SECA Core Technology Program: SOFC Technology Development

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Acknowledgements

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Outline

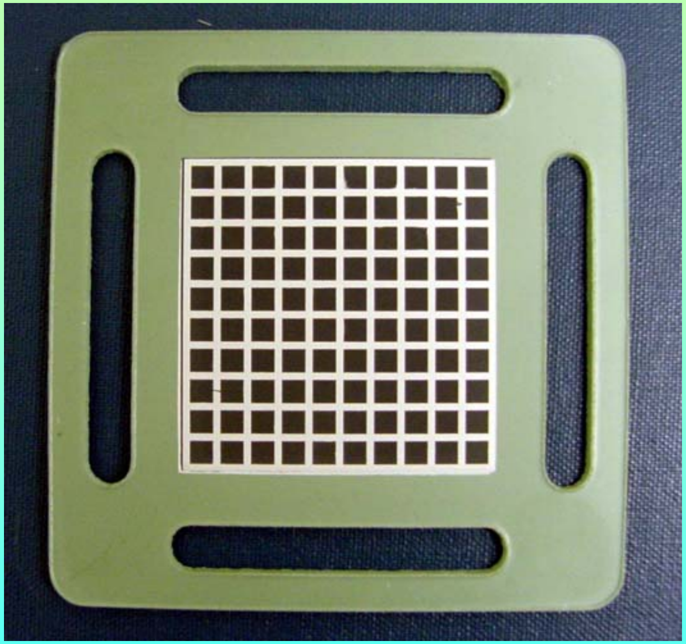
- SOFC Component Development Activities
  - 1. Cells
    - Anode supported Cell Fabrication
    - Performance Optimization
    - Advanced Anode Materials
  - 2. Interconnect Development
  - 3. Seal Development

- (SOFC Modeling discussed in Moe Khaleel's presentation)

Anode-supported Cell Fabrication

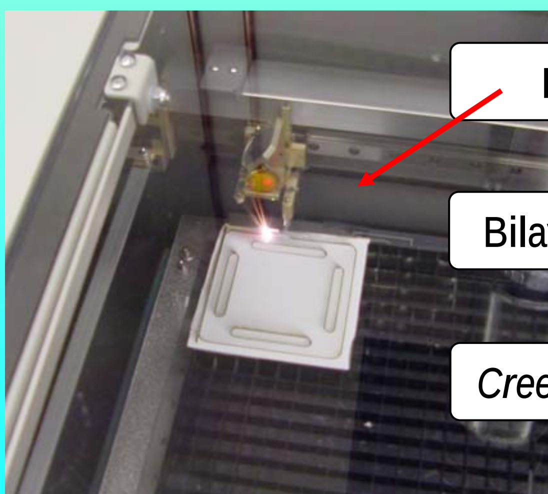
Cell Development Approach

- Goal: Develop cost-effective fabrication techniques for high performance, stable anode-supported YSZ cells.
- YSZ electrolyte
  - Time-tested solid electrolyte
- Anode-supported SOFCs (<10 μm YSZ)
  - Allows for operation at 800ºC or below; advantageous for interconnect, balance of plant, thermal management and cycling
- Fabrication by lamination of cast tapes
  - Proven as low-cost method of manufacturing planar ceramic structures
- Cosintering of anode and electrolyte in air
  - Reduces number of heat treatments

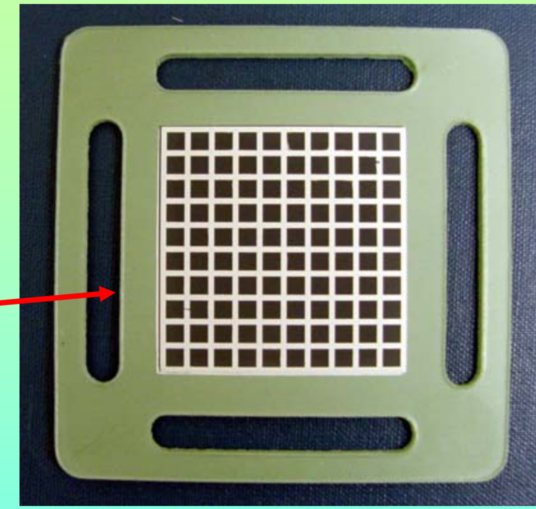


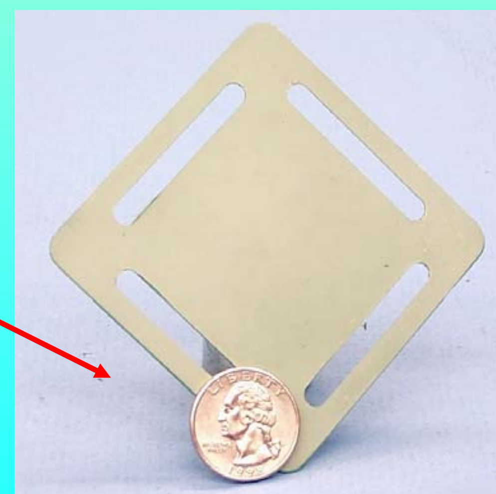
Cell Fabrication Process

- Attrition Milling
- Tape Batching
- Casting
- Lamination
- Laser Cut
- Bilayer Sintering
- *Creep Flattening**



