The Solid State Energy Conversion Alliance

SECA Core Technology Program

Third Annual SECA Workshop

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SECA Program Coordinator

www.netl.doe.gov/scng

SECA Core Technology Program Solicitation

- **Fuel Processing**
  - Contaminant Resistant Anodes and Reforming Catalysts for Intermediate Temperature Solid Oxide Fuel Cell Systems
  - High Temperature Sulfur Removal
- **Manufacturing**
  - Low Cost Production of Precursor Materials
- **Controls and Diagnostics**
  - Sensors
  - Active Sealing Systems
- **Power Electronics**
  - Interaction Between Fuel Cell, Power Conditioning Systems and Application Loads
  - DC-to-DC Converters for Solid-Oxide Fuel Cells
- **Modeling & Simulation**
  - Fuel Cell Failure Analysis
  - Manufacturing Models
- **Materials**
  - Cathodes
  - Interconnects
  - Innovative Sealing Concepts

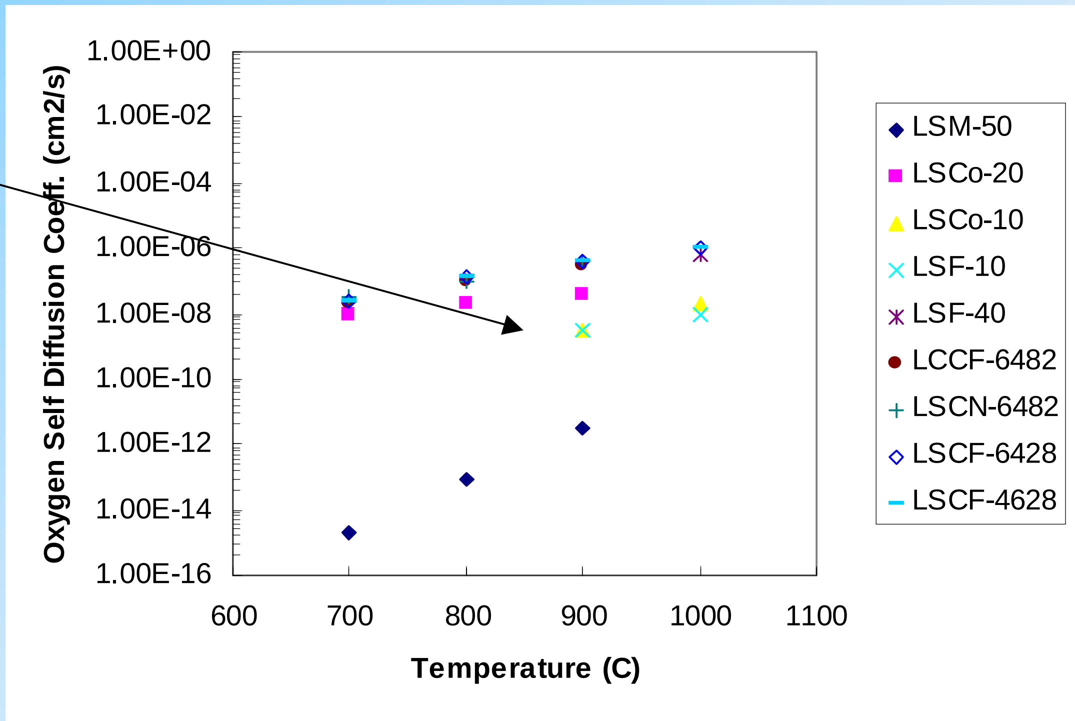
SECA Core Technology Program Activities at PNNL

Core Technology - Areas of Emphasis

- **SOFC component development**
  - Anode Supported Cell Fabrication & Performance Optimization
    - Tape casting process
    - Anode & cathode materials
    - Interconnects
    - Seals
- **SOFC modeling**
    - Modeling of cells and stacks – transient and steady state
    - System modeling

Advantages of LSF Cathode

High oxygen diffusion coefficient (relative to LSM) increases "effective" TPB at the cathode / electrolyte interface, thereby reducing the cathode overpotential



Other advantages of LSF as cathode material:

High oxygen surface exchange coefficient; TEC is compatible with other cell components; high electronic conductivity

Data from PNNL (LSCF compositions) and others (CRC Handbook of Solid State Electrochemistry p. 505)

Temperature Dependence of Anode-supported Cell Performance

<u>Cell:</u>

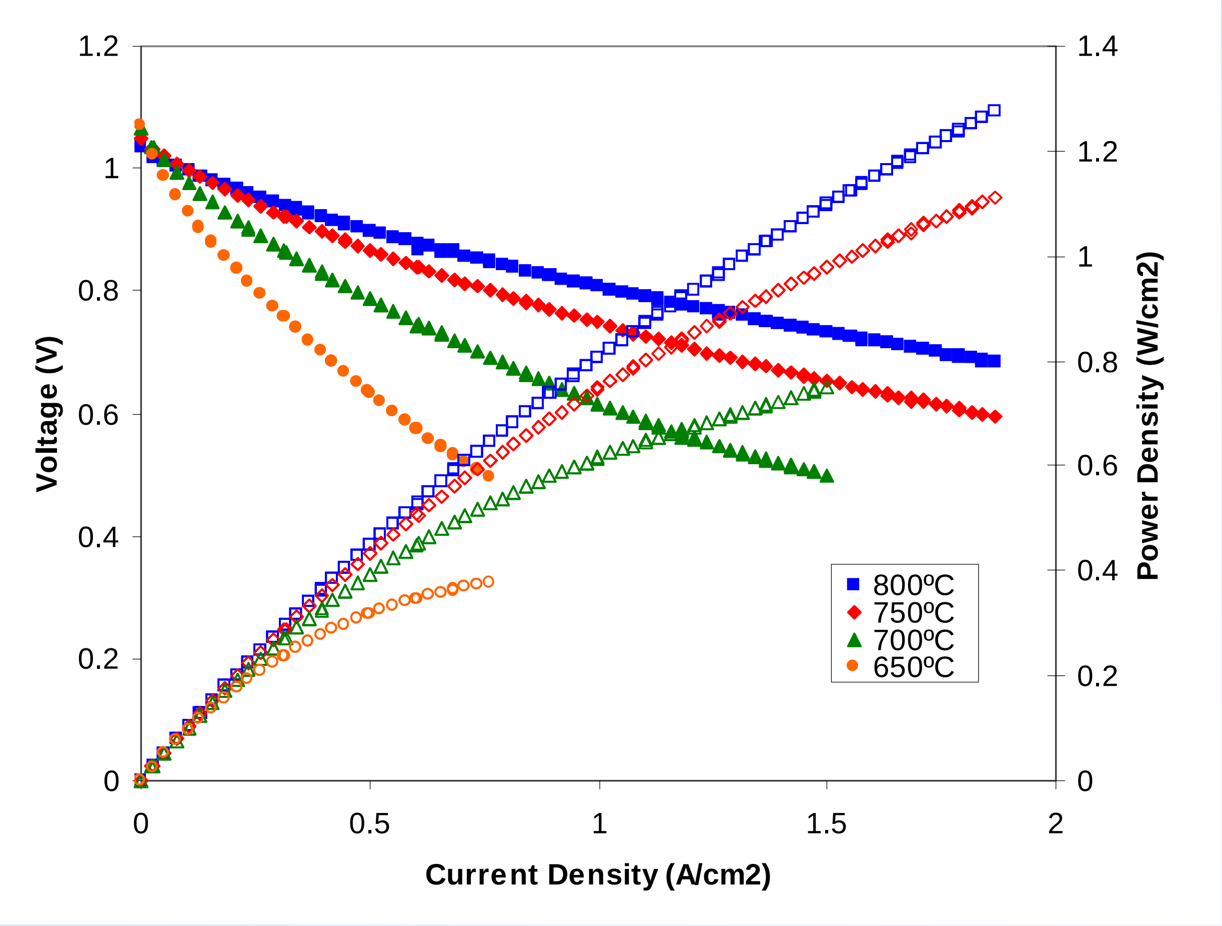
LSF Cathode / SDC Interlayer / YSZ Electrolyte / Ni-YSZ anode

<u>Fuel:</u>

97% H_2 / 3% H_2O (Low Fuel Utilization)

<u>Oxidant:</u>

Air



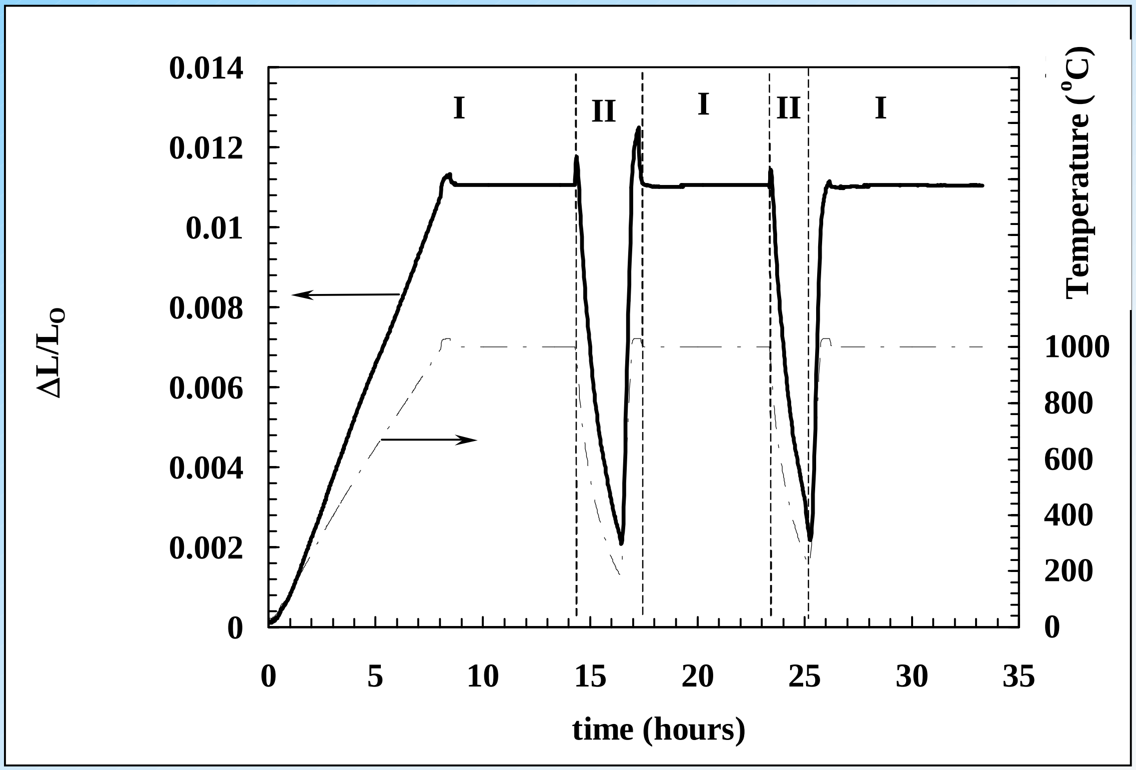
Advanced Red/Ox Tolerant Anode

Doped $SrTiO_3$ compositions show promise as red-ox tolerant anode materials

Simulated Thermal Cycles-

I: Exposure to reducing environment at 1000ºC (corresponding to SOFC anode environment during operation)

