SECA Core Technology Program - PNNL: SOFC Component Materials Development

Jeff Stevenson

Pacific Northwest National Laboratory

Richland, WA 99352

Presented at the SECA CTP Review Meeting

Sacramento, CA, Feb. 19, 2003

SECA Core Technology Program - PNNL: SOFC Component Materials Development

Program Scope:

- Intermediate Temperature Cathode Materials Development
- Advanced Anode Materials Development
- Metallic Interconnect Materials Evaluation and Development
- SOFC Stack Seal Development

Presentation Outline

- Intermediate Temperature Cathode Materials Development
- Metallic Interconnect Materials Evaluation and Development

- For each task:
  - Objective
  - Previous Status
  - Results
  - Future Work

Intermediate Temperature Cathode Materials Development

Cathode Materials Development

- Objective: Develop and optimize high performance, stable cathode materials for intermediate temperature SOFC

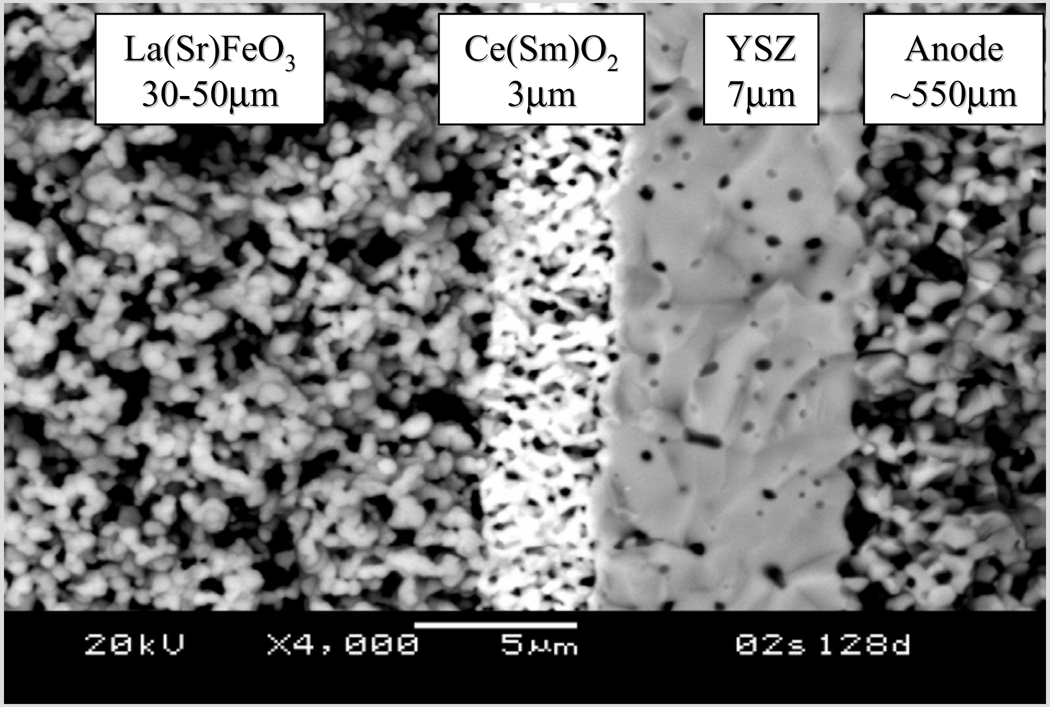
- **Variables:**
  - **Base composition, type and amount of dopant**
  - **Initial particle size distribution (calcination and milling conditions), fugitive phases**
  - **Sintering temperature and time**
- **Approach:**
  - **Synthesis (glycine-nitrate) and characterization of candidate cathode powders (XRD, dilatometry, SEM, PSA, TGA, electrical conductivity)**
  - **Fabrication of cathodes on anode-supported membranes via screen printing and sintering**
  - **Evaluation of cathode performance by electrochemical testing and SEM**

Sr-Doped $LaFeO_3$ Cathode Development

Advantages:

- High ionic conductivity
- Rapid oxygen surface exchange kinetics
- TEC match to other components
- High electronic conductivity
- Iron is inexpensive B-site constituent

Introduction of doped ceria layer improves performance

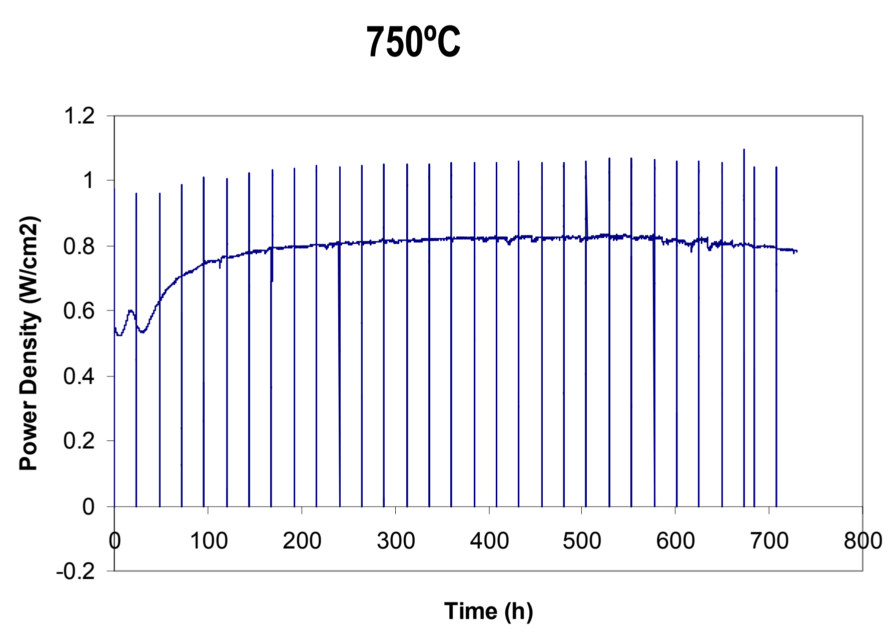


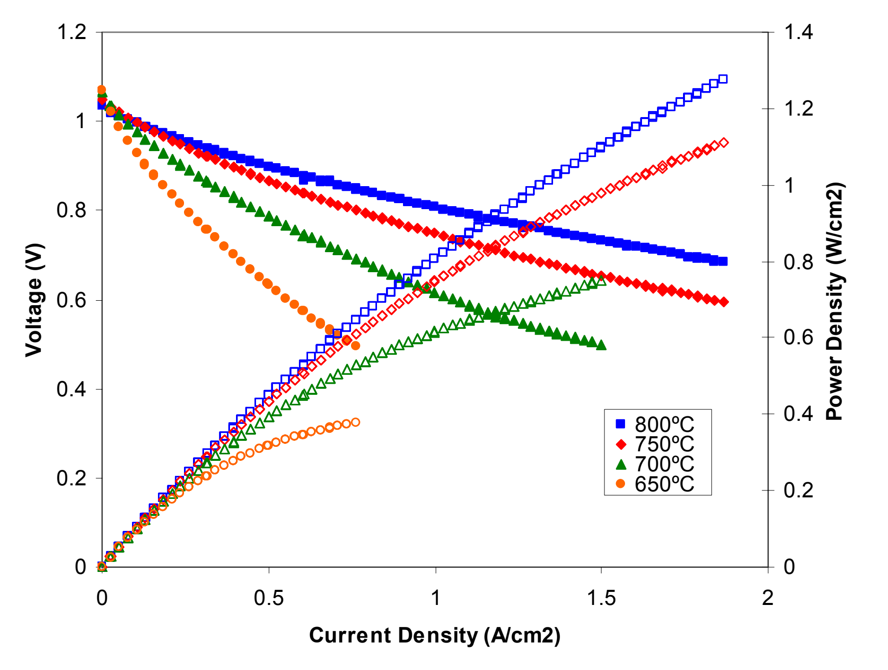
Anode-supported cell w/ LSF-20 cathode (Previous status)

