Advanced Interconnect Development

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Battelle

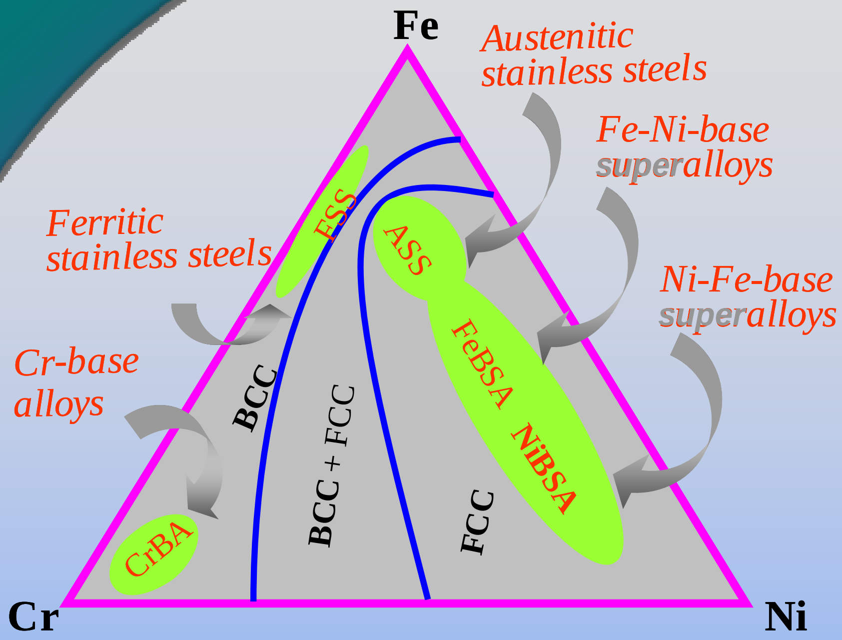
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Objectives

- Develop cost-effective, optimized materials for intermediate temperature SOFC interconnects and interconnect/electrode interface applications.

- Identify and understand degradation processes in interconnects and at their interfaces with electrodes and seals.

Approach



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

<u>Oxidation resistant alloys</u>:

Alumina–forming alloys
Chromia-forming alloys

Body-centered–cubic (BCC)
e.g. ferritic steels
Face-centered-cubic (FCC)
e.g. austenitic Fe-Cr, Ni-Cr-base alloys

- Screening-studies of conventional and newly developed alloys
- Investigation and understanding of degradation in metallic interconnects and at their interfaces under SOFC operating conditions.
- Materials development
  - Surface modification
  - Bulk alloy development
  - Electrode/interconnect interfaces

Focus Areas & Accomplishments

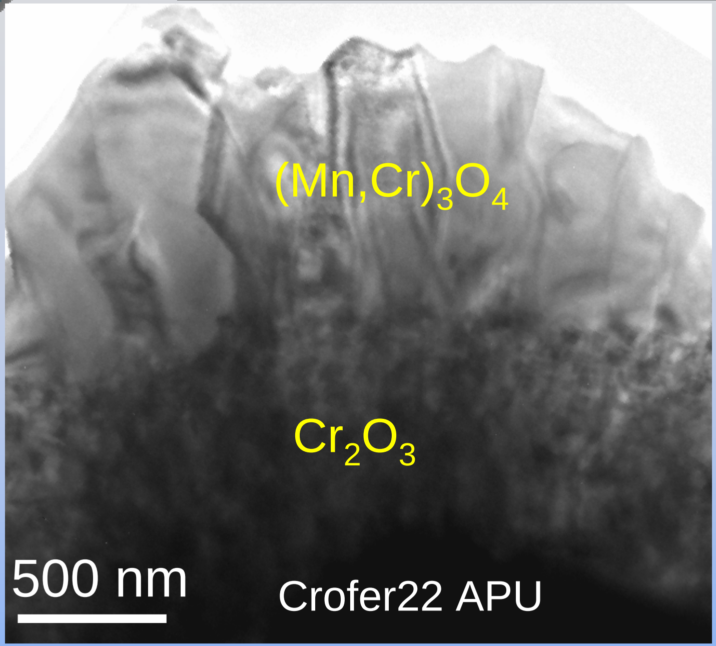
- Ferritic stainless steel interconnects with spinel protection layer
  - Thermally grown $(Mn,Co)_3O_4$ spinel protection layers on FSS;
  - Characterized thermally, electrically, and electrochemically.
- Austenitic-base alloys and laminated, composite interconnect structures
  - Developed Ni-base alloys for improved scale properties.
  - Investigated the feasibility of cladding approach for fabrication of laminated, composite metallic interconnects.
- Interactions and contact layer b/w cathode and interconnect
  - Screening-studied perovskites as an electrical contact layer and interactions b/w metallic interconnects and the perovskites;
  - Developed new electrical contacts and methods of making them.
- Degradation of metallic interconnects under SOFC operating conditions
  - Investigated oxidation behavior of metals and oxidation resistant alloys under dual exposures;
  - Carried out advanced analyses to gain fundamental understanding.

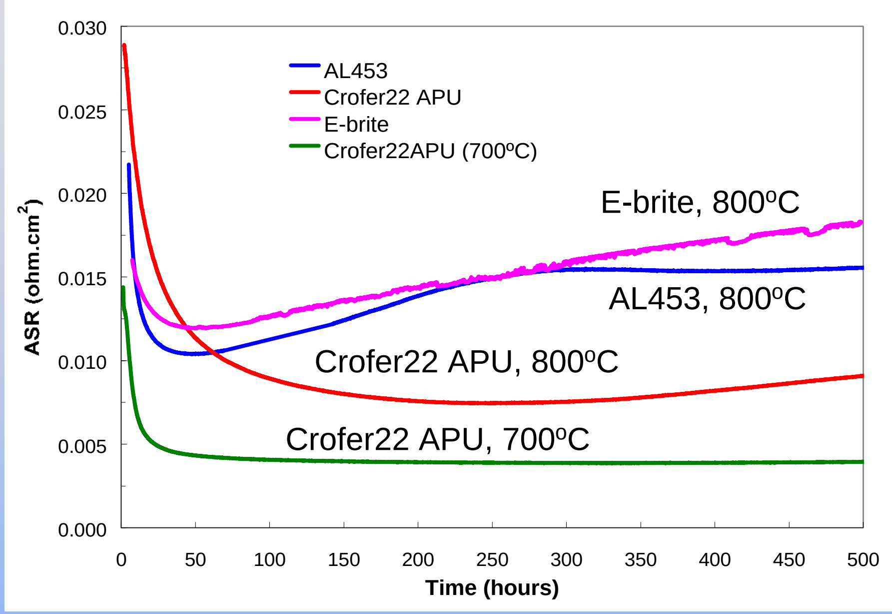
Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions

Protection Layer: The Need

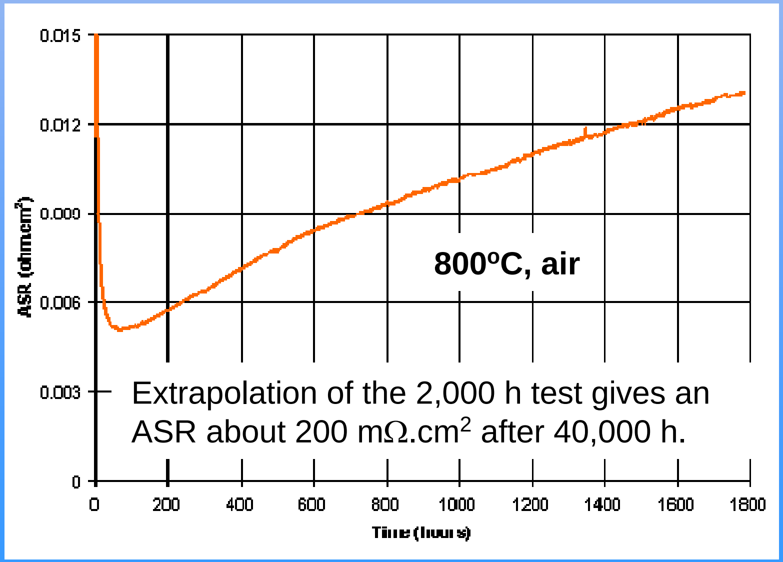
- To improve long term scale structural and electrical stability.

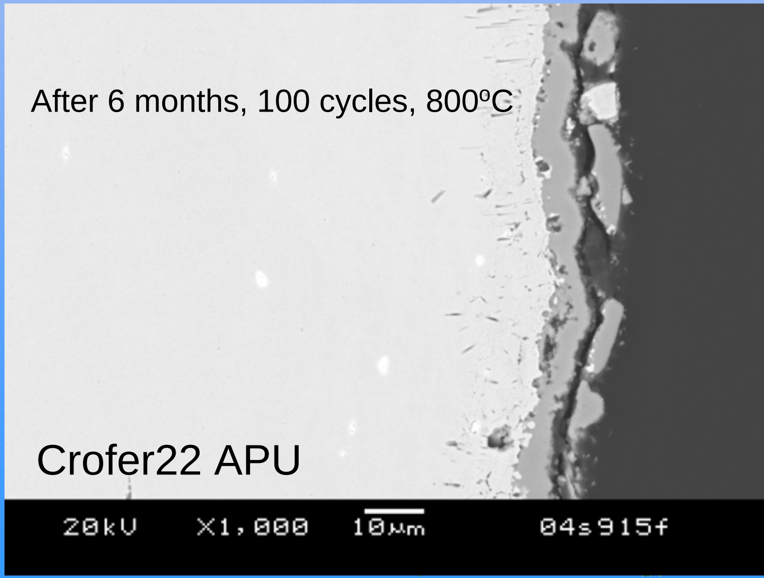




Yang, Hardy, Walker, Xia, Simner, Stevenson, J. Electrochem. Soc., 151 (2004) A1582.

Yang, Stevenson, Meinhardt, Solid State Ionics, 160, 213 (2003).





