SECA Core Technology Program - PNNL: SOFC Component Development

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Presented at the SECA CTP Review Meeting

Pittsburgh, PA, June 18, 2002

Battelle

Topical Outline

- SOFC Component Development Activities
  - 1. Cells
    - Advanced Cathode Materials Development – Steve Simner
    - Advanced Anode Materials Development – Olga Marina
  - 2. Metallic Interconnect Development – Gary Yang (Scott Weil, Dean Paxton)
  - 3. Compressive Seal Development – Matt Chou

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

SOFC Cathode Materials Development

Cathode Materials Development

- Objective: Develop and optimize high performance, stable cathode materials for intermediate temperature SOFC.
- **Approach:**
  - **Synthesis (glycine-nitrate) and characterization of candidate cathode powders (XRD, dilatometry, SEM, PSA, TGA, electrical conductivity)**
  - **Fabrication of cathodes on anode-supported membranes via screen printing and sintering**
  - **Evaluation of cathode peformance by electrochemical testing and SEM**

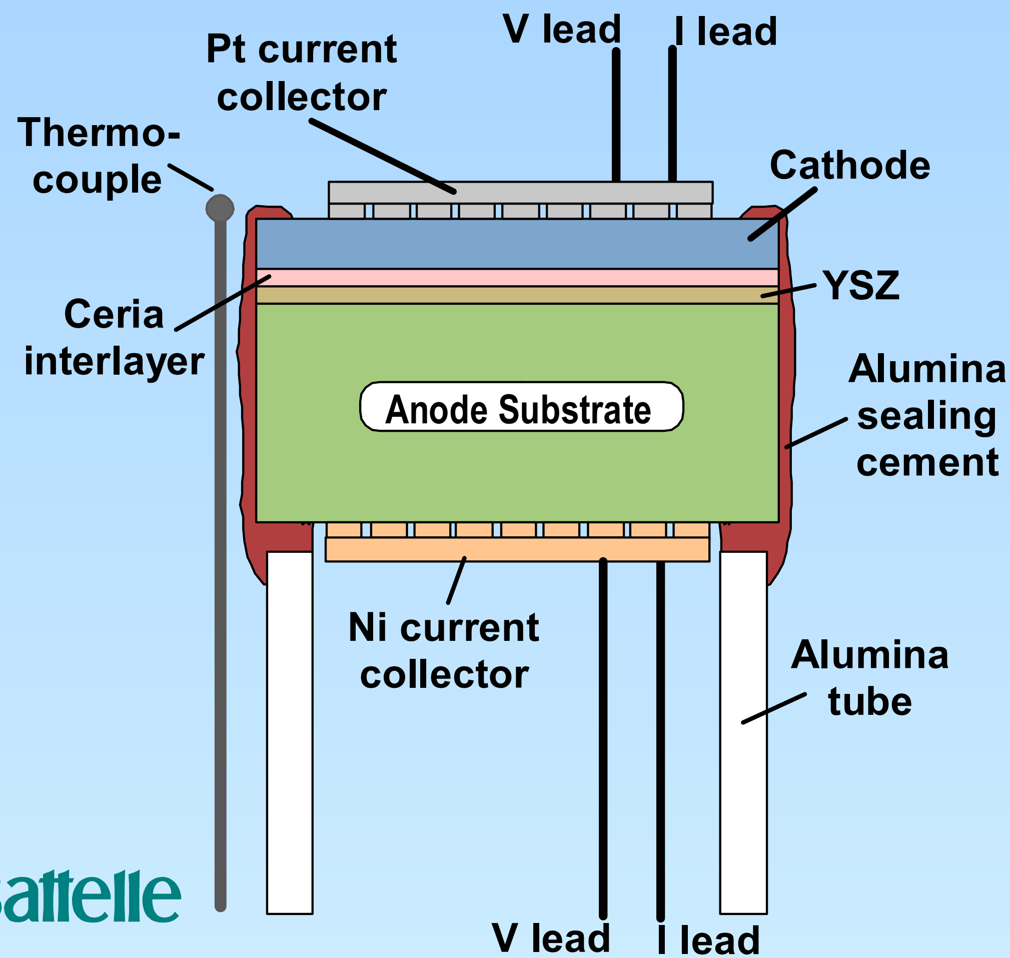
SOFC Cathode Material Challenges

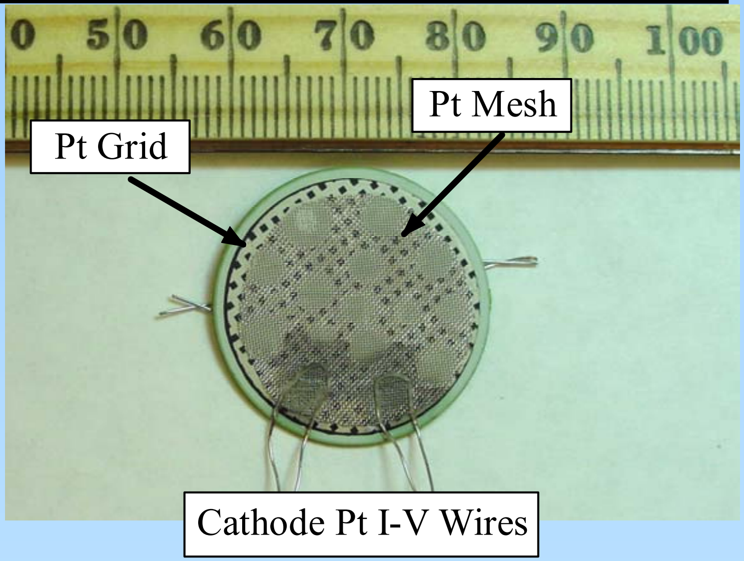
- Intrinsic Properties
  - High electrocatalytic activity towards oxygen reduction
    - High ionic conductivity, high surface exchange kinetics
  - Thermal expansion compatible with other SOFC materials
  - Minimal chemical interaction with the electrolyte and interconnect materials during fabrication and operation
  - High electronic conductivity
- Processing Related
  - Porous, stable microstructure to allow gas transport
  - Optimized interfacial mictrostructure to maximize oxygen reduction kinetics:
    - ½ O_2 (g) + 2 e' (cathode) ---------> O^{2-} (electrolyte)
  - Stability (chemical, phase, microstructural, dimensional) at high temperature in oxidizing atmosphere (1 to 10^{-6} atm. $P(O_2)$)
  - Adhesion to electrolyte surface – dependent on sintering temperature
  - Ease of fabrication
  - Low cost

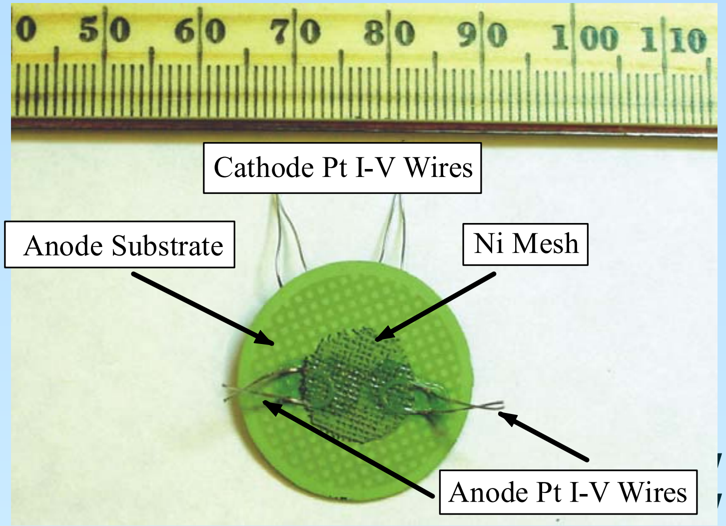
Single Cell Experimental Set-Up

NOT TO SCALE

Gas Flow Rates
Anode: 200 sccm H_2-3%H_2O
Cathode: 300 sccm air







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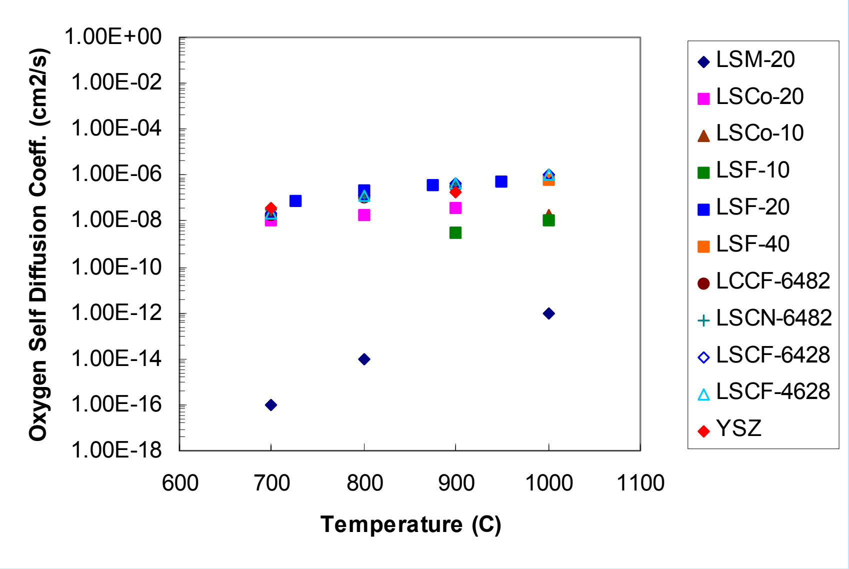
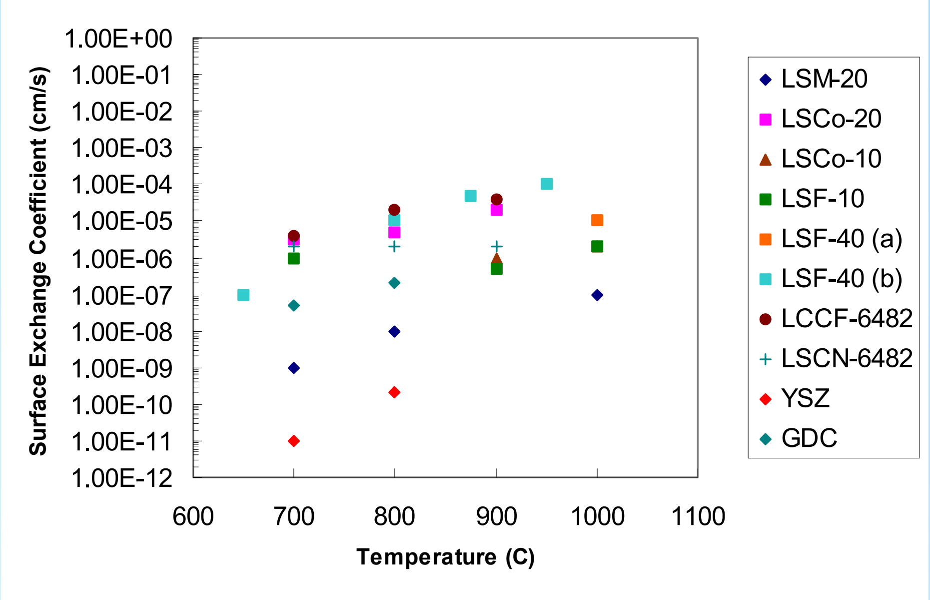
Advantages of LSF Cathode

- Mixed ionic-electronic conduction
  - High oxygen diffusion coefficient, D, and surface exchange coefficient, k, relative to LSM.





  - Potentially reduces cathodic polarization by extending the cathodic reaction sites beyond the triple phase boundaries (TPB).