II: Exposure to air during thermal cycling (corresponding to conditions an unprotected anode would experience during sytem startup and shutdown)

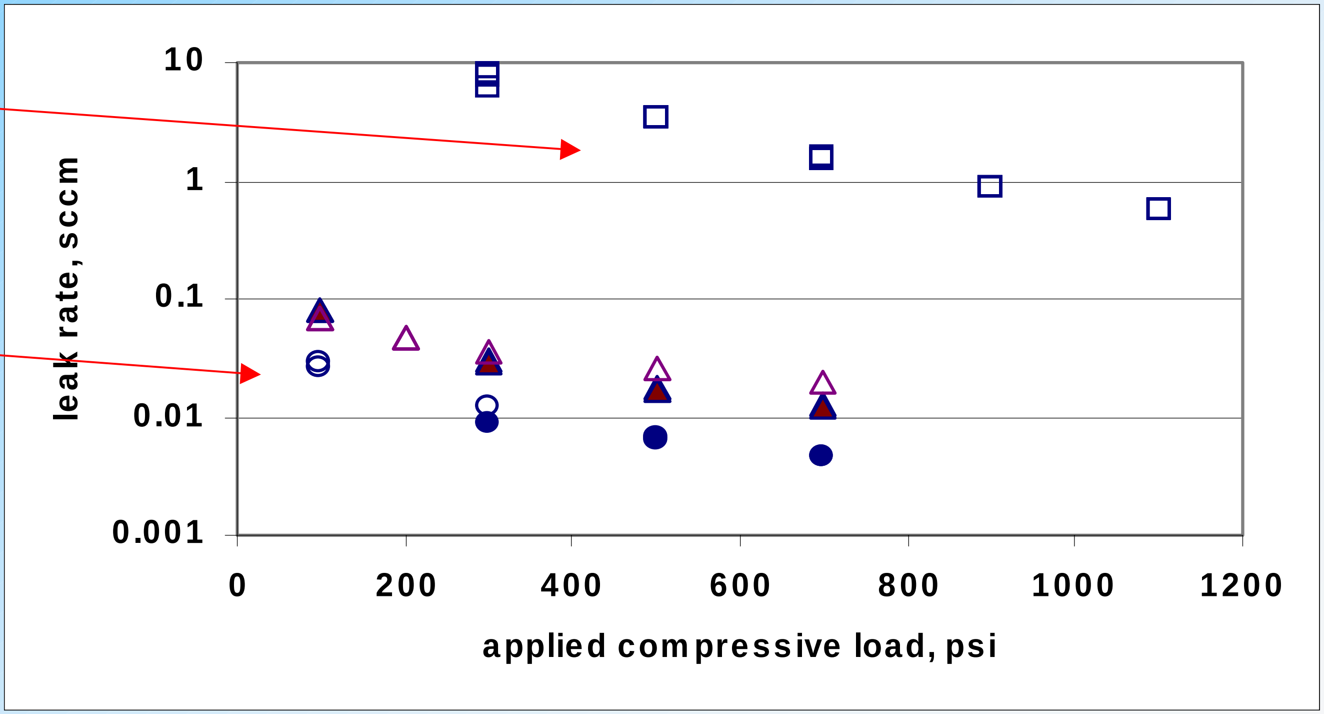


"Advanced" compressive seal concept

In coupon testing, mica gaskets exhibited relatively high leak rates under moderate compressive loads. In recent testing, advanced compressive seals exhibited leak rates approximately 2 orders of magnitude lower relative to simple mica gasket. Test conditions: 800ºC in air

Simple Mica Seal

"Advanced" Seals



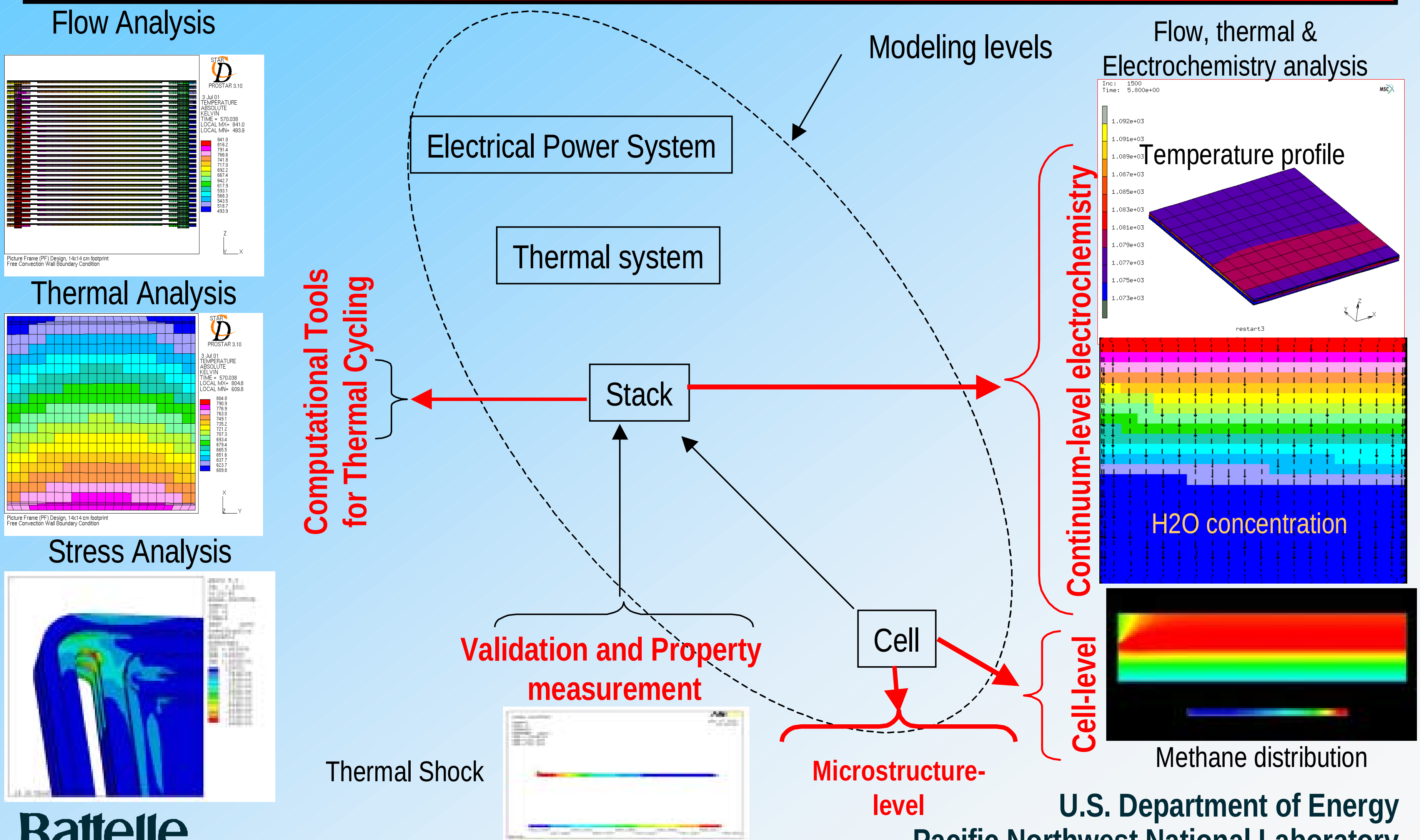
Metallic Interconnect Development

3-step Screening & Testing Study to Evaluate Candidate Alloys

- Goals: Identify candidate alloys for SOFC interconnect; Develop understanding of corrosion processes and mechanisms

- Step 1 – *completed* – compiled metallurgical database; reduced candidate list from ~300 to ~15 alloys
- Step 2 – *in progress* – screening tests
  - chemical – stability in fuel and oxidant environment, compatibility and bonding strength with seal materials
  - electrical – effects of environment on scale resistance
  - mechanical – effects of environment on mechanical properties
  - fabrication – formability and joinability testing

Overview of Modeling and Simulations



Accomplishments:

- Low cost tape casting process for anode & electrolyte fabrication
- Single step sintering process for anode-supported electrolyte co-sintering
- Non-nickel base anode for oxygen tolerance
- Sr doped lanthanum ferrite cathode electrode for superior performance
- Engineering performance models for cell & stack operations
- Data base compilation for candidate metallic current collector

NETL SOFC Model Capabilities

- **Three-dimensional, steady-state, with fluid dynamics, heat transfer, species transport, chemical reaction, porous media flow**
  - Water-gas shift reaction
  - Species diffusion in flow channels and porous media
- **Electrochemical SOFC submodel**
  - H_2 and CO Electrochemistry

$$3H_2 + 3O^{2-} \Rightarrow 3H_2O + 6e^-$$

$$CO + O^{2-} \Rightarrow CO_2 + 2e^-$$

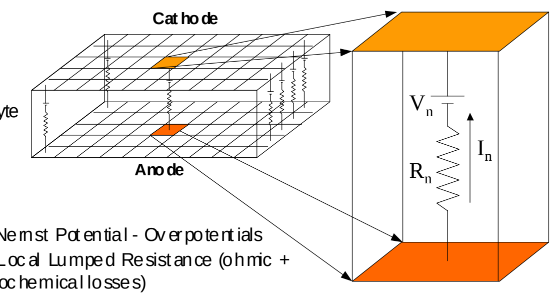
$$2O_2 + 8e^- \Rightarrow 4O^{2-}$$

$$N = E^o + \frac{R_u T}{8F} \ln\left(\frac{P_{H_2}^3 P_{CO} P_{O_2}^2}{P_{H_2O}^3 P_{CO_2} P_{tot}^2} \right)$$