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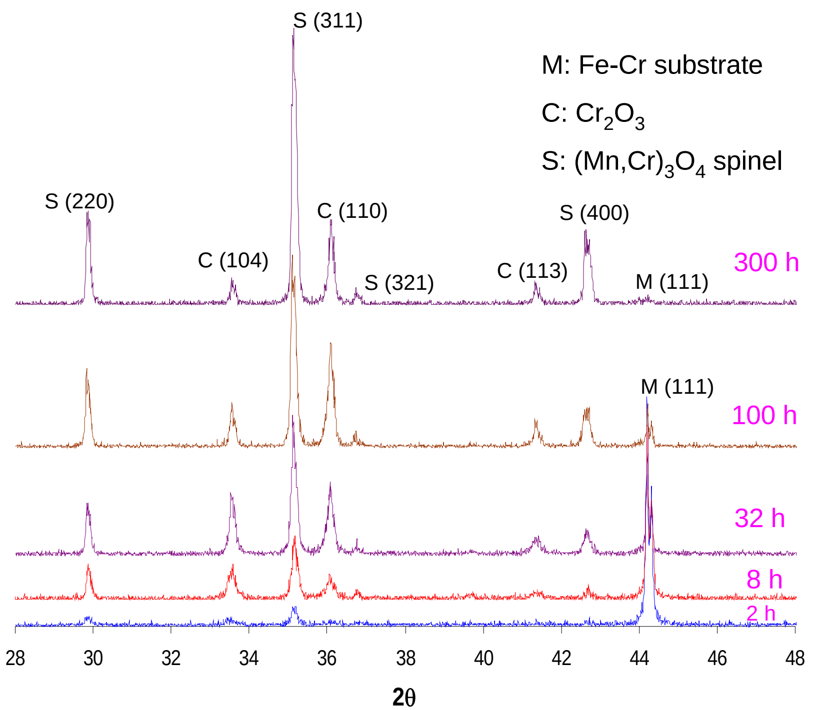
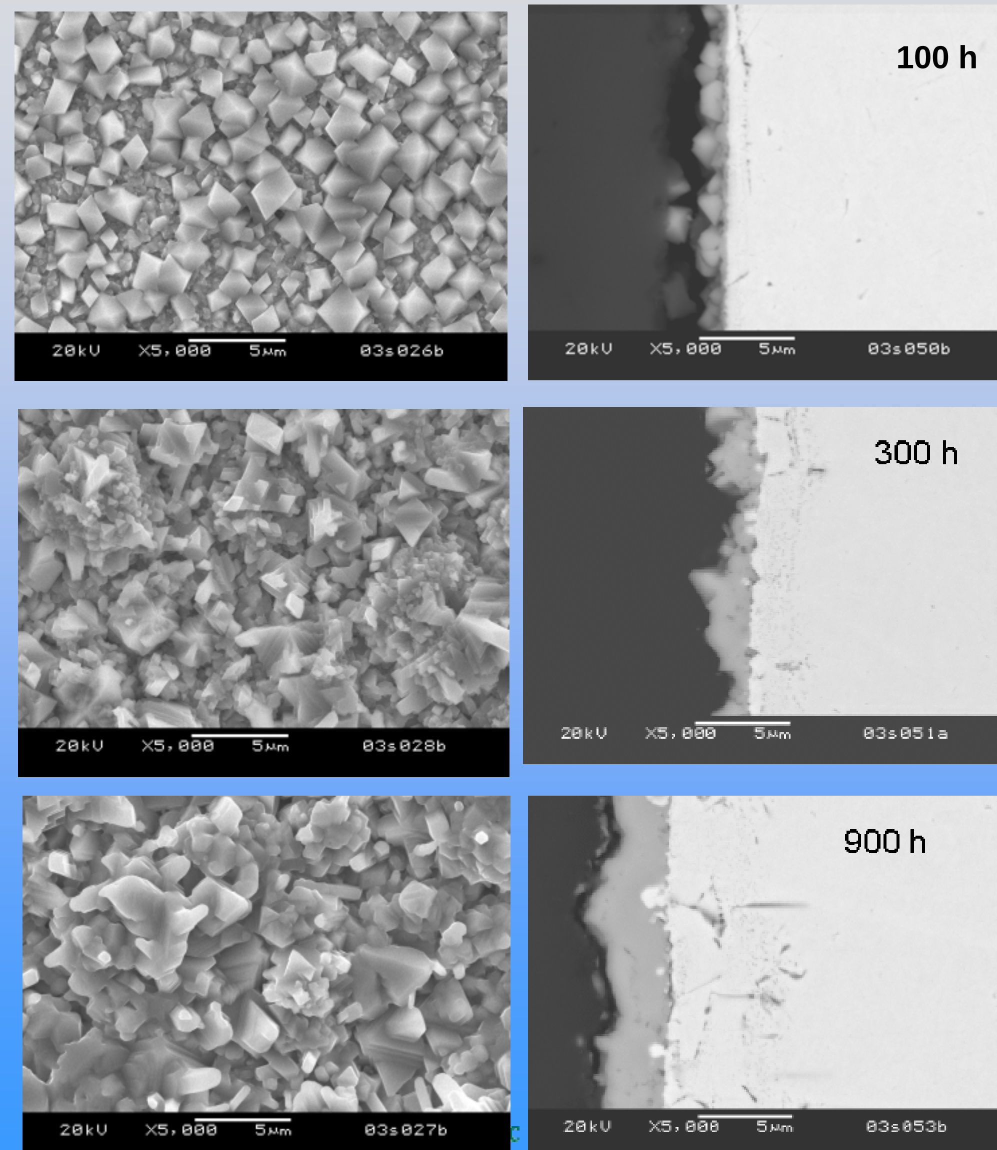
Protection Layer: The Need

- To mitigate or prevent Cr migration and potential poisoning.

Crofer22 APU, 800ºC, in air

In-situ X-Ray Diffraction Analysis





Simner, Anderson, Xia, Yang, Pederson, Stevenson, J. Electrochem. Soc., 152 (2005) A740.

Yang, Meinhardt, Stevenson, J. Electrochem. Soc., 150, A1095 (2003).

Development of $(Mn,Co)_3O_4$ Spinel Protection Layer

Why $(Mn,Co)_3O_4$ spinel?

- Electrical conductivity:

$$\sigma_{(Mn,Co)_3O_4} = 10^{3\sim4}\sigma_{Cr_2O_3} = 10^{2\sim3}\sigma_{MnCr_2O_4}$$

- Appropriate CTE:

$$CTE_{Mn_{1.5}Co_{1.5}O_4} = 11.5\times10^{-6}K^{-1}, 20-800^oC$$

- Non-Cr containing: Cr-containing oxides will release Cr
- Flexibility of fabrication: THERMAL GROWTH

Why thermal growth?

- Strong adherence to the substrate;
- Introduction of porosity for strain tolerance;
- Improved thermomechanical stability;
- Cost effectiveness.

Larring, Norby, J. Electrochem., Soc., 147, 3251 (2000).
Yang, Xia, Singh, Stevenson, SECA Annual Workshop, Boston, May 11-13, 2004.
Yang, Xia, Stevenson, Electrochem. & Solid State Lett., 8 (2005) A168.

Approach

Preparation of $(Mn,Co)_3O_4$: SS or GNP

↓

Solution based coating

↓

Heat-treated in reducing environments

↓

Thermally grown during heating in oxidizing environments or during first SOFC stack heating

Thermal Growth of $Mn_{1.5}Co_{1.5}O_4$ on FSSs

Reduction

In H_2/Ar+3% H_2O, 800ºC, 24h

$$[MnCo_2O_4]_{cubic} + 3H_2 \uparrow \Rightarrow 2Co + MnO + 3H_2O \uparrow$$

$$[Mn_2CoO_4]_{tet} + 2H_2 \uparrow \Rightarrow Co + 2MnO + 2H_2O \uparrow$$

$$4Mn_{1.5}Co_{1.5}O_4 + 5H_2 \uparrow \Rightarrow 6Co + 6MnO + 5H_2O \uparrow$$

Oxidation

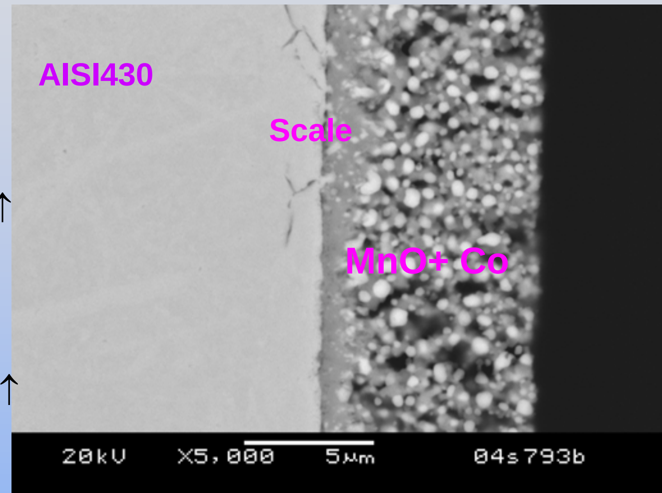
Air+3% H_2O, 800oC, 100h

$$4Co + 2MnO + 3O_2 \uparrow \Rightarrow 2[MnCo_2O_4]_{cubic}$$

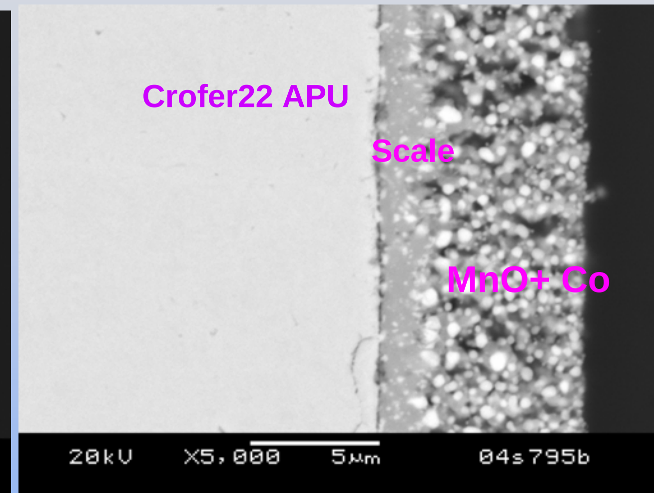
$$2Co + 4MnO + 2O_2 \uparrow \Rightarrow 2[Mn_2CoO_4]_{tet}$$

