DOE Hydrogen Program

# Development of a Novel Efficient Solid-Oxide Hybrid for Co-generation of Hydrogen and Electricity Using Nearby Resources for Local Application

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**Project ID#: PDP 33**



MSRI

# Overview

## Timeline

- Project started: 02/10/2006
- Project ends:  07/31/2009
- Percent completed: 70%

## Budget

- Total budget funding
  - DOE $2,480k
  - Contractor $ 620k
- Funding received in FY07
  - $ 1,265k
- Funding for FY08
  - $ 755k

## Barriers

Hydrogen generation by water electrolysis

- G – Capital cost
  - Low-cost, durable high-temperature materials development
  - Lower operating temperature
- H – System Efficiency
- K – Electricity costs

## Partners

- University of Alaska Fairbanks – anode supports fracture mechanisms and modeling of residual stresses (S. Bandopadhyay; N. Thangamani)
- University of Missouri-Rolla – cathode & seal materials development (H. Anderson; R. Brow)
- University of Utah – interconnect development (A. Virkar)

# Objective

| | |
|---|---|
| Overall Objective | • To develop a low-cost and highly efficient 5 kW SOFC-SOFEC hybrid system co-generating both electricity and hydrogen to achieve the cost target of < \$3.00/gge when modeled with a 1500 gge/day hydrogen production rate.<br>• The project focuses on materials R&D, stack design & fabrication, and system design & verification. |
| 2007 | • 5 kW SOFC-SOFEC hybrid system development<br>– Materials development and application (electrodes & seals)<br>– Stack design and development<br>– Hybrid system design<br>– BOP components design and development |
| 2008 | • 5 kW SOFC-SOFEC hybrid system fabrication and assembly<br>– Cell & non-cell repeat units fabrication<br>– BOP components fabrication<br>– Stack assembly and integration<br>– Hybrid module evaluation<br>– Control system assembly & programming |

# Milestones

| Quarters, FY | Milestone or Go/No-Go Decision |
|---|---|
| 1st Quarter, FY07 | Go/No-Go decision: assess the appropriate load and strains that SOFC-SOFEC can withstand. |
| 2nd Quarter, FY07 | Go/No-Go decision: assess the viability of 1 kW hybrid module for cogeneration based on performance. |
| 4th Quarter, FY07 | Go/No-Go decision: finalize the cathode system for hybrid application. |
| 4th Quarter, FY07 | Milestone: Complete the design of the 5 kW system and major BOP components. Down select two "invert" glass compositions from 81 compositions that are thermal-mechanically compatible and thermal-chemically stable. Finalize the cathode system for SOFEC applications. |
| 3rd Quarter, FY08 | Milestone: Complete the high temperature flexural tests and creep studies of SOFEC anode substrates. |
| 4th Quarter, FY08 | Milestone: Complete fabrication of all cell/non-cell repeat units. Complete fabrication and pre-test of BOP components. Transfer the glass seal technology from the subcontractor to MSRI. |

# Approach

## Materials Development

A. Cathode materials Dev.

B. Anode optimization

C. Electrolyte optimization

D. Catalyst studies

E. Seals development

F. Fabrication Q.A.

**80% complete**

## Cell / Stack /System Design

A. Stack design

B. 5kW system design

C. BOP design/dev.

D. Stresses analyses

E. Seals application

F. Economic analysis

**80% complete**

## Experimental Verification

A. Short stacks in dif. modes

B. 1 kW hybrid stack

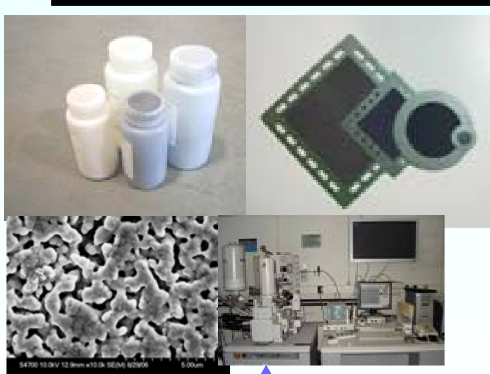
C. Durability evaluation

D. BOP design & evaluation

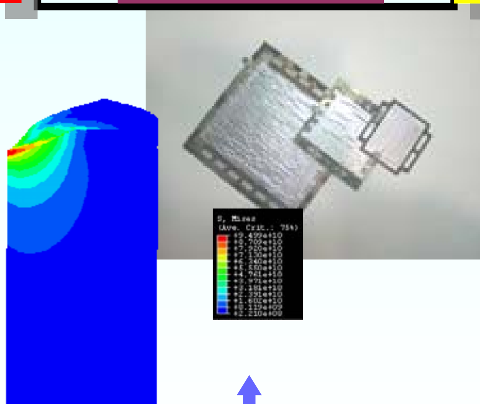
E. 5 kW hybrid system development & evaluation

**50% complete**

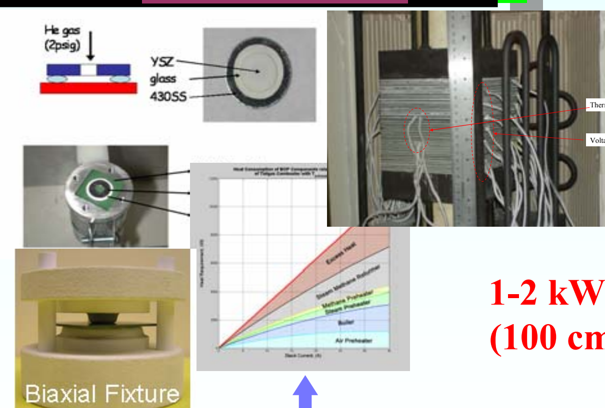
**Success**



**MSRI, UMR**



**MSRI, UAF, UMR, UU**

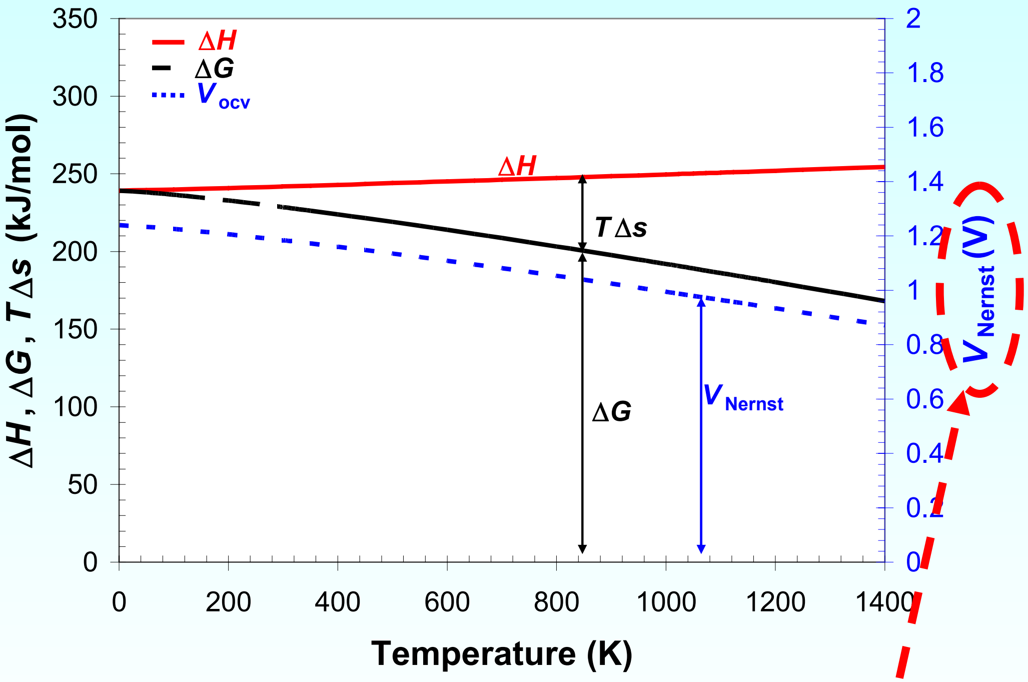



**1-2 kW Stack**
**(100 $cm^2$/cell)**

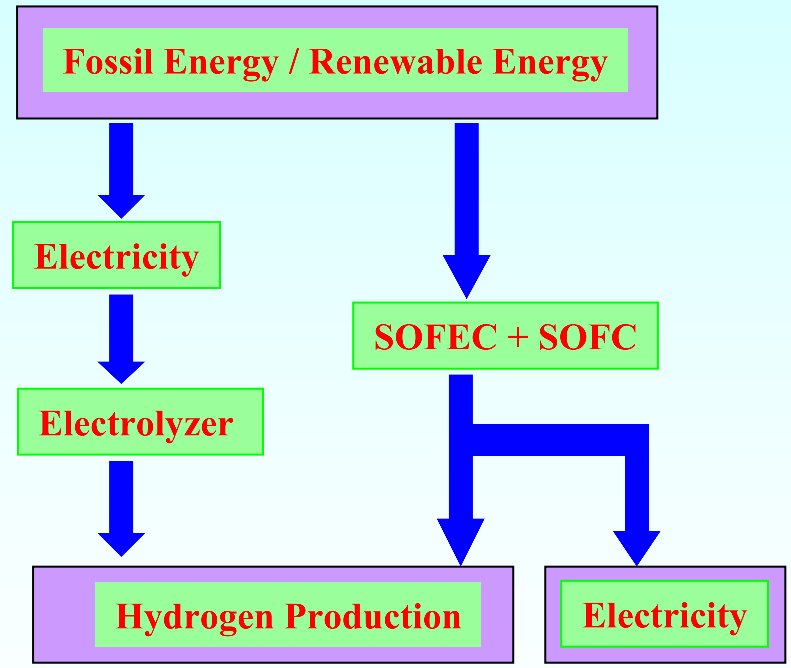
**MSRI, UU, UMR**

# Background

**A Solid Oxide Fuel-Assisted Electrolysis Cell (SOFEC) directly applies the energy of a chemical fuel to replace the external electrical energy required to produce hydrogen from water/steam; decreasing the cost of energy relative to a traditional electrolysis process.**