- **Electrical field submodel to calculate electrical potential field in all conducting regions including electrodes, current collectors, interconnects**
  - Ohmic heat generation
  - Current Flow

$$\nabla \cdot \underline{i} = \rho_i$$

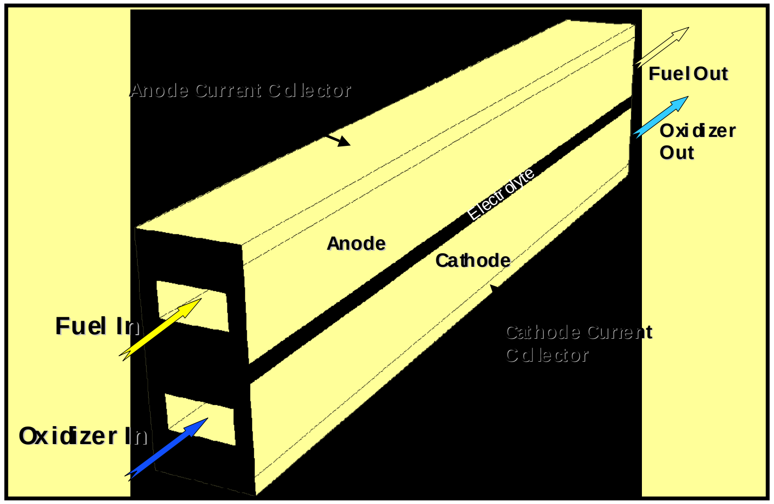
$$\underline{i} = -\sigma \nabla \phi$$

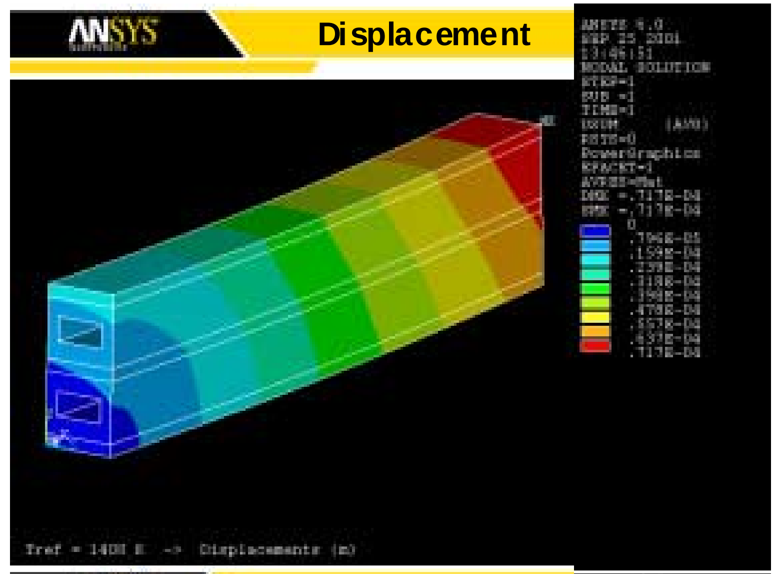


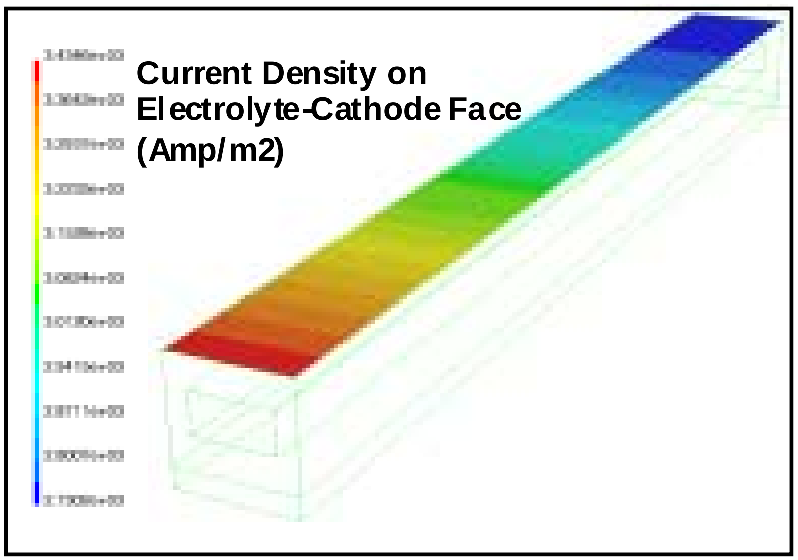
V_n = Nernst Potential - Overpotentials
R_n = Local Lumped Resistance (ohmic + electrochemical losses)

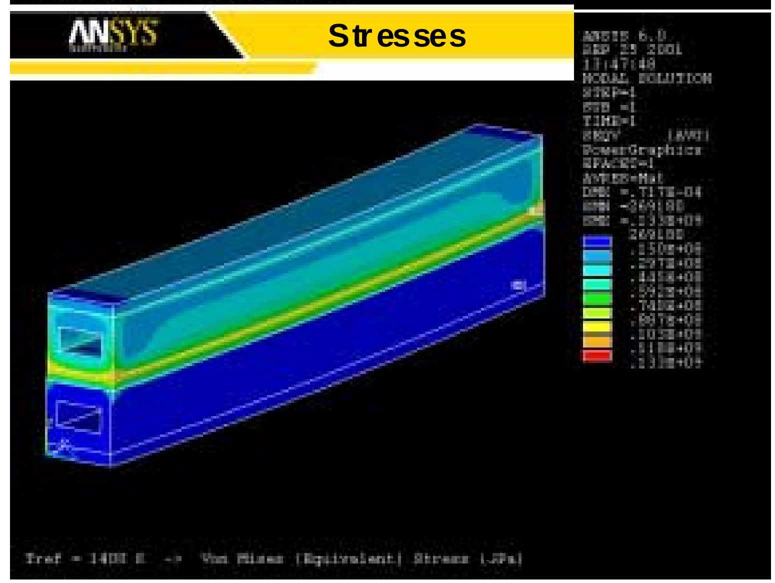
- **Parallel Code for PC cluster computing**
- **Model temperature output coupled to ANSYS FEA code for stress analysis**

Example: Simple Co-Flow Channel



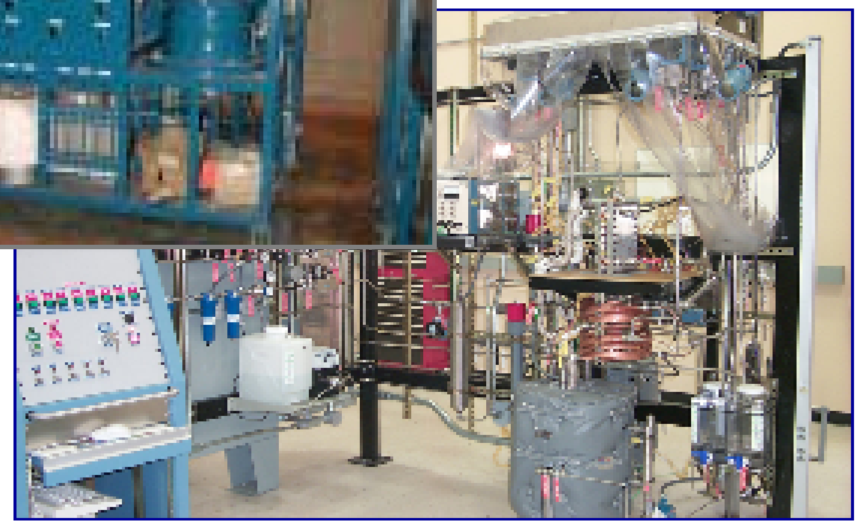






Planned Capabilities and Validation

- **Extend to Stacks**
- **Internal Reforming**
- **Include Contact Resistance**
  - Current collector-electrode
  - Electrode-electrolyte
  - Current collector-interconnect



- **Complete Model Validation**
  - Data from open literature
  - Data from NETL testing facilities
  - Data from SECA partners

- **Working with SECA partners in Model Validation and Application**
  - Delphi
  - Siemens-Westinghouse

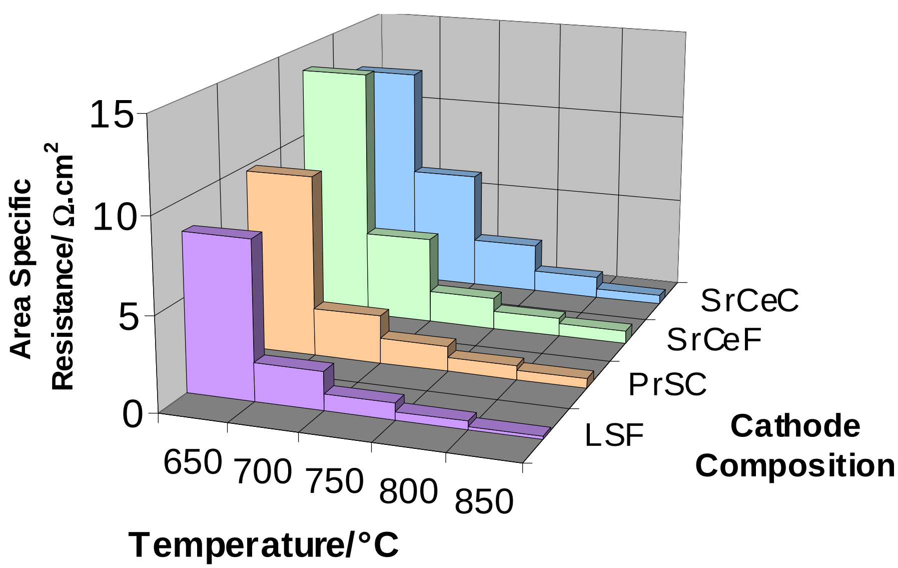
Solid Oxide Fuel Cell Materials Research at Argonne National Laboratory

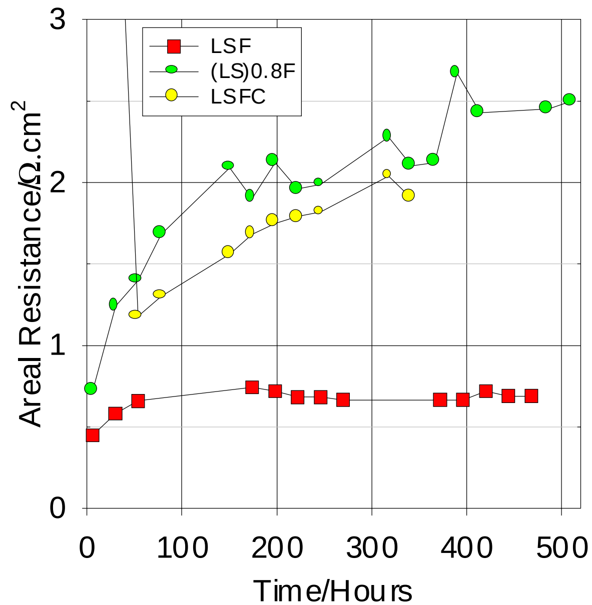
Drivers for the research

- A major approach to lowering fuel cell and balance-of-plant costs is to reduce SOFC operating temperatures to $\leq 800^{o}C$. At the lower temperatures, however,
  - Conventional LSM cathode performance is inadequate
    - Need to develop perovskite and other cathode materials with high electrochemical activity, low resistivity at $\leq 800^{o}C$
  - Sulfur-poisoning of Ni anode is exacerbated
    - Need anode materials tolerant to 1-100 ppm or more of H_2S
  - Metallic interconnect (bipolar) plates become feasible
    - Need new alloys or coatings as presently available metals and alloys degrade rapidly in SOFC environments

Single-phase cathode materials

- Accomplishments
  - Identified Sr-doped lanthanum ferrates as the most promising candidate cathode materials
  - Verified stable performance to 500 h

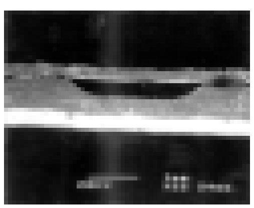




Metallic Interconnect Materials

Approach

- Alloys similar to ferritic stainless steels
  - reduce Cr, other elements that can degrade fuel cell performance
  - additives to improve properties and protective scale
- Materials of graded composition to impart optimum chemical stability at each surface
- Novel processing technique can yield almost any desired shape
  - flat, corrugated, textured, functionally graded
  - can incorporate flow fields, internal manifolds