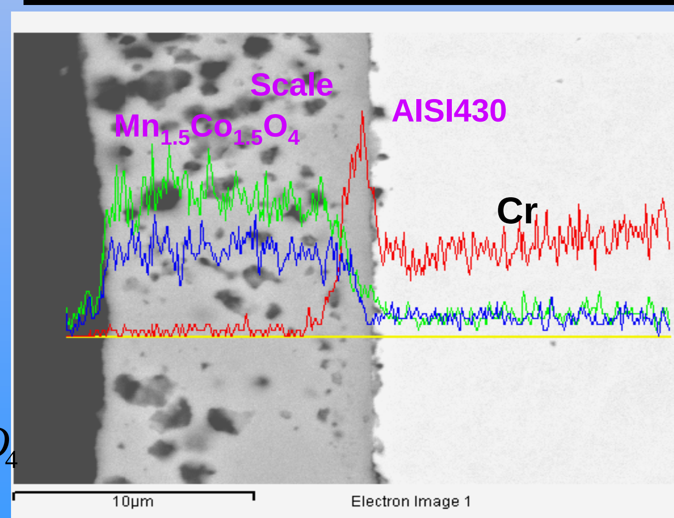
$$6Co + 6MnO + 5O_2 \uparrow \Rightarrow 4Mn_{1.5}Co_{1.5}O_4$$