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

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

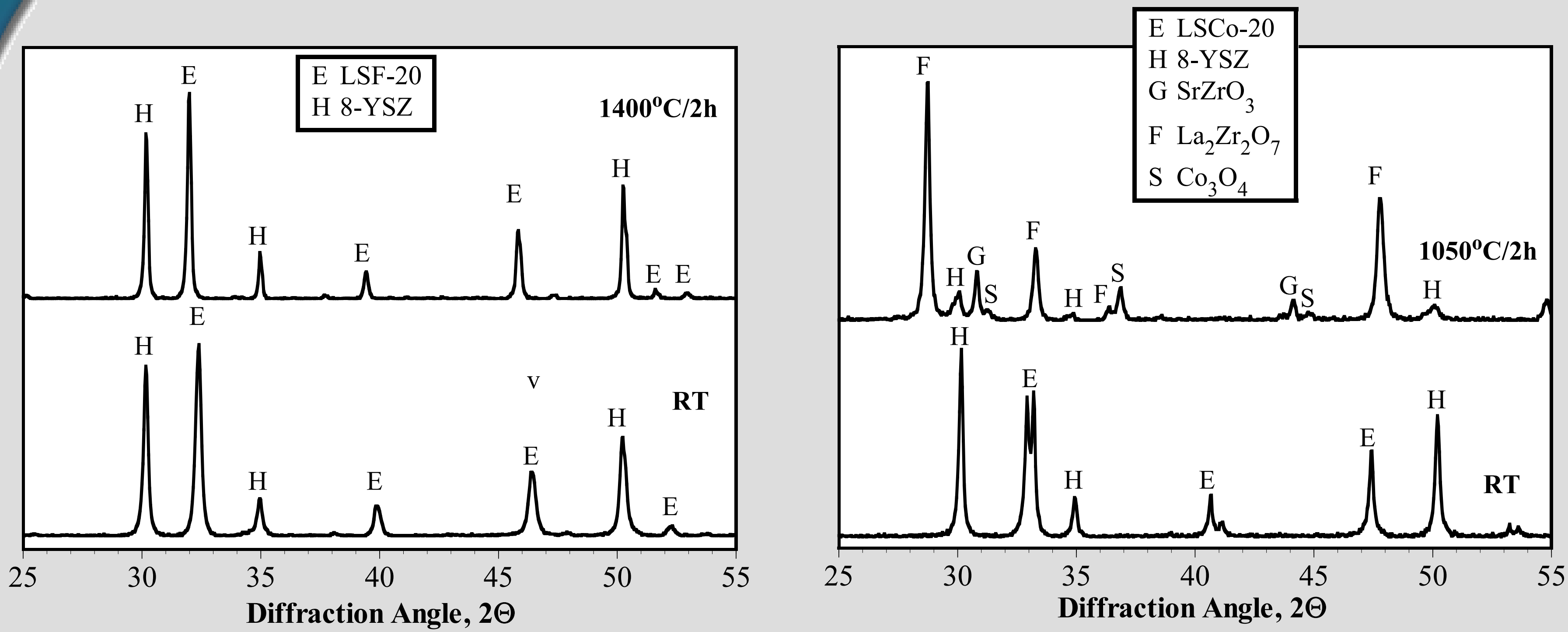
Oxidant: Air





T(ºC)	Power at 0.7V (W/cm^2)
650	0.36
700	0.63
750	0.85
800	1.21

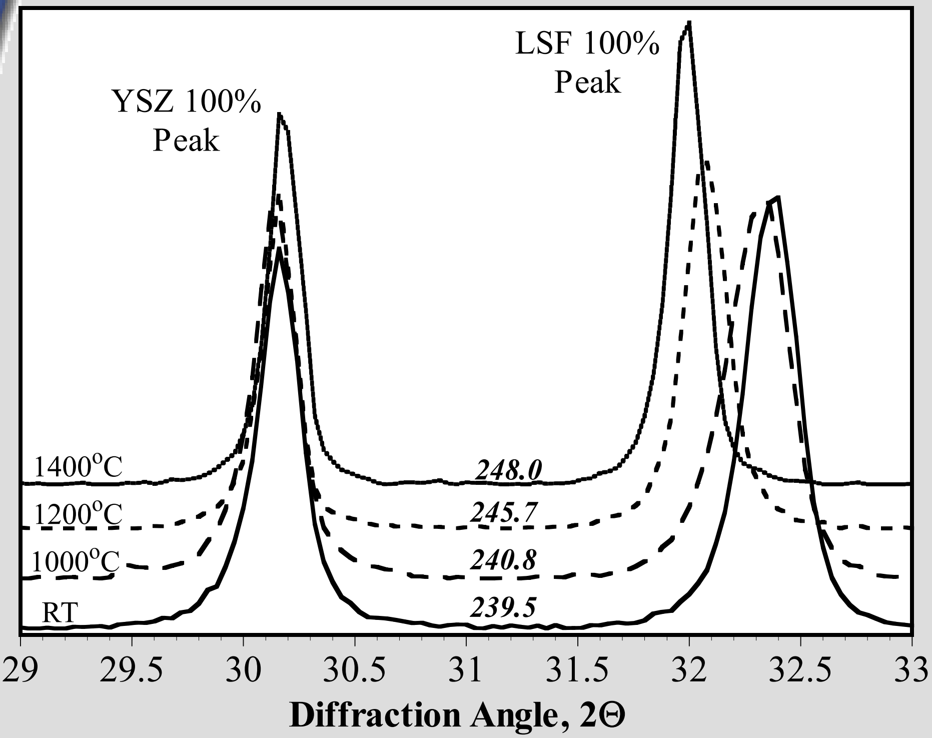
Role of ceria layer:
Prevention of reaction between YSZ and LSF?

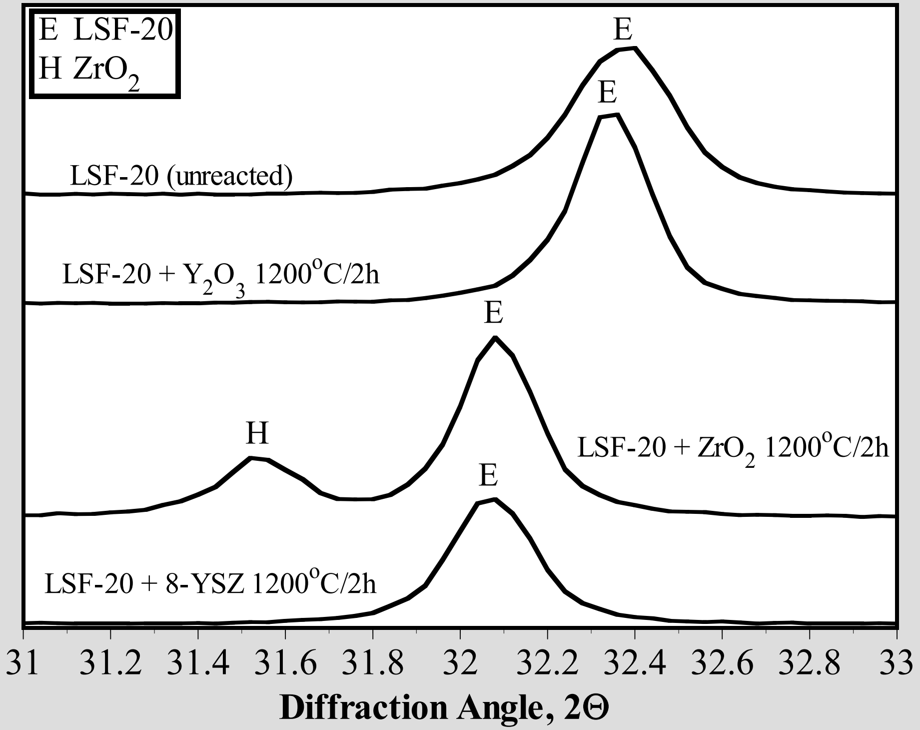


Mixtures of LSF and YSZ, heated to 1400ºC for 2 h, showed no evidence of zirconate formation. (Contrary to case with LSCo and YSZ).

Role of ceria layer:
Prevention of reaction between YSZ and LSF?

However, for T ≥ 1000ºC, LSF peaks were shifted, indicating expansion of lattice due to change in composition of perovskite phase.