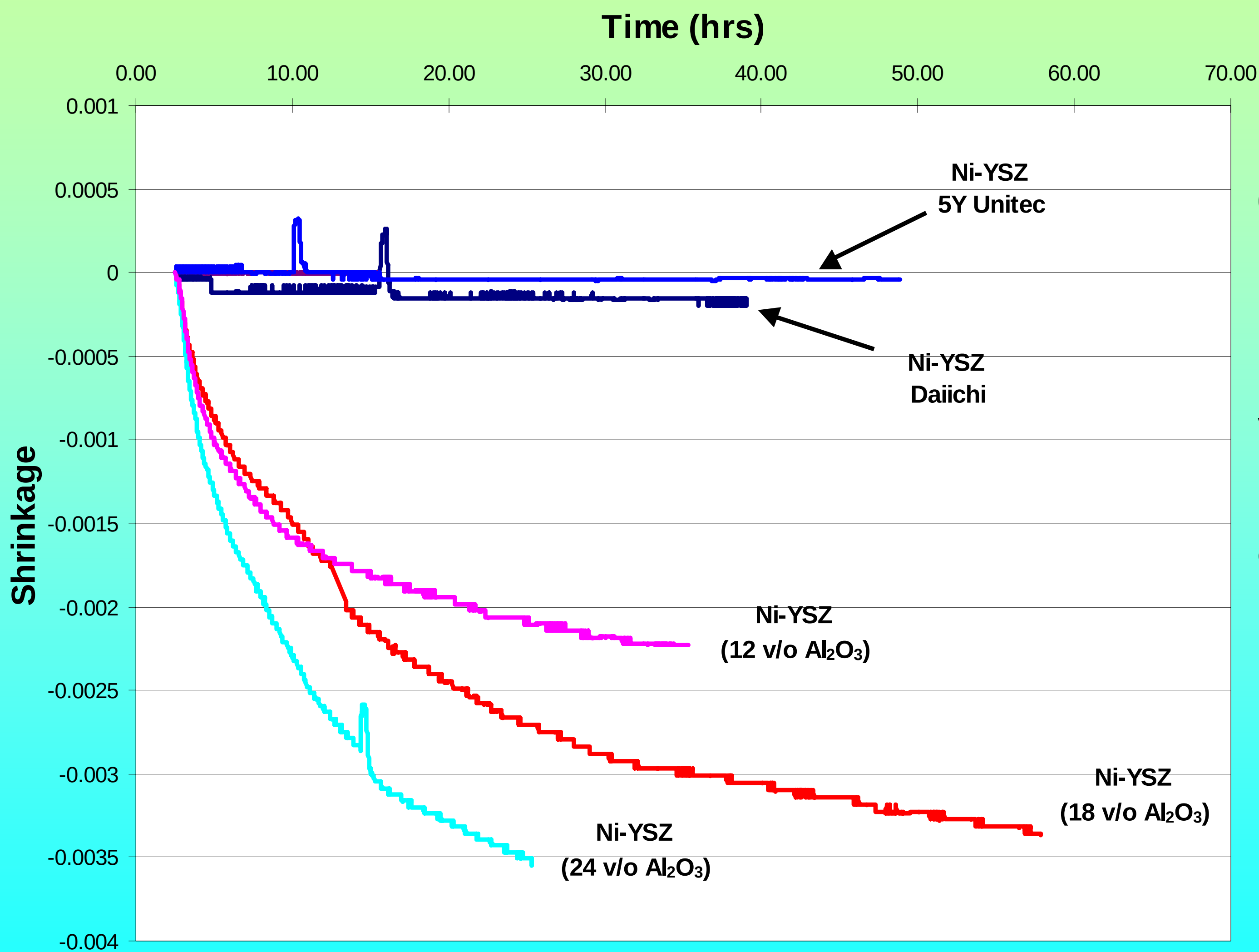
- Screen Print
- Sintering
- Reduction of NiO





*likely to be eliminated

Changes in Anode Composition to Improve Stability of Reduced Anode



Modified anode composition and microstructure to minimize sintering of reduced anode after NiO is reduced to Ni

Minimizing camber of sintered bilayers

- To minimize cost, mass, volume, and gas diffusion distances, targeted cell thickness is <600 μm; thinner cells offer improved flexibility, but also exhibit camber due to TEC mismatch

Sintered bilayers: 7 cm x 7 cm	Center Deflection, D (mm)	Part Thickness, t (mm)	Camber (D/t)
Typical Bilayer (US/CF)	0.36	0.56	0.64
Typical Bilayer (CS)	0.28	0.57	0.49
Bilayer w/ High TEC electrolyte	0.10	0.53	0.19
Double sided Bilayer (YSZ/Anode/YSZ)	0.03	0.54	0.06
Modified Bilayer (US/CF)	0.25	0.57	0.44
Modified Bilayer (CS)	0.15	0.52	0.29

Recent changes in bilayer fabrication yield substantial improvement in flatness

- US/CF = Unconstrained Sintering followed by Creep Flattening
- CS = Constrained Sintering (Sintering Conditions: 1375ºC/1hour)

Fabrication of Anode-supported SOFC

- Status:
  - Cells are produced by combination of tape casting, lamination, and screen-printing. Range of anode substrate thickness: 300 – 1200 μm.
  - Typical cells consist of ~600 μm thick bulk anode; 10 μm active anode; 7 μm YSZ membrane; 5 μm ceria layer; 20 μm cathode
  - Optimizing anode/electrolyte bilayer processing to minimize or eliminate camber due to TEC mismatch between anode and electrolyte
  - Improved dimensional stability (after reduction of NiO to Ni) by optimizing bulk anode composition and microstructure