Formed Flow Field in Dense Material

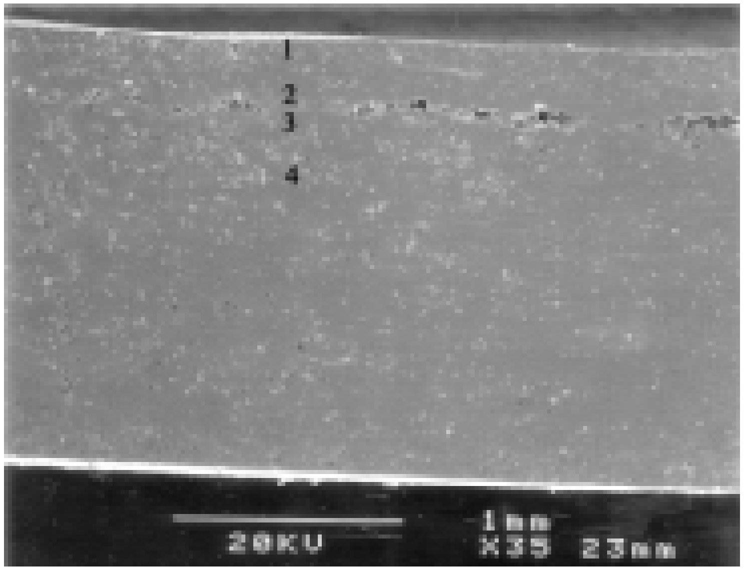
Formed Flow Field with Porous Layers

Macroporous Flow Field

Metallic Interconnect Materials

Multi-layer plates are easily formed

- Compositionally graded specimens can be fabricated
- Samples show excellent bonding
- After 400 h at 800ºC, there was no observed elemental diffusion between layers



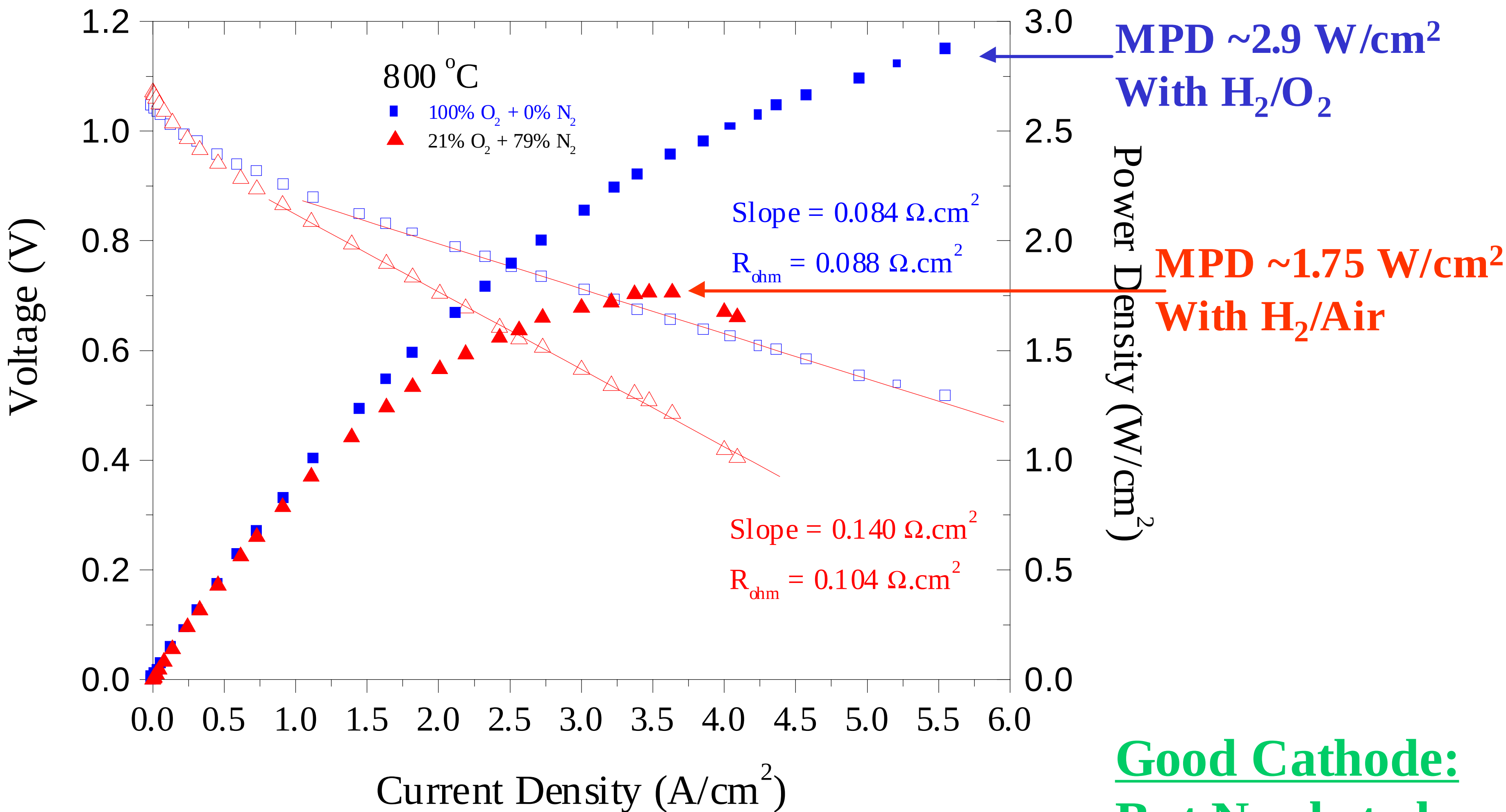
SEM Micrograph of compositionally-graded sample

- 10-Layer specimen
  Two surface layers: Fe-Cr-La-Y-Sr alloy
  Bulk: SS Type 434
- Points 1,2: ~1.5 - 2.0 wt% La
- Points 3,4: no measurable La

Summary
Future directions

- Micro-engineer the cathode-electrolyte interface to further improve cathode performance
- Evaluate anode materials with 0-100 ppm H_2S in fuel gas
- Characterize oxide scale on metallic bipolar plates for growth rates and electrical conductivity
- Test developed materials in full cell and short stack configurations

Effect of Oxidant Composition on a High Performance, Anode-Supported Cell



Good Cathode: But Needs to be Better

Funding: DOE/NETL

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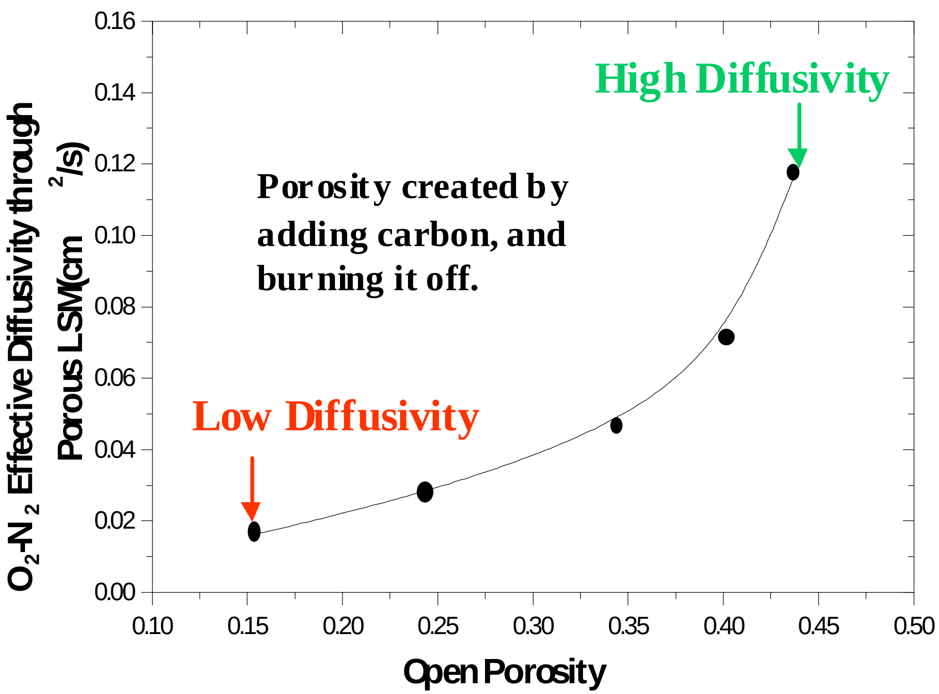
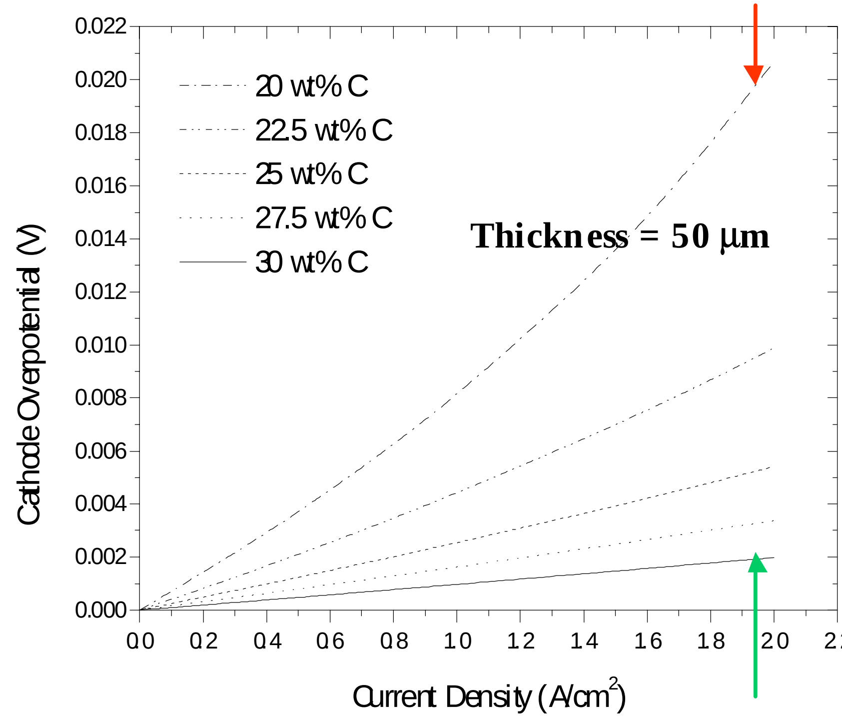
O_2-N_2 Effective Diffusivity through Porous LSM and Cathodic Concentration Polarization