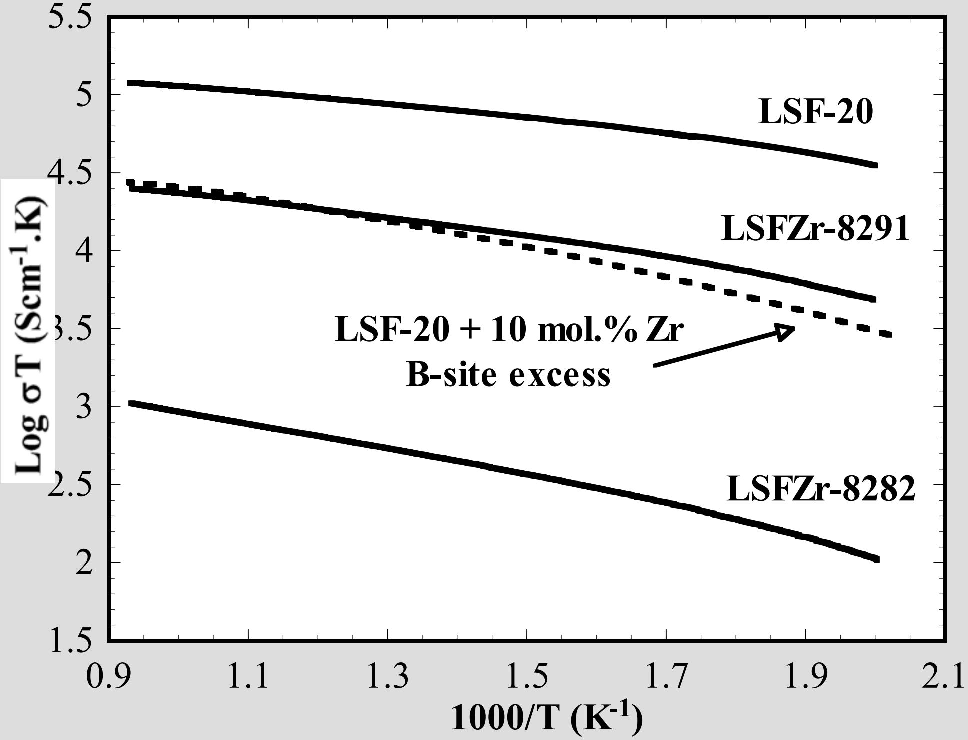




Results using ZrO_2 and Y_2O_3 indicate Zr^{4+} from YSZ incorporated onto B-site of perovskite lattice; conclusion is supported by EDX results

Impact of Zr^{4+} on LSF Conductivity

Significant reduction in electrical conductivity of LSF w/ increasing Zr content:

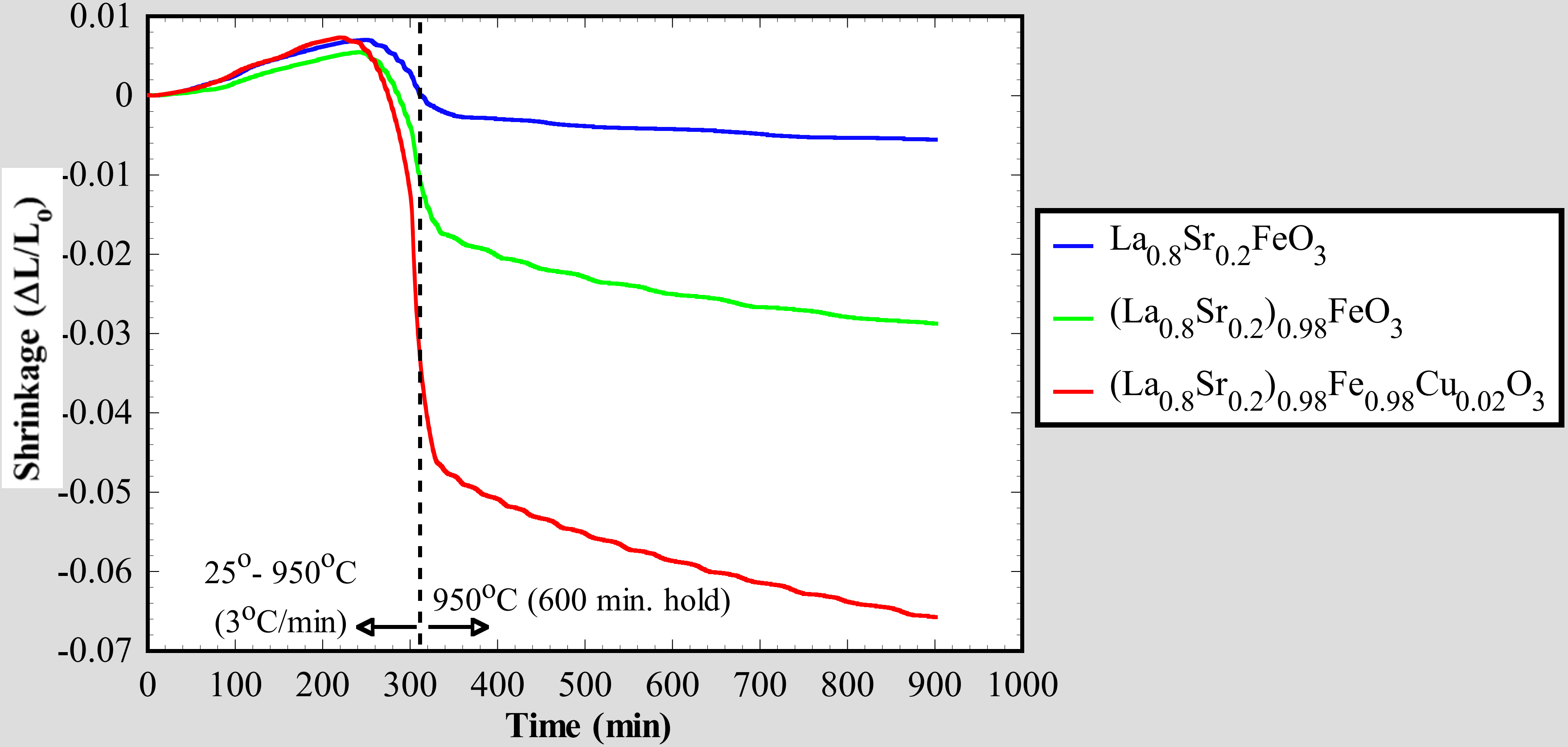


$$\left[Sr_{La}^{'}\right]+\left[Fe_{Fe}^{'}\right]=\left[Fe_{Fe}^{\bullet}\right]+2\left[V_{O}^{\bullet\bullet}\right]+\left[Zr_{Fe}^{\bullet}\right]$$