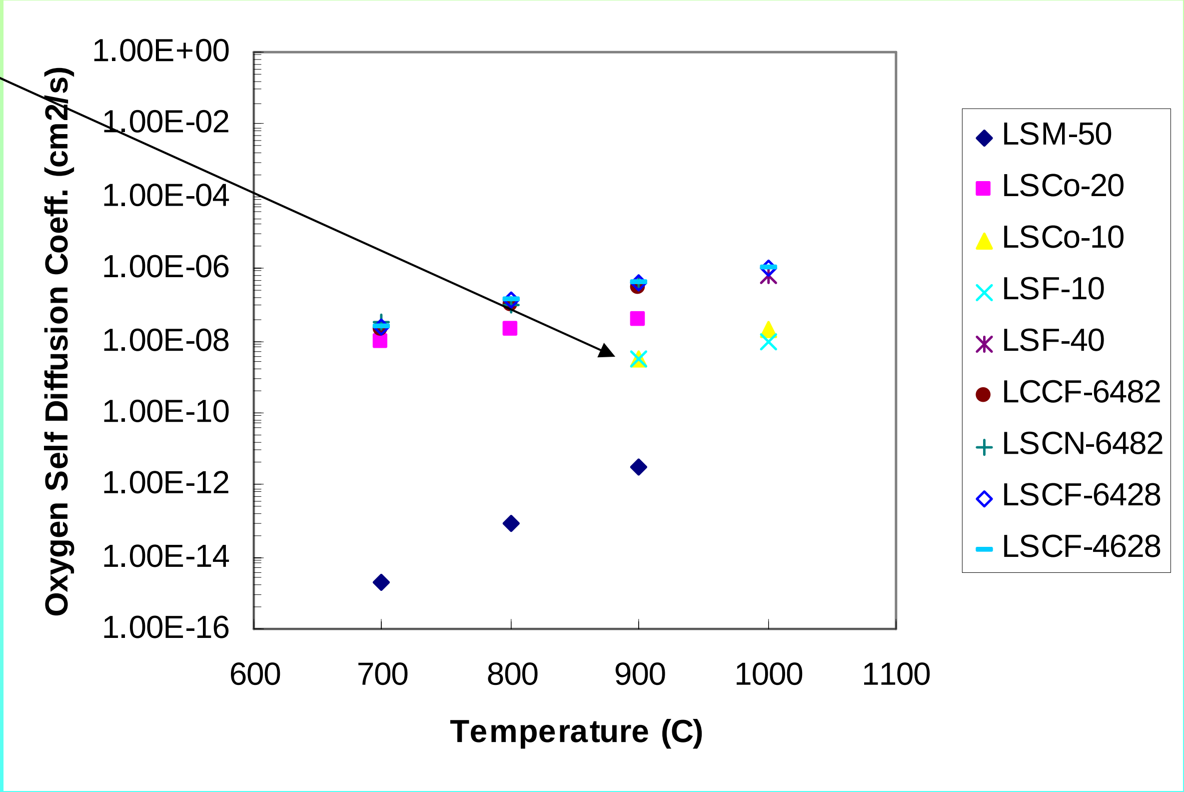
Performance Optimization

Electrode Development

- Goal: Develop and optimize high performance, stable electrodes for intermediate temperature SOFC.
- To date, most of performance improvement effort has focused on cathode:
- Composition
  - Lanthanum Strontium Manganite (LSM), and LSM/YSZ – early focus of cathode work
  - Lanthanum Strontium Ferrite (LSF) – best results to date
  - Lanthanum Strontium Nickel Ferrite
  - Lanthanum Strontium Cobaltite
- Microstructure
  - Porosity, Grain size
  - Interfacial layers
- Processing Variables
  - Base composition, Type and amount of dopant
  - Initial particle size distribution (calcination and milling conditions), Fugitive phases
  - Sintering temperature and time

Advantages of LSF Cathode

High oxygen diffusivity (relative to LSM) enhances oxygen reduction kinetics at cathode/electrolyte interface



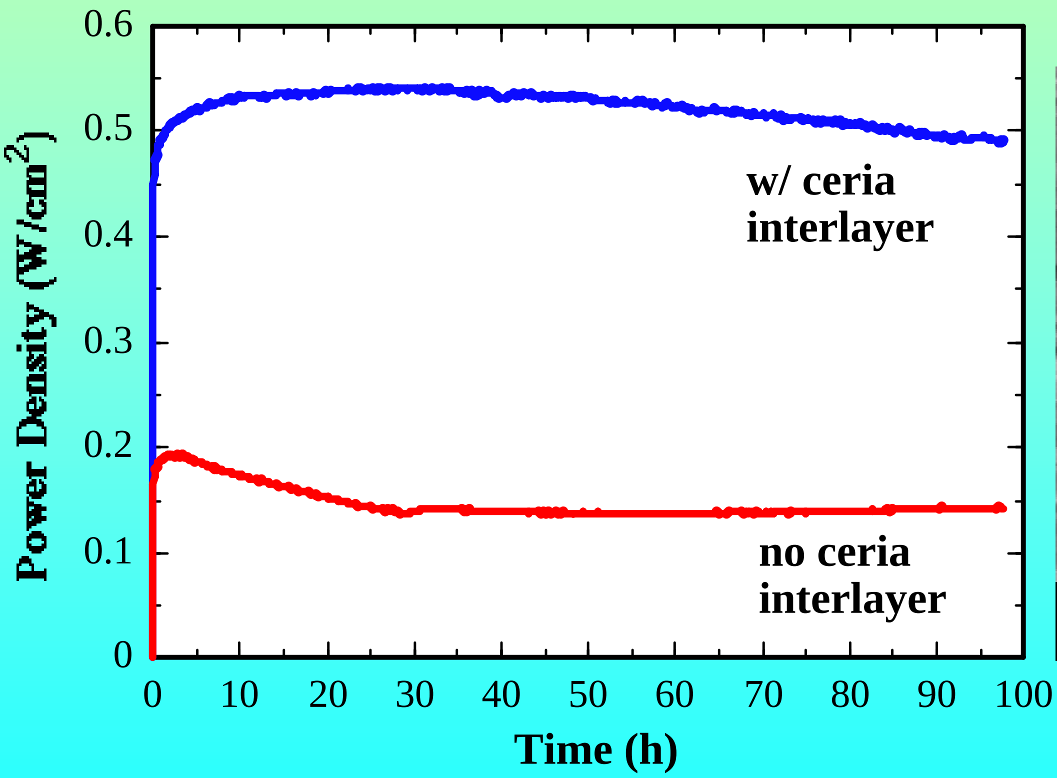
Data from PNNL (LSCF) and others (CRC Handbook of Solid State Electrochemistry p. 505)

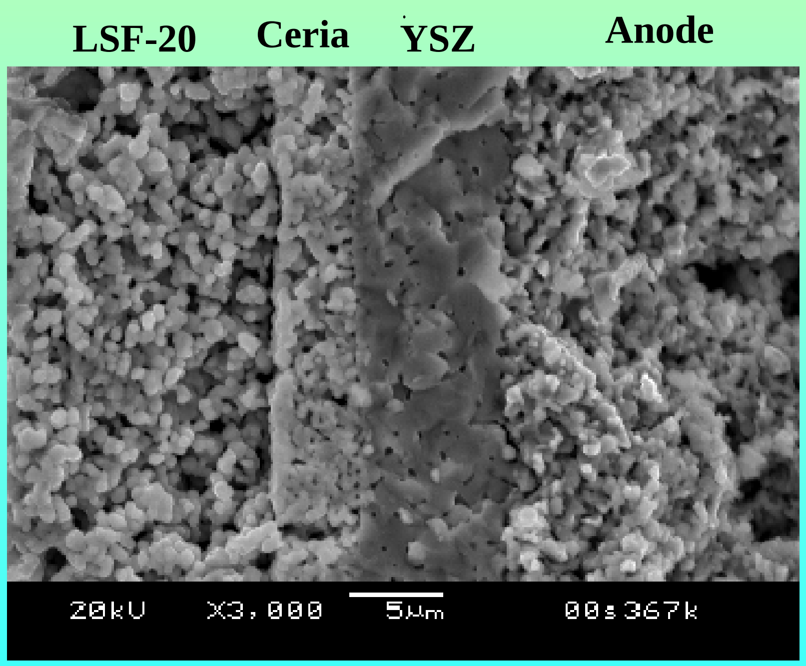
Other advantages of LSF as cathode:

High oxygen surface exchange coefficient; TEC is compatible with other cell components; high electronic conductivity (similar to LSM)

Sr-Doped $LaFeO_3$ Cathode Development

- Introduction of a ceria interlayer substantially increases the performance.





