SOFC IC Overview and CTP Status

Gary Yang, Steve Simner, Jeff Stevenson, and
Prabhakar Singh

Presented at SECA CTP IC Meeting,

Argonne National Laboratory

July 28-29, 2004

Prabhakar.singh@pnl.gov;

outline

- IC Requirements
- IC/ SOFC Exposure Conditions
- IC Materials - Ceramic, Alloys, Coatings
- Technology Status

Prabhakar.singh@pnl.gov;

SECA CTP Priorities

	What	How
1	Gas seals	Glass and compressive seals
1	Interconnect	Modifying components in alloys Coatings
2	Modeling	Models with electrochemistry Structural characterization
2	Cathode performance	Micro structure optimization Mixed conduction Interface modification
2	Anode/ fuel processing	Metal oxides with interface modification Catalyst surface modification Characterize thermodynamics/kinetics
3	Power electronics	Direct DC to AC conversion DC to DC design for fuel cells
4	Material cost	Lower cost precursor processing Cost model methodology

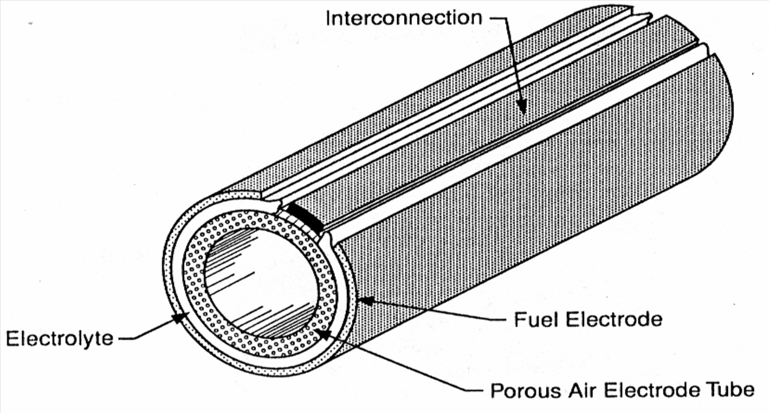
Prabhakar.singh@pnl.gov;

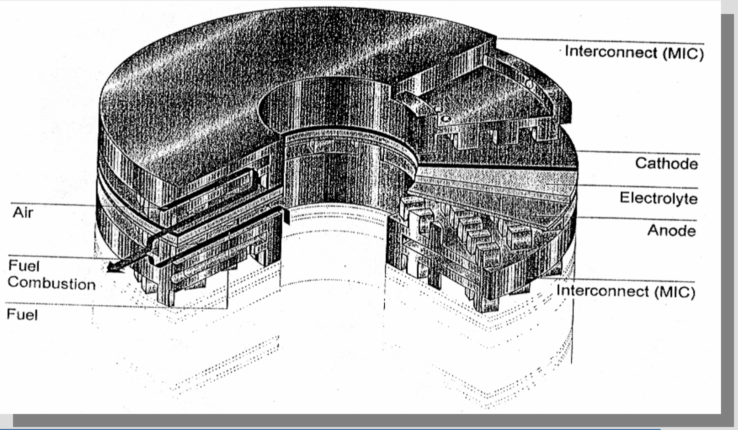
Workshop Findings

(Workshop held in Atlanta, 2001)

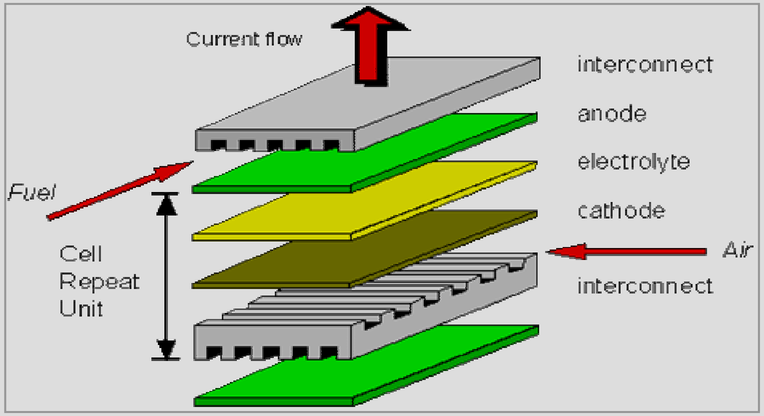
Topical Area	Top 3 Development Needs
Cell/Stack Materials & Manufacturing	1. Stable Interconnect 2. Fuel/ Oxidant Seals 3. Internal Reforming/ Direct oxidation
Fuel processing	1. Sulfur Tolerant Anode 2. Catalyst Kinetics, Parameters & Deactivation 3. On anode Fuel Utilization
Stack/ Systems Performance & Modeling	1. Fast start up and Thermal Cycles 2. Cell & Stack Performance Model 3. Low Cost HX, Insulation, Blowers & sensors
Power electronics	1. Fuel cell / PE Interface 2. Materials & Fabrication Processes 3. Modeling: Electrical Interfaces

SOFC Configurations





Both ceramic and metallic interconnects have been used in SOFC systems



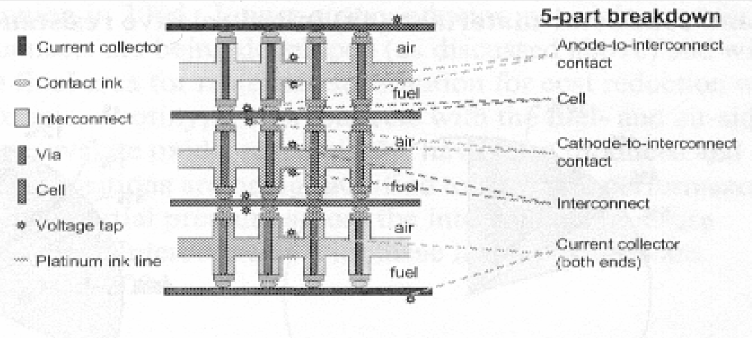
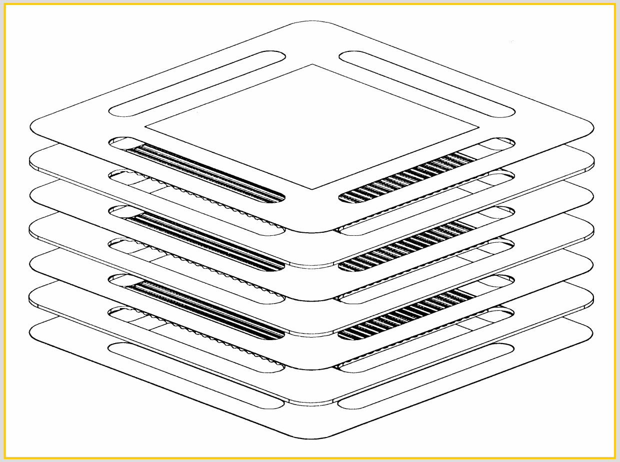
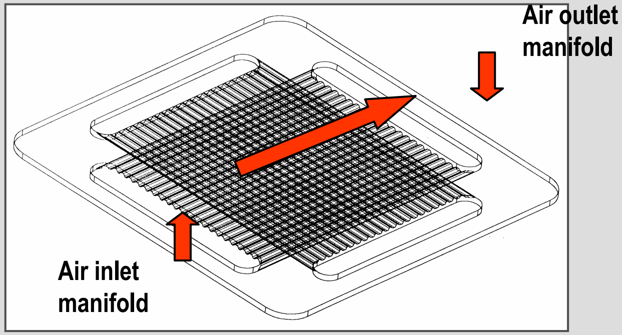


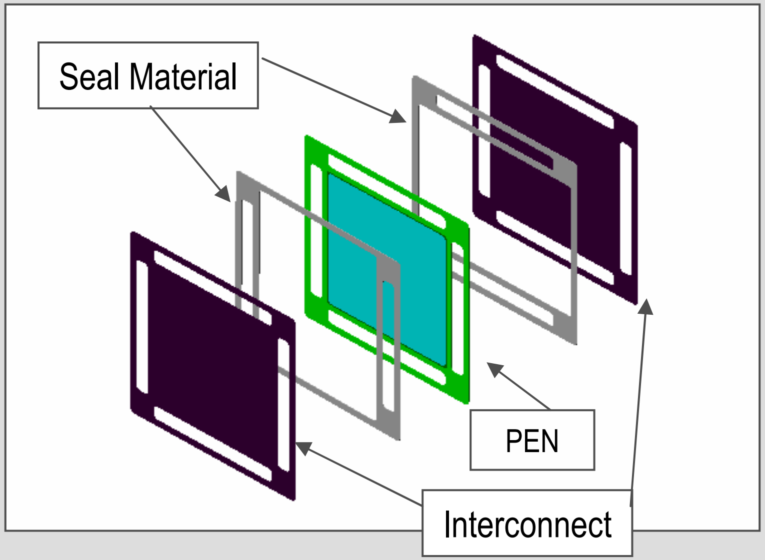
Figure 3. Illustration of short stack using voltage taps to isolate resistance contributions.

Prabhakar.singh@pnl.gov;

Planar SOFC Configurations







Design Variables
- Gas flow distribution channel dimensions/types
- Ceramic or metallic interconnect
- Material thickness and PEN strength
- Rigid or compression seals
- Manifold dimensions and Flow configuration

Operational Variables
- 600-800C or higher
- Air as oxidant
- Hydrocarbon or reformed fuel
- 60-85% fuel utilization

Interconnection Functional Requirements

An integrated approach for IC development has been designed and implemented

SOFC Interconnection Materials

Electrical	Chemical	Mechanical	Fabrication	Cost
• Metal & Oxide electrical conductivity	• Resistance to oxidation and volatilization in air and multi-component fuel gases • Resistance to interfacial interactions	• Thermal expansion match • High temperature yield strength • Creep resistance	• Fabricability • Joinability	• Low raw materials cost • Low processing cost • Materials of non-strategic importance

A Collaborative Program with Universities, National Laboratories, Manufacturers and Users

Prabhakar.singh@pnl.gov;

SECA CTP IC Development

Evaluation of metals and alloys:
- Fe base FSS, ASS
- Ni base alloys
- Silver and others

Evaluation of Coatings:
- Ceramic w/wo Cr
- Claddings

Evaluation of degradation mechanisms
- Corrosion in single & dual atmospheres
  - Interaction with Seals
  - Interaction with electrodes / interface layers

- Growth kinetics
- Electrical conductivity
- Chemical stability
- Interface stability
- Electrode compatibility

Prabhakar.singh@pnl.gov;

SECA CTP Interconnect Activities

PNNL

Evaluation of candidate alloys, surface modification of alloys, development of interconnect/cathode interfaces, evaluation/mitigation of Cr poisoning

ANL

Evaluation/mitigation of Cr poisoning, development of alloy interconnects

LBNL

Metal supported cells, protective coatings for alloys

Univ. of Pittsburgh

Evaluation of chromia-forming alloys, accelerated testing, mechanisms

Ceramatec

Protective coatings for interconnect alloys

New Starts

Arcomac Surface Engineering, LLC

Oxidation Resistant, Cr Retaining, Electrically Conductive Coatings on Metallic Alloys for SOFC interconnects

Southwest Research Institute

Surface Modified Ferritic Interconnects for SOFCs

Southern Illinois University at Carbondale

Novel alloy system, based on TiC-Ni-Ni3Al to develop a superior interconnect material for SOFC.

Tennessee Technological University

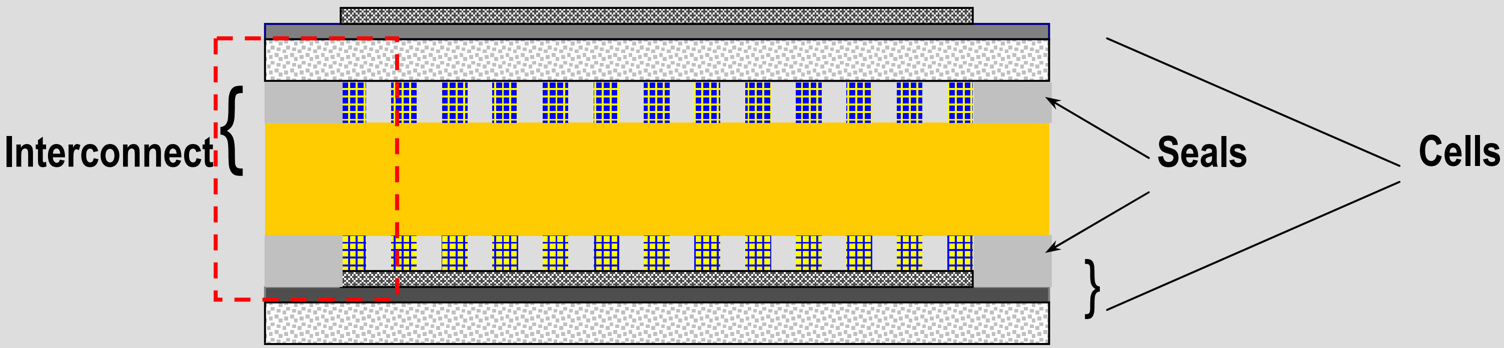
Utilize alloy design principles to thermally-grow multi-layer structure with an outer layer of Cr-free nickel ferrite spinel and an inner layer of Ni-rich or Cr-rich protective oxide's

University of Utah

Synthesize and characterize coating materials with ultra-low oxygen diffusion that are electronically conducive using site-specific doping and through fundamental understanding of the underlying defect chemistry

Prabhakar.singh@pnl.gov;

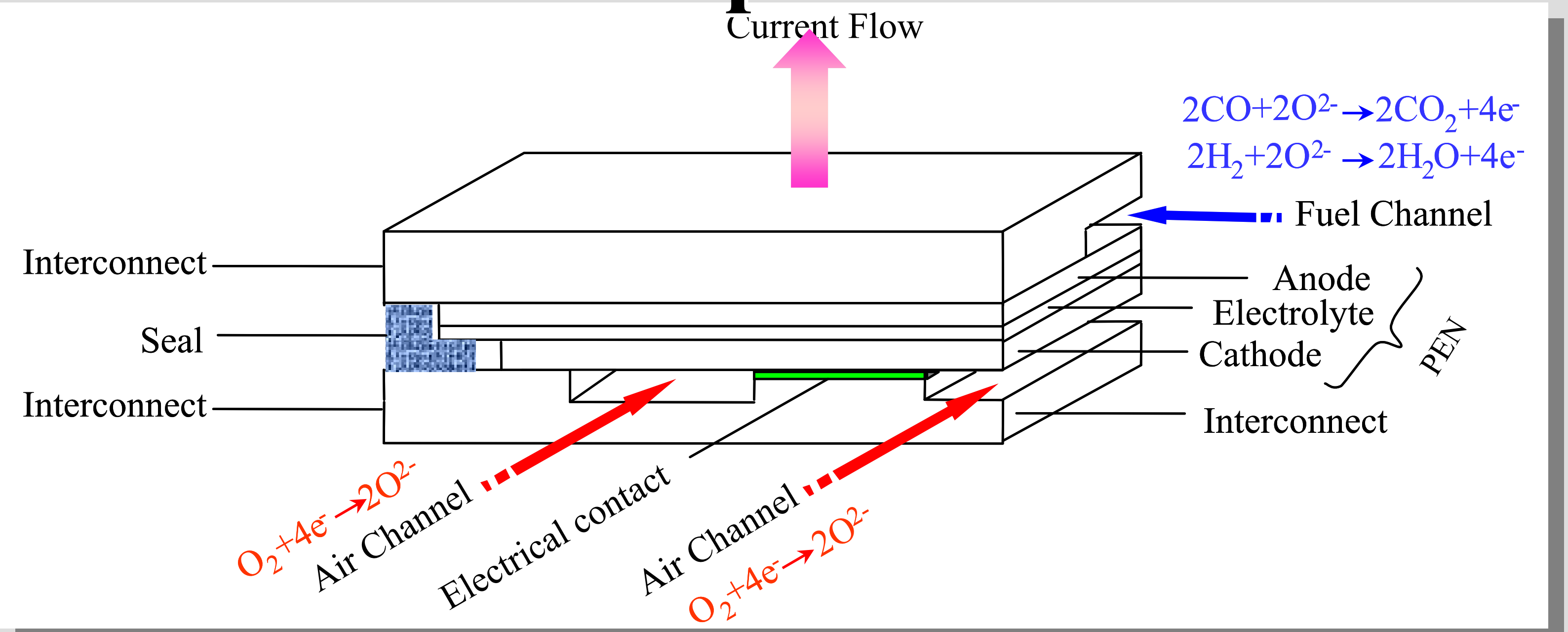
The Interconnect : Function

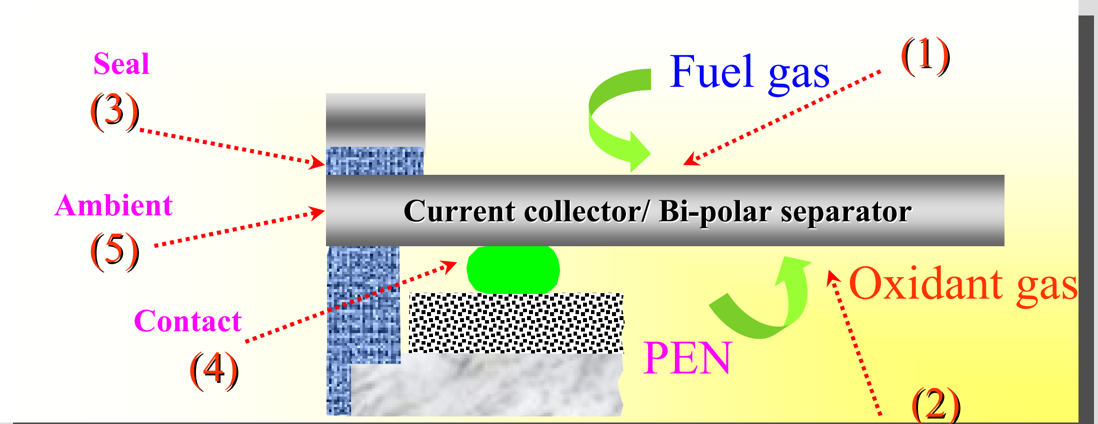


- ✓ Acts as a physical barrier between the fuel and oxidant (hermetic, chemically and mechanically stable, and thermally shock resistant)
- ✓ Acts as a low resistivity electrical conduit over the lifetime of the device
- ✓ Provides mechanical support and stability to the stack