Conclusion: Ceria interlayer required for LSF cathodes sintered at T ≥ 1000ºC

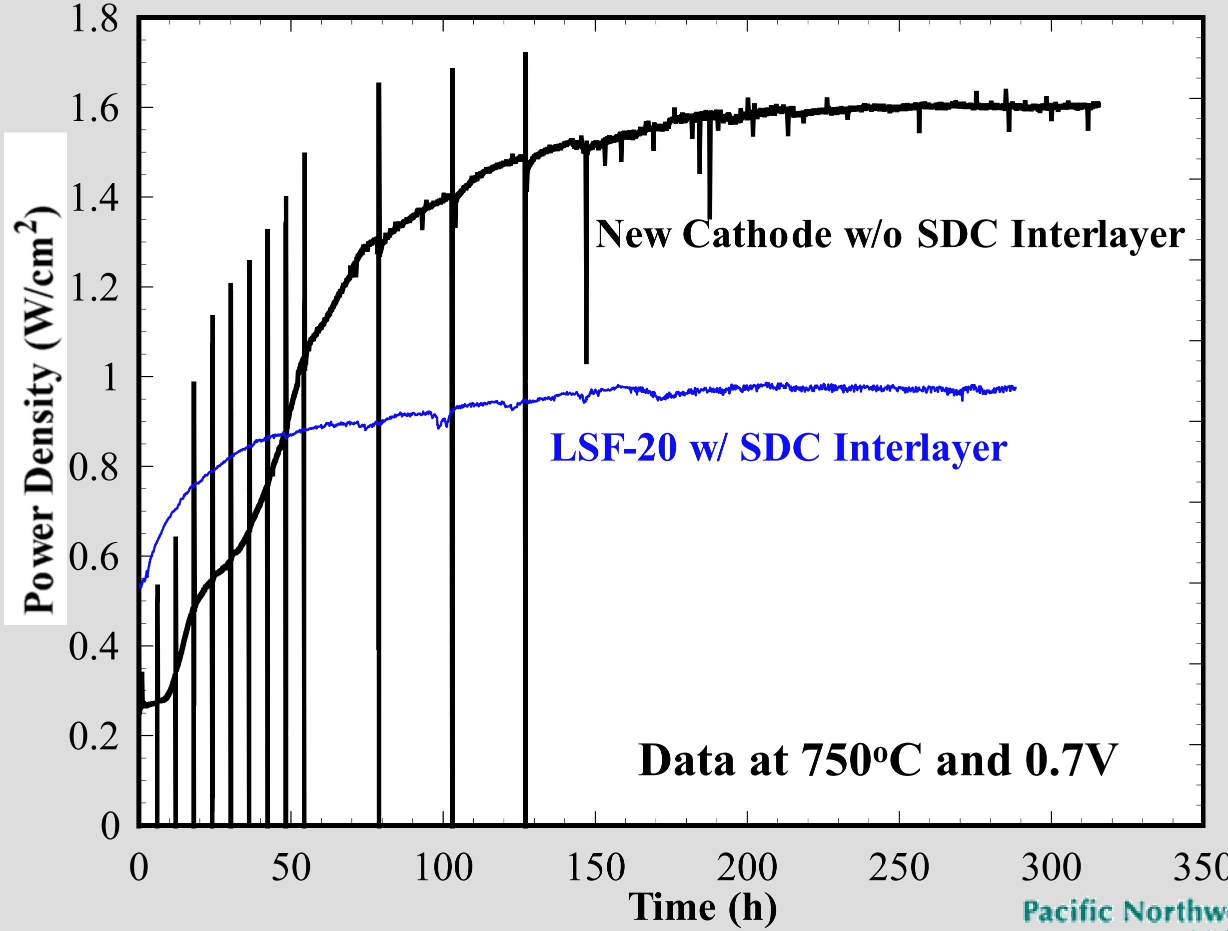
Enhancing LSF Sinterability

- **Goal: Modify the LSF cathode to sinter onto YSZ below 1000°C to avoid the LSF-YSZ interaction. Compositions of the type $(La_{0.8}Sr_{0.2})_{0.98}Fe_{0.98}M_{0.02}O_3$ are being considered.**



$(La_{0.8}Sr_{0.2})_{0.98}Fe_{0.98}Cu_{0.02}O_3$ Performance Data

- Initial performance data indicates significantly improved power density (1.4-1.8 W/cm^2 at 750°C and 0.7V) for the new cathode material sintered on YSZ at 950°C.



Metallic Interconnect Materials Evaluation and Development

Metallic Interconnects for SOFC

- Objectives:
  - Identify and quantify degradation processes in candidate alloys
  - Develop a cost-effective optimized material for intermediate temperature interconnect applications

- Approach:
  - Screen testing of candidate alloys (chemical, electrical, mechanical properties)
  - Materials development
    - Surface modification (surface doping, protective coatings)
    - Bulk modification

Screen testing of candidate alloys

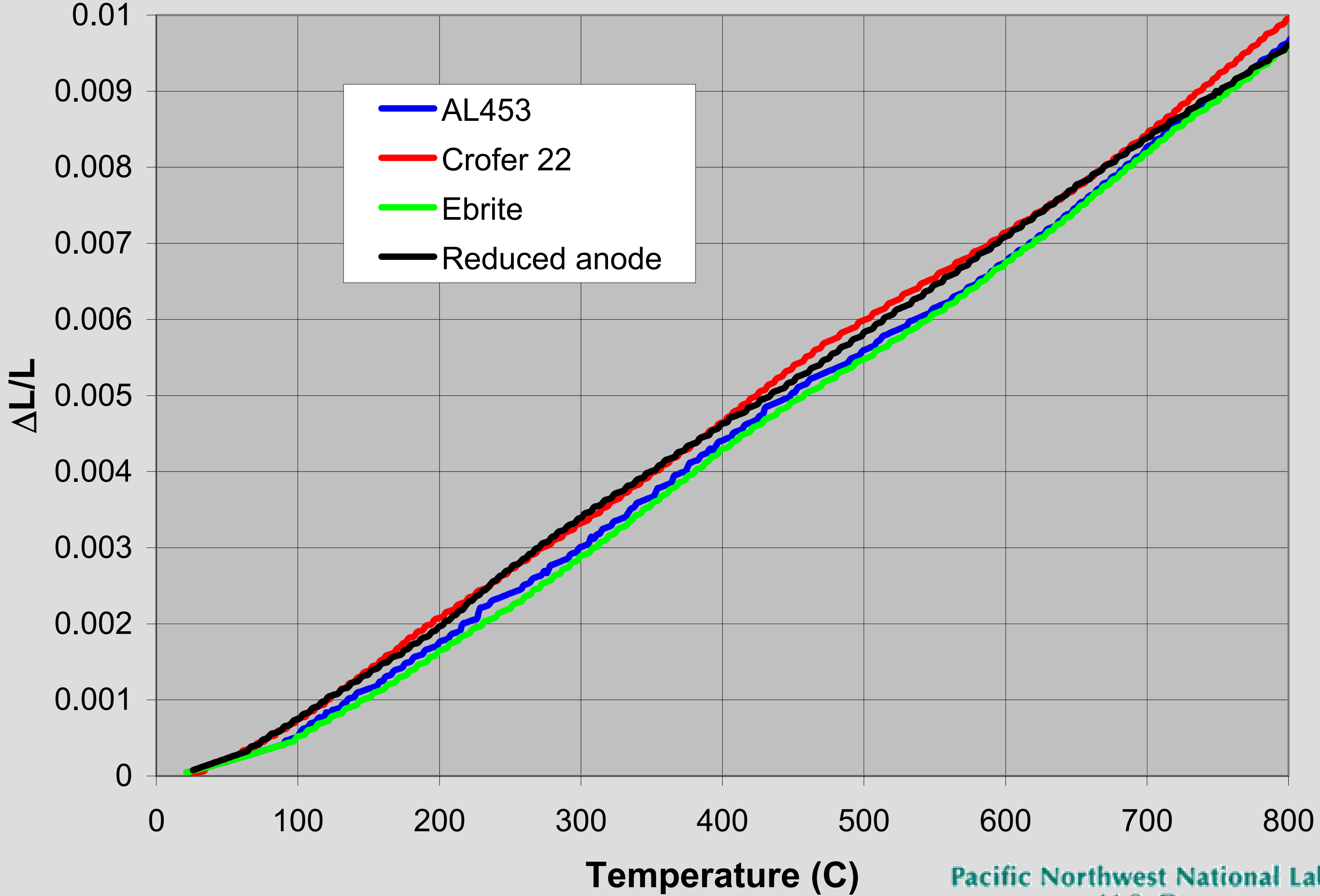
- **Emphasis on "Chromia-forming" Ferritic Stainless Steels:**
  - **CTE match, conductive oxide scale, low cost, ease of fabrication**

- **Screening Studies**

Chemical Screen	▪ Oxidation in air, fuel, and dual atmosphere environments (scale thickness, composition, and microstructure) ▪ Chemical compatibility with alkaline earth-aluminosilicate glass seals ▪ Oxide scale thermodynamic stability
Electrical Screen	▪ ASR measurements under SOFC exposure conditions
Mechanical Screen	▪ Investigation of thermal expansion ▪ Interfacial bonding strength with glass seals

