SECA Core Technology Program: Materials Development at PNNL

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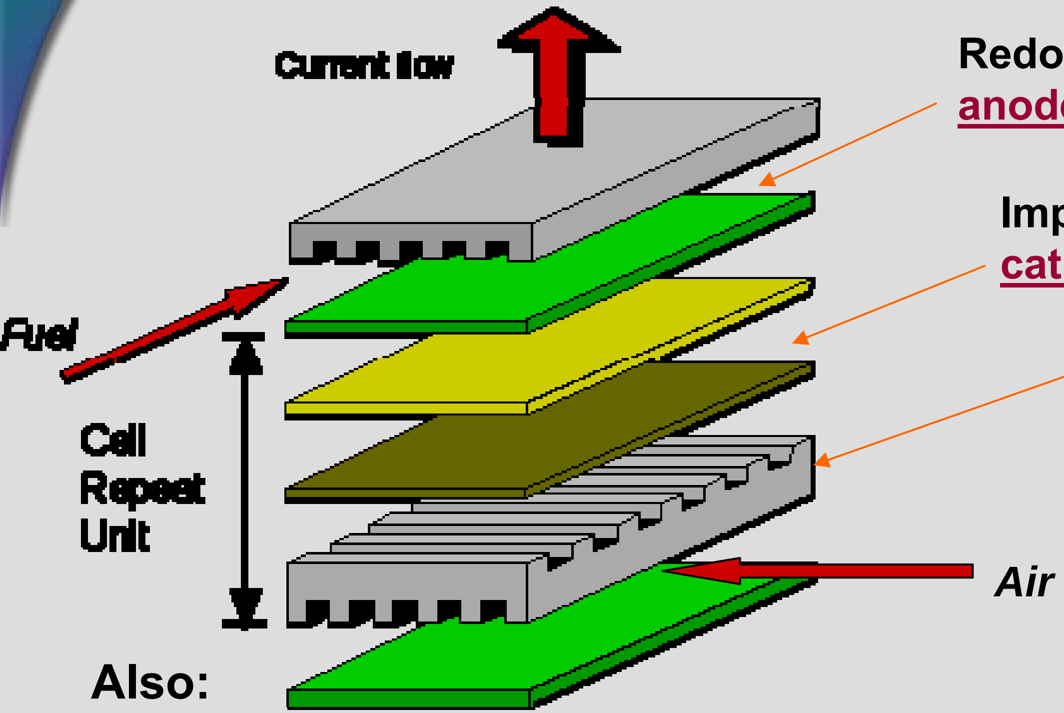
Outline

- SOFC Materials Development Activities Overview / Technical Issues Being Addressed
- 5 Development Topics
  - Results & Discussion
  - Summary
  - Future Work
- Acknowledgements

SECA CTP at PNNL: SOFC Materials Development
“Technical Issues Addressed”



Redox-, hydrocarbon-, and sulfur-tolerant anode materials

Improved intermediate temperature cathode materials - (LSM, LSCF)

Stable metallic interconnect materials - Performance evaluation (screen testing); Bulk/surface modification for enhanced performance

Also:

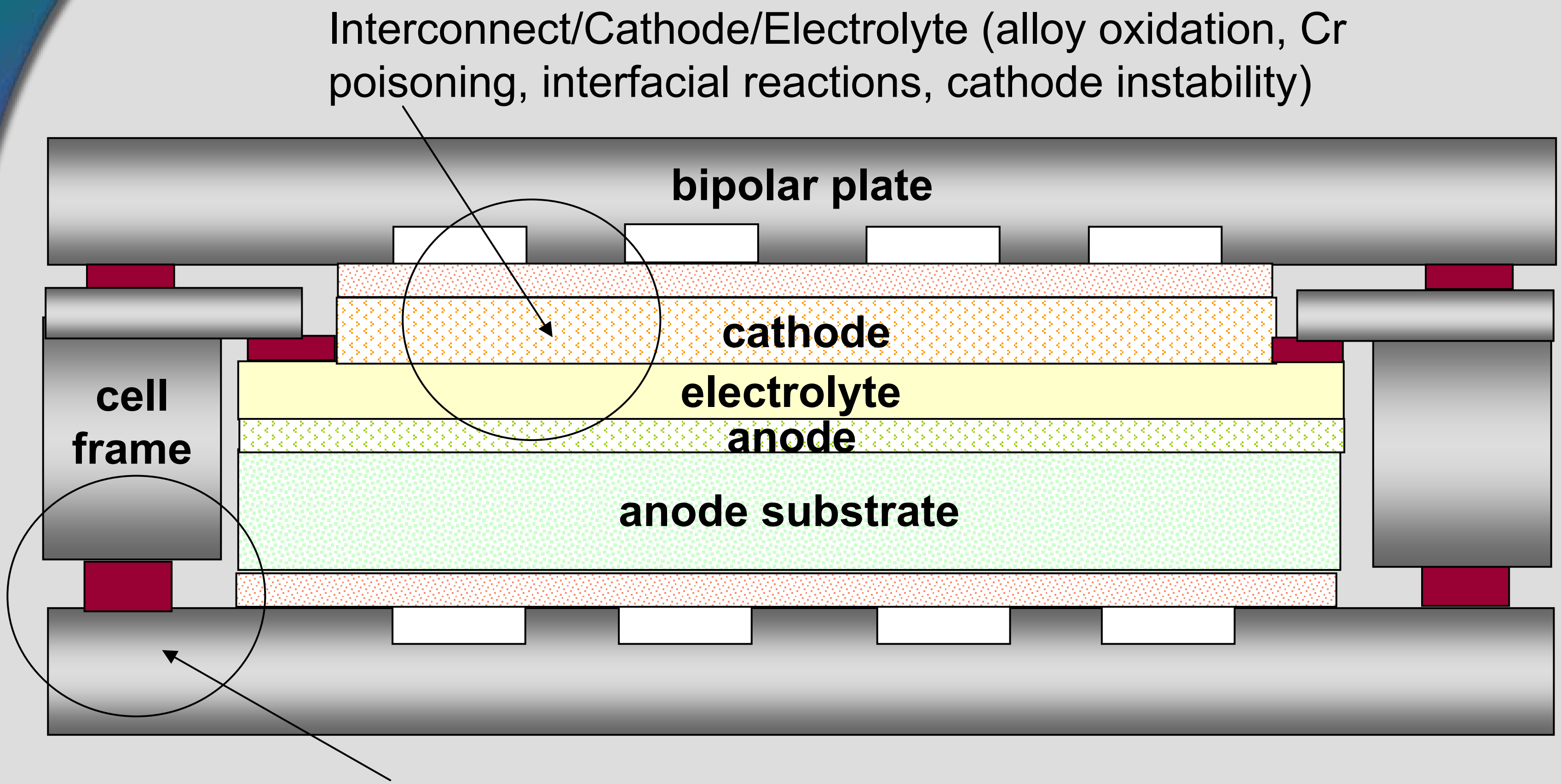
Stable, low resistance contact materials – electrode/interconnect interfaces

Stable, thermally cyclable seals (glass-ceramic, reactive air brazes, compressive, compliant)

Cost-effective fabrication techniques

Understanding/eliminating degradation mechanisms

Degradation Regions Addressed in Presentation



Interconnect/Cathode/Electrolyte (alloy oxidation, Cr poisoning, interfacial reactions, cathode instability)

Seal/Interconnect/Seal Interface (CTE-related stresses, interfacial reactions, seal volatility)

Accomplishments

- Initiated joint study on Cr degradation effects on LSM cathodes
- Characterized behavior of LSM and LSCF cathodes
- Studied interconnect alloy behavior in SOFC environment
- Developed and tested protective coatings for alloys
- Initiated development of “refractory” glass-ceramic seals

Presentation Topics

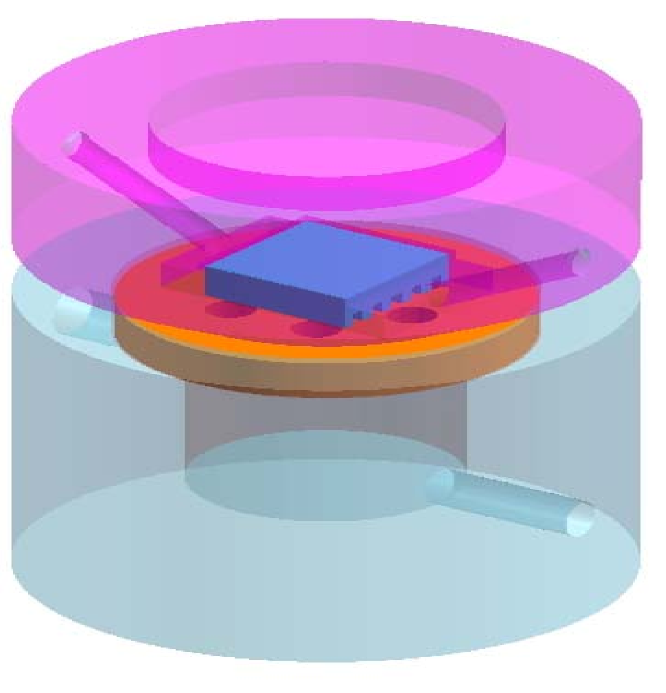
- Effects of Cr on Cathode Performance (Joint study w/ GE Energy and ANL)
- Degradation Mechanisms in Mixed-Conducting Cathode Materials
- Environmental Effects of Interconnect Oxidation
- Protective Coatings for Interconnects
- “Refractory” Glass-Ceramic Seals

Effects of Cr on Cathode Performance

- Objective: To quantitatively assess, under realistic conditions, effects of Cr species on cathode performance
  - Determine under what conditions, if any, chromium transport has a detrimental effect on LSM-based cathodes
  - Determine if the observed Cr transport is predominantly vapor phase, solid state or both
  - Determine Cr compounds formed at cathode/electrolyte interface and cathode/interconnect interface regions
  - Correlate Cr observed at interfaces vs. observed performance degradation (if any)

Effects of Cr on Cathode Performance

- **Approach: Collaboration with GE Energy & ANL**
- **Test Conditions**
  - InDEC cells w/ LSM-YSZ cathodes
    - 700, 800ºC; 1000 hours; realistic airflow conditions
  - Cr sources evaluated:
    - E-brite flow field (ANL, GE)
    - Vapor phase delivered from upstream w/ Au flow field (PNNL)
    - Transpiration experiments (PNNL)
- Further discussion in next presentation (Atul Verma from GE Energy)



Presentation Topics

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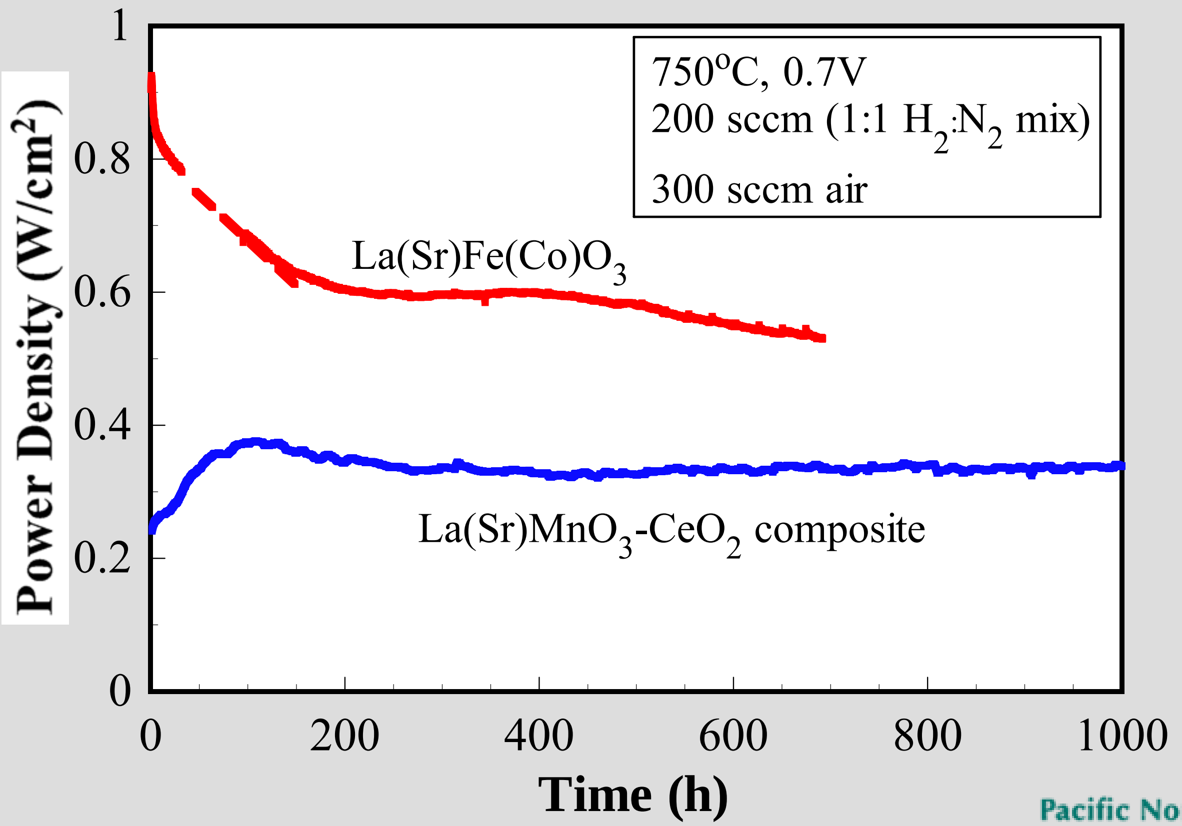
Degradation Mechanisms in Mixed-Conducting Cathode Materials

Experimental Approach

- Long-term cell tests (750°C/0.7V) for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF-6428) cathodes on anode-supported YSZ cells.
- Standard potentio-static/dynamic analysis (0.7 V, 750°C), and full cell impedance spectroscopy to separate ohmic and non-ohmic degradation.
- Processing and testing variables affecting degradation.
  - Cathode calcination temperature – phase homogeneity.
  - Constant voltage or OCV hold.
  - Cathode-interconnect contact pastes
- Pre- and post-test analysis.
  - SEM, XPS, EDS, TEM, adhesion

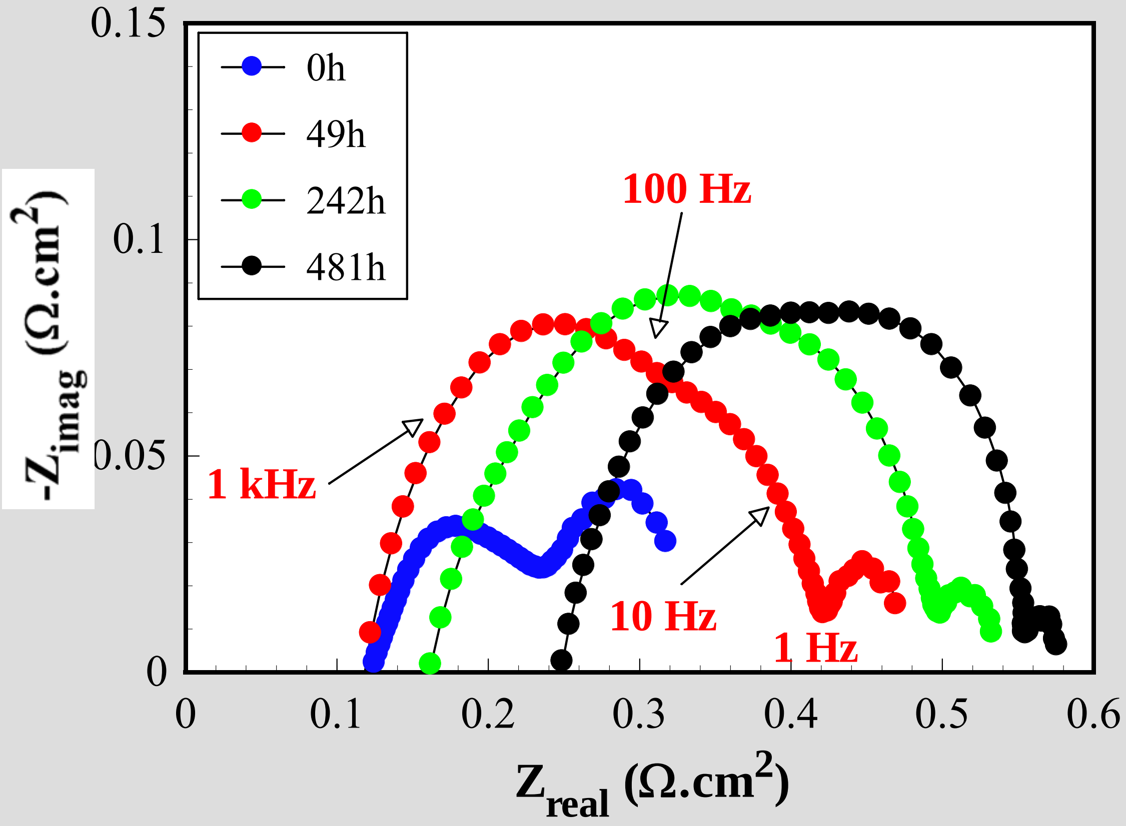
LSM-20 vs. LSCF-6428 - Power Density and Long-Term Stability

- LSM-20/SDC-20 composite cathode is relatively stable over >1000 hour period. LSCF offers significantly higher power densities but exhibits substantial degradation.