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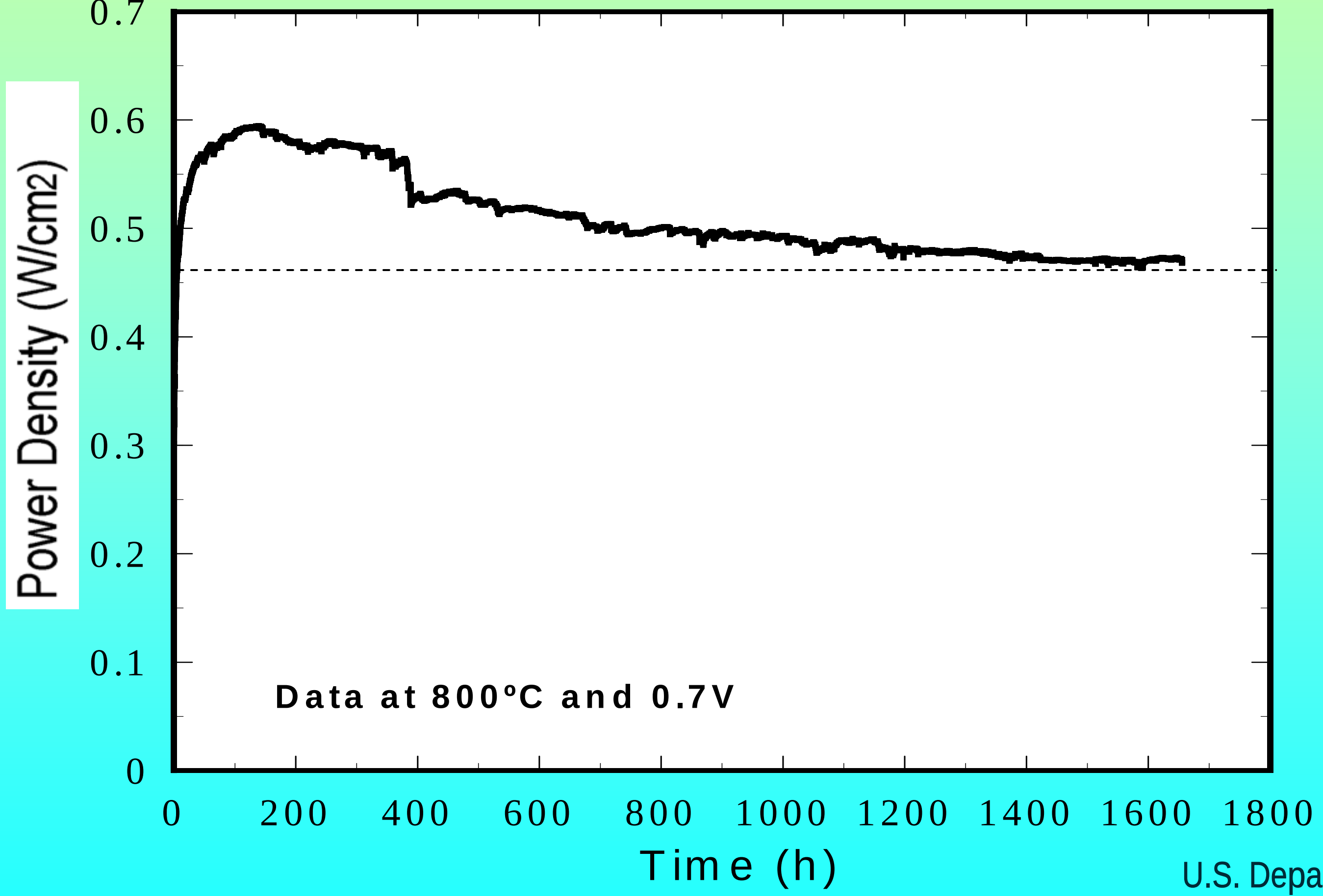
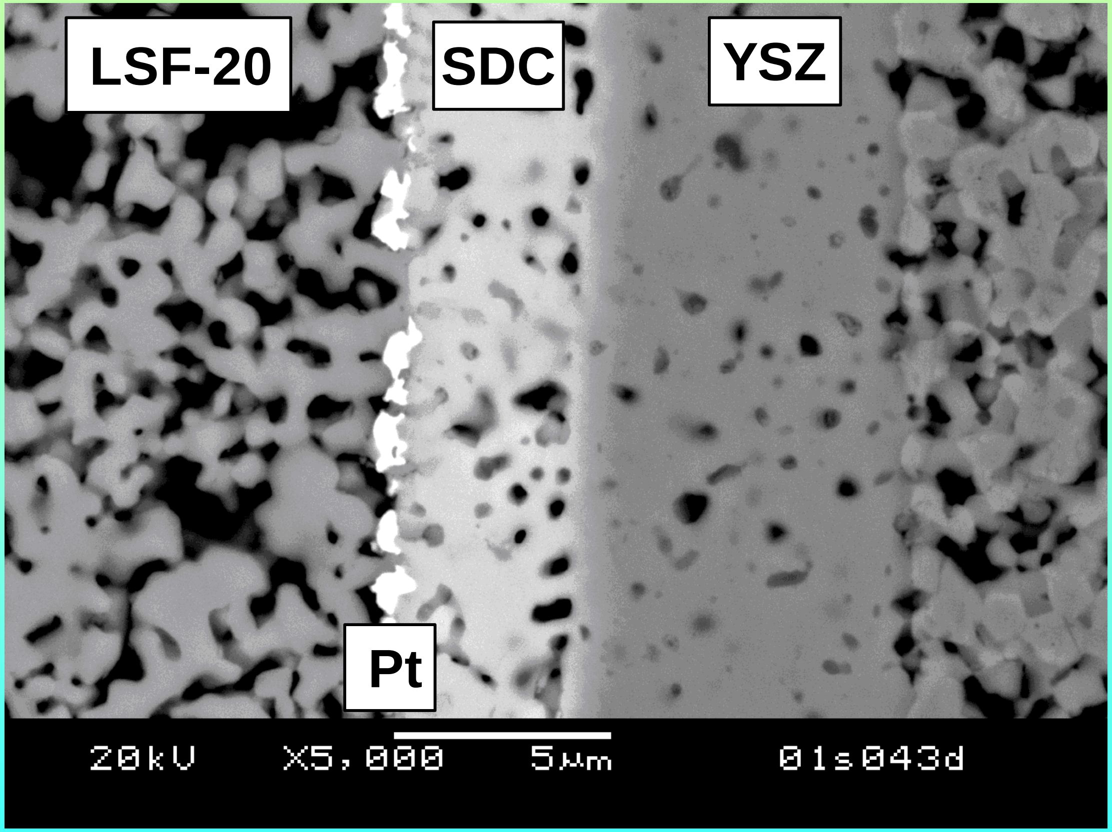
Long-Term Cell Test: January 2001