Unique process




Co-generation

$CH_4$-assisted SOFEC Reaction

Electrochemical Process

$4H_2O + 8e' \rightarrow 4H_2 + 4O^{2-}$ at cathode

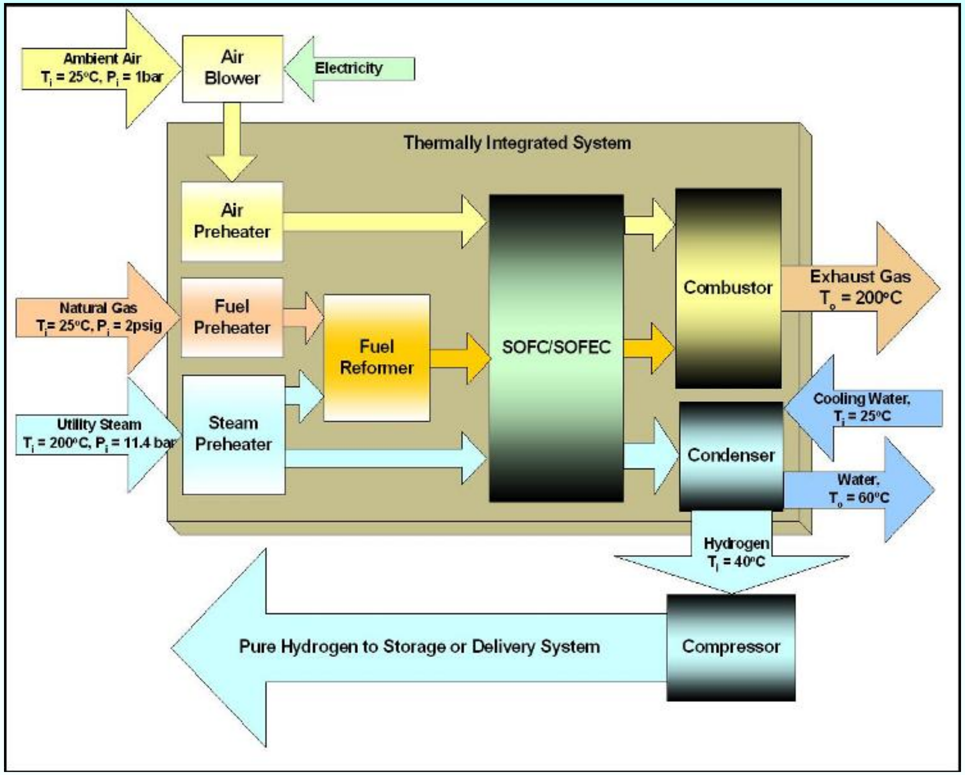
$4O^{2-} + CH_4 \rightarrow CO_2 + 2H_2O + 8e'$ at anode

$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

Pure $H_2$ formed. No need for $H_2$ separation membranes. Lower electricity requirement.

# Concept of Hybrid SOFC-SOFEC Integral System

## Technical Challenges and Solutions




Cost of Hydrogen

**SOFC-SOFEC performance**

- cathode materials: composition, microstructure, catalytic characterisitcs;
- anode material: porosity, tortuosity, composition;
- low operating temperature: inexpensive materials, non-precious metal catalysts;
- manufacturability.

**System efficiency**

- SOFC-SOFEC hybrid architecture;
- thermal integration;
- co-generation concept.

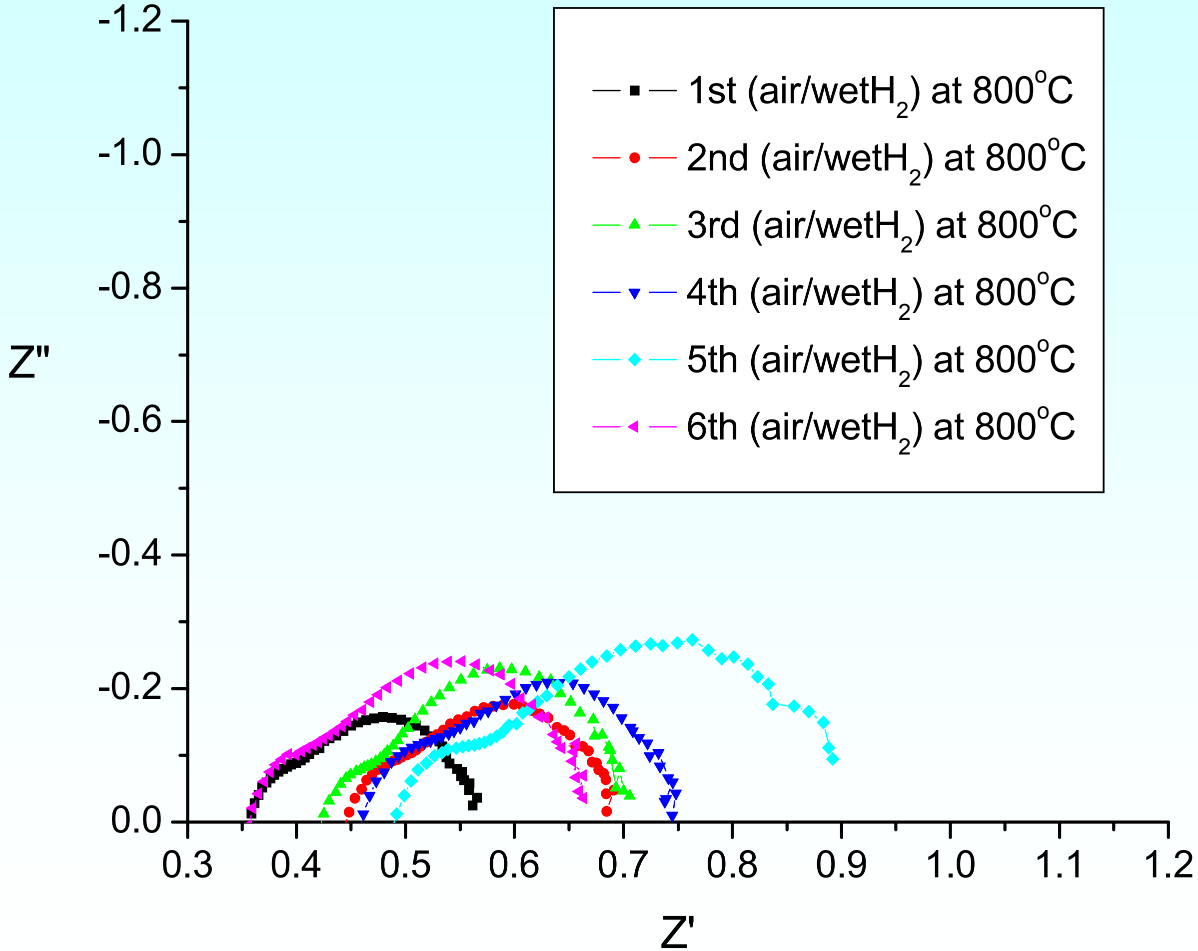
**Long-term durability**

- "invert" seal material thermalmechanical compatibility and thermalchemical stability;
- anode mechanical strength.