(Tested in absence of Cr)

LSCF-6428 – *Long-Term Impedance*



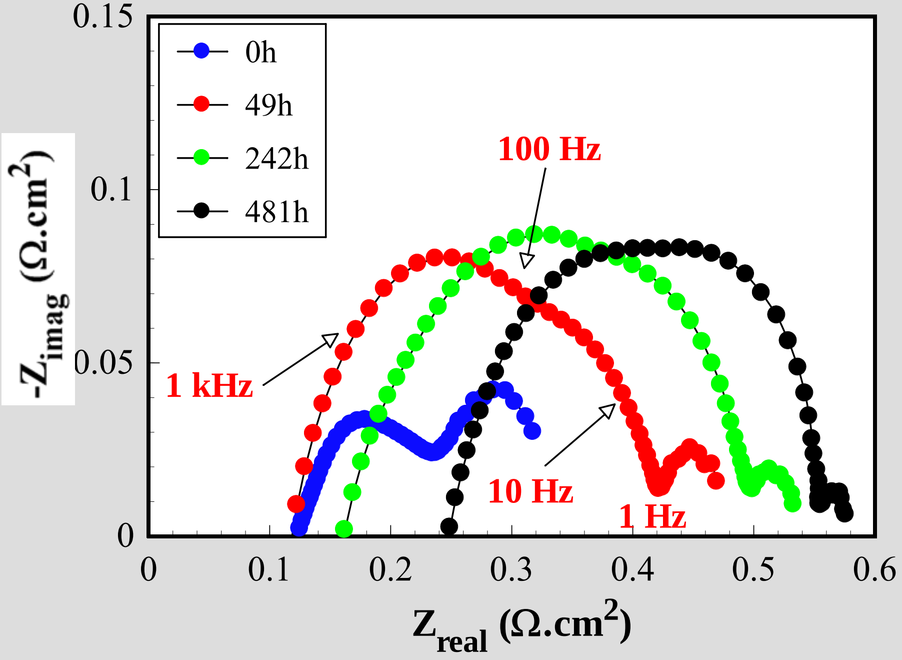
- Initial degradation attributed to substantial increase in cathode polarization (>1Hz).
- After 50-100 hours degradation predominantly associated with increased ohmic resistance.

Possible Sources of Degradation – *Non-Ohmic*

- ***Increased Cathode Polarization***
  - Coarsening of cathode microstructure
    - loss of active electrochemical reaction area and/or impeded gas flow
    - no evidence from standard SEM but may be too subtle to detect; FE-SEM required.
  - Phase segregation within cathode
    - changes in defect chemistry, and electrochemical activity (e.g. Sr precipitation leading to reduced acceptor dopant concentration).
  - Interdiffusion at interfaces
    - forming solid solutions with altered defect chemistry.

Possible Sources of Degradation - *Ohmic*

- To attribute the increased ohmic resistance to a reduction in bulk electronic conductivity of an individual layer:
  - LSCF ➔ 10^3 decrease
  - Anode ➔ 10^2 decrease
  - SDC or YSZ ➔ 10^1 decrease

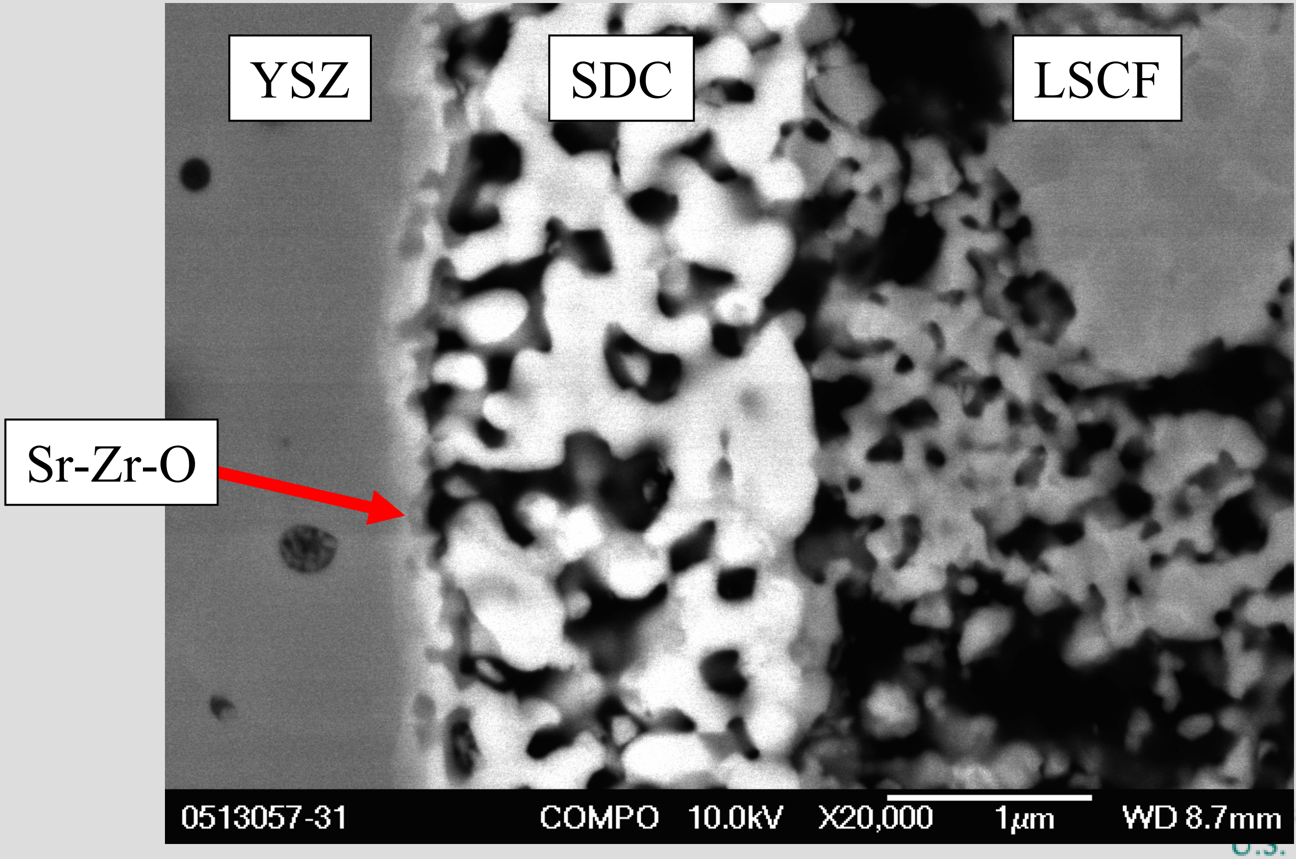


- Delamination at interfaces
  - Loss of contact area

- Formation of resistive interfacial phases ➔ 5 nm reaction layer with conductivity 10^{-5} S/cm would account for the observed increase in ohmic resistance.

LSCF Degradation – *$SrZrO_3$ Formation?*

- Sr-Zr-O diffusion (s_{pure} ~10^{-6} S/cm at 750^{o}C) layers are sometimes observed after sintering of the cathode, but the layers do not discernibly increase in thickness during testing, and may even disappear.



LSCF Degradation – *XPS (Sr Enrichment)*

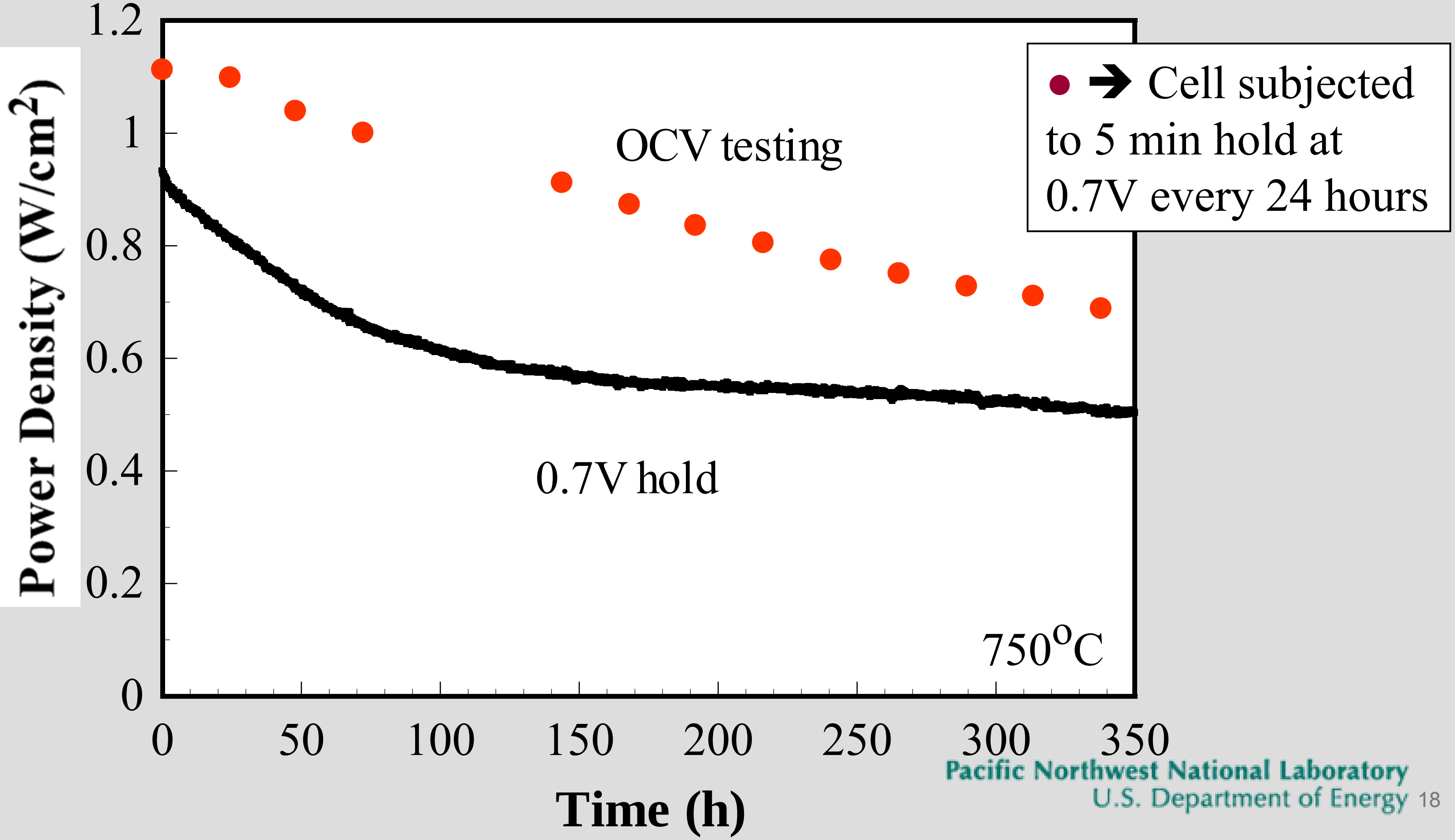
- Detailed microscopy of pre- and post-tested samples is being conducted but to date indicates no discernible changes in microstructure to account for the observed degradation.
- However, initial XPS analysis of pre-and post-tested samples suggests increased Sr segregation at the cathode-current collector interface after cell operation.
  - *For the pre-tested sample* ➔ Sr / (La+Sr) ≈ 0.5 (should be 0.4)
    - Some Sr enrichment during cathode fabrication
  - *For the post-tested sample* ➔ Sr / (La+Sr) ≈ 0.65 with regions up to 0.9
    - Extensive Sr enrichment during cell operation
  - Pure SrO conductivity at 750°C ~5 x 10^{-5} S/cm (W.D. Copeland, *J. Phys. Chem. Solids* 29 [1968] 313)➔ 15-20 nm layer would account for observed ohmic increase.

LSCF Degradation – *Influence of Processing and Test Variables*

- Variables studied to date:
  - *Calcination temperature of cathode powder* – higher calcination temperatures improve phase homogeneity but provide no benefit to long-term stability.
  - *Thickness of ceria barrier layer* – thicker interlayers prevent (or reduce) $SrZrO_3$ formation but have no effect on long-term degradation.
  - *Constant voltage (0.7V) or OCV* – cell continues to degrade in non-operation mode.
  - *Cathode-interconnect contact* – manipulating this interface appears to have the most significant effect on long-term stability.

LSCF Degradation at Zero Current

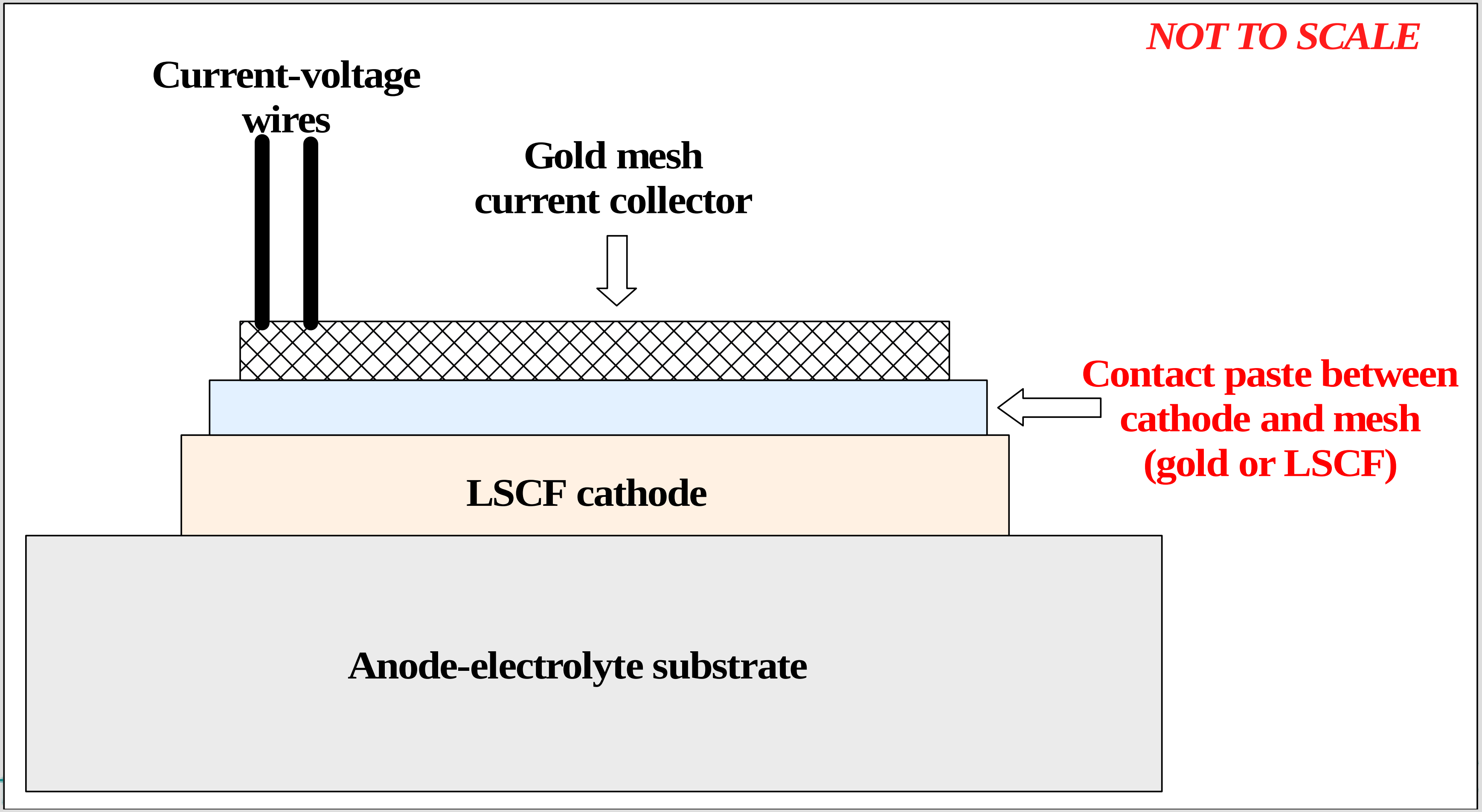
- Testing at zero current (with intermittent I-V/impedance measurement) indicates cell degradation ➔ thermally induced degradation.



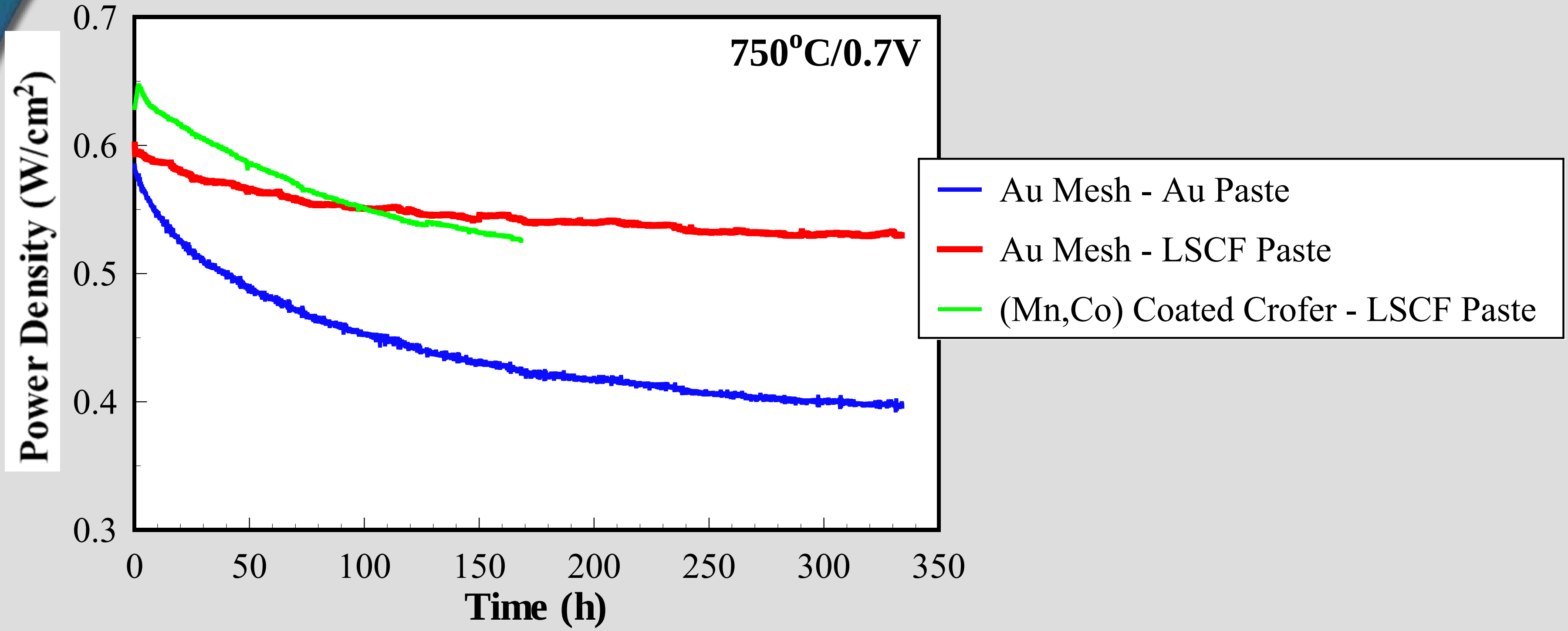
● ➔ Cell subjected to 5 min hold at 0.7V every 24 hours

Cathode Current Collector

- Initial data indicates that changing the contact paste between the LSCF cathode and gold mesh current collector has the most significant effect on cell stability.

