

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

Greg Tao, Mike Homel, Bruce Butler, and Anil Virkar

Materials & Systems Research Inc., Salt Lake City, UT

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**Project ID#: PDP 14**

# Overview

## Timeline

- Project started: 02/10/2006
- Project ends: 07/31/2008
- Percent completed: 40%

## Budget

- Total budget funding
  - DOE \$2,480k
  - Contractor \$ 620k
- Funding received in FY06
  - \$ 452k
- Funding for FY07
  - \$ 1,000k

## Barriers

Hydrogen generation by water electrolysis

- G – Capital cost
  - Low-cost, durable high-temperature materials development
  - Lower operating temperature
- J – Renewable integration
- K – Electricity costs

## Partners

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

# Objective

Overall Objective	<ul style="list-style-type: none"><li>• To develop a low-cost and highly efficient 5 kW SOFC-SOFEC hybrid co-generating both electricity and hydrogen to achieve the cost target &lt; \$3.00/gge when modeled in a 1000 gge/day hydrogen production.</li><li>• The project focuses on materials R&amp;D, stack design &amp; fabrication, and system design &amp; verification</li></ul>
2006	<ul style="list-style-type: none"><li>• SOFC-SOFEC cell &amp; stack development<ul style="list-style-type: none"><li>— Materials development (electrodes &amp; seals)</li><li>— Stack design &amp; development</li><li>— Cell fabrication</li><li>— Proof-of-concept hybrid stack verification</li></ul></li></ul>
2007	<ul style="list-style-type: none"><li>• 5 kW SOFC-SOFEC hybrid system development<ul style="list-style-type: none"><li>— Materials development and application (electrodes &amp; seals)</li><li>— Hybrid system design</li><li>— BOP components design &amp; development</li><li>— Fabrication</li><li>— Hydrogen generation cost analysis</li></ul></li></ul>

# Approach

## Materials Development

- A. Ca materials Dev.
- B. An optimization
- C. Electrolyte optimization
- D. Catalyst studies
- E. Seals development
- F. Fabrication Q.A.

40% 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

40% complete

## Experimental Verification

- A. Short stacks in dif. modes
- B. 1 kW hybrid stack
- C. BOP Manufact.& Eva.
- D. 5 kW sys. development
- E. 5kW hybrid system Exp. Evaluation

30% complete

Success

MSRI, UMR

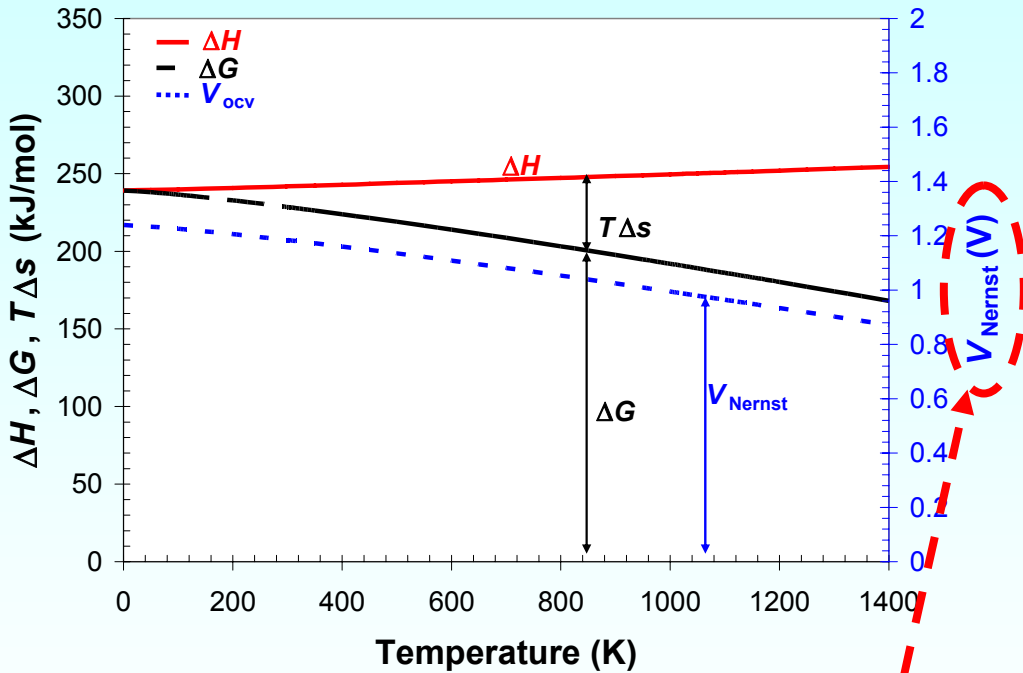
MSRI, UAF, UMR, UU

MSRI, UU, UMR

1-2 kW Stack  
4" x 4"

# Background

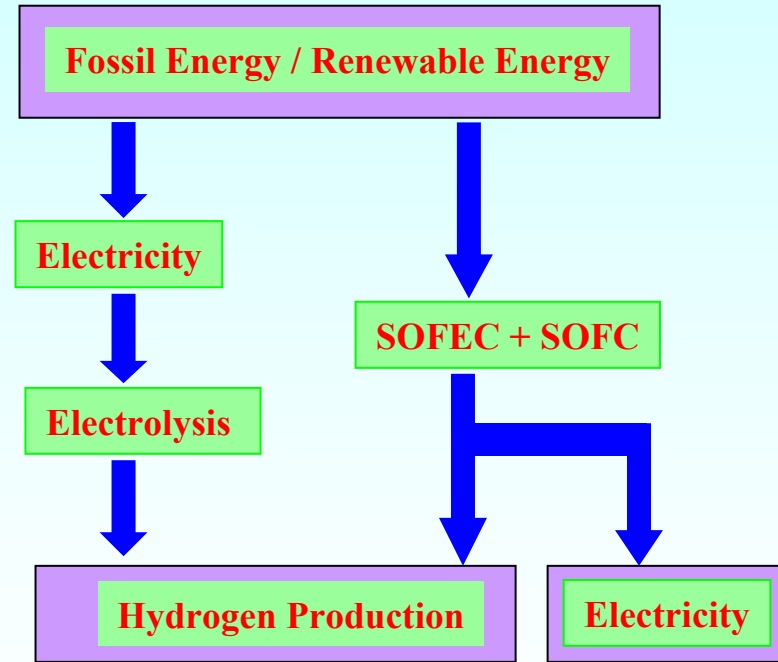
A Solid Oxide Fuel-Assisted Electrolysis Cell (SOFEC) directly applies the energy of a chemical fuel to replace the external electrical energy required to produce hydrogen from water/steam; decreasing the cost of energy relative to a traditional electrolysis process