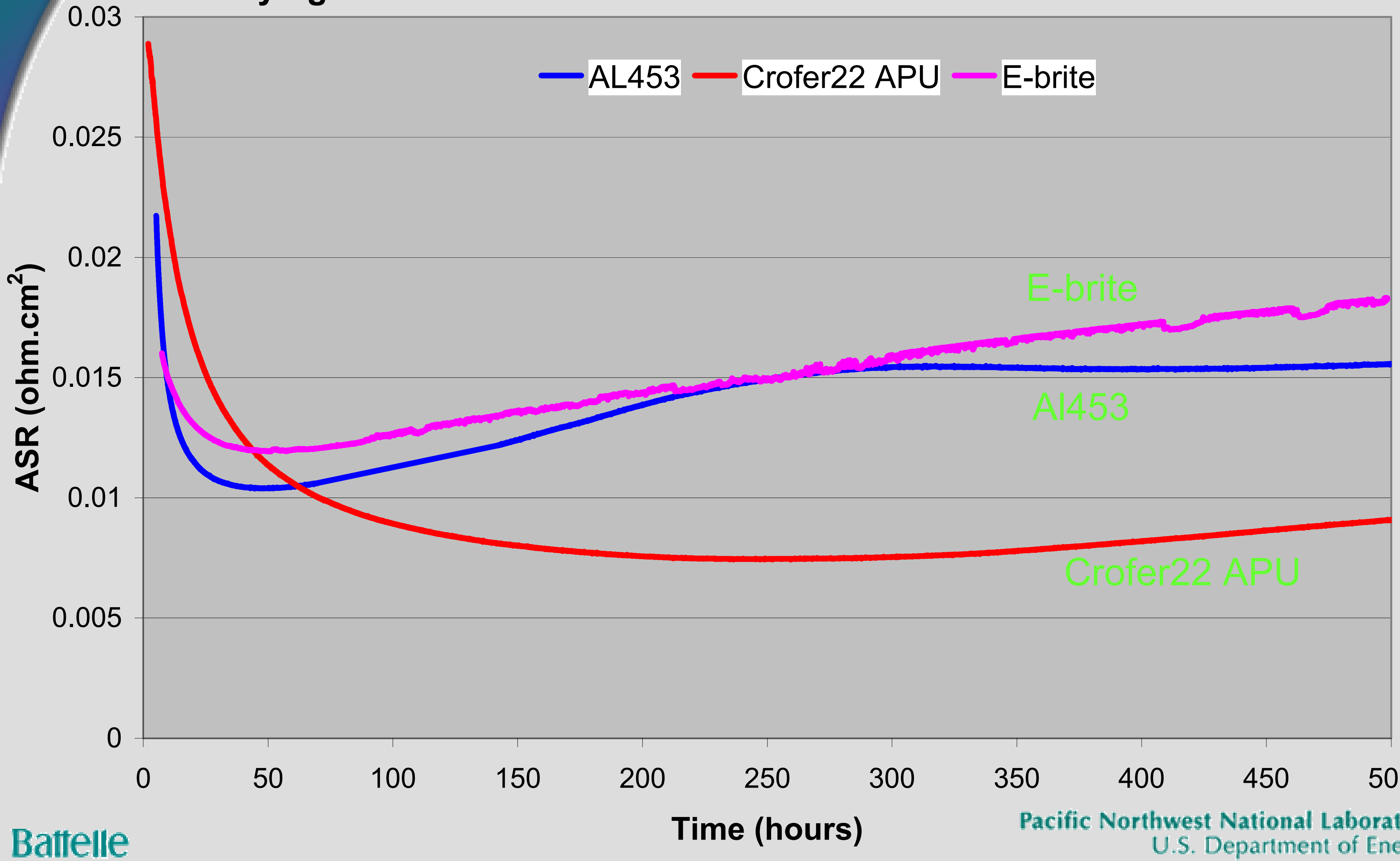
Thermal expansion

Selected alloys offer good CTE match to SOFC components

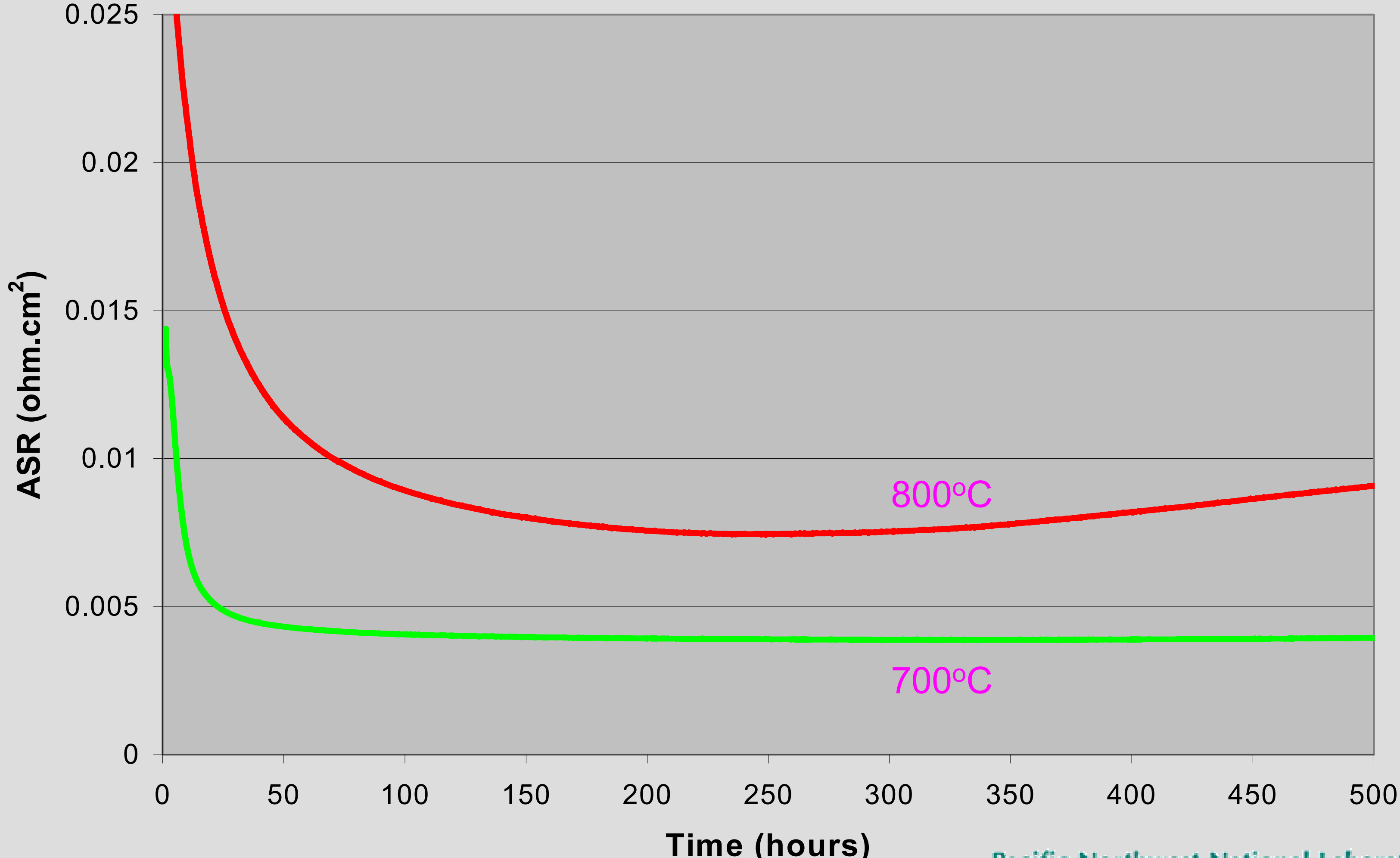


Electrical Resistance of Scales on Selected FSS

Coupon samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.

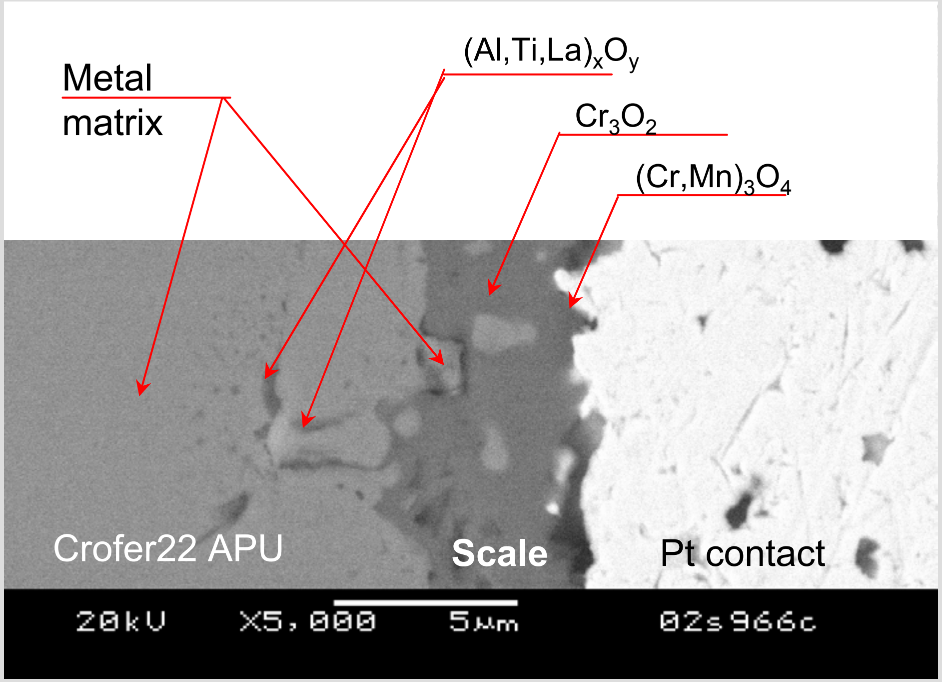


Scale Resistance for Crofer22APU at 700, 800ºC (in air)

