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

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. • The project focuses on materials R&D, stack design & fabrication, and system design & verification.
2007	• 5 kW SOFC-SOFEC hybrid system development – Materials development and application (electrodes & seals) – Stack design and development – Hybrid system design – BOP components design and development
2008	• 5 kW SOFC-SOFEC hybrid system fabrication and assembly – Cell & non-cell repeat units fabrication – BOP components fabrication – Stack assembly and integration – Hybrid module evaluation – 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

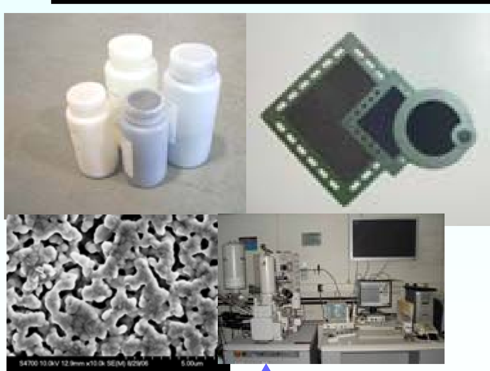
C. Durability evaluation

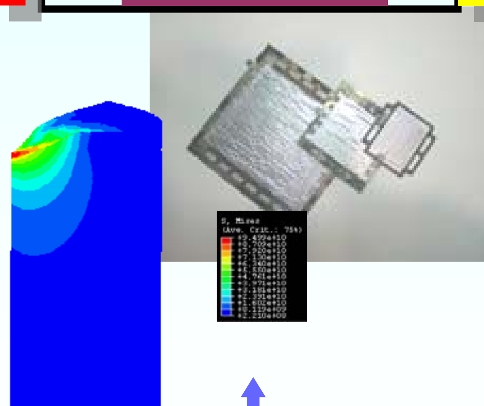
D. BOP design & evaluation

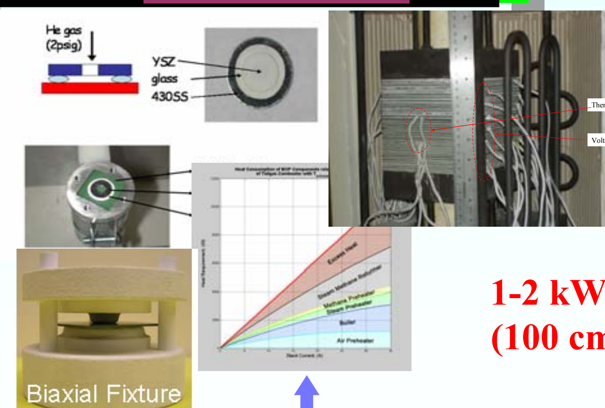
E. 5 kW hybrid system development & evaluation

50% complete

Success







1-2 kW Stack (100 cm²/cell)

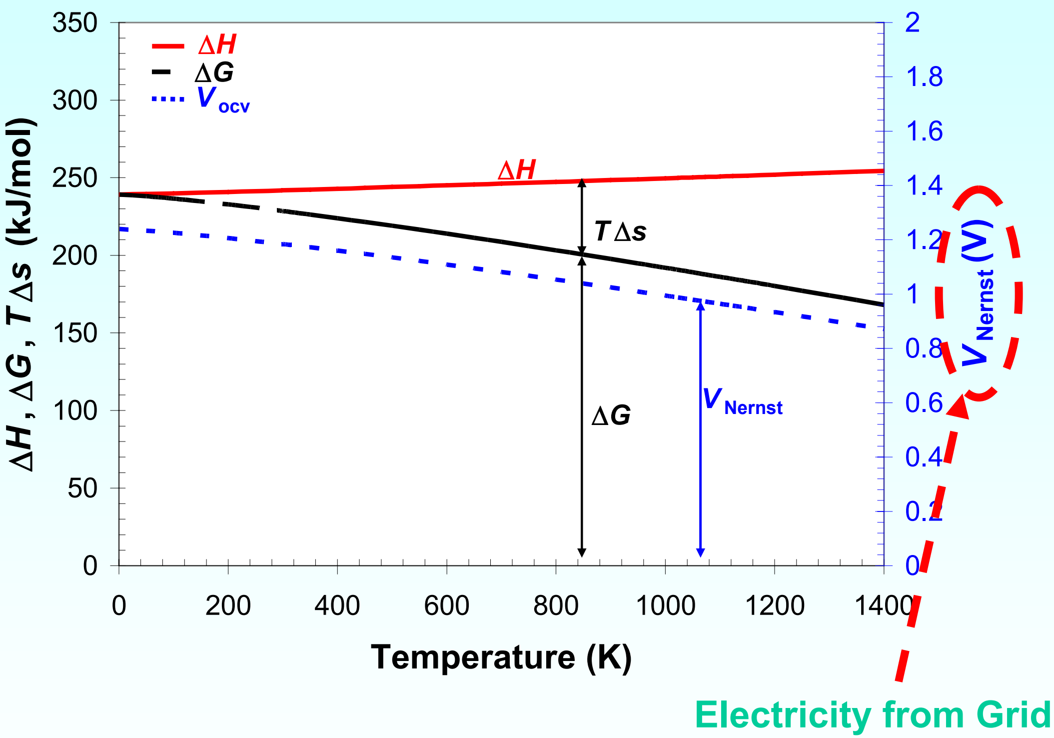
MSRI, UMR

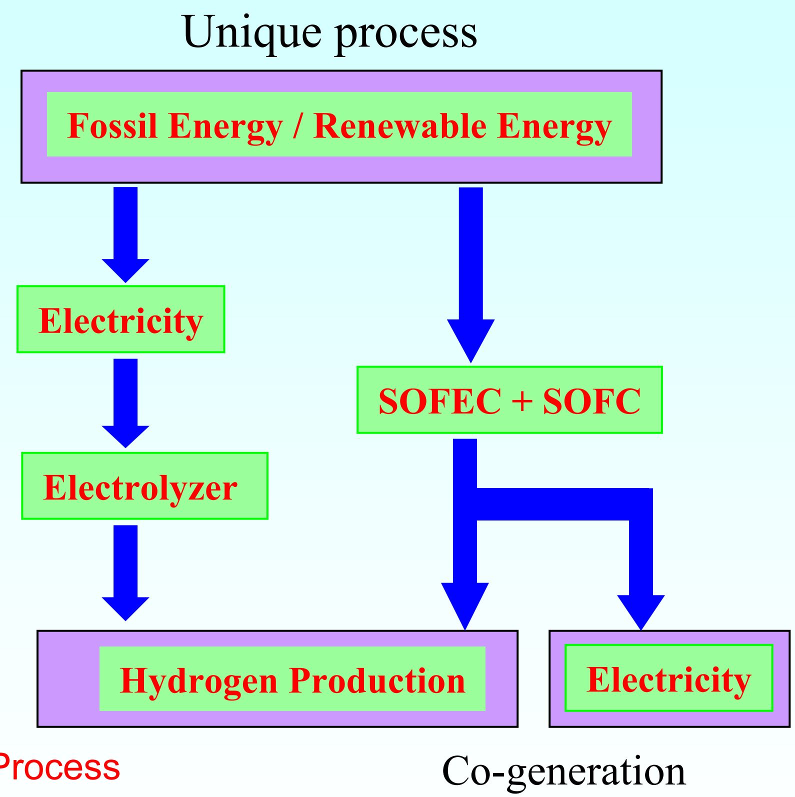
MSRI, UAF, UMR, UU

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.