Electricity from Grid

Electrochemical Process  
at cathode  
at anode

Unique process



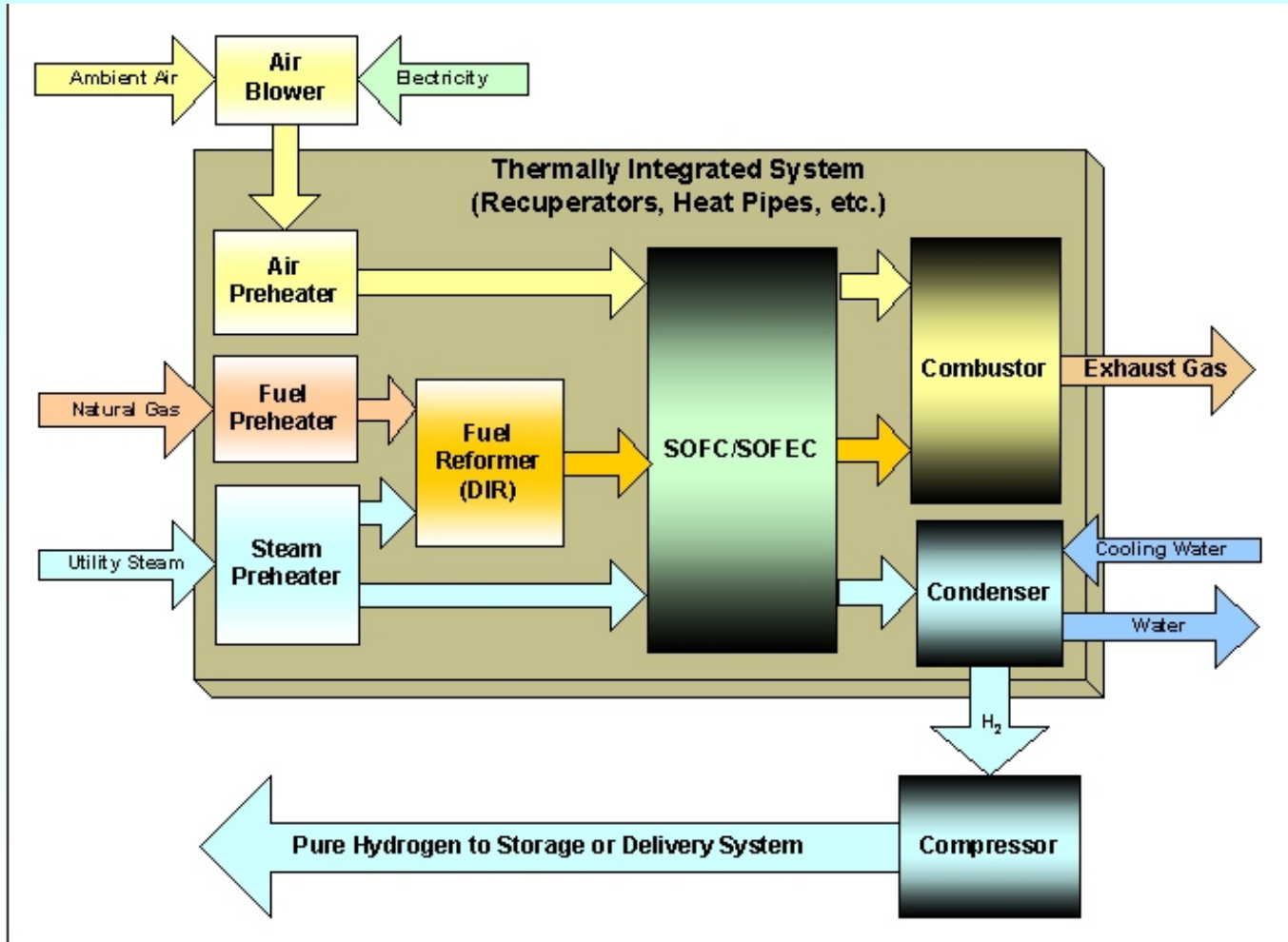
Co-generation

CH<sub>4</sub>-assisted SOFEC Reaction



Pure H<sub>2</sub> formed. No need for H<sub>2</sub> separation membranes. Lower electricity requirement.

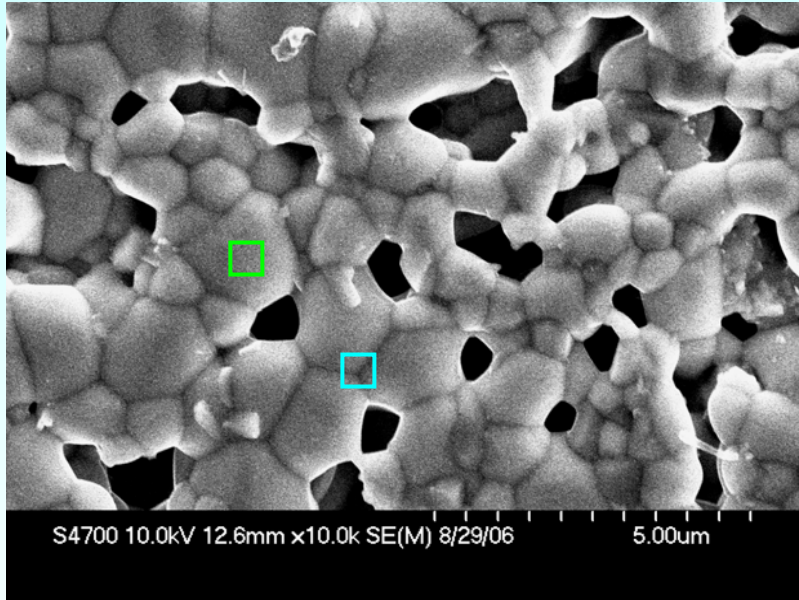
# Concept of Hybrid SOFC-SOFEC Integral System



- Pure H<sub>2</sub> & e<sup>-</sup> generated from fuel, steam, and air
- SOFECs produce pure hydrogen
- SOFCs generate electricity; increase H<sub>2</sub> production rate
- Thermal integration improves system efficiency

# SOFEC Cathode Materials Development

## Chemical analysis of LST/LSCM



Element	Wt %	At %
O K	15.29	49.09
SrL	10.82	6.35
TiK	15.89	17.05
LaL	47.83	17.69
CrK	5.96	5.89
MnK	4.21	3.93
Total	100	100

Element	Wt %	At %
O K	24.16	63.03
SrL	11.06	5.27
TiK	13.68	11.92
LaL	41.97	12.61
CrK	5.35	4.29
MnK	3.8	2.89
Total	100	100

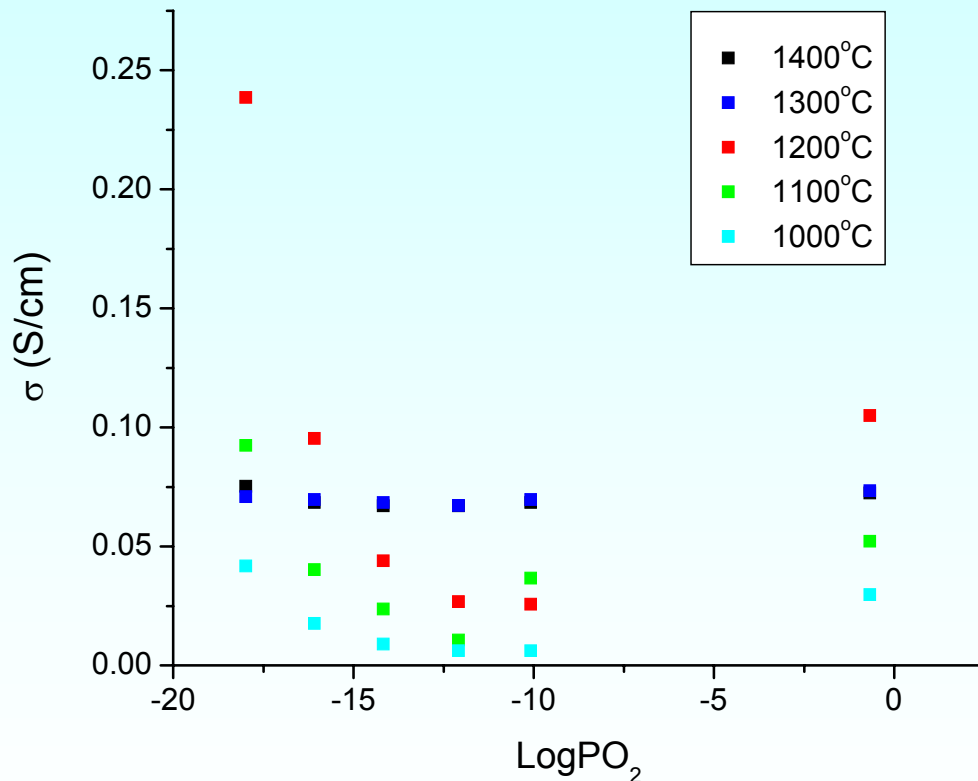
Wt% of  $\text{La}_{0.8}\text{Sr}_{0.2}\text{TiO}_{3-\delta}$  and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$