- LSF/SDC/YSZ/Ni-YSZ Cell operated for 1700 hours at 0.7V and 800˚C with a power density >400 mW/cm². Fuel was 97% H_2 / 3% H_2O (~20% utilization); Oxidant was air.



Microstructure of 1700 h cell

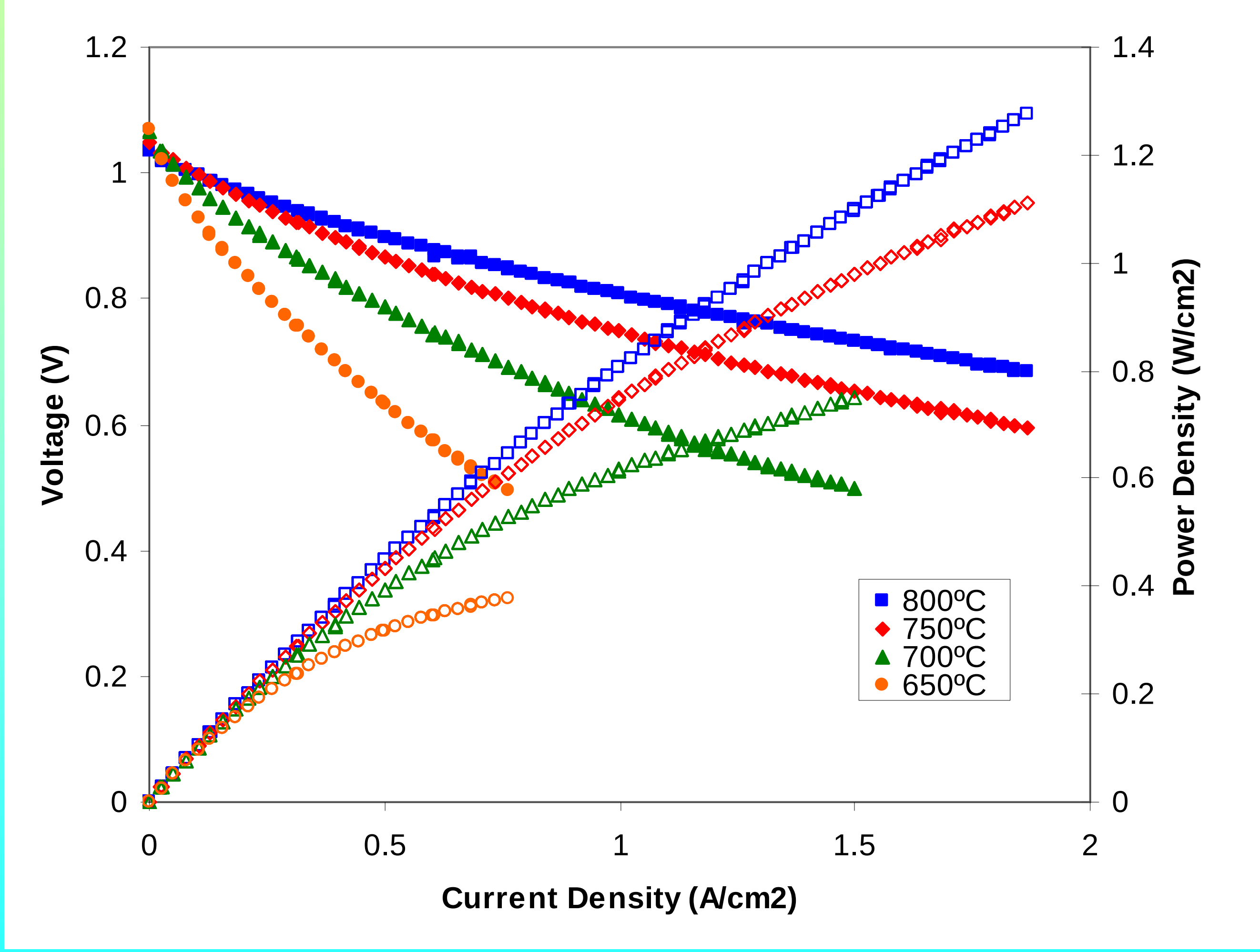
Performance degradation explained (at least in part) by migration of Pt from current collector on back of cathode



Temperature Dependence of Cell Performance

Single cell (LSF / SDC / YSZ / Ni-YSZ) operating on 97% H_2 / 3% H_2O at 750ºC and 0.7 V