- Pure $H_2$ & electricity co-production from feedstock: hydrocarbon fuel, steam, and air
- Hybrid comprised of SOFCs and SOFECs
- SOFECs produce pure $H_2$ and SOFCs generate electricity for a high $H_2$ production rate
- Thermal integration improves system efficiency

# SOFEC Cathode Materials Development

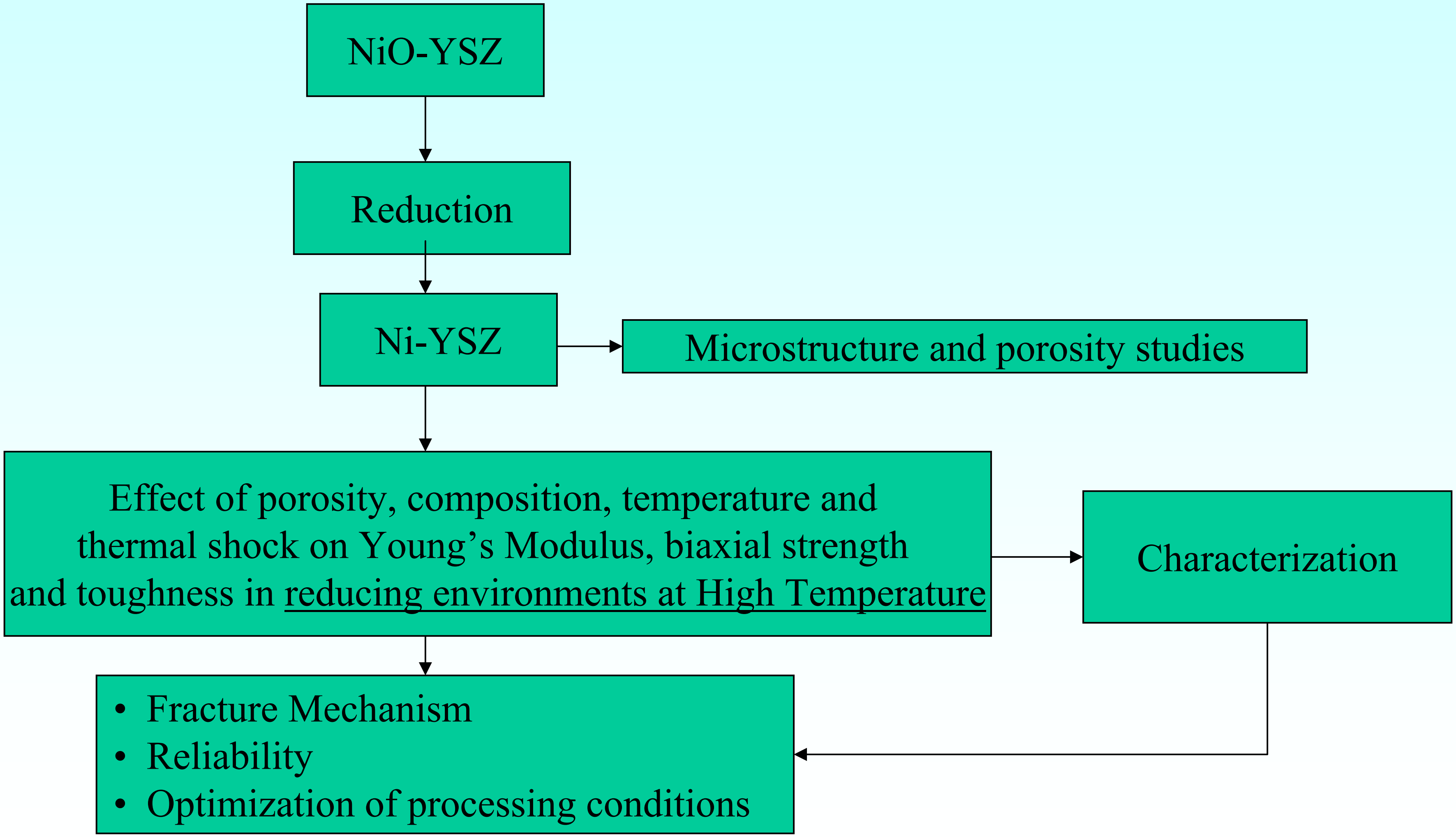
## LSCM Redox Stability Study




- Previous studies show that $(La,Sr)(Cr,Mn)O_3$-based cathode material is electrocatalytically and chemically stable in both reducing and oxidizing atmospheres
- Previous long-term tests show degradation rate < 1% per 1000hrs over a 4500 hrs continuous test in the SOFC mode.
- Redox stability is desired for reversible applications

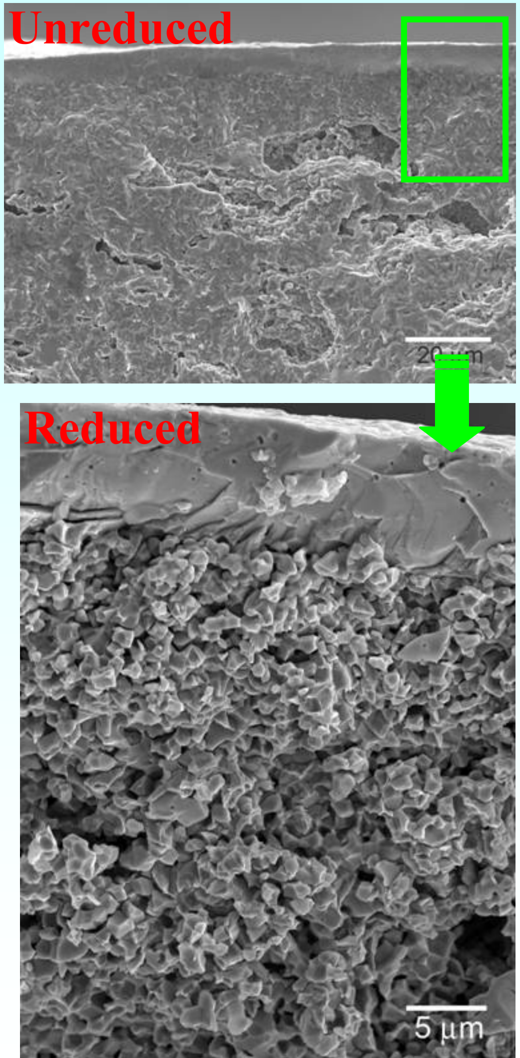
# SOFC-SOFEC Anode Substrate Development

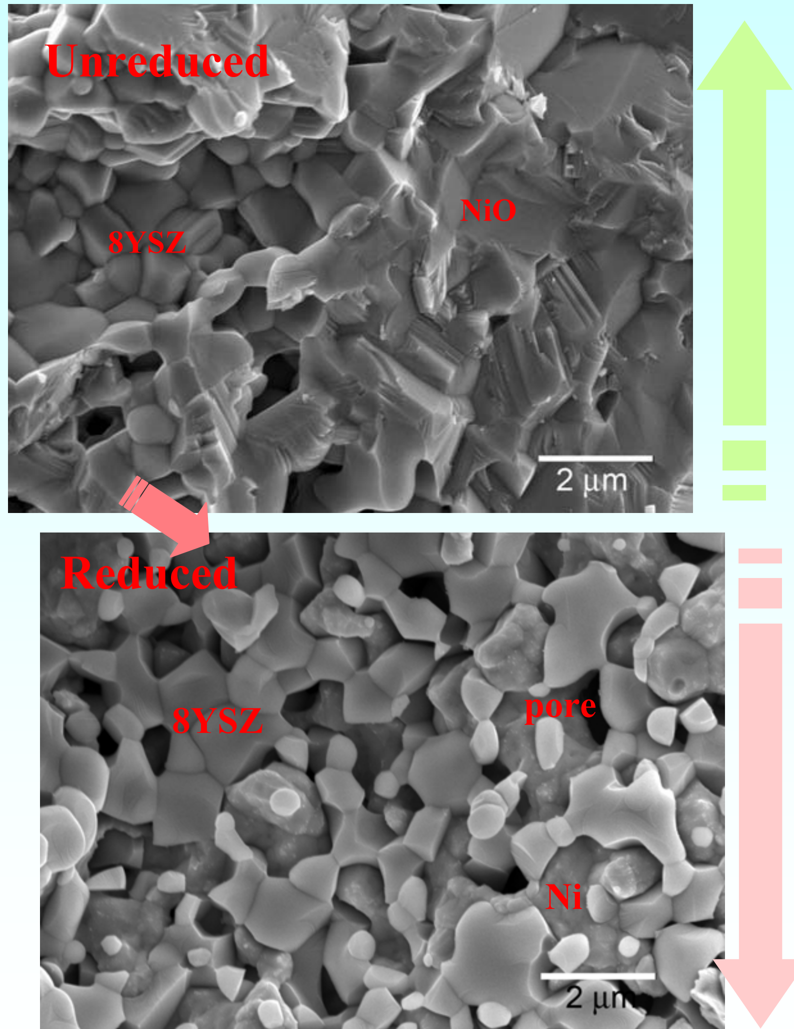
**Effects of Residual/Chemical/Applied Stresses on Mechanical Integrity**