Prabhakar.singh@pnl.gov;

Current collector exposure conditions





1. Fuel gas/Metal interface
2. Oxidant gas/Metal interface
3. Compliant seal/Metal interface
4. Electrical contact/metal interface
5. Ambient/Metal interface

Candidate IC Materials

Three groups:

1. Electronically conducting Ceramic
   La Chromite (Doped)

2. Metals and Alloys
   Fe Base FSS & ASS, Ni base Alloys, Ag

3. Coatings & Claddings
   Perovskites, Spinals, Ni (Anode)
   Bi & tri layer clad

Bulk (groups 1–2)

Surface (group 3)

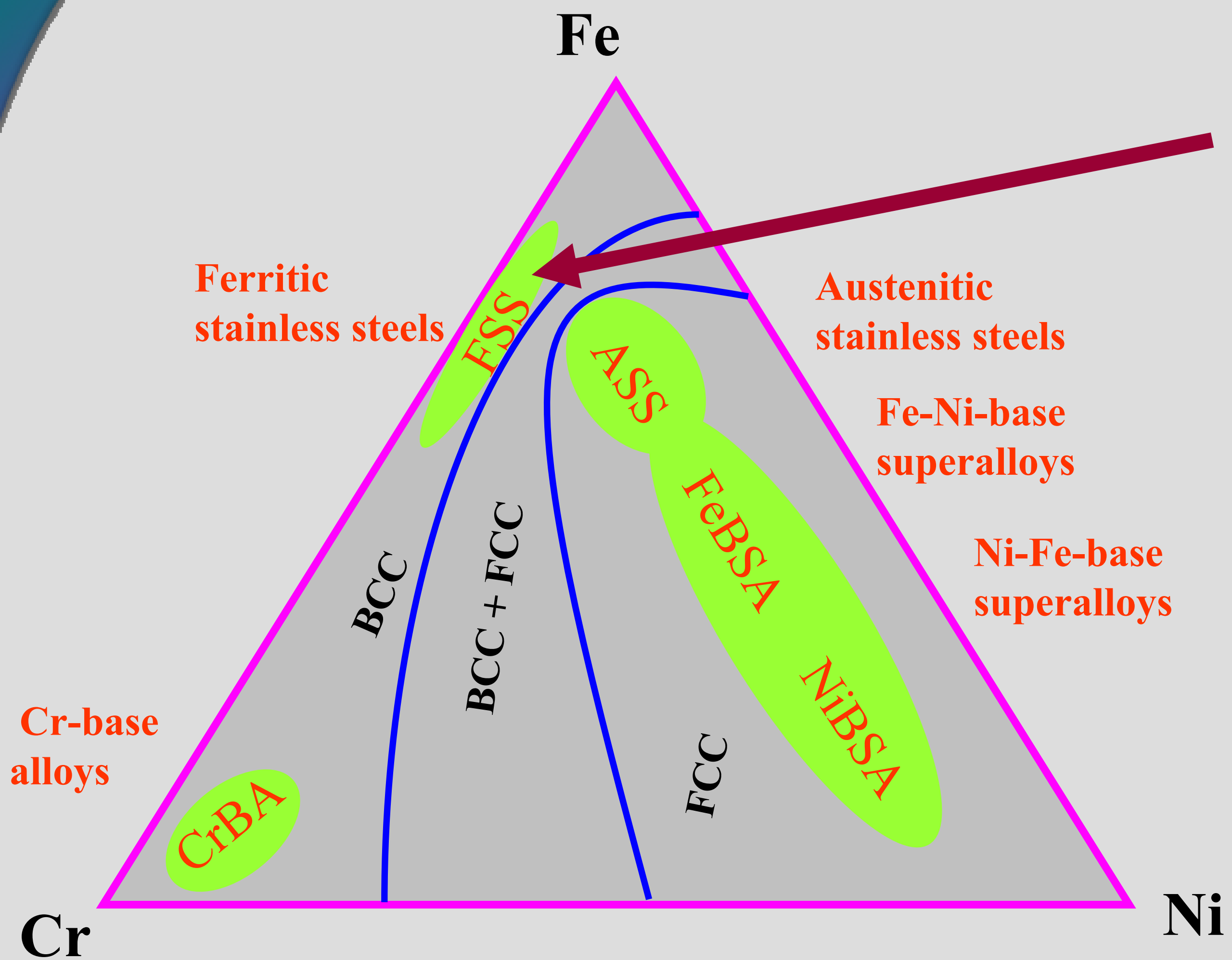
Prabhakar.singh@pnl.gov;

key properties of different alloy groups

Alloys	Matrix structure	TEC $\times 10^{-6}.K^{-1}$	Oxidation resistance	Mechanical strengths	Manufactur-ability	Cost
CrBA	BCC	11.0-12.5 (RT-800°C)	Good	High	Difficult	Very expensive
FSS	BCC	11.5-14.0 (RT-800°C)	Good	Low	Fairly readily	Cheap
ASS	FCC	18.0-20.0 (RT-800°C)	Good	Fairly high	Readily	Cheap
FeBSA	FCC	15.0-20.0 (RT-800°C)	Good	High	Readily	Fairly expensive
NiBSA	FCC	14.0-19.0 (RT-800°C)	Good	High	Readily	Expensive

Prabhakar.singh@pnl.gov;

Potential Candidate Alloy Systems

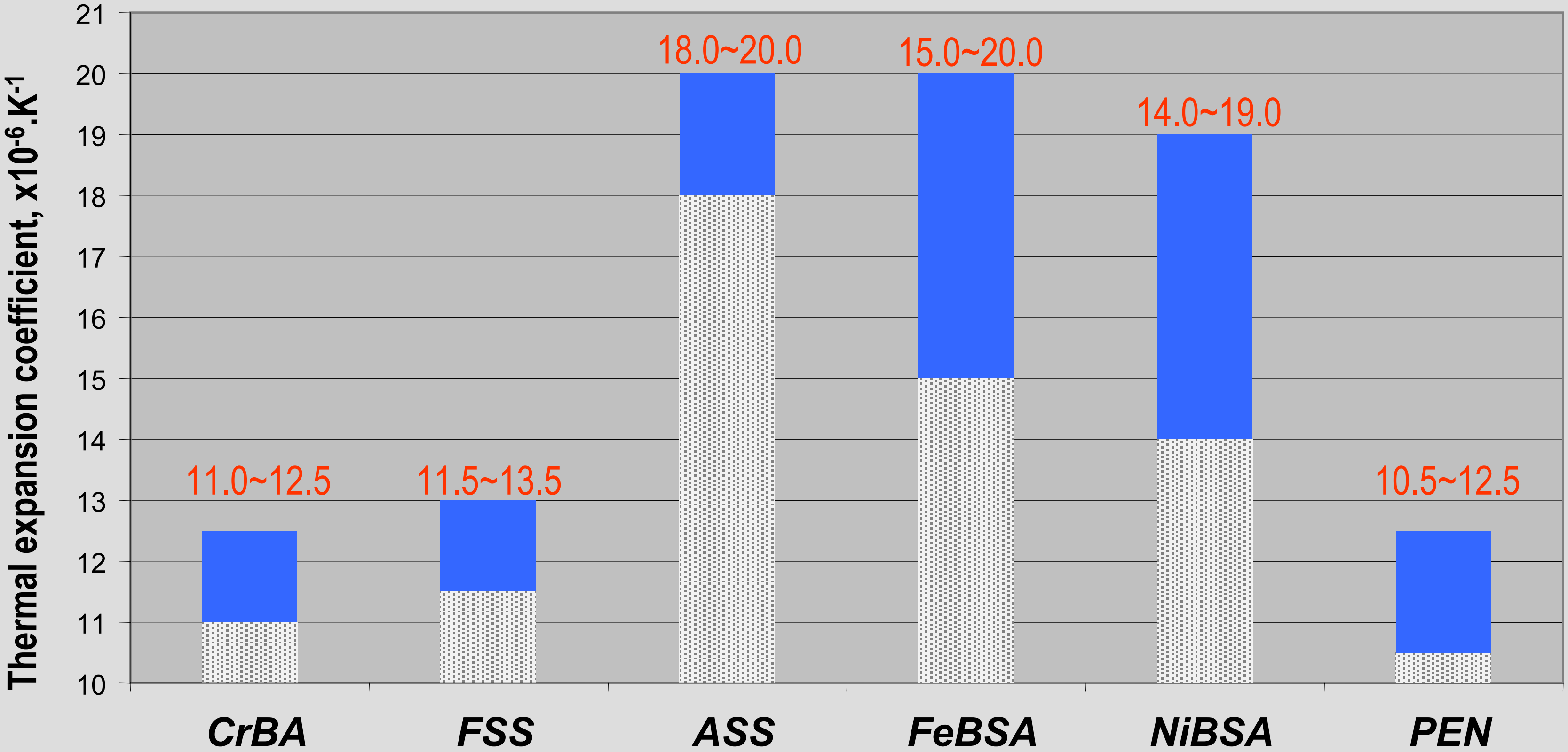


Emphasis on "Chromia-forming" Ferritic Stainless Steels:

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

Prabhakar.singh@pnl.gov;

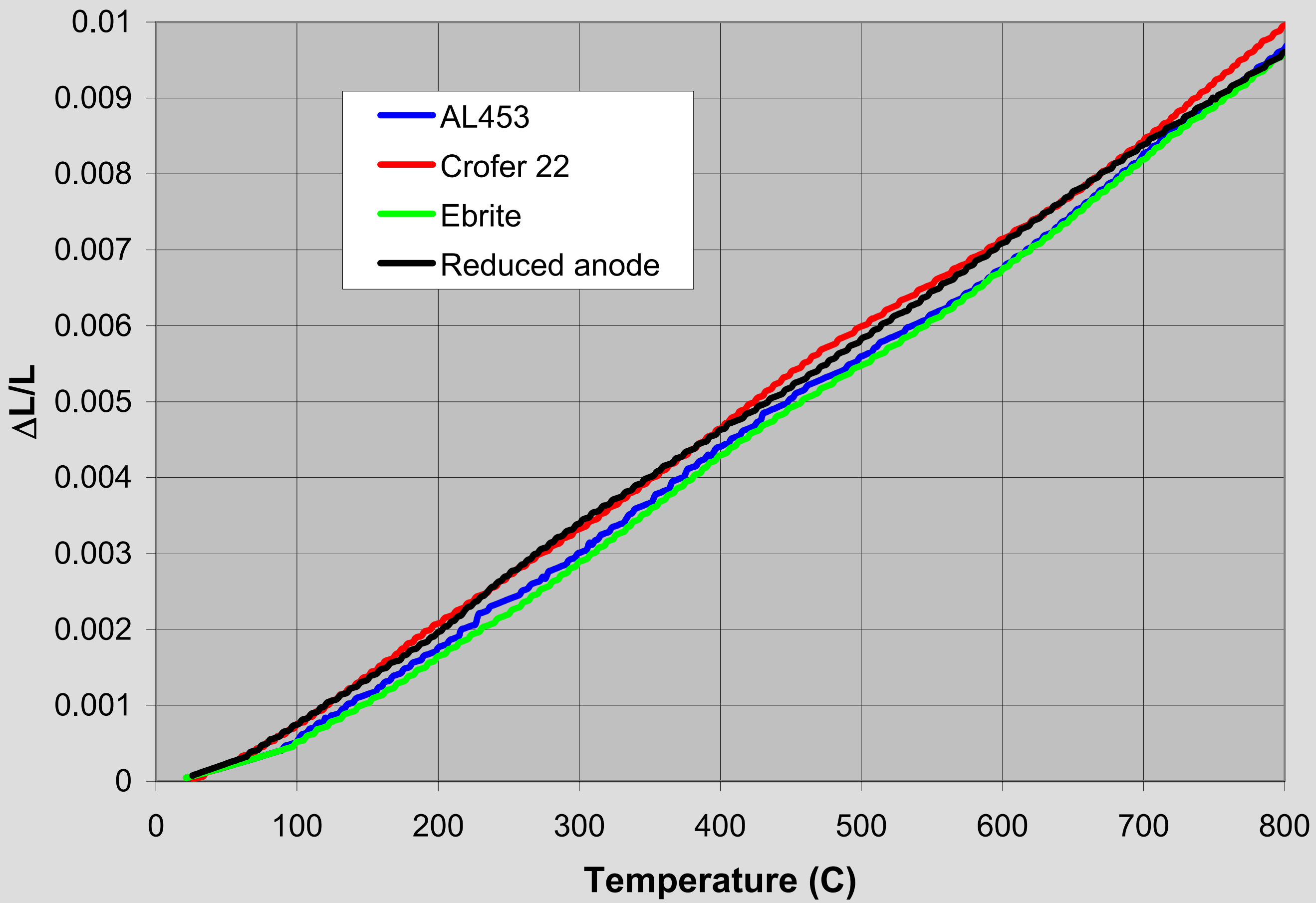
CTE of different alloy groups



- *BCC matrix alloys (CrBA, FSS) have a lower CTE than that of FCC matrix alloys (ASS, FeBSA, NiBSA);*
- *FSS, including Fecralloy offer better CTE match to PEN.*

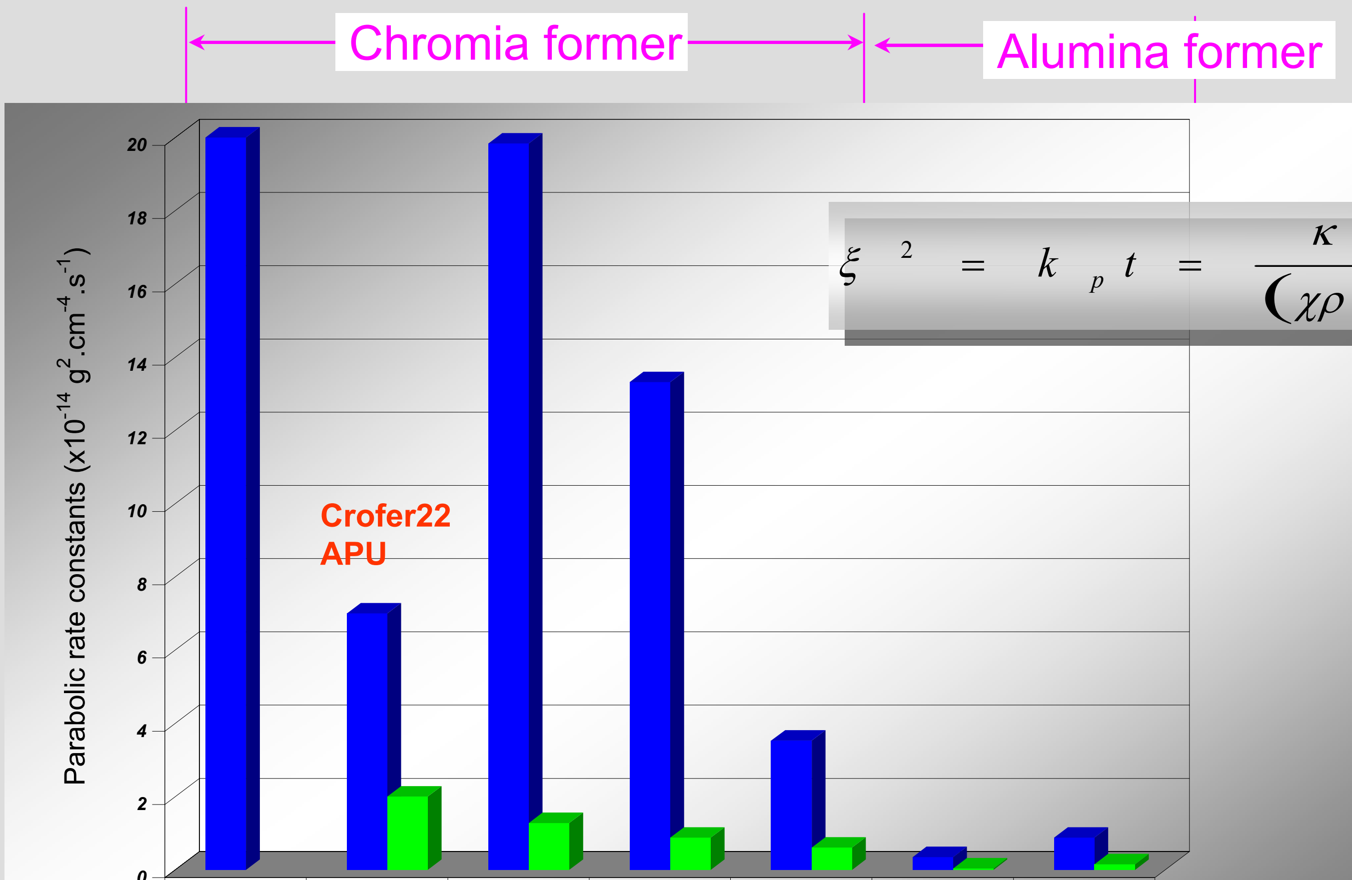
Thermal expansion

Selected alloys offer good CTE match to SOFC components



Prabhakar.singh@pnl.gov;