- The LST/LSCM sintered at 1200°C has no significant variation of composition between grain and grain boundary
- The active diffusion process appears to be started between 1100 and 1200°C

		La	Sr	Ti	Cr	Mn	O
LST(0.8/0.2/1)	Wt/mol	138.9	87.6	47.9			16
	Wt%	49.5	8	21.2			21.3
LSCM(0.8/0.2/0.5/0.5)	Wt/mol	138.9	87.6		52	55	16
	Wt%	48.3	7.6		11.3	12	20.8

# SOFC Cathode Materials Development

## Conductivity investigation of LST/LSCM

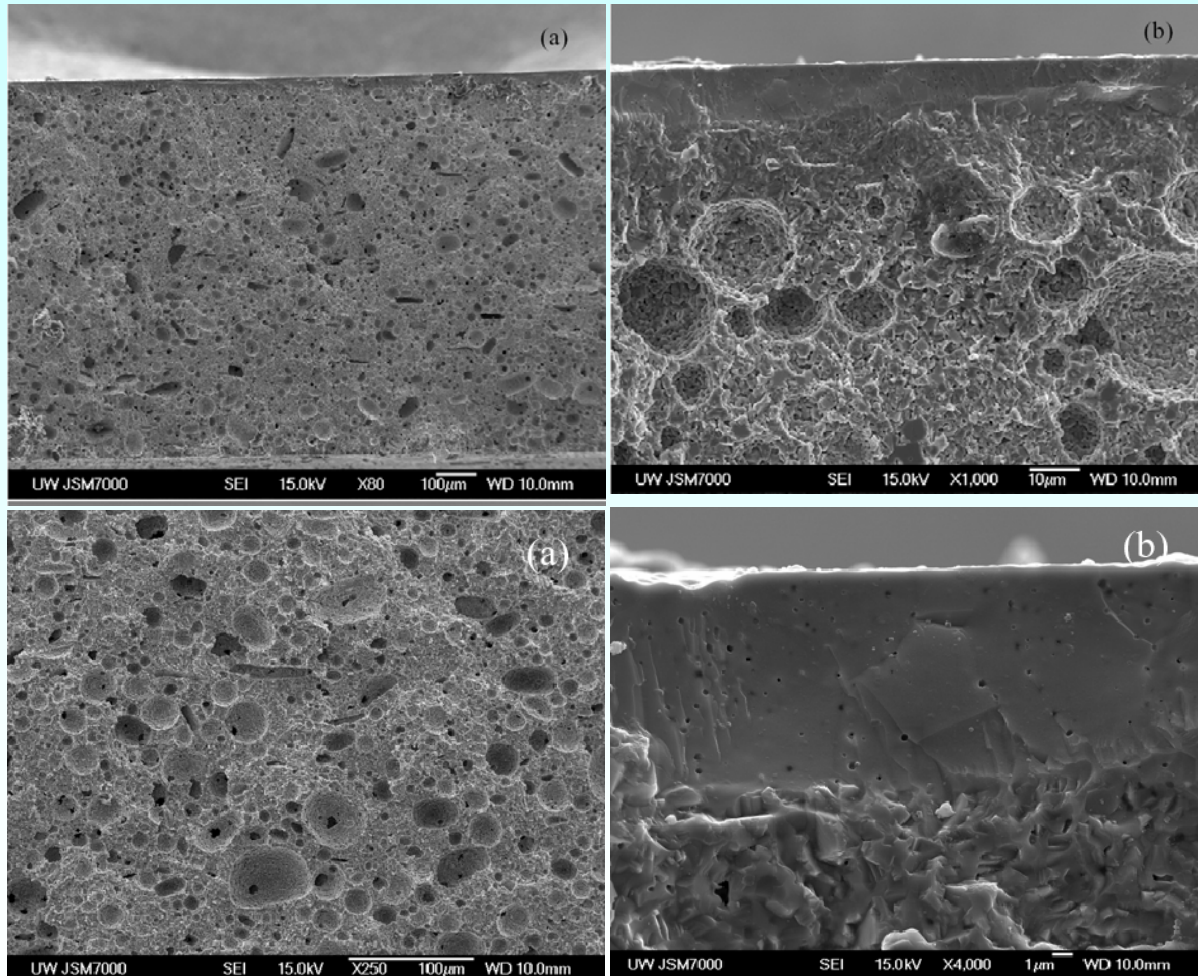


- The higher conductivity at 1200°C is due to  
(1) the higher density  
(2) early stage of inter-diffusion process  
(3) LST and LSCM co-exists without losing their original material properties
- The total conductivity behavior of the LST/LSCM is dominated by the low conductivity of the LST

Measured at 900°C



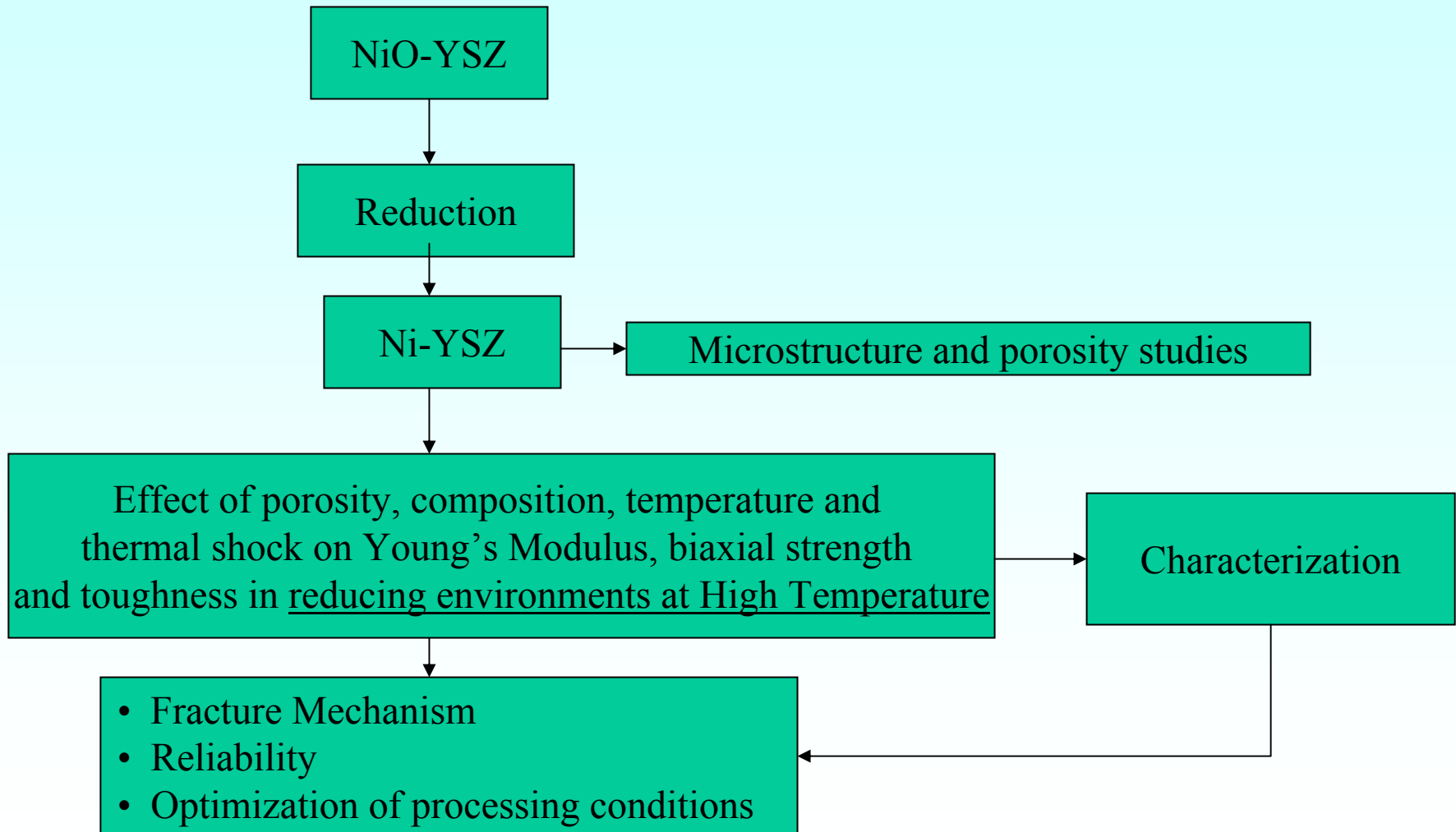
# SOFC-SOFEC Anode Substrate Development