# Reduction of Half-cells

$NiO\ (s) + H_2\ (g) \longrightarrow Ni\ (s) + H_2O\ (g)$

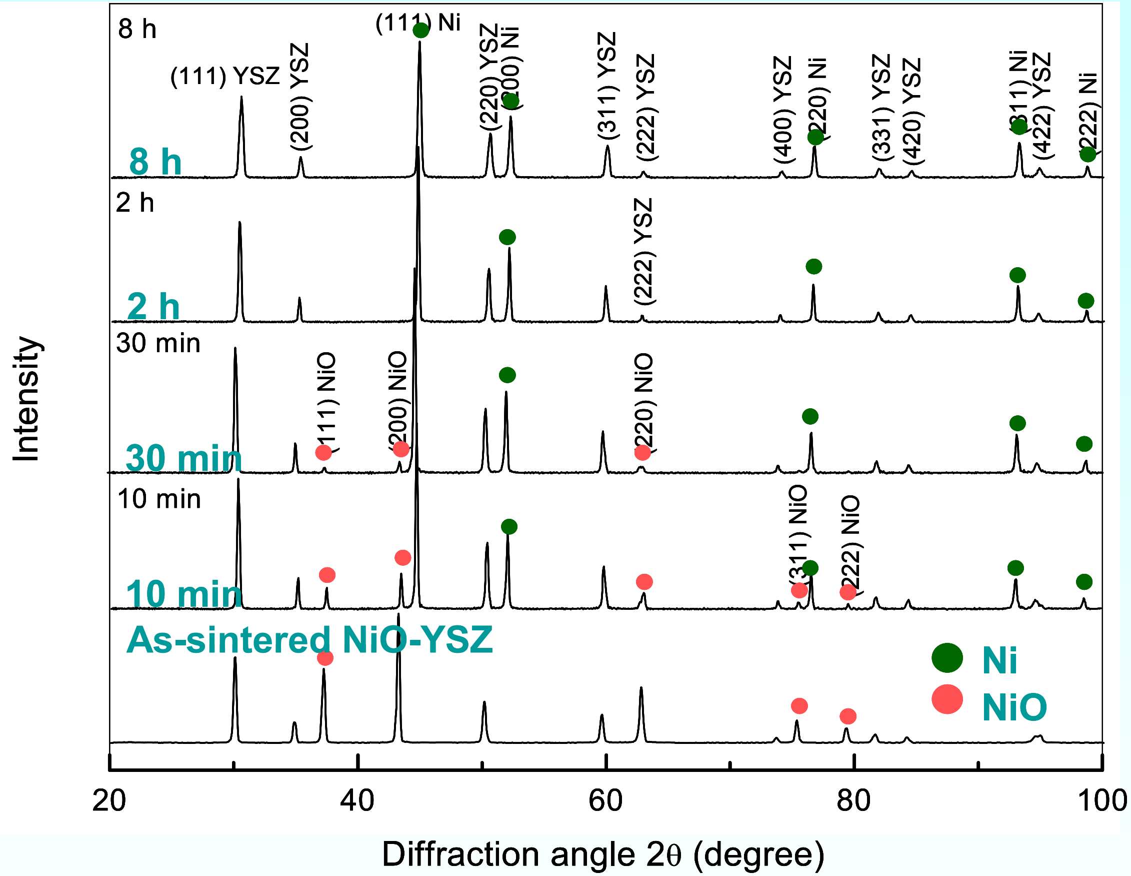


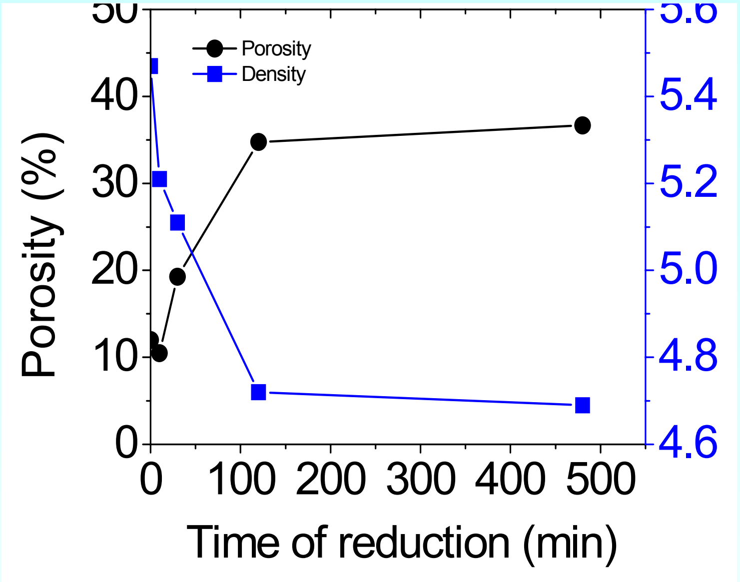



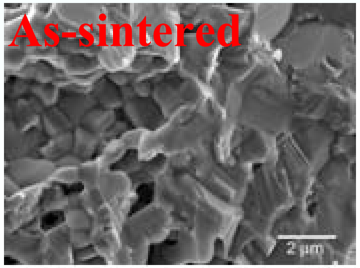

- Porosity
- Triple phase boundary (TPB)

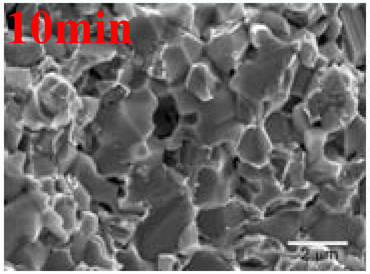
- Density
- Mechanical properties

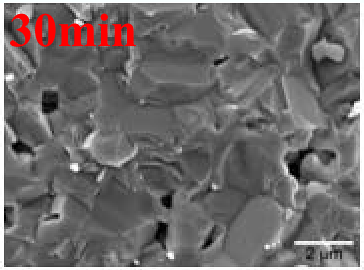
# Effect of Reduction on Phases & Microstructure