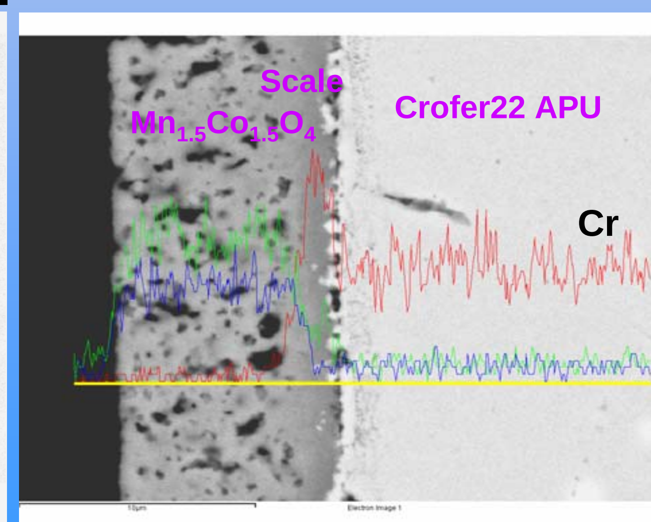
AISI430



Crofer22APU

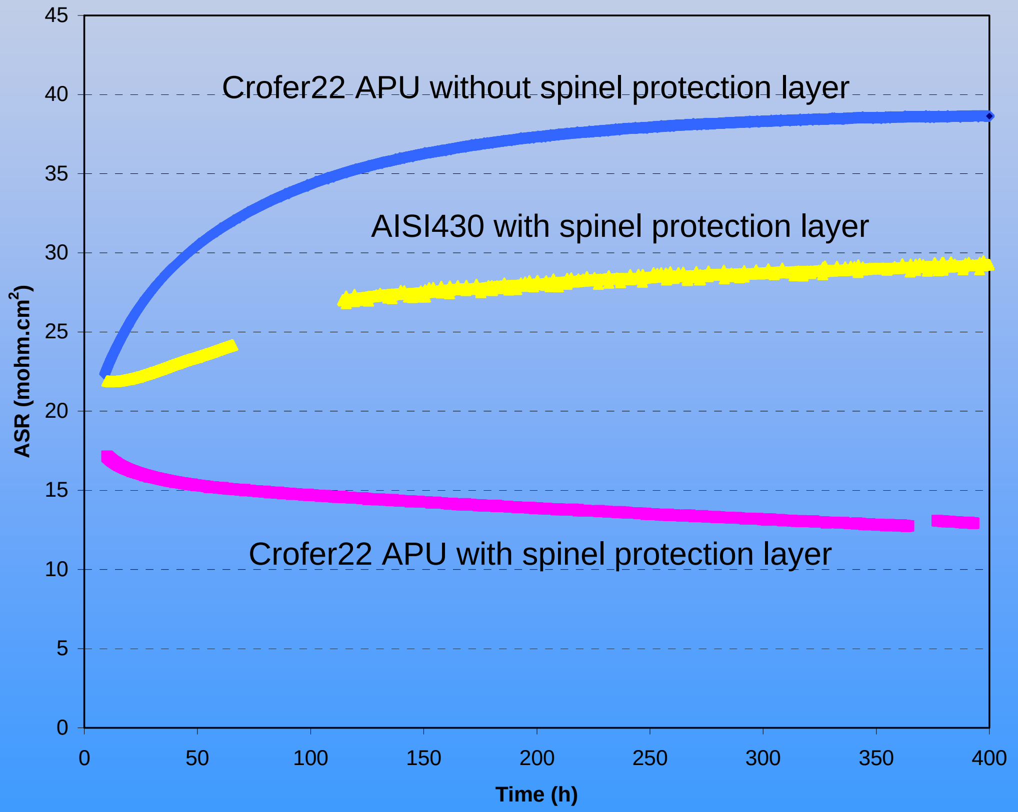


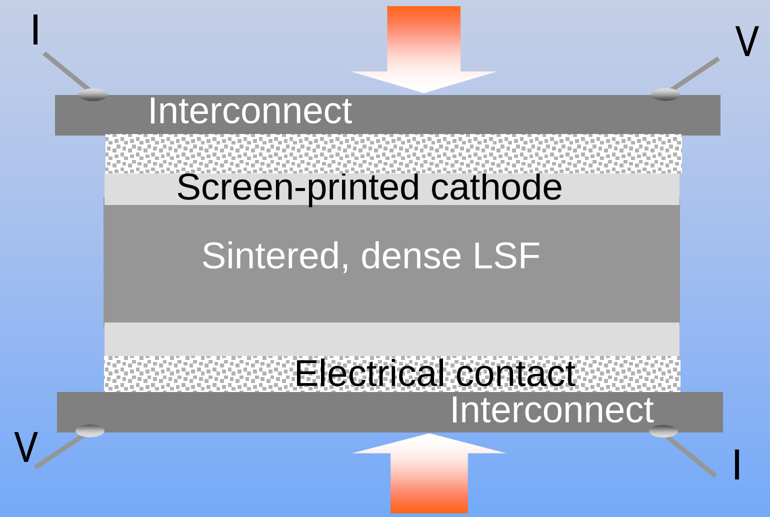




Contact ASR w & w/o Protection Layers

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





6.5 PSI Load

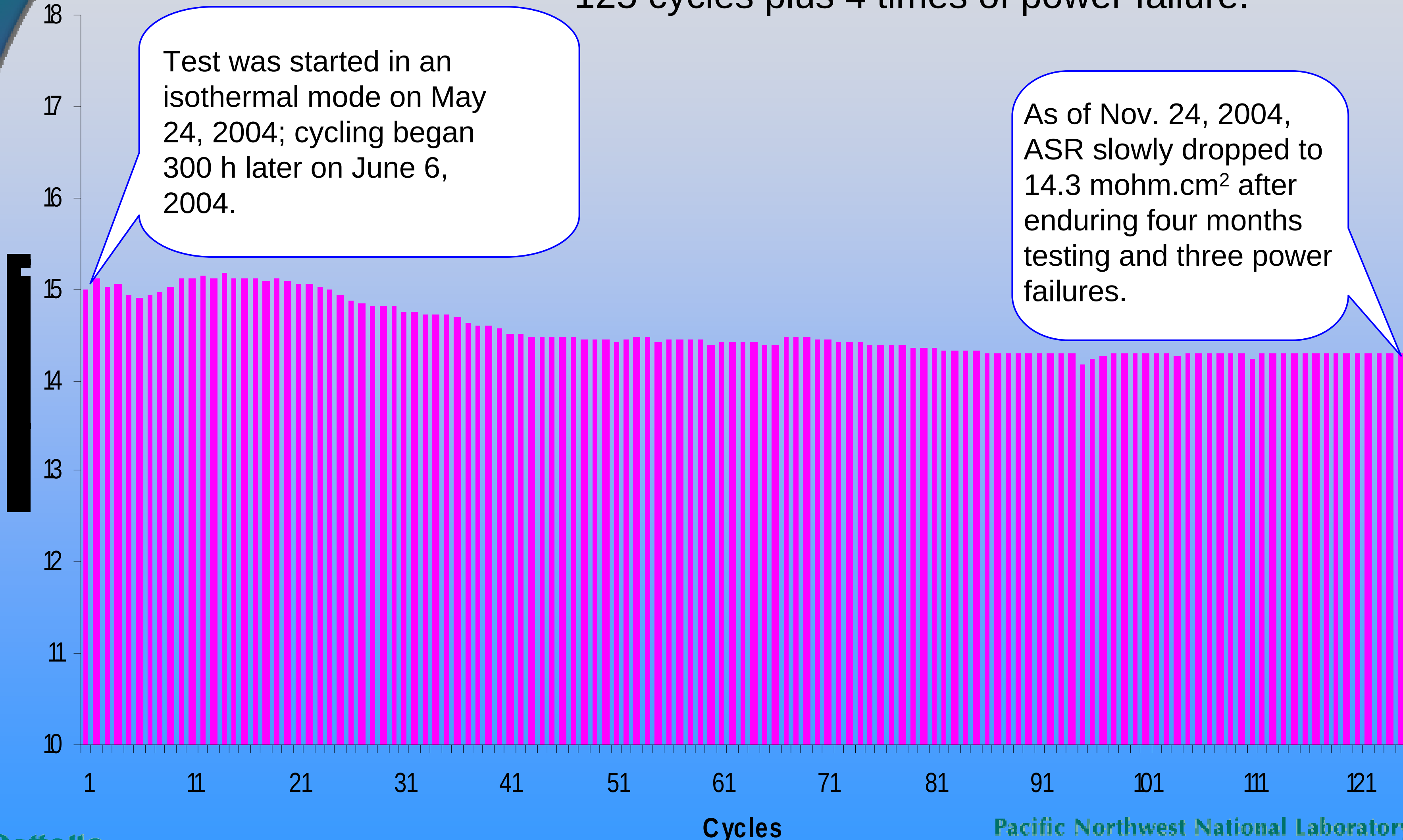
$500 mA.cm^{-2}$

LSCM electrical contact, 800ºC, air

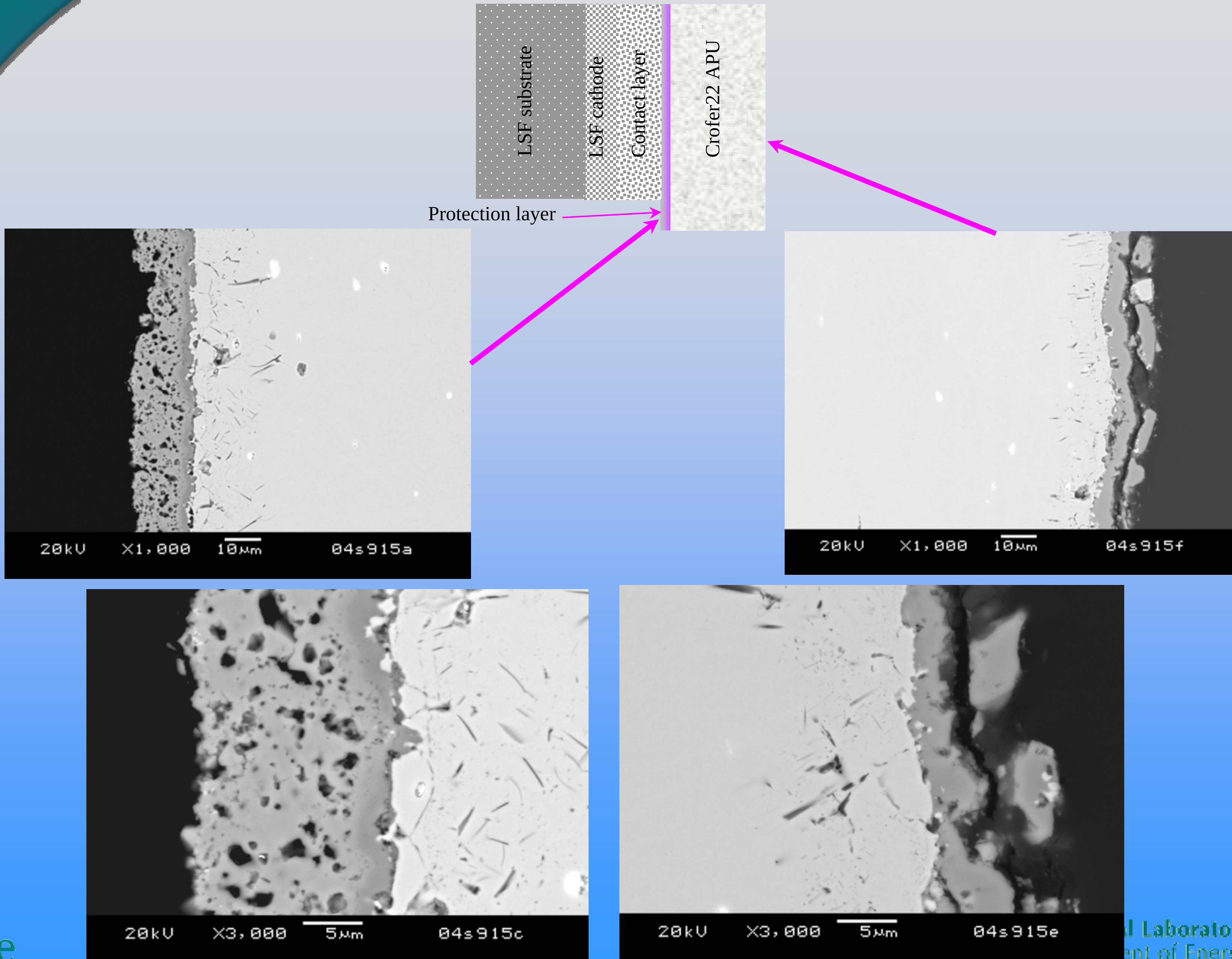
Six Month Thermal Cycling Test

IRU test: 800°C, air, cycling from 80-800°C,

125 cycles plus 4 times of power failure.

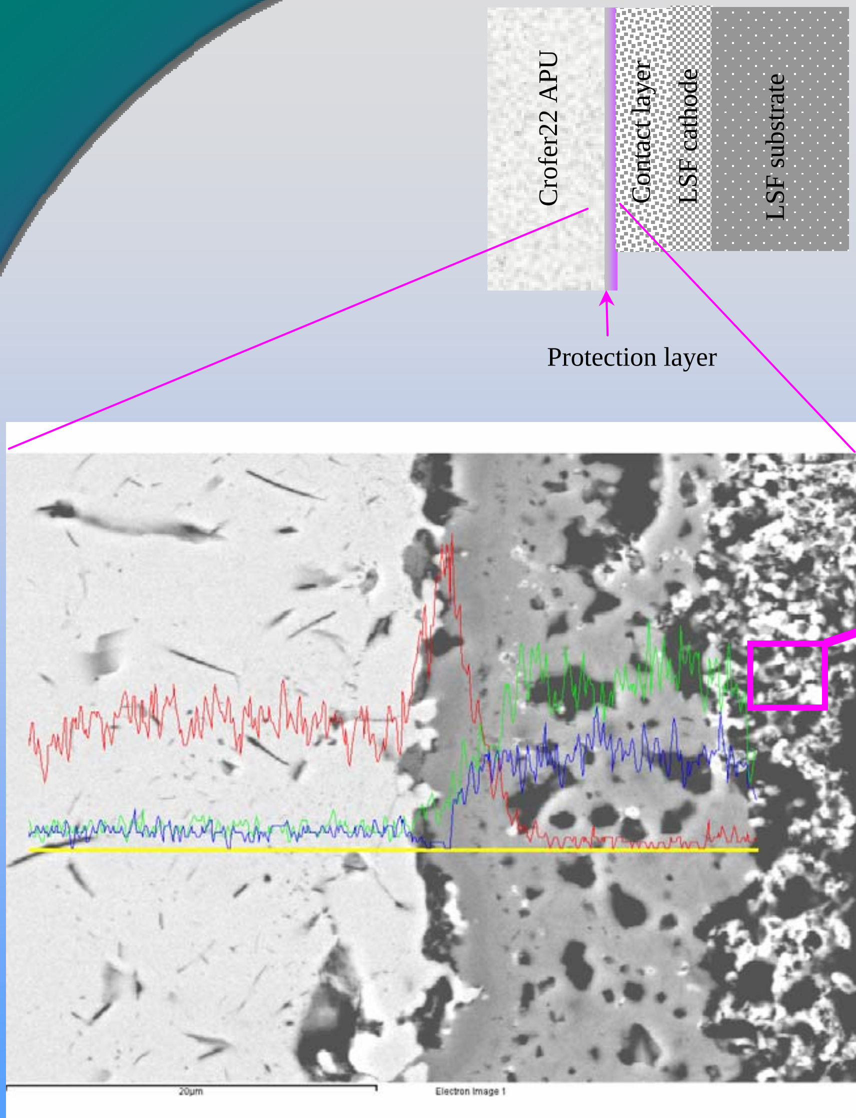


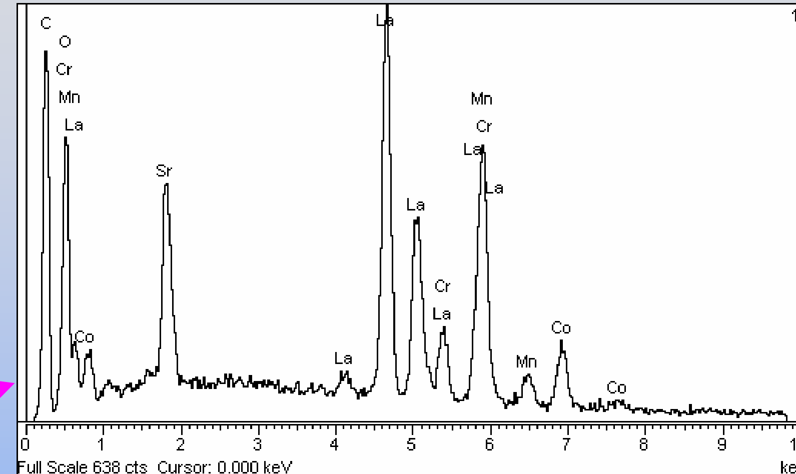
Improved Surface Stability



Effective Cr-Barrier

No Cr migration across the spinel protection layer after six months of heating and cycling.





Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	11.20	1.1185	16.01	0.63	51.91
Cr K	0.00	1.0284	0.00	0.00	0.00
Mn K	10.78	0.9163	18.79	0.46	17.74
Co K	3.77	0.9180	6.56	0.36	5.77
Sr L	4.64	0.6073	12.20	0.56	7.23
La L	29.51	1.0148	46.45	0.68	17.35

Yang, Xia, Stevenson, Electrochem. & Solid State Lett., 8 (2005) A168.

Yang, Xia, Simner, Stevenson, J. Electrochem. Soc., in press (2005).

Simner, Anderson, Xia, Yang, Stevenson, J. Electrochem. Soc., in press (2005).

Summary

- $Mn_{1.5}Co_{1.5}O_4$ spinel protection layers can be thermally grown on ferritic stainless steel interconnects.
- The thermally grown $Mn_{1.5}Co_{1.5}O_4$ spinel protection layer:
  - improved surface stability
  - minimized contact resistance
  - prevented Cr migration
- The spinel protection layer demonstrated excellent long-term stability.

Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions

Modification of Haynes 230

Evaluation:

- Oxidation and scale growth in moist air as well as under dual environments
- Scale constitution and structure
- Scale electrical conductivity
- Thermal expansion

High purity metal elements → Vacuum induction melting → Electroslag remelting → Hot rolling → Cold rolling → 40 mil sheets

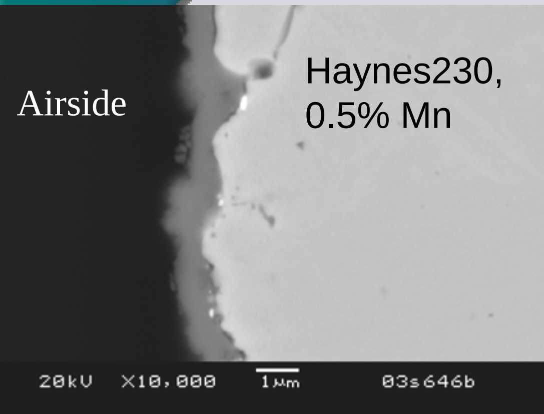
Heat No.	8305 7804	M1	M2
Chem. Comp.	0.5% Mn Haynes 230	1% Mn EN1304-4-812	2% Mn EN1404-4-813
Al	0.34	0.31	0.38
B	0.002	0.005	0.006
C	0.100	0.111	0.095
Co	<5.0	< 0.01	< 0.01
Cr	22.45	20.96	20.73
Cu	0.05	0.03	0.04
Fe	1.54	< 0.01	< 0.01
La	0.017	< 0.005	< 0.005
Mn	0.52	1.08	2.06
Mo	1.42	2.02	1.95
Ni	Bal	60.67	59.49
P	0.005	0.005	0.006
S	<0.002	0.003	0.002
Si	0.38	0.42	0.42
Ta	<0.100	0.06	0.06
Ti	<0.01	< 0.010	< 0.010
W	14.23	13.62	14.34

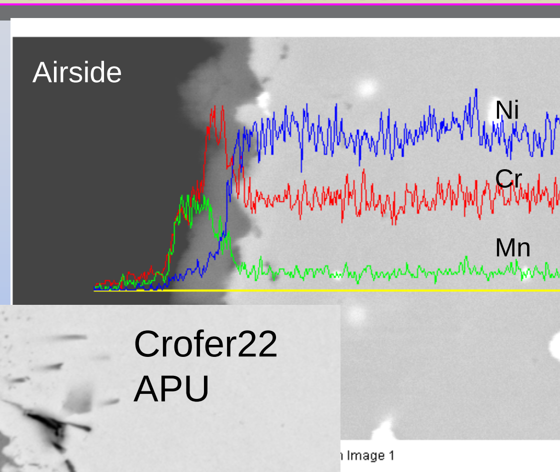
** Alloys were made at Haynes International Inc.*

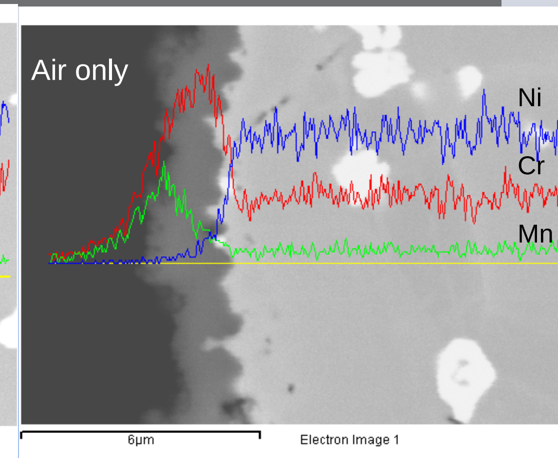
Scale Structure and Growth of M Alloys

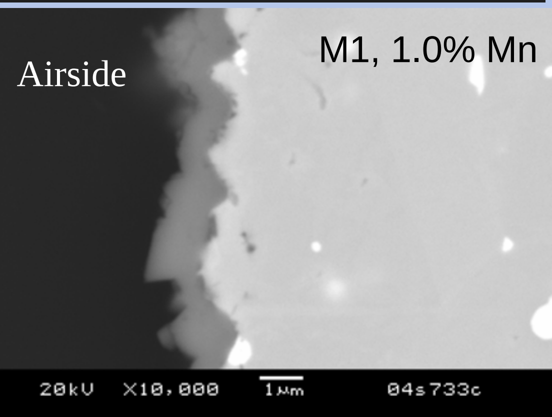
- Scale structure similar to Crofer, i.e. $(Mn,Cr)_3O_4$+Cr_2O_3;
- Mn addition increased scale growth, but still better than Crofer;
- Superior oxidation resistance under dual environments.

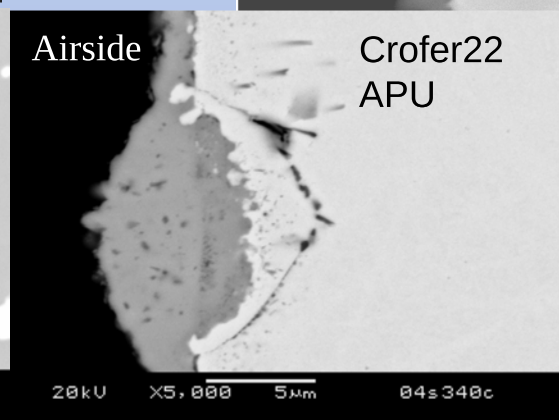
800°C, 300h

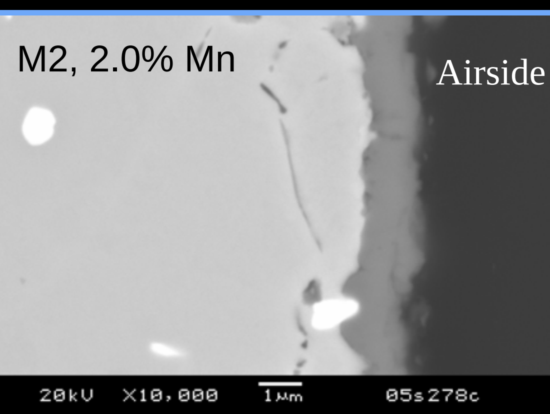


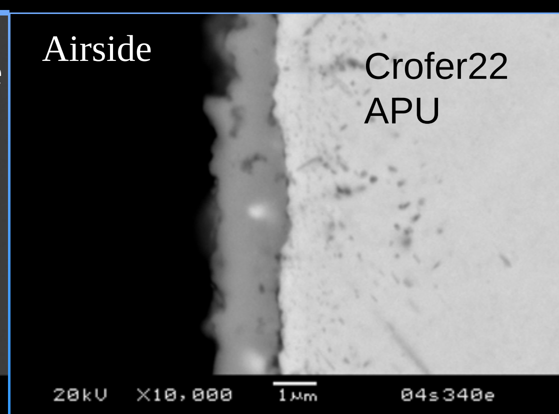


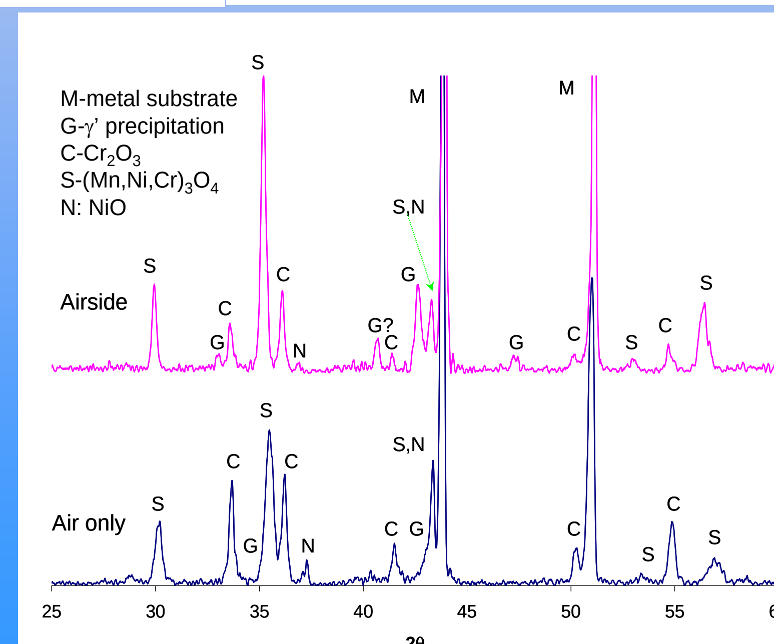






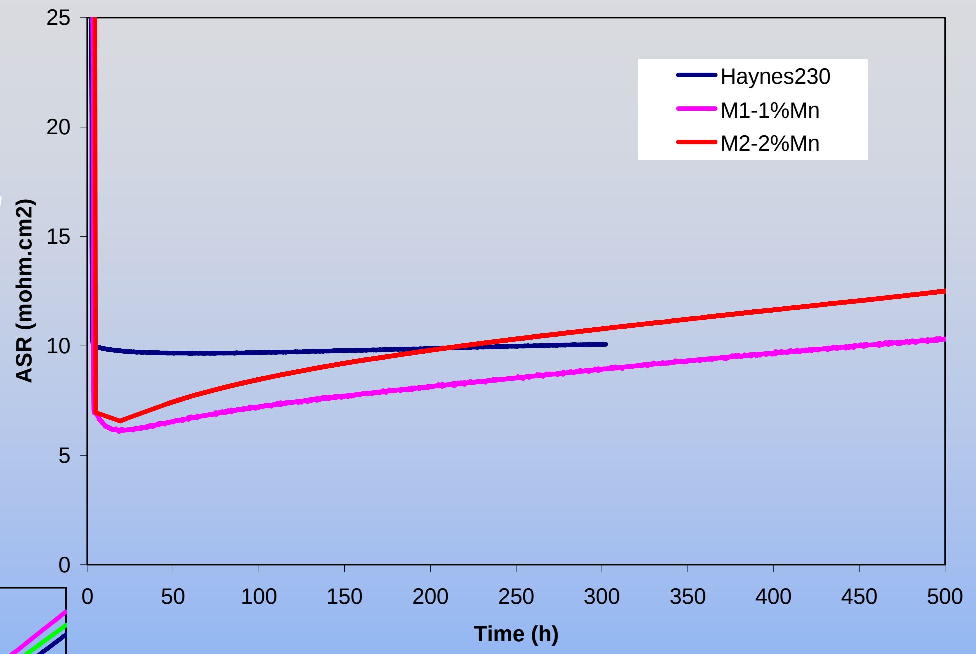


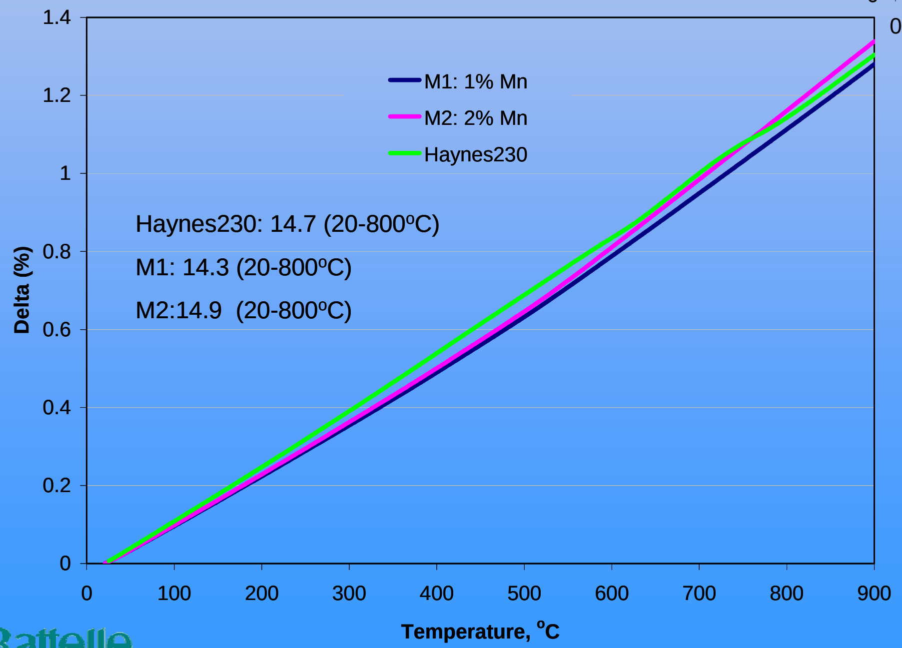




Properties of M Alloys

- $(Mn,Cr)_3O_4$ spinel help improved scale conductivity,
- Mn addition increased scale growth rate and thus the scale electrical resistance.