Oxidation Resistance



$$\xi^2 = k_p t = \frac{\kappa_g}{(\chi\rho)^2} t$$

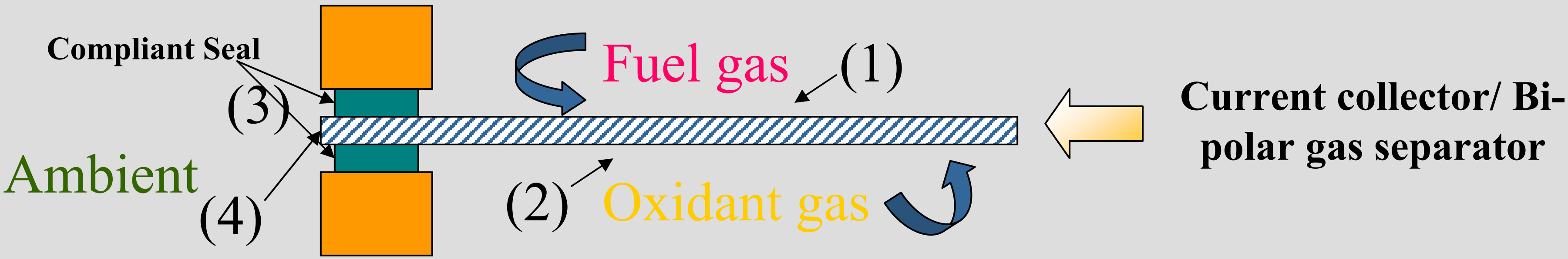
	430	Crofer22 APU	AL 453	446	E-brite	Fecralloy	Alpha-4
800oC	35	7	19.84	13.32	3.53	0.35	0.88
700oC		2	1.28	0.88	0.61	0.04	0.15

Prabhakar.singh@pnl.gov;

SOFC Exposure : Corrosion & Oxidation

Prabhakar.singh@pnl.gov;

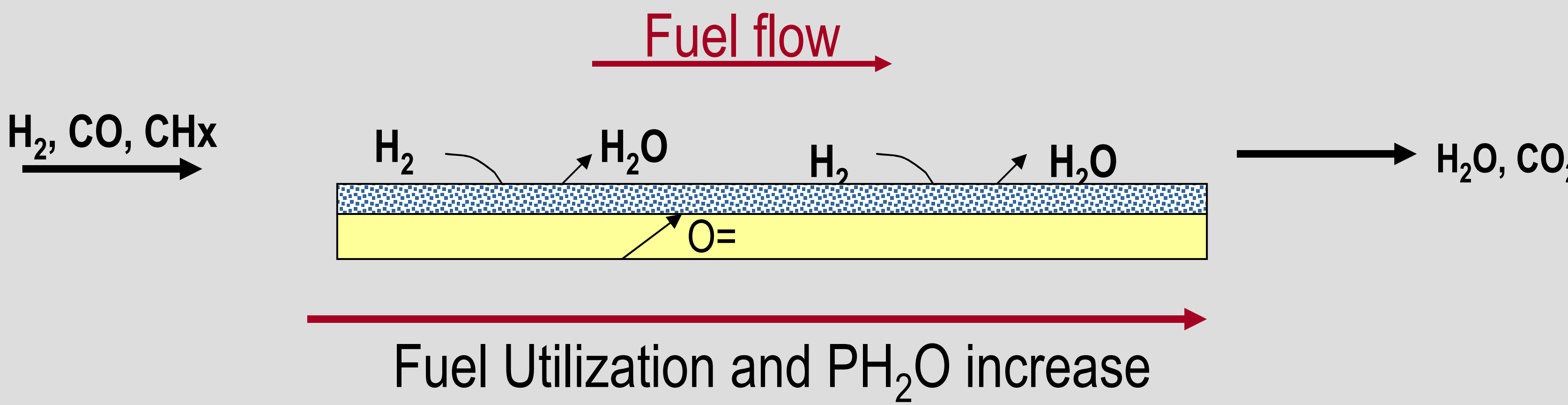
Current collector exposure conditions



1. Fuel gas / Metal interface
2. Oxidant gas/ Metal interface
3. Compliant seal/ Metal interface
4. Ambient/ Metal interface

Prabhakar.singh@pnl.gov;

Fuel Utilization: H_2O Formation



$CHx + H_2O = H_2 + CO$ (Consumption of H_2O)

$H_2 + O^{=} = H_2O$ (Production of H_2O)

$CO + H_2O = CO_2 + H_2$ (Consumption of H_2O)

Fuel Utilization	PH2O/PH2	logPO2/600	logPO2/800
0	0.031	-26.89	-21.38
20	0.28	-24.98	-19.46
40	0.724	-24.16	-18.64
60	1.56	-23.5	-17.98
80	4.26	-22.62	-17.1
99	102.09	-19.87	-14.34
99.995	1999	-17.27	-11.76

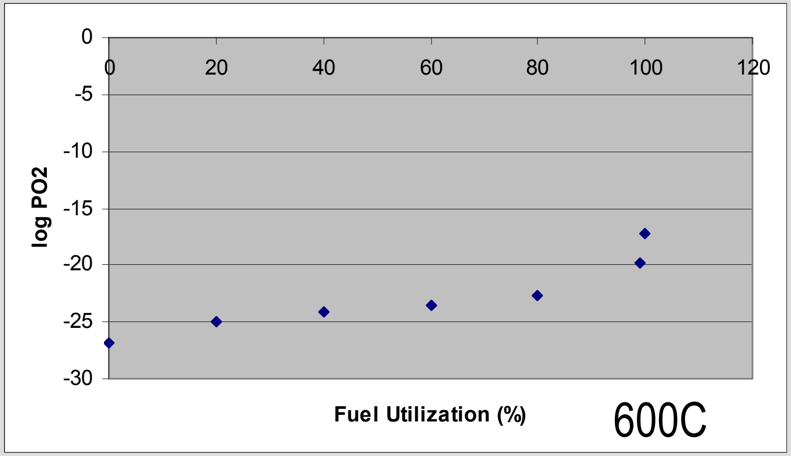
Consider H2-3%H2O Fuel

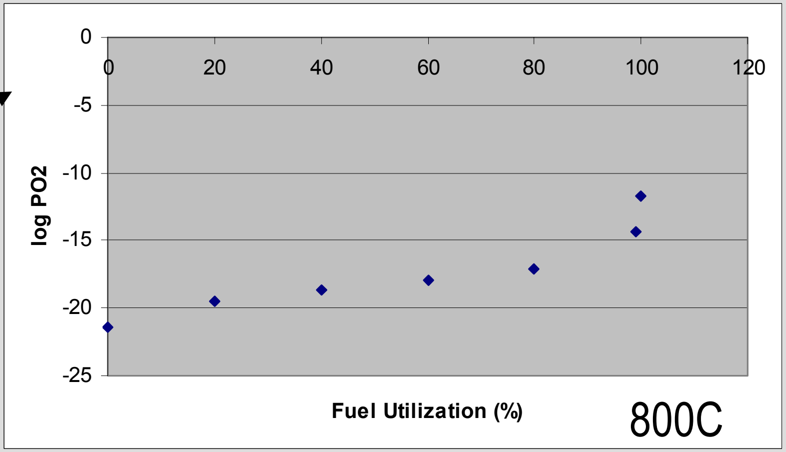
Prabhakar.singh@pnl.gov;

Oxide formation in fuel gases

- Ni &Cu remain metallic up to 99% FU
- Fe, Cr, Al, Si etc. will oxidize at all utilizations
- Most alloys will form Al,Cr, Si base oxides in fuel/ utilized fuel gases

M/MO	PO2eq/600	PO2eq/800
Ni/NiO	-19.16	-13.91
Cu/Cu2O	-12.52	-8.775
Fe/FeO	-24.8	-18.91
Cr/Cr2O3	-36.21	-27.82
Co/CoO	-20.62	-15.42

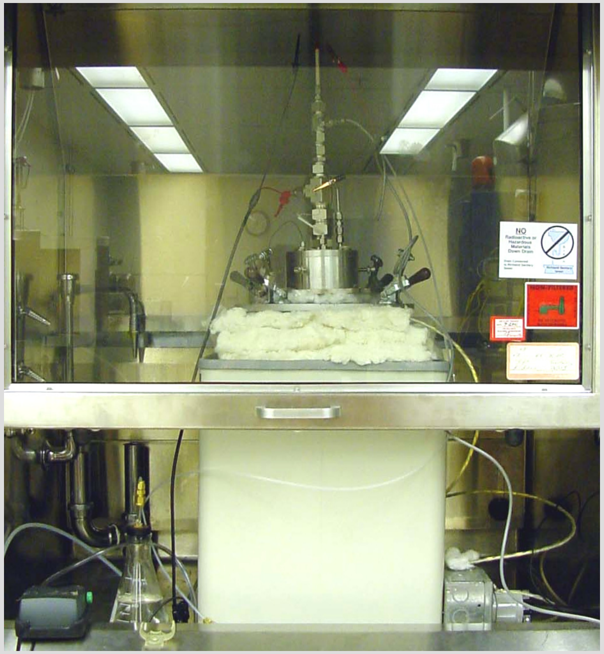


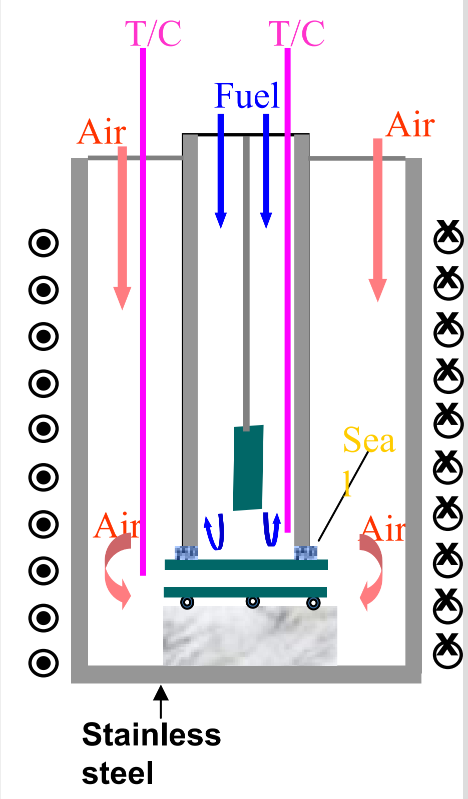


Prabhakar.singh@pnl.gov;

Dual Atmosphere Study

	FSS	Fe	Ni	Cr	C	Mn	Si	Mo	W	Ti	Al	RE
FeSS	AISI430	Bal.	--	16.0	0.1	1.0	1.0	--	--	--	--	--
FeSS	Crofer22 APU	Bal.	--	22.0	0.005	0.5	--	--	--	0.08	--	0.06La
NiBS	E-brite	Bal.	--	26.0	0.001	0.01	0.025	--	--	--	--	--
NiBS	Haynes 230	1.5	Bal.	22.0	0.10	0.5	0.4	1.4	14	--	0.3	0.02La .005B





Variables:

Temperature, 700~800°C

Time, 300 hours

Fuel, H_2+3% H_2O

Heating, isothermal and cycling.

Materials Evaluated:

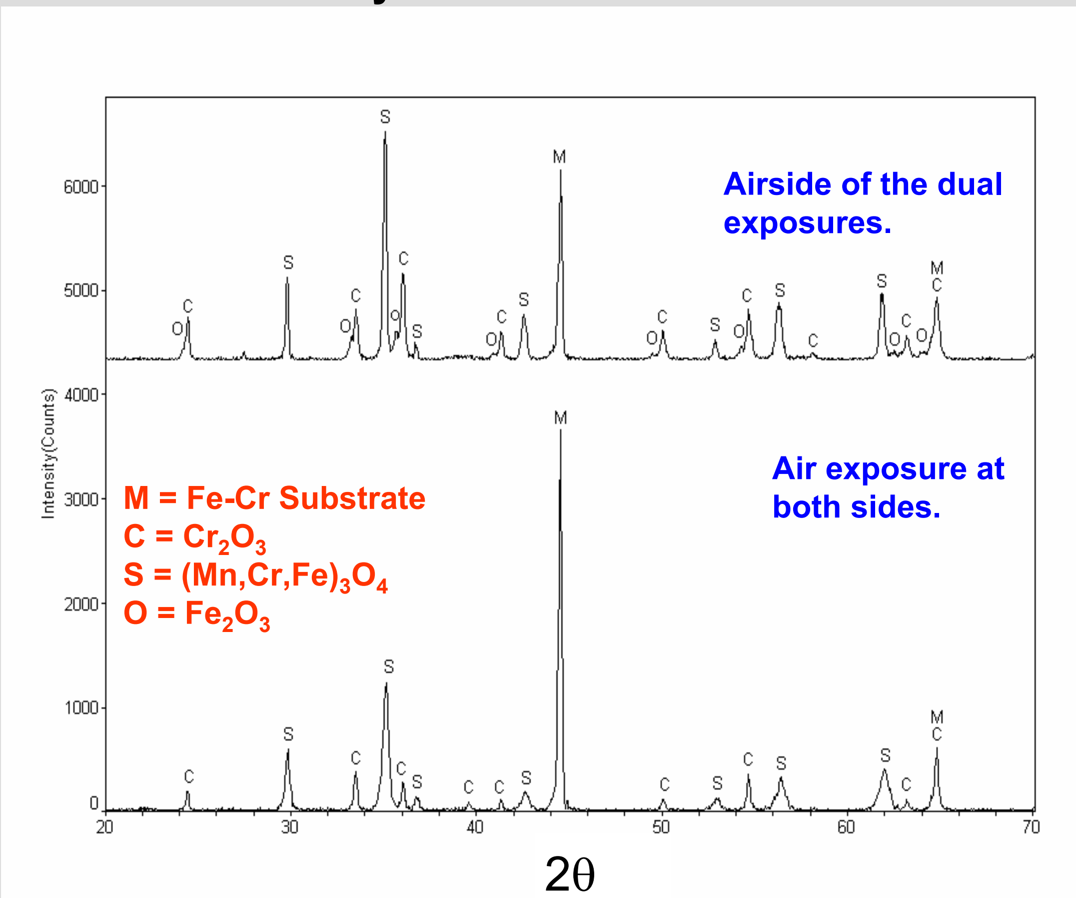
Fe & Ni Base Alloys

Ag

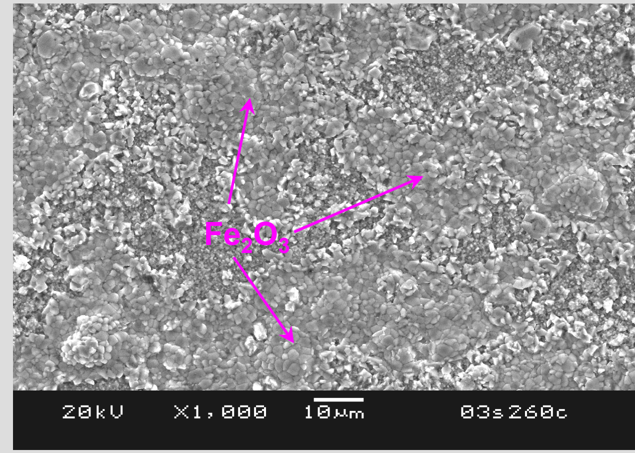
Prabhakar.singh@pnl.gov;

Crofer22 APU: Structure of Scales

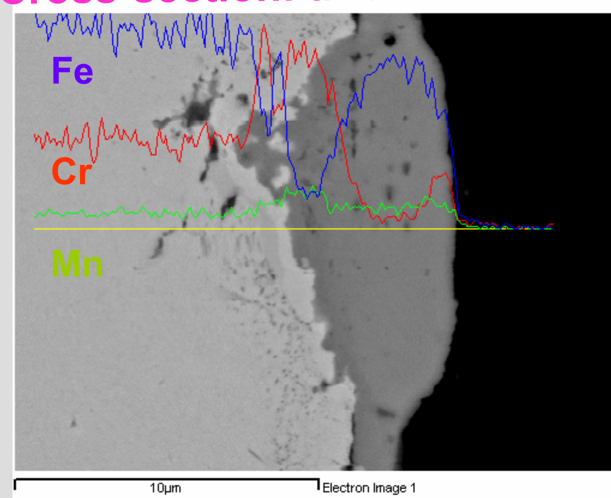
Grown on the coupon in air only and on the air side; heat-treated at 800ºC for 300 hours, with three thermal cycles.