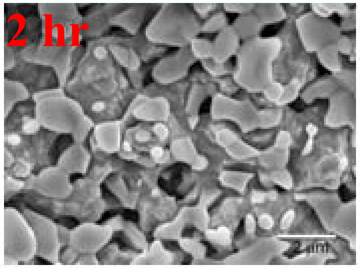


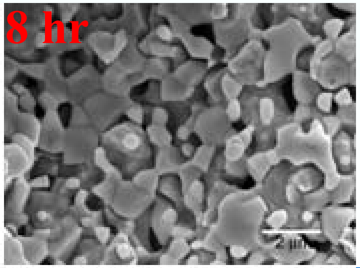



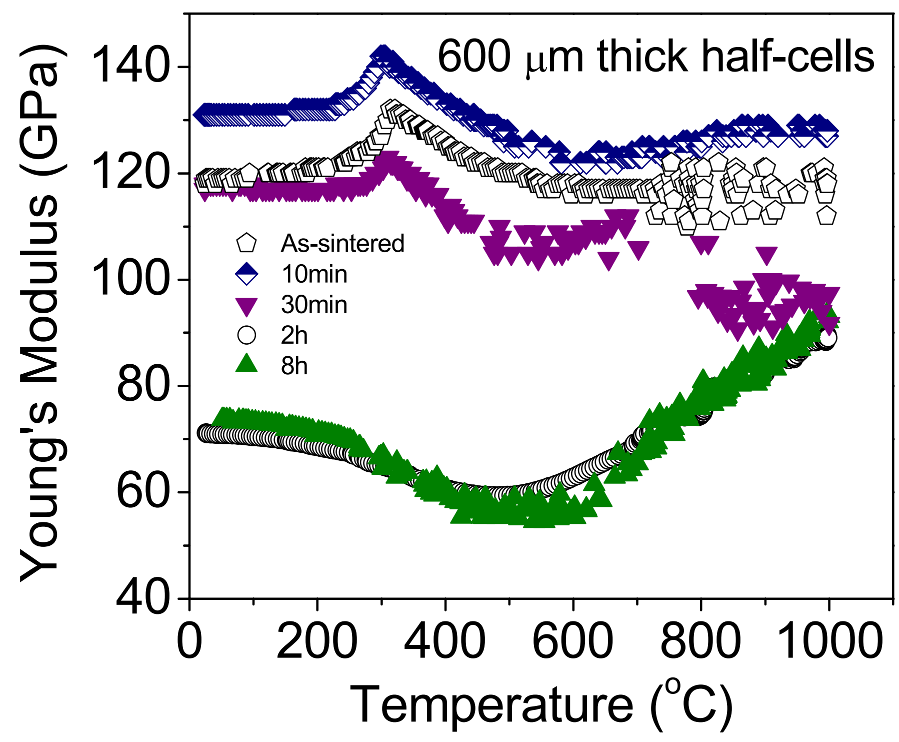



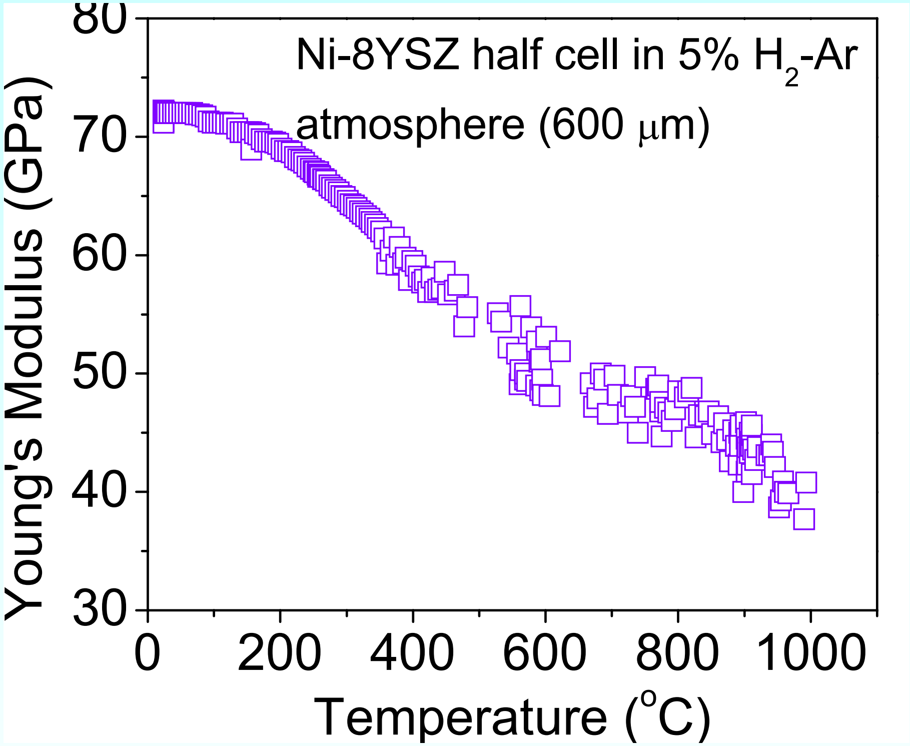



# Effect of Reduction on Mechanical Properties



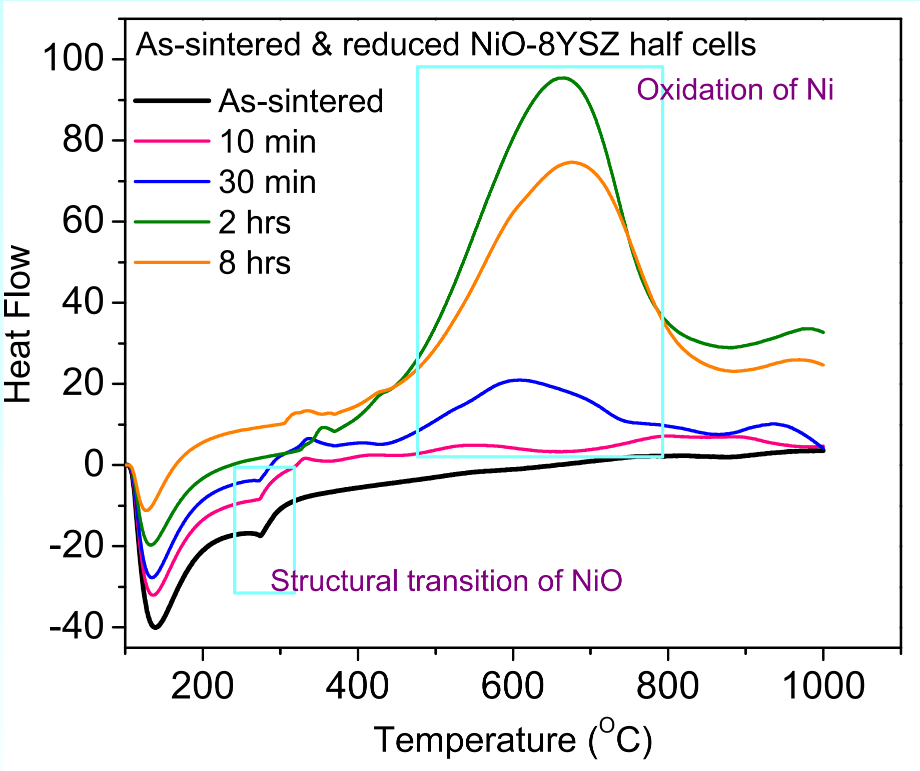

***<u>Half-cells that have NiO:</u>***

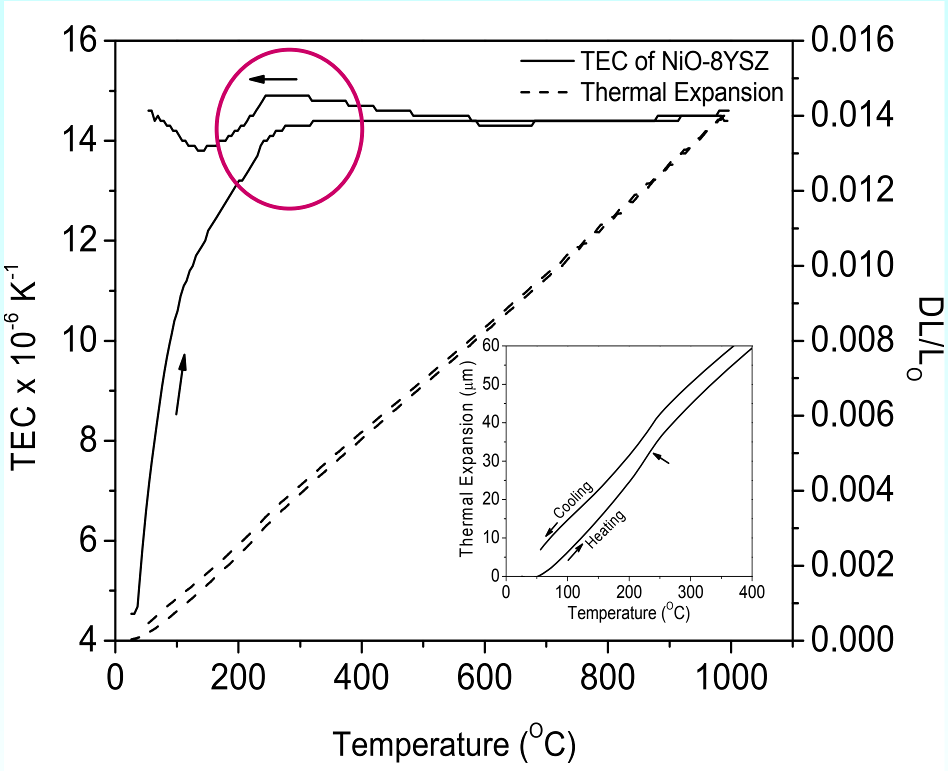
- Higher initial E and a peak in E at 300°C due to rhombohedral to cubic transition

***<u>Half-cells that have no or negligible NiO:</u>***

- No structural transition assisted change in E; Oxidation of Ni increases E
- Scattering of E at high temperatures due to thermodynamic instability of c-$ZrO_2$

# Events Affecting 'E' at Elevated Temperatures



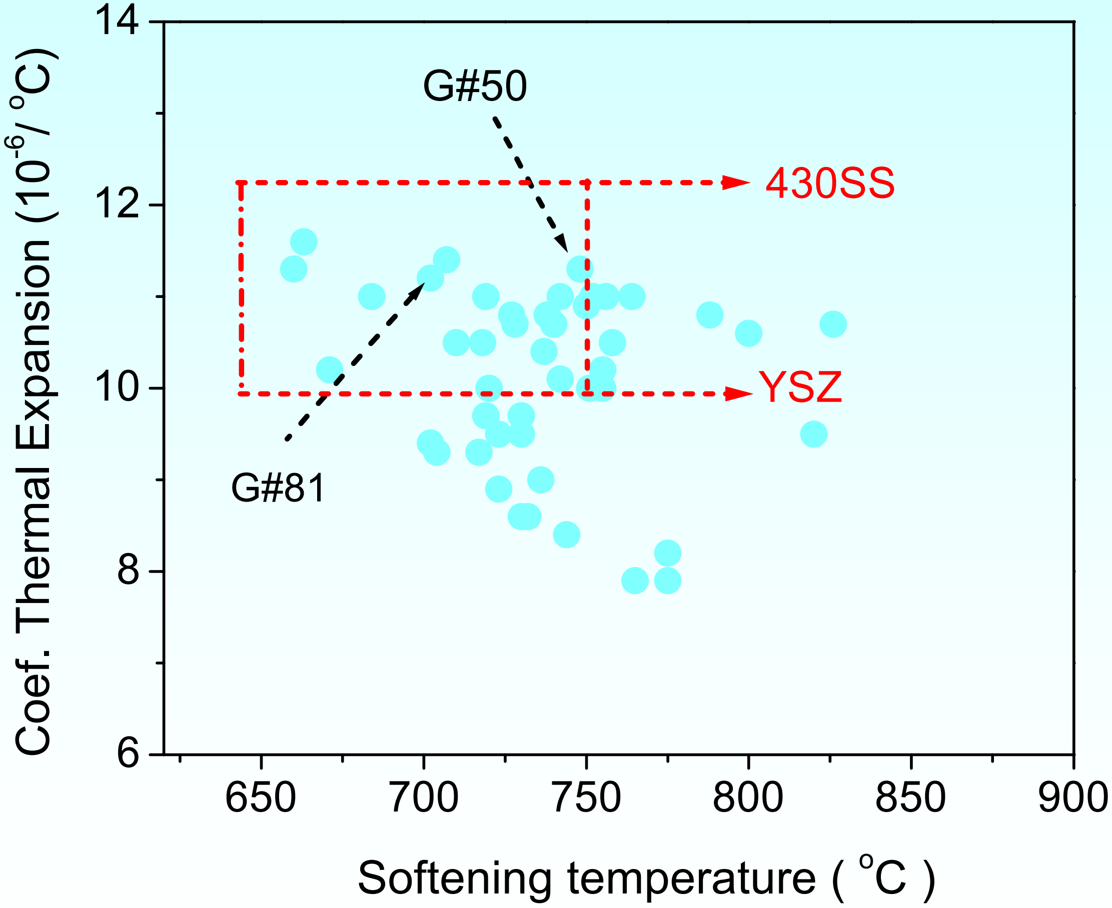

- Rhombohedral to cubic transition of NiO that affects the thermal expansion and Young's modulus @ ~ 300°C
- Oxidation of Ni @ ~ 500°C