Experimentally Measured Effective Diffusivities



Calculated Cathodic Concentration Polarization

Low Diffusivity High Polarization



High Diffusivity Low Polarization

Cathode Concentration Polarization is Small When Porosity is High

Funding: DOE/NETL

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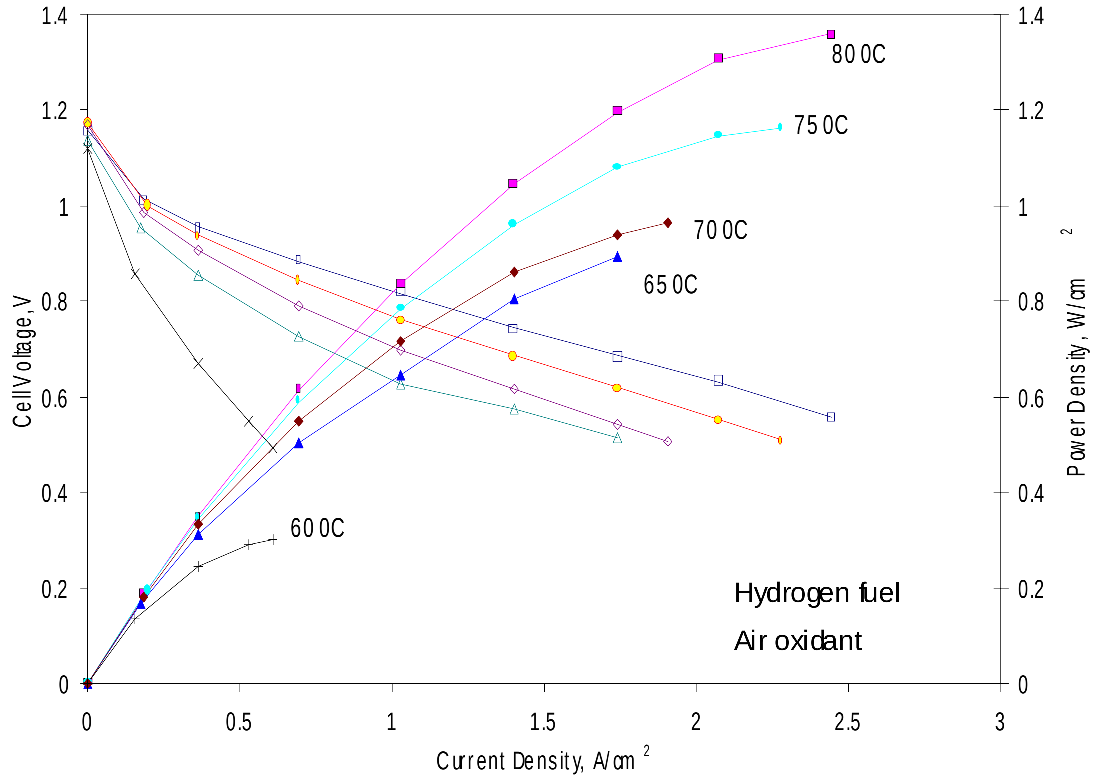
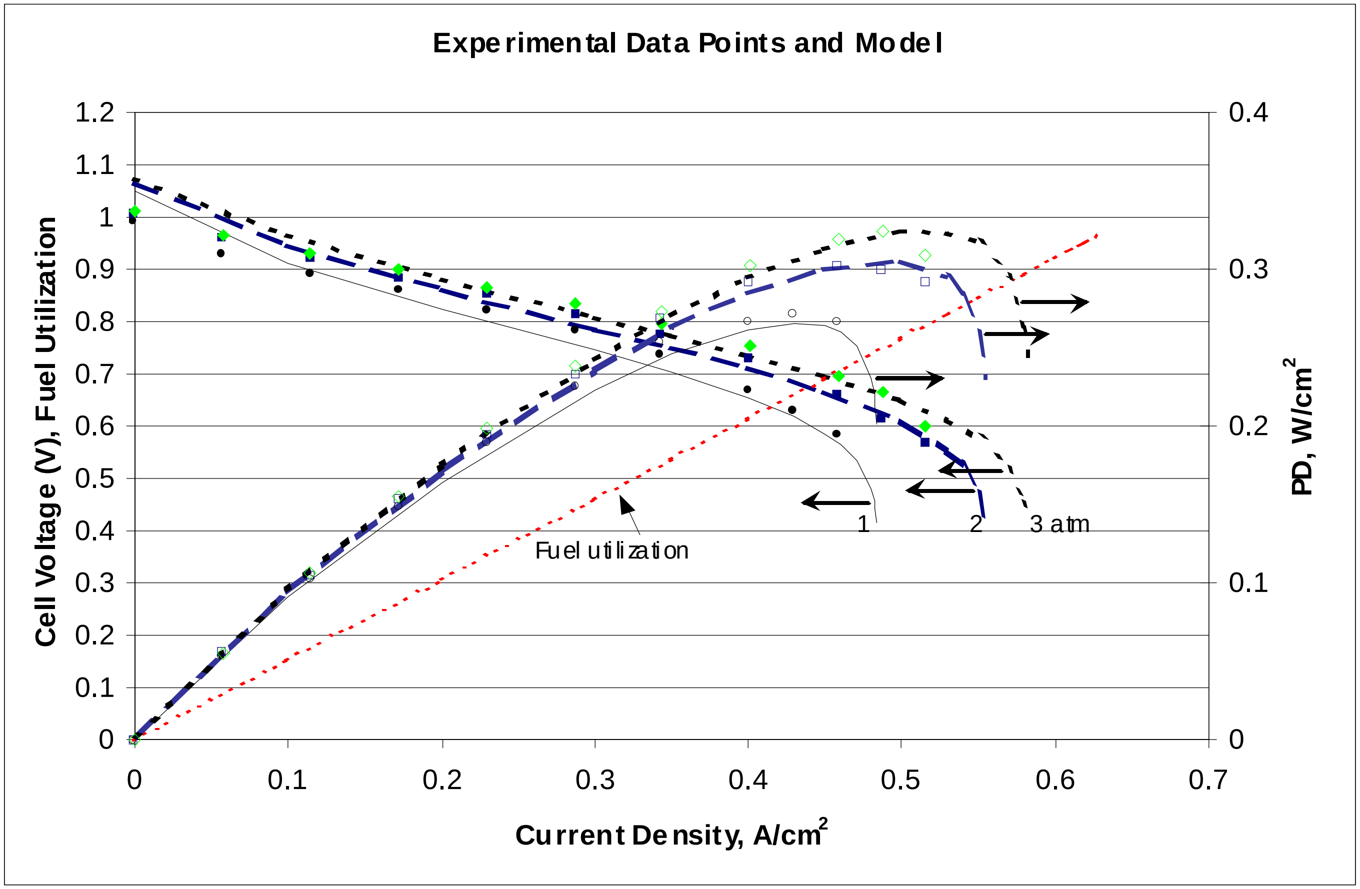
SOFC Cell Performance at Reduced Temperatures



• **High power densities (e.g., 0.9 W/cm² at 650°C) achieved at reduced temperatures (<800°C) with anode-supported thin-electrolyte cells**