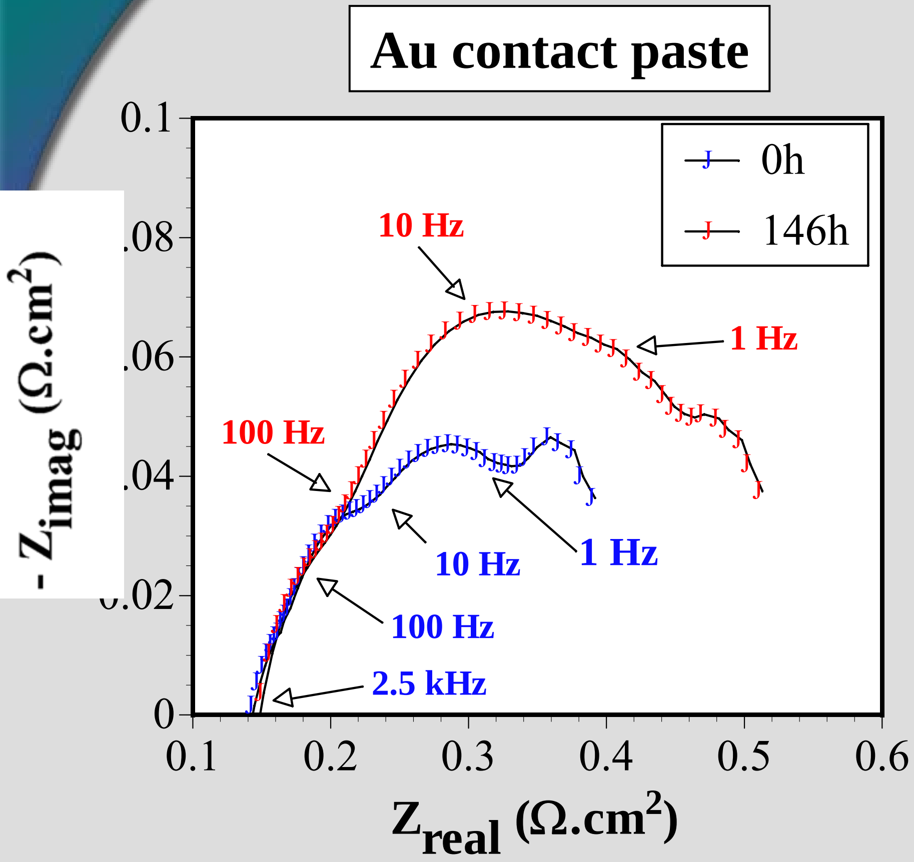


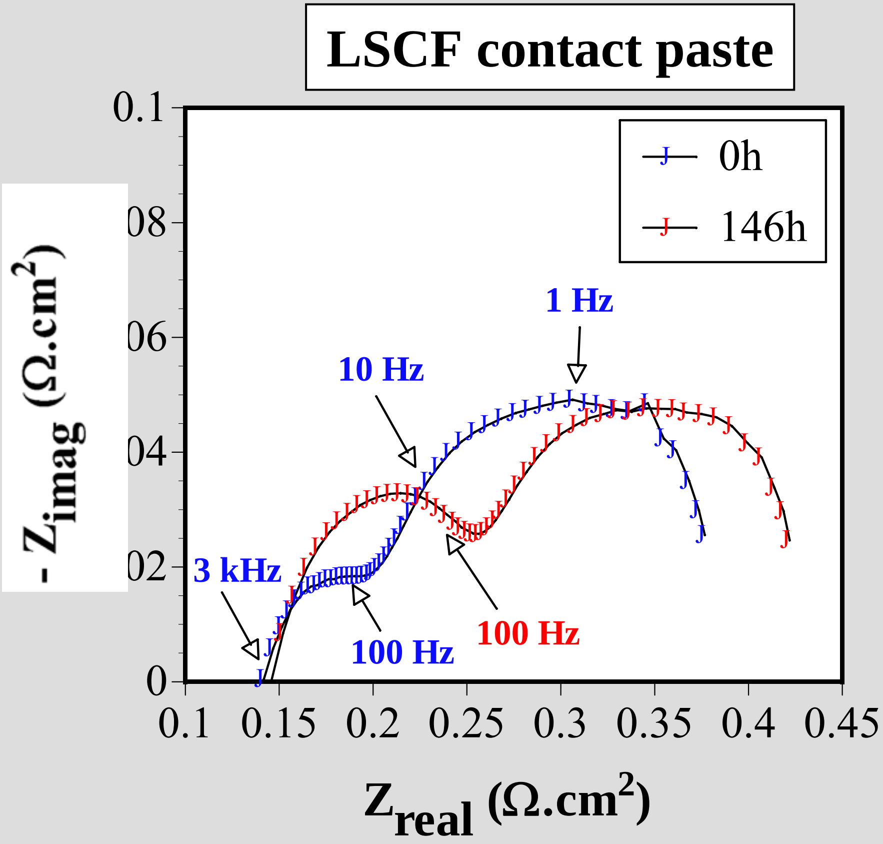
Effects of Cathode Current Collector



Contact Paste	**Degradation (%/hour)**		
	0 - 100 h	100 - 200 h	200+ h
Au	0.2	0.08	0.04
LSCF	0.07	0.02	<0.01

Cathode Current Collector – *Effect on Stability*


Au contact paste


LSCF contact paste

- Similar ohmic resistance in both cases; for Au paste, non-ohmic degradation mechanism(s) correlated with frequencies < 100 Hz; for LSCF, with frequencies > 100 Hz
- Phenomena are reproducible

Summary

- LSCF-6428 offers higher power density than LSM but exhibits degradation over time.
  - Both ohmic and non-ohmic factors associated with observed degradation in performance
  - Degradation mechanisms may include the formation of SrO at the cathode surface.
  - Manipulation of the cathode-current collector interface results in significant changes in stability ➔ reason(s) not yet established.

Future Work

- Complete Cr degradation study (with GE Energy and ANL)
- Complete investigation of LSCF degradation mechanisms, considering the effects of:
  - Materials - Sr content, A-site deficiency, acceptor dopant (Sr or Ca).
  - Processing – cathode firing temperature, cathode and ceria thickness.
  - Testing – temperature, air or O_2 cathode gas, cathode-current collector configuration.
- Evaluate dependence of performance of LSM-based cathodes on various composition/processing parameters
- Optimize LSM-based cathodes for higher stable performance

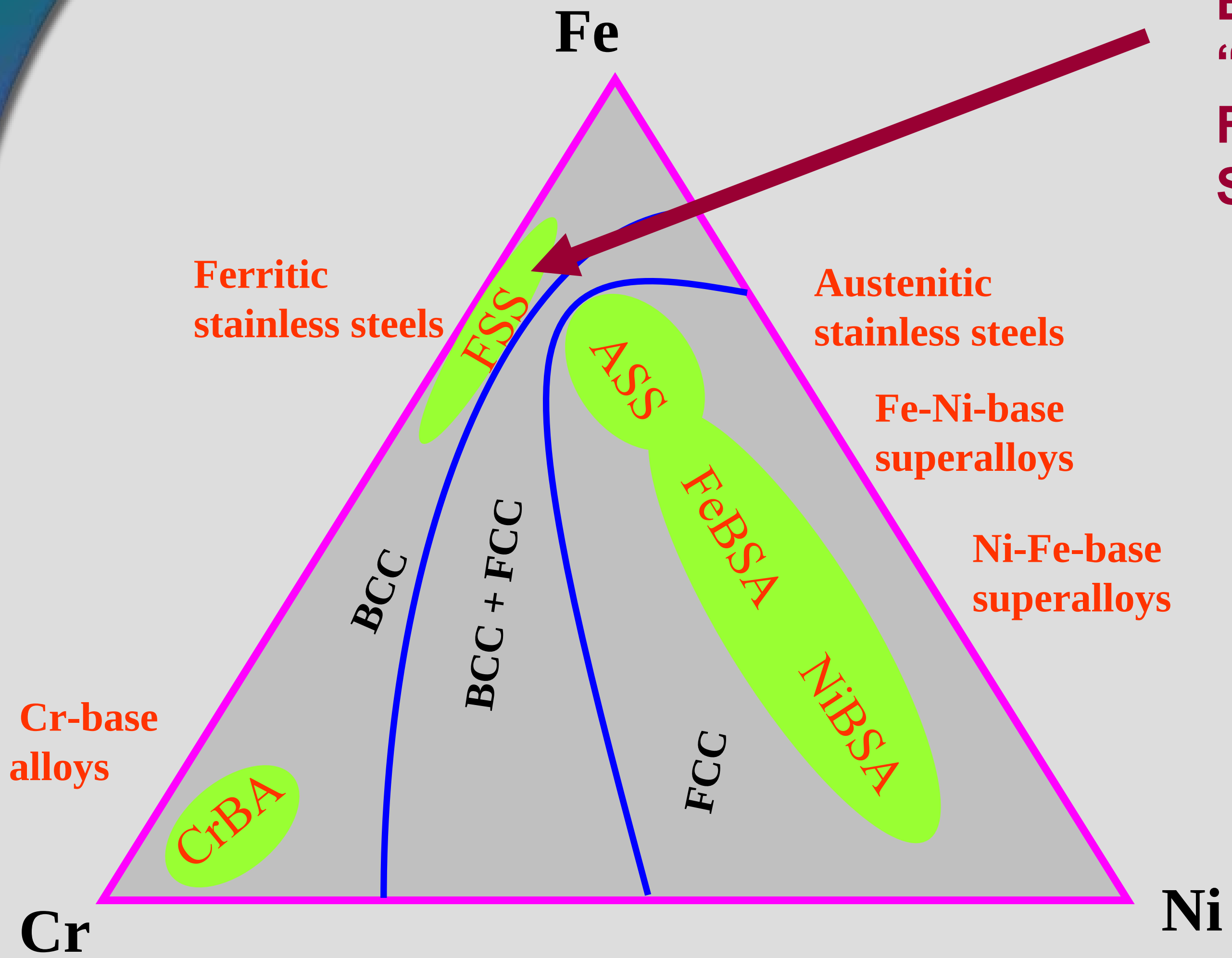
Presentation Topics

- Effects of Cr on Cathode Performance (Joint study w/ GE Energy and ANL)
- Degradation Mechanisms in Mixed-Conducting Cathode Materials
- Environmental Effects on Interconnect Oxidation
- Protective Coatings for Interconnects
- "Refractory" Glass-Ceramic Seals

Environmental Effects on Interconnect Oxidation

- Objective: To evaluate and understand oxidation and corrosion behavior of SOFC interconnect alloys under simulated stack operating conditions
- Approach:
  - Conduct oxidation tests of selected alloys under single and dual (oxidizing/reducing) environments representative of SOFC interconnection exposure conditions
  - Examine alloy and oxide scale chemistry and structure using metallography, SEM, XRD, XPS, EDS etc

Potential Candidate Alloy Systems



Emphasis on "Chromia-forming" Ferritic Stainless Steels:

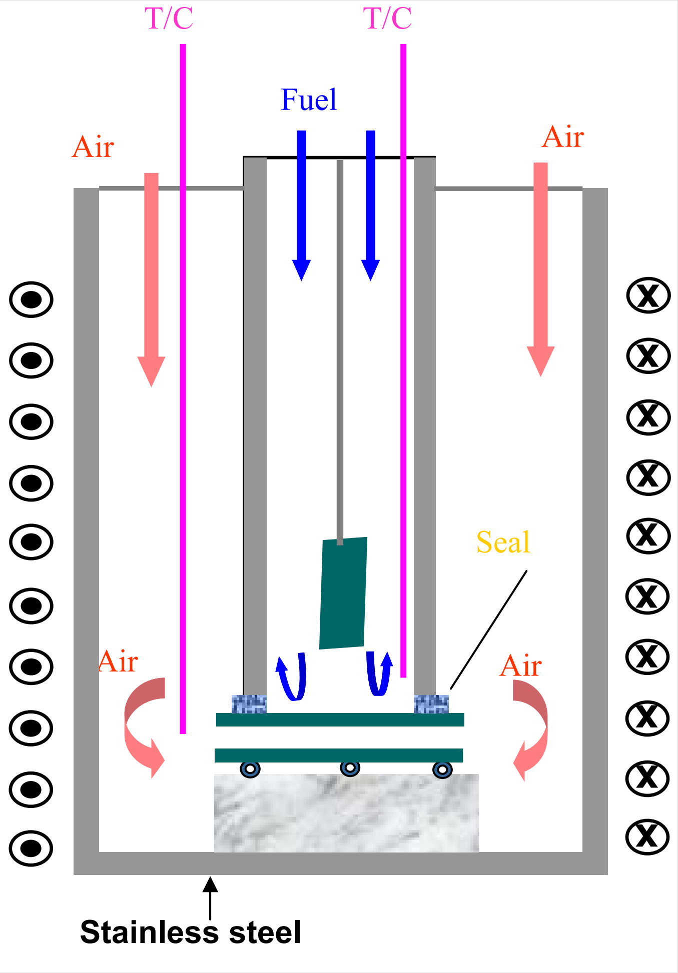
- CTE match
- Conductive, protective oxide scale
- low cost
- ease of fabrication

- **Ni-base superalloys also of interest**

Also: Co-base superalloys

Yang, Weil, Paxton, Stevenson, J. Electrochem. Soc., 150, A1188 (2003).

Dual Atmosphere Study: Experimental Approach:



Materials studied:

FeSS
- E-brite-27%Cr
- Crofer22-22%Cr
- AISI430-17%Cr

NiBA
- Haynes 230-22%Cr
- Hastelloy S-17%Cr
- Haynes 242-9%Cr

Ag, Ni

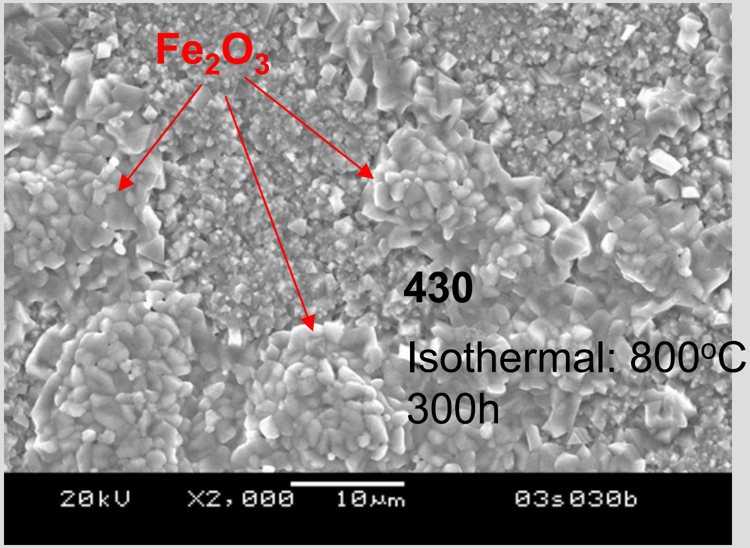
Variables:

- ➢Alloy composition
- ➢Isothermal vs. cycling
- ➢Hydrogen & **Simulated reformate**

Oxidation of Alloys in Dual (Air/Hydrogen) Environment

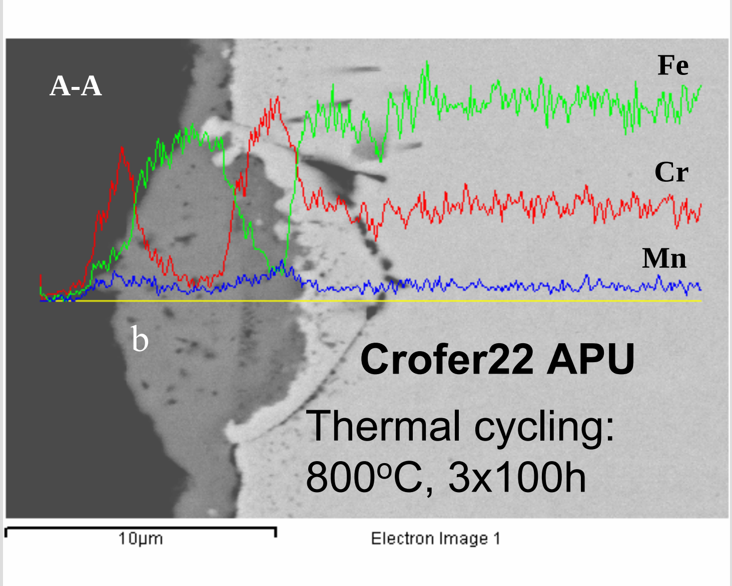
Previous PNNL results:

- Air-side oxidation of FSS is function of Cr content, thermal history, environment
- Effects of dual atmosphere on oxidation (iron incorporation into oxide scale; local attack via formation of iron oxide nodules) increases with decreasing Cr content:
  - Ebrite (25% Cr): no significant effect
  - Crofer22 APU (22% Cr) and 430 (17% Cr) both significantly affected
- The presence of moisture in air, thermal cycling, and higher temperatures further accelerate the anomalous air side oxidation
- Little difference observed on fuel side
- Ni and Ni-base alloys did not exhibit significant dual atmosphere effect



430

Isothermal: 800°C, 300h



Crofer22 APU

Thermal cycling: 800°C, 3x100h

Related work at Allegheny Tech., Univ. of Pitts., ARC; also MCFC (FuelCell Energy)

Extension to Carbon-containing environments

- Motivation: SOFCs will operate on partially and fully reformed hydrocarbons and syngas containing various levels of CHx, CO and CO_2. There is a need to understand effects of C species in fuel gas on alloy oxidation/corrosion behavior:
  - Accelerated metal loss (e.g., pitting) has been reported in complex gas atmospheres (Birks, Meier, Natesan, Pettit and others)
  - Carburization and sensitization of stainless steels have been reported via molecular and chemical transport of gaseous (CO,CO_2, CHx) species.
  - Ni clad FSS experienced extensive carburization (carbide formation) due to C diffusion through Ni cladding (Jian)

Question: Will thermally grown oxide scales provide effective protection and diffusion barrier at 600-800ºC?