CH_4-assisted SOFEC Reaction — Electrochemical Process

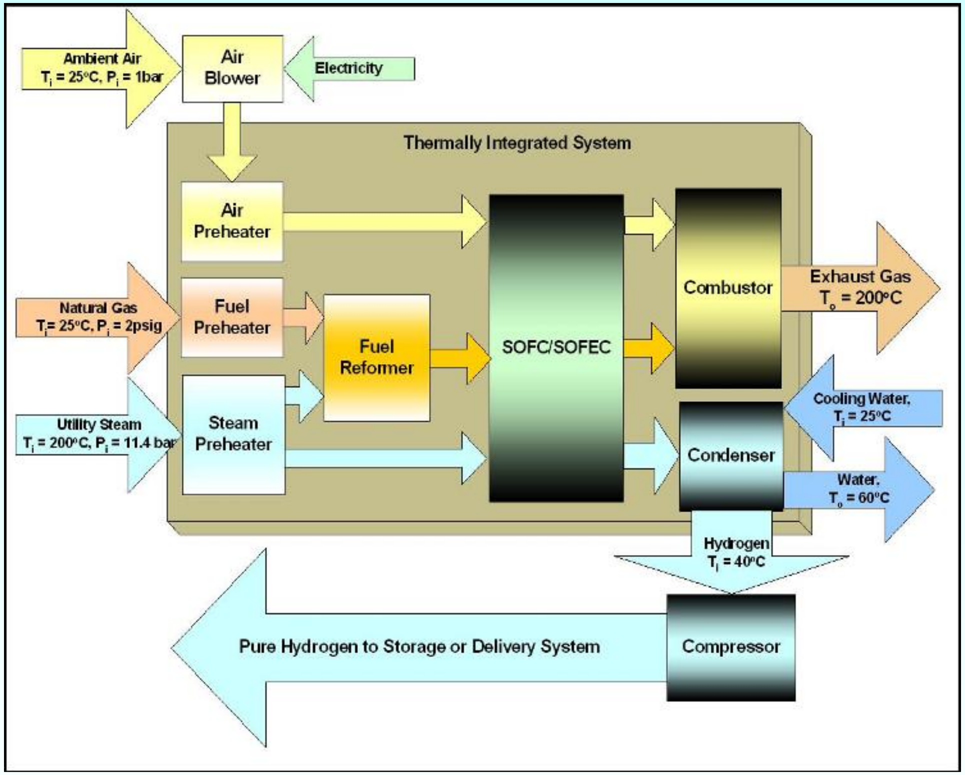
$4H_2O + 8e' \rightarrow 4H_2 + 4O^{2-}$ — at cathode

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

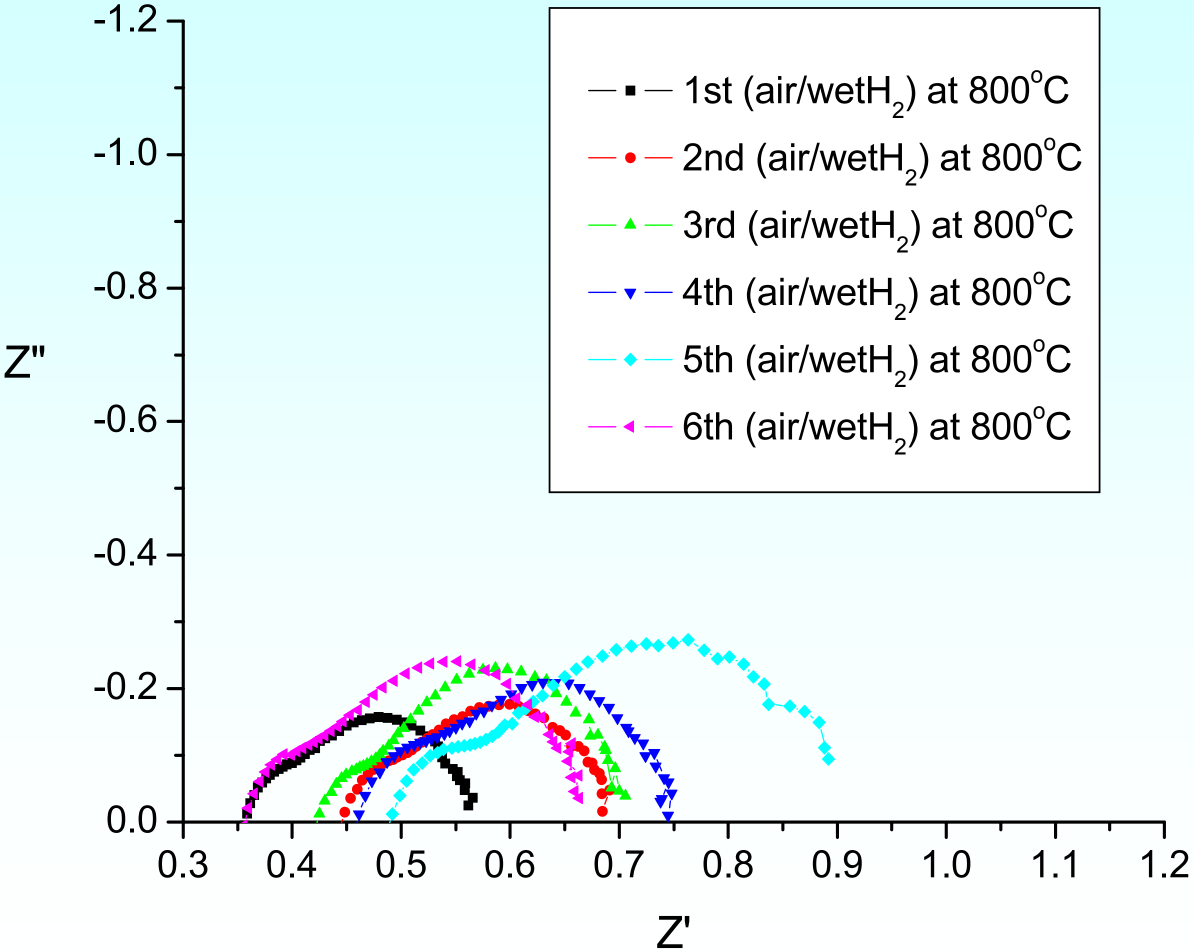
System efficiency
- SOFC-SOFEC hybrid architecture;
- thermal integration;
- co-generation concept.