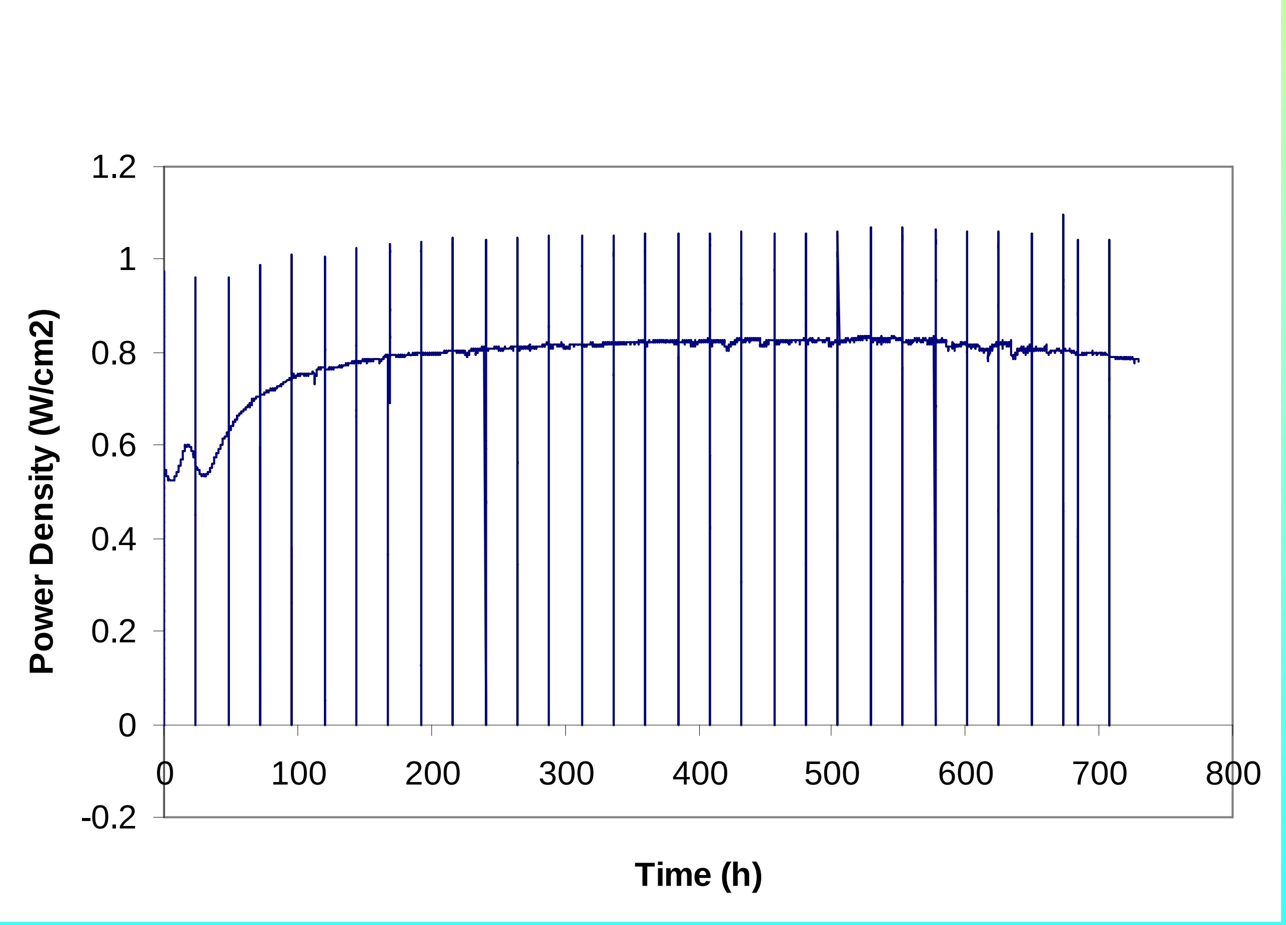
Low fuel utilization



Long-term Cell Test: July 2001

Status:

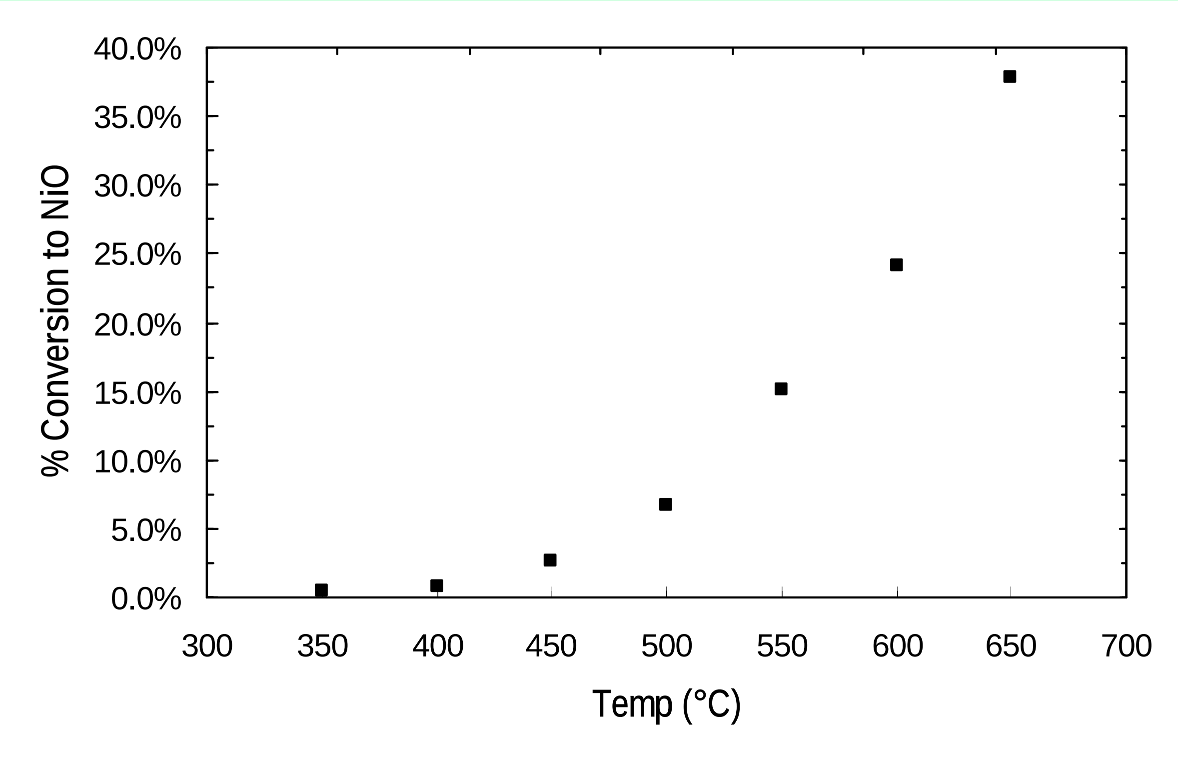
Single cells operating on 97% H_2 / 3% H_2O (~20% fuel utilization) at 750ºC and 0.7 V, deliver ~800 mW/cm²