Air-side of dual test



Cross-section: airside of dual test

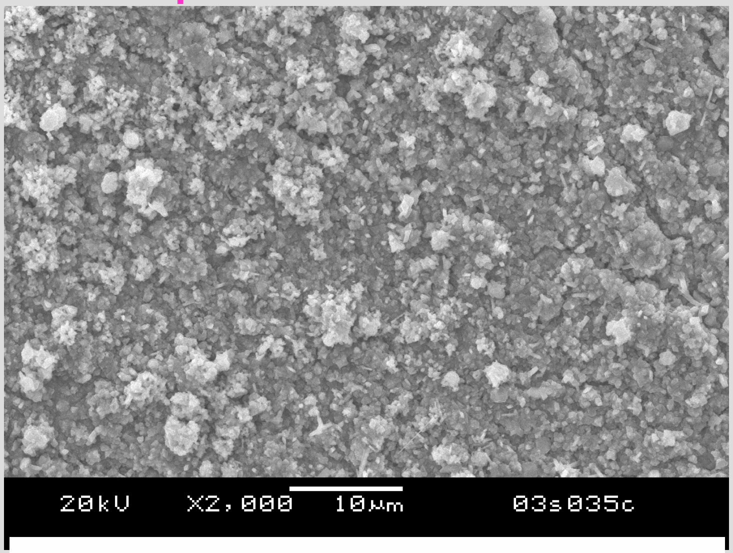


Prabhakar.singh@pnl.gov;

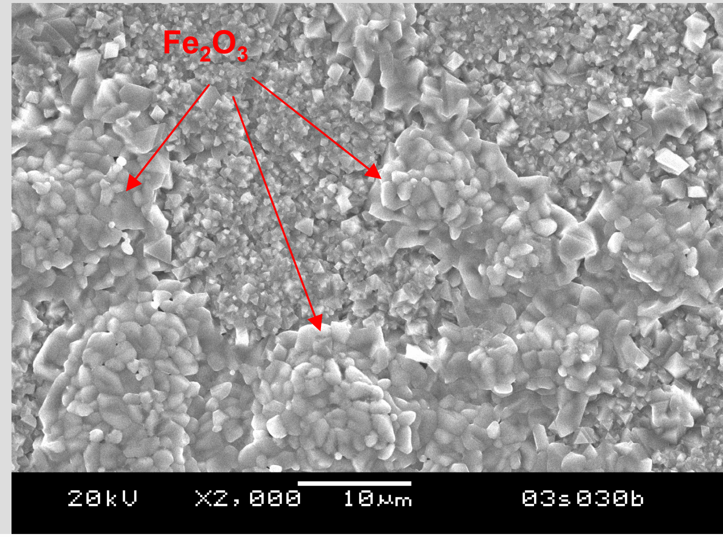
AISI430: Scale Microstructures

Surface microstructures

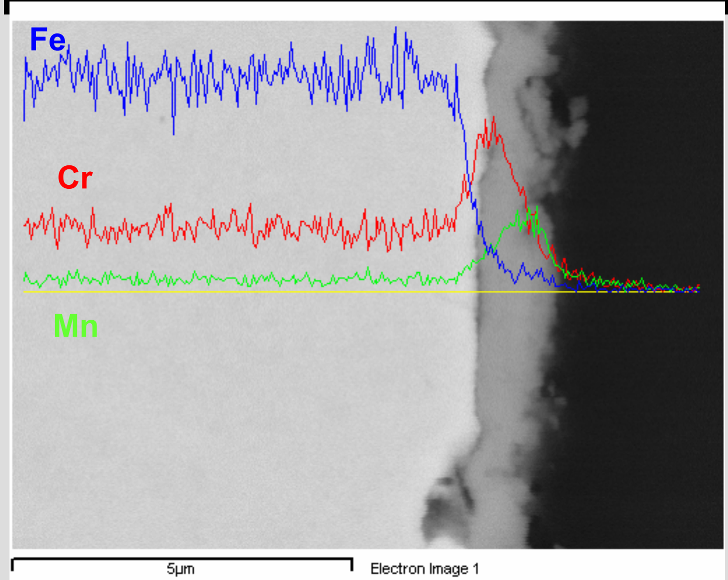
Air exposure at both sides

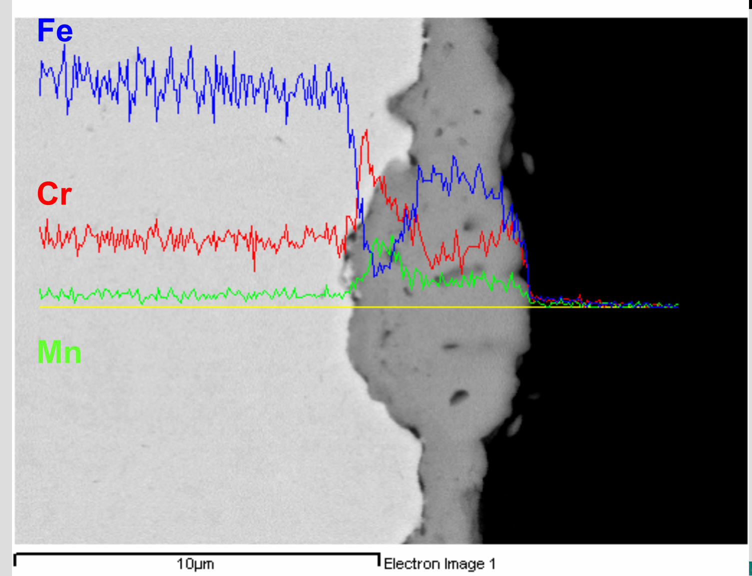


Air-side of dual exposures



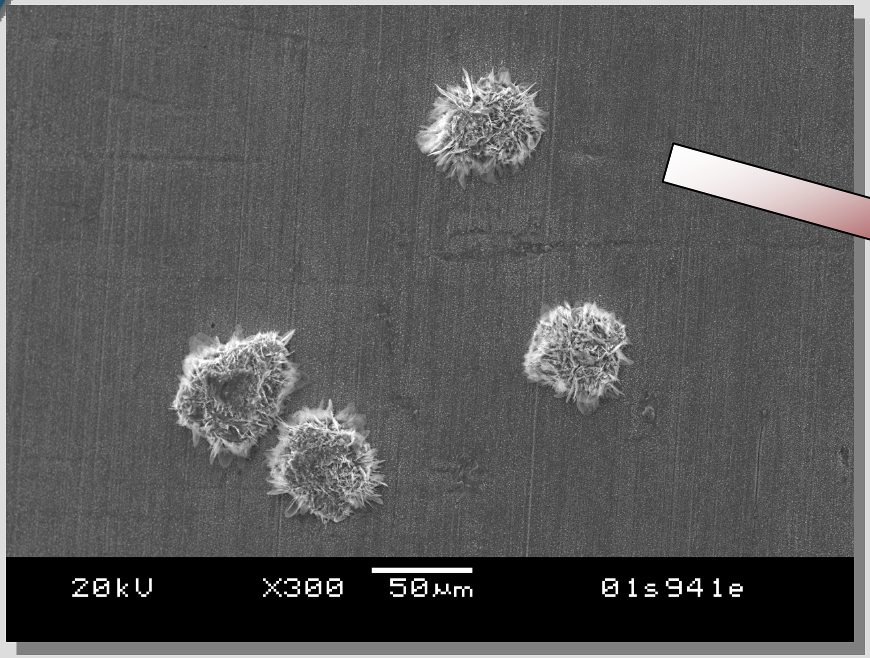
Cross-sections

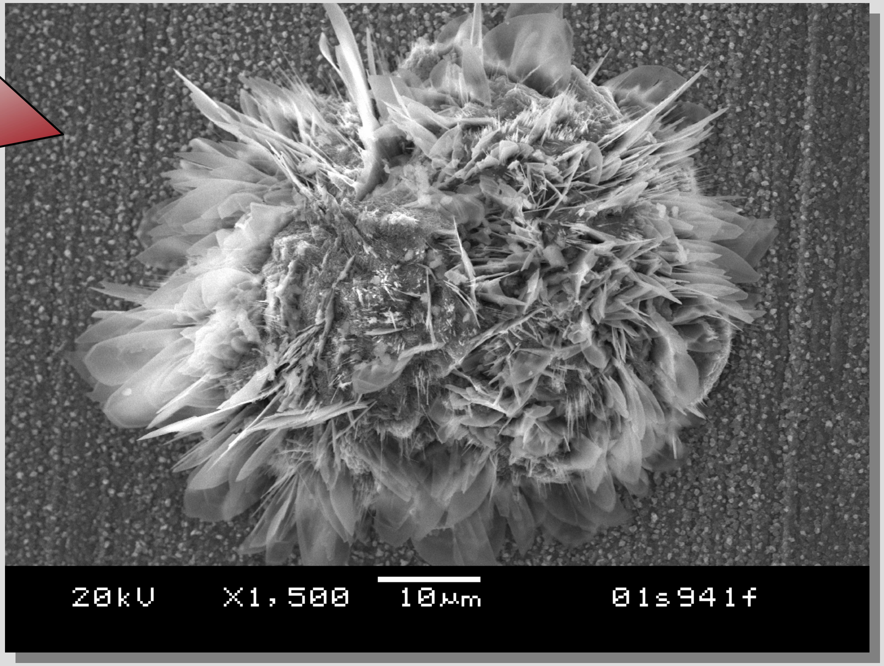


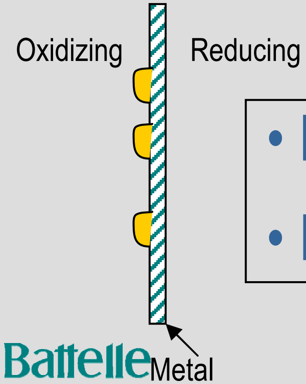


Prabhakar.singh@pnl.gov;

Localized Overgrowth of Scale





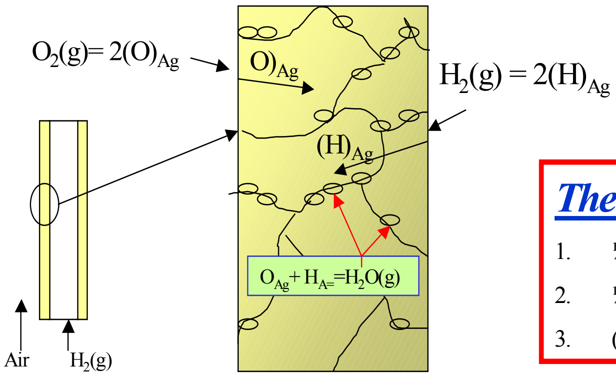


- Localized Scale Overgrowth – FeOx Rich Oxide
- Platelets/ Whiskers Formation- Preferred Growth

Prabhakar.singh@pnl.gov;

Bi-polar effect

Mechanistic understanding of corrosion processes are being developed for addressing long term performance of materials



Reaction Steps

1. $(H_2)_g = 2(H)_{Ag}$ Ag/Fuel interface

2. $(O_2)_g = 2(O)_{Ag}$ Ag/ Air Interface

3. $2(H)_{Ag} + (O)_{Ag} = (H_2O)_g$ Bulk Ag

Thermochemical Data

1.	$\frac{1}{2}(H_2)_g = (H)_{Ag}$,	$-G$
2.	$\frac{1}{2}(O_2)_g = (O)_{Ag}$,	$-G$
3.	$(H_2)_g + \frac{1}{2}(O_2)_g = (H_2O)_g$,	$-G$

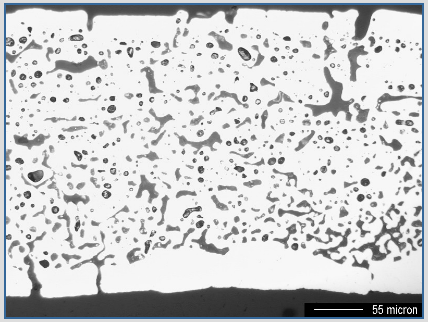
Bulk Degradation Related to :

1.Dissociation and dissolution of H and O in the bulk metal

2. Interaction between dissolved H & O to form High pressure H_2O gas

3. Nucleation and growth of steam bubbles/voids at GB/defects

Air/ Air



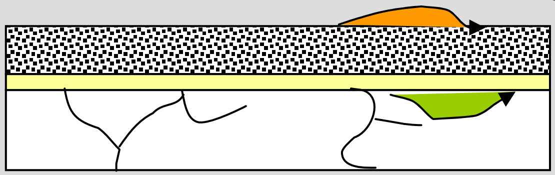
Air/ Fuel

Prabhakar.singh@pnl.gov;

Dual Atmosphere effect

Presence of multi-oxidant / H_2O leads to :

- Accelerated corrosion
- Multi-phase oxide formation
- Uneven metal / metal oxide interface formation
- Localized oxide growth and metal penetration

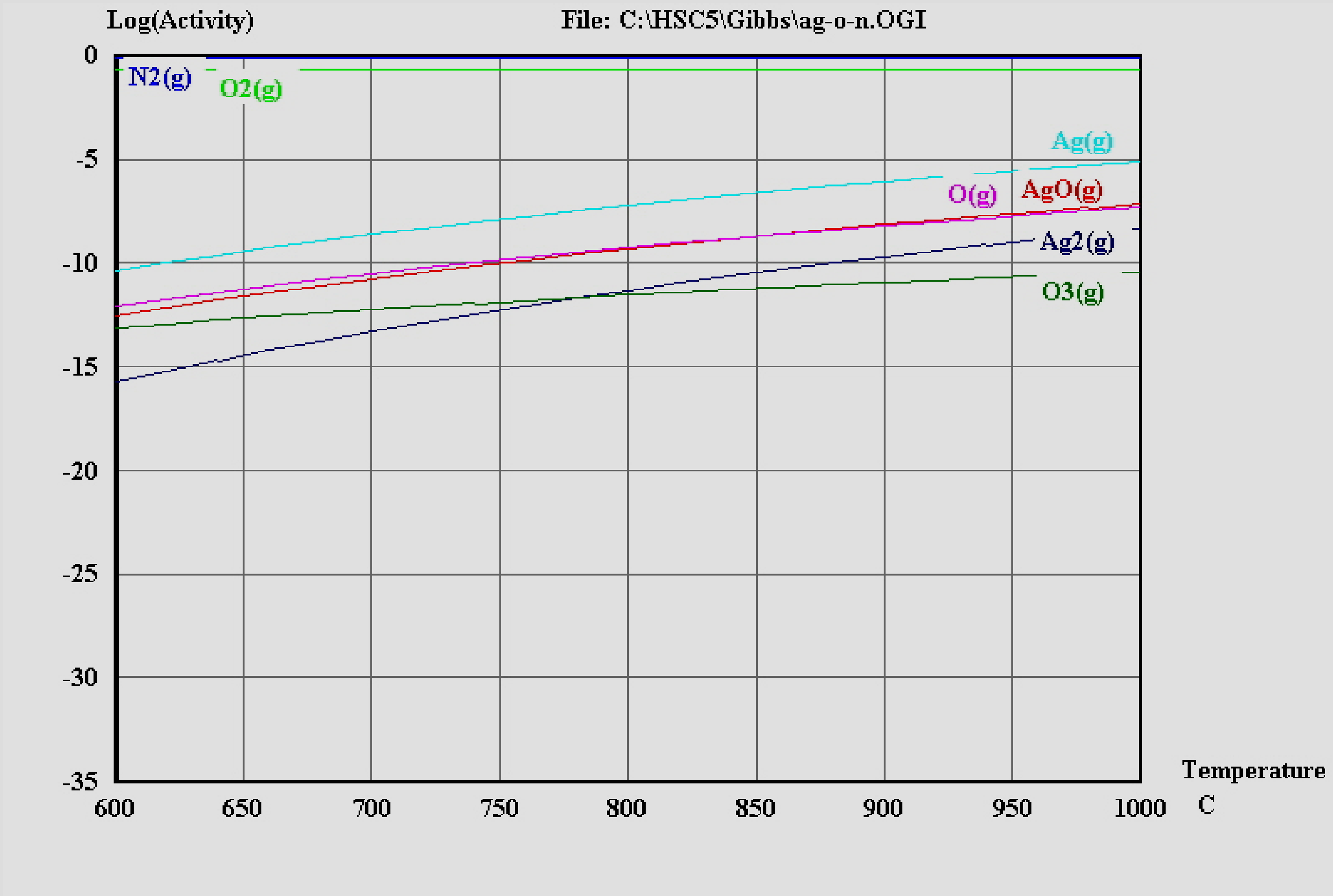


Possible Reaction Mechanisms:

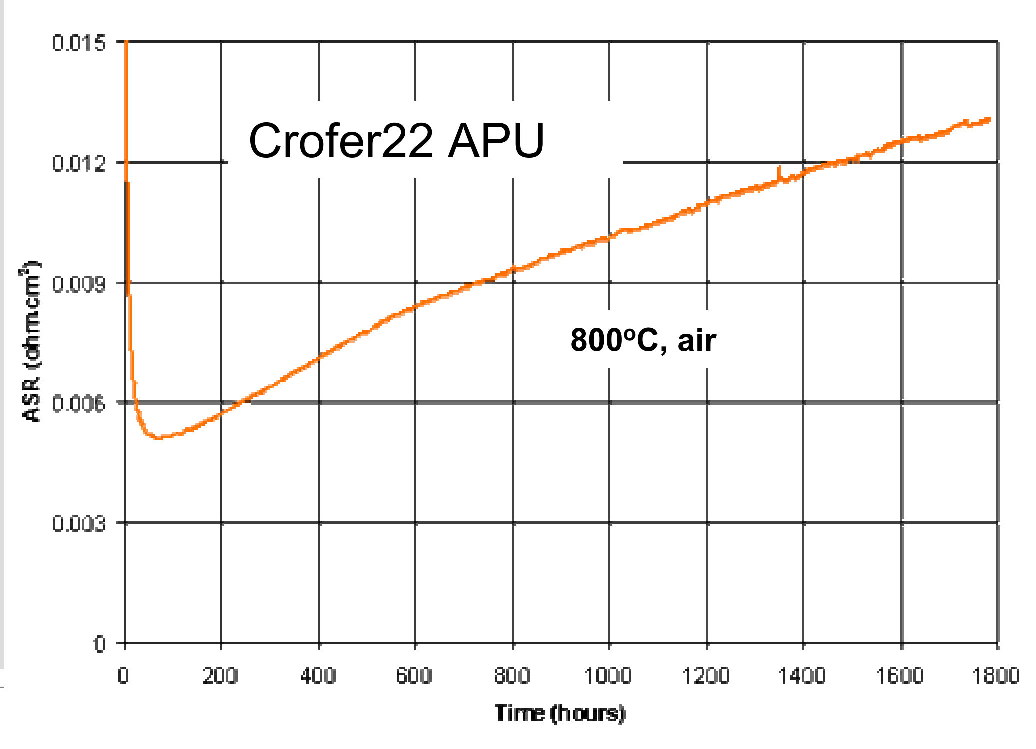
- Porous oxide formation
- Defect structure modification
- Red / ox gas chemistry