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

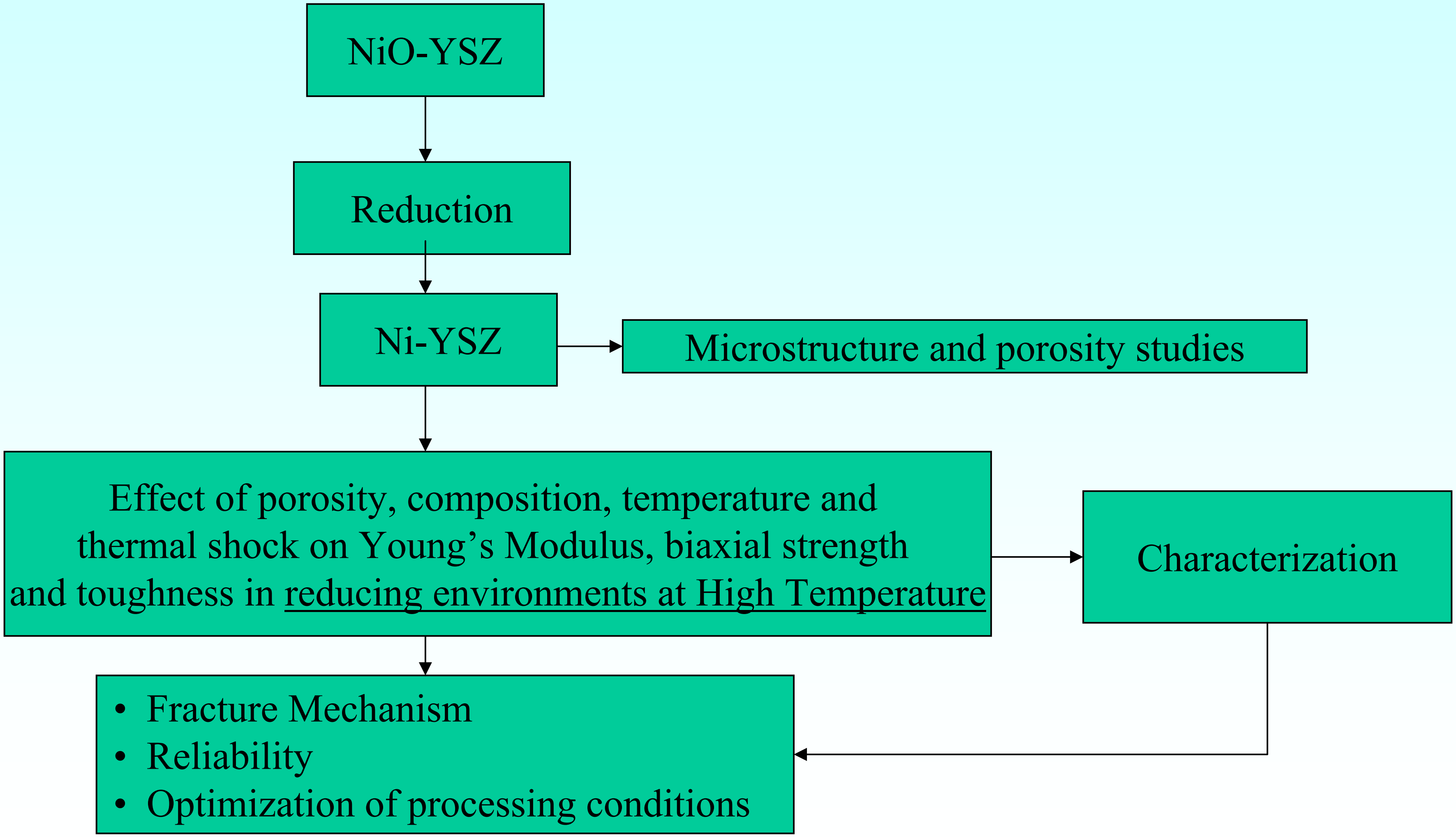
LSCM Redox Stability Study



- 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

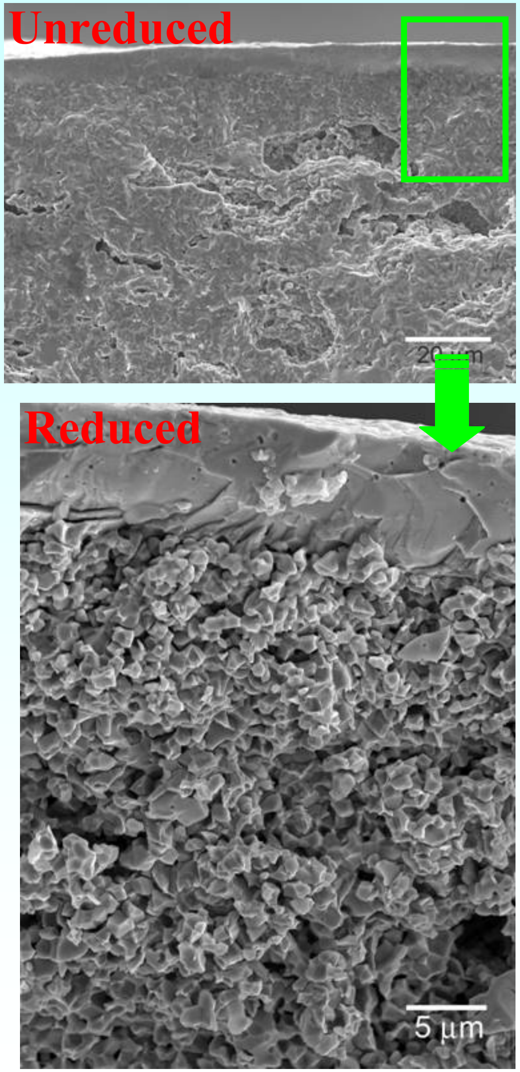
SOFC-SOFEC Anode Substrate Development

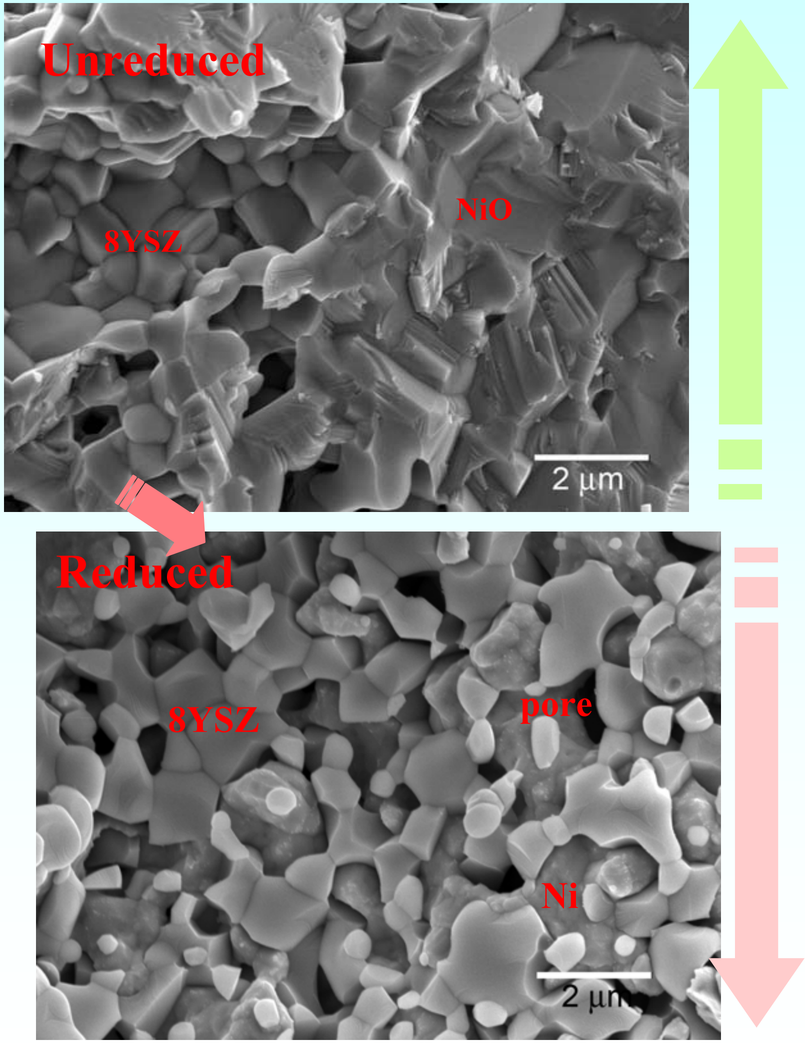
Effects of Residual/Chemical/Applied Stresses on Mechanical Integrity