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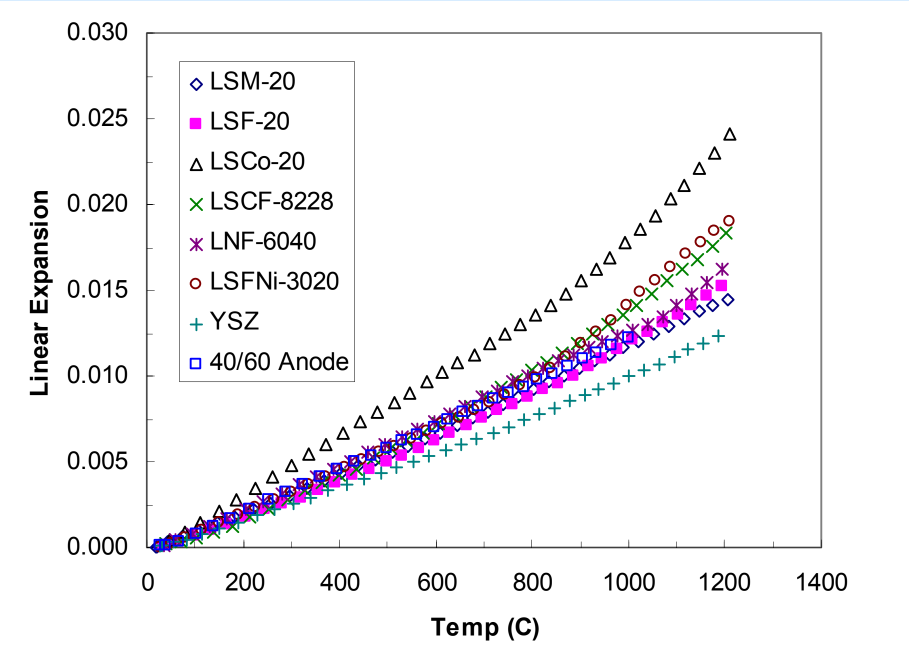
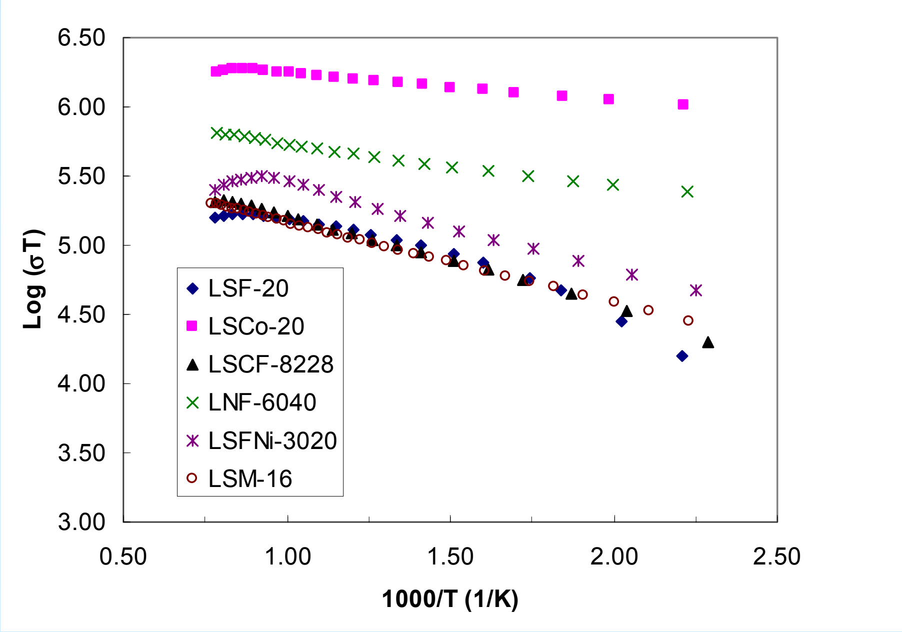
Data from PNNL and other sources

U.S. Department of Energy
Pacific Northwest National Laboratory

Advantages of LSF Cathode

- TEC is compatible with other cell/stack components
- High electronic conductivity (similar to LSM)



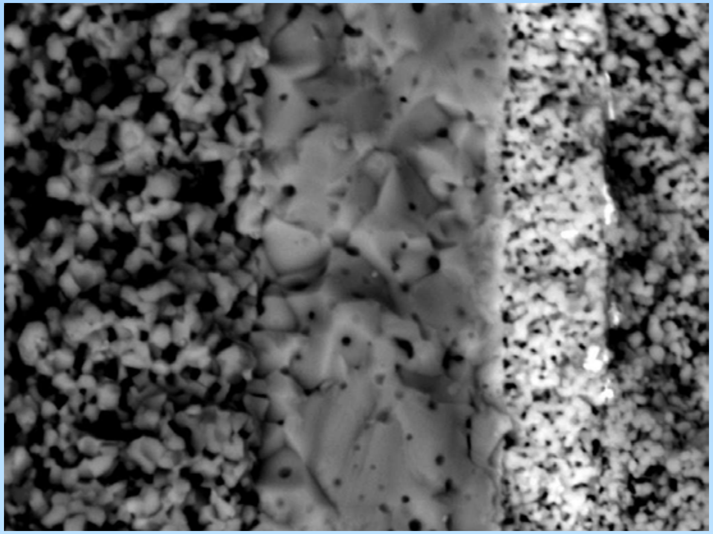


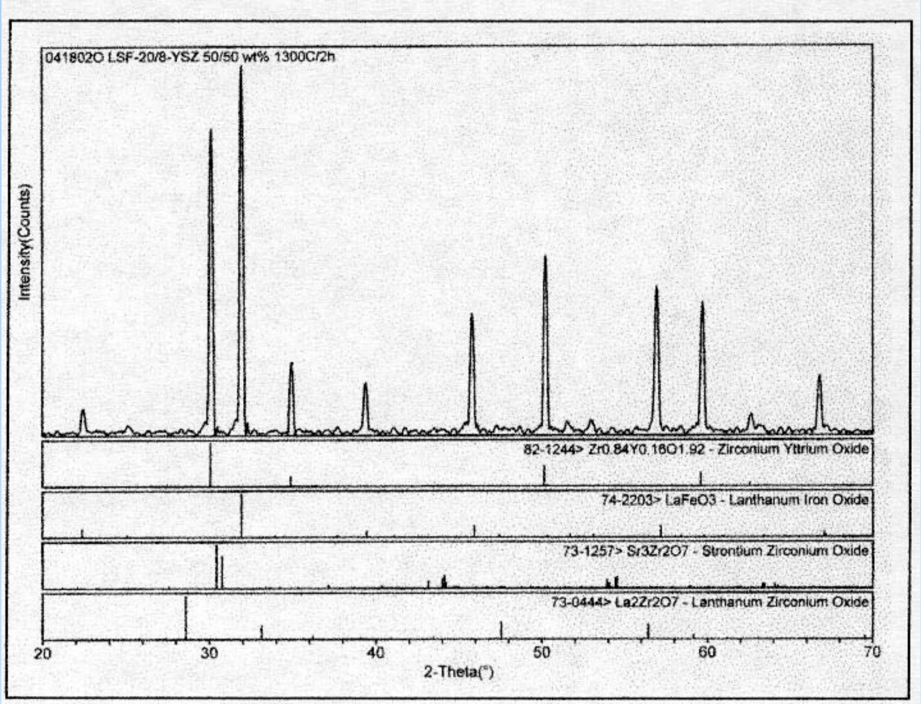
PNNL Data

Sr-Doped $LaFeO_3$ Cathode Development

- Introduction of a ceria interlayer substantially improves the performance.

Anode YSZ SDC LSF





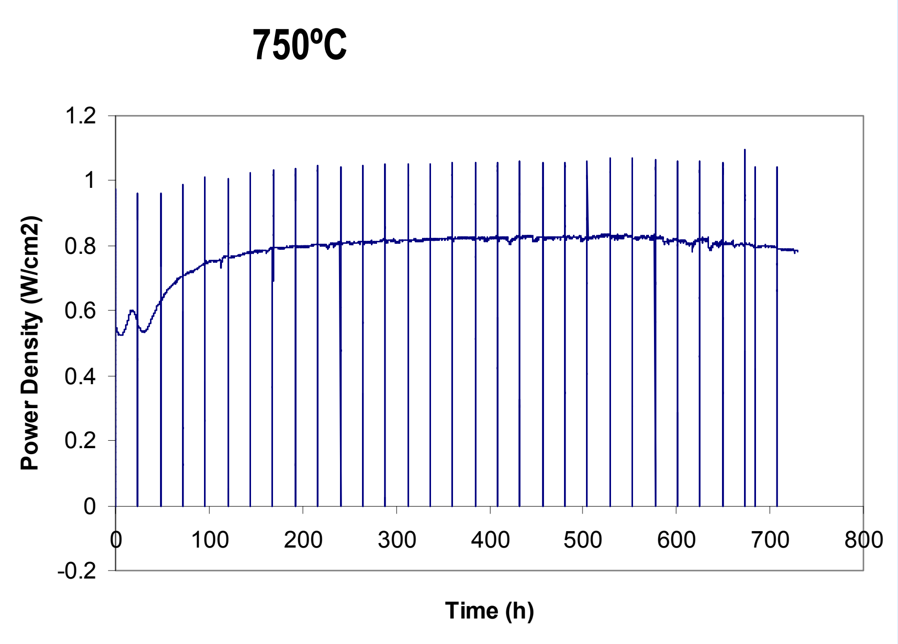
Mixtures of LSF and YSZ, heated to 1300ºC for 2 h, showed no evidence of zirconate formation. LSF peaks were shifted somewhat, possibly due to change in oxygen nonstoichiometry. Enhanced performance may be due to high ionic conductivity and surface exchange kinetics of the ceria vs. zirconia.

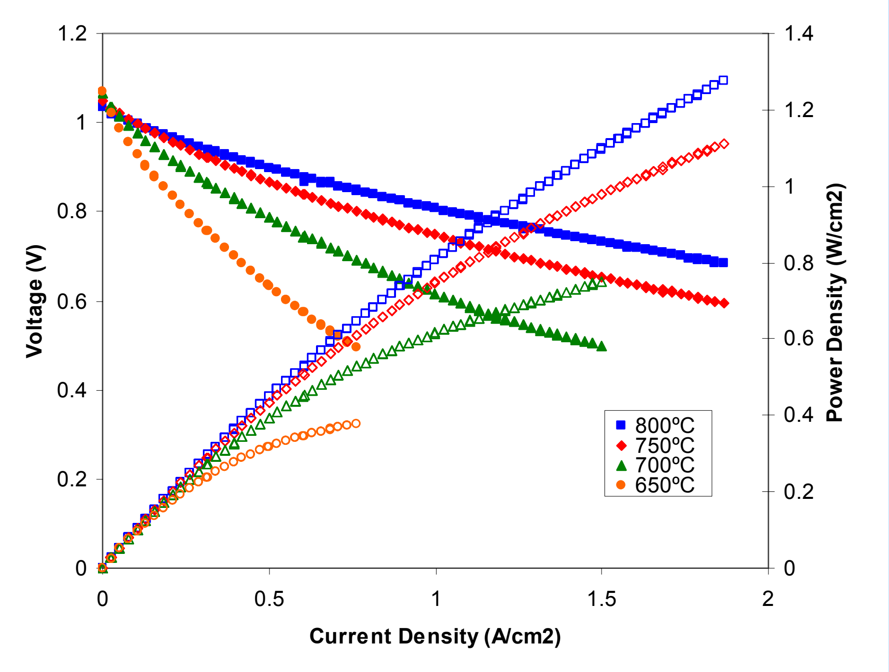
Anode-supported cell w/ LSF-20 cathode

<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





S.P. Simner et al., "Optimized Lanthanum Ferrite-Based Cathodes for Anode-Supported SOFCs," Electrochemical and Solid-State Letters, <u>5</u>, A173 (2002).

Achieving Further Improvement

- LSF demonstrates good performance and stability, but requires further improvement:

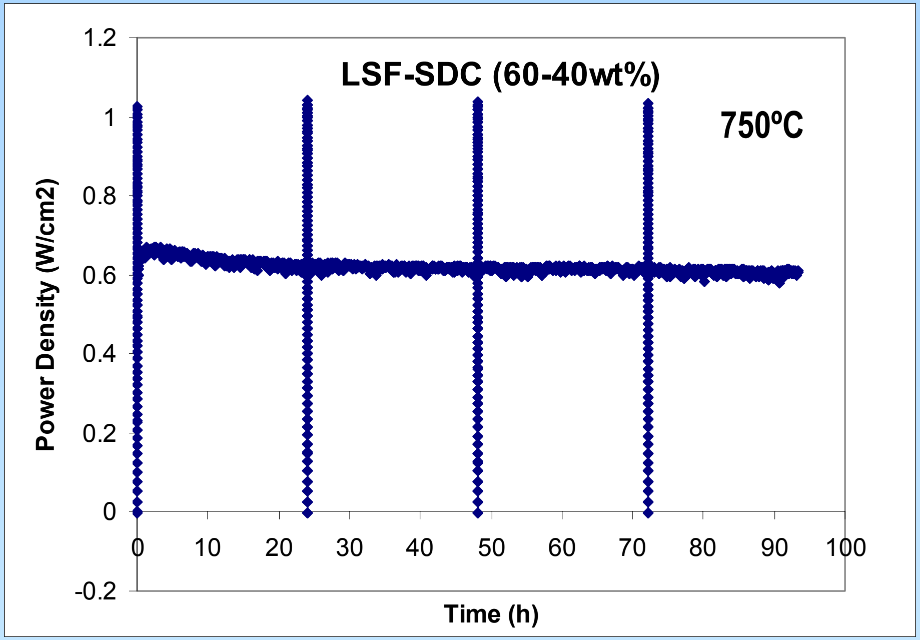
  1) **LSF – SDC mixtures**

     –Optimize composition and morphology

  2) **Engineering ceria layer**

     –Optimize density, thickness, surface texture

  3) **Compositional modification of LSF: e.g., B-site dopants**



Advantage of LSF-SDC mixtures:
no "burn-in" period during initial operation

SOFC Anode Materials Development

SOFC Anodes: Advantages and Disadvantages of Ni/YSZ Anode

- Advantages:
  - Relatively inexpensive; chemically and physically compatible with YSZ electrolyte
  - High electronic conductivity
  - High catalytic activity for fuel oxidation and for steam reforming of methane
  - With these advantages, conventional Ni/YSZ cermet has proven adequate for operation on clean H_2 or fully reformed fuels
- Disadvantages:
  - **Unstable in oxidizing atmosphere at high temperatures**
  - **Easily poisoned by sulfur**
  - Tends to promote carbon deposition during internal reformation; high catalytic activity for steam reforming can cause excessive thermal gradients
  - Sintering during operation (particularly at high steam partial pressures occuring at high fuel utilization) may decrease activity of anode-electrolyte interface; may cause warping in anode-supported cells