# Hermetic Seals Development

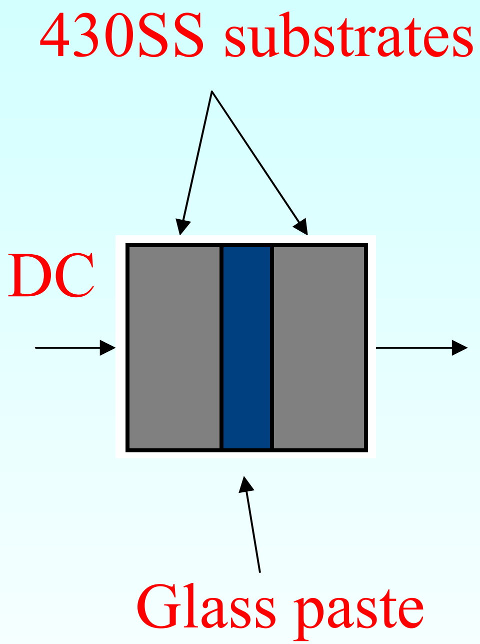
**Evaluated More Than 81 'Invert' Glass Compositions**

"Invert" silicate:
Glasses with
$SiO_2$<45 mole%

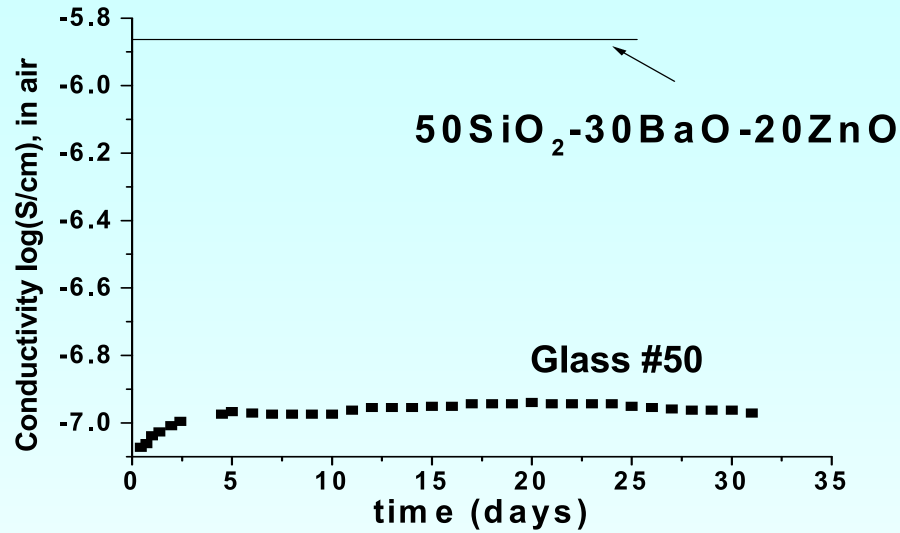
Compositions based on:
Pyrosilicate
and
Orthosilicate

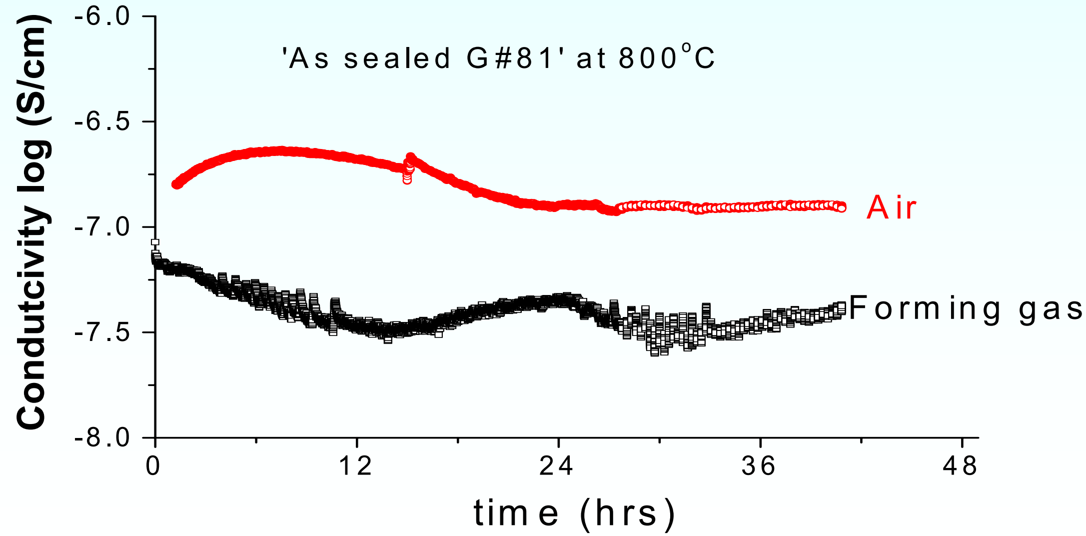


# Electrical Conductivity in Air and Forming Gas




Test conditions:
800°C in air and
forming gas



# Thermal Cycle Effects on Seals

## Hermetic Seals After Initial Multiple Thermal Cycles

| Sealing materials | Test conditions | Notes |
|---|---|---|
| 430SS/G50[1] (45µm)/Ni-YSZ | wet forming gas | Failed after 20 cycles; Ni-YSZ fracture |
| 430SS/G50[1](45µm)/YSZ | air | Failed after 60 cycles; YSZ fracture |
| 430SS/G81[2] (20µm)/Ni-YSZ | forming gas | 10 cycles; Ni-YSZ fracture |
| 430SS/G81[2] (20µm)/Ni-YSZ | forming gas | Failed after 30 cycles; Ni-YSZ fracture |
| 430SS/G81[2](25µm)/Ni-YSZ | forming gas | 32 cycles without failure |

(Samples held at pressure for 24 hours at 800°C; tested for leaks using a 4 psig differential in the testing gas)

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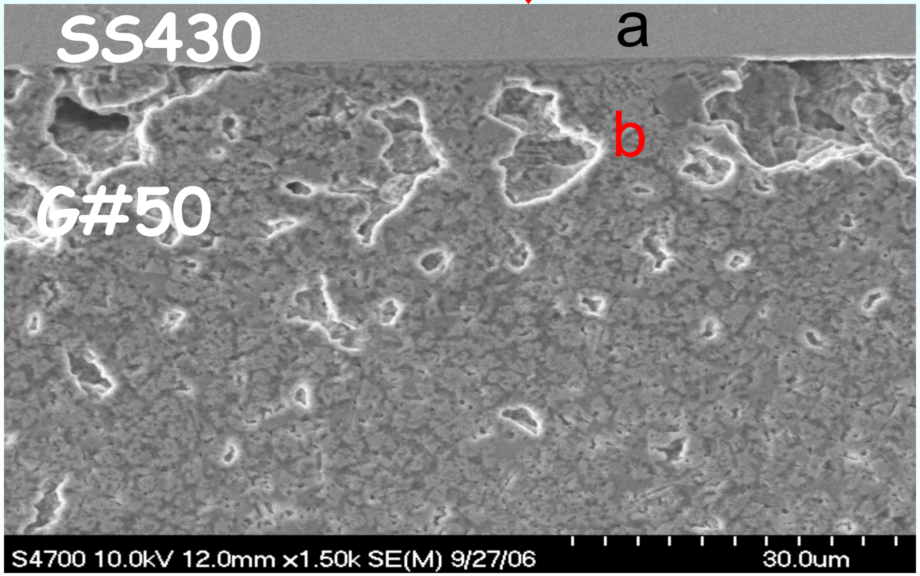
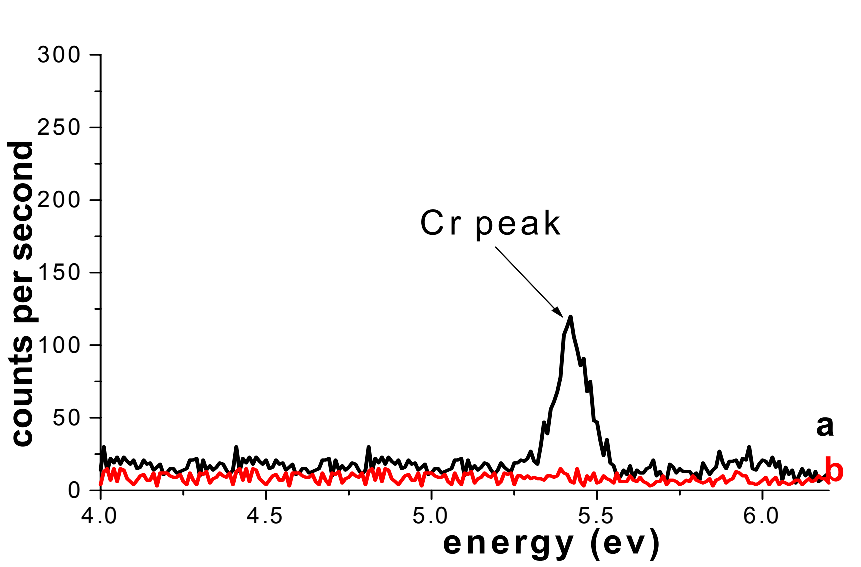
[1] Glass prepared by a commercial vendor (MO-Sci)
[2] Glass prepared at UMR