- Estimated effects of temperature and load on hardness and fracture toughness of the rectangular and button cells
- Investigated microstructure of the membranes
- Investigated Young's modulus of the membranes at RT
- Studied thermal expansion
- Initiated modeling of the indentation stress distribution
- Designed and fabricated high temperature Equibiaxial flexural strength fixture
- Fabricated an equipment for measuring high temperature modulus using Impulse Excitation technique (IET)

# SOFC-SOFEC Anode Substrate Development

## Effects of residual/chemical/applied stresses on Mechanical Integrity



# Hermetic Seals Development

More than 60 'invert' glass compositions have been evaluated

"Invert" silicate:

Glasses with

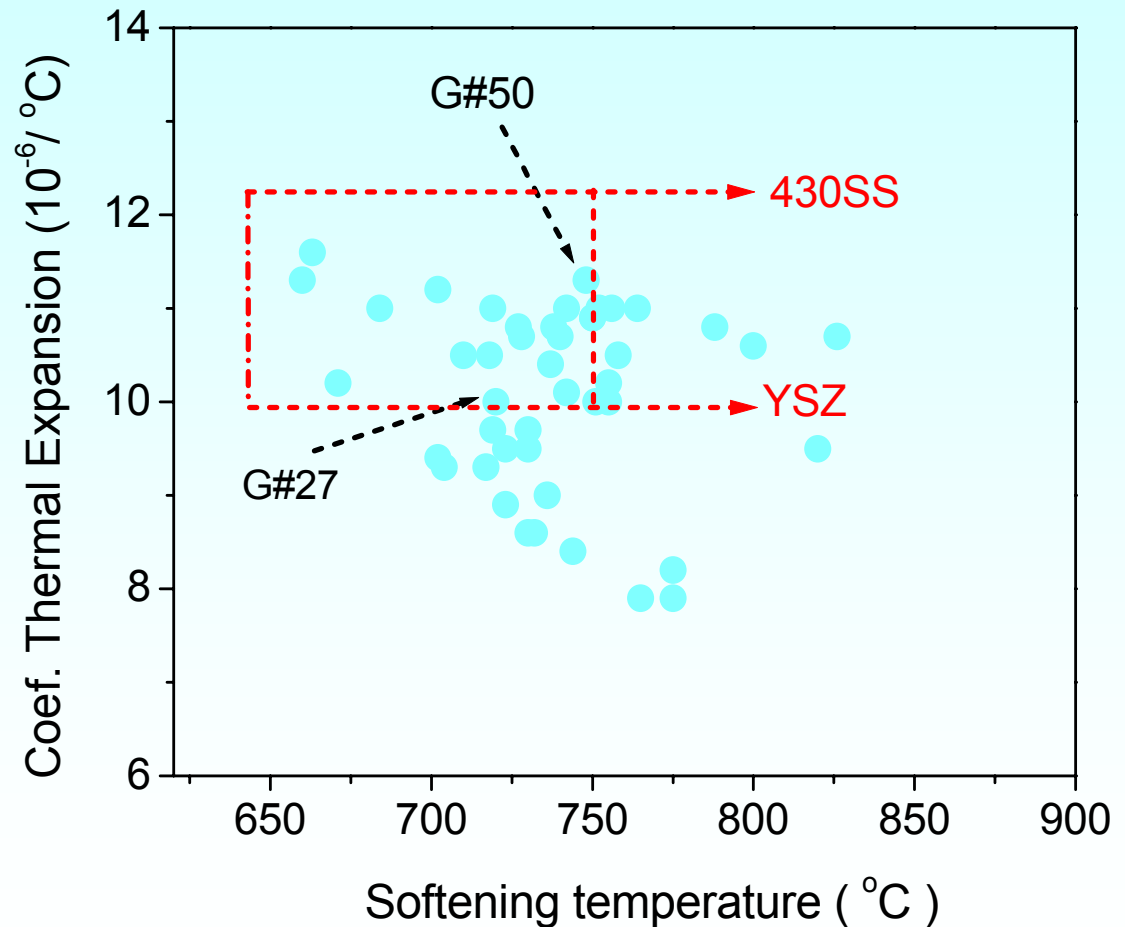
$\text{SiO}_2 < 45 \text{ mole\%}$

Compositions based on:

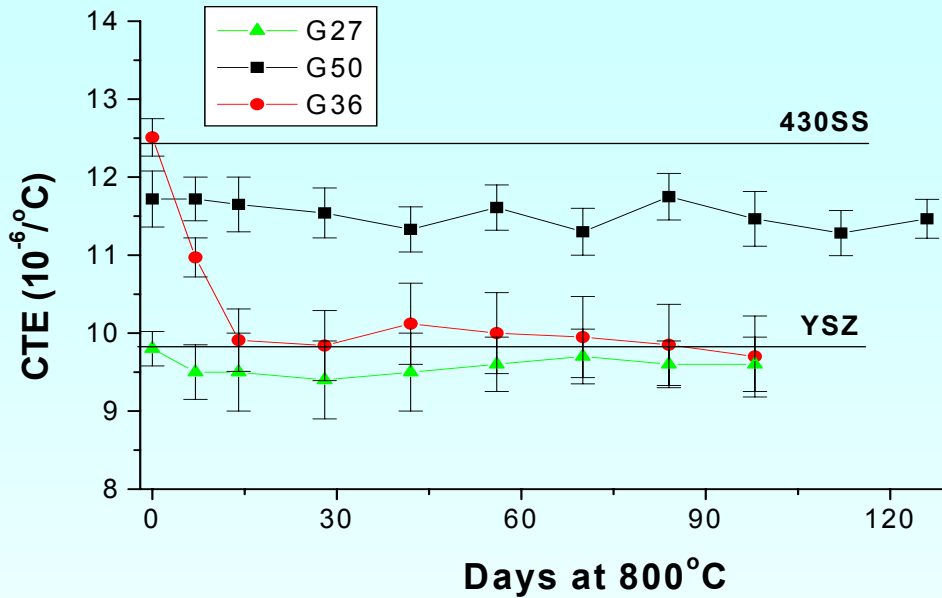
Pyrosilicate

and

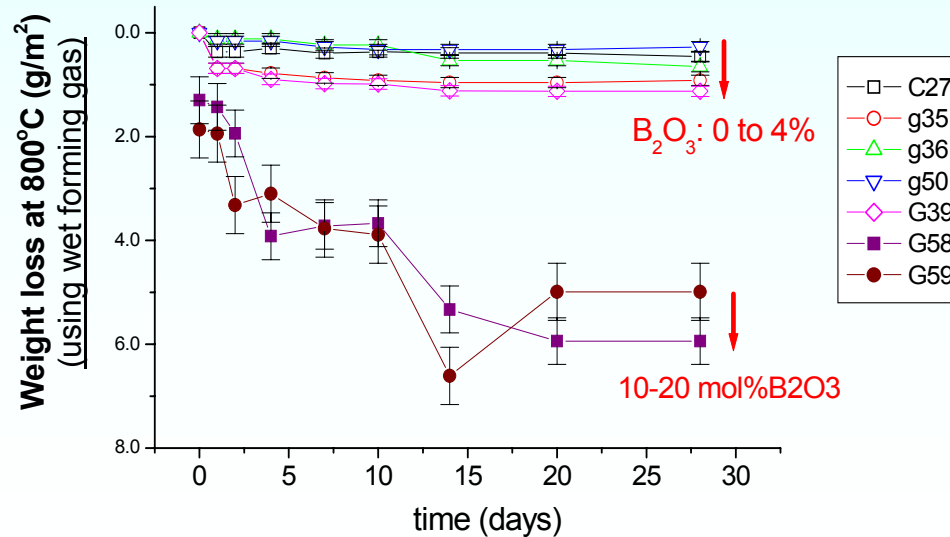
Orthosilicate



# Hermetic Seals Development

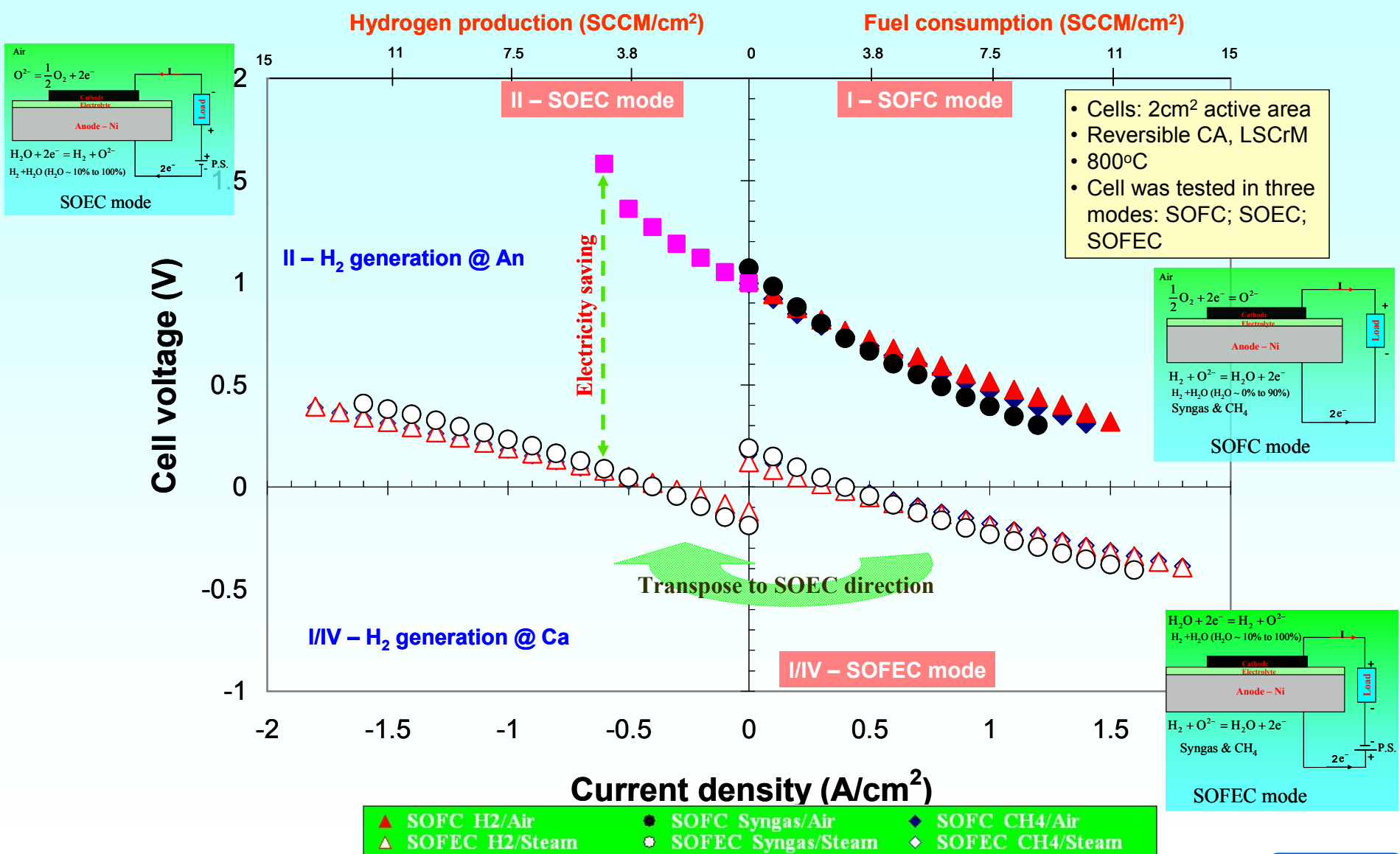


**Thermomechanical compatibility is a significant property design target**

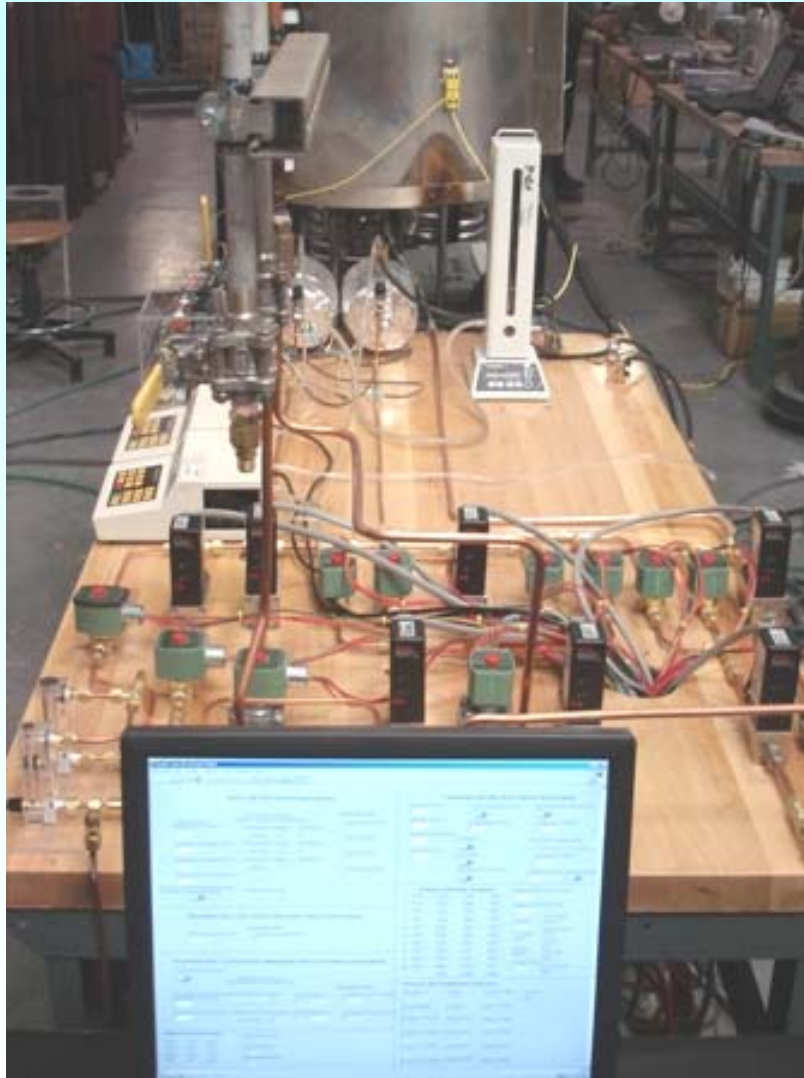


**Thermochemical stability depends on glass composition**

# Cathode Characteristics in SOFC/SOEC/SOFEC Modes

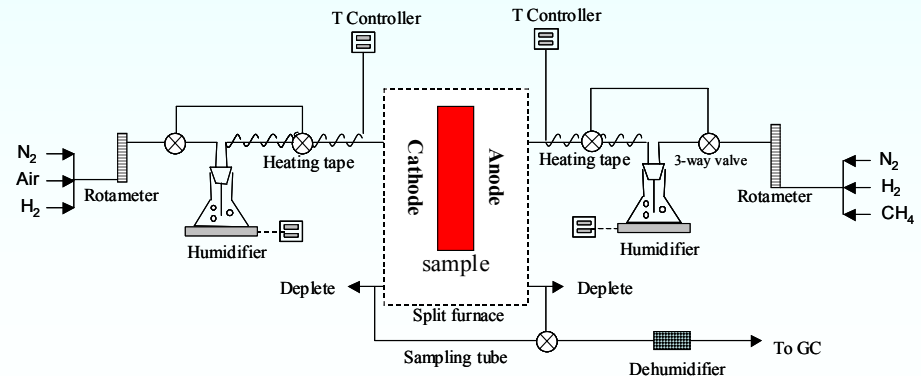


# Proof-of-concept Hybrid Stack Testing



Hybrid stack testing station

- Station capable of operating in three modes: SOFC/SOEC/SOFEFC