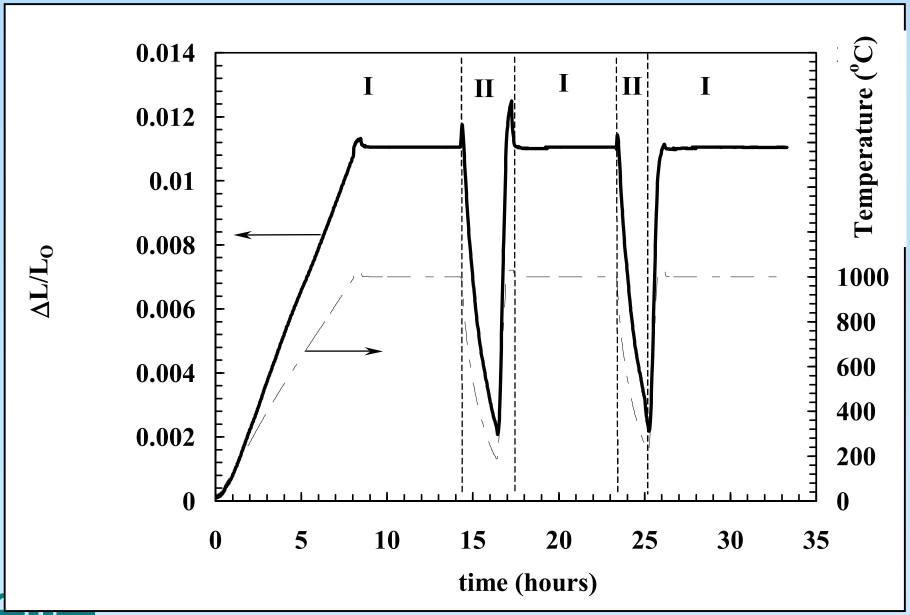
Advanced Red/Ox Tolerant Anode

- Objective: Develop alternative to Ni-based anode that offers higher tolerance to oxidizing environments (to allow fuel to be turned off during system startup and shutdown) and tolerance to sulfur-containing environments

- **Approach:**
  - **Synthesis (glycine-nitrate) and characterization of candidate anode powders**
  - **Fabrication of anodes on electrolyte-supported cells via screen printing and sintering**
  - **Evaluate candidate oxide materials using electrical conductivity measurements, 2- and 3-electrode cell tests (*I-V*, impedance spectroscopy), dilatometry, XRD, SEM**

Candidate Material for Oxidation Tolerant Anodes

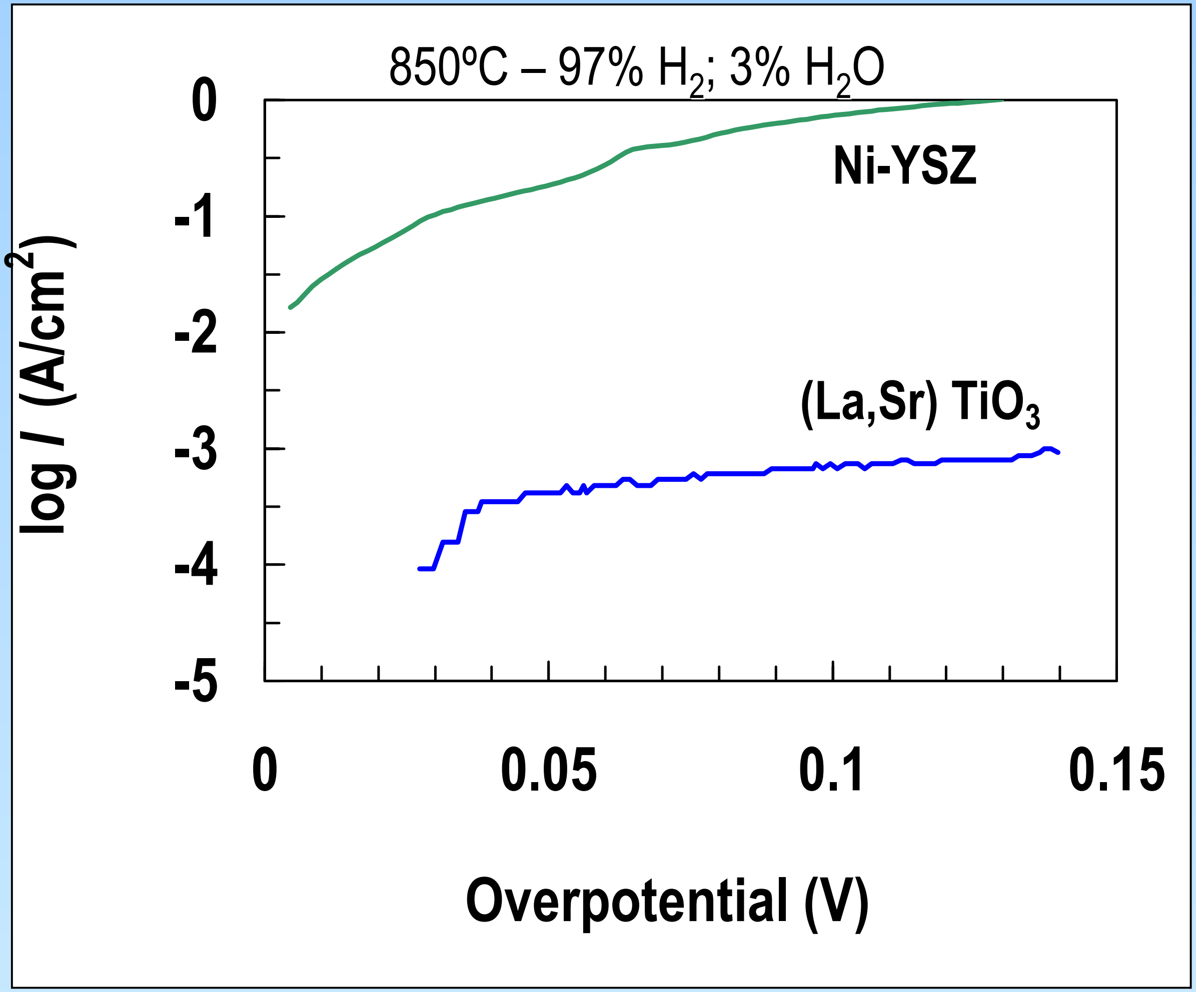
- La-doped $SrTiO_3$
  - Reasonable electrical conductivity (up to 15 S/cm)
  - Dimensional and chemical stability under redox cycling
  - TEC match to SOFC components
  - But, LST exhibits poor activity for hydrogen oxidation



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)

Half-cell polarization curves

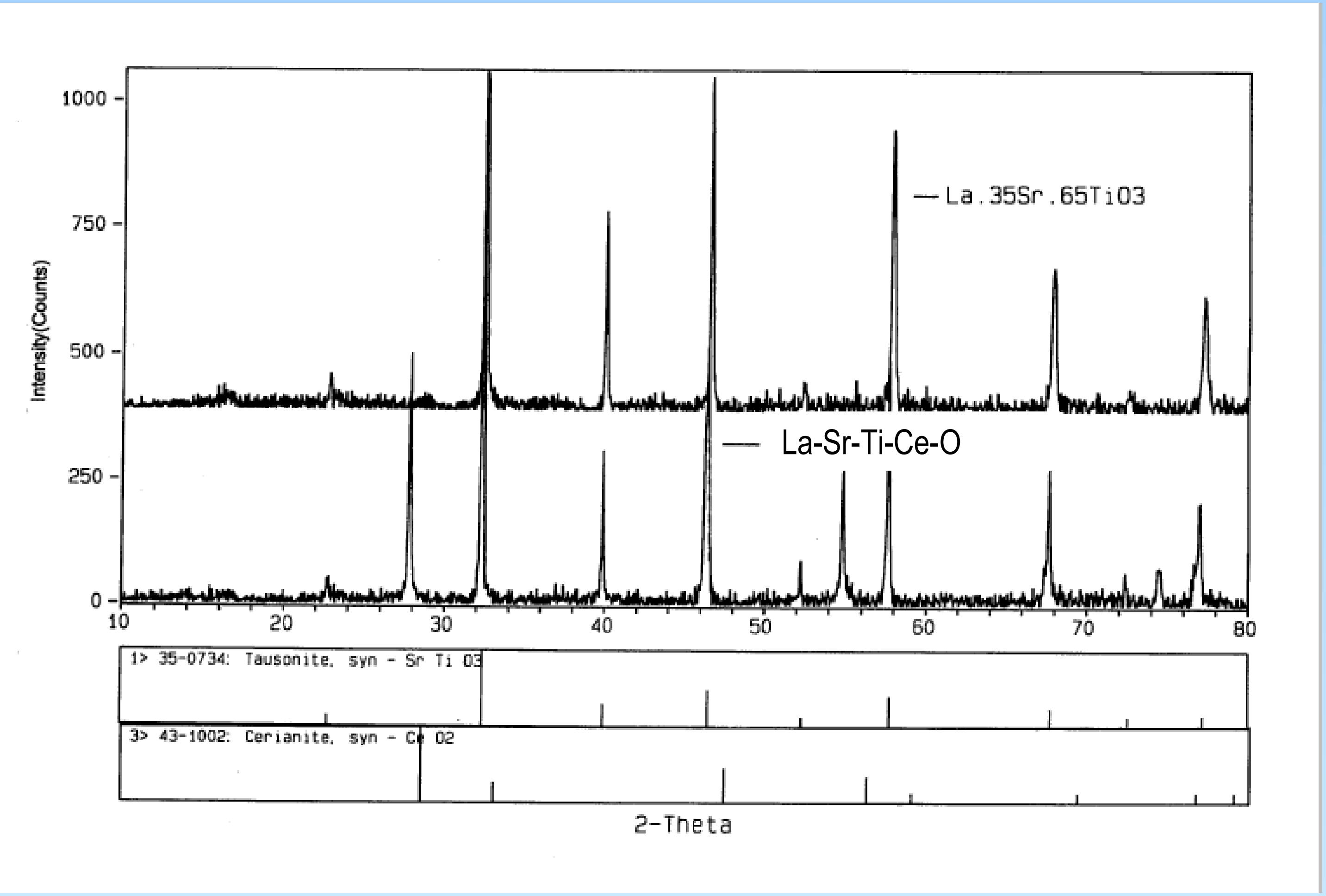


- LST exhibits poor anodic performance
  - low catalytic activity
- Approaches to improve performance:
  - Adding a catalytically active second phase
  - B-site doping

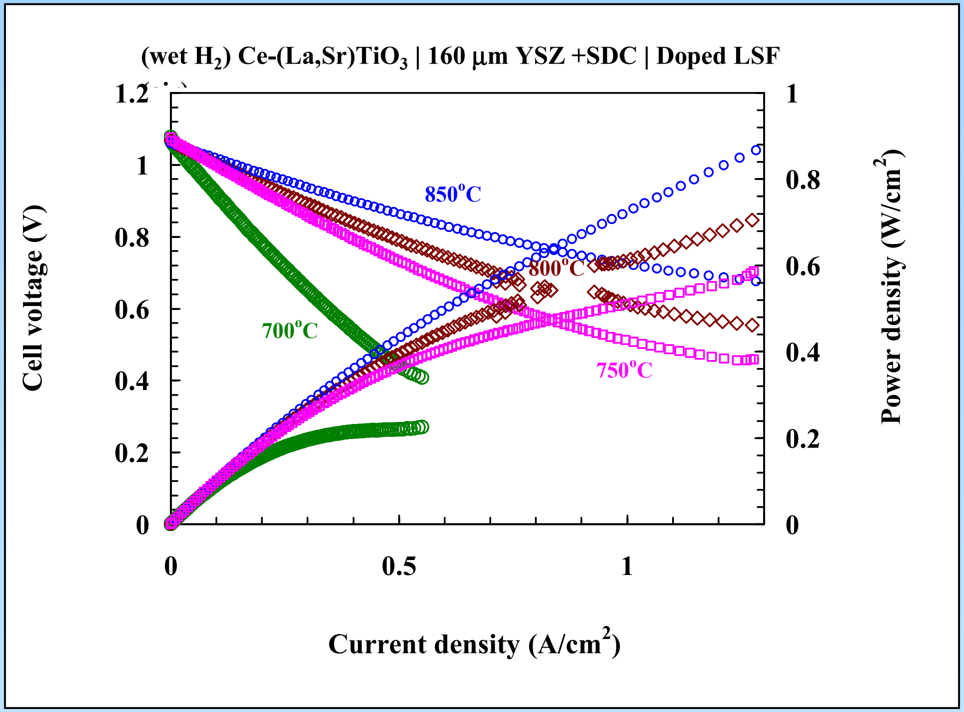
Polarization resistances at the doped $SrTiO_3$ / YSZ interface at 850°C in H_2/H_2O=97/3 vs. Pt/air