Reduction of Half-cells

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

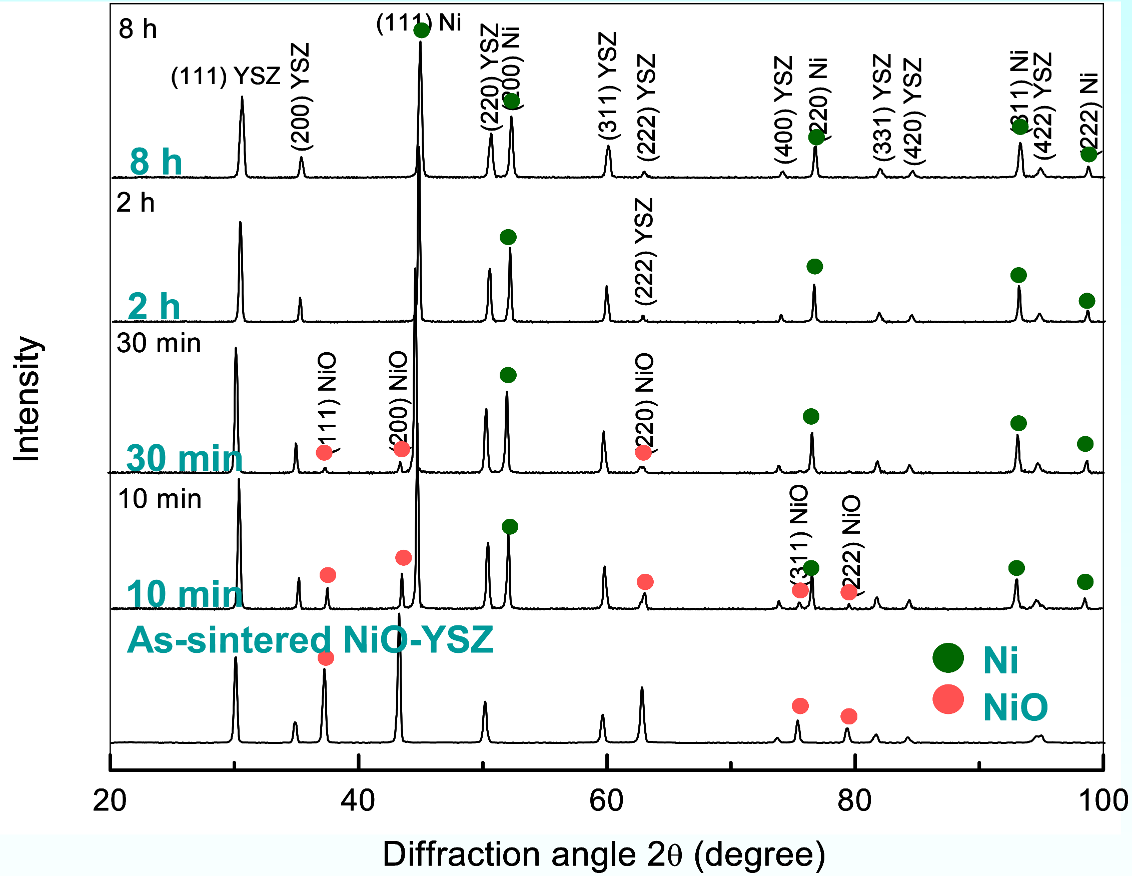


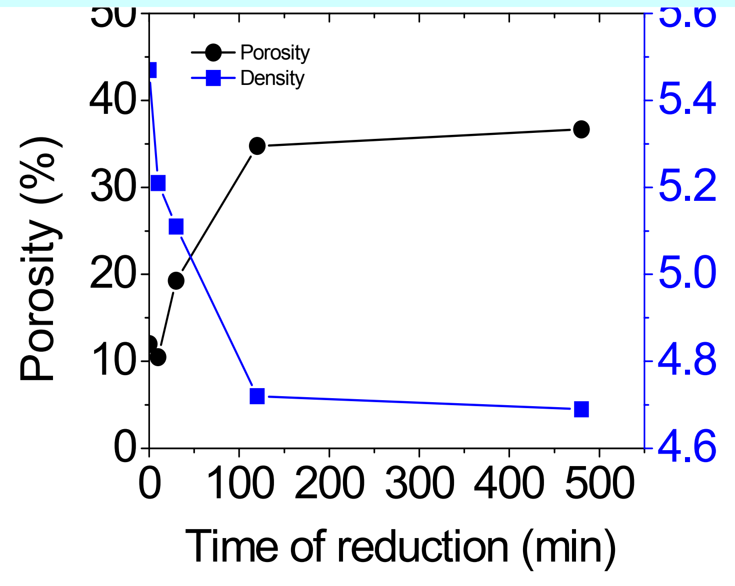


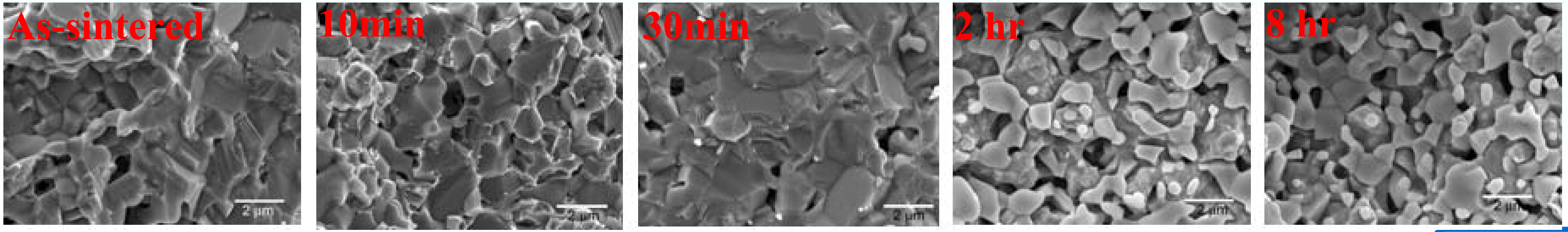
- Porosity
- Triple phase boundary (TPB)

- Density
- Mechanical properties

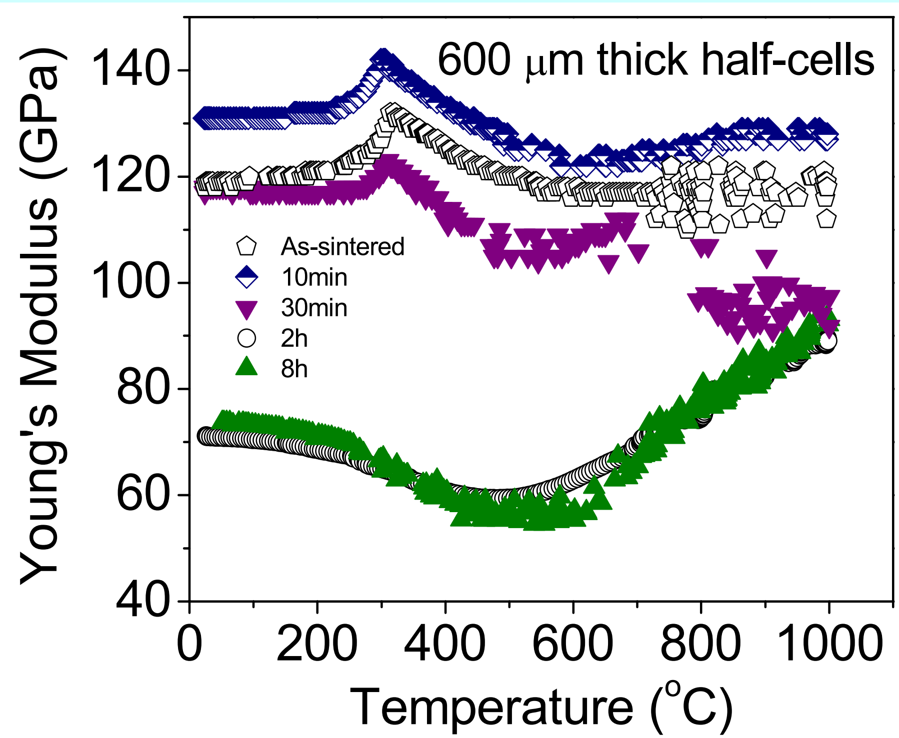
Effect of Reduction on Phases & Microstructure