Preliminary results

- **Crofer22 APU; 0.5mm thick; 1000 hours; 800ºC**
- Air vs. "Fuel"
  - "Fuel" composition:

Temp. (ºC)	H_2	CO	CH_4	CO_2	H_2O
800 (calc.)	**72.1**	**12.4**	**0.2**	**2.5**	**12.8**
800 (exp.)*	**74.2**	**9.8**	**0**	**6.2**	**9.7**

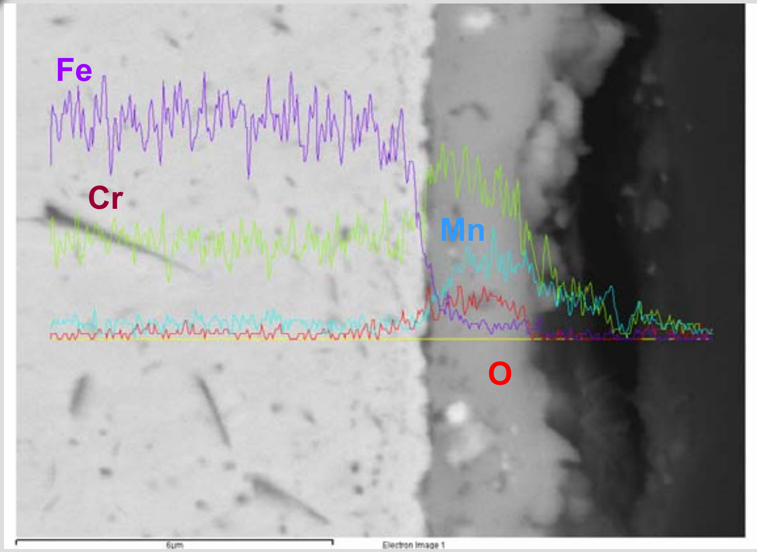
*Outlet composition analyzed with GC

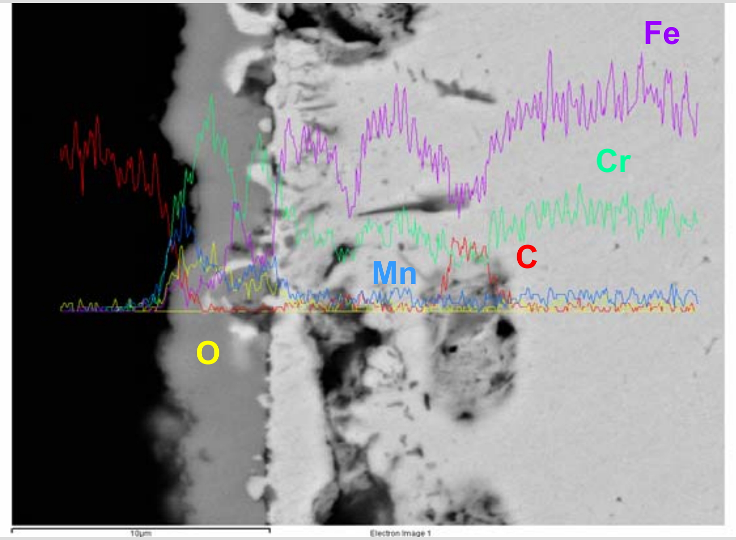
- Oxide scale chemistry and structure similar to previous C-free tests (air vs. moist hydrogen)
- Some evidence of highly localized carbon diffusion into the metal

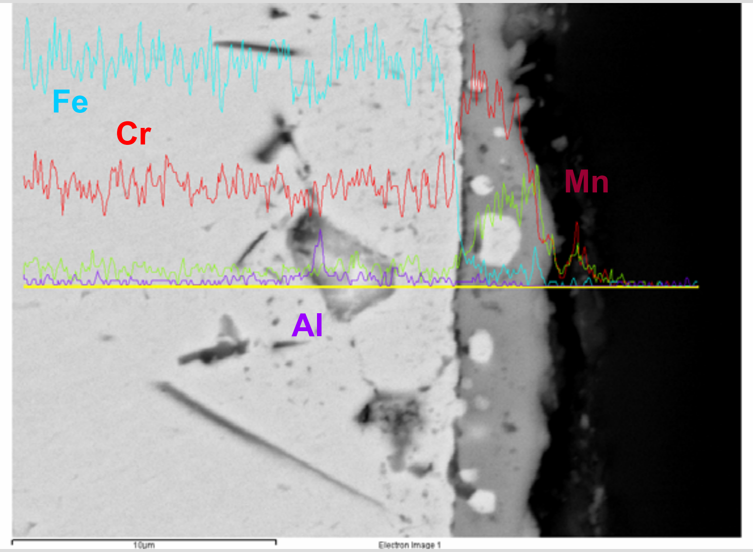
Preliminary results

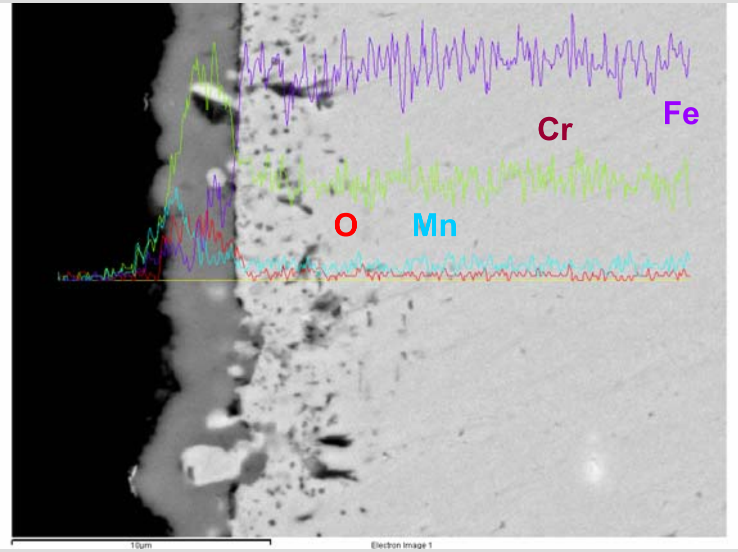
Airside

Fuel side









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- ○ Degradation Mechanisms in Mixed-Conducting Cathode Materials
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- ● Protective Coatings for Interconnects
- ○ “Refractory” Glass-Ceramic Seals

Protective Coatings for Interconnects

- Objective: To develop protective coatings for SOFC interconnect alloys which will reduce oxidation kinetics and, if necessary, mitigate Cr volatility
- Approach:
  - Synthesize and characterize coating materials
  - Fabricate coatings onto interconnect alloy coupons
  - Evaluate structure and performance of coatings and alloy substrate by SEM, XRD, resistance measurements, etc.

Oxidation of Alloy Interconnects

Long-term issues:

Increased scale resistance

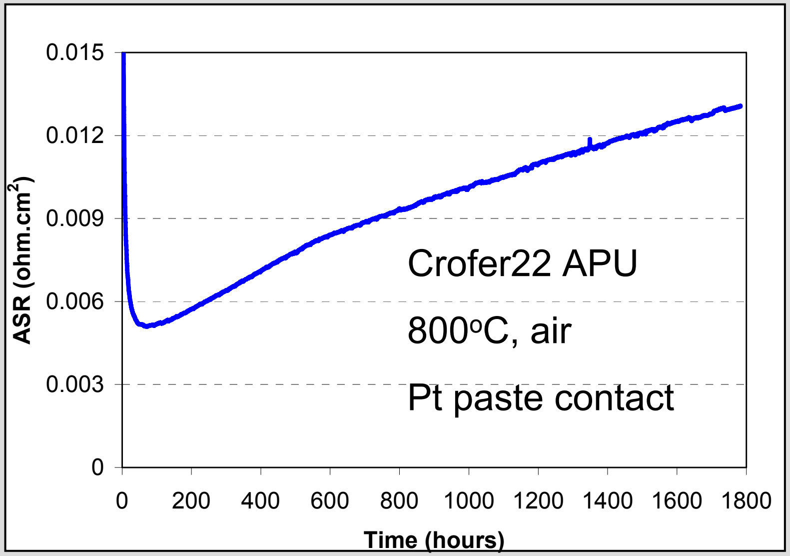
Scale spallation

Localized metal loss

Cr volatility

Approaches to solution:

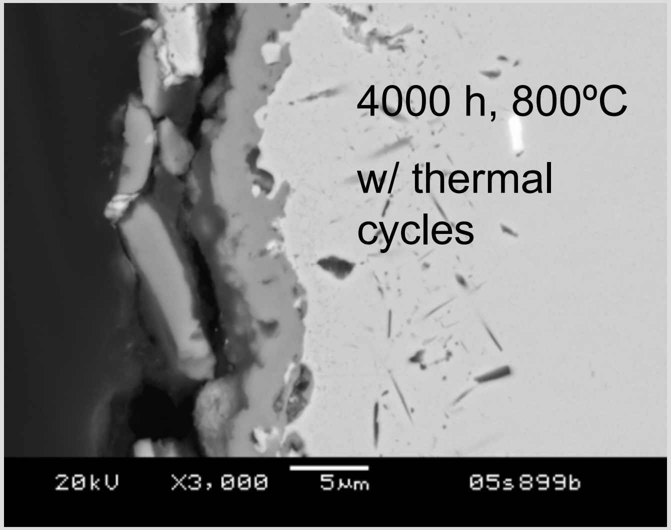
Bulk alloy modification, cladding, surface modification (including coatings)



Crofer22 APU

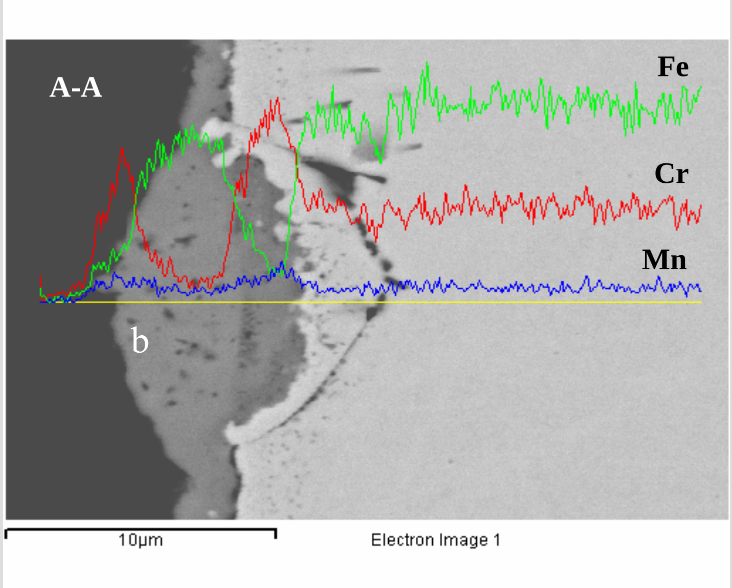
800°C, air

Pt paste contact



4000 h, 800°C

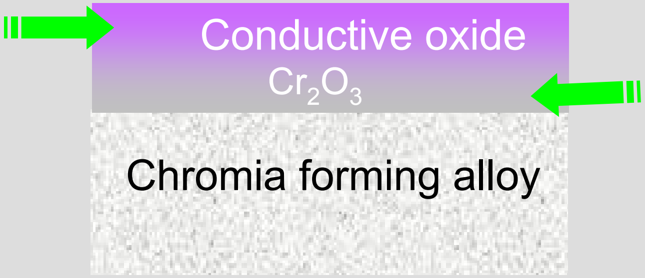
w/ thermal cycles



Protection Layers on Interconnects

Conductive oxide layer:

- ❖ Acts as a mass transport barrier to both Cr^{3+} outward and O^{2-} inward diffusion
- ❖ Reduce subscale growth rate
- ❖ Minimize scale resistance
- ❖ Prevent Cr release from metal substrate



Chromia subscale:

- ❖ Slow growth via O^{2-} inward diffusion;

Requirements:

High electrical conductivity, stability over SOFC temperature range, appropriate thermal expansion, low/no Cr volatility

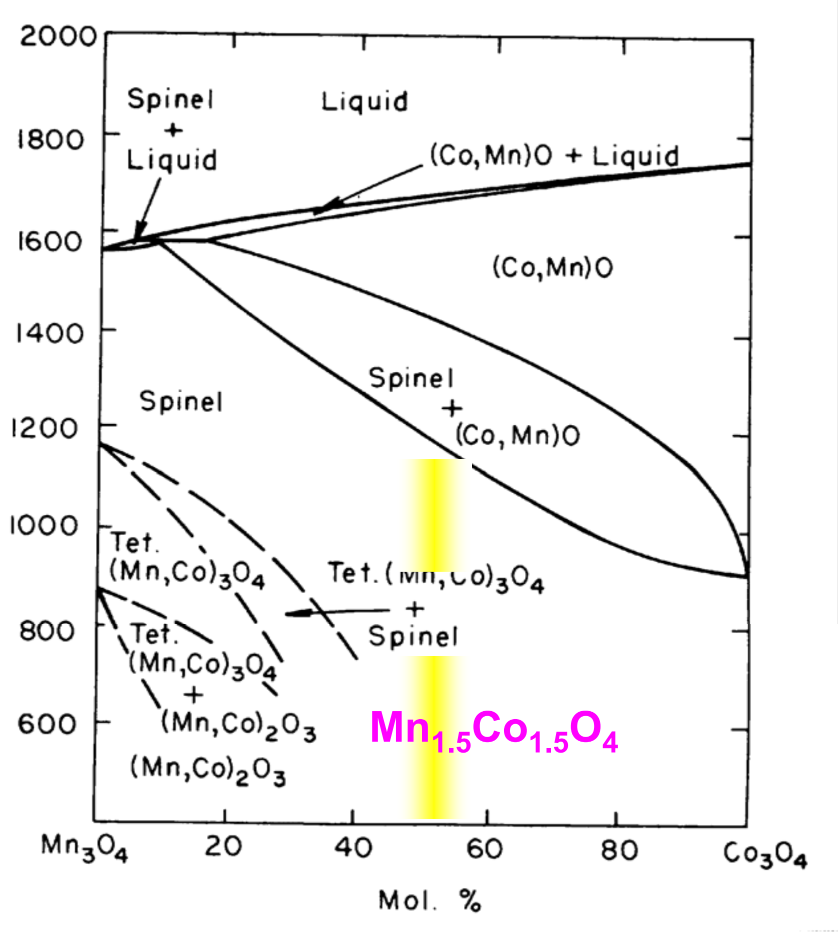
Candidate Oxides:

Perovskites: LSM, LSCr, LSCo, LSCF, LSF

Spinels: $(Mn,Co)_3O_4$

$(Mn,Co)_3O_4$ Spinel

- Extensive solid solution between Mn_3O_4 and Co_3O_4
- Wide range of compositions available for consideration

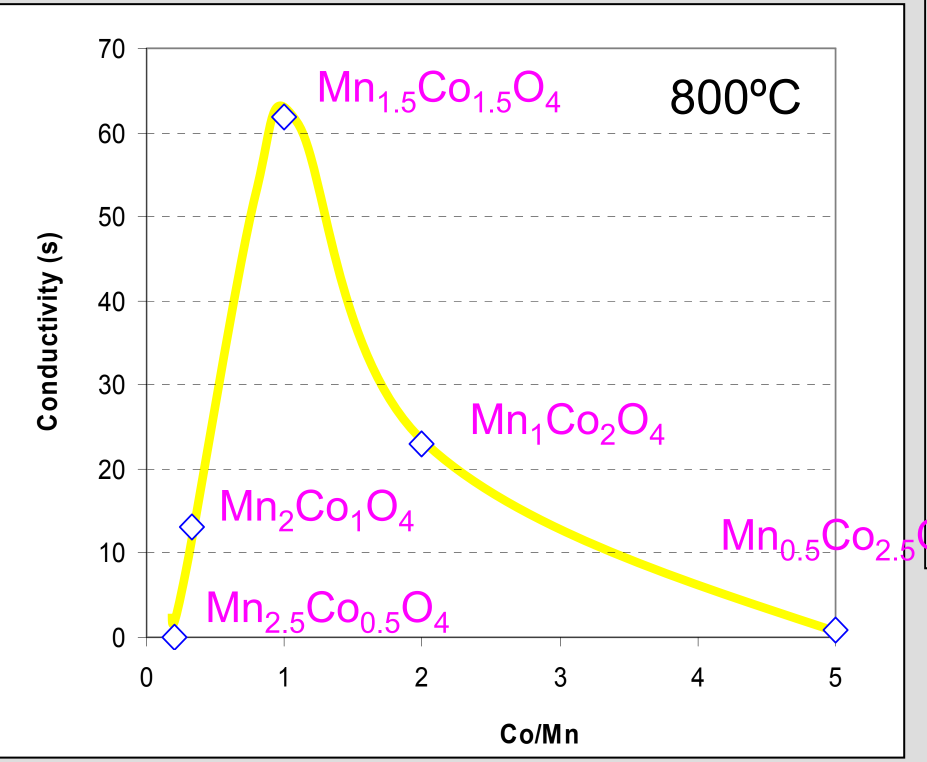


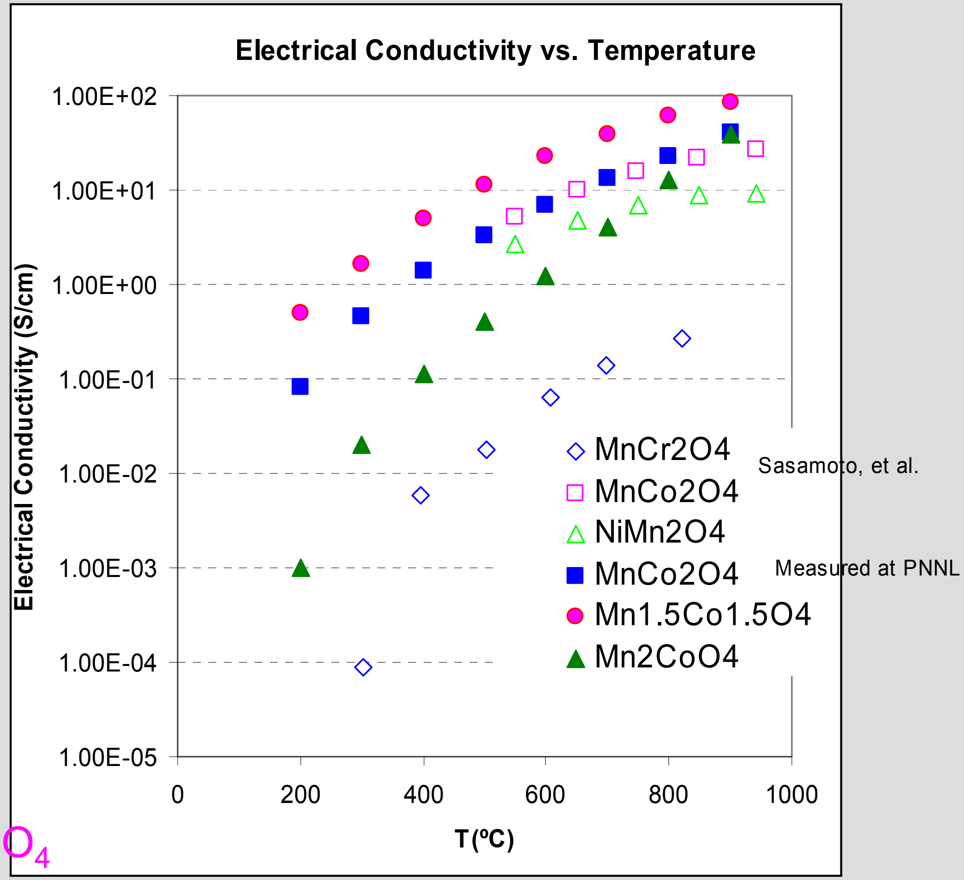
- Related work:
- Larring & Norby, J. Electrochem. Soc., 147, 2000
- LBNL