# Hermeticity and Materials Compatibility

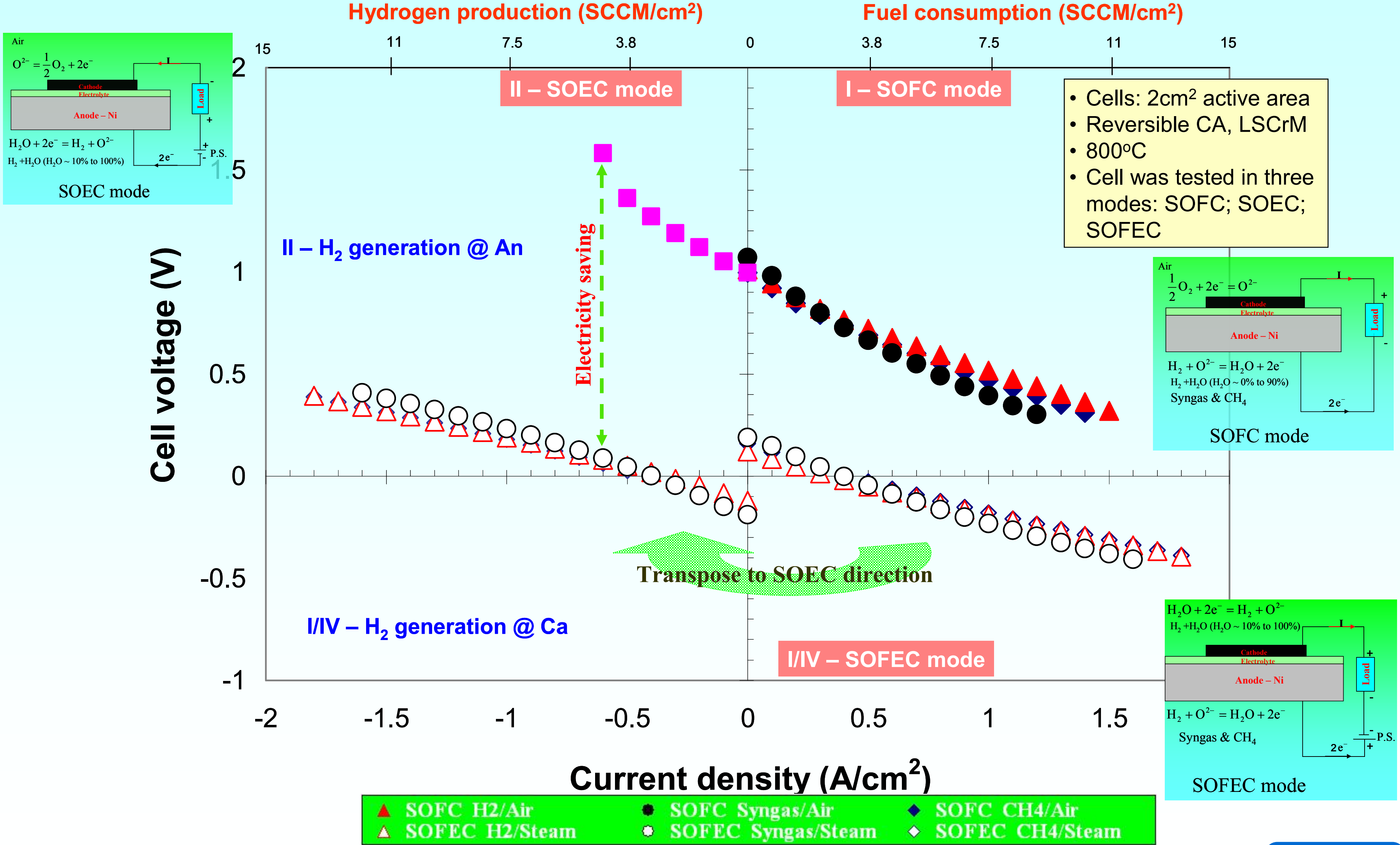
## Little Evidence for Significant Reactions @ Seal Interfaces

Ten days in wet forming gas at 800$^{o}$C

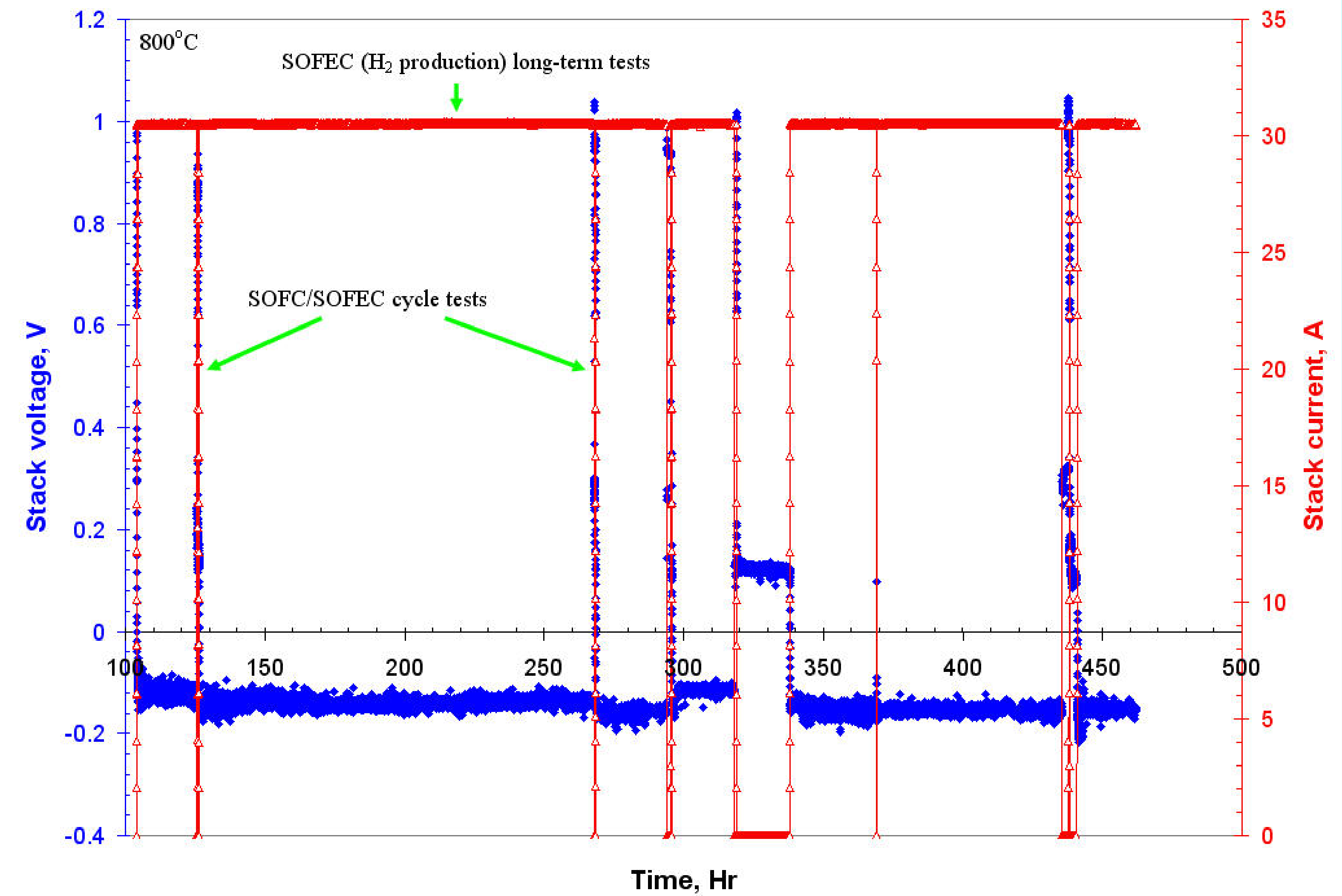
# Cathode Characteristics in SOFC/SOEC/SOFEC Modes




- Cells: 2cm² active area
- Reversible CA, LSCrM
- 800°C
- Cell was tested in three modes: SOFC; SOEC; SOFEC