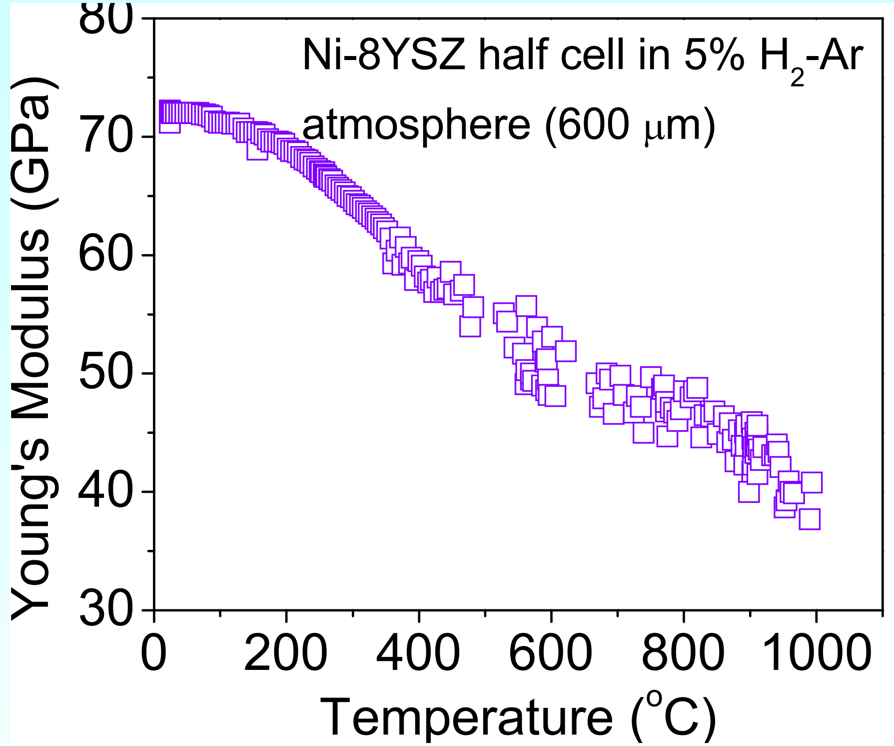






Effect of Reduction on Mechanical Properties





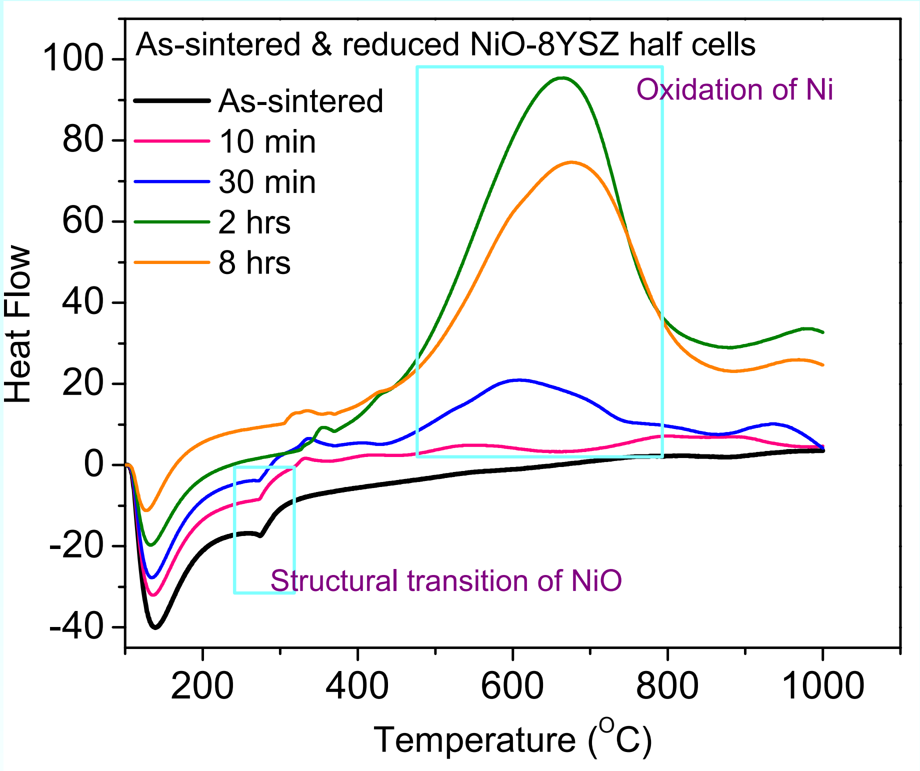
<u>Half-cells that have NiO:</u>

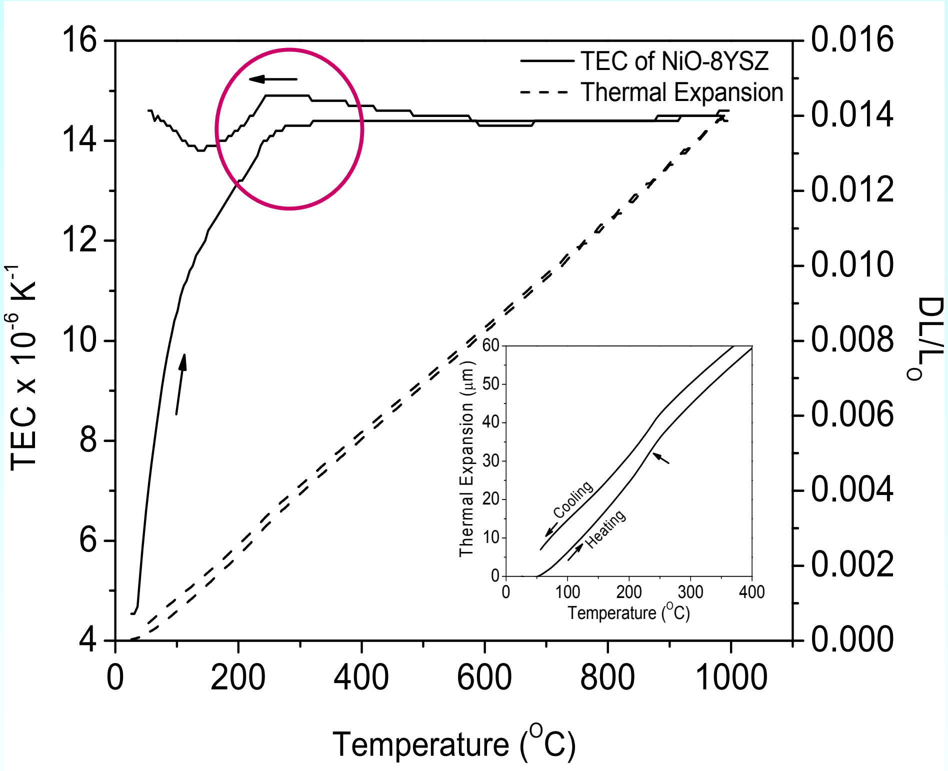
- Higher initial E and a peak in E at 300°C due to rhombohedral to cubic transition

<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

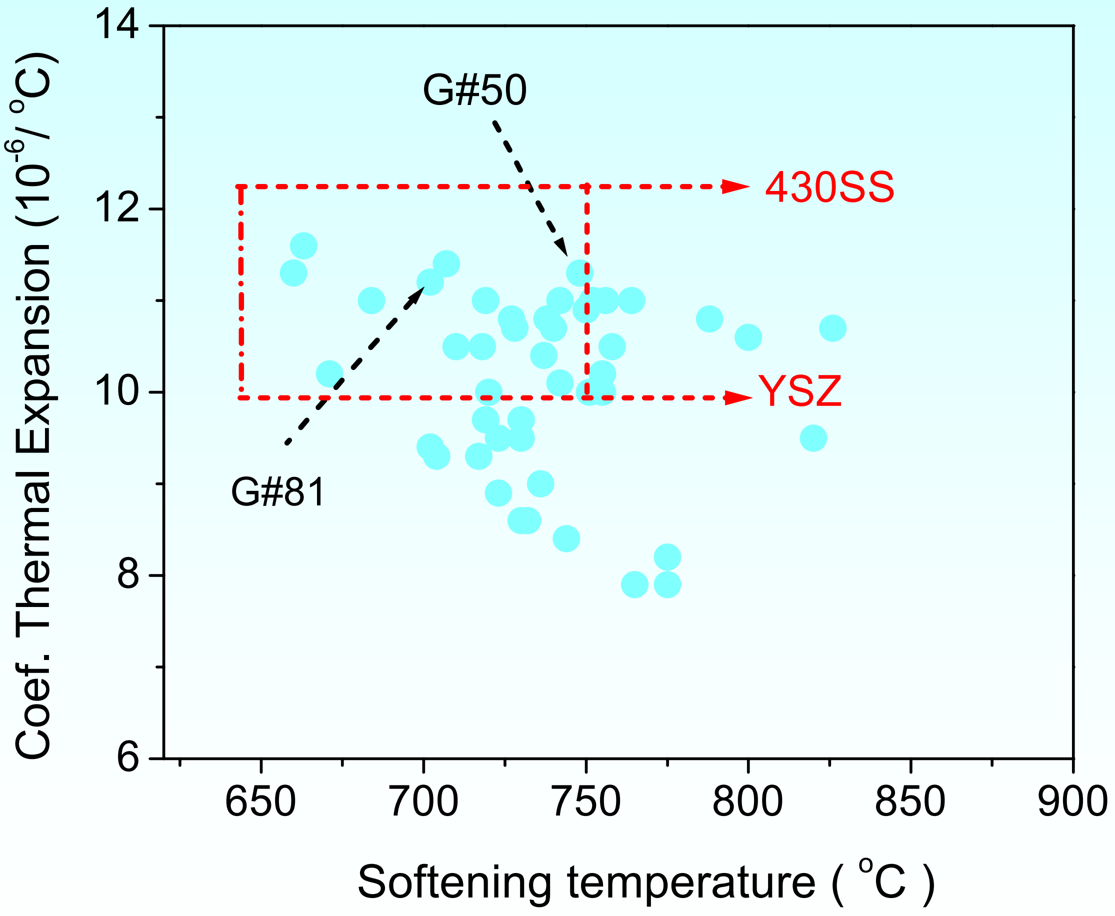
SiO_2<45 mole%

Compositions based on:

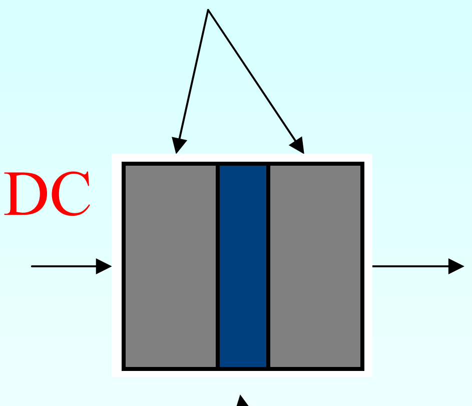
Pyrosilicate

and

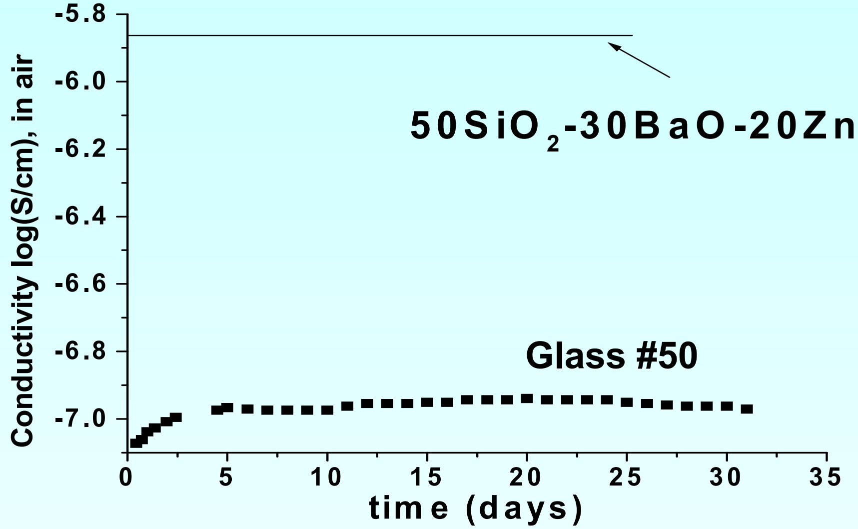
Orthosilicate

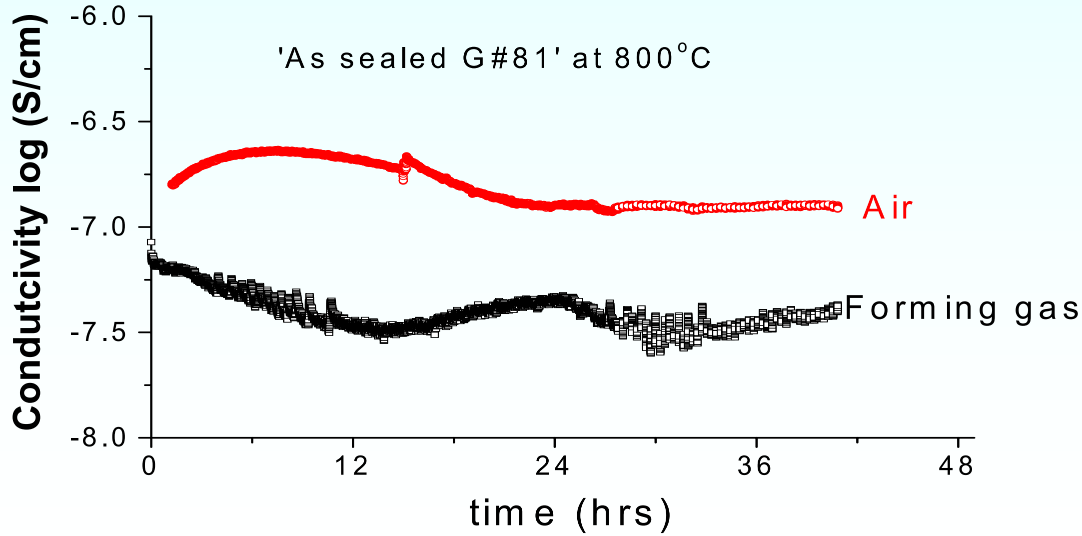


Electrical Conductivity in Air and Forming Gas



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

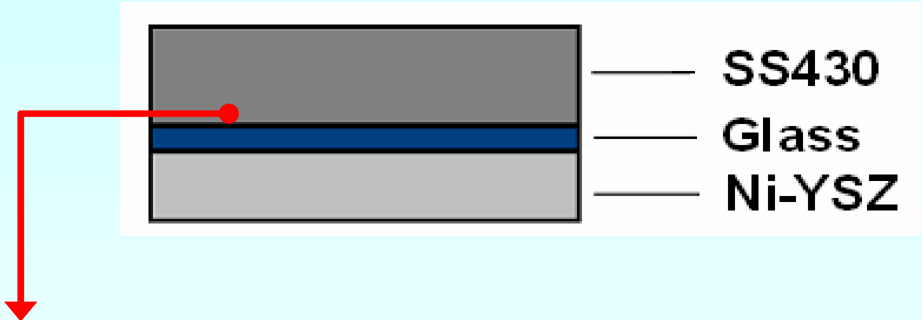
(Samples held at pressure for 24 hours at 800°C; tested for leaks using a 4 psig differential in the testing gas)

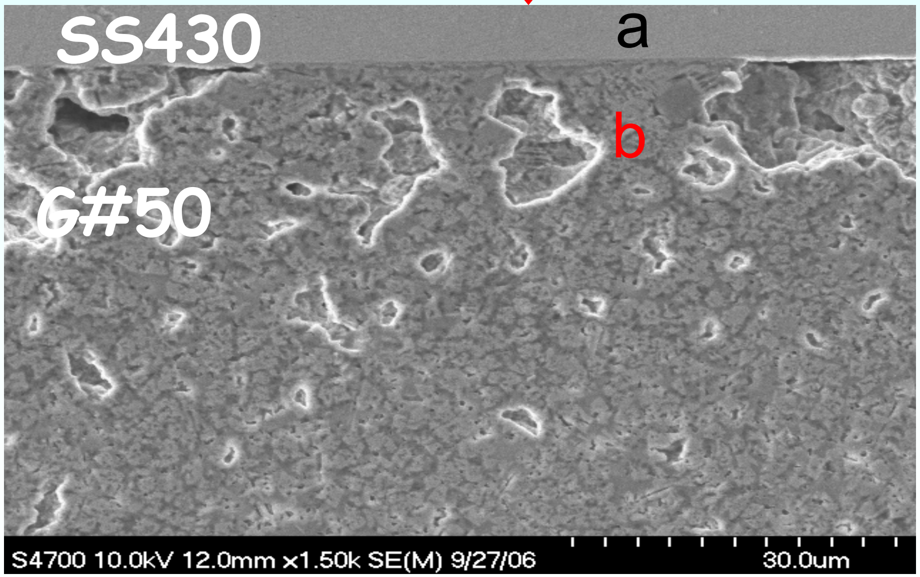
[1] Glass prepared by a commercial vendor (MO-Sci)
[2] Glass prepared at UMR