- Capable of 40+ cell stack
- Capable of hybrid stack
- Automation testing
- Self protection in case of power outage
- Stack IR evaluation
- Gas chromatograph analysis
- Hydrogen production measurement





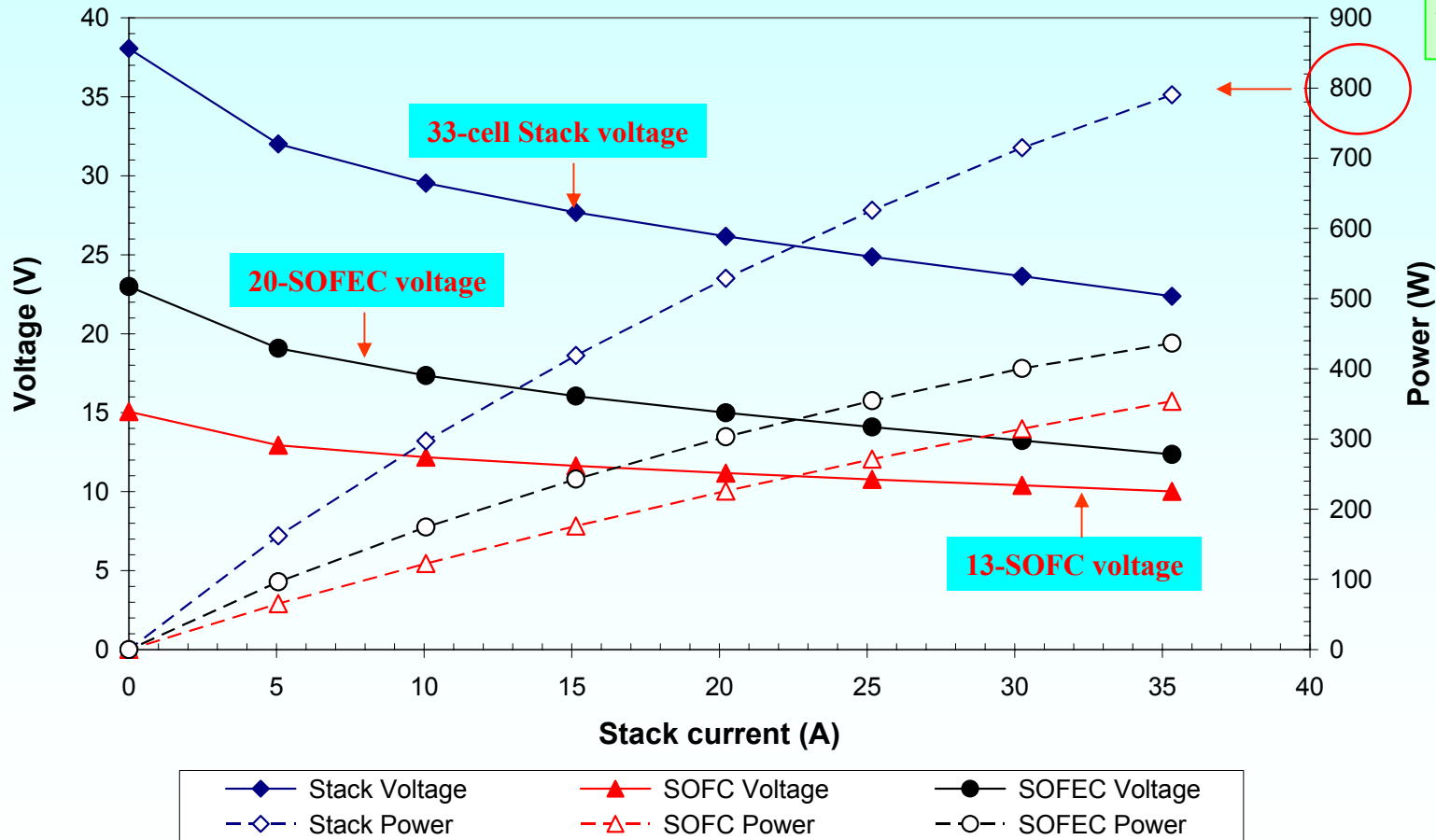
# kW Class SOFC-SOFEC Hybrid Stack Power Generation

**SOFC (13-cell) + SOFEC (20-cell) Hybrid Stack**  
**Baseline Test in SOFC Mode (Stack vs. SOFC & SOFEC)**  
 Furnace temperature 750°C, 50%H<sub>2</sub>+N<sub>2</sub> U<sub>f</sub>/U<sub>air</sub>=40/40

## Power generation

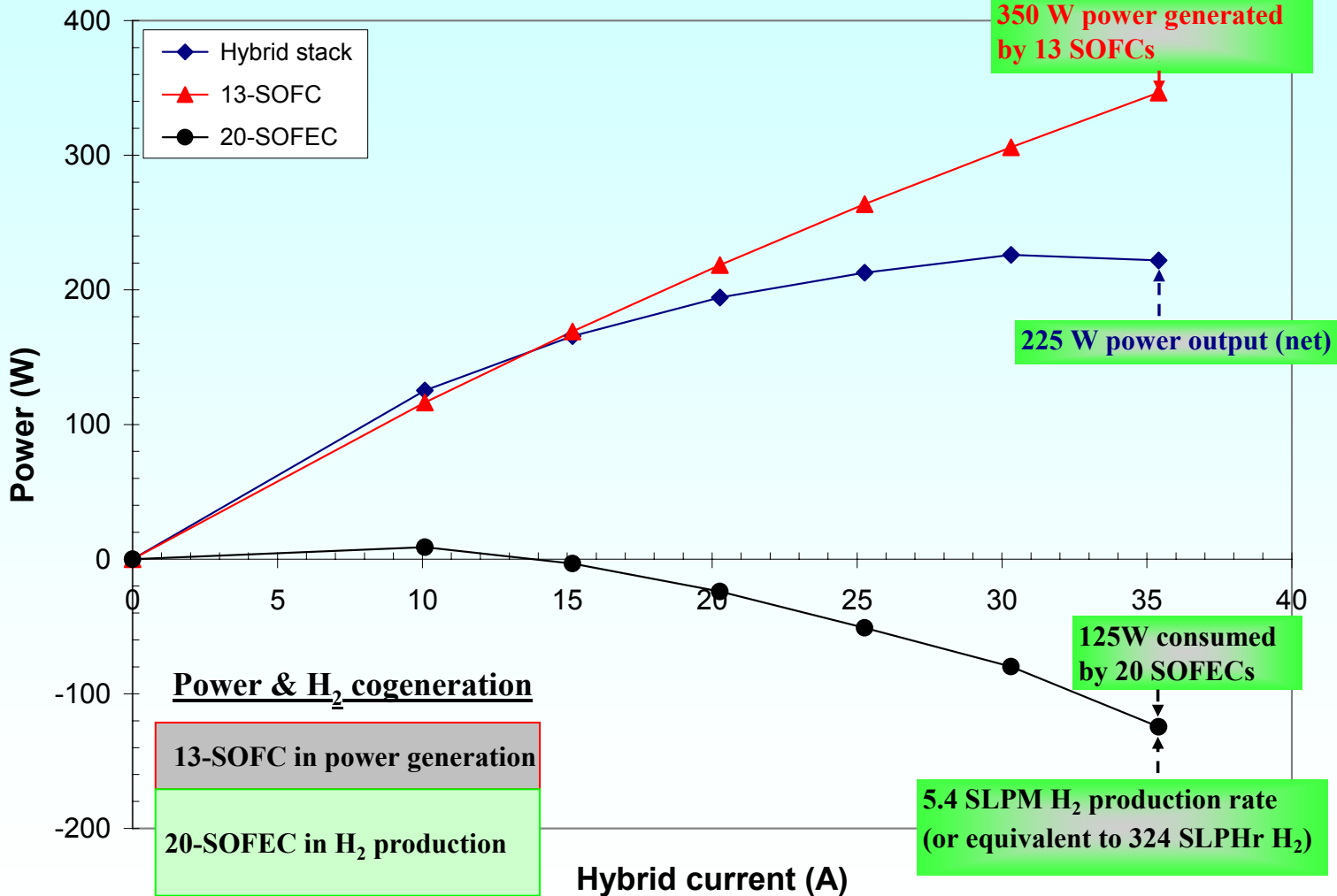
13-SOFC in power gen.