E. Aukrust and A. Muan, J. Am. Ceram. Soc., 46, 511, 1963

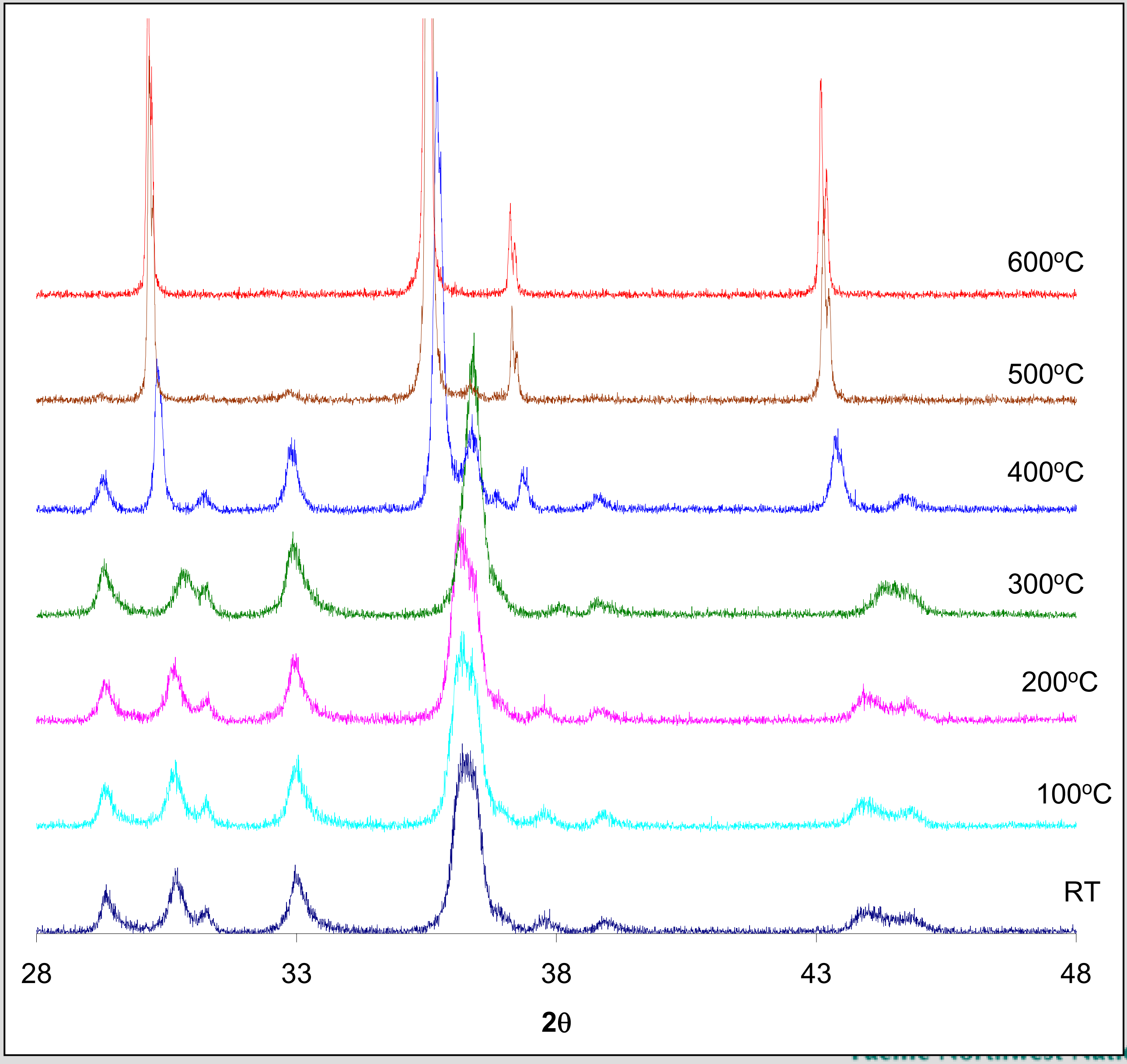
Electrical Conductivity of $(Mn,Co)_3O_4$ Spinels

$$\sigma_{Mn_{1.5}Co_{1.5}O_4} = 10^2\sigma_{MnCr_2O_4} = 10^{3\sim4}\sigma_{Cr_2O_3}$$





HT XRD of $Mn_{1.5}Co_{1.5}O_4$: from RT to 600°C, 5°C/min

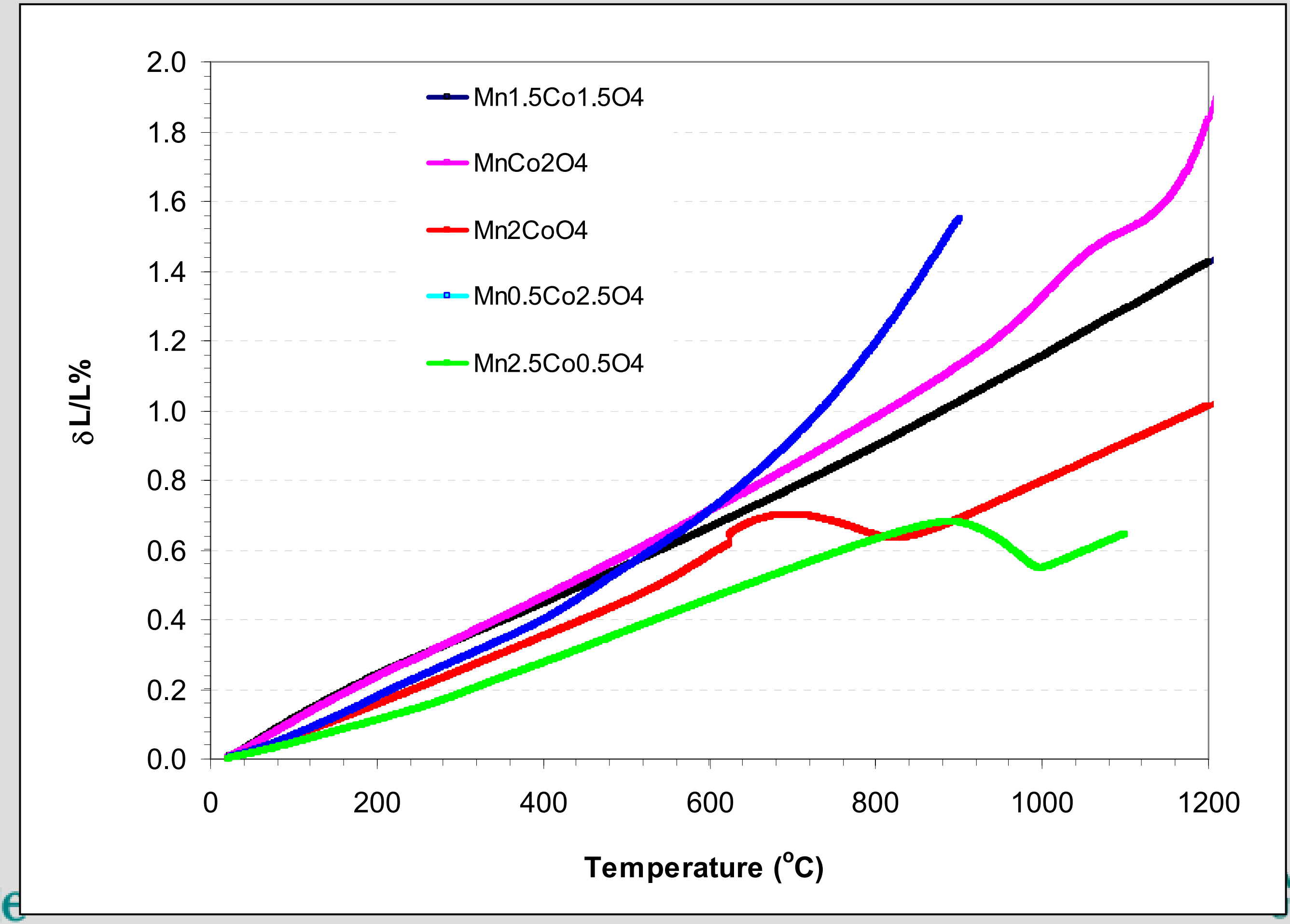


Thermal Expansion

Structurally stable up to 1,200°C

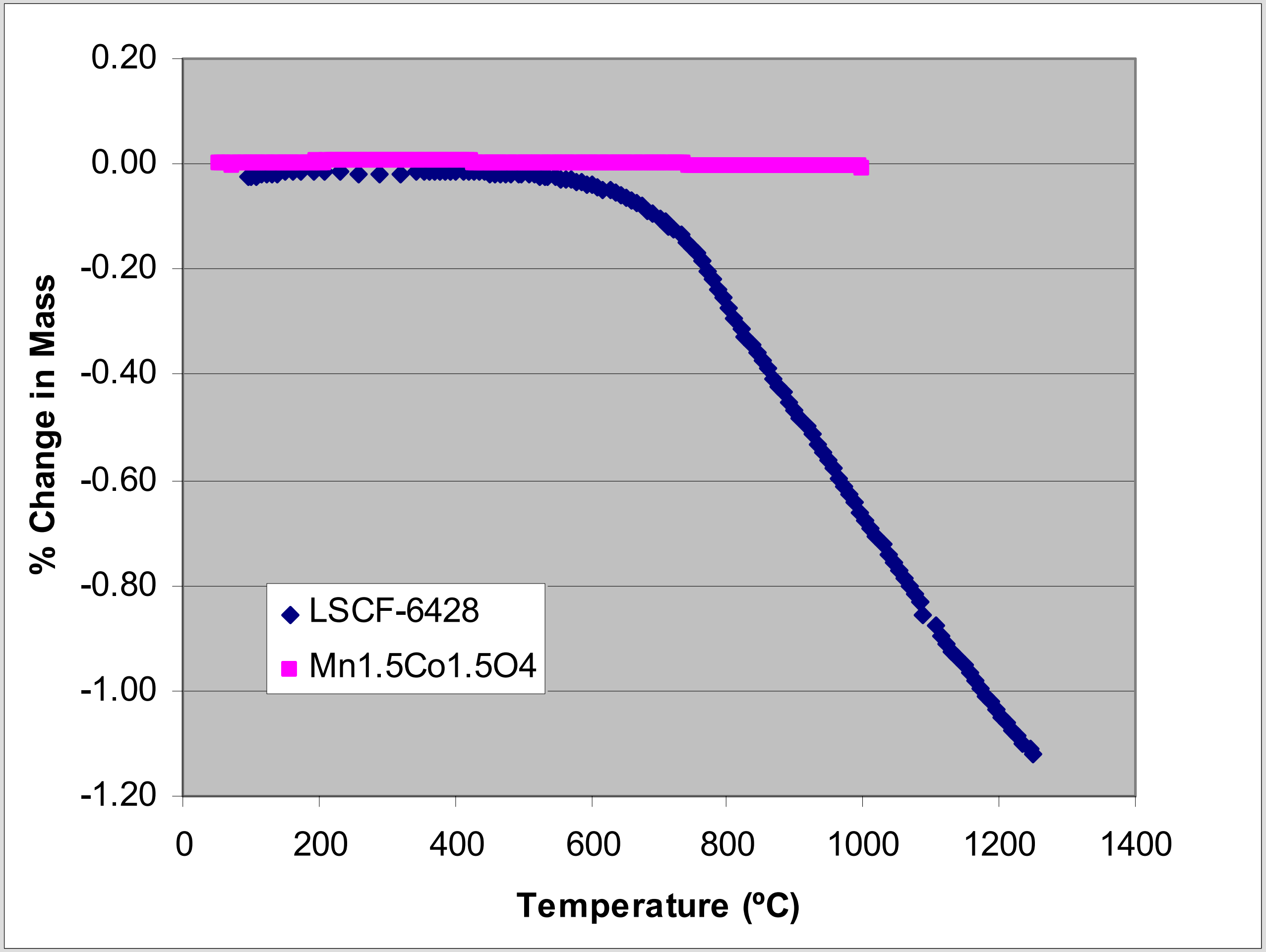
Good CTE matching to the FSS substrate:

$$CTE_{Mn_{1.5}Co_{1.5}O_4} = 11.5 \times 10^{-6} K^{-1}, 20 - 800^{o}C$$



Thermogravimetric Analysis

Minimal change in oxygen stoichiometry of spinel with temperature



Measured in air

Thermal Growth of $Mn_{1.5}Co_{1.5}O_4$ Spinel Protection Layer

Approach

Synthesis of $Mn_{1.5}Co_{1.5}O_4$ Powder

Solid state reaction or combustion synthesis

Preparation of slurry and application of coating

Screen printing, dip coating, brush application

Heat treatment in reducing environment

$$4Mn_{1.5}Co_{1.5}O_4 \Rightarrow 6Co + 6MnO + 5O_2 \uparrow$$

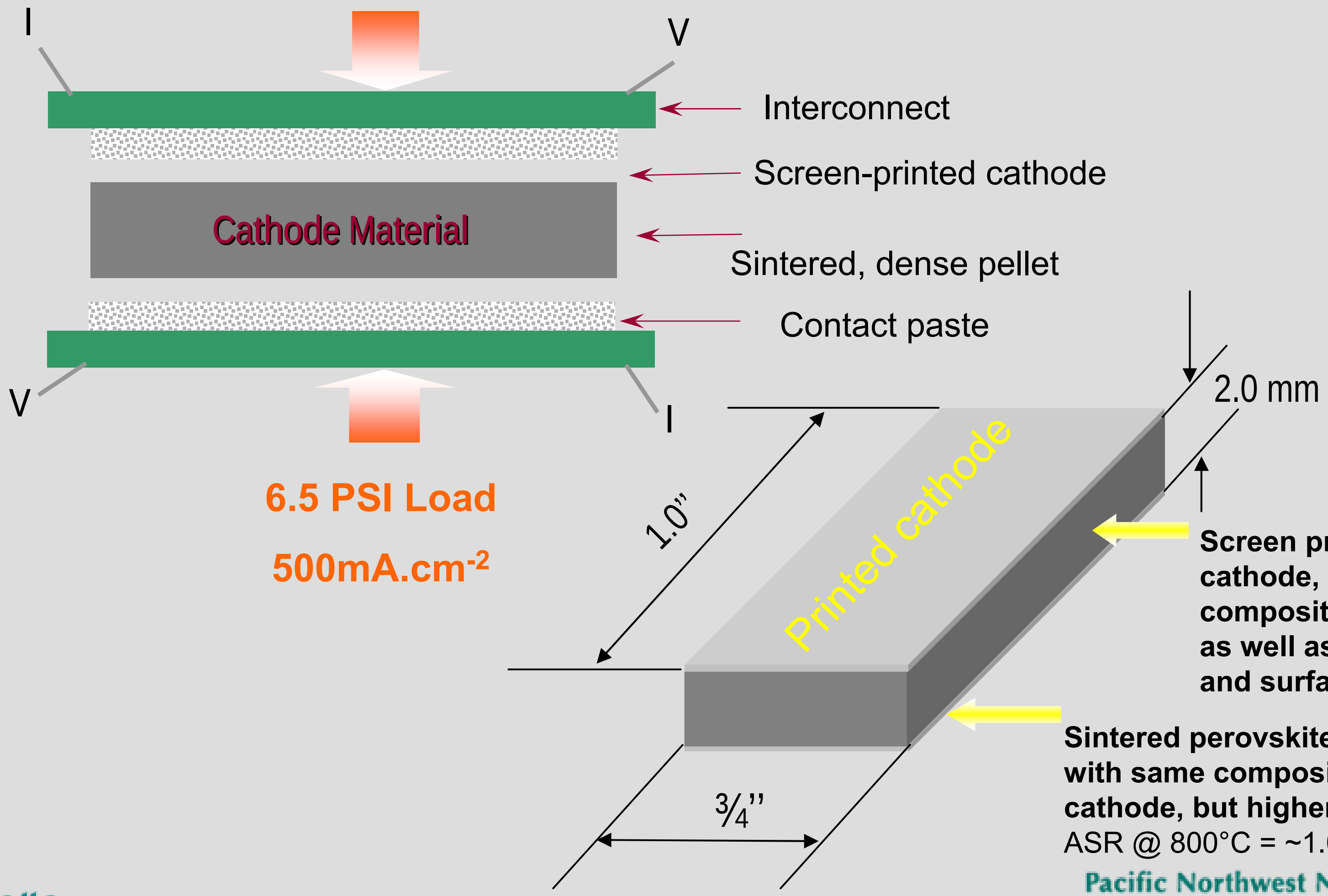
Oxidation and reaction-sintering in oxidizing environment

$$6Co + 6MnO + 5O_2 \uparrow \Rightarrow 4Mn_{1.5}Co_{1.5}O_4$$

Reaction sintering of Co, MnO mixture provides increased coating density at 800ºC