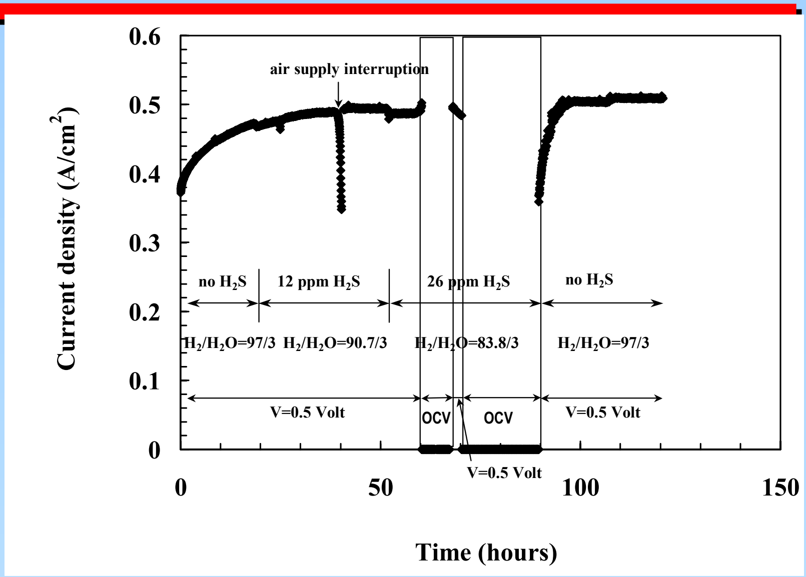
Anode composition	*Tsint*, °C	R_p, Ωcm^2
$La_{0.35}Sr_{0.65}TiO_3$	1000	52
$La_{0.4}Sr_{0.6}TiO_3$	1000	44
5 wt% Ni+ $La_{0.4}Sr_{0.6}TiO_3$	1000	1
$La_{0.35}Sr_{0.65}Ti_{0.8}Ni_{0.2}O_3$	1000	48
$La_{0.35}Sr_{0.65}Ti_{0.8}Co_{0.2}O_3$	1000	39
$La_{0.35}Sr_{0.65}Ti_{0.8}Cu_{0.2}O_3$	1300	60
$La_{0.35}Sr_{0.65}Ti_{0.8}Cr_{0.2}O_3$	1000	47
$La_{0.35}Sr_{0.65}Ti_{0.8}Fe_{0.2}O_3$	1000	21
(La,Sr)(Ti,Ce)O_3, Ti/Ce=19	1000	1.5
(La,Sr)(Ti,Ce)O_3, Ti/Ce=9	1000	0.4
(La,Sr)(Ti,Ce)O_3, Ti/Ce=5.7	1000	0.3
(La,Sr)(Ti,Ce)O_3, Ti/Ce=4	1000	0.2
(La,Sr)(Ti,Ce)O_3, Ti/Ce=1	1000	3.6
(La,Sr)(Ti,Ce)O_3, Ti/Ce=4, Sr/La=9	1000	1
(Y,Sr)(Ti,Nd)O_3	1000	10
(Y,Sr)(Ti,Pr)O_3	1000	43
(Y,Sr)(Ti,Ce)O_3	1000	16

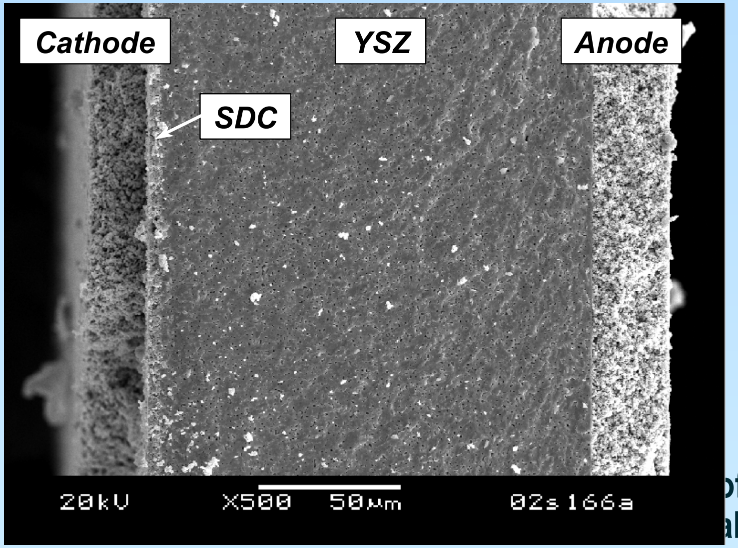
XRD patterns (calcined 1200°C/1h)



All-ceramic SOFCs: Electrochemical Performance







Fuel: H_2/H_2O=97/3 (Low Utilization)

Oxidant: Air

Work in progress / Future work

- Optimize composite phases for electrical conductivity and electrocatalytic activity
- Perform sulfur tolerance tests
- Perform long-term carbon tolerance test
- Test steam-reforming of methane and higher hydrocarbon fuels
- Determine mechanical properties

SOFC Interconnect Development

SOFC Interconnects: Challenges

Mechanical and chemical stability:

- High temperature oxidation/corrosion resistance
- 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

Low resistance path for electric current

Low materials and fabrication cost

Preferred high temperature interconnect material: Doped lanthanum chromite

High temperature alloys may satisfy these requirements for lower temperature (<800ºC) SOFC stacks

Metallic Interconnects for SOFC

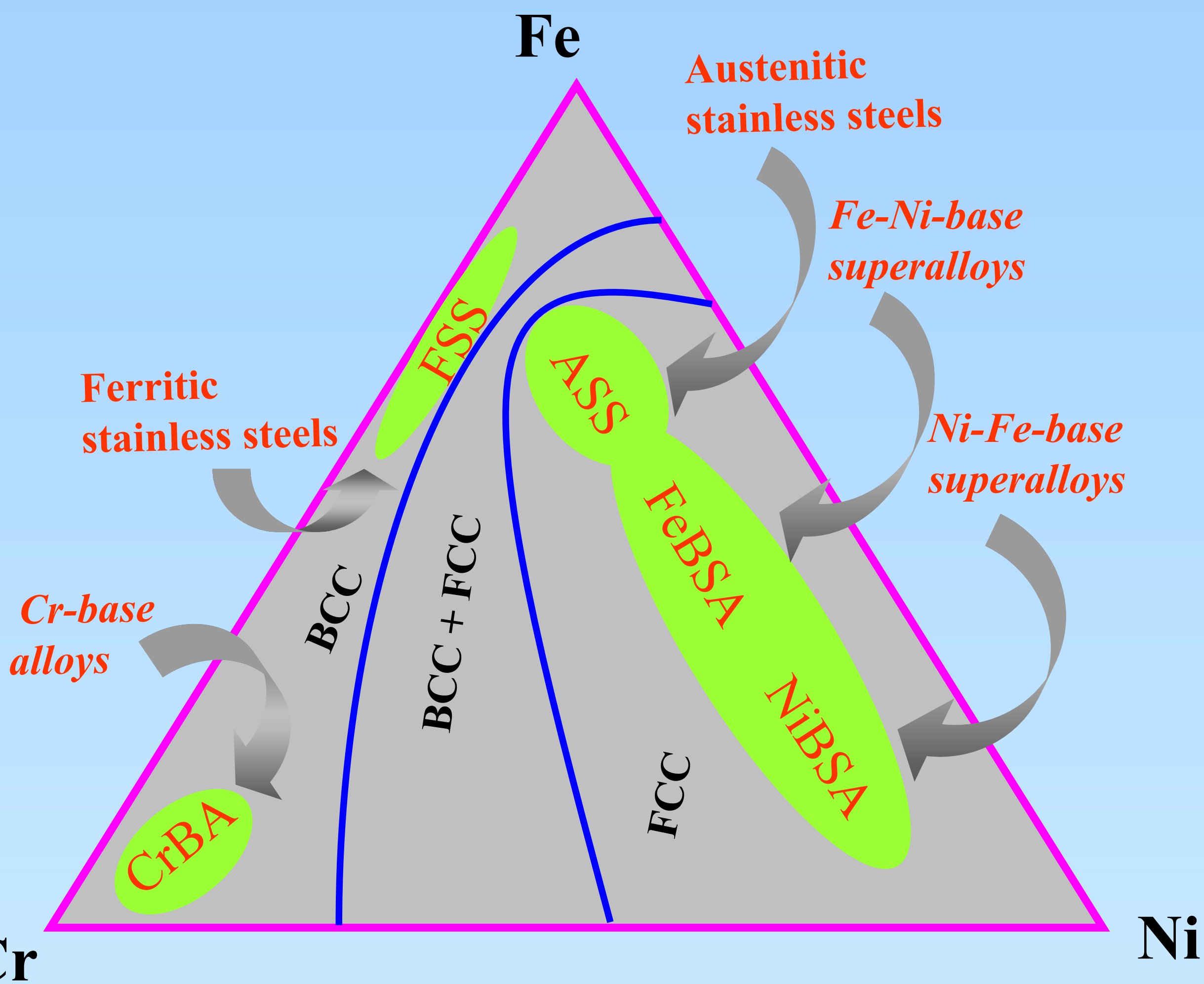
- Objectives:

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

Approach:

- **Pre-screening of candidate alloys (completed)**
- **Screen testing (evaluation of chemical, electrical, mechanical properties)**
- **Materials development**

Potential Candidates



Overall, heat resistant alloys could be potential candidates, including

- Ferritic stainless steels
- Austenitic stainless steels
- Fe-Ni-base superalloys
- Ni-Fe-base superalloys
- Cr-base alloys

Plus

- Co-base superalloys

Pre-selection process

Data collection/ Literature studies

From handbooks, textbook, journal publications, producer's WebPages, etc

↓

Properties Database*

Compilation of composition and property information of about three hundred heat resistant alloys.

↓

Pre-selection of Candidate Alloys

Composition criteria for pre-selection

- **Chromia formers**

  Cr ≥18 wt% for Ni- and Fe-bases;

  Cr ≥ 22 wt% for Co-bases;

- **Alumina formers**

  Al ≥ 3~4 wt%

  Cr ≥ 15 wt%

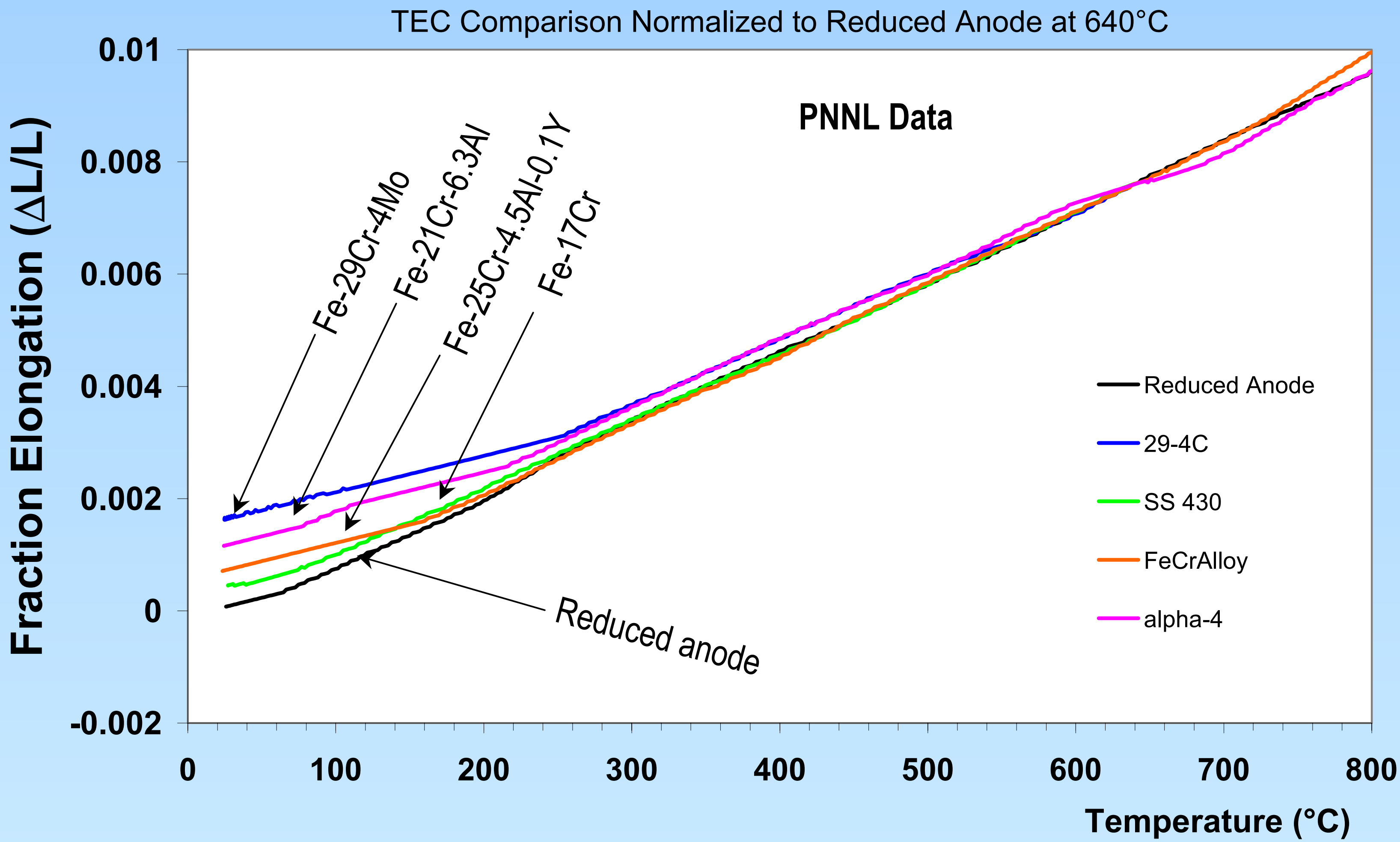
*Available upon request

Screen testing of candidate alloys

- Selected alloys
  - Ni-Fe-base superalloys: G-30, Nicrofer 6025, Haynes 230, Haynes 214, Rene 41;
  - Fe-Ni-base superalloys: Haynes 120, Pyromet, Haynes 556;
  - Ferritic stainless steels: 430, 446, Ebrite, 29-4C, Al 453
    - Advantages: CTE match, cost, ease of fabrication
  - Alumina formers: Fecralloy, alpha-4.
- Screen testing