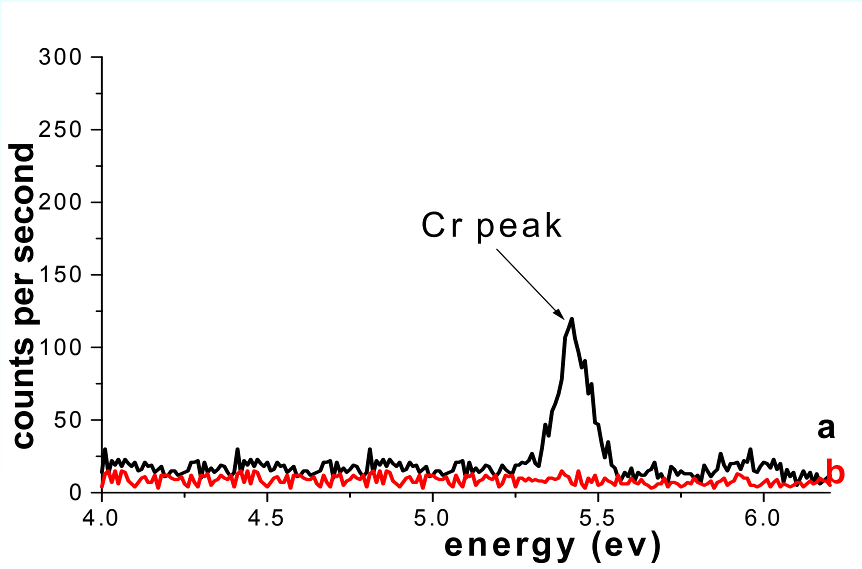
Hermeticity and Materials Compatibility

Little Evidence for Significant Reactions @ Seal Interfaces

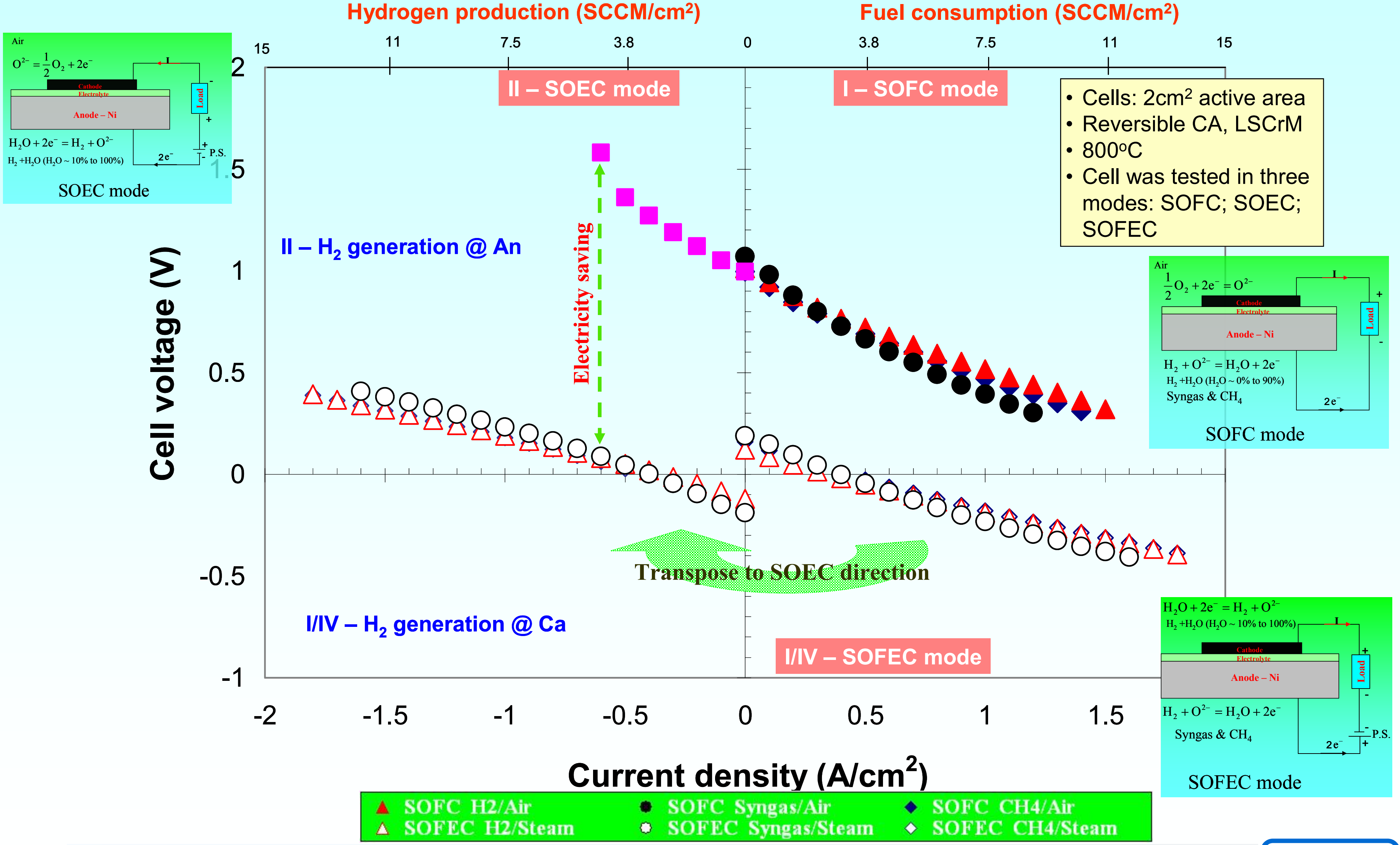
Ten days in wet forming gas at 800^{o}C





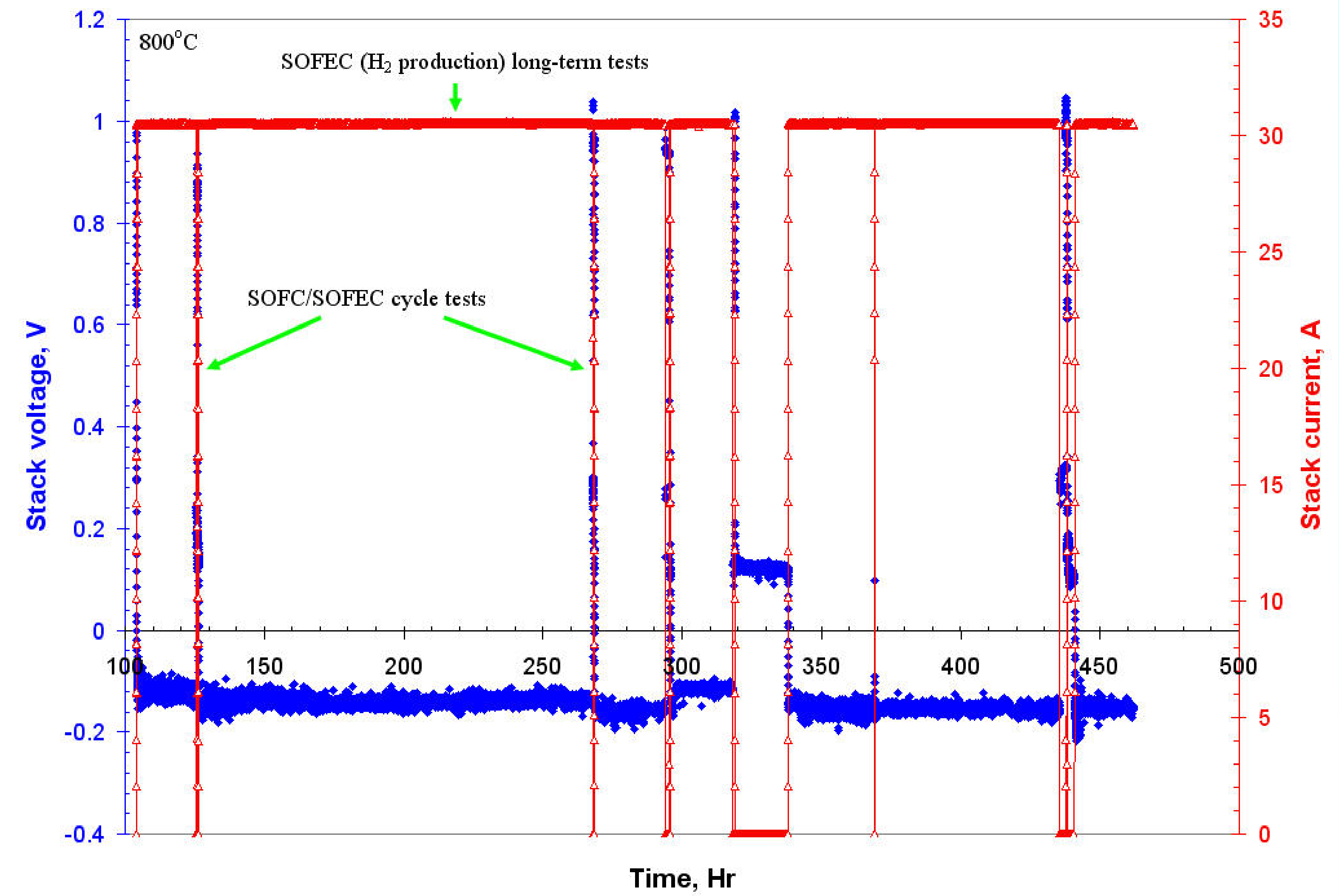


Cathode Characteristics in SOFC/SOEC/SOFEC Modes



SOFEC Stability Test

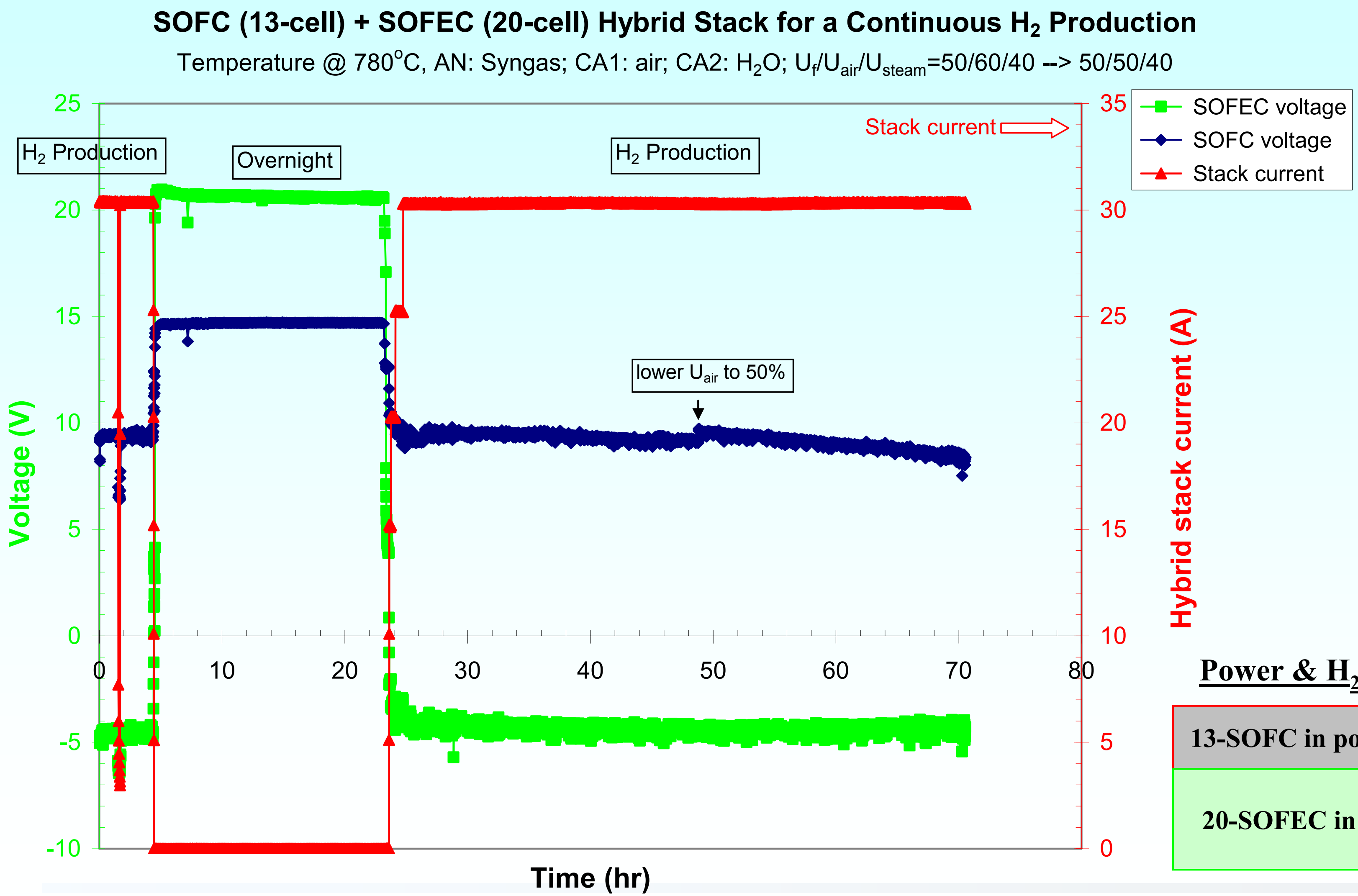
Single-cell Stack with 100 cm² Per-cell Active Areas



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

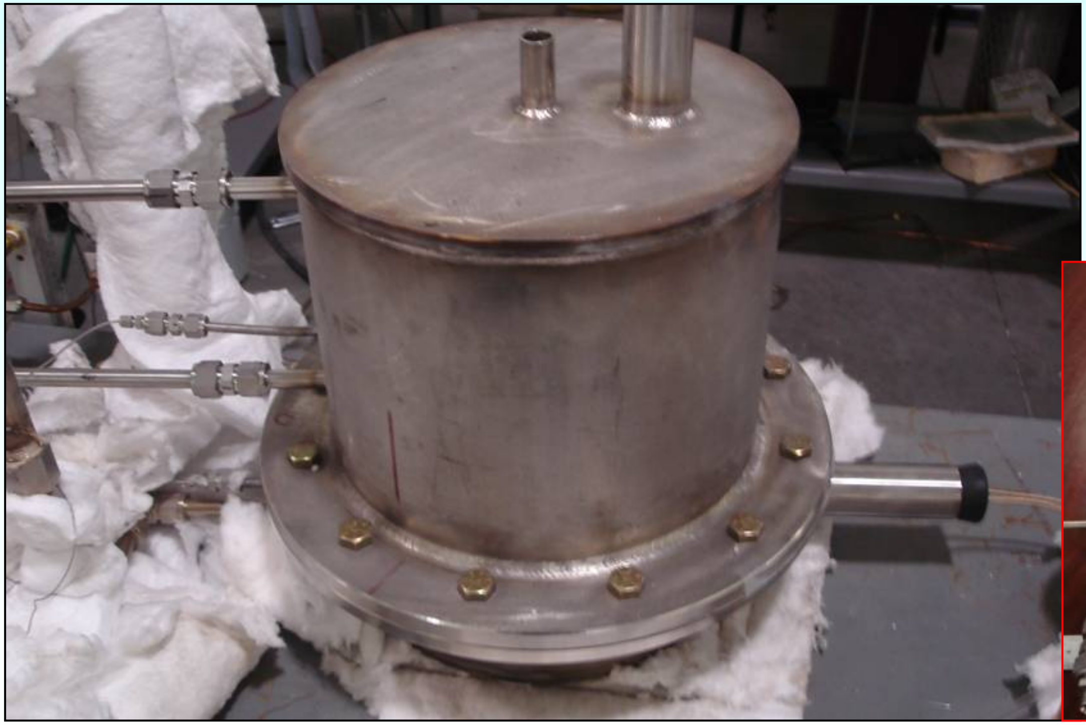