Pressurized Operation of Planar SOFCs

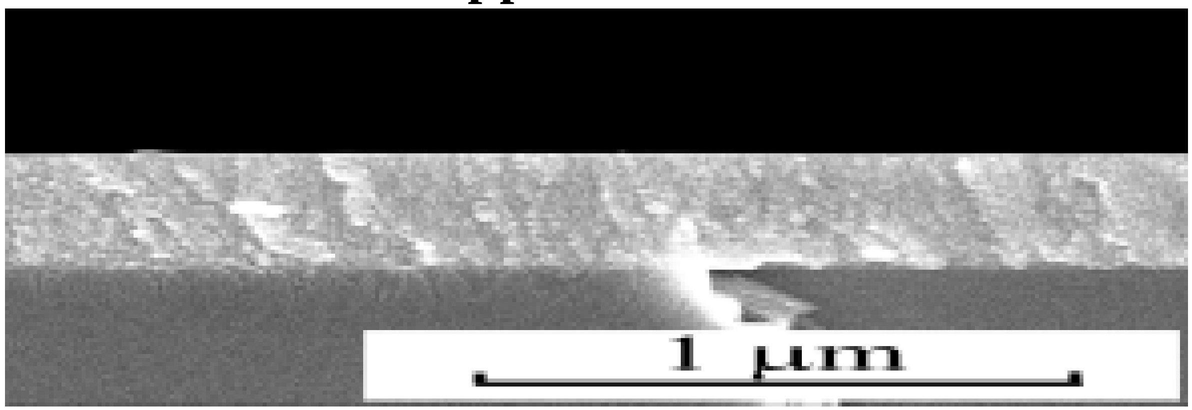


• **First pressurized SOFC with planar anode-supported thin-electrolyte cells**

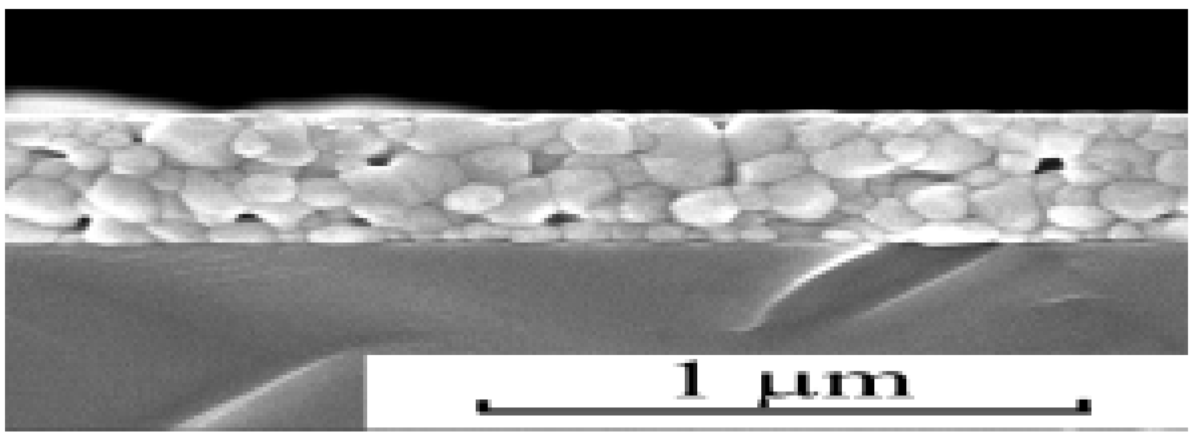
Honeywell

EMARC
ELECTRONIC MATERIALS APPLIED RESEARCH CENTER

YSZ film deposited from polymeric precursor on sapphire substrate



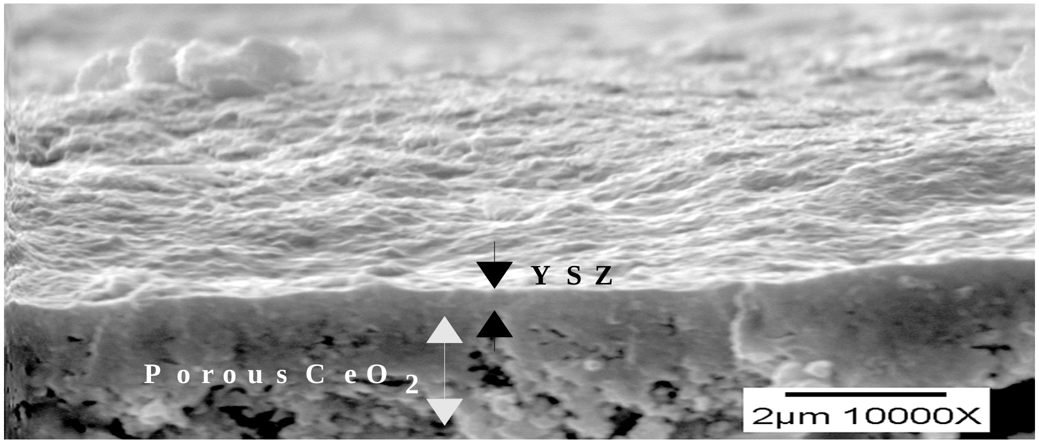
A) Annealed at 400°C for 4 hours



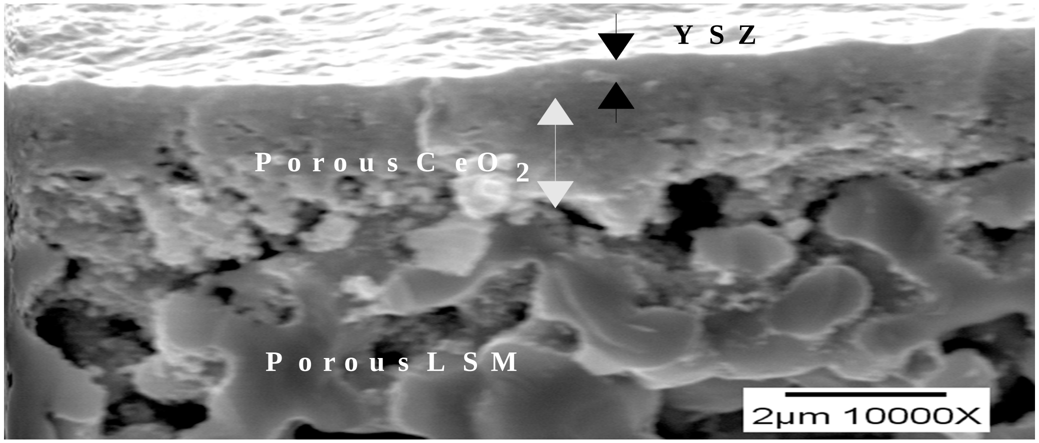
B) Annealed at 1000°C for 4 hours

UMROLLA

Cross section - 1

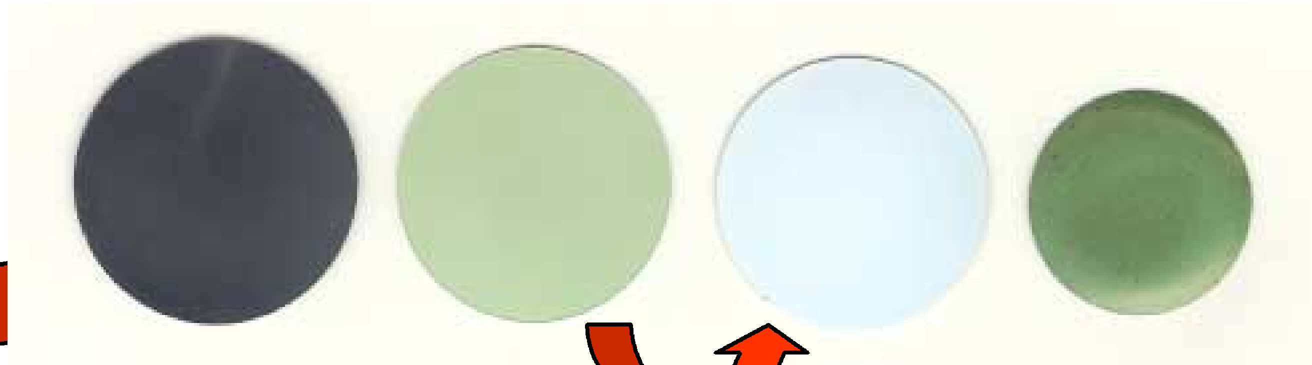


Cross section - 2



LBNL Developed Colloidal Deposition Technique for SOFCs

NiO/YSZ substrate (pressed)	NiO/YSZ fired at 950 °C	NiO/YSZ substrate with green YSZ film	NiO/YSZ-YSZ bilayer fired at 1400 °C



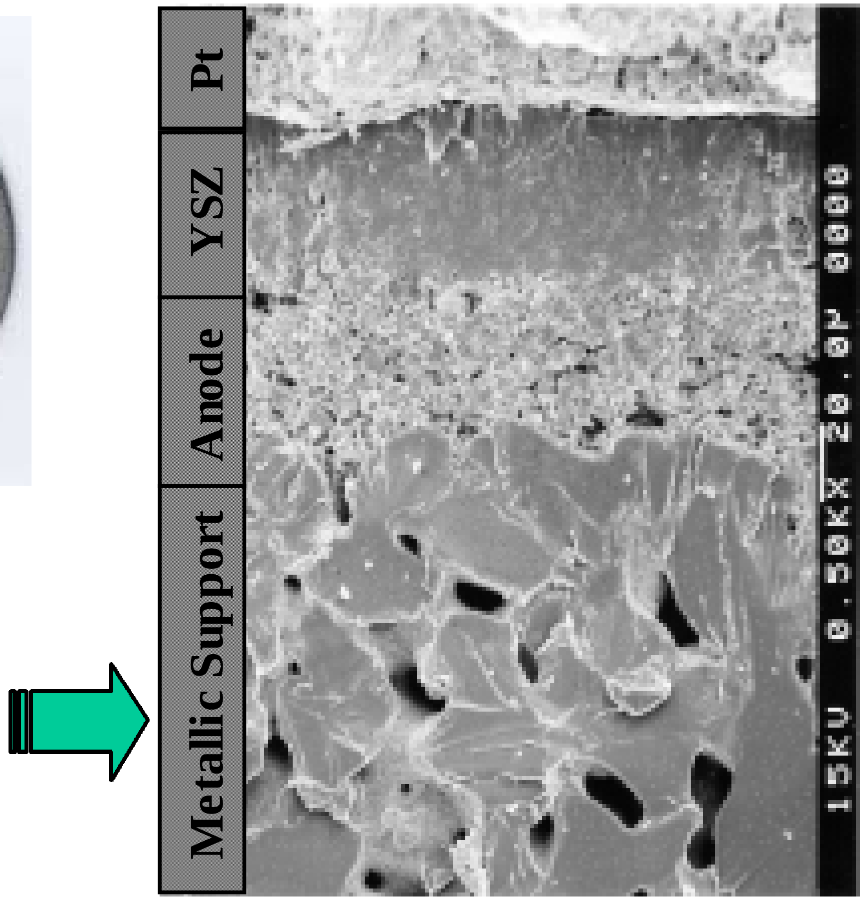
Dip-coat, aerosol spray, EPD…

- Geometry Independent
- Low Cost
- Scaleable

Development of Alloy Supported Thin-film SOFC Structures to Reduce Stack Cost and Improve Reliability

Top view of a YSZ/Ni-YSZ/FeCr alloy SOFC bilayer (looking through transparent YSZ film).

Bottom view of a YSZ/Ni-YSZ/FeCr alloy SOFC bilayer (at porous FeCr electrode)



ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Objectives and Tasks

Objectives:

- Develop technology leading to reforming of diesel fuel for APU applications.
- Understand parameters that affect fuel processor lifetime and durability.
  - Examine fuel components, impurities and additives
  - Quantify fuel effects on fuel processor performance
  - Understand the parameters that affect fuel processor lifetime and durability
    - Catalyst durability
    - Carbon formation and catalyst durability

Tasks:

- Carbon Formation Measurement of Diesel Fuel(s)
  - Equilibrium and component modeling
  - Experimental carbon formation measurement
- Fuel Mixing
  - Vaporization / Fuel atomization
  - Direct liquid injection
- 'Waterless' Partial Oxidation of Diesel Fuel
  - Start-up
  - SOFC anode recycle

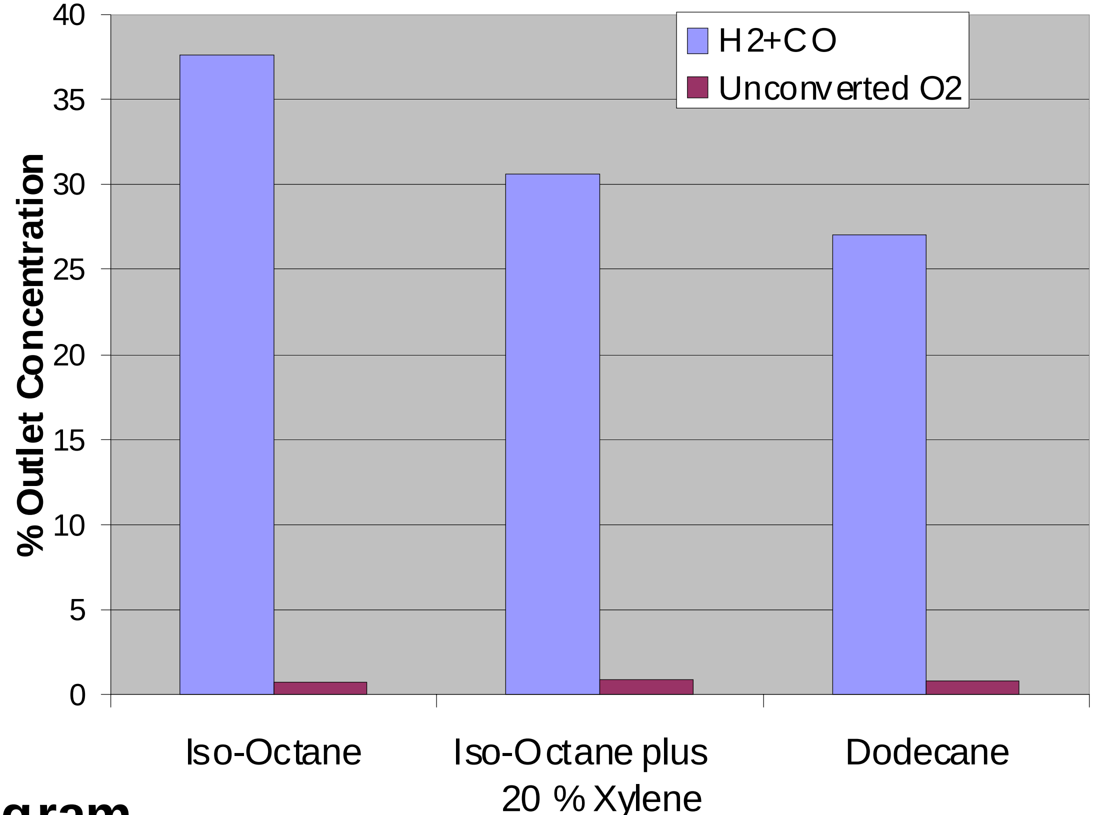
Partial Oxidation Stage Outlet Concentrations
(for similar oxygen conversion)