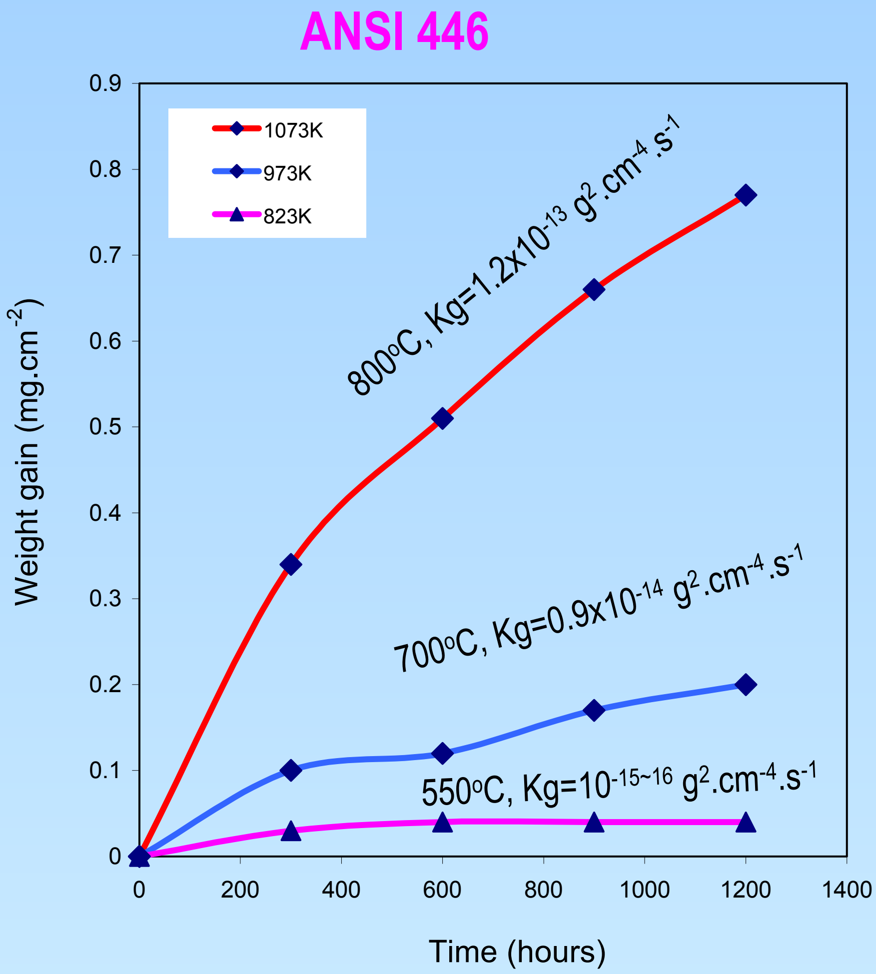
Chemical Screen	Oxidation in fuel and oxidant environment Chemical compatibility with barium-calcium-aluminosilicate base glass seals Oxide scale thermodynamic stability
Electrical Screen	ASR measurements under cell exposure conditions (air & dual atmosphere)
Mechanical Screen	Investigation of thermal expansion Interfacial bonding strength with glass seals

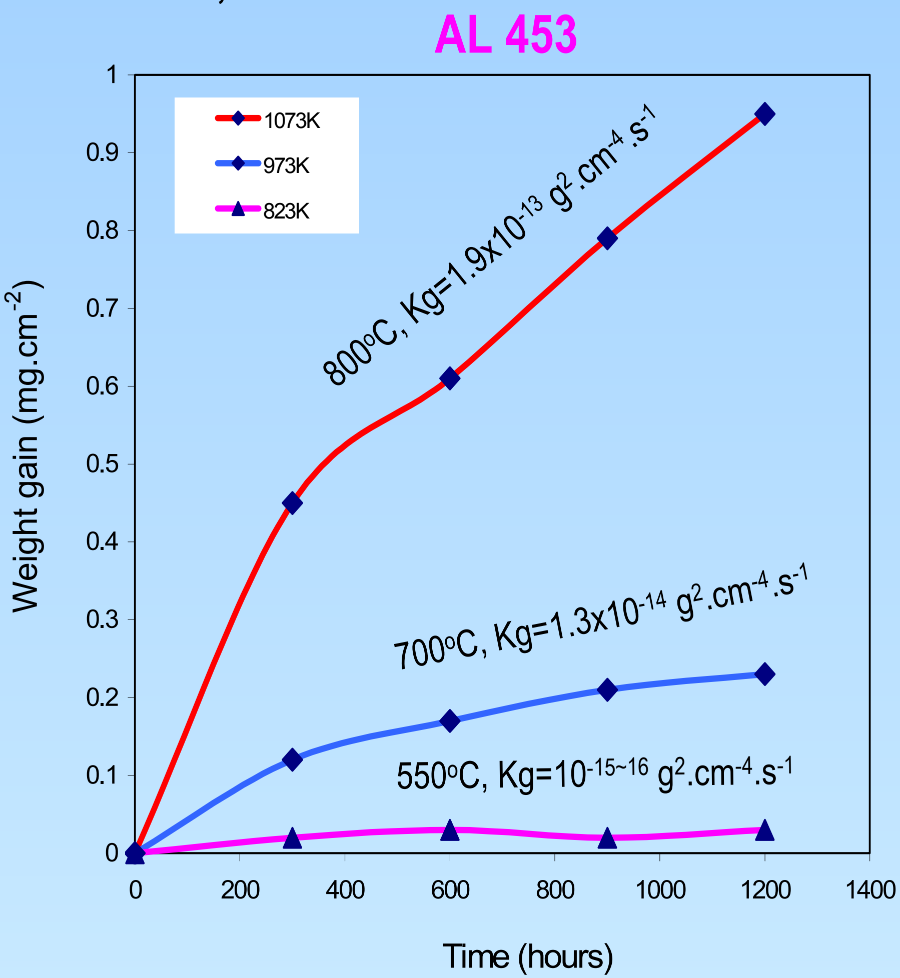
CTE of Ferritic Stainless Steels



Oxidation Resistance of 446 and AL 453

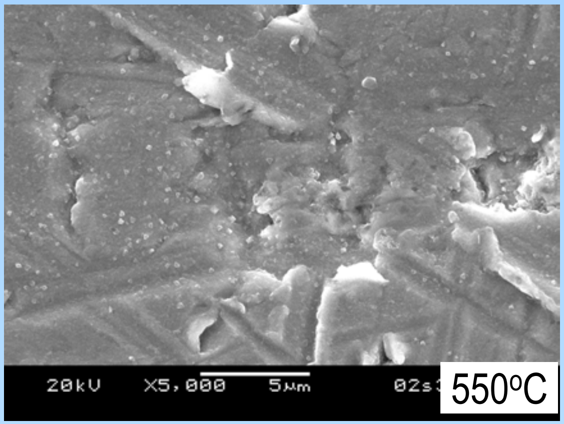
Oxidation resistance was measured as a function of time at 550, 700 and 800°C in air.

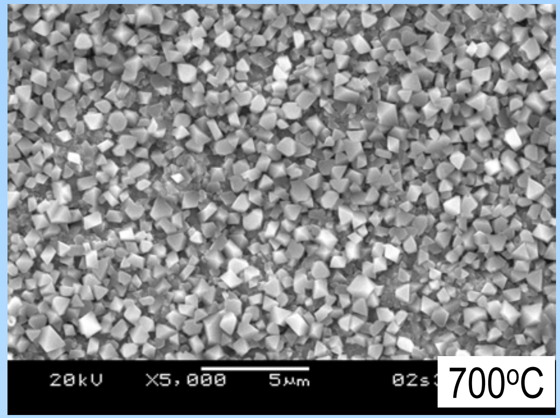


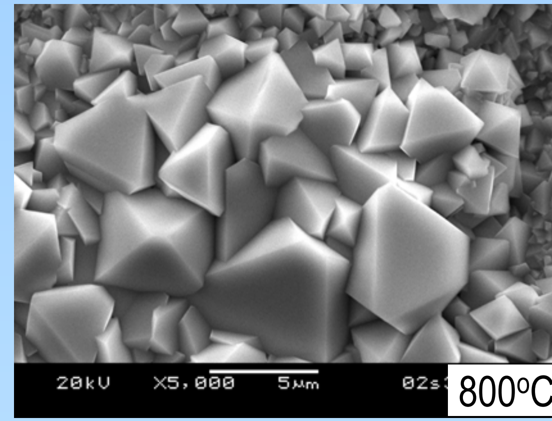


Oxidation Study – Surface Analysis of Scale

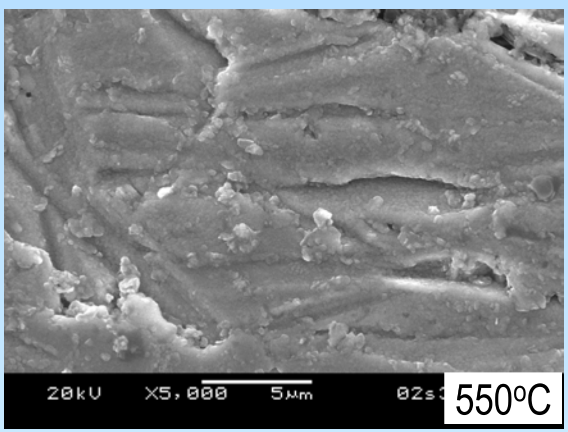
ANSI 446: Preoxidized for 300 hours in air at 550, 700 and 800°C. **XRD – 800°C - $MnCr_2O_4$, Cr_2O_3**

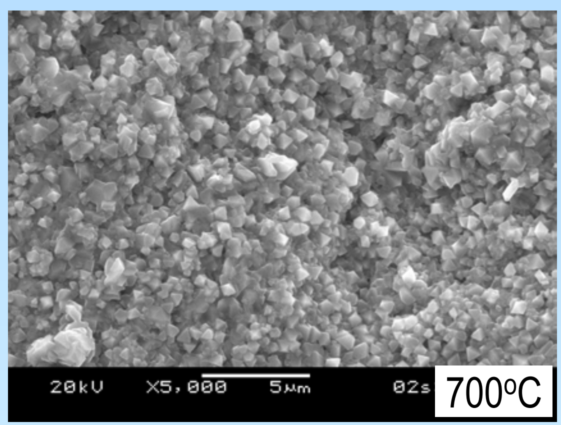


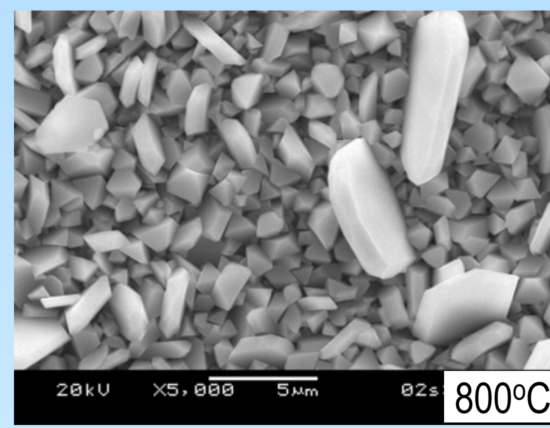




AL 453: Preoxidized for 300 hours in air at 550, 700 and 800°C. **XRD – 800°C – Cr_2O_3, $MnCr_2O_4$**







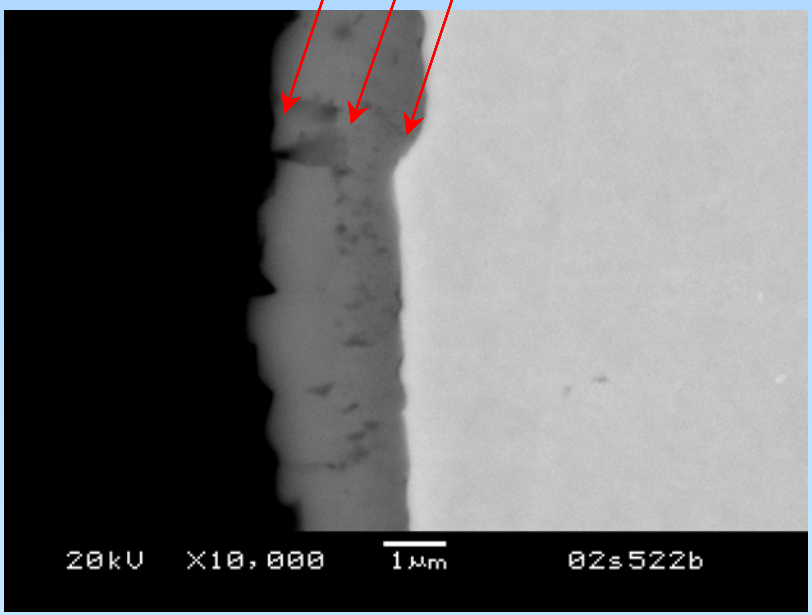
Scale microstructures of 446 and AL 453

Samples were pre-oxidized at 800°C for 300 hours in air.

