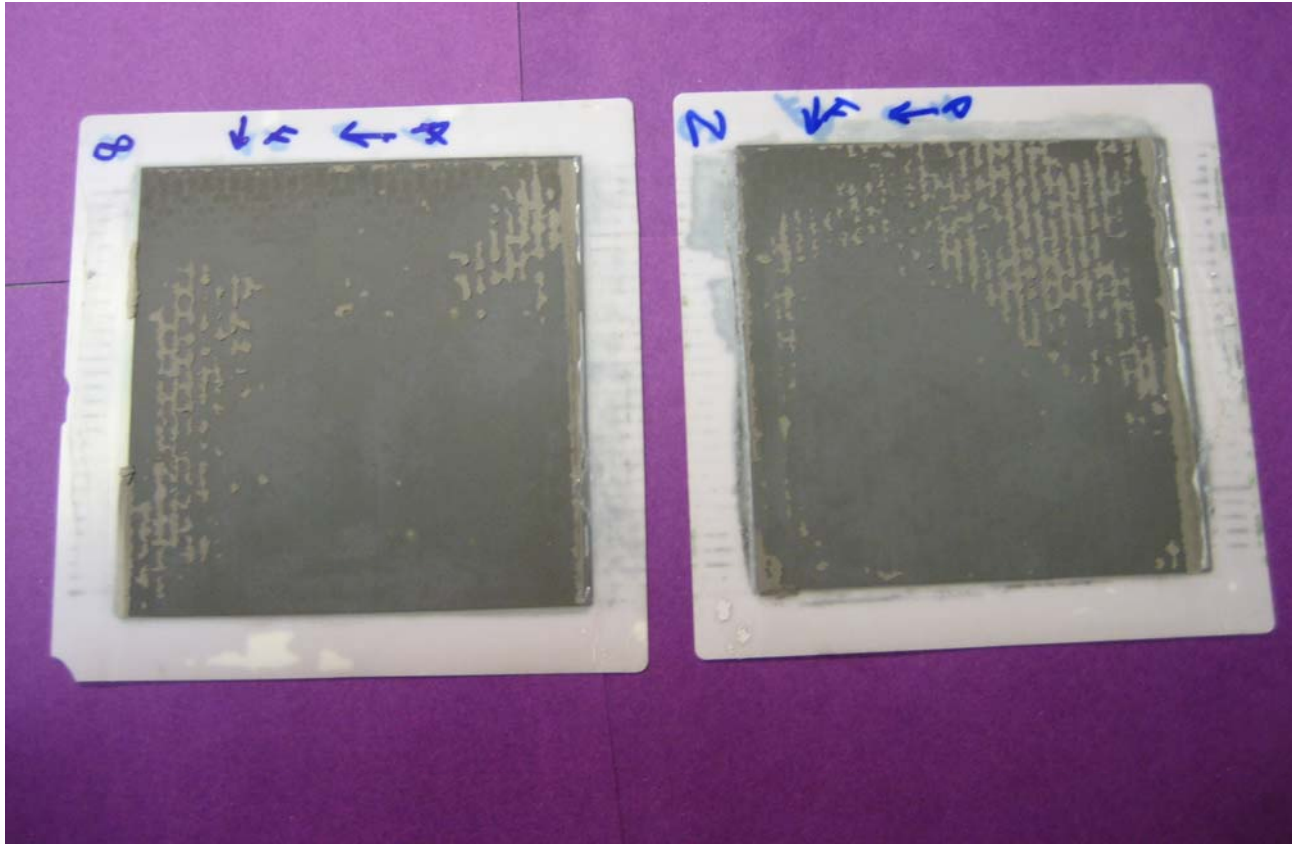


- At fixed total stack voltage
 - Manganite groups: increase in voltage (ASR) with time
 - cobalt-ferrite groups: decrease in voltage with time
 - Mixed group: net decrease in voltage with time



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Post-test: Comparison Stack Hydrogen Electrode & Bond Layer