Study of Interfacial Resistance

$$ASR_{cathode/interconnect} = \Phi(scale, contacts, reactions)$$



Interconnect

Screen-printed cathode

Sintered, dense pellet

Contact paste

6.5 PSI Load

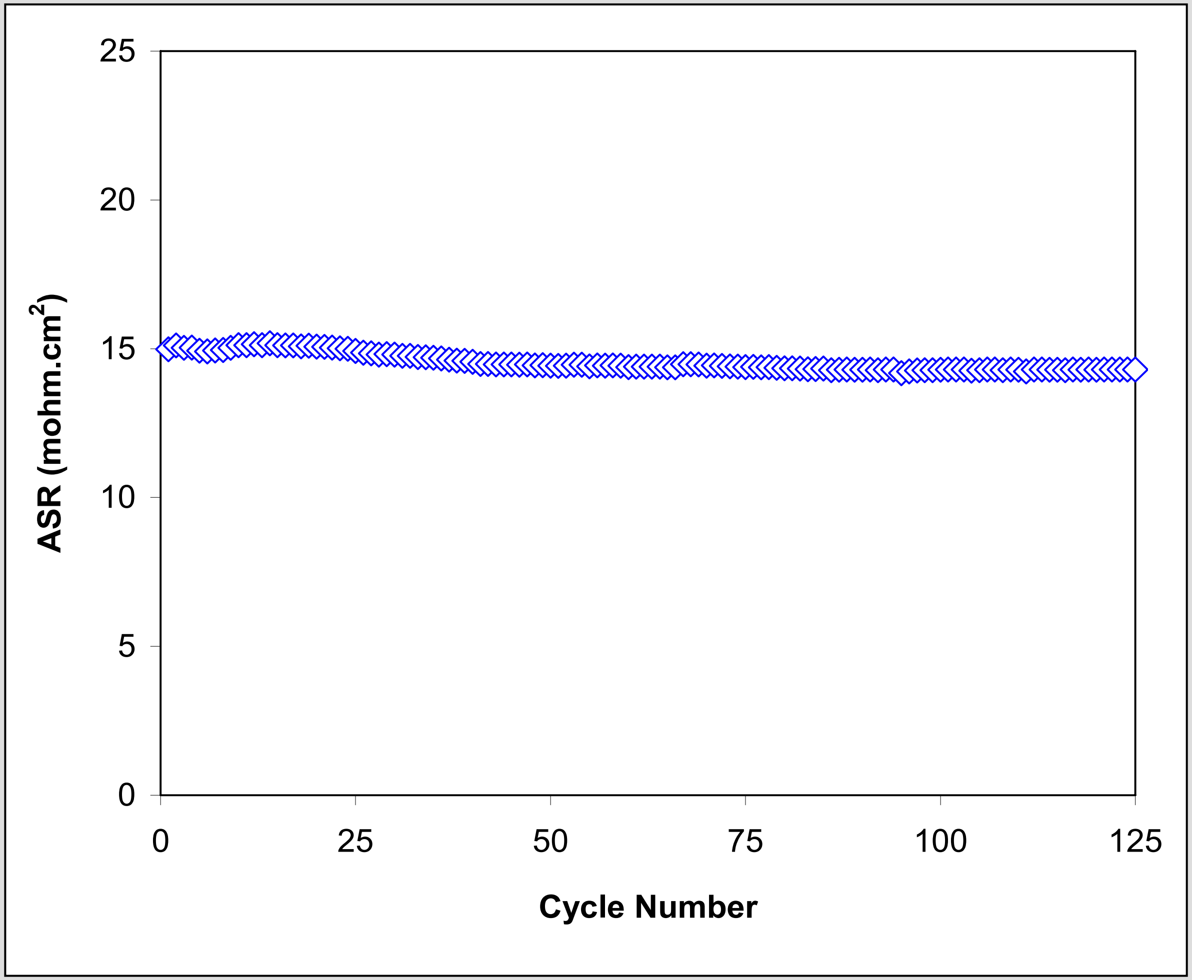
500mA.cm^{-2}

Screen printed, sintered cathode, with same composition as a real cathode, as well as thickness, density and surface finish.

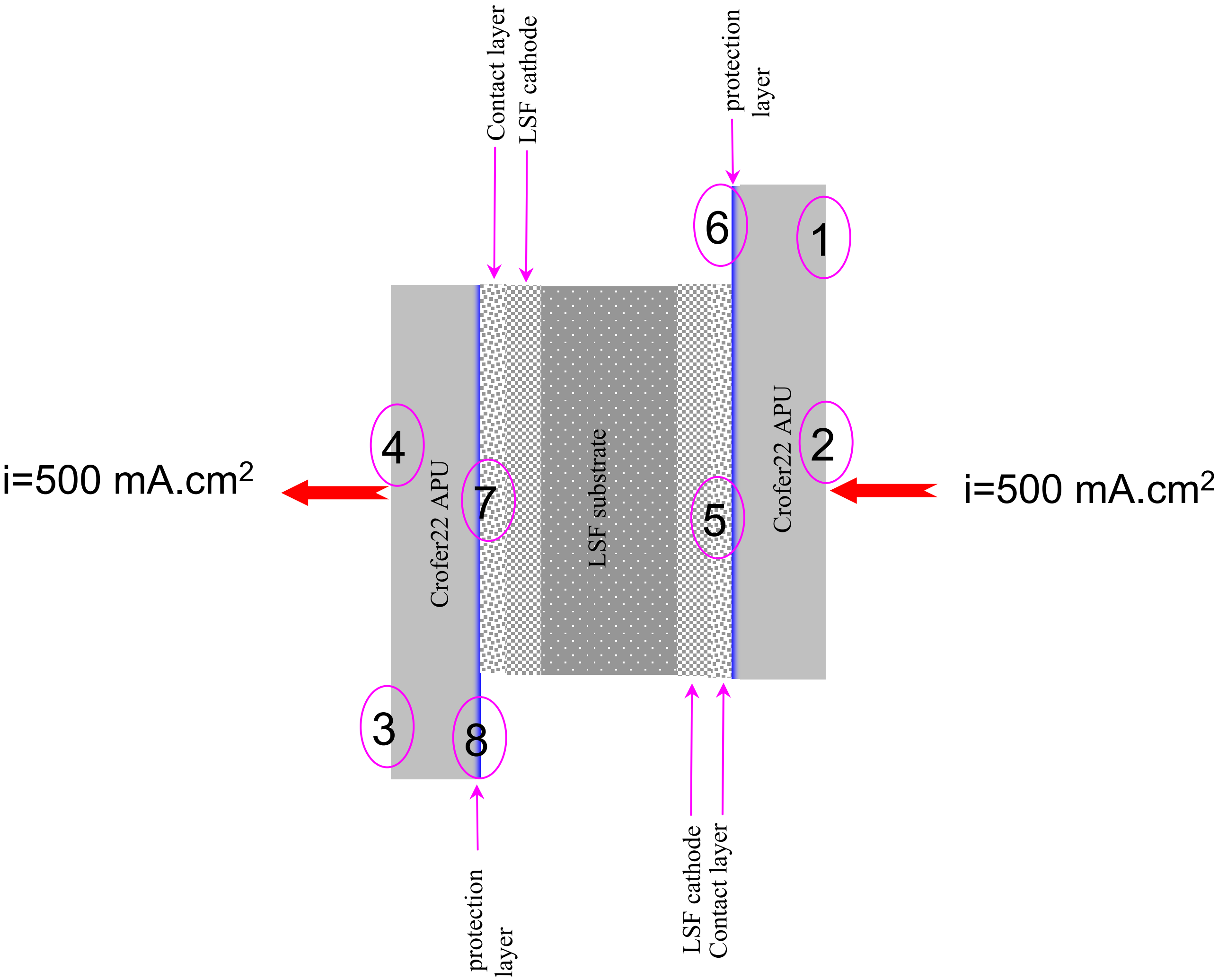
Sintered perovskite pellet with same composition as cathode, but higher density.
ASR @ 800°C = ~1.0 mΩ-cm^2

ASR Test: 6 months, 125 thermal cycles

- Spinel-coated Crofer22 APU, LSCM contact paste, LSF “cathode”
- Thermally cycled from RT to 800ºC in air



SEM/EDS Analysis



Effective Cr and O Barrier

No Cr penetration after 6 months of test and 125 cycles

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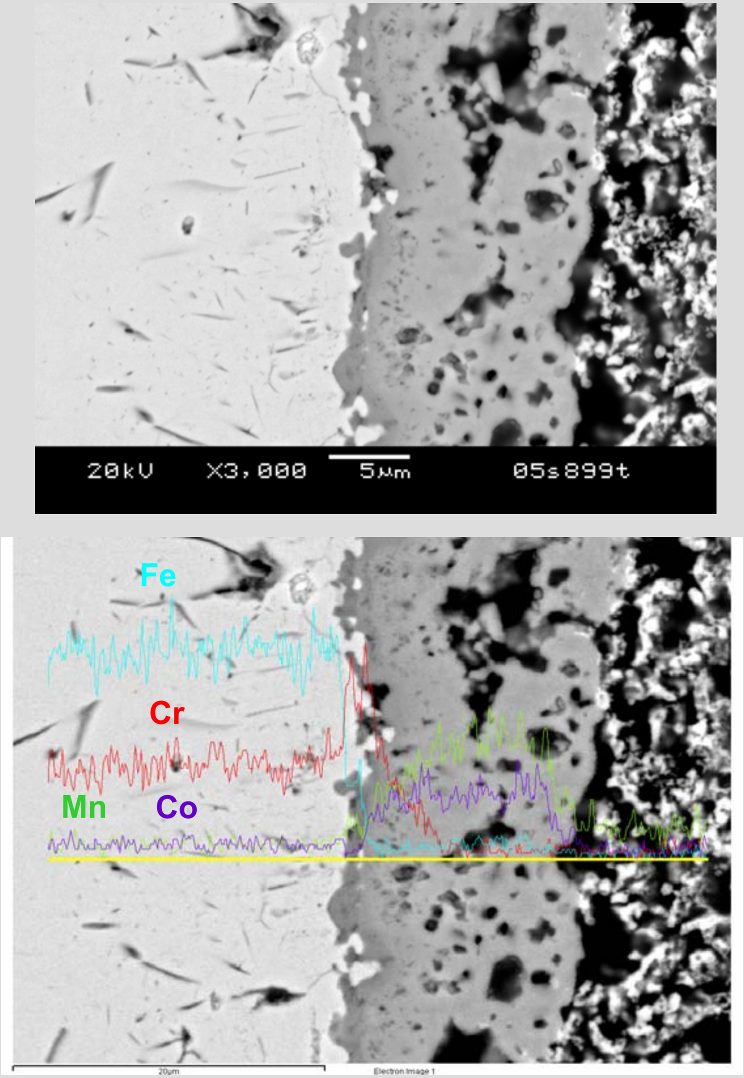
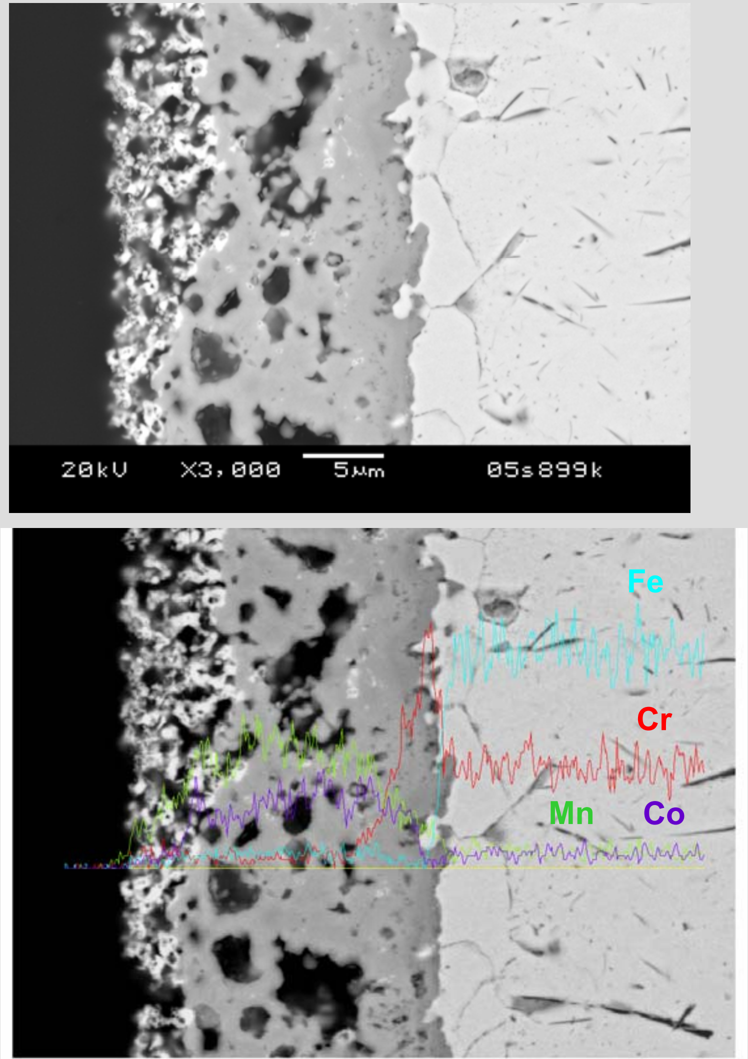


5-5

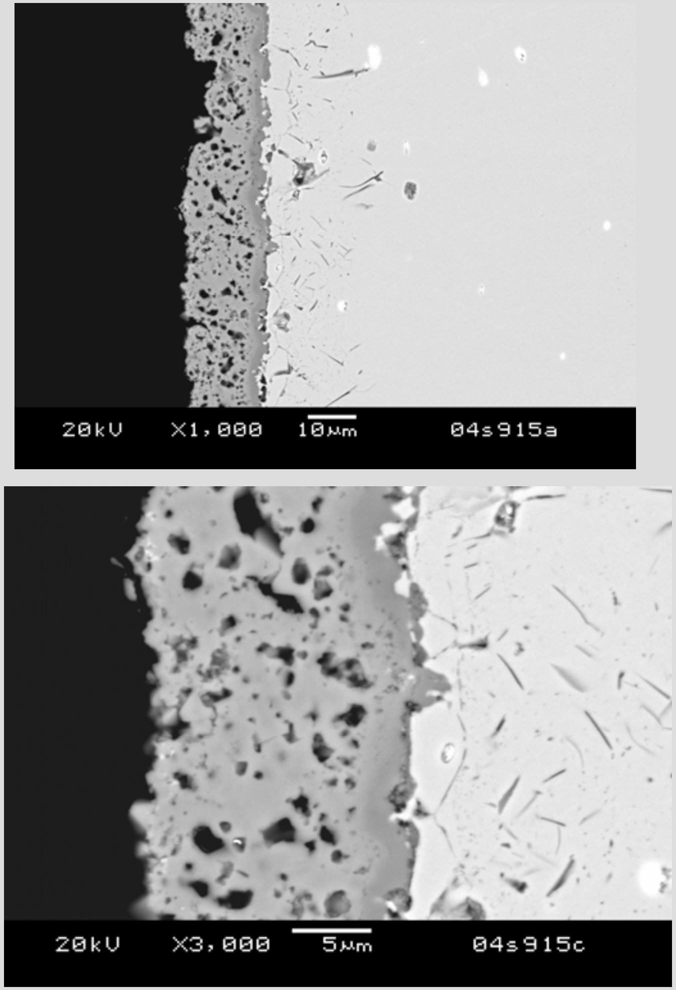


Improved Surface Stability

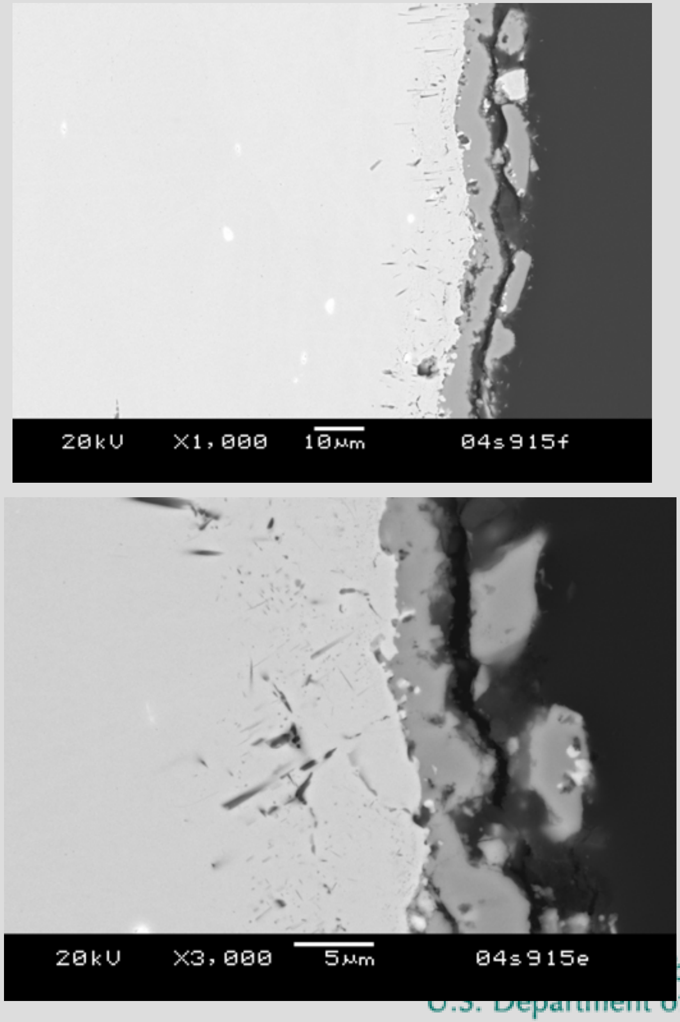
No spallation was observed at areas with protection layer