$(Cr,Mn)_3O_4$, Cr_2O_3

Cr_2O_3, Fe_2O_3, $(Cr,Mn)_3O_4$

Cr_2O_3, $(Cr,Mn)_3O_4$, SiO_2

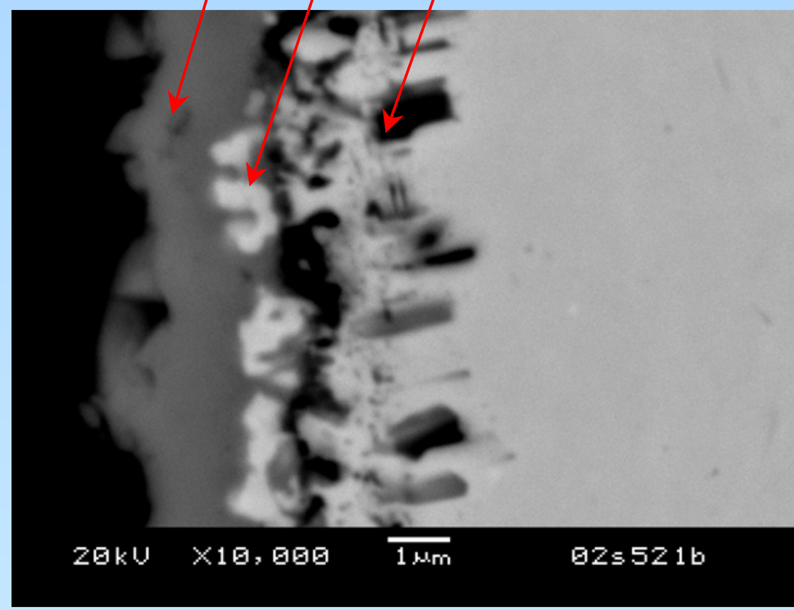


ANSI 446

Cr_2O_3, $(Cr,Mn)_3O_4$

Fe_2O_3, Cr_2O_3, …

Al_2O_3, Cr_2O_3, Fe_2O_3

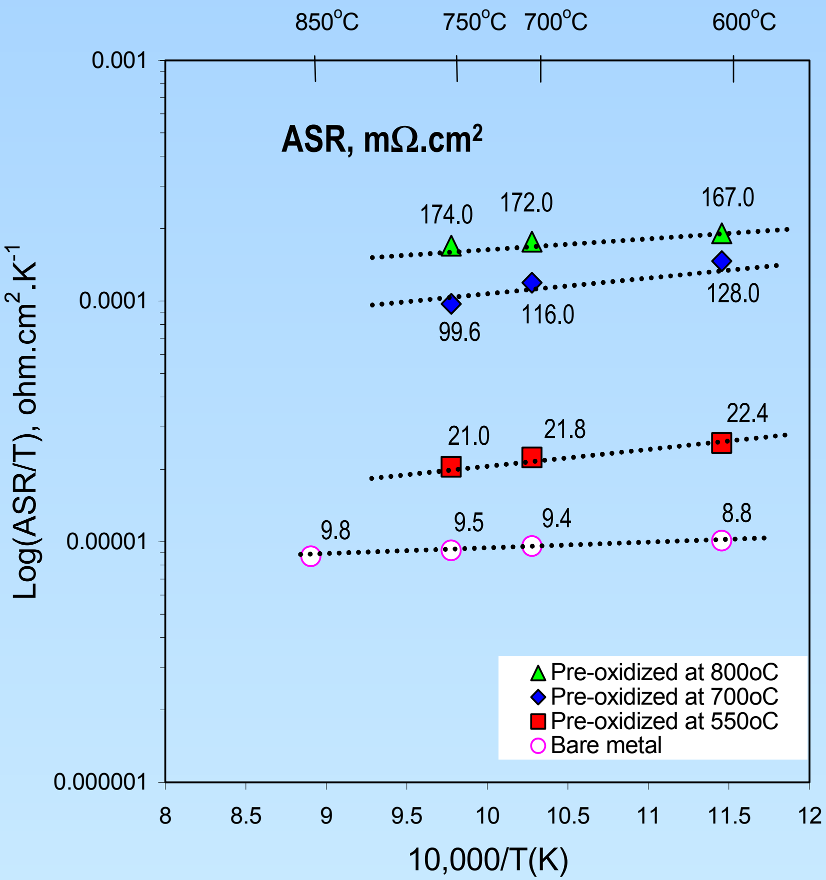


AL 453

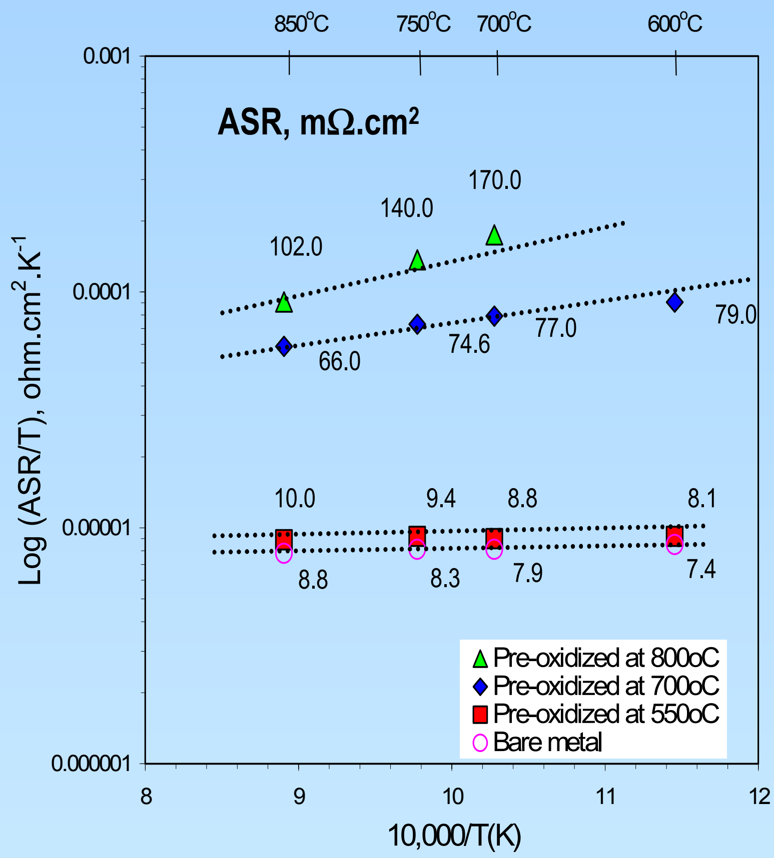
Measured ASR of SS446 and AL 453

ASR was measured as a function of temperature, after heat treatment at 550, 700 and 800°C for 300 hours in air.

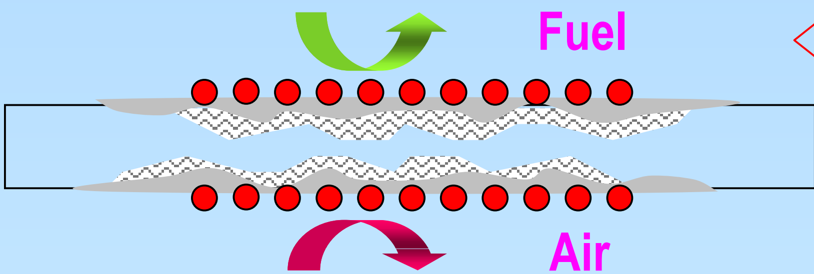
ANSI 446

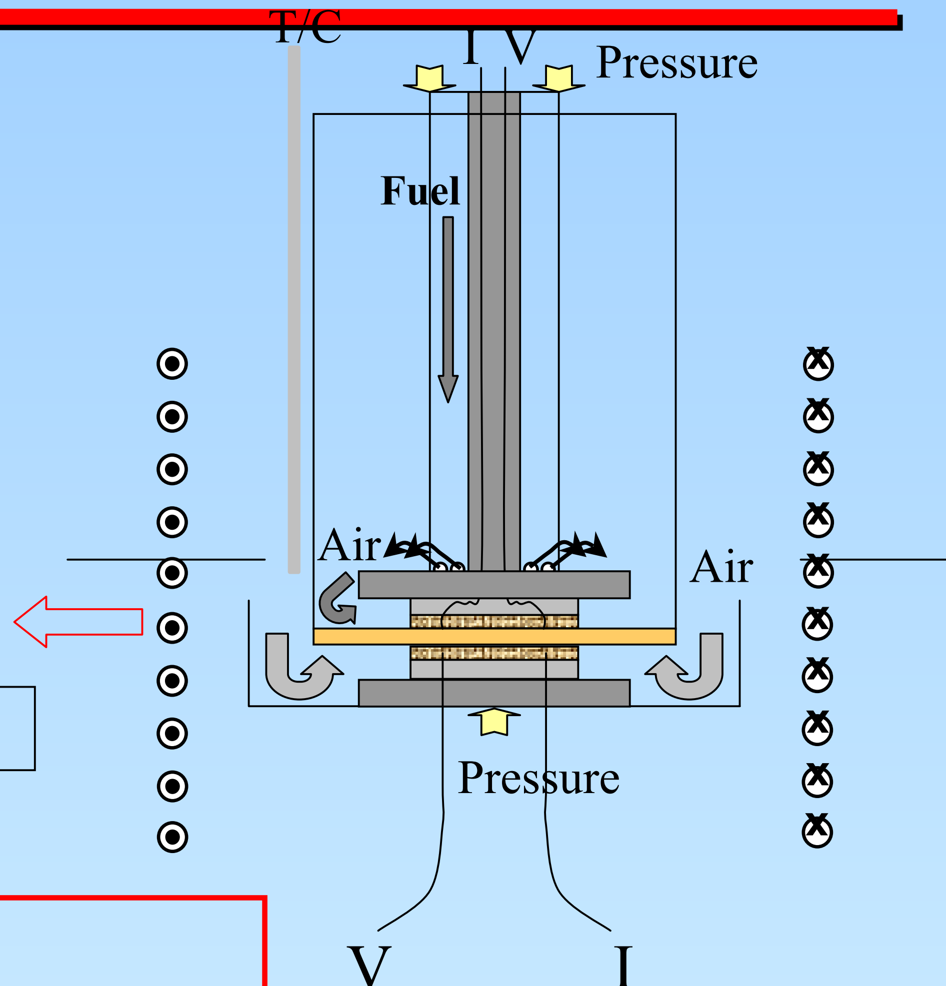


AL 453



2-Atmosphere Oxidation/Conductivity Test





Temperature: R.T. - 1000°C
Current Density: 0 - 4.0 A/cm²
Time at Temperature: Variable
Atmospheres: Air and Various Fuels
Sample Type/Thickness: Variable

Issues / Future Work

- Ferritic stainless steels offer best CTE match to PEN
  - Concerns include thickness and integrity of scale, resistance of scale, volatilization of chromium species, and strength of interfacial bonds (oxide/metal, oxide/glass)
  - May require modification of alloy bulk, modification of alloy surface, and/or application of protective coatings

- Future work:
  - Complete screening study (oxidation, scale resistance)
  - Bulk modification
  - Surface modification (oxide coatings, surface alloying)

SOFC Seal Development

SOFC Seals: Challenges

Requirements for seals in planar SOFC stacks

- High degree of sealing (hermetic or allowable leak rate) under minimal compressive load
- Matching CTE (especially for rigid seals)
- Electrically insulating
- Long-term stability at high T in oxidizing/reducing and humid environments
- Inexpensive
- Thermal cycle stability
- Chemically and physically stable
- Thermal shock resistance

Rigid seals (i.e., glass-ceramic) require very close TEC matching of all stack components to minimize stresses; Compressive seals may relax these requirements somewhat by providing compliance in "x-y" plane.