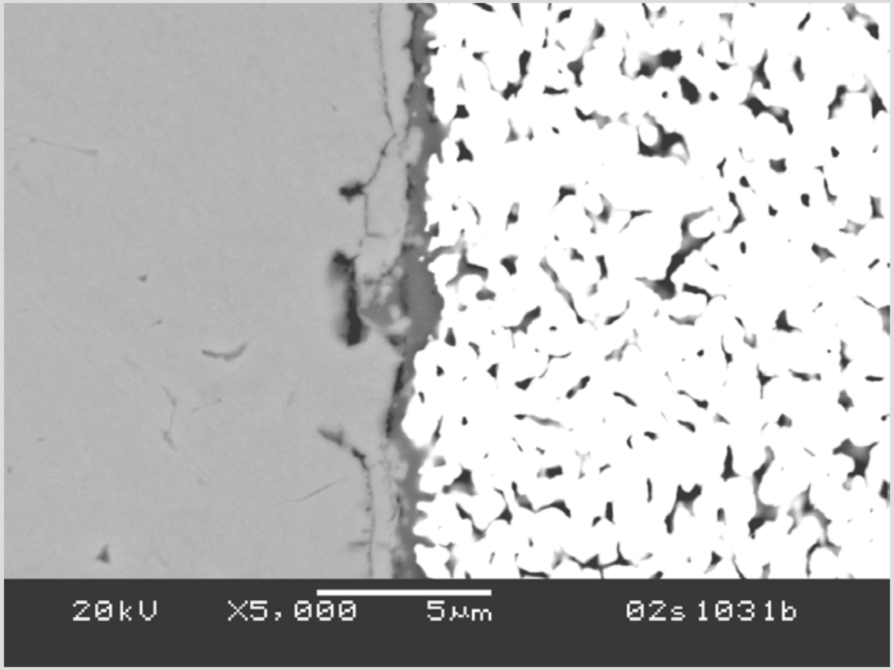


Microstructures of cross-sections of samples from conductivity tests (in air)

800^{o}C, 500h



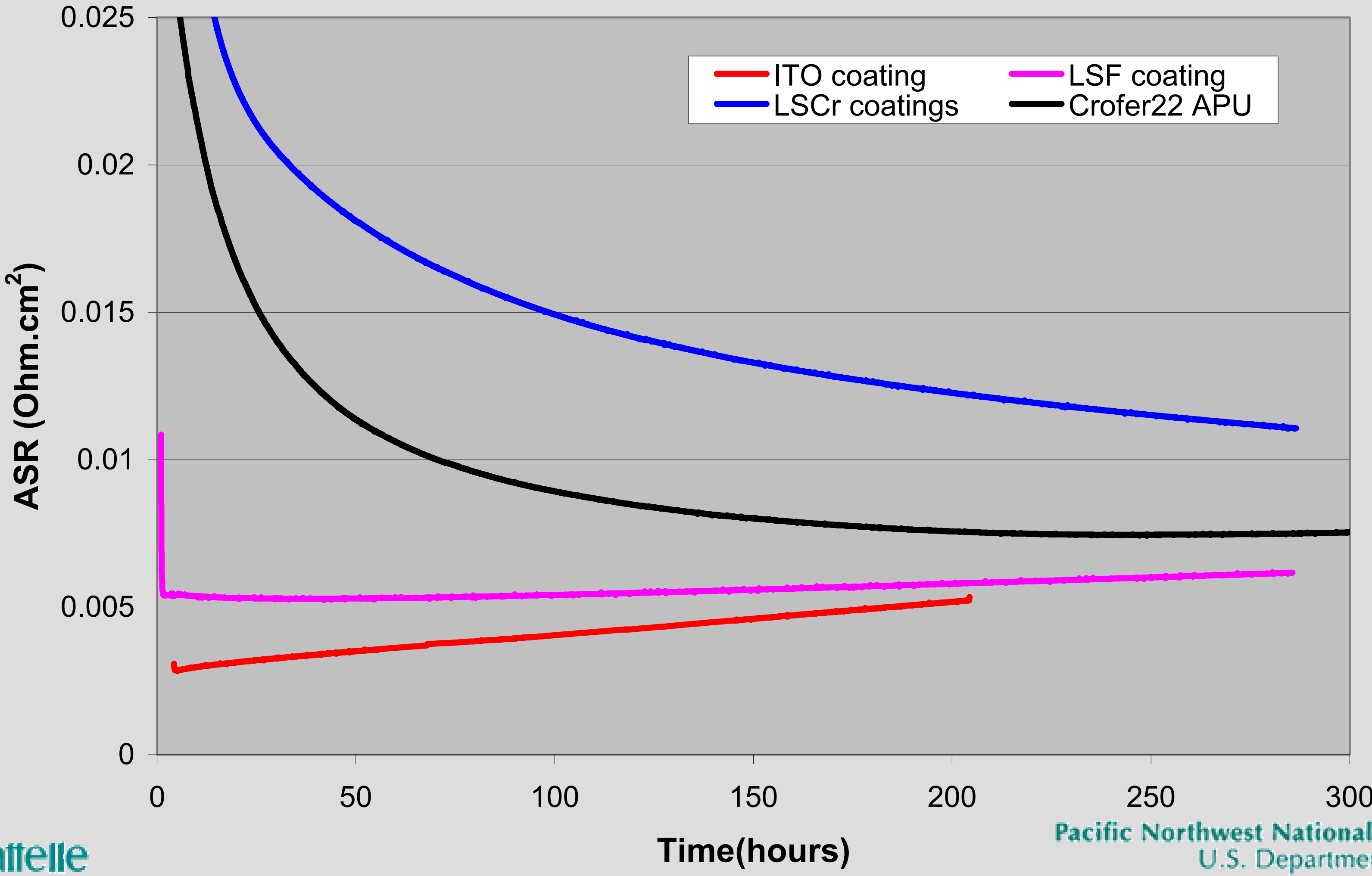
700^{o}C, 500h



Note: Reduced Cr volatility due to $(Cr,Mn)_3O_4$ outer scale

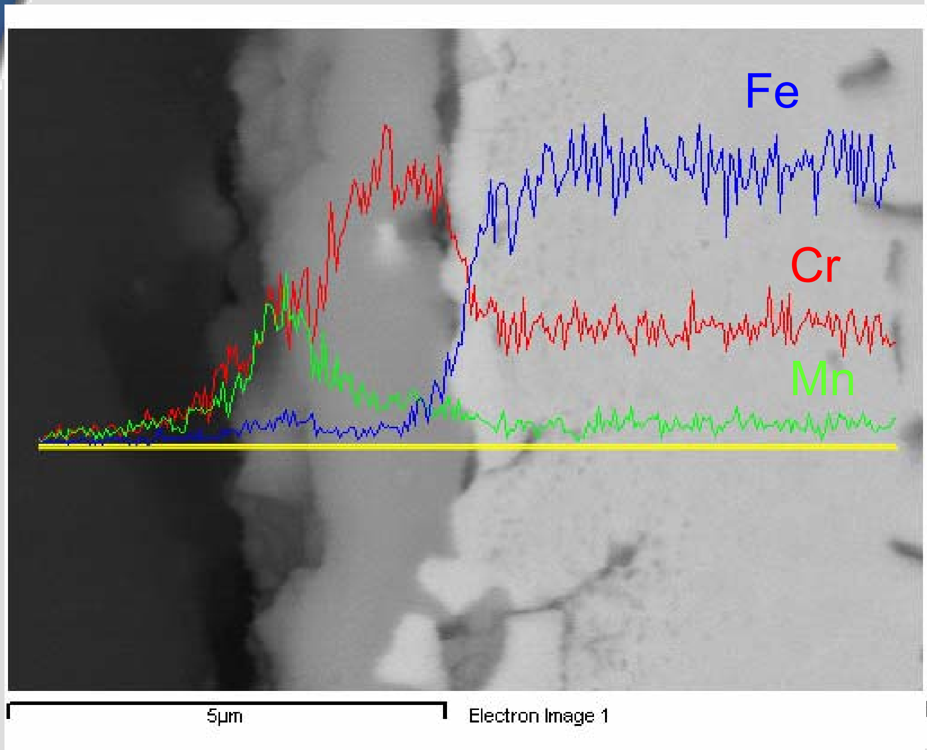
ASR of Crofer22 APU and Effects of Conductive Oxide Coatings

Both bare and coated samples were pre-oxidized in air at 800°C for 100h before carrying out tests in air at 800°C.