Significant spallation of Mn-Cr spinel was found on surfaces without protection layers

6-6

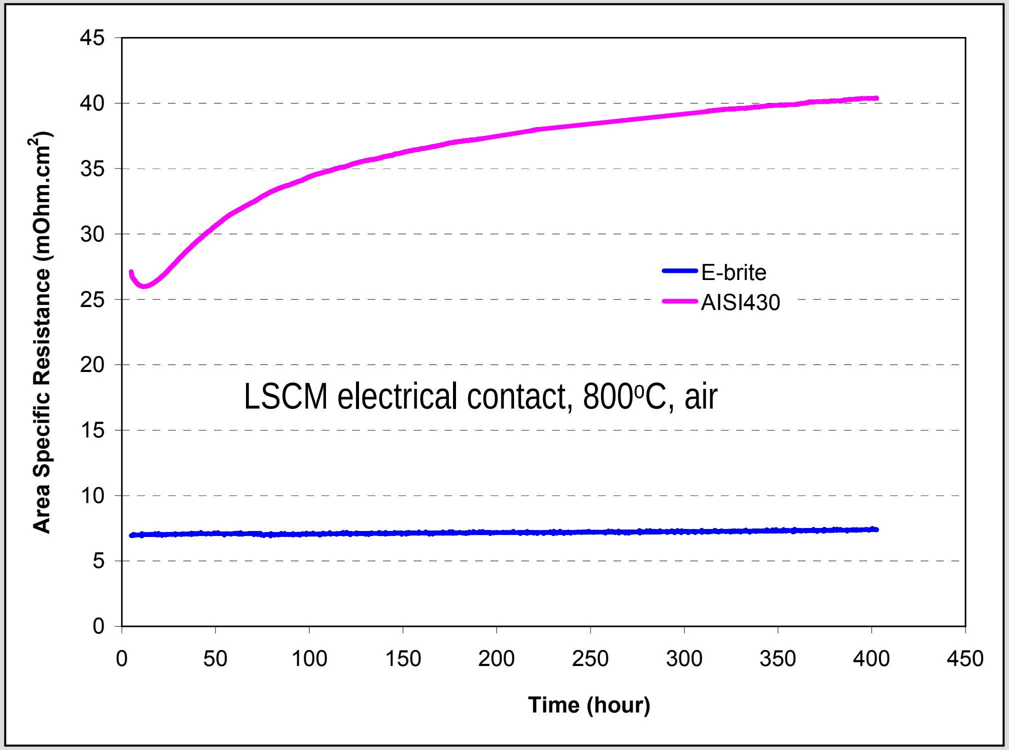


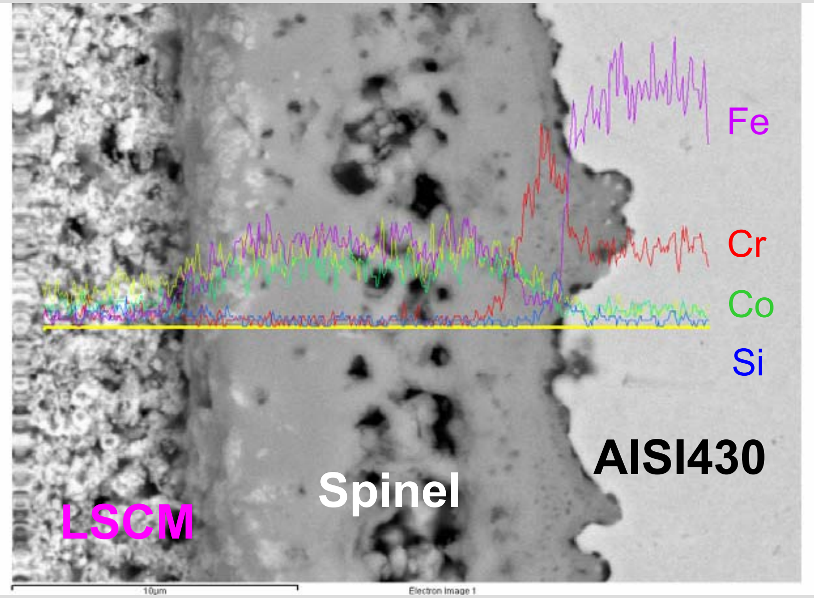
1-1

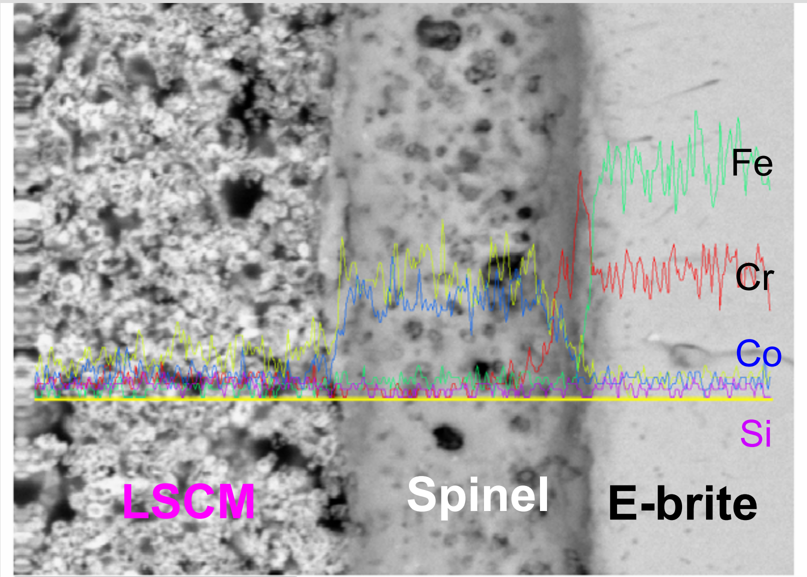


Fabrication and performance of $Mn_{1.5}Co_{1.5}O_4$ Protection Layers on Other FSSs

- $(Mn,Co)_3O_4$ protection layers applicable to other ferritic stainless steels as well
- Stability and performance depend on their ferritic substrate composition







Summary

- Initiated dual atmosphere studies with simulated reformate; observed Fe enrichment of fuel side scale.
- In 1000 hour test on Crofer22 APU at 800ºC, no iron oxide nodules observed on air side, and no pitting corrosion observed on fuel side
- Spinel protection layers successfully fabricated onto several different FSS; substantial reduction of subscale growth and Cr transport observed.

Future Work

- Interconnects:
  - Continue to investigate impact of dual atmosphere (air/reformate) tests on alloy oxidation/corrosion behavior
  - Optimize composition, structure, and thickness of spinel coatings
  - Evaluate alternative approaches for coating fabrication

Presentation Topics

- Effects of Cr on Cathode Performance (Joint study w/ GE and ANNL)
- Degradation Mechanisms in Mixed-Conducting Cathode Materials
- Environmental Effects of Interconnect Oxidation
- Protective Coatings for Interconnects
- “Refractory” Glass-Ceramic Seals

“Refractory” Glass-Ceramic Seals

▶ Objectives

- To develop and evaluate new “refractory” sealing glasses with higher sealing temperatures than typical SOFC sealing glasses to minimize seal reactivity and increase seal stability
- Evaluation includes sealing temperature, crystallization behavior, CTE, chemical compatibility, leak testing, and thermal cycle stability
- Standardized tests allow for meaningful comparison between different sealing materials (PNNL or other SECA participants)

Why "refractory" glass (glass-ceramics) for sealing?

•State-of-the-art sealing at ~850ºC: G18 (US Pat.: 6430966)

BaO	35
CaO	15
Al_2O_3	5
SiO_2	35
B_2O_3	10

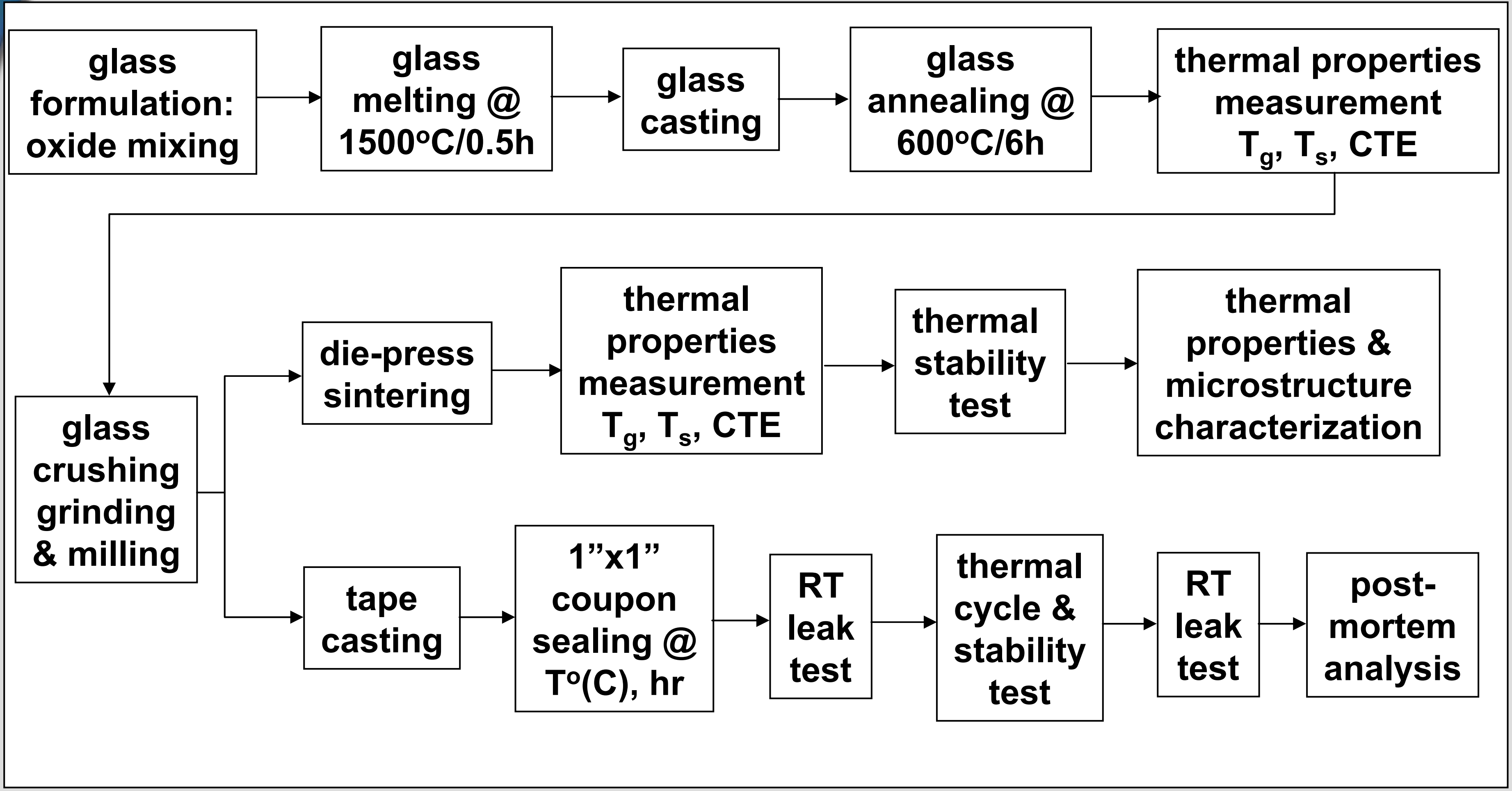
•Initial CTE: ~$12.5\times10^{-6}/^{o}C$

•Aged CTE (1000hrs/750°C) ~$11.1\times10^{-6}/^{o}C$ due to formation of mono-celsian phase

•Reaction with alloy to form $BaCrO_4$ (α_a=16.5, α_b=33.8, α_c=20.4)

- Glasses (including residual glass in glass-ceramics) are more reactive near or above their melting point. Residual glass likely to have high boria content.
- Glasses of higher sealing temperatures (≥ 950°C) may exhibit lower interfacial reactivity and better thermal stability (e.g., lower mobility, volatility) during long-term operation at 700-800°C.

Experimental Approach



glass formulation: oxide mixing

glass melting @ 1500°C/0.5h

glass casting

glass annealing @ 600°C/6h

thermal properties measurement T_g, T_s, CTE

glass crushing grinding & milling

die-press sintering

thermal properties measurement T_g, T_s, CTE

thermal stability test

thermal properties & microstructure characterization

tape casting

1”x1” coupon sealing @ T°(C), hr

RT leak test

thermal cycle & stability test

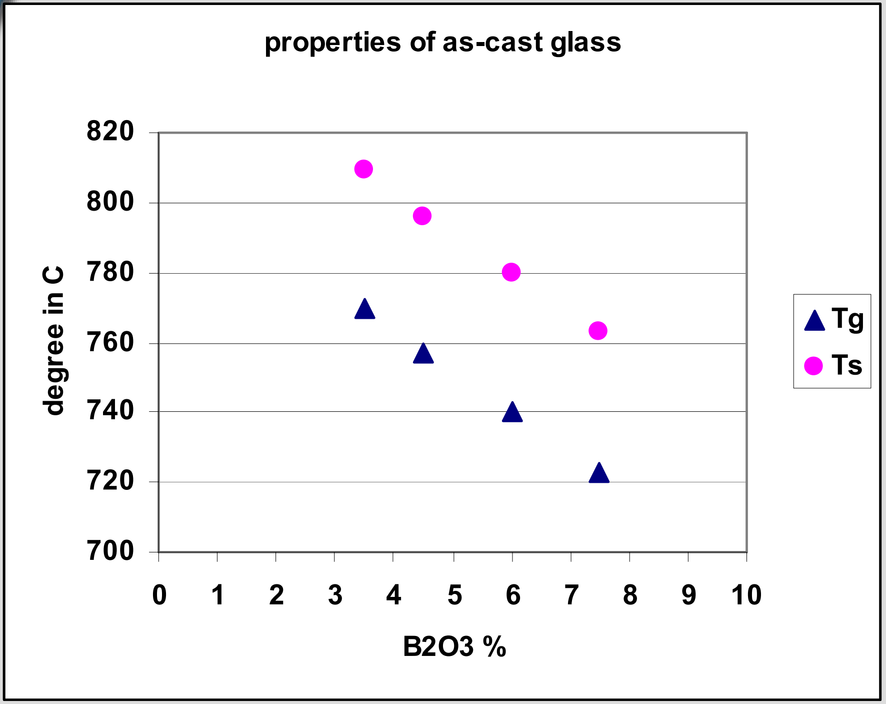
RT leak test

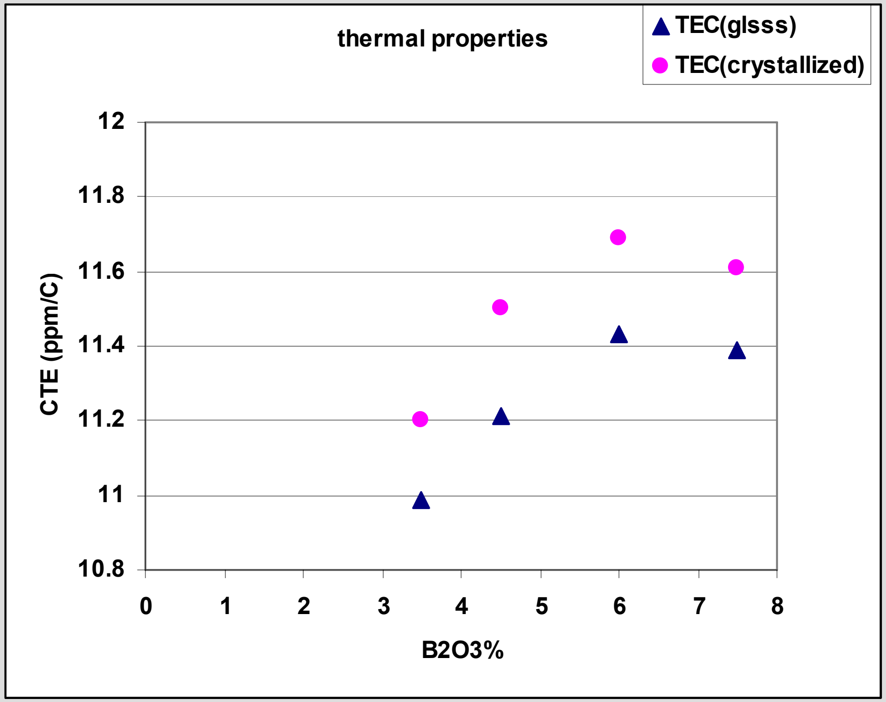
post-mortem analysis

“Refractory” Glass-Ceramic Seals

- Compositional Approaches:
  - Minimize B_2O_3 content
    - Glass former, also acts as flux, so reduction of B_2O_3 increases glass refractoriness
    - Evaluate compositional effects on CTE, reactivity
  - Alkaline earth substitution (MgO, CaO, SrO, BaO)
    - Evaluate compositional effects on sealing temp, CTE, reactivity