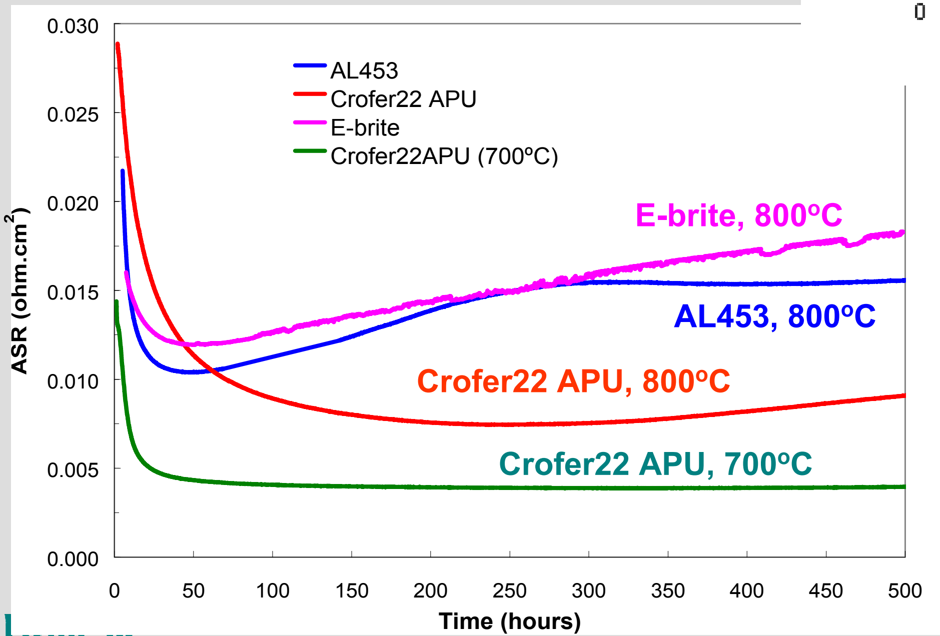
Prabhakar.singh@pnl.gov;

Silver evaporation in air



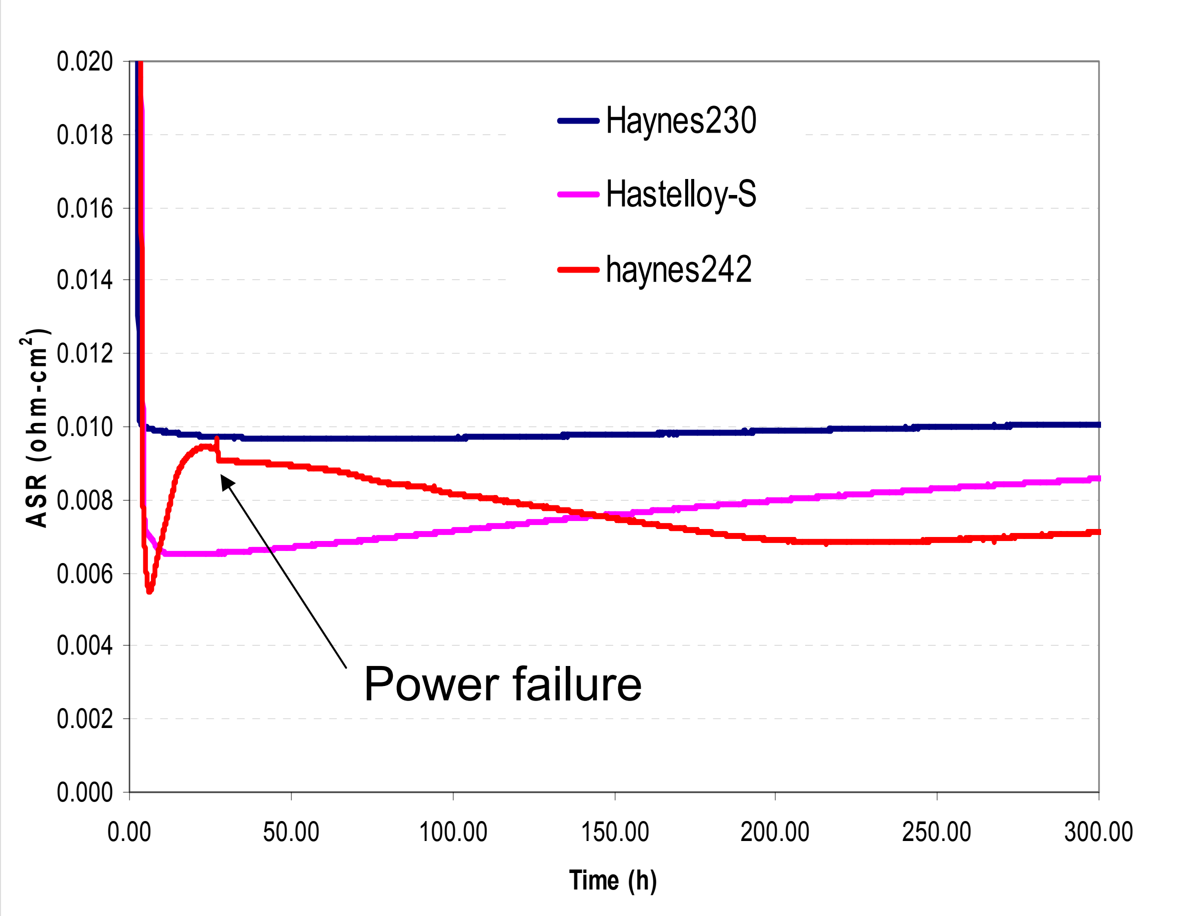
FSS Scale Electrical Conductivity





Coupon samples were pre-oxidized in air at temperature for 100h before carrying out tests in air

Scale ASR of Ni-based Alloys



Coupon samples were pre-oxidized in air at temperature for 100h before carrying out tests in air at 800ºC

Comparison

	Haynes230 **Ni-base superalloy** **Ni-22Cr-14W-2Mo-.5Mn**	**Crofer22 APU** **Stainless steel** **Fe-22Cr-.5Mn**
Thermal expansion $X10^{-6}.K^{-1}$	**15.2** **RT-800°C**	**12.2** RT-800°C
Oxidation resistance Kg, $10^{-13}.g^2.cm^{-4}.s^{-1}$	**0.36, 800°C** **0.05, 700°C**	**7.0**, 800°C **2.0**, 700°C
ASR, $m\Omega.cm^2$ After 600h of oxidation	**10.0, 800°C** **5.0, 700°C**	**9.0, 800°C** **4.0, 700°C**
Dual atmosphere Corrosion resistance	**Enhanced formation of uniform chromia scale**	**Grow hematite to accelerate attack**
Ultimate tensile stength, σ_u (MPa)	**865, RT** **605, 760°C**	**443, RT** **<100, 760°C**
Manufacturability	**Very easy**	**Fairly easy**
Raw materials cost	**Fairly expensive**	**Inexpensive**

Interaction with Seal

Prabhakar.singh@pnl.gov;

Interaction with Glass seals

For un-optimized alloys:

- Weaker interface
- Cr dissolution
- Localized porosity formation at the interface

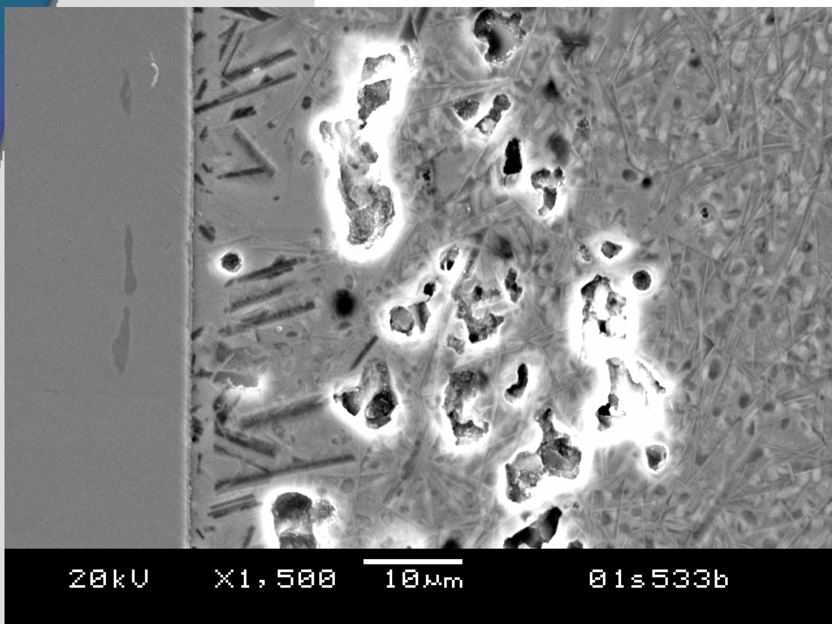
Modified interface/Coating improves the strength and stability

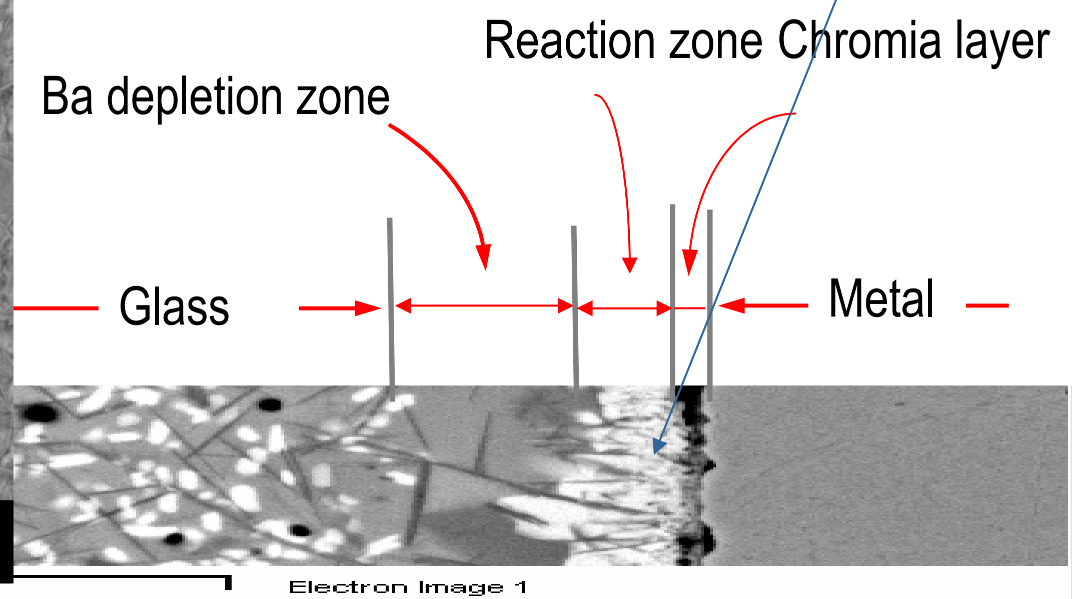
Prabhakar.singh@pnl.gov;

Un-optimized Seal/Alloy Interfaces

SECA

$$2Cr_2O_3+4BaO+3O_2 = 4BaCrO_4$$

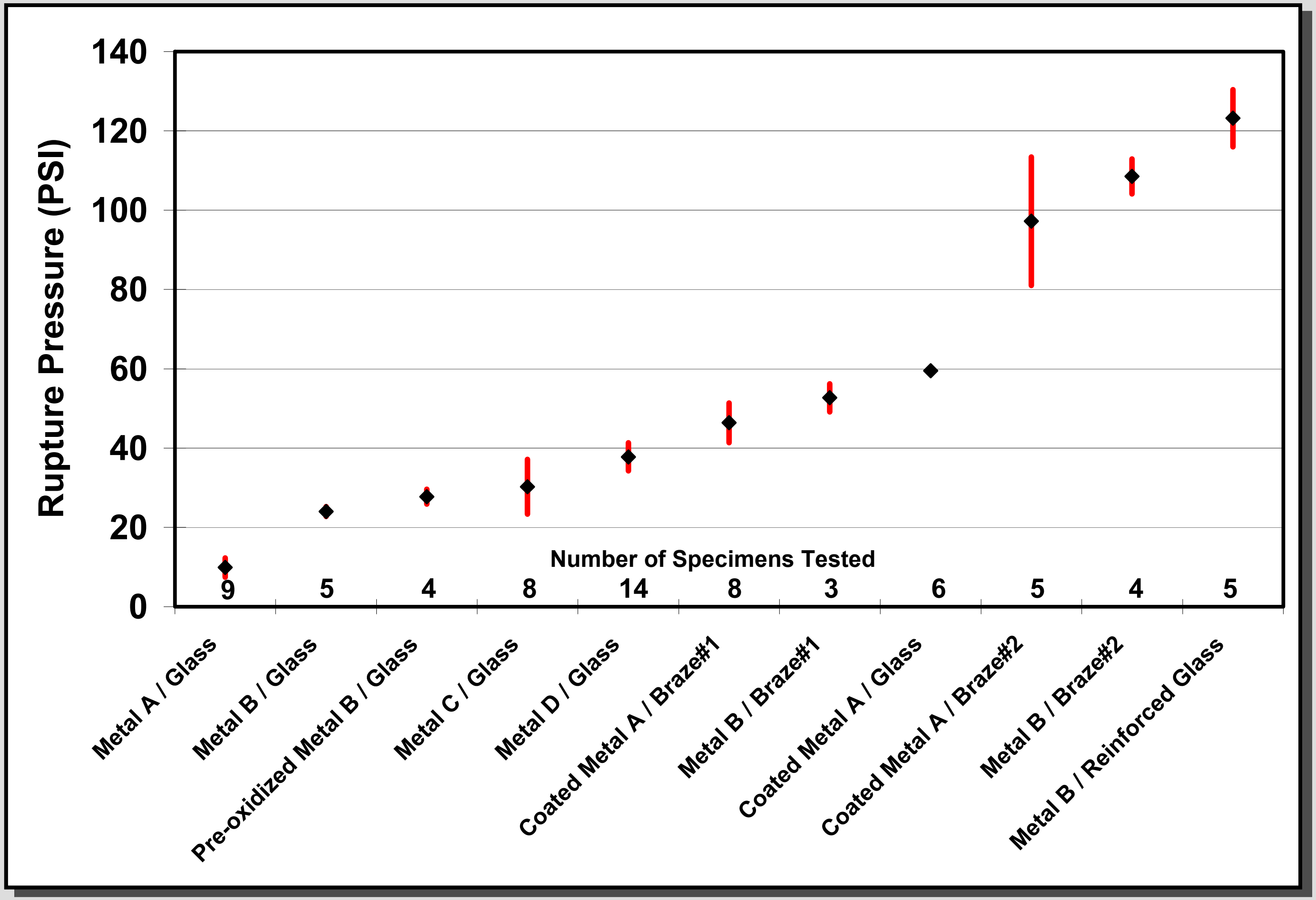




Localized porosity formation at the interface

Weakening of interfaces due to secondary phase formation

Improvement of Seal Strength for Generation 3



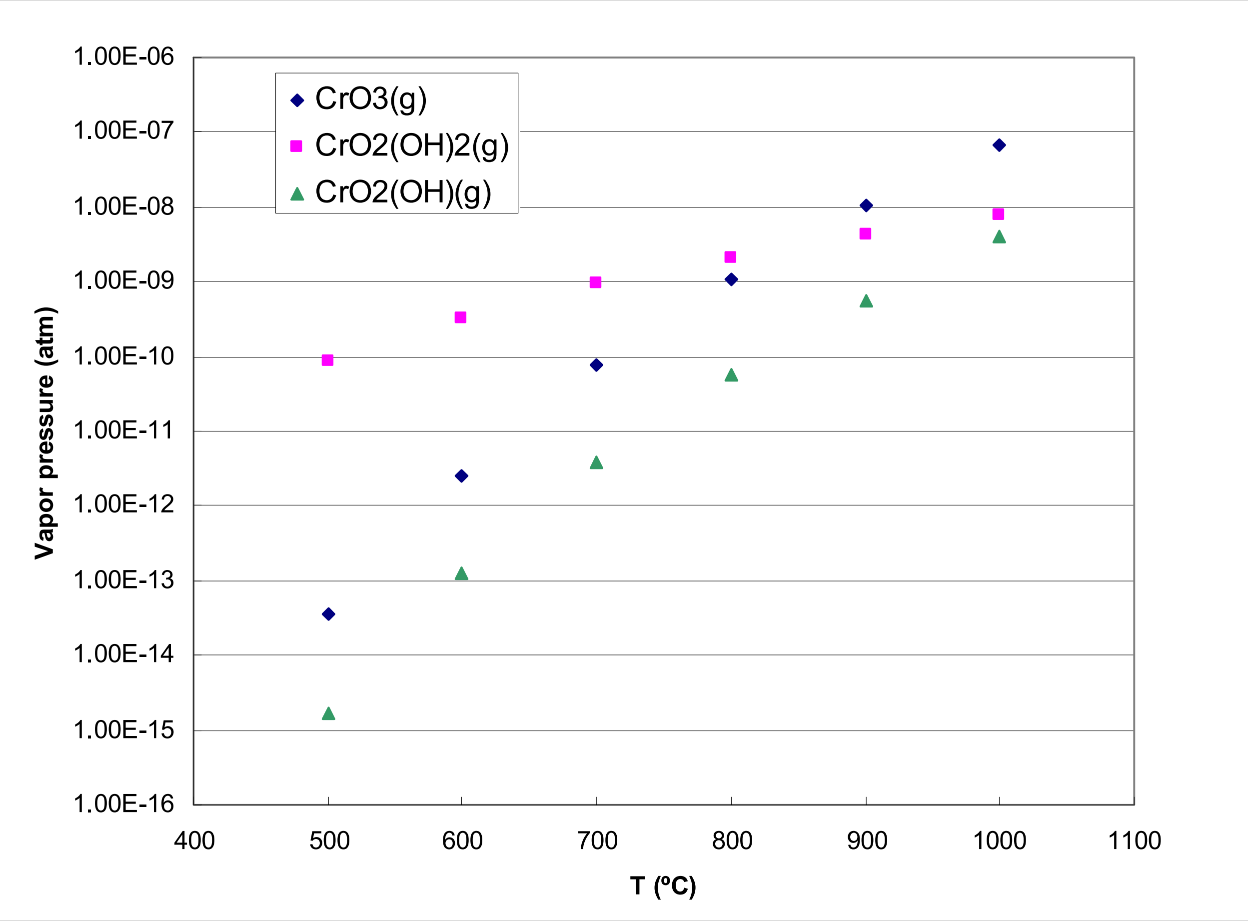
(Slide Courtesy of Delphi/BMI)