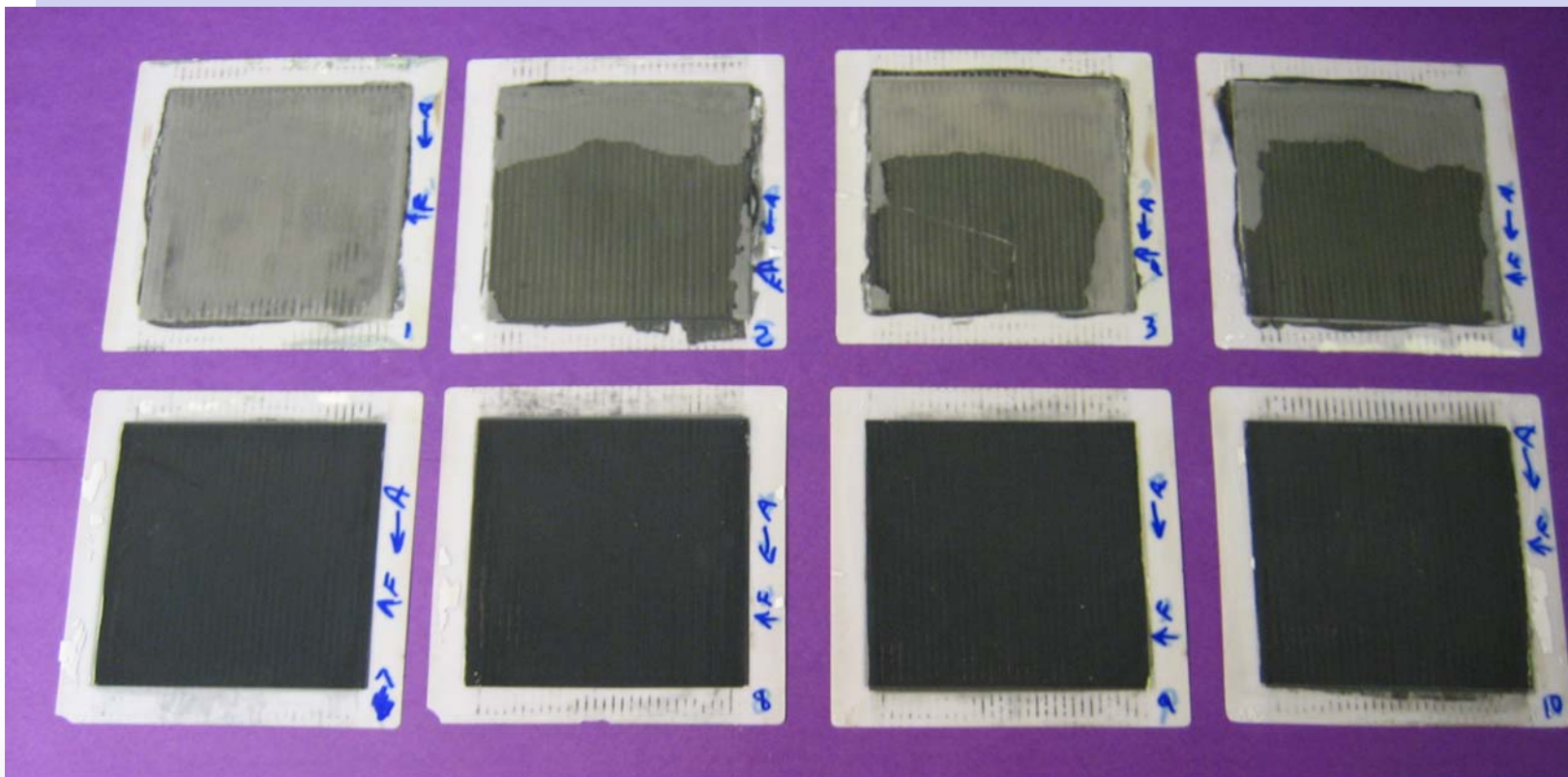
**Adherent and conductive hydrogen electrode
Most areas of bond layer separated with flowfield**