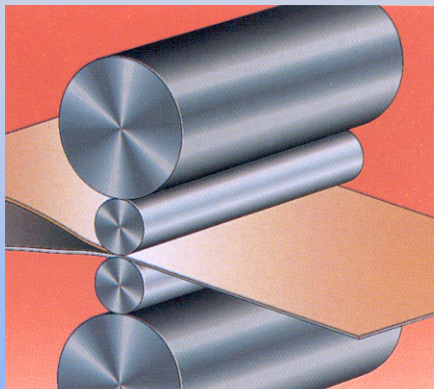


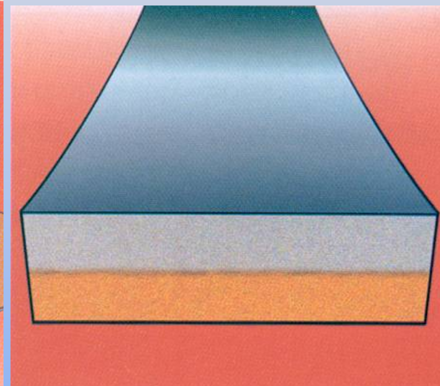


- CTE of M alloys is comparable to Haynes230 and higher than that of ceramic cells,
- Mn addition slightly increased CTE.

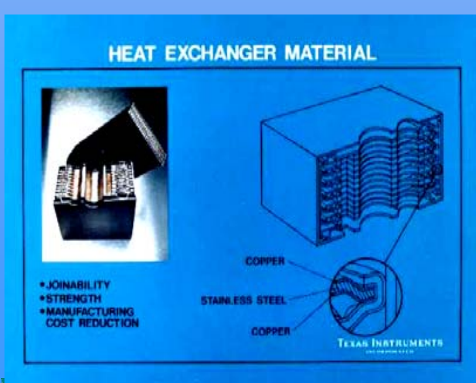
Laminated, Composite Interconnect Structures via Cladding*

- **Clad Metal:**
  - A layered, composite metallic material





  - Cost-effective and widely used in Industries as well as in our daily life

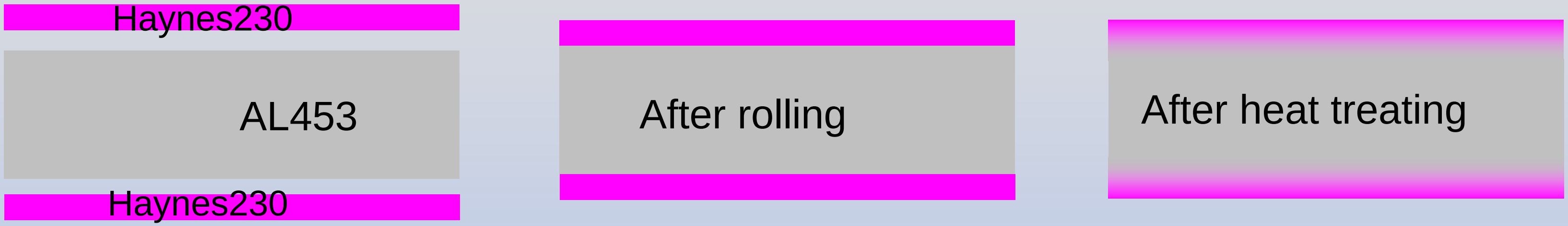


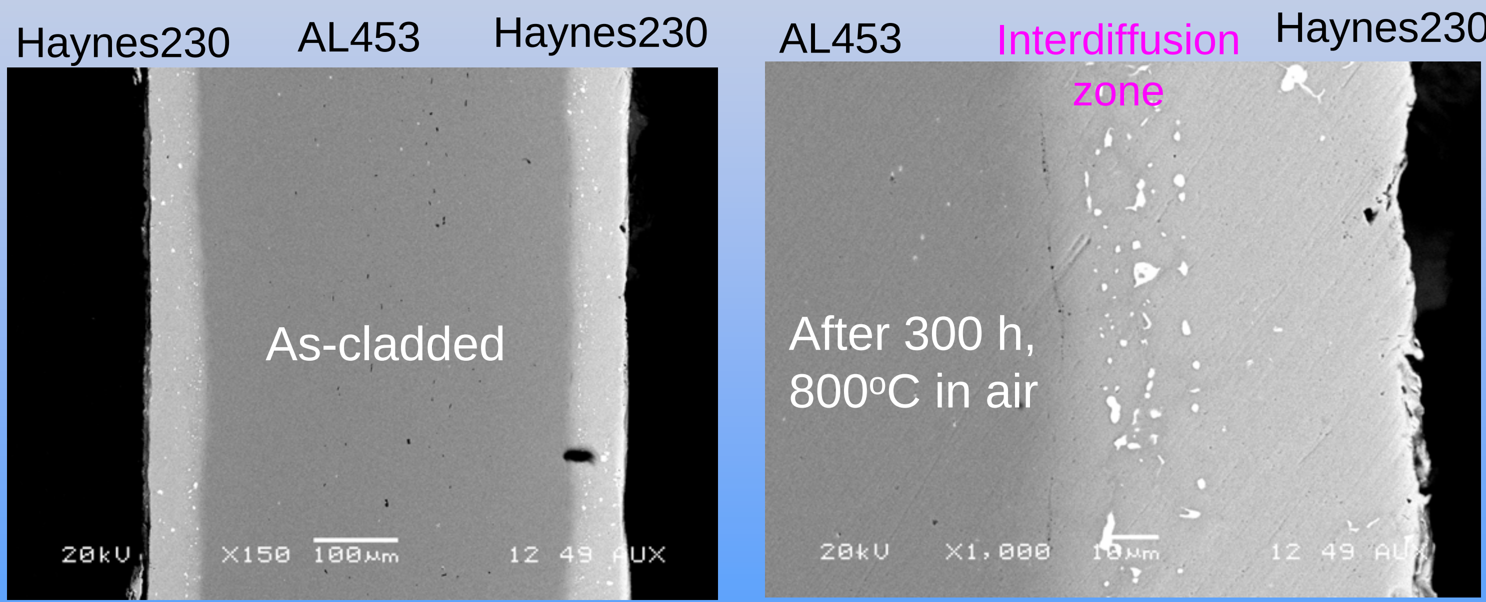
- **Clad Metal for interconnect applications**

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

** Collaboration with Leigh Chen, Engineered Materials Solutions Inc.*

Proof-of-Concept: Haynes230||AL453||Haynes230

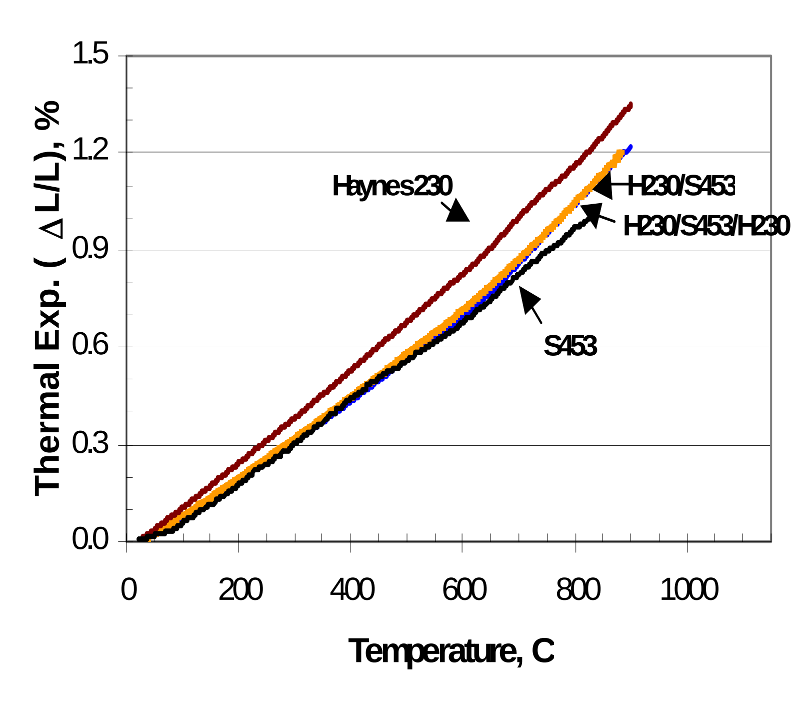




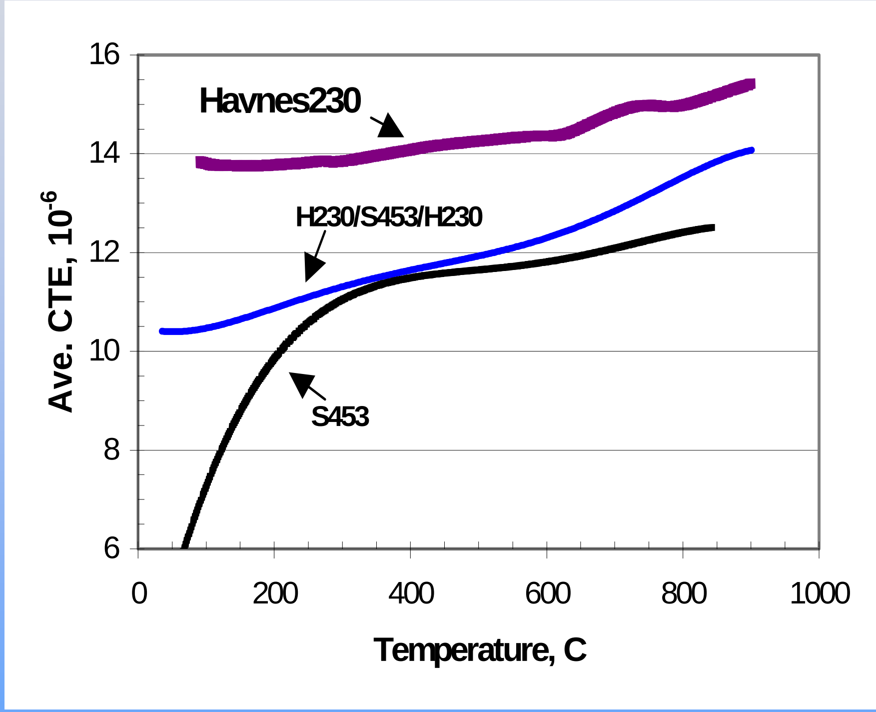
- The proof of concept work proved the viability of cladding FSS with Ni-based alloys and another piece of FSS;
- The cladded structures were stable during a subsequent heat treatment.