Prabhakar.singh@pnl.gov;

Cr Evaporation and Electrode Poisoning

Prabhakar.singh@pnl.gov;

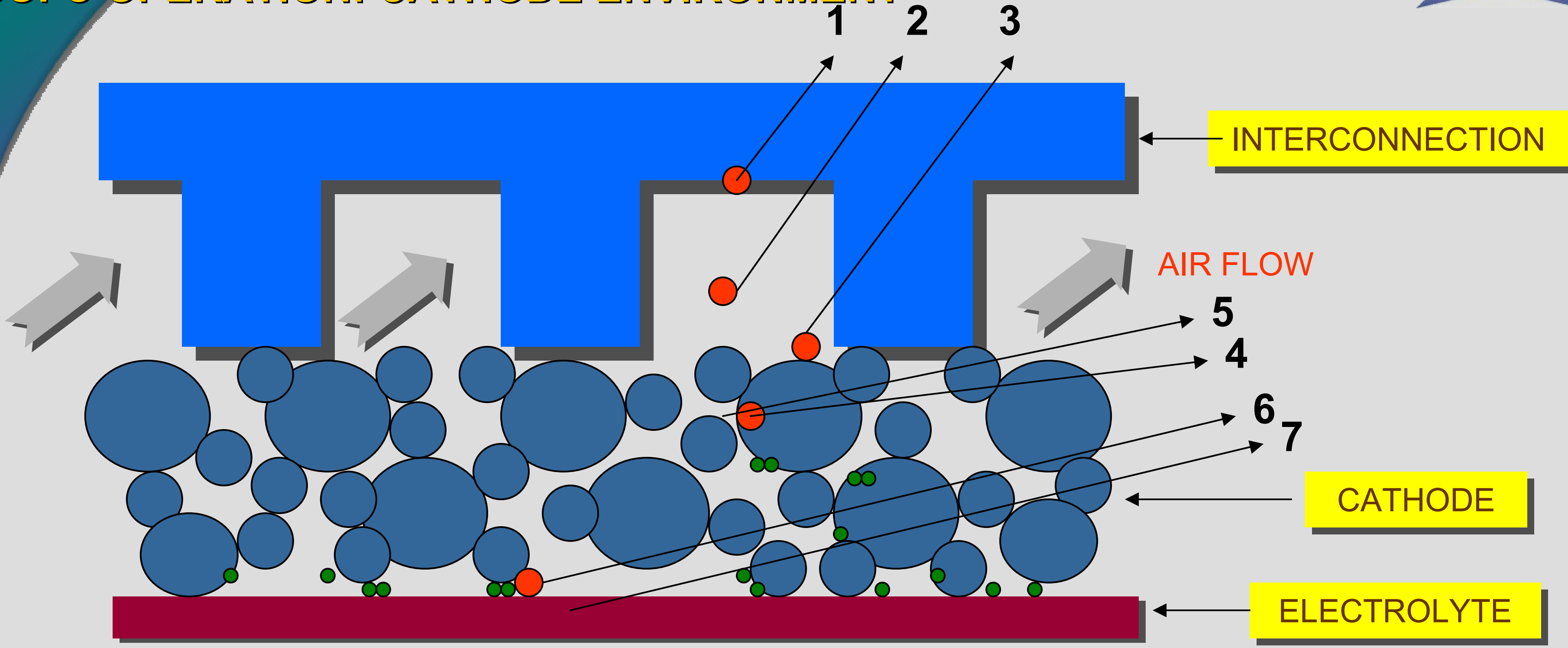
Chromium Species Evaporation



Calculated equilibrium vapor pressure of Cr species (CrO_3, $CrO_2(OH)$, and $CrO_2(OH)_2$) above Cr_2O_3 in air (w/ 3% water) at 1 atm.

Prabhakar.singh@pnl.gov;

FORMATION, TRANSPORT AND INTERACTION OF CR SPECIES DURING SOFC OPERATION: CATHODE ENVIRONMENT



1: CHROMIUM EVAPORATION FROM IC SURFACE
2: GAS PHASE TRANSPORT OF CHROMIA VAPOR
3: CONTACT WITH CATHODE SURFACE
4: REACTION WITH CATHODE SURFACE
5: DIFFUSION INTO CATHODE
6: REDUCTION AND DEPOSITION AT CATHODE/ELECTROLYTE INTERFACE
7: DIFFUSION INTO ELECTROLYTE/ BARRIER LAYER

FORMATION, TRANSPORT AND INTERACTION OF CR

CHROMIA EVAPORATION FROM IC SURFACE
$Cr_2O_3 + 2H_2O + 1.5O_2 + CrO_2(OH)_2$ (g) k1

GAS PHASE TRANSPORT OF CHROMIA VAPOR
$CrO_2(OH)_{2\ IC} = CrO_2(OH)_2$ (Elec) k2

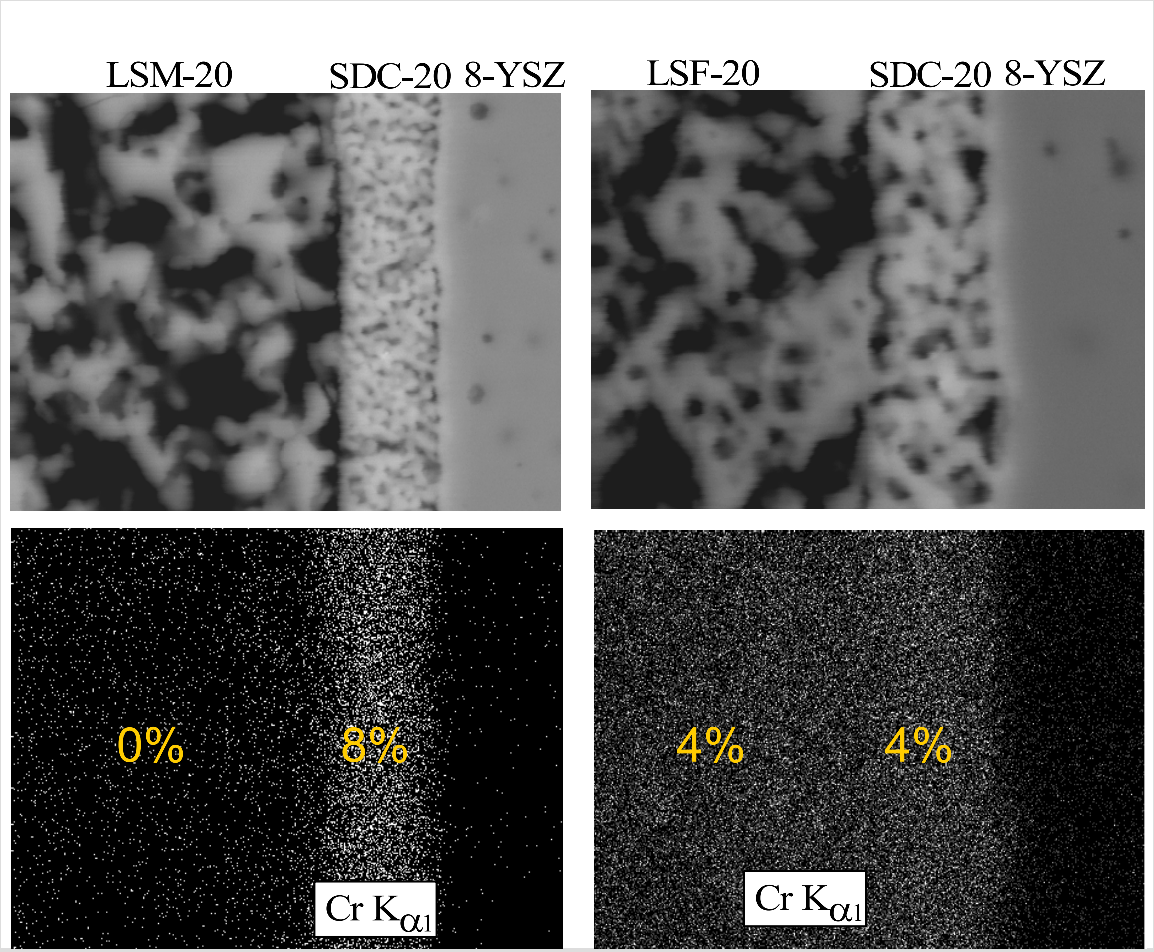
SURFACE COVERAGE OF AIR ELECTRODE
$CrO_2(OH)_2$ (Elec) = Elec * $CrO_2(OH)_2$ k3

INTERACTION WITH AIR ELECTRODE
Elec*$CrO_2(OH)_2$ = Cr_2O_3 (Surface) k4
Elec*$CrO_2(OH)_2$ = MO. CR_2O_3 k5

REDUCTION AND DEPOSITION
$CrO_2(OH)_2$ (g) +e = Cr_2O_3, (or Spinel) k6

Prabhakar.singh@pnl.gov;

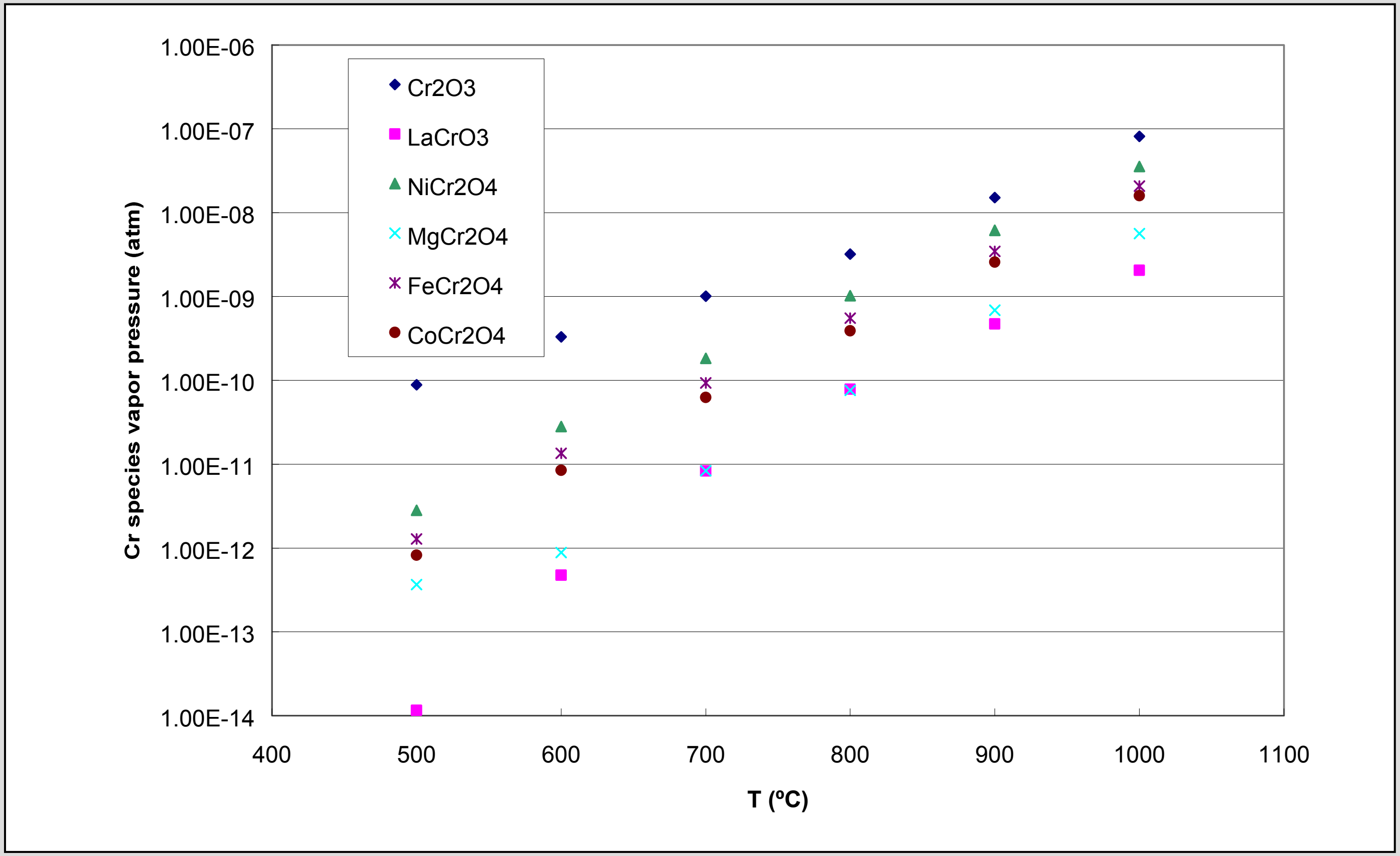
Cr Deposition in Cathode



Prabhakar.singh@pnl.gov;

Chromium Species Evaporation

SECA



Calculated total equilibrium vapor pressure of Cr species (CrO_3, $CrO_2(OH)$, and $CrO_2(OH)_2$) above the indicated oxides in air (w/ 3% water) at 1 atm.

Prabhakar.singh@pnl.gov;

Cr Evaporation and its effects

Cr poisons cathode
Severity of poisoning varies with materials and cell/stack design

Mitigation approaches:

- Reduce Cr activity in the oxide (lower partial pressure of Cr above oxide)
- Add “Cr absorbing “ materials at the interface
- Provide Cr free coatings for IC
- Optimize gas flow path to allow “Flow By” situation

Prabhakar.singh@pnl.gov;

Coatings and Claddings

Prabhakar.singh@pnl.gov;

Cladded Interconnect Structures

Concept

After rolling After heat treating

Advantages

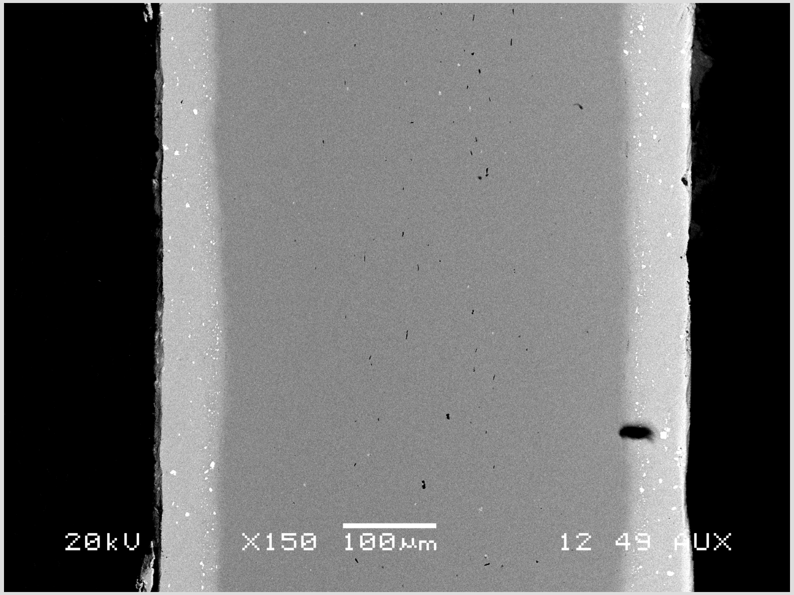
- Integrate advantages of different alloys, while avoiding disadvantages.
  - Solve the issue of thermal expansion mismatch;
  - Optimize the interconnect mechanical and structural stability.
- Allow to address cathode- and anode-side issues separately;
- Mass production and very cost effective.