# SOFEC Stability Test

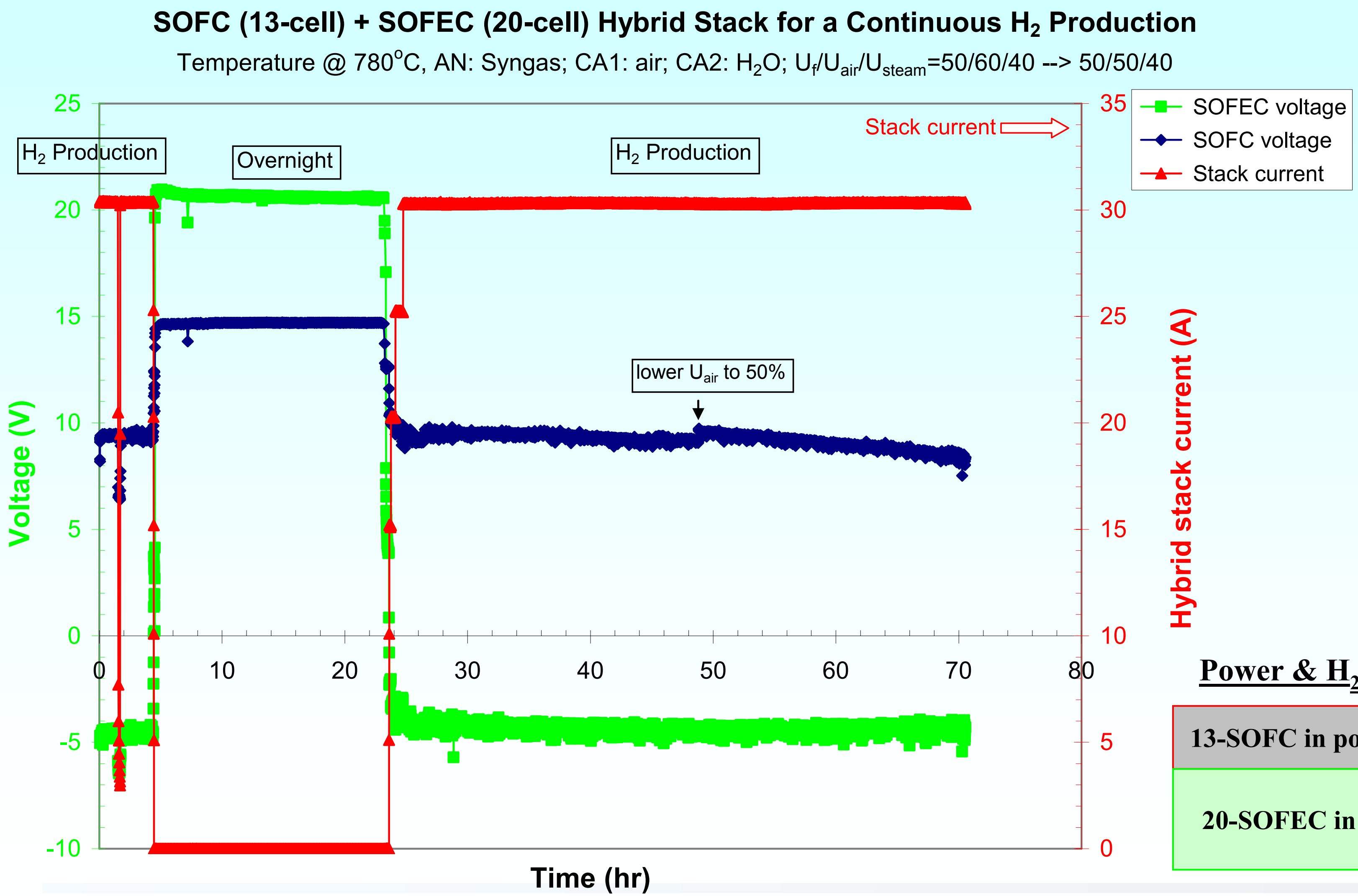
## Single-cell Stack with 100 cm² Per-cell Active Areas




**Per cell production rate: 13.92 standard liters of $H_2$ per hour, or 27.54 grams per day**

# SOFC-SOFEC Hybrid Power & $H_2$ Cogeneration

**Co-Production rate: Net power output @ 130 Watts and 270 standard liters of $H_2$ per hour (or 0.534 kg/day)**




**Power & $H_2$ cogeneration**

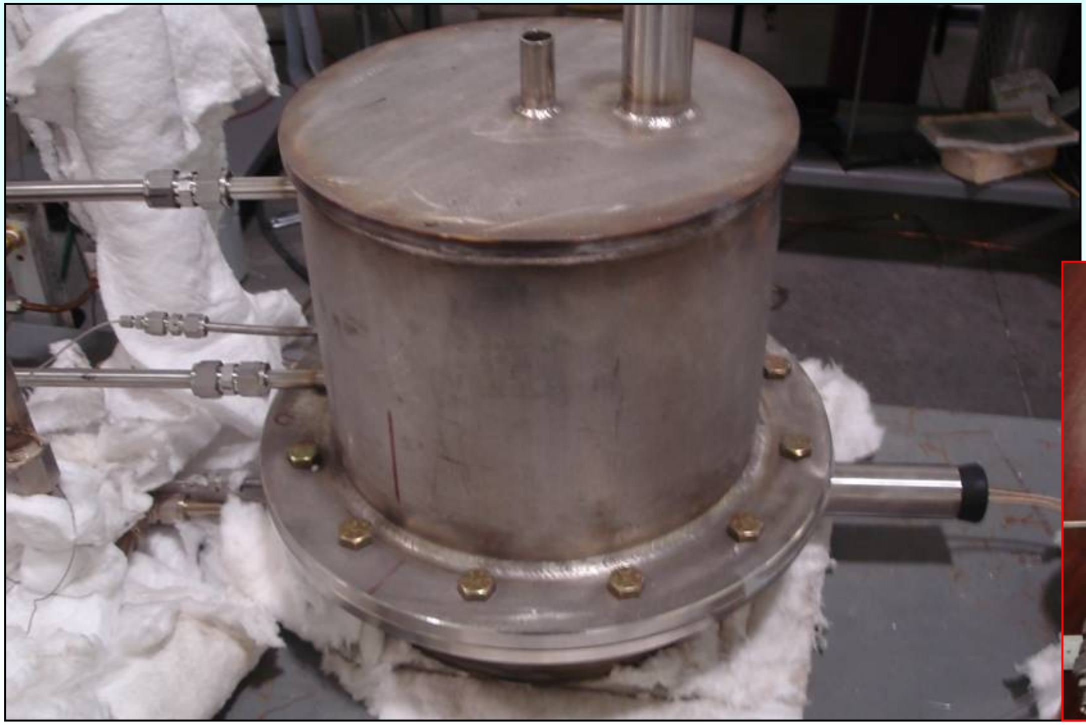
| |
|---|
| 13-SOFC in power generation |
| 20-SOFEC in $H_2$ production |

# Next Generation Stack Design for the 5 kW System

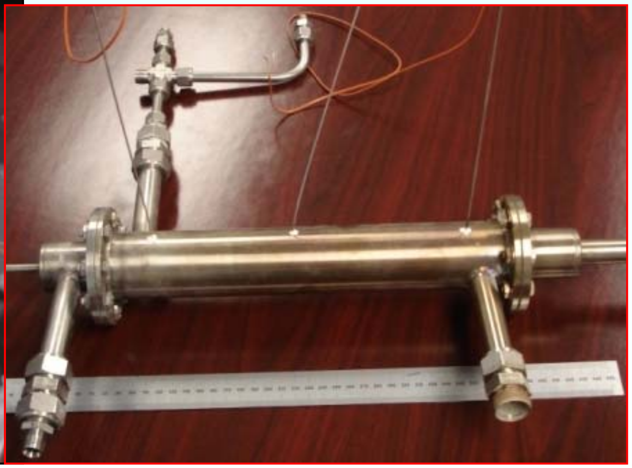
- Larger stacks (60+ cells per stack)
- Thermal and flow management
  - Novel flow geometry for in-stack temperature and flow optimization
- Improved sealing
- Design for assembly
  - Stack components have been minimized to reduce stacking time and error
  - Improved reliability
- Reduced pressure drop over previous designs

# Balance of Plant Hardware

- Combustors, reformers and steam generators are being fabricated and tested prior to system integration.
- Catalytic combustors ensure minimal noxious byproducts.



**Catalytic combustor**



# Control System

- Design of electronic control algorithm for the SOFC-SOFEC hybrid system.
- Autonomous operation enables to perform all stacks at maximum fuel efficiency and producing hydrogen from excess capacity.
- Multiple stacks in parallel operation to increase reliability and disrupt failure cascades.
- Acquisition of electronic control hardware and integration with system software.
- Pre-test of power electronics and load leveling systems before being integrated into the overall system.

# Future Work (FY 08 – FY 09)

**FY 08**

- Materials Development
  - ➢ Exploring an advanced cathode material
  - ➢ Continuous investigation of anode substrates: equi-biaxial test and flexural strength under both air and $H_2$ at working temperatures; effect of thermal cycles on strength
- 5 kW Hybrid System Fabrication
  - ➢ BOP components fabrication
  - ➢ Stack assembly, integration and burn-in
  - ➢ Implementation and optimization of system controls

**FY 09**

- 5 kW Hybrid System Assembly and Evaluation
  - ➢ 5 kW hybrid system assembly
  - ➢ System testing and evaluation
  - ➢ Hydrogen production cost analysis using H2A model

# Project Summary

| | |
|---|---|
| Relevance: | Investigate an alternative approach to provide low-cost and highly efficient distributed electricity and hydrogen |
| Approach: | Develop a 5 kW SOFC-SOFEC hybrid system based on innovative materials development and system design research to co-generate hydrogen and electricity |
| Technologies Accomplishments and Progresses: | Materials development: - Evaluated redox stability and long-term stability of the promising cathode material for SOFEC applications. - Finalized two promising "invert" glass compositions from 81 candidates. Seals survived after 30+ thermal cycles in reducing/oxidizing atmospheres. - Investigated effects of reduction on microstructure development and phase formation, elastic properties as a function of temperature, and effects of porosity, composition & microstructure on strength. 5 kW hybrid system development: - Evaluated long-term stability tests of hydrogen production to reduce cost. – Finalized the design of hybrid modules with improved thermal management and flow optimization. – Designed and fabricated major BOP components. – Designed hybrid system control algorithm and acquired control hardware. |
| Proposed Future Research: | Continue implementing mechanical/thermal analyses of anode supports; fabricate and evaluate BOP components and optimize hybrid system controls; implement 5 kW system experimental evaluation and perform cost analyses using DOE H2A model. |