Advanced Anode Materials

Advanced Red/Ox Tolerant Anode

- Goal: Develop alternative to Ni-based anode that offers higher tolerance to oxidizing environments to allow fuel to be turned off during system shut down



NiO formation in porous Ni/YSZ anode after 10 minutes exposure to air at indicated temperature (calculated from weight gain data)

Candidate Material for Oxidation Tolerant Anodes

- La-doped $SrTiO_3$
  - Reasonable electrical conductivity (5-20 S/cm)
  - Dimensional and chemical stability under redox cycling
  - TEC match to SOFC components
  - LST exhibits poor activity for hydrogen oxidation, but <u>recent modifications to base composition have substantially improved performance</u>

Optimization of LST anode through additional doping

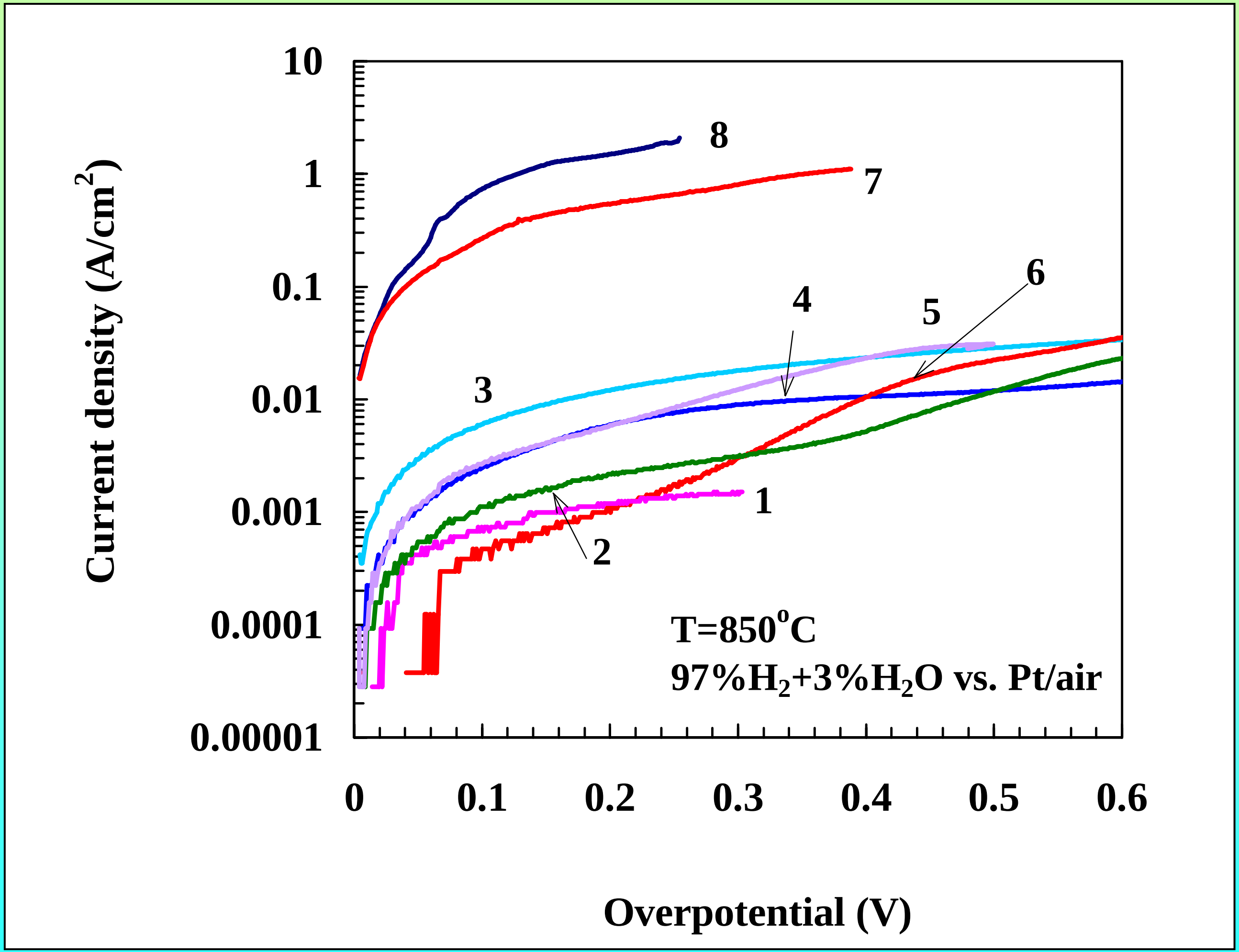
1: LST

2-7: Doped LST

8: Ni/YSZ

Status:

Continuing optimization of electrical conductivity and activity towards hydrogen oxidation through compositional and microstructural optimization



Metallic Interconnects

Metallic Interconnects for SOFC

- Goals:

1. Identify and quantify degradation processes
2. Develop a cost effective material (bulk and /or coatings) for intermediate temperature operation.

Challenging environment for interconnect:

- Multi component gas streams (H_2O, CO_2, O_2 etc.)
- Changing fuel composition (as result of fuel utilization)
- Simultaneous fuel and oxidant gas exposures
- Isothermal (high temperature) and thermal cyclic exposures

Stage 1 of Interconnect Development: 3-step Screening & Testing Study

Motivation for Screen Testing:

- Identification of candidate alloys.
- Understanding of corrosion processes and mechanisms
- No published inclusive study on suitable "lower" temperature (T_{oper} ~ 750°C) SOFC interconnect materials. Lack of agreement in the literature on oxidation rate and rate of conductivity deterioration for high temperature alloys.
- Purpose: Determine which high temperature alloys can best meet the application specifications. Identify the issues that will need to be addressed for enhanced long-term interconnect performance