Prabhakar.singh@pnl.gov;

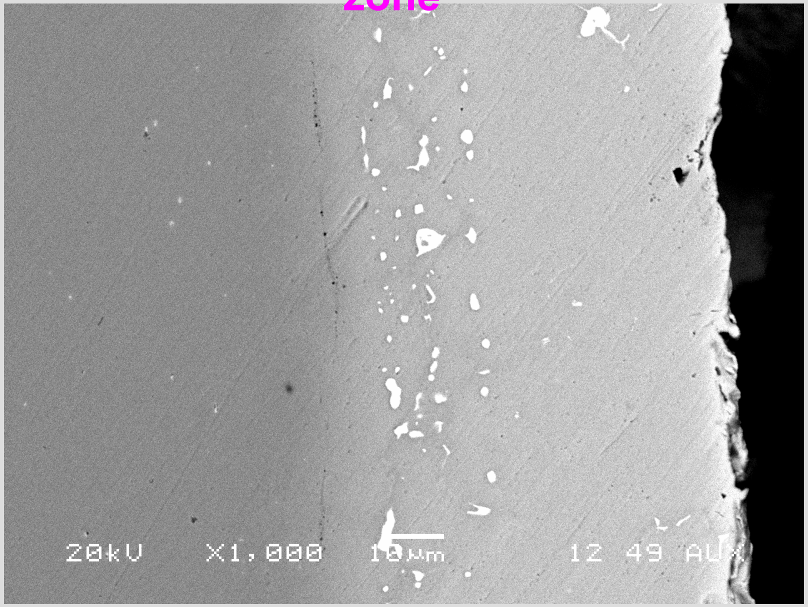
Proof of Concept

Sample No	Cladding couples	Final rolling gauges
System1	Inconel625 || AL453CRE || Inconel625	0.010"
System2	Inconel625 || AL453CRE || AISI316	0.010"
System3	Haynes230 || AL453CRE || Haynes 230	0.010"
System5	Haynes230 || AL453CRE || Haynes 230	0.020"
System6	Haynes230 || AL453CRE	0.010
System7	Haynes230 || AISI430	0.020"
system8	Haynes230 || AISI430	0.010"

Haynes230 AL453 Haynes230

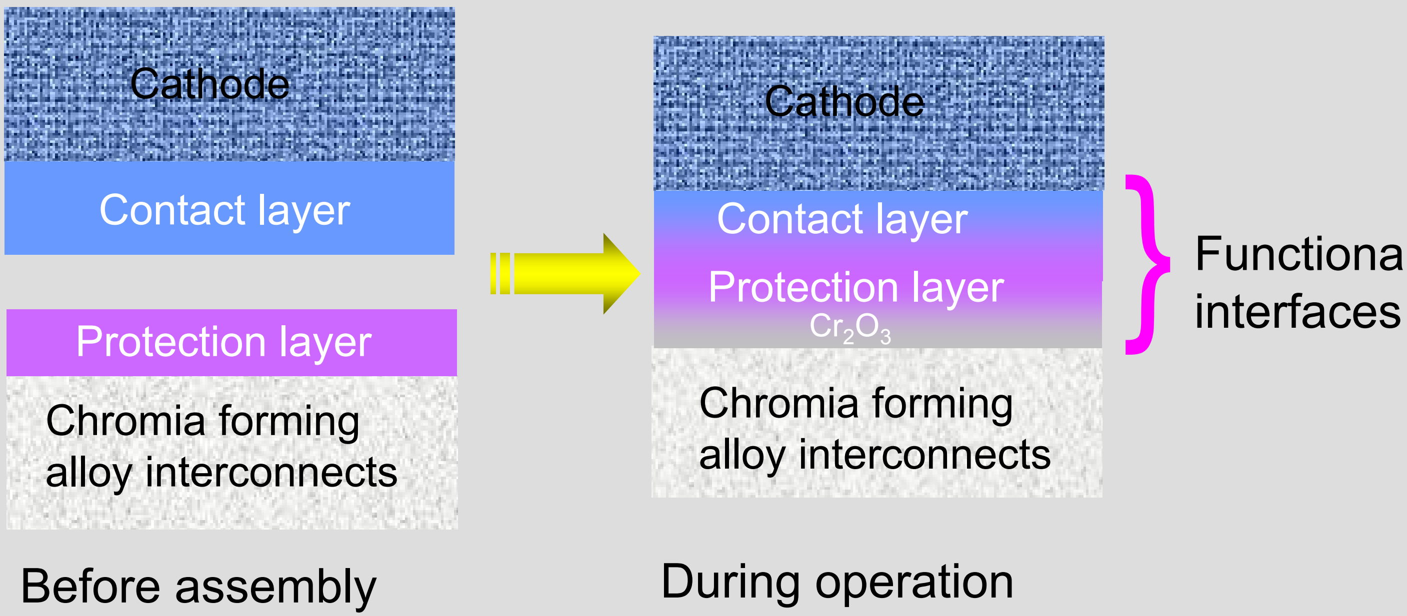


AL453 **Interdiffusion zone** Haynes230



Prabhakar.singh@pnl.gov;

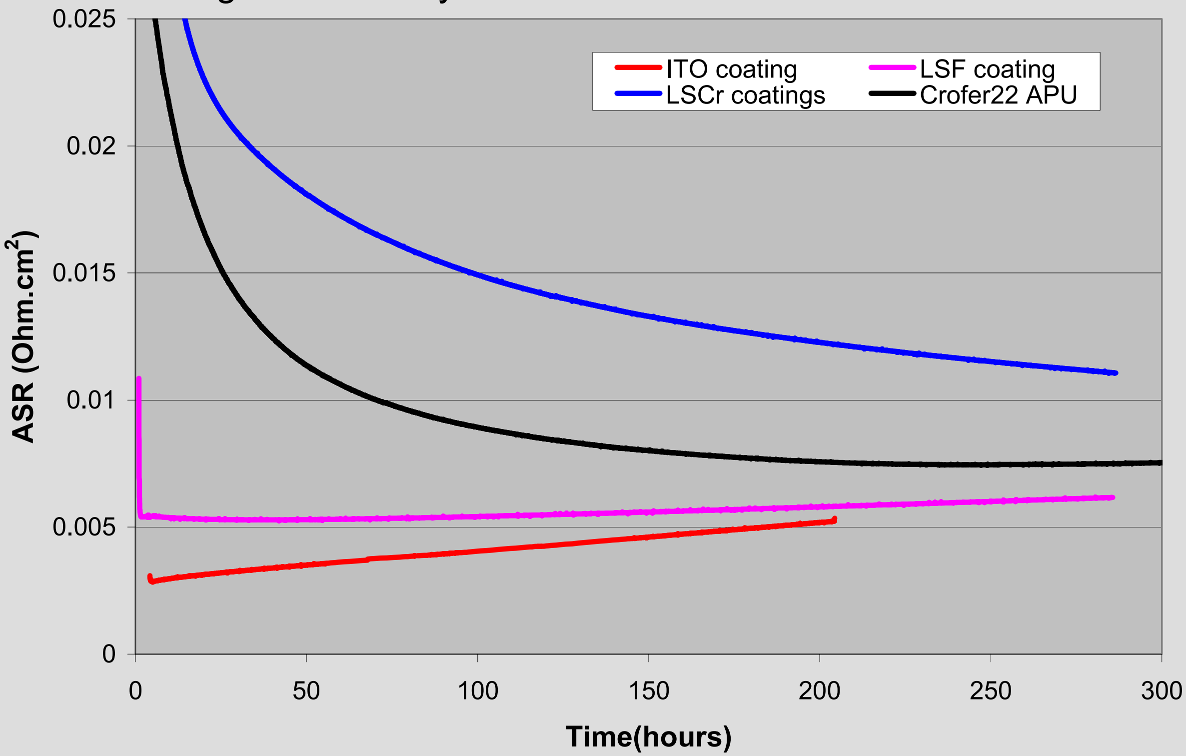
Cathode-Side Functional Interfaces

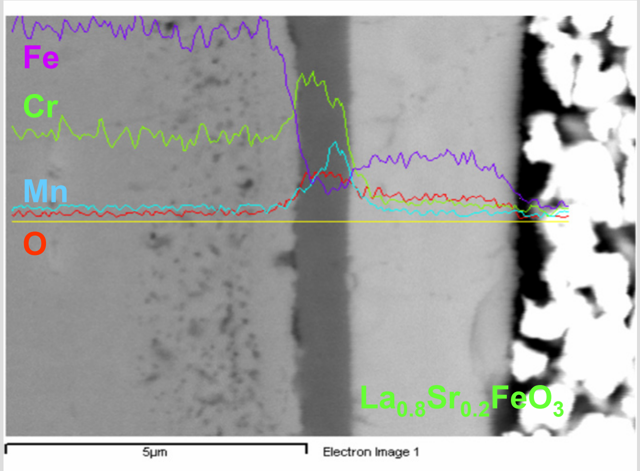


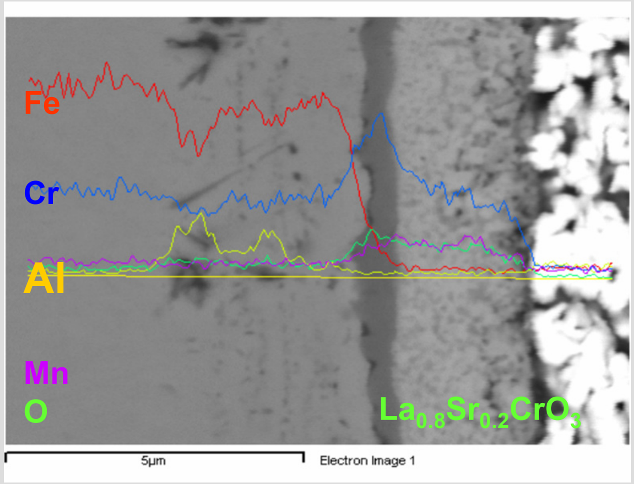
- **Protection layer acts as a mass barrier to mitigate or prevent Cr migration via both gas transport and solid state reactions, as well as to decrease electrical contact resistance. The subsequently grown chromia sub-scale serves as cation and anion transport barrier, protecting the alloy interconnect.**
- **Contact layer promotes contact between cathodes and interconnects, and helps minimize interfacial resistance and power loss.**

Perovksite Protection Layers

- The provskite coatings decrease electrical resistance and mitigate or prevent Cr migration;
- The growth rate of the chromia beneath the coatings and the eventual scale depends on the ionic conductivity of coatings.
- Long term stability needs to be further studied.







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

Prabhakar.singh@pnl.gov;

Development of Protection Layers

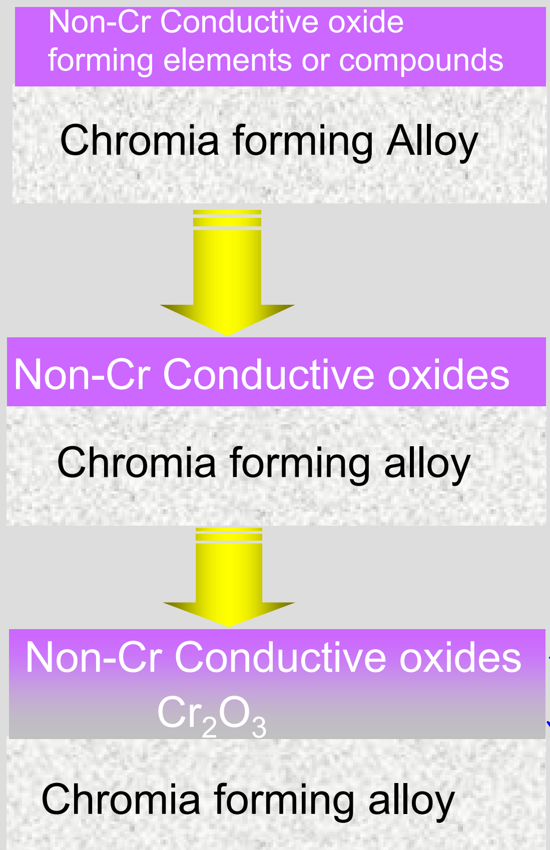
SECA

Concept

Starting Materials

After thermal treatment

During SOFC operation



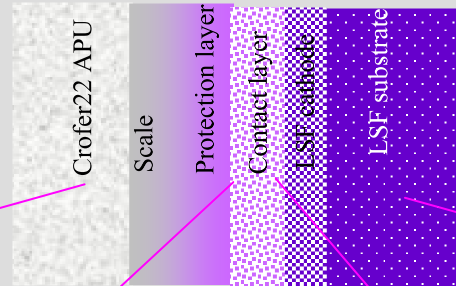
- The conductive oxide top layer acts as a mass barrier to prevent Cr migration via both the gas transport and solid state reaction, as well as to decrease electrical contact resistance.

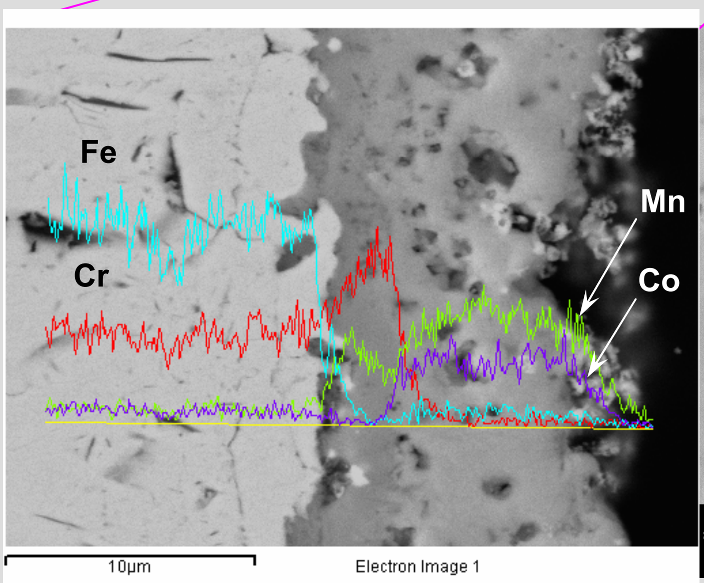
- The subsequently grown chromia sub-scale serves as cation and anion transport barrier, protecting the alloy interconnect.

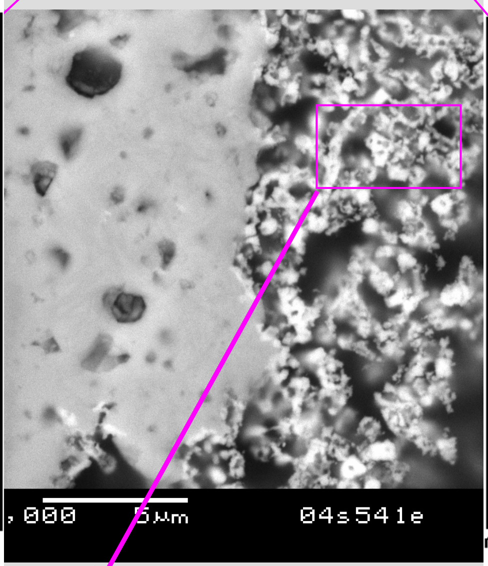
Prabhakar.singh@pnl.gov;

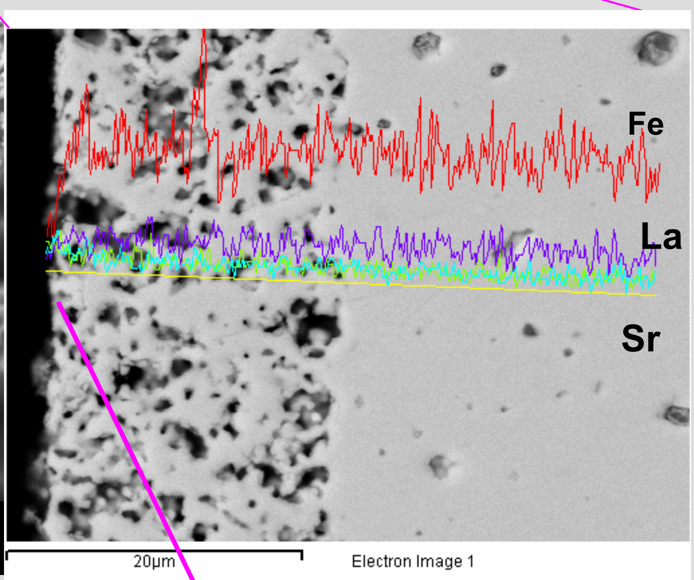
SEM/EDX of Cross-Section

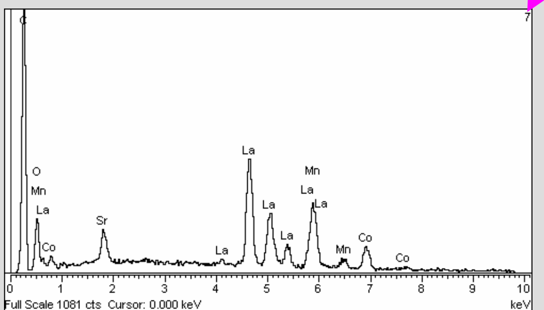
No Cr activity at the surface of spinel coating after 1,000h at 800°C in air