Thermal Expansion of Clad Metals

Thermal expansion of clad metals, compared to Haynes 230 and Al453



CTE* of the clad metal in comparison with that of Haynes230 and AL453



- The cladding is a viable approach to modify the thermal expansion of metallic interconnect and help improve its cost-effectiveness.

Chen, Yang, Jha, Xia, Stevenson, J. Power Sources, in press (2005).

Summary

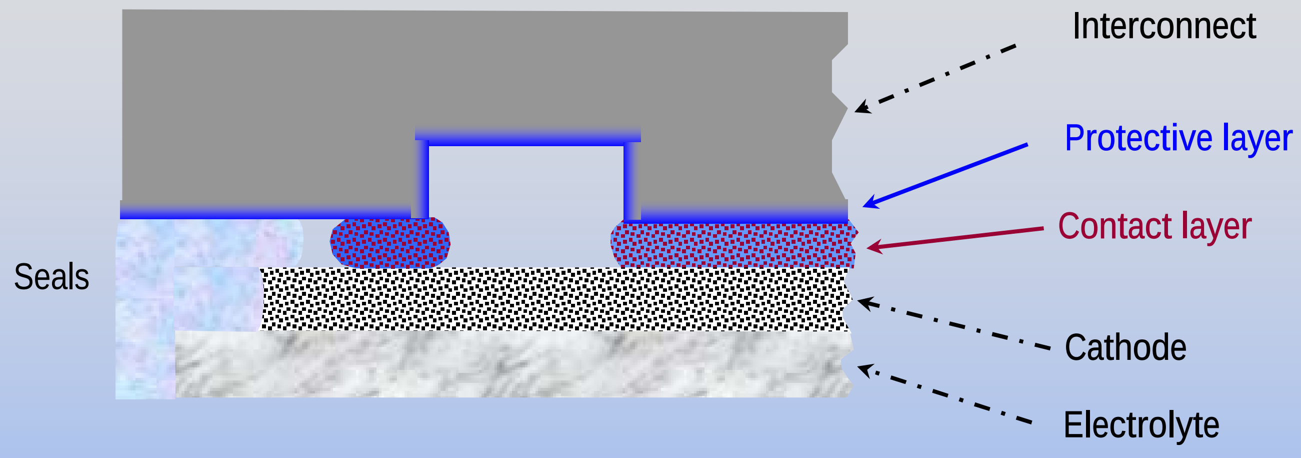
- The austenitic Ni-Cr-base alloys can be modified for improved properties for SOFC applications.

- The initial work demonstrated that cladding is a viable approach to fabricate laminated, composite interconnect structures that integrate the advantages of different alloys, while avoiding their disadvantages.

Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions

Contact Layers



Functions

- Promote electrical contact
- Facilitate stack assembling
- Act as a buffer zone to trap Cr

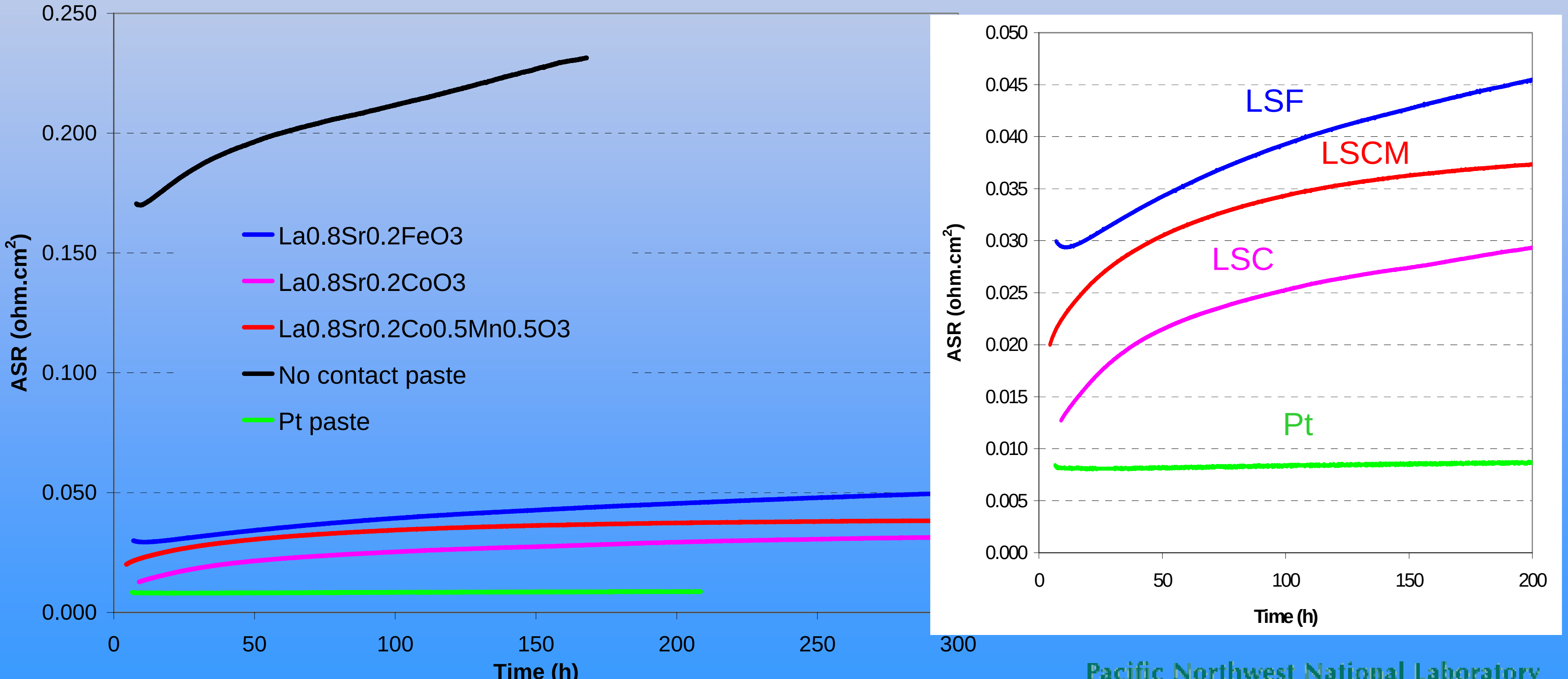
Materials requirements

- High electrical conductivity
- Chemical compatibility
- Thermal expansion matching
- Thermochemical stability
- Low cost

Contact Resistance

$$ASR_{contact} = \Phi\begin{pmatrix} Scale: conductivity, growth-rate; \\ contact: area, conductivity; \\ reactions: scale \mid contact \mid electrodes \end{pmatrix}$$

- $SrCrO_4$ can be formed via both solid-solid and solid–gas reactions.
- LSM and LSCM facilitate $(Mn,Cr)_3O_4$ spinel formation.



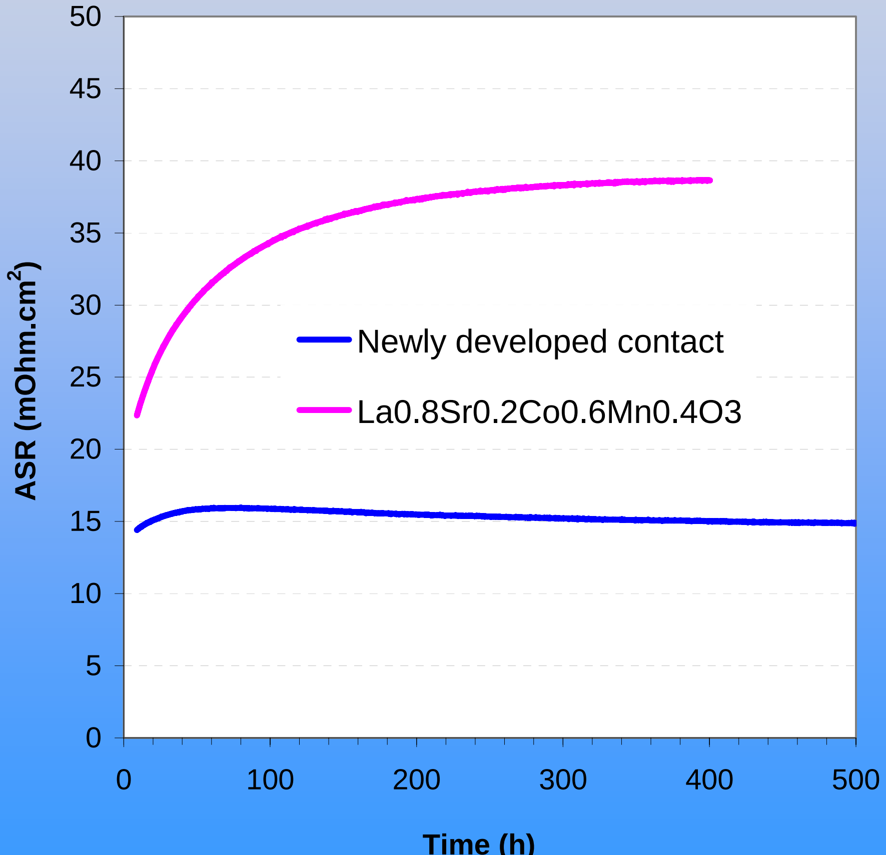
Yang, Xia, Singh, Stevenson, J. power Sources, accepted (2005).