Approach 1: minimize B_2O_3 content
Thermal properties





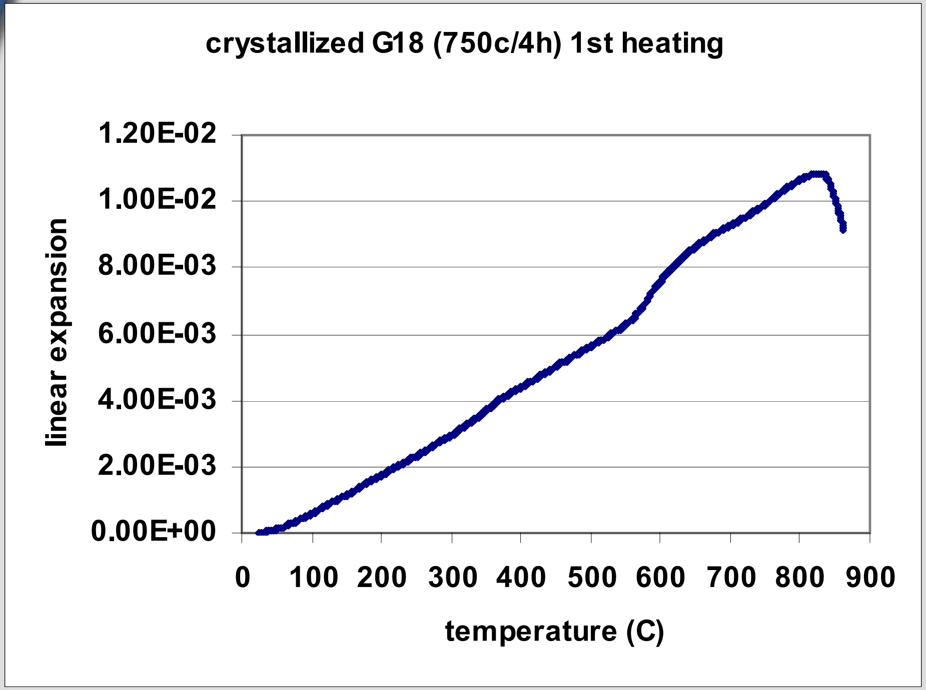
G18:

Tg – 630ºC

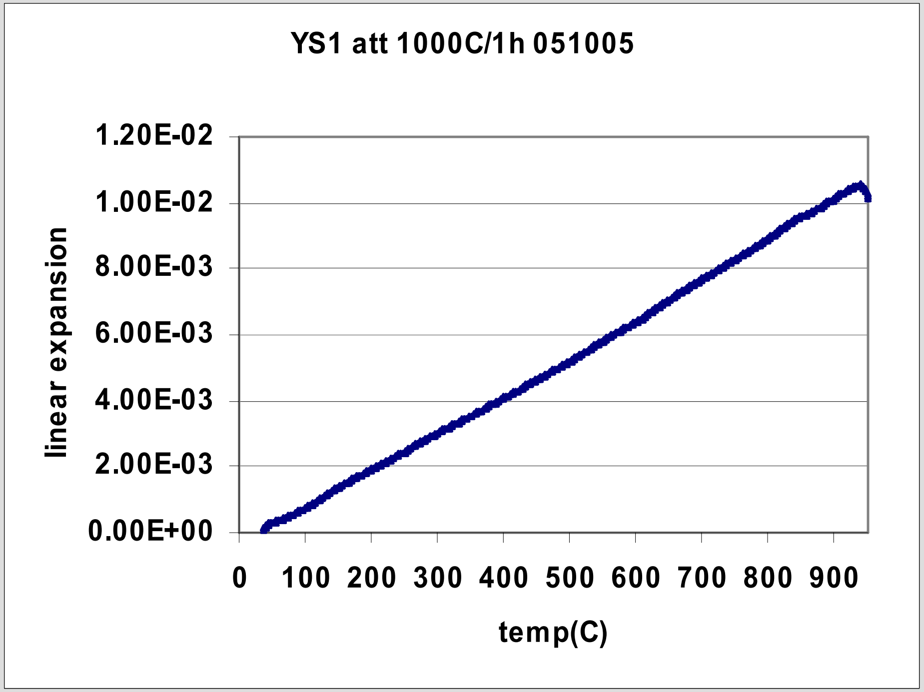
Ts – 685ºC

#ID	SrO	CaO	Al2O3	Y2O3	B2O3	SiO2	note
YS1	42.5	10	4	6	7.5	30.0	clear glass
YS61	42.5	10	4	6	6.0	31.5	clear glass
YS7	42.5	10	4	6	5.5	32.0	clear glass with very light skin
YS8	42.5	10	4	6	4.5	33.0	clear glass with very light skin
YS9	42.5	10	4	6	3.5	34.0	1/3 opaque
YS11	40.0	10	4	6	7.5	32.5	clear glass
YSO1	42.5	10	0	6	7.5	34.0	clear glass

Dilatometric behavior



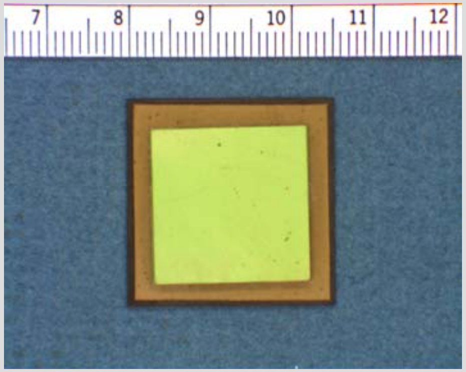
G18, 850°C/1h, 750°C/4h



YS1, 1000°C/1h, 800°C/4h

RT leak test of sealed coupons

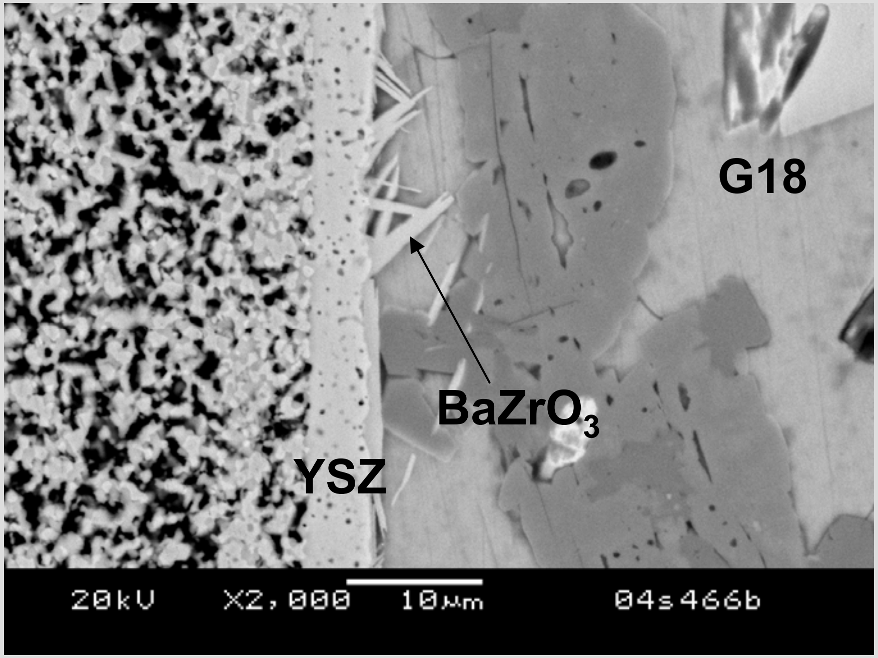
Metal squares (1”x1”) and YSZ-bilayer (0.75”x0.75”) are sealed with glass at ~5 psi



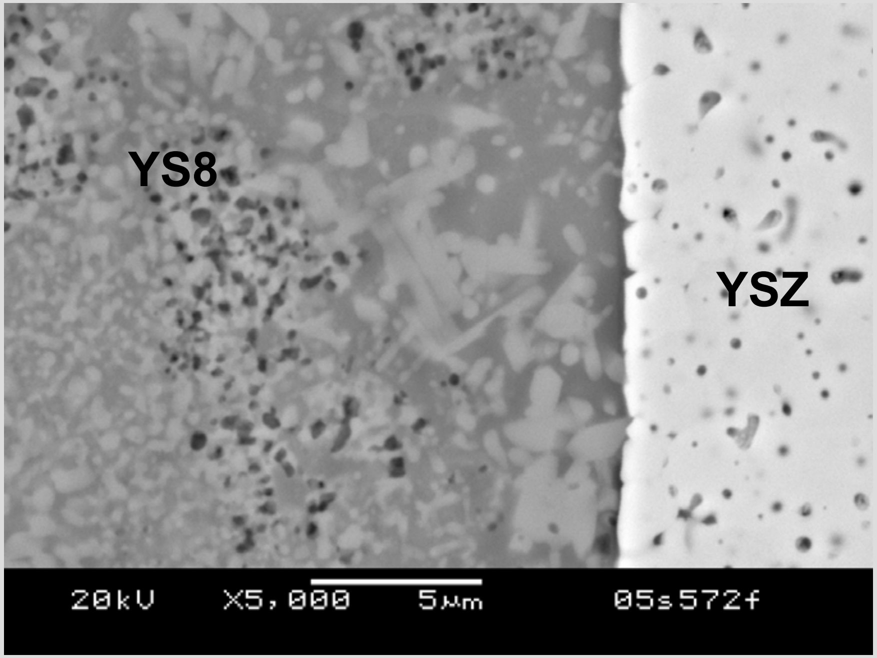
All tests remained hermetic through 10 thermal cycles; indication of acceptable CTE match and minimal reactivity; larger and longer tests required

glass#	metal	sealing	as-sealed	10 T.C./air	10 T.C./red.
YS8	Crofer-ox	1050/1	hermetic	hermetic	hermetic
YS8	Crofer-ox	950/1	hermetic	hermetic	
YS8	Crofer-ox	1100/1	hermetic	hermetic	hermetic
YS1	Crofer-ox	850/1	hermetic	hermetic	hermetic
YS1	Crofer-ox	900/1	hermetic	hermetic	hermetic
YS1	Crofer-ox	950/1	hermetic	hermetic	
YS1	Crofer-ox	1000/1	hermetic		
YSO1	Crofer-ox	900/1	hermetic		hermetic
YSO1	Crofer-ox	950/1	hermetic		hermetic
YSO1	Crofer-ox	1000/1	hermetic		hermetic
YSO1	Crofer-ox	1050/1	hermetic		hermetic
YSO1	Crofer-AR	900/1	hermetic		hermetic
YSO1	Crofer-AR	950/1	hermetic		hermetic
YSO1	Crofer-AR	1000/1	hermetic		hermetic
YSO1	Crofer-AR	1050/1	hermetic		hermetic

Interfacial reactions (glass/YSZ)

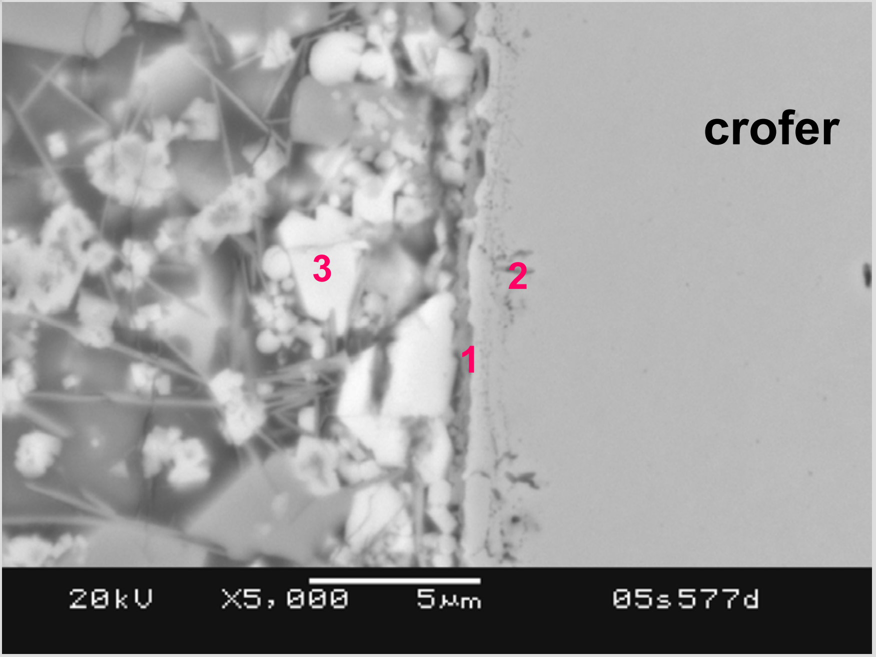


G18, 850°C/1h+750°C/4h

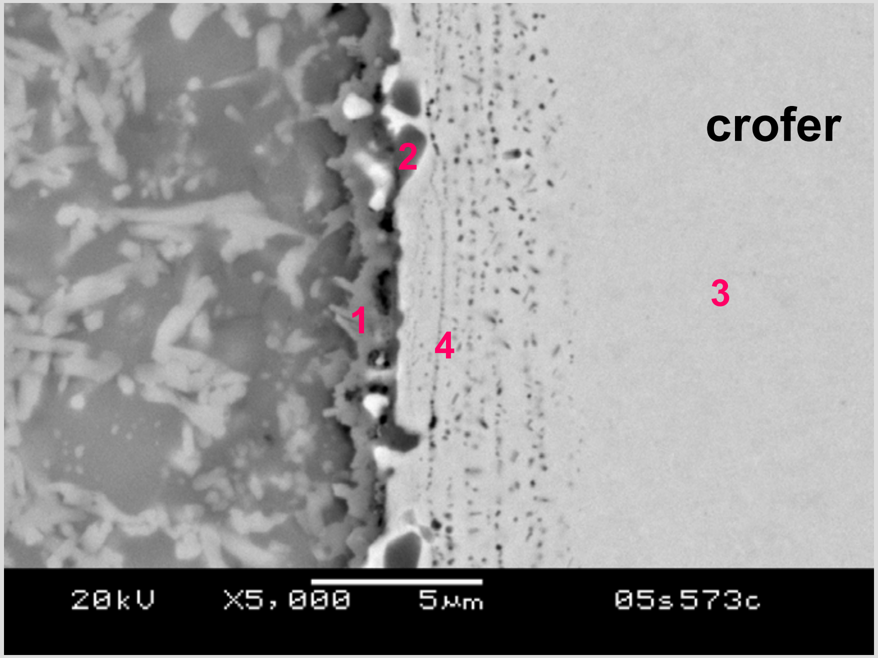


YS8, 1050°C/1h+800°C/4h

Interfacial reactions(glass/crofer22APU)



G18m, 850°C/1h+800°C/4h



YS8, 1050°C/1h+800°C/4h

ponit #	O	Al	Si	Ca	Cr	Mn	Fe	Ba
1	39.11	1.77	2.21	0.82	**34.51**	1.49	13.6	6.50
2	10.97	12.5			**16.38**		60.17	
3	48.91		1.29		**24.86**		1.28	23.7

ponit #	O	Al	Si	Ti	Cr	Mn	Fe	Sr
1	37.42	1.83	1.56	0.33	**35.82**	1.40	20.91	0.73
2	26.23	2.32	0.86		**27.59**	7.9	34.72	0.38
3			0.59		**22.93**		76.48	
4		1.73	0.75	1.31	**22.96**		73.24	

Approach 2: Replacement of Ca with other alkaline earth (Mg, Ba, Sr)

Ba^{+2} (1.36Å), Sr^{+2} (1.16Å), Ca^{+2} (1.00Å), Mg^{+2} (0.72Å)

# ID	SrO	MgO	CaO	BaCO3	Y2O3	B2O3	SiO2	note
YSP4	45.0	**7.5**	0	0	6	10.0	31.5	clear glass
YSP5	45.0	0	**7.5**	0	6	10.0	31.5	clear glass
YSP6	45.0	0	0	**7.5**	6	10.0	31.5	clear glass
YSP7	52.5	0	0	0	6	10.0	31.5	clear glass

glass #	Tg	Ts	TEC(glsss)	TEC(crystallized)	heat treatment
YSP4	653	708	11.45	9.91 (RT-866C)	600/2,1000/1,800C/4h
YSP5	661	713	11.84	11.51 (RT-873C)	600/2,1000/1,800C/4h
YSP6	660	704	12.10	12.43 (30-860C)	600/2,1000/1,800C/4h
YSP7	661	711	11.92	12.27 (30-928C)	600/2,1000/1,800C/4h

Thermal stability: effect of ageing on CTE

glass#	CTE (as-sintered)	CTE (1000hr air aged)	ageing temp
G18	12.50 (RT-570C)	11.10 (RT-850C)	750
YS1	11.61 (RT-946C)	11.33 (RT-961C)	900
YS61	11.69 (100-934C)	10.89 (RT-940C)	900
YS8	11.50 (RT-1000C)	10.84 (RT-986C)	900
YSO1	11.73 (RT-870C)	11.51 (RT-962C)	900
YSP5	11.51 (RT-873C)	to be determined	900
YSP6	12.43 (30-860C)	to be determined	900
YSP7	12.27 (30-928C)	12.43 (RT-1000C)	800

Short-term ageing test in 30%H_2O/70%H_2

glass #	as-sealed	850C/200h/30%H2O	850C/500h/30%H2O
G18	hermetic	leak	
G18	hermetic	hermetic	leak
YS1	hermetic	hermetic	hermetic
YS1	hermetic	hermetic	hermetic
YS1	hermetic	hermetic	hermetic
YS1	hermetic	hermetic	hermetic
YSO1	hermetic	hermetic	hermetic
YSO1	hermetic	hermetic	hermetic
P5	hermetic	hermetic	hermetic
P5	hermetic	hermetic	hermetic
P6	hermetic	hermetic	hermetic
P6	hermetic	leak	
P7	hermetic	hermetic	hermetic
P7	hermetic	hermetic	hermetic

- Tests included 3 thermal cycles
- Survival of seals attributed to minimal chemical interaction and good CTE match

Summary

- “Refractory” sealing glasses were formulated and characterized. The effects of reducing B_2O_3 content, and substitution of various alkaline earths, were evaluated.
- Coupon tests showed hermetic sealing to Crofer22 APU for several glasses even after 10 thermal cycles in air and/or in reducing (70% H_2/30% H_2O) environment.
- No distinct interfacial reaction of “refractory” glasses with YSZ or Crofer22 APU was observed.
- Several refractory glasses retained hermetic sealing to FSS after 850^{o}C/500 hrs ageing in air and reducing environments, indicating good CTE match and chemical stability with Crofer22 APU.

Future Work

- Glass-ceramic seals:
  - Continue optimizing the refractory sealing glass formulations with respect to sealing temperature, CTE, crystallization rate
  - Study the chemical compatibility of the refractory sealing glasses with interconnect alloys; testing extended to include coated alloys.
  - To evaluate the thermal stability (1000 hrs) of the refractory glasses in simulated SOFC environments.
  - Validation of results on larger samples (4”x4”); thermal cycle tests in dual environments.

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