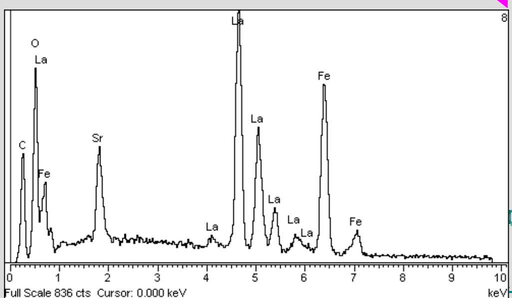






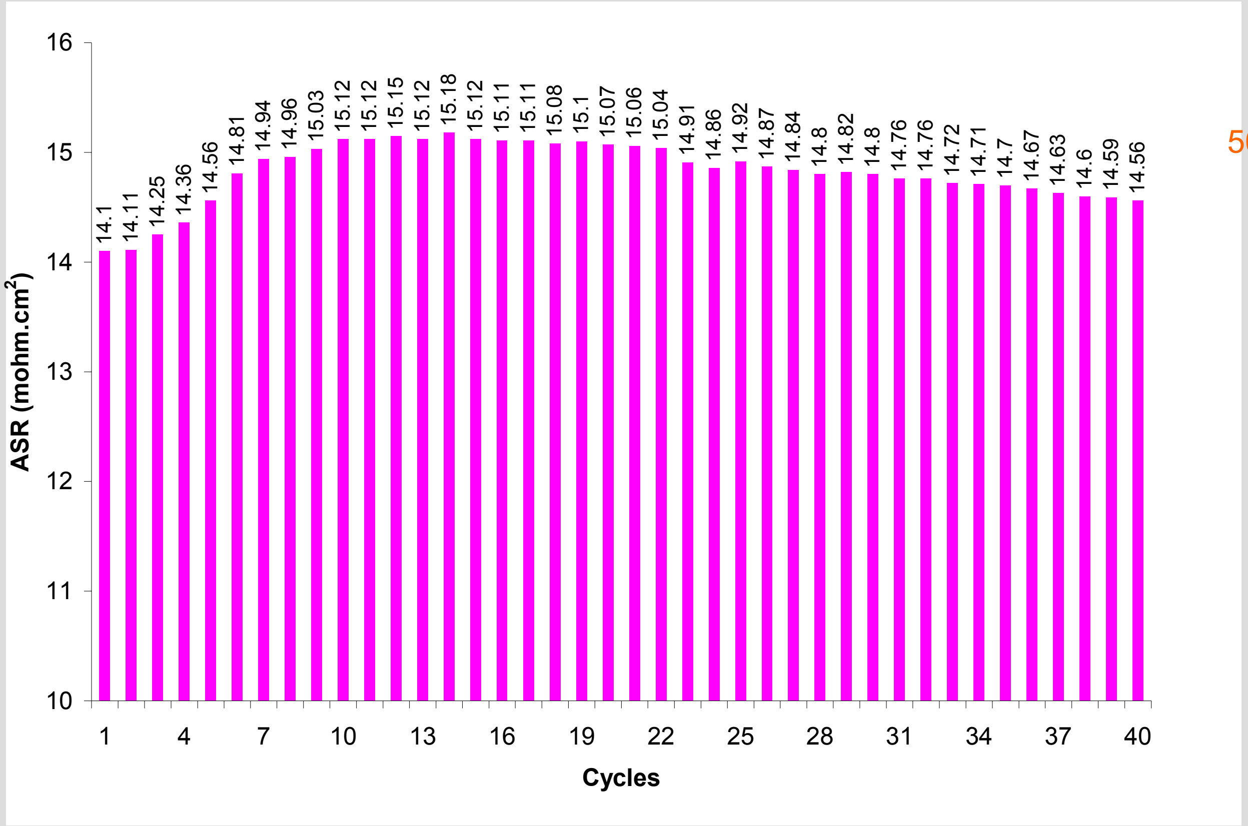




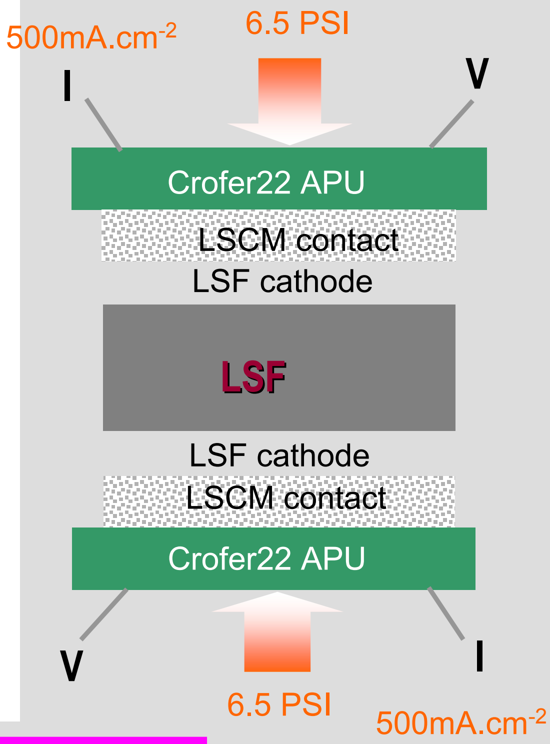


Interfacial ASR of Crofer22 APU Grown with Spinel Protection Layers

The $(Mn,Co)_3O_4$ spinel protection layer on Crofer22 APU minimizes the interfacial resistance; $(La_{0.8}Sr_{0.2})Co_{0.5}Mn_{0.5}O_3$ used electrical contact.



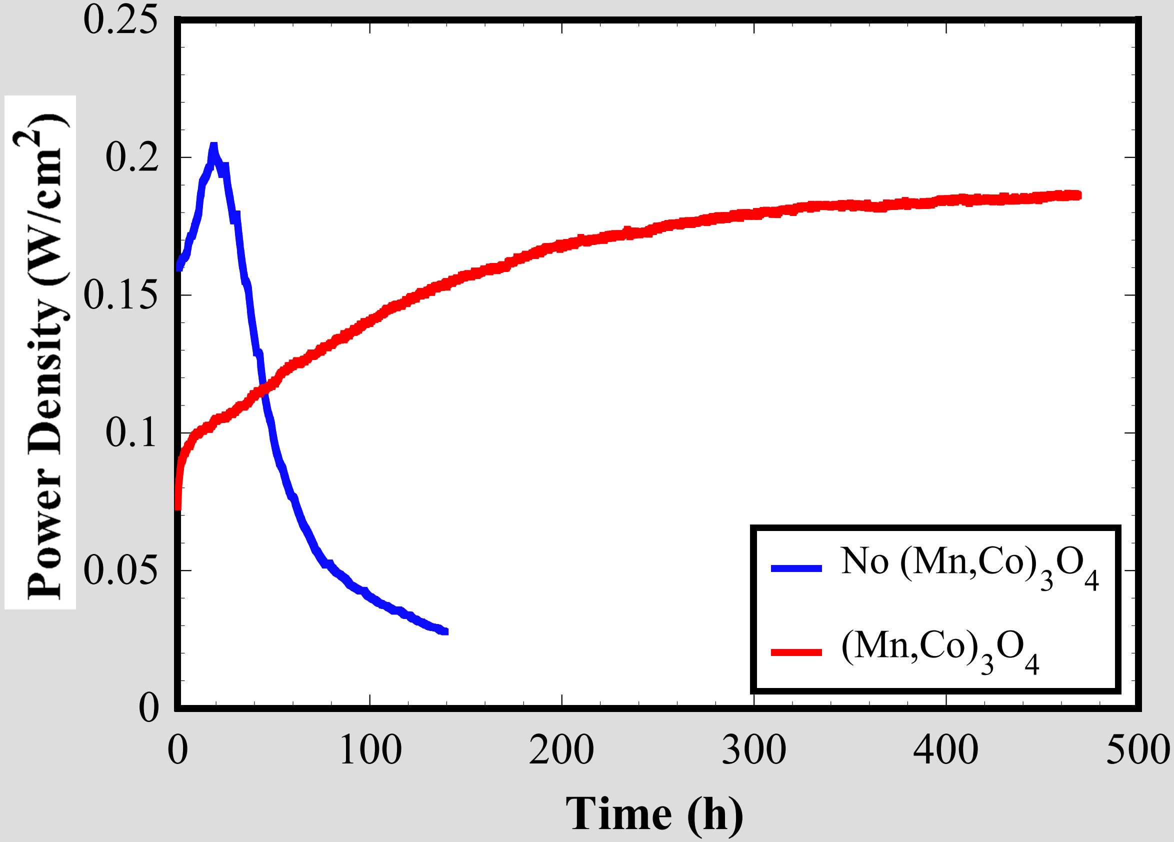
Thermal cycles: 80-800ºC



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

Prabhakar.singh@pnl.gov;

Cr mitigation w/ Mn Co spinel surface layer



Anode supported cell w/ LSM-20 with and without $(Mn,Co)_3O_4$ protective layer on Crofer foil.

Prabhakar.singh@pnl.gov;

Summary

- Alloys show promise for IC applications due to low cost, ease of fabrication, high thermal conductivity and low electrical resistance.
- Issues to be addressed include oxidation and corrosion under SOFC operating conditions
    - Metal loss (localized, carburization, sensitization, scale spalling etc.)
    - Increasing electrical resistance
    - Cr evaporation / Poisoning
    - Interaction with seals and contact materials
- Development approaches include alloy modifications, coatings, claddings.
- Essential to focus on system solution (complete electrode – contact materials – interconnect structure and materials)

Prabhakar.singh@pnl.gov;

Acknowledgements

- US DOE Office of Fossil Energy
  - SECA Core Technology Program
    - Wayne Surdoval, Lane Wilson, Don Collins and Travis Schultz
- PNNL Technical Staff
- Professor G.H. Meier for helpful technical discussions
- Dr. N.Q. Minh of GE Power Systems for discussions and suggestions

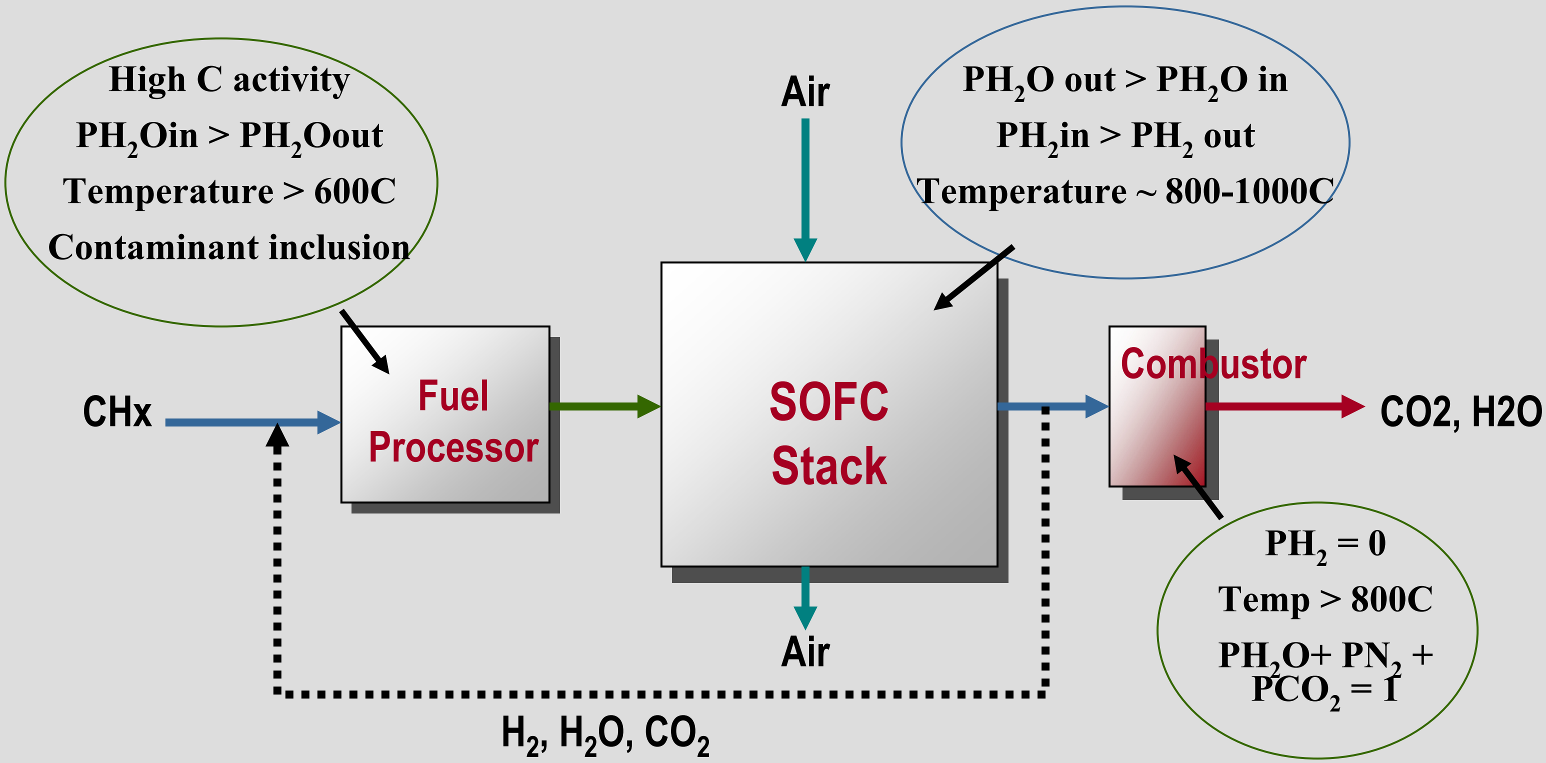
Prabhakar.singh@pnl.gov;

Workshop Objectives and Goals

- Utilize technical expertise of attendees to address interconnect challenges
- Achieve consensus regarding the technical status, issues and on going activities
- Identify and prioritize potential approaches for solving remaining challenges
- Develop a technology "Road Map" for future R&D activities

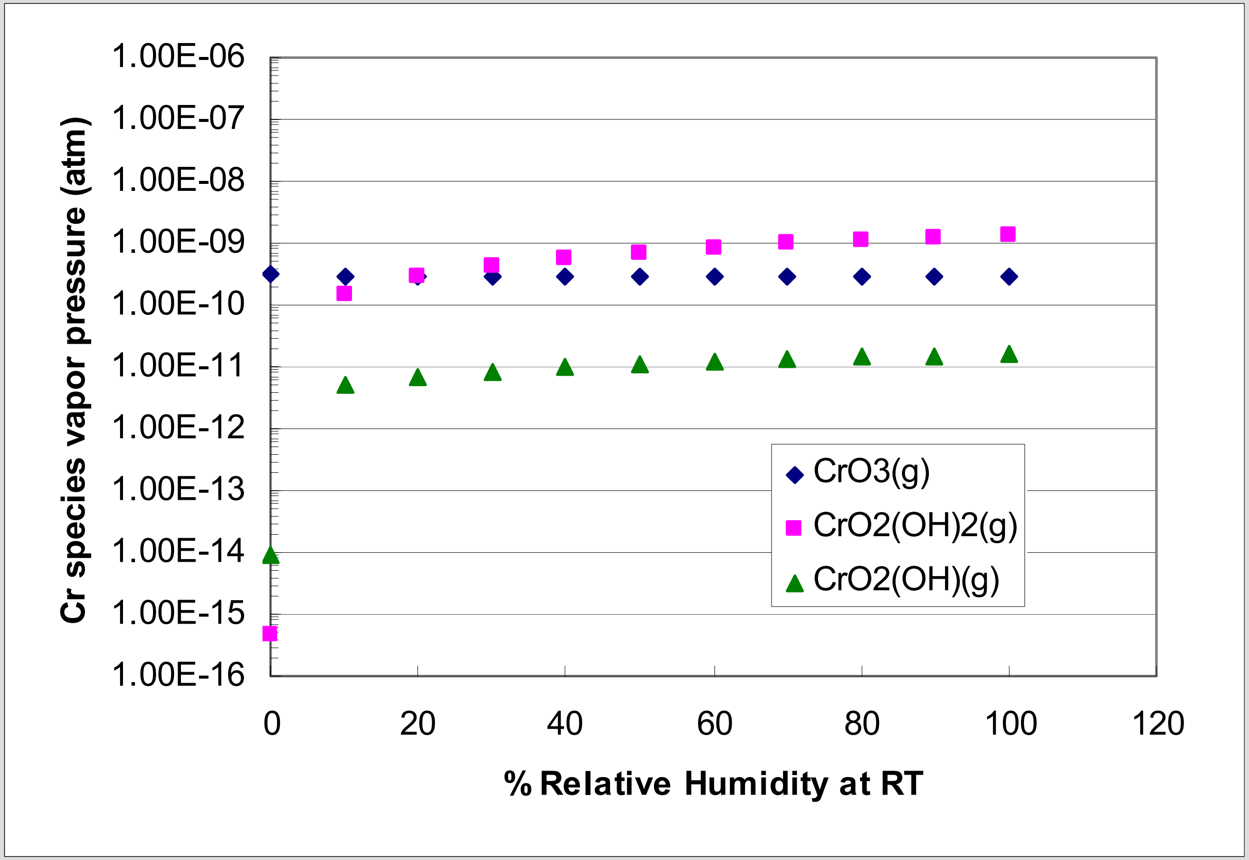
Prabhakar.singh@pnl.gov;

SOFC System



Prabhakar.singh@pnl.gov;

Chromium Species Evaporation



Calculated equilibrium vapor pressure of Cr species (CrO_3, $CrO_2(OH)$, and $CrO_2(OH)$ as a function of relative humidity in air above Cr_2O_3. Temperature: 750ºC; Pressure: 1 atm.