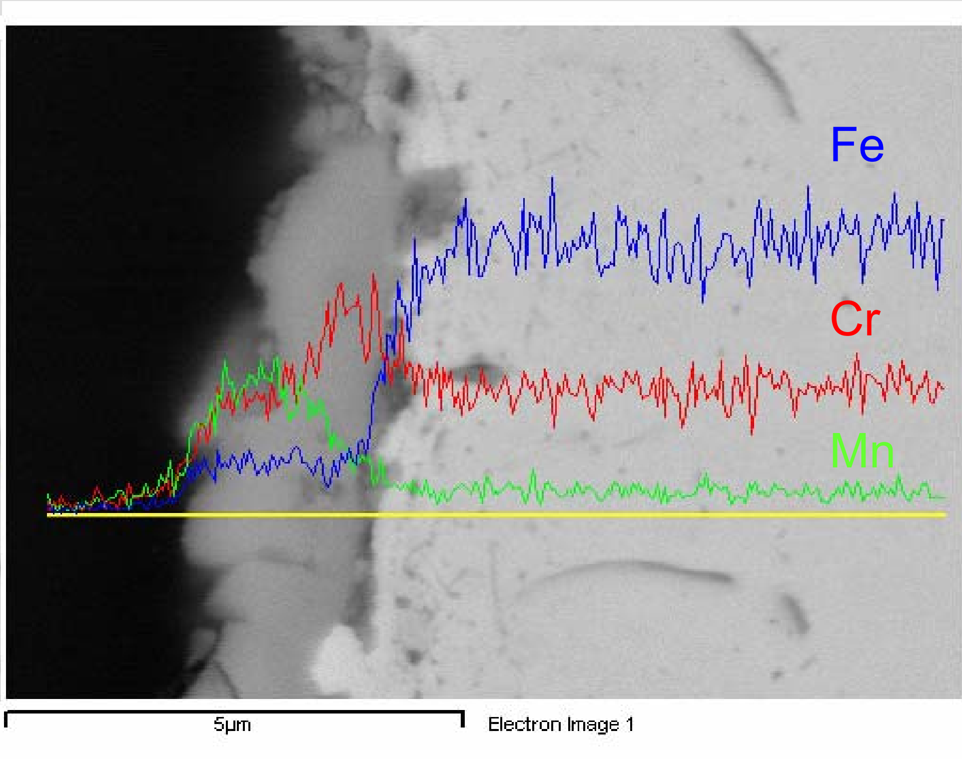


Oxidation Behavior of Crofer22APU: Dual Atmosphere vs. Air

Air exposure at both sides



Air-side of dual exposure



Repeated EDX analyses on Crofer22APU tested under dual exposure indicate the presence of Fe in the scale

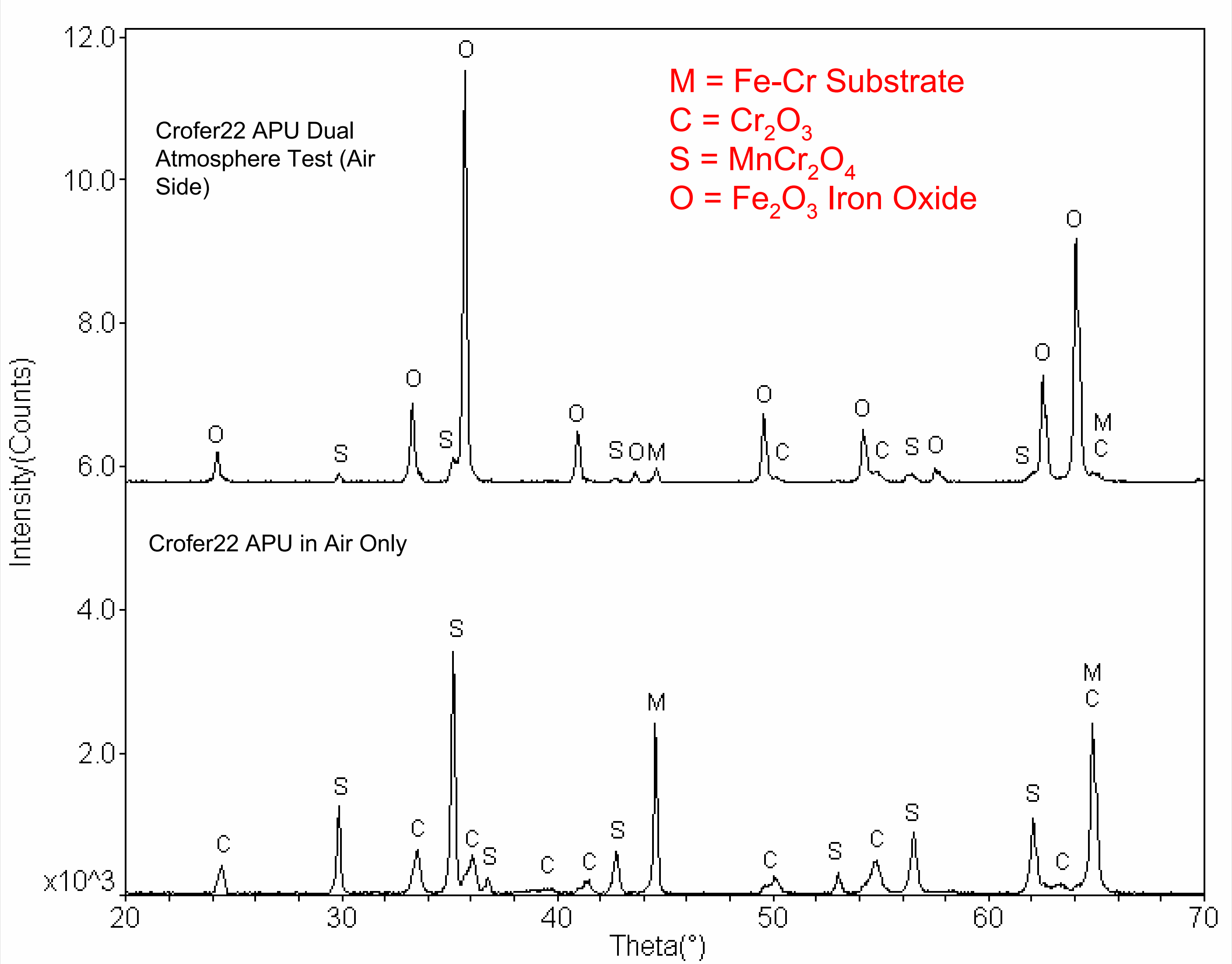
Dual Atmosphere w/ Thermal Cycling

Thermal cycling tests:

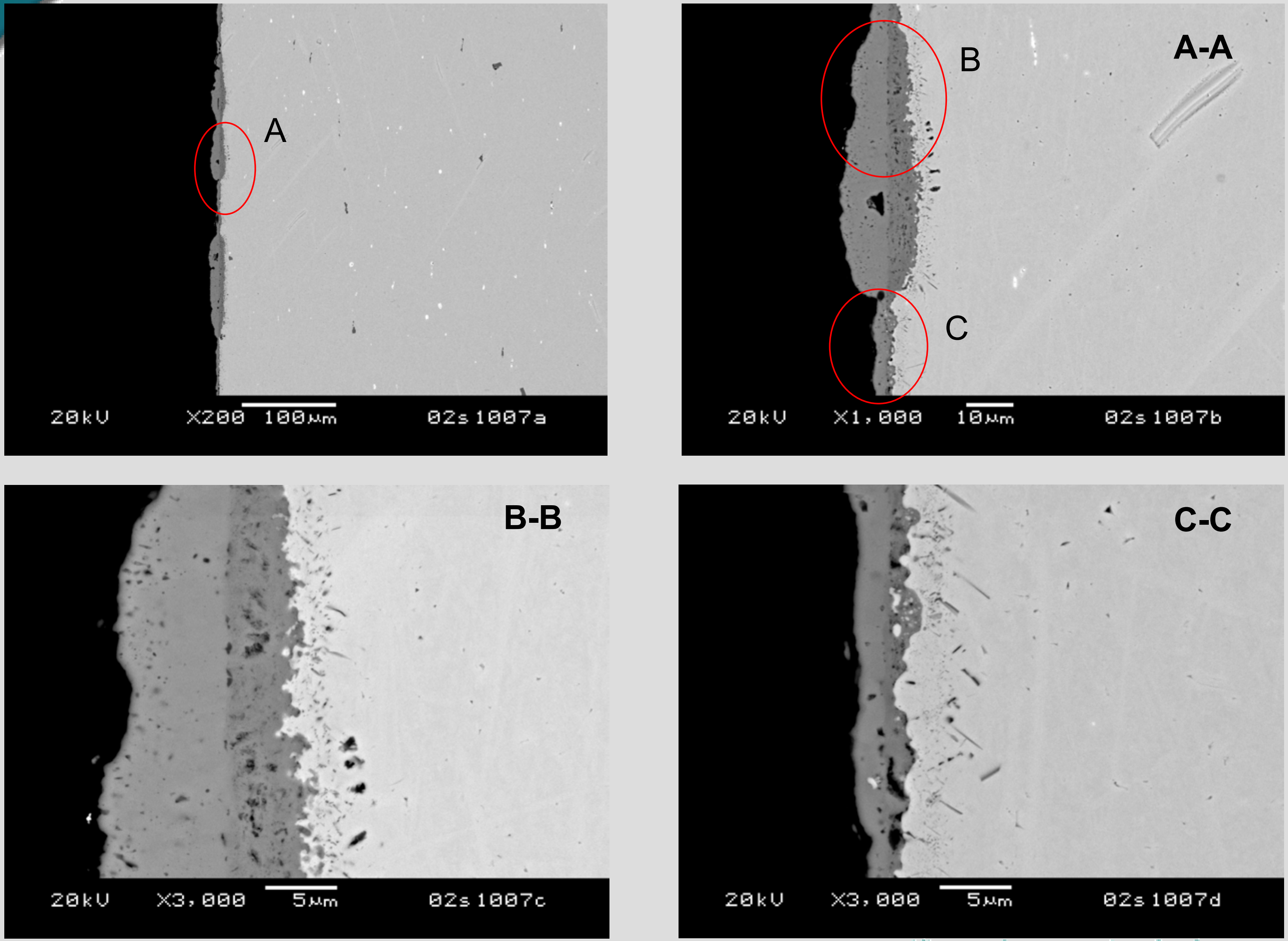
5ºC/min to 800ºC, 100h dwell

3 cycles

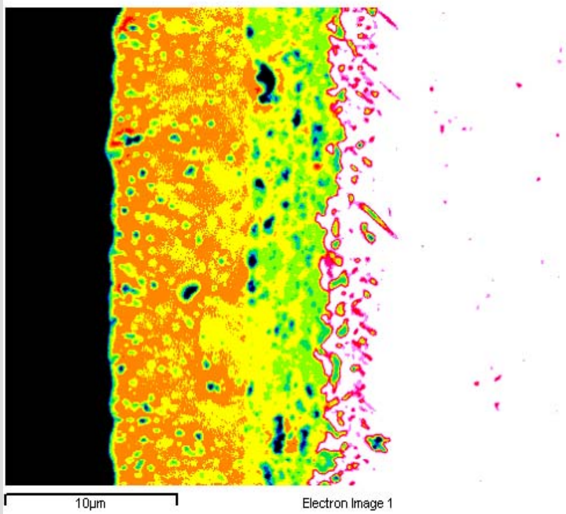
XRD patterns from the airside of dual test vs. air exposure only

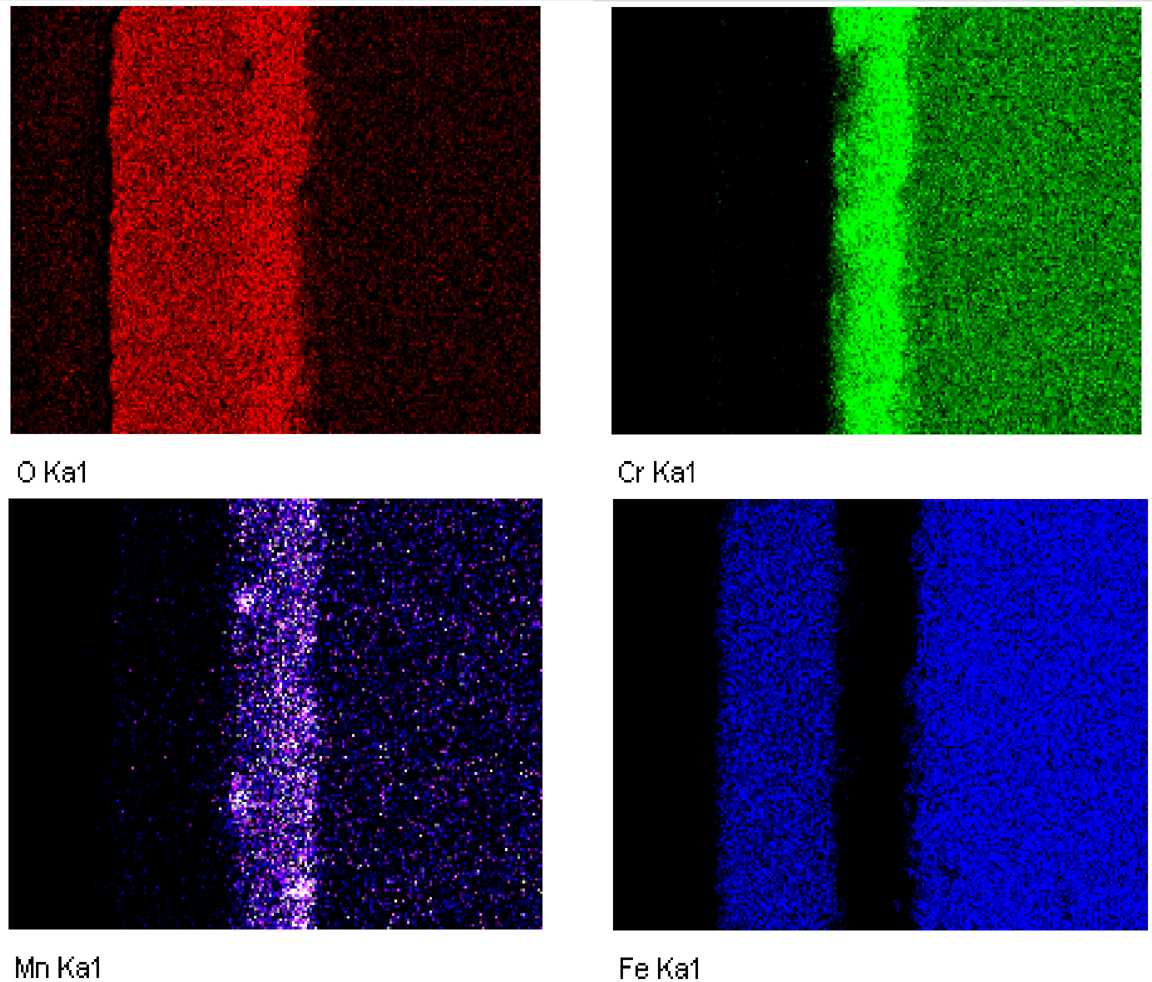


Airside under dual exposure w/ cycling



Elemental mapping of scale formed at the air side





Future Work (Short-term)

- Continue to study role of dual atmosphere exposure on corrosion of alloys
- Extend screening studies to include ZMG232, a new ferritic stainless composition developed by Hitachi Steel for SOFC applications
- Study the evaporation of scale on metallic interconnect
- Investigate the feasibility of doping interconnect surface to minimize scale growth / electrical resistance

Acknowledgements

- Cathode Development: Steve Simner, Mike Anderson
- Interconnect Development: Gary Yang, Prabhakar Singh, Matt Walker

- Financial Support:
  - Solid-State Energy Conversion Alliance Core Technology Program (SECA)

Compositions of FSS

FSS	Fe	Cr	C	Mn	Si	Mo	Ti	Al	P	S	La+Ce
AISI430	Bal.	16.0	0.1	1.0	1.0	--	--	--	0.03	0.03	--
AISI446	Bal.	26.0	0.2	1.5	1.0	--	--	--	0.04	0.03	--
E-brite	Bal.	26.0	0.001	0.01	0.025	--	--	--	0.02	0.02	--
AL453	Bal.	22.0	0.03	0.3	0.3	--	0.02	0.6	0.02	0.03	0.1
Crofer22 APU	Bal.	22.0	0.005	0.5	--	--	0.08	--	0.016	0.002	0.06La
ZMG232	Bal.	22.0	+ other elements								