Step 1: Pre-Screen - completed

- Identified nearly 300 high temperature, oxidation resistant alloys which fall into one of five categories
  - Chromia-forming Ni-, Fe-, and Co-based superalloys
  - Alumina-forming Ni-, Fe-, and Co-based superalloys
  - Cr-based alloys
  - Stainless steel: austenitic and ferritic
  - Noble metals and intermetallics
- The candidate list was narrowed to ~35 alloys by preparing a metallurgical database and grading the reported alloy properties against nine parameters:
  - Thermal expansion coefficient
  - Rate of oxide scale growth
  - Raw material cost
  - Yield strength at 800°C
  - Creep rate at 800°C
  - Formability
  - Susceptibility to hydrogen embrittlement
  - Susceptibility to sulfidization
  - Joinability

Step 2: Screen Testing of Alloy Properties – in progress

Chemical Screen	• Isothermal / thermal cyclic stability in fuel and oxidant environment • Chemical compatibility and bond strength with glass seals • Thermal cycle and duration testing with glass and compressive seal materials
Electrical Screen	• ASR measurements under cell exposure conditions (dual atmosphere)
Mechanical Screen	• Metal loss rate measurements as a function of time at temperature and thermal cycling in dual atmosphere • High temperature mechanical testing after long-term exposure
Fabrication Screen	• Erichsen and bulge formability testing • Initial joinability testing
Cost Screen	• Estimate of the overall interconnect cost

- Step 3: Long-Term Testing: Narrow the list to ~ 3 leading candidates and measure their performance under prototypical conditions

Metallic Interconnects for SOFC

- Status:
  - Developed metallurgical database for high temperature alloys
    - Thermal expansion coefficient, Rate of oxide scale growth, Raw material cost, Yield strength, Creep rate, Formability, Hydrogen embrittlement, Sulfidization, Joinability
  - Screening of alloy properties in progress:
    - Chemical, Electrical, Mechanical, Fabrication, Cost

Seal Development

- Prior development of glass seal materials on AR&TD Program
- Present emphasis in CTP: compressive seals

Seal Development for SOFC Stacks

- Rigid Seals or Compressive Seals?
  - Rigid seals (Glass or glass/ceramics) require:
    - TEC matched to components
    - Good wetting of adjacent component surfaces
    - Minimal creep or viscous flow
    - Minimal chemical interaction with other components and gases
  - Compressive seals -- questions to be answered include:
    - Quality of Seal? Measure leak rates, degradation and/or interaction with other cell components under SOFC operating conditions
    - Effect of compressive load structure on stack components, stack cost, and thermal management?

Compressive seals for SOFC

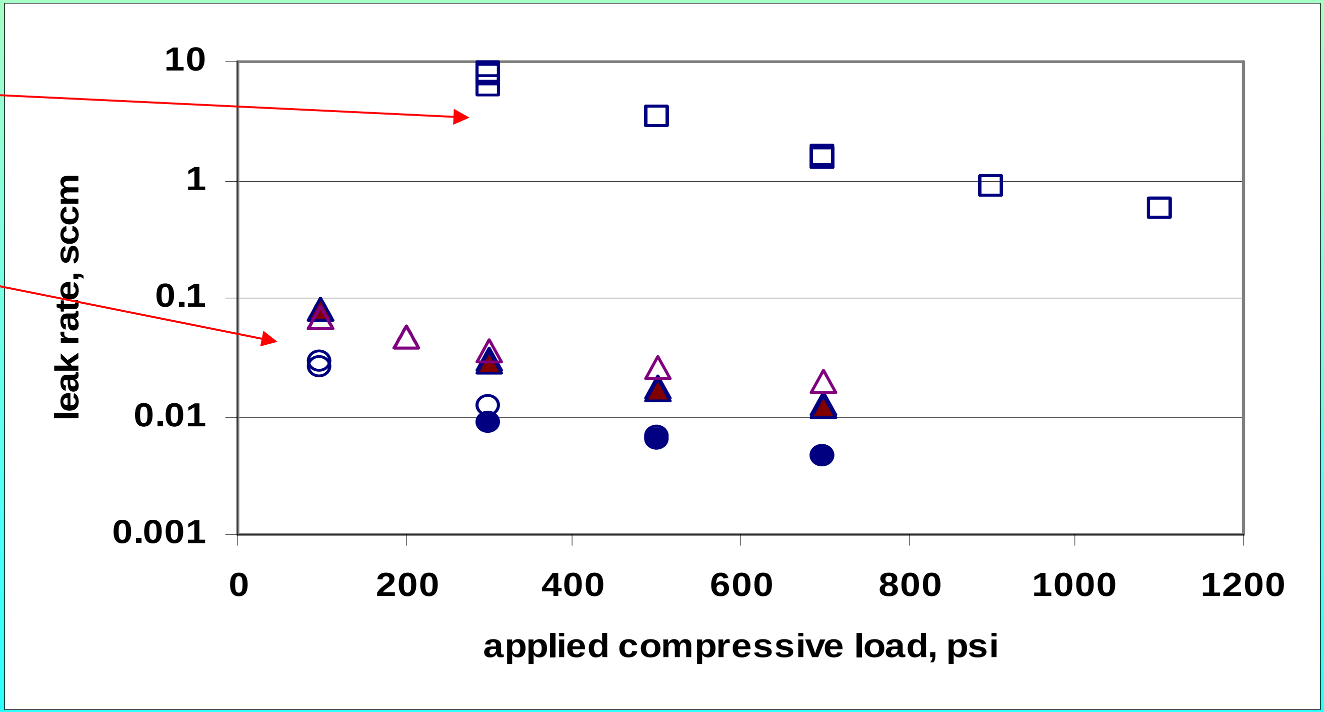
- Goal: to develop inexpensive, reliable compressive seal materials, offering adequate sealing and stable performance under minimal compressive load, as an alternative to glass or glass-ceramic seals.
- Requirements include:
  - High degree of sealing (minimal leakage) under minimal compressive load
  - Compliant at temperature of interest
  - Electrically insulating
  - Long-time stability in dual environments at T
  - Easy to handle and fabricate
  - Inexpensive
- Candidate “off-the-shelf” materials: Muscovite and phlogopite mica

Preliminary results for "advanced" compressive seal concept

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

Mica

"Advanced"



Summary

- Fabrication and processing techniques for anode-supported cells are being optimized for improved structural stability, electrical performance, and cost.
- Anode-supported cells using LSF cathode, YSZ electrolyte, and Ni/YSZ anode exhibit stable, high power density.
- Screening study for metallic interconnects in progress
- Red-ox tolerant ceramic anode and advanced compressive seals are being developed.