13-SOFC in power generation
20-SOFEC in H_2 production

Next Generation Stack Design for the 5 kW System

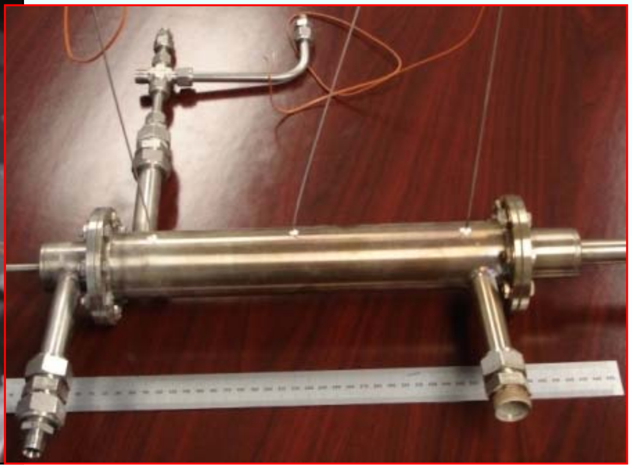
- Larger stacks (60+ cells per stack)
- Thermal and flow management
  - Novel flow geometry for in-stack temperature and flow optimization
- Improved sealing
- Design for assembly
  - Stack components have been minimized to reduce stacking time and error
  - Improved reliability
- Reduced pressure drop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