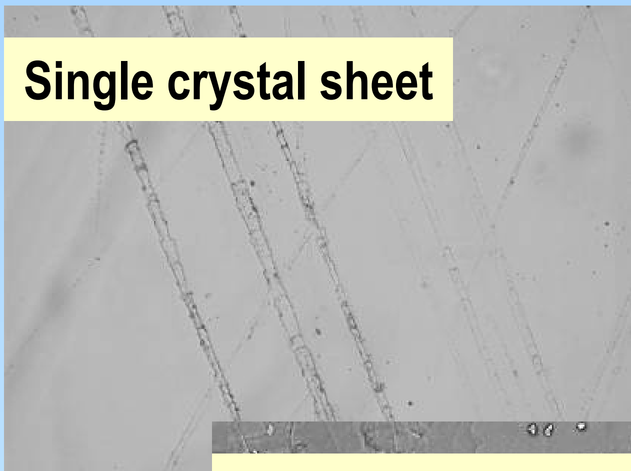
Compressive seals for SOFC

- Objective: 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.

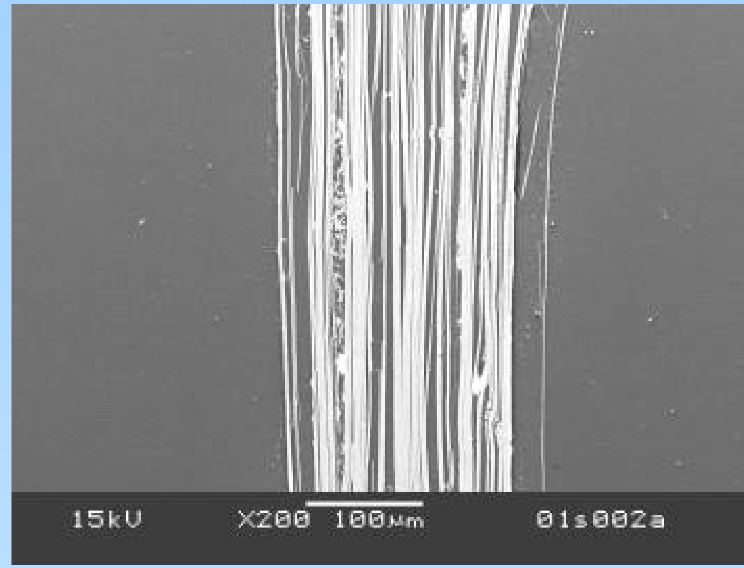
- Approach:
  - Evaluate "hybrid" seal concept (combination of mica and compliant material, e.g., glass)
  - Leak rate measurements on simulated SOFC seals
  - Post-test evaluation (SEM)

Basis of seal: Mica

- Muscovite: $KAl_2 (AlSi_3O_{10}) (F,OH)_2$
- Phlogopite: $KMg_3(AlSi_3O_{10})(OH)_2$



Single crystal sheet

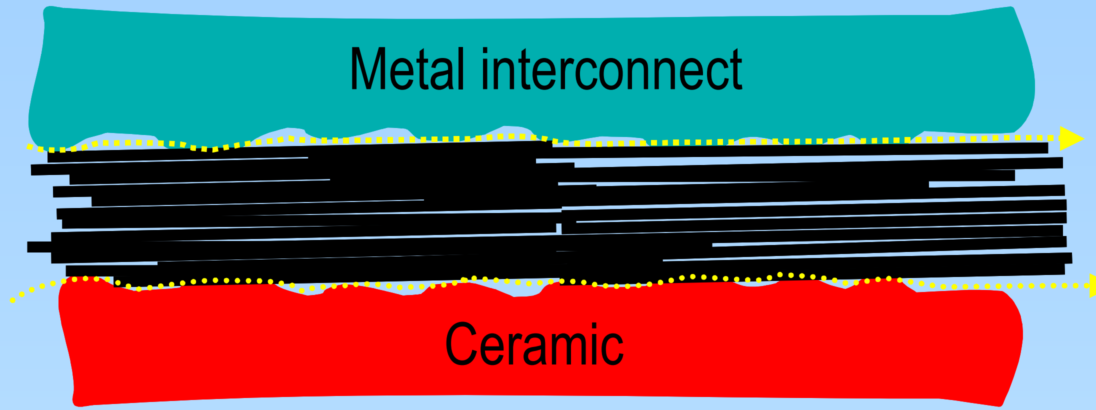


Layered silicate structure

Paper: Discrete flakes with binders

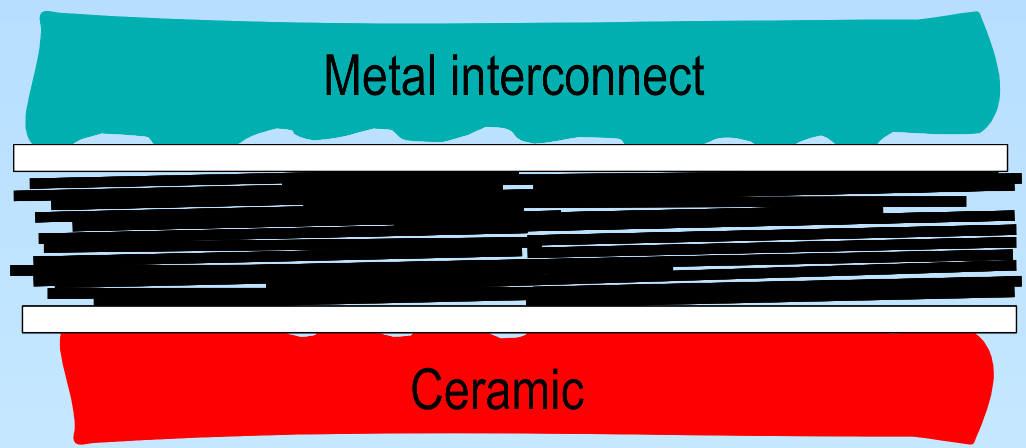
Concept of hybrid compressive seal

Simple mica layer yields excessively high leak rates through interfaces

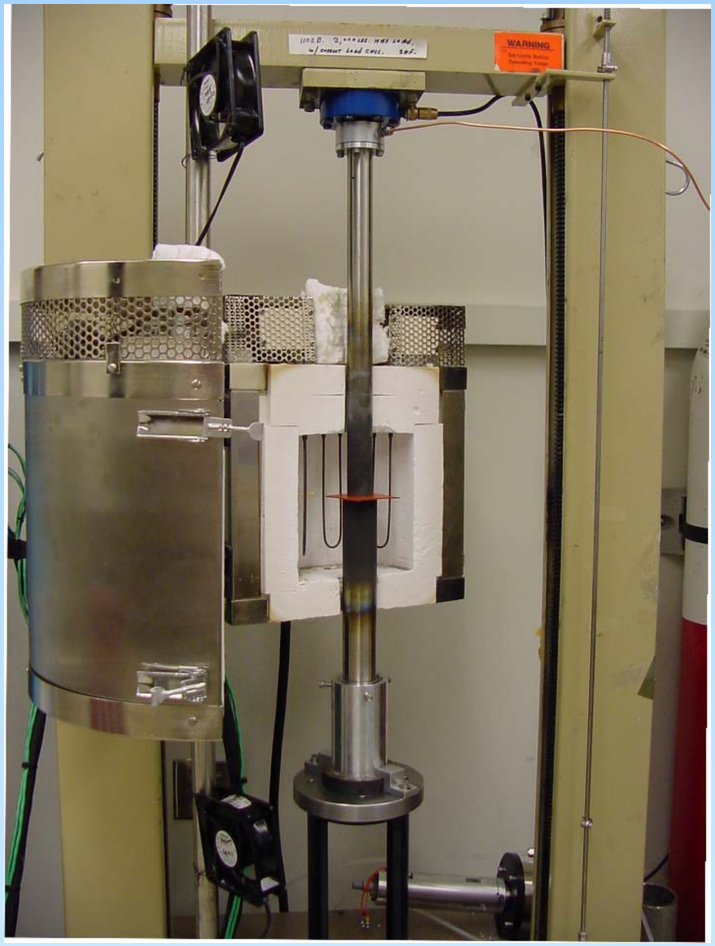


Mica: compliant in 2-D (x-y plane)

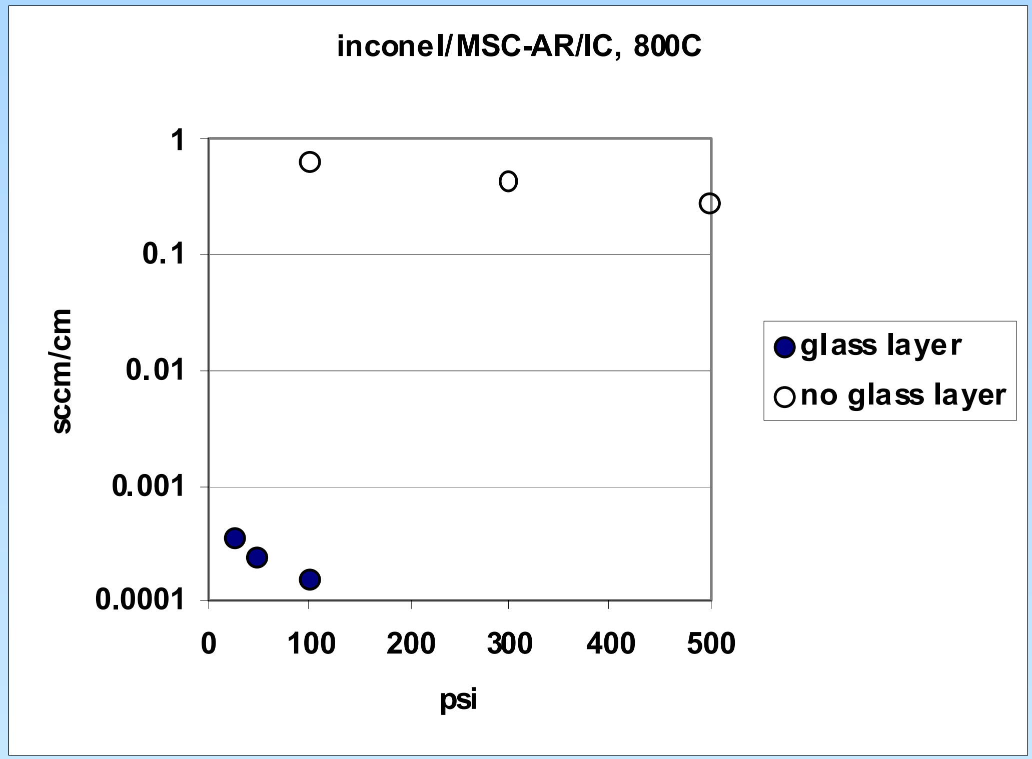
Metal/glass interlayer: compliant in 3-D; seals off interfaces



Reduction of leak rate by insertion of glass interlayers



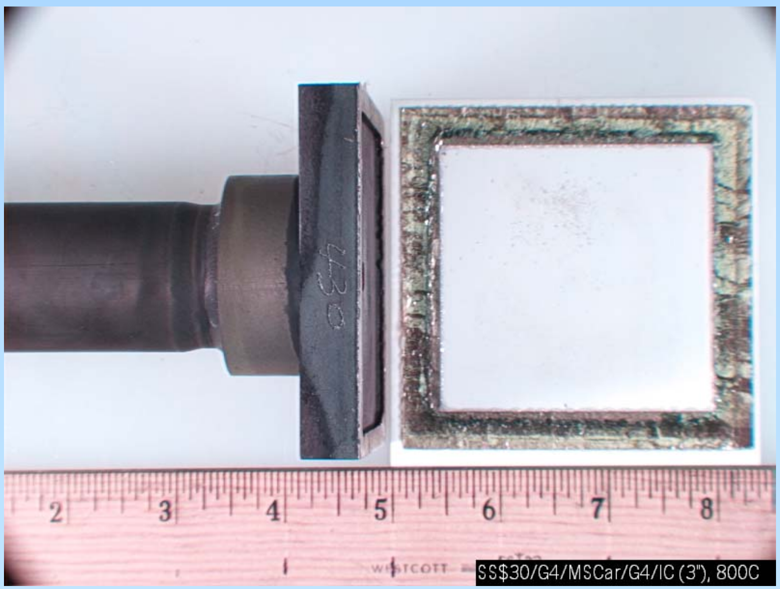
Orders of magnitude reduction in leak rate (vs. plain mica) for single crystal type mica in hybrid design with glass interlayers