20-SOFEC in power gen.



# kW Class SOFC-SOFEC Hybrid Power & H<sub>2</sub> Cogeneration

## Power – Current curve: Hybrid vs. 13-SOFC vs. 20-SOFEC



### Hybrid stack

- 13 SOFCs
- 20 SOFECs
- T = 770°C
- Anode: Syngas
- Cathode 1: air
- Cathode 2: steam
- U<sub>f</sub> = 40%
- U<sub>air</sub> = 40%
- U<sub>steam</sub> = 40%

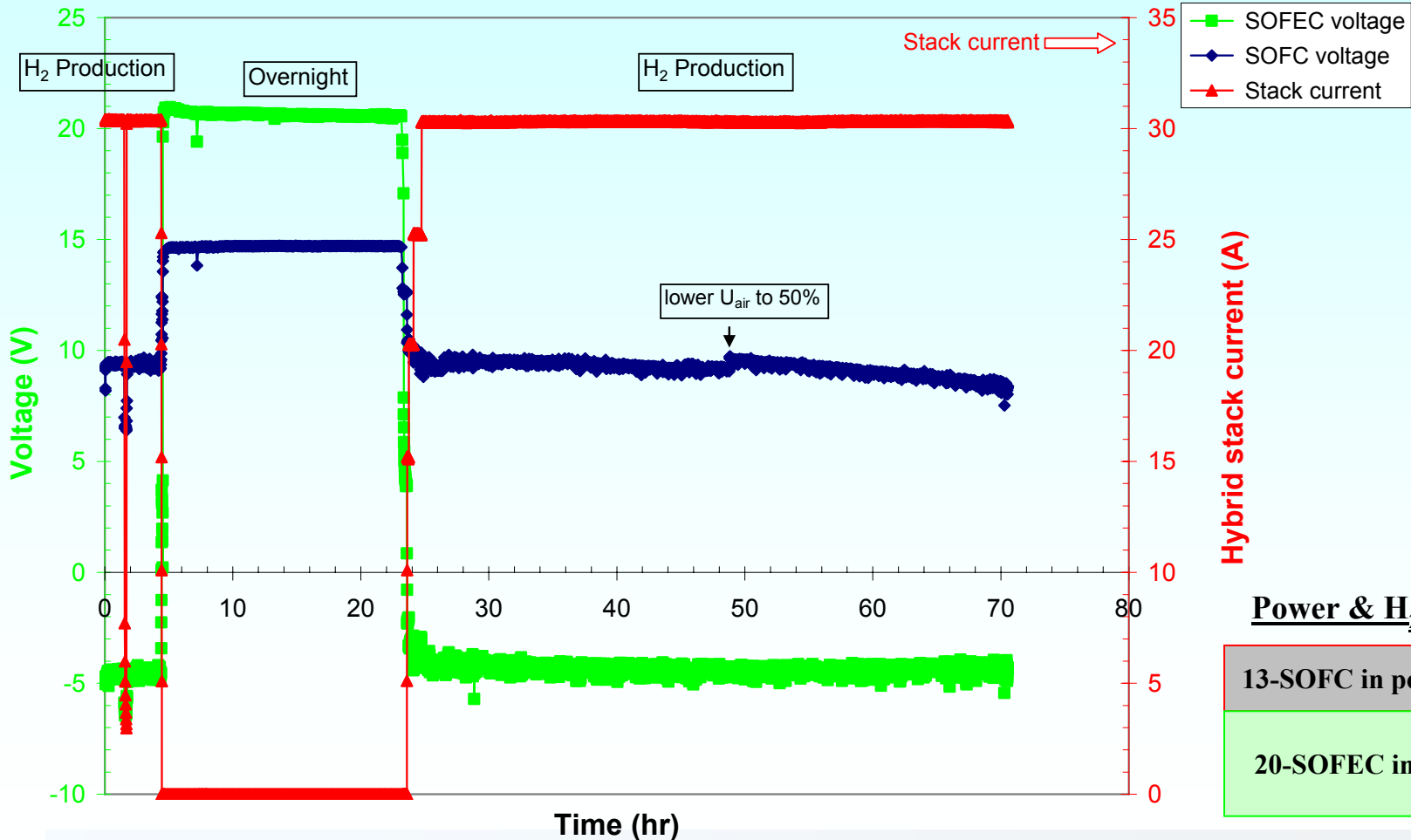


# kW Class SOFC-SOFEC Hybrid Power & H<sub>2</sub> Cogeneration

**H<sub>2</sub> Production Rate: 270 standard liters per hour, AND, Net Power Output: 130 Watts**

**SOFC (13-cell) + SOFEC (20-cell) Hybrid Stack for a Continuous H<sub>2</sub> Production**

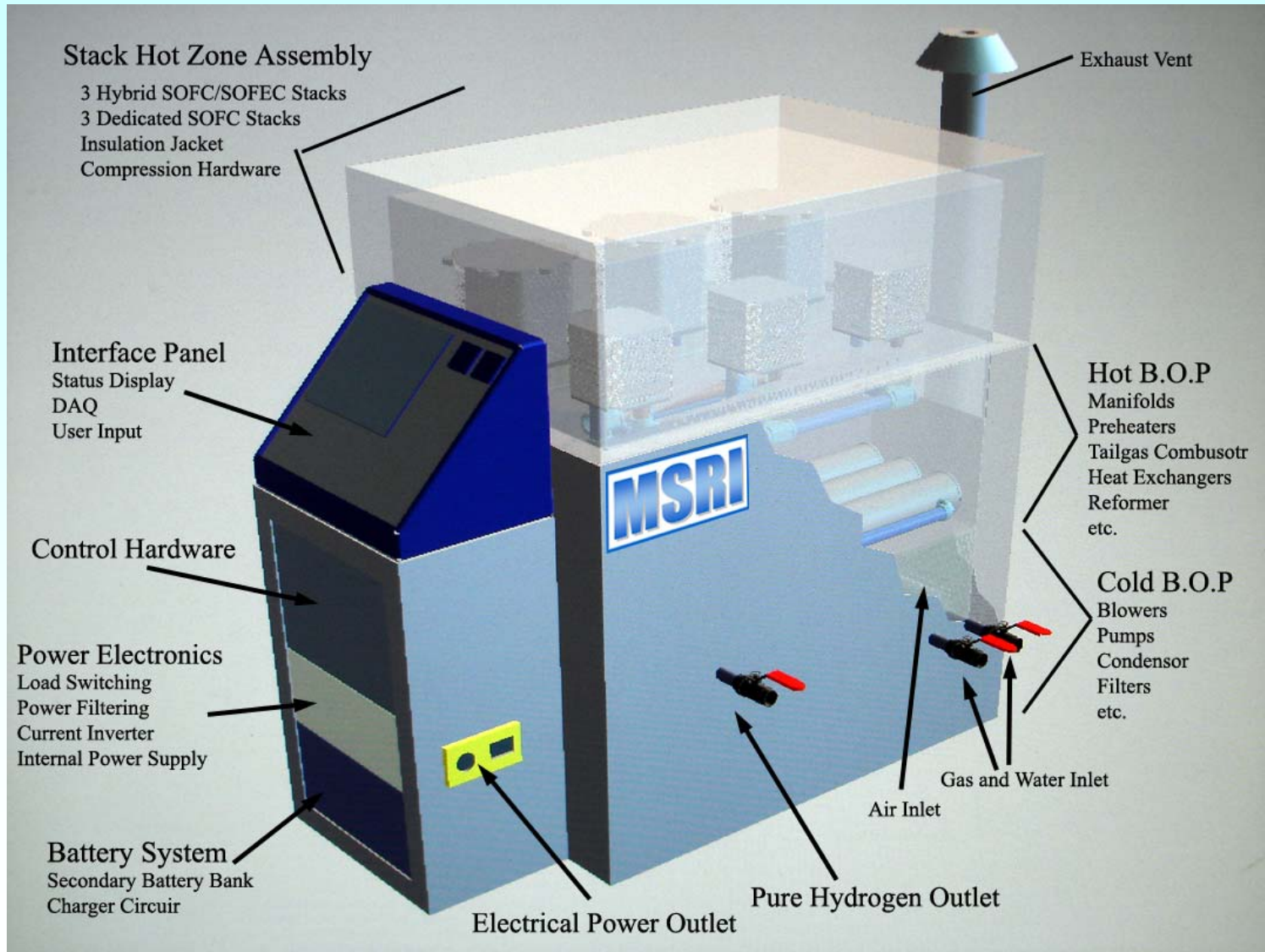
Temperature @ 780°C, AN: Syngas; CA1: air; CA2: H<sub>2</sub>O; U<sub>f</sub>/U<sub>air</sub>/U<sub>steam</sub>=50/60/40 --> 50/50/40



**Power & H<sub>2</sub> cogeneration**

- 13-SOFC in power generation
- 20-SOFEC in H<sub>2</sub> production

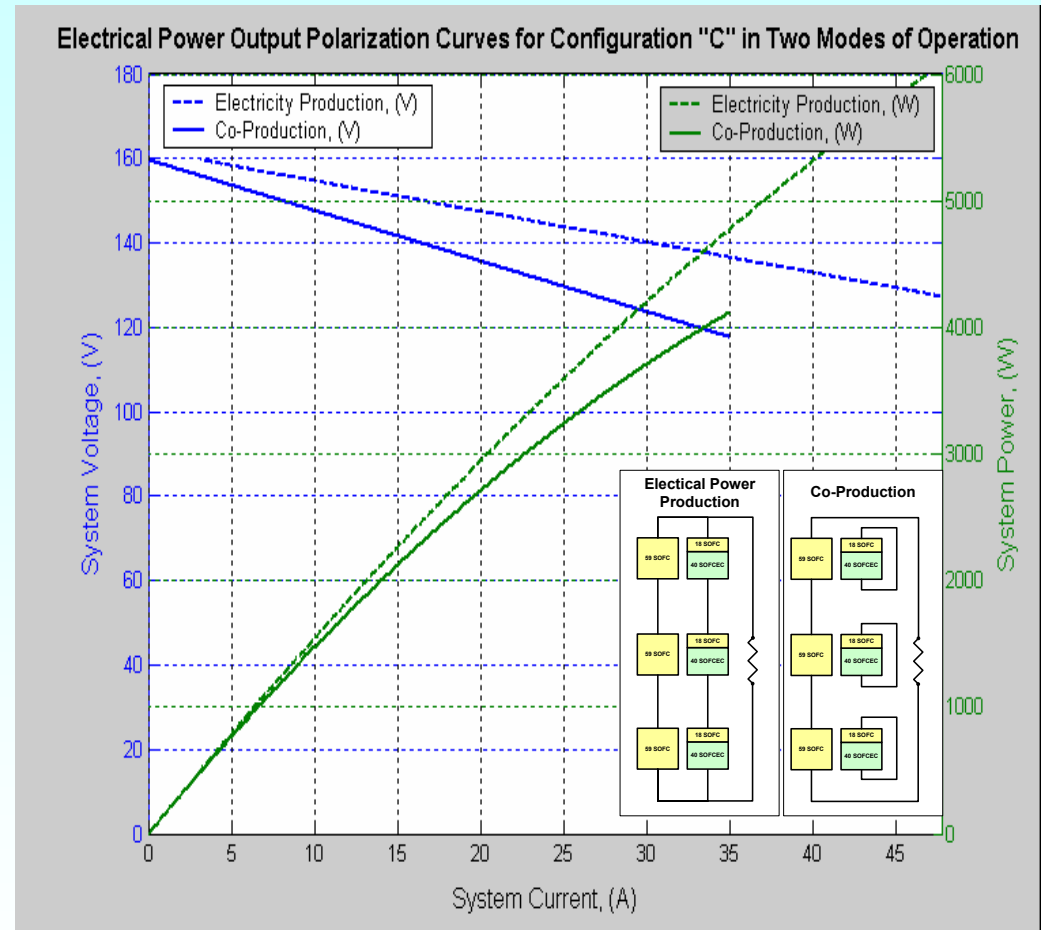
# 5 kW Hybrid System Design



# Optimization of System Configuration

## 2 Modes of Operation:

- Co-generation
  - ❖ Hybrid stacks self driven, dedicated SOFC stacks in series
  - ❖ Electrical load following independent of hydrogen production rate
- Electrical Power Production
  - ❖ Series/parallel configuration of hybrid and dedicated stacks
  - ❖ Allows for peak power output with dedicated and hybrid stacks each at optimal current density



# Future Work (FY07 – FY08)

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- Materials Development

- Cathode optimization and long-term stability investigation in reducing & oxidizing atmospheres