Higher Temperatures (O/C ratio's) are required for long chained hydrocarbon conversion for similar residence times – leads to H2 dilution

Longer residence times required for similar conversion (same Temperature / O/C)

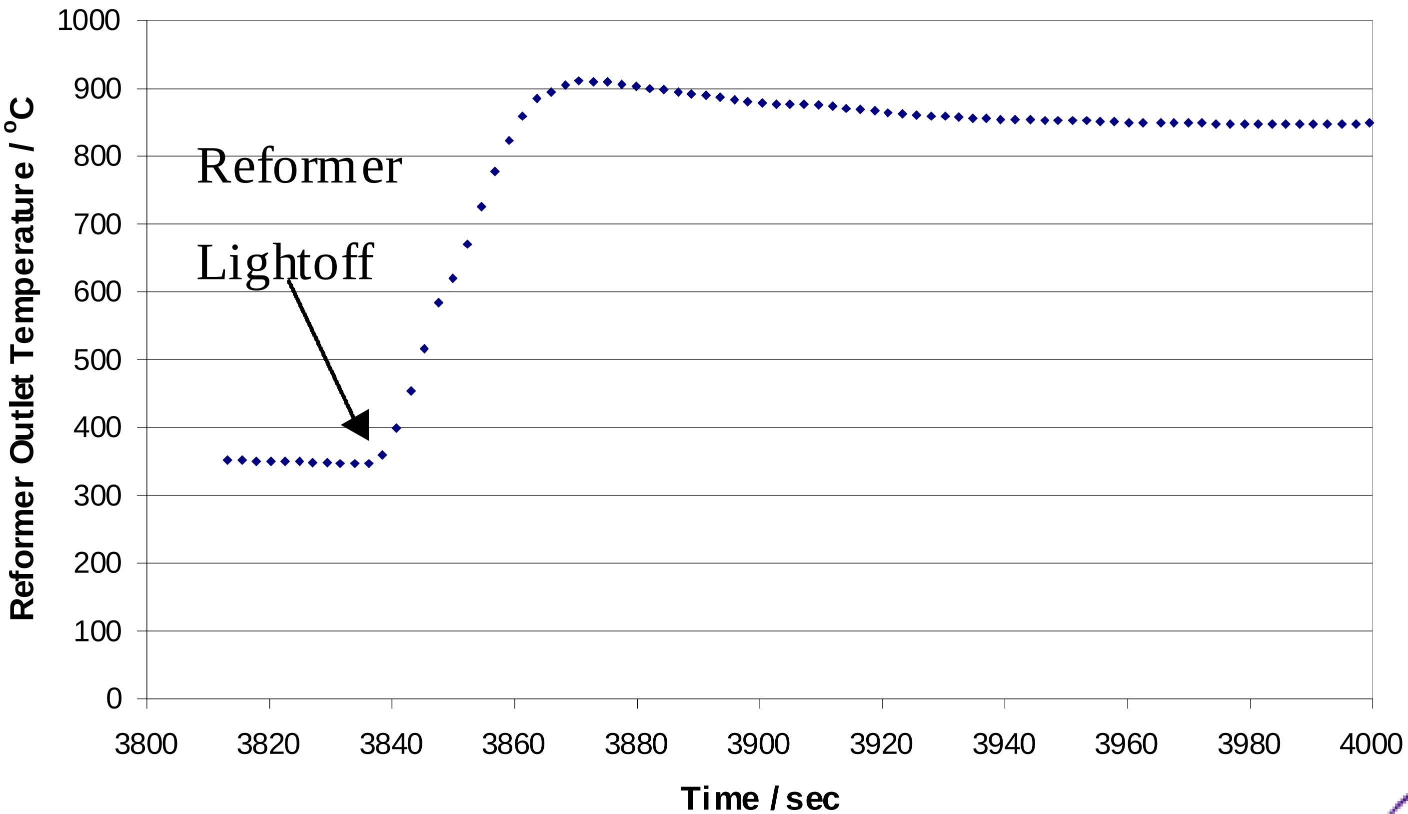
residence time (iso-octane ~ 10 msec)

residence time (dodecane ~ 45 msec)



Diesel POx/Reforming Light-off

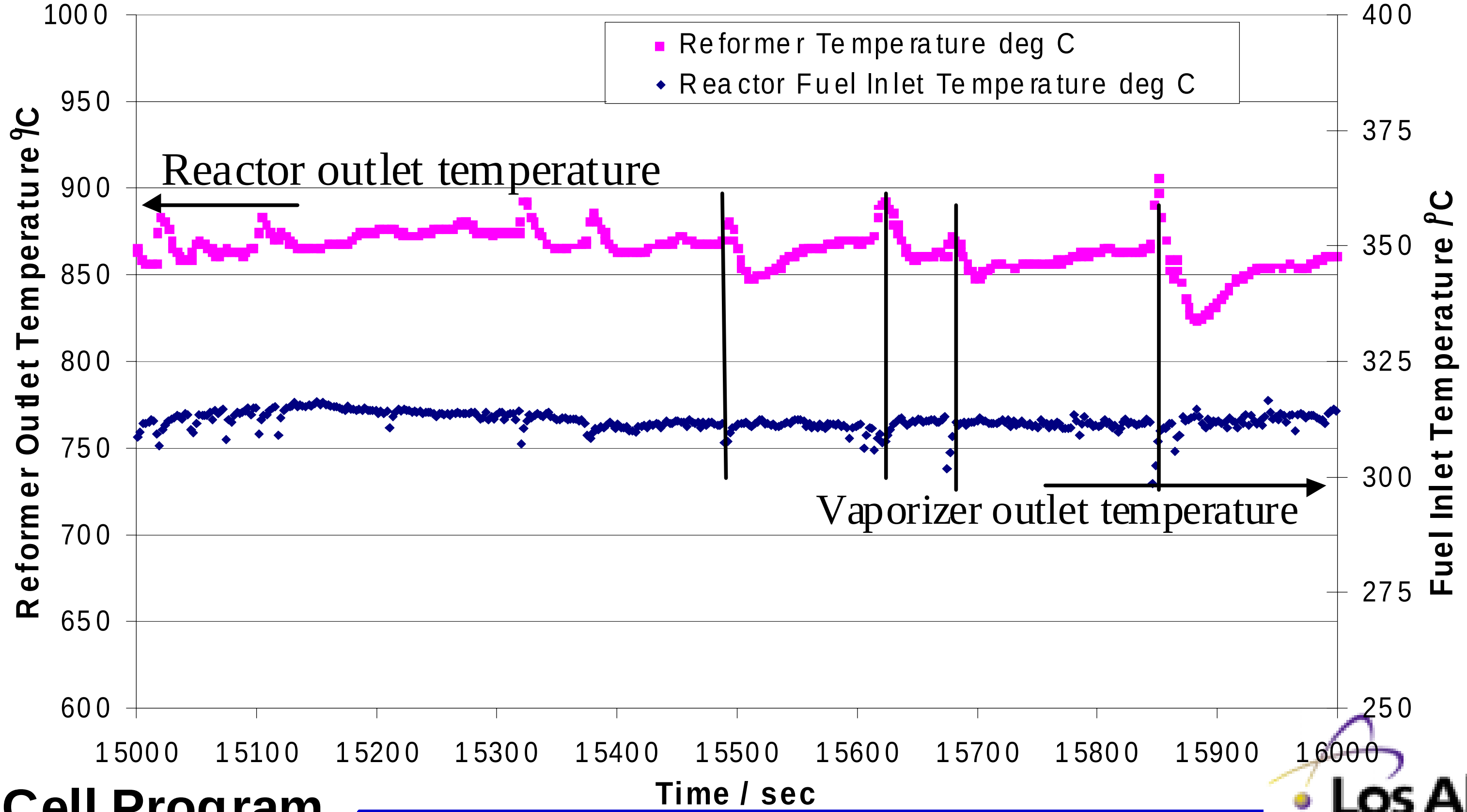
Reactor start-up with kerosene / no water
water availability during initial operation



Fuel / Water co-vaporization Issues

Co-vaporization of water and fuel in external vaporizer uses water as carbon formation suppressant / fuel carrier

Co-vaporization produces periodic ‘distillation’ and reactor temperature exotherms

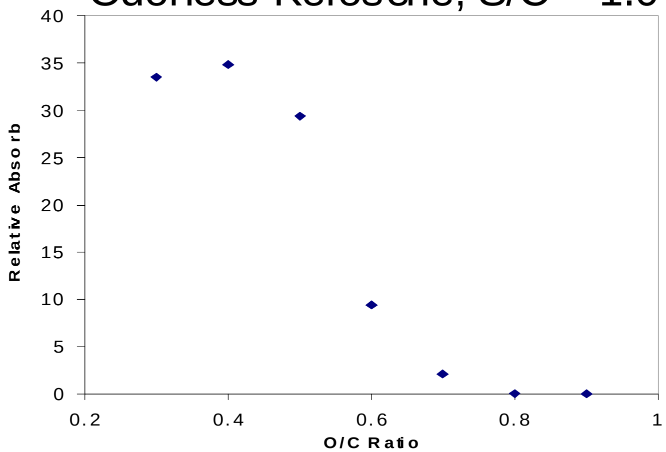


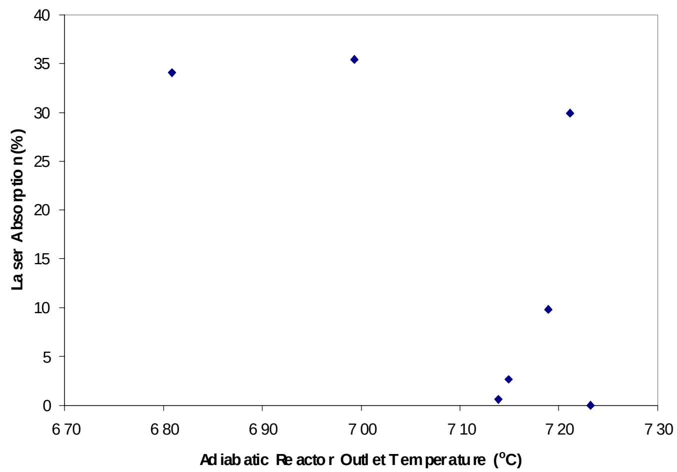
Technical Summary/Findings

- Catalytic oxidation / reforming
  - Diesel Fuel Components (Dodecane)
    - Long chained hydrocarbons require higher residence time for conversion
    - aromatics slow and inhibit overall reaction rate
- Pre-combustion
  - Diesel fuels much more likely for pre-combustion
    - Kerosene has higher pre-combustion tendencies than de-odorized kerosene
- Carbon Formation
  - Hysteresis observed after on-set of carbon formation
  - Greater carbon formation with aromatics