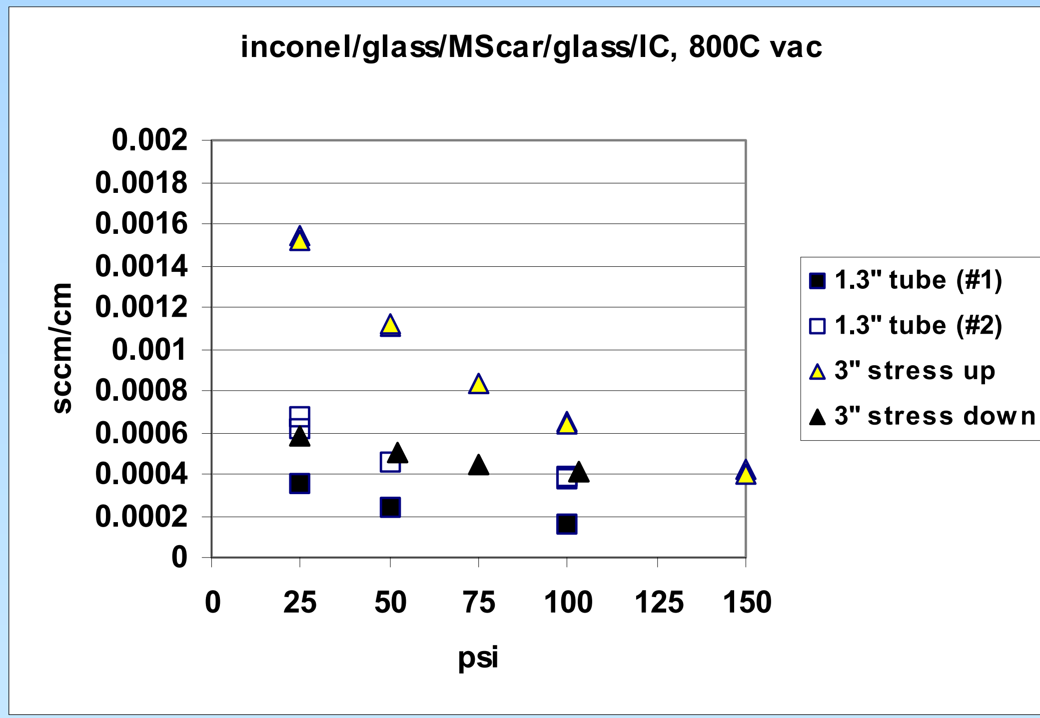


Results for larger (3" square) compressive seal test

Inconel/glass/MSC/glass/alumina, 800^{o}C air

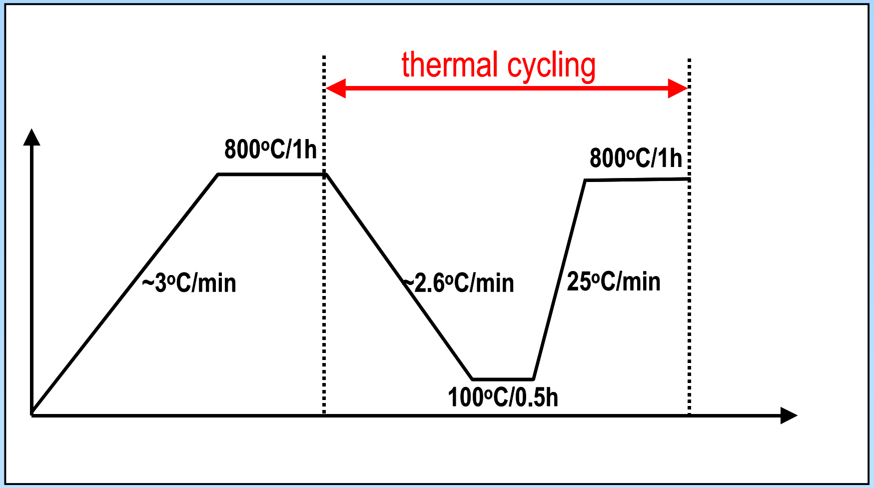
Consistent results with small (1.3") sample

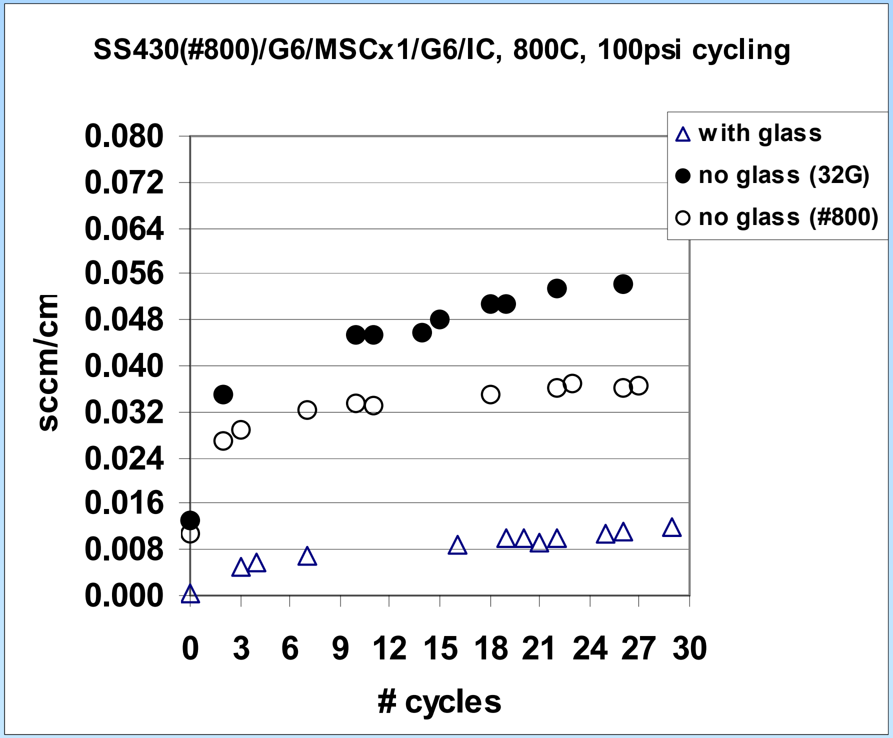




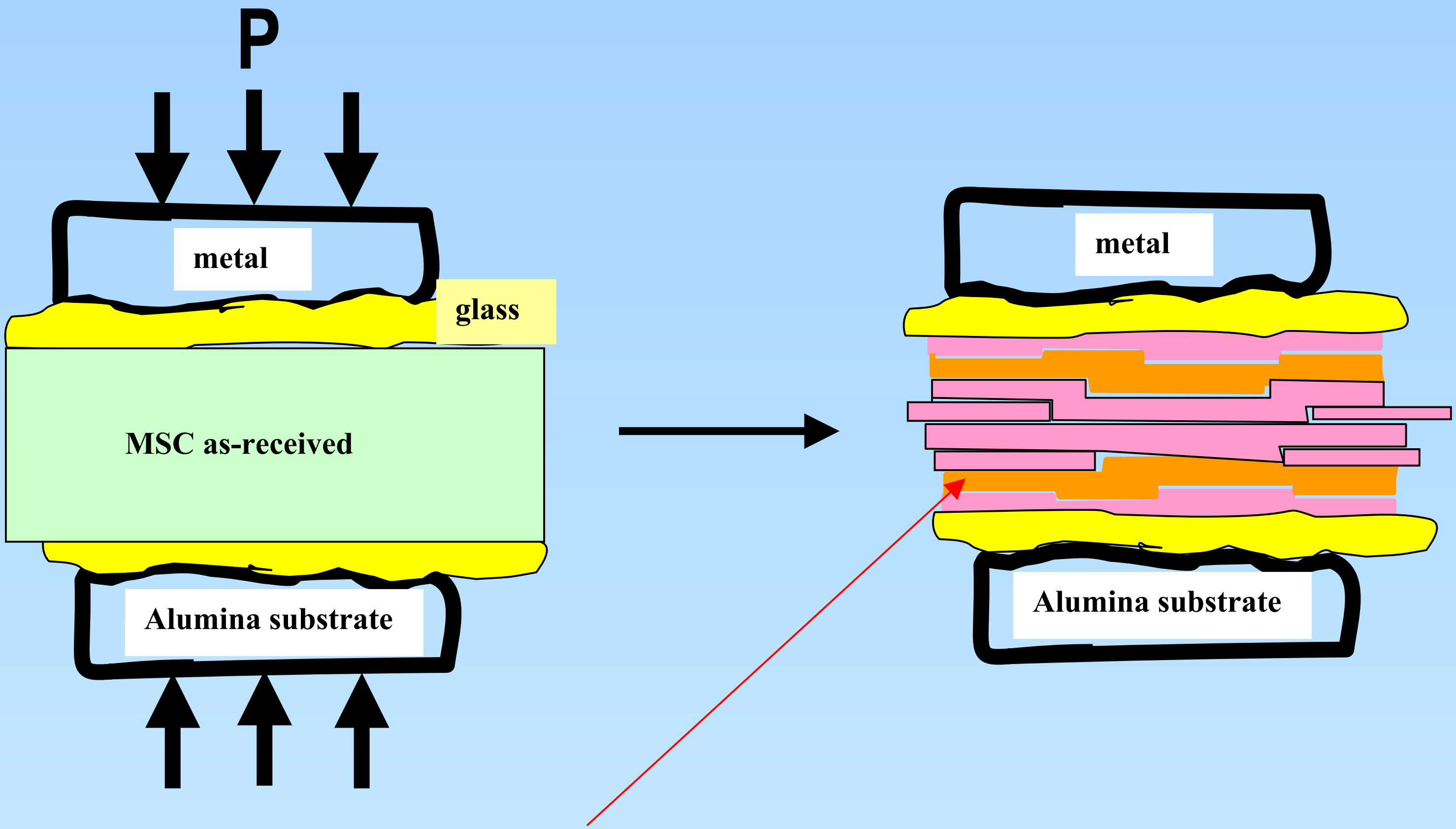
Thermal cycling of hybrid seal

Abrupt increase in leak rate during initial cycles –
Modest increase in leak rate subsequently





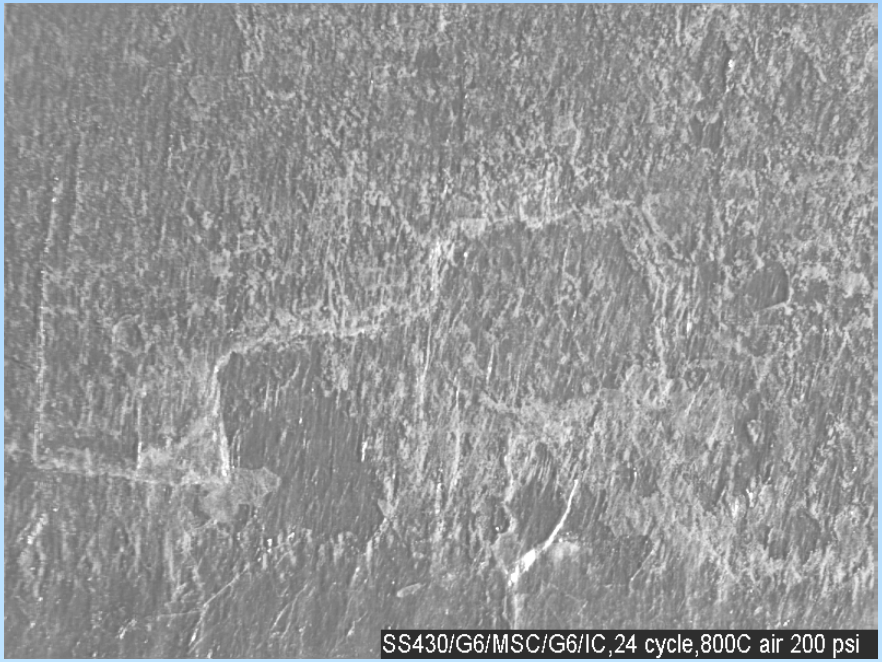
Thermal cycling degradation with hybrid seals



Frictional damage is limited to the first several sub-layers below glass/mica interface; CTE of mica (~6.9 ppm/K) substantially less than CTE of SS or glass (10-13 ppm/K)

Degradation to mica after thermal cycling

MSC after 24 thermal cycling to 800ºC in air (applied stress:100 psi (SS430/G6/MSC-ar/G6/IC))



■Future Work: Extend leak rate experiments from coupon testing in air to testing of SOFC single cells under typical operating conditions.

- Leak rate measurements
- Effects of leaks on SOFC OCV and I-V behavior

Summary / Status

- Cathode Development
  - LSF cathodes exhibit low polarization losses, stable performance in anode-supported cell tests
- Anode Development
  - La-Sr-Ti-Ce oxide anodes exhibit redox and sulfur tolerance, and low anodic polarization losses
- Interconnect Development
  - Database of high temperature alloy properties completed / screen testing in progress
- Seal Development
  - Glass/mica “hybrid” compressive seals exhibit very low leak rates under moderate applied loads (25-100 psi)