- G#50 in-stack implementation, long-term & thermal cycling tests
- Investigation of fracture mechanism and modeling residual stresses
- Continuous of investigating effects of residual/chemical/applied stresses on the mechanical integrity of the SOFC-SOFEC

- SOFC-SOFEC Hybrid Stack Optimization

- Evaluate new interconnect design with enhanced thermal/fluid management
- Evaluate stack design integrated with heat exchanger

- 5 kW Hybrid System Design and Evaluation

- BOP components design and fabrication
- 5 kW hybrid system assembly and evaluation
- Implementation of hydrogen production cost analysis using H2A model

# Project Summary

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Relevance:	Investigate an alternative approach to provide low-cost and highly efficient distributed co-production of 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:	Developed/characterized perovskite-type oxides (p and n-type) cathode materials over a wide range of oxygen activities; studied the influences of combined stresses ( residual, chemical, thermal and applied stresses) for understanding and improving SOFC-SOFEC structures in service conditions; developed hermetic seal materials; characterized the selected materials in SOFC/SOEC/SOFEC modes; proof-of-concept kW hybrid stack co-generating hydrogen and electricity; designed a 5 kW hybrid system
Proposed Future Research:	Continue developing electrodes and sealing materials; implement mechanical/thermal analyses of anode supports; optimize the 5 kW hybrid system; fabricate and evaluate BOP components; implement system experimental investigation and cost analyses