Technical Results:
Carbon formation measurements

Carbon formation monitoring with laser scattering
Odorless Kerosene; S/C = 1.0





Results

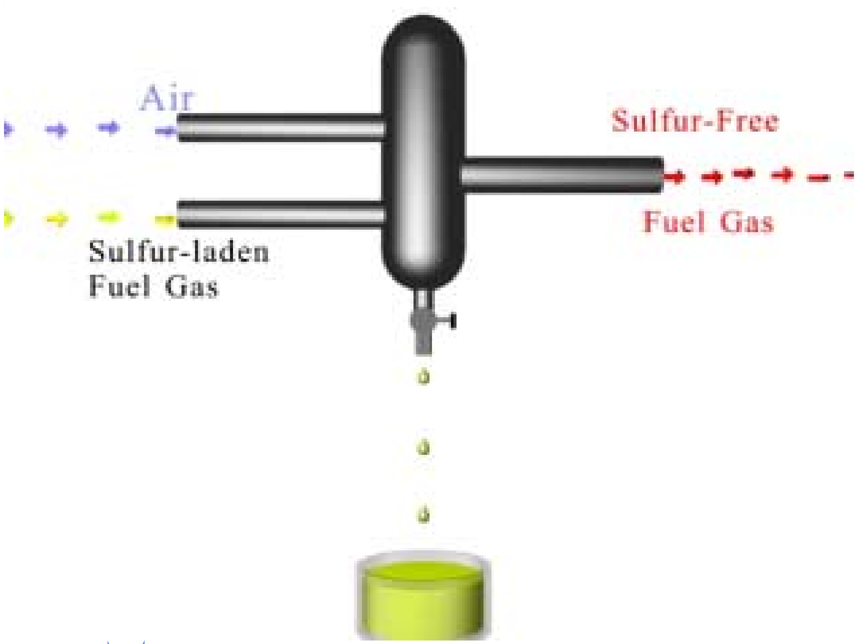
- Partial oxidation of
  - odorless kerosene
  - kerosene
  - dodecane
  - hexadecane
- Carbon formation monitoring by laser optics
- Carbon formation shown at low relative O/C ratios and temperature with kerosene (left)
- Demonstrated start-up with no water – carbon formation observed after ~ 100 hrs of operation

NETL Fuel Processing Team

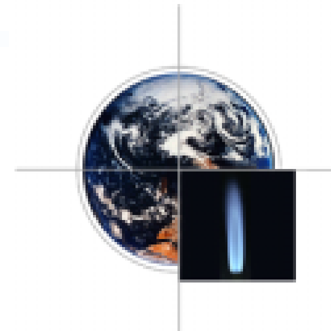
Fuel Desulfurization - "SCOHS"

- **Challenge:** *Limited sulfur tolerance in fuel cell reformer & stack*
- **NETL Research:** *Selective Catalytic Oxidation of H_2S*
- **Benefit:** *Fuel cells using coal gas, nat. gas, transportation fuels*

$$H_2S + 1/2\,(O_2 + 3.76\,N_2) = 1/n\,S_n + H_2O + 1.88\,N_2$$

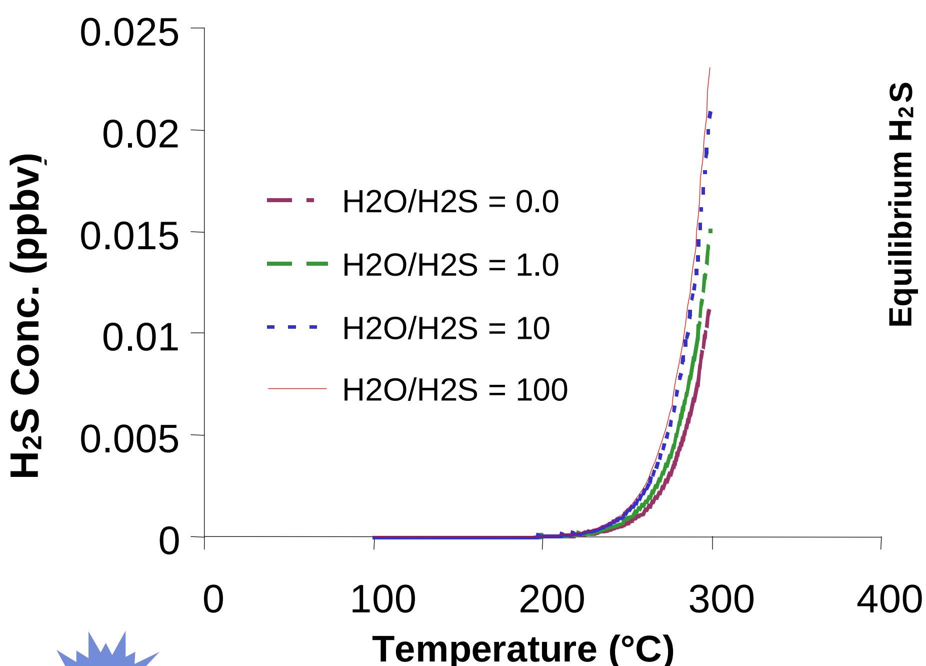


NETL Fuel Processing Team
Fuel Desulfurization - "SCOHS"

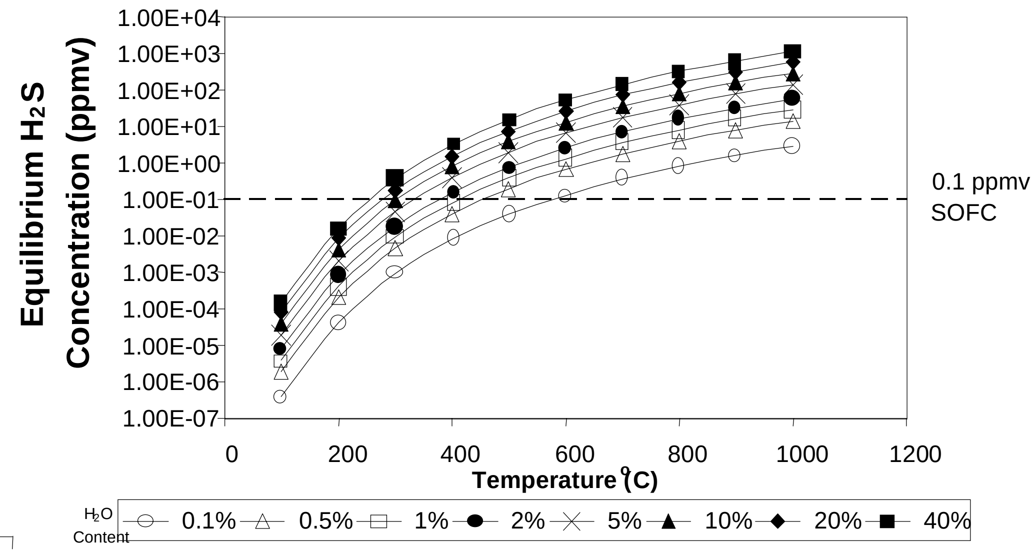


- **Removal Efficiency:** *SCOHS has part per trillion (ppt) thermodynamic sulfur removal efficiencies.*
- **Water Sensitivity:** *Unlike most metal oxide based systems, SCOHS is relatively insensitive to water content, which can be found in high concentrations in some reformate streams.*

SCOHS - Thermodynamic Removal Eff.

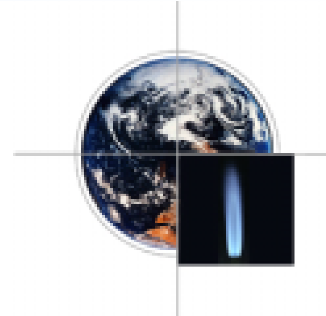


Zinc Titanate - Thermodynamic Removal Eff.

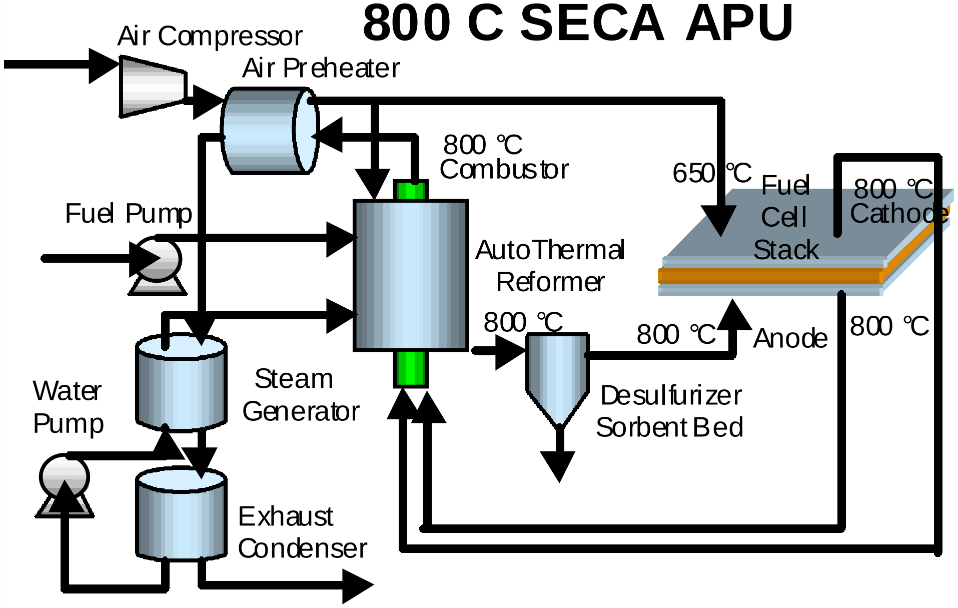


NETL Fuel Processing Team

Fuel Processor - "APU"



800 C SECA APU



ATR Oxygen-to-Carbon Ratio - 0.25
ATR Steam-to-Carbon Ratio - 0.7
Fuel Cell / Reformer Temperature - 800 C

Desulfurizer Temperature	**150/400 C**	**800 C**
Efficiency	**52.82**	**55.09**
Net Power Output	**5 kW**	**5 kW**
Mass Specific Fuel Consumption	**.75E-3 kgmol / kW hr**	**.722E-3 kgmol / kW hr**

Additional SECA Core Program Participants

Technology Management, Inc. Benson Lee	Demonstrate the operation of two SOFC modules as a single unit. Develop Screen Printing Manufacturing Technique
University of Florida Eric Wachsman	Develop Bi-Layer Ceria, Bismuth Oxide electrolyte for low temperature operation. Develop ionic conduction model.
Northwestern University/ Applied Thin Films Scott Barnett	Develop segmented in series SOFC design. Develop internally reforming anode as discussed in “Nature”
Georgia Institute of Technology/ Meilin Liu	Development of ultra-low (500 C) temperature SOFC materials. Development of in-situ FTIR emission spectroscopy for evaluation of gas-solid interactions in fuel cells.
NexTech Materials, Ltd. Bill Dawson	Development of cathode supported SOFC designs. Development of manufacturing techniques for low temperature SOFC materials
Ceramatec S. Elangovan	Interconnects Development of Low Temperature material set.
Oak Ridge National Lab Edgar Laura-Curzio Don Adams	SOFC material property and reliability evaluations Power Electronics evaluation.