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

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)**



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

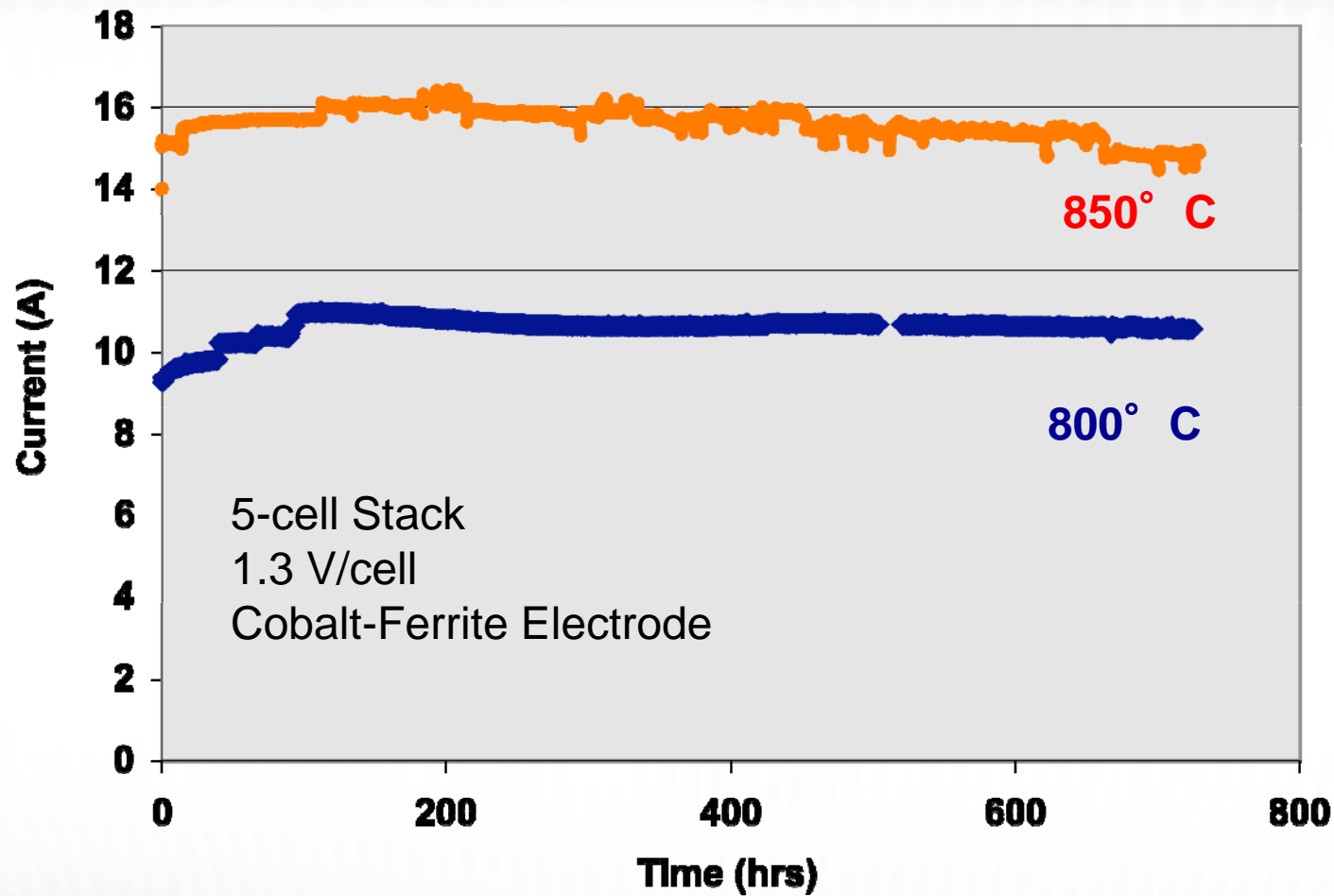
Verification Stack

- 5-cell stack tested Q3-09
 - All cells with cobalt-ferrite electrode
 - Ceria interlayer between P-ScSZ and electrode



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

New O₂ Electrode Improves Stack Stability



Best SOEC stack stability to-date



CERAMATEC®
TOMORROW'S CERAMIC SYSTEMS

Recap: Materials Changes Made

- Cobalt-ferrite air electrode
 - more catalytic for oxygen evolution
- Underlayer
 - reduction in cation diffusion into electrolyte
 - improved adhesion
- Spinel coating of metal Interconnect
 - Cr suppression



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS

Pending Materials Work

- Some promising directions emerging
 - Electrolyte composition screening still ongoing
 - Cobalt-ferrite electrode provides equivalent performance to manganite
 - Initial cell test shows improved stability
 - Cr suppression using published SOFC approach
- Screening of bond layer composition
 - Reduction or elimination of reactive species, Mn, Sr, Co
- Completion of interconnect coating evaluation
- Stack testing for stability and post-test evaluation



Acknowledgement

- Office of Naval Research
 - Contract No. N0014-08-C-0680
 - Project Manager: Dr. David Shifler

- Department of Energy
 - Through a sub-contract from Idaho National Lab.
 - INL Technical Lead: Dr. Stephen Herring
 - DOE Project Manager: Mr. Carl Sink



CERAMATEC
TOMORROW'S CERAMIC SYSTEMS