Performance of Newly Developed Contacts

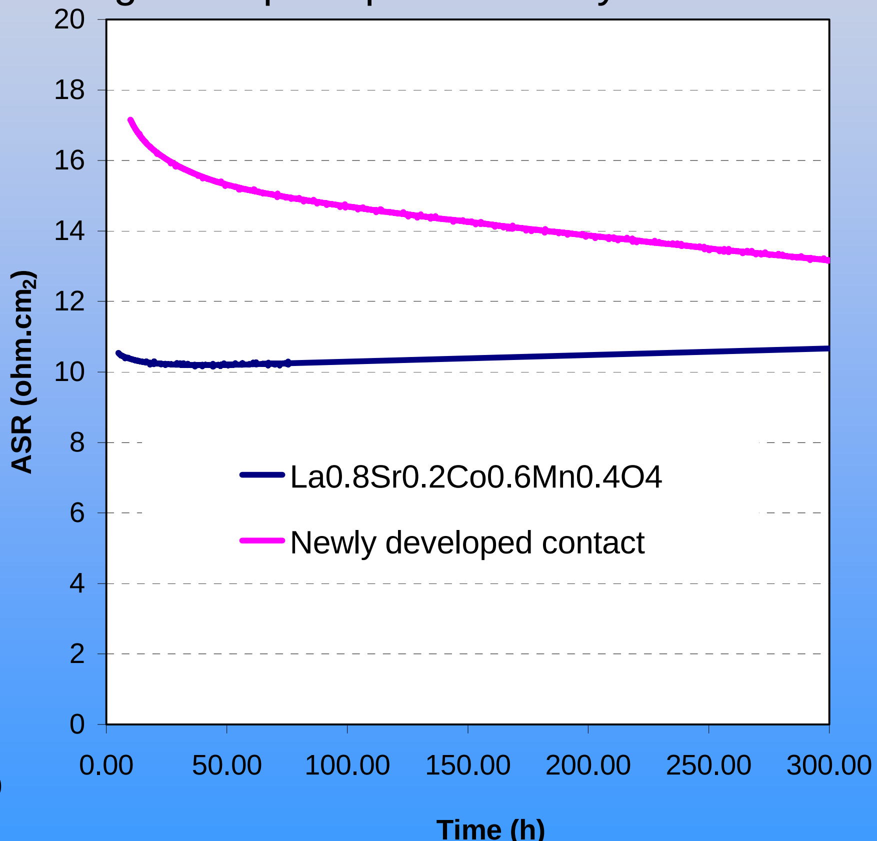
- **Combination of the spinel protection layer and a newly developed contact led to a significantly minimized contact ASR.**

IRU test: LSF cathode; Temperature: 800°C

LSF cathode and bare Crofer22 APU as interconnect



Crofer22 APU with thermally grown spinel protection layer



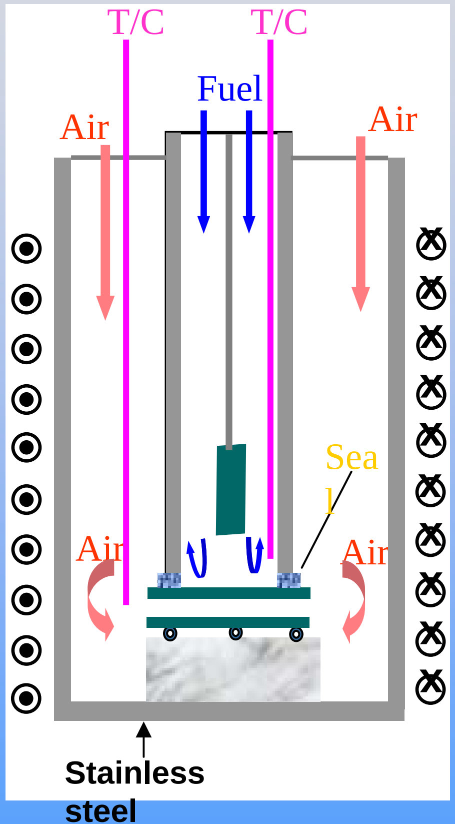
Summary

- It is desirable to have an electrical contact layer to minimize the contact resistance between oxide cathodes and metallic interconnects.
- Screening study on perovskite contacts indicated that the contact ASR depends on scale conductivity, contact area, and conductivity of contact materials, as well as interactions between interconnects and electrical contacts.
- The combination of spinel protection layer and the newly developed contact materials demonstrated a very low contact ASR.

Focus Areas

- Ferritic stainless steel interconnect with spinel protection layer
- Austenitic-base alloys, and laminated, composite interconnect structures
- Interactions and contact layer b/w cathode and interconnect
- Degradation of metallic interconnects under SOFC operating conditions

Oxidation Behavior of Alloys under Interconnect Dual Exposures



- **Oxidation study has been a common area of interest, but typically in a single exposure.**
- **Oxidation behavior under interconnect dual exposures can be very different from that in a single exposure.**
- **Understanding helps develop robust materials.**

Materials studied:

NiBS:
- Haynes 230-22%Cr
- Hastelloy S-17%Cr
- Haynes 242-9%Cr
- Pure Ni, Ag, etc.

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

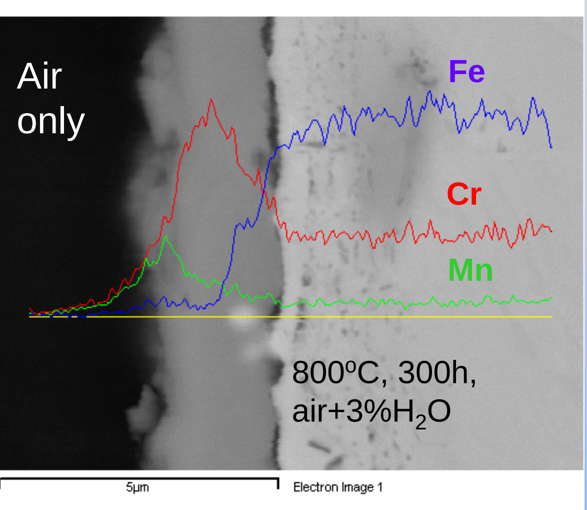
Variables:

- Alloy composition
- Thermal history: isothermal vs. cycling
- Fuels: Hydrogen & Reformates

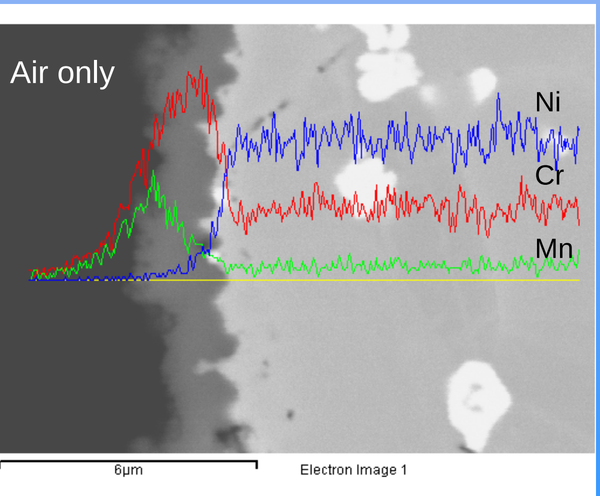
Yang, Walker, Singh, Stevenson, *Electrochem. & Solid State Lett.*, 6, B35-37 (2003).
Yang, Walker, Singh, Stevenson, Norby, *J. Electrochem. Soc.*, 151, B669-678 (2004).
Singh, Yang, Viswanathan, Stevenson, *J. Mater. Eng. & Perform.*, 13, 287-294 (2004).
Yang, Xia, Singh, Stevenson, *Solid State Ionics*, in press (2005).

Anomalous Oxidation of Alloys under Dual Exposures: A Summary

Crofer22 APU



M1 alloy



Ferritic stainless steels (FSS):

FSS demonstrate anomalous oxidation behavior under dual exposures.

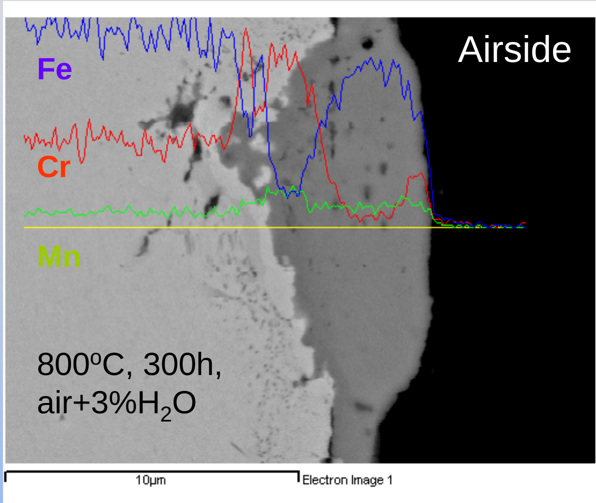
Depending on alloy composition, thermal history, and surrounding environment, the anomalous oxidation can lead to a localized attack by formation of hematite nodules,

Ni-Cr-base alloys (NCA):

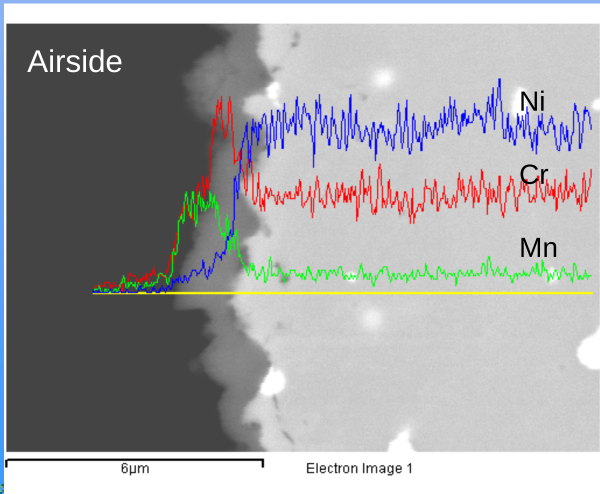
NCA also demonstrate anomalous oxidation behavior under dual exposures.

The anomalous oxidation usually leads to less defects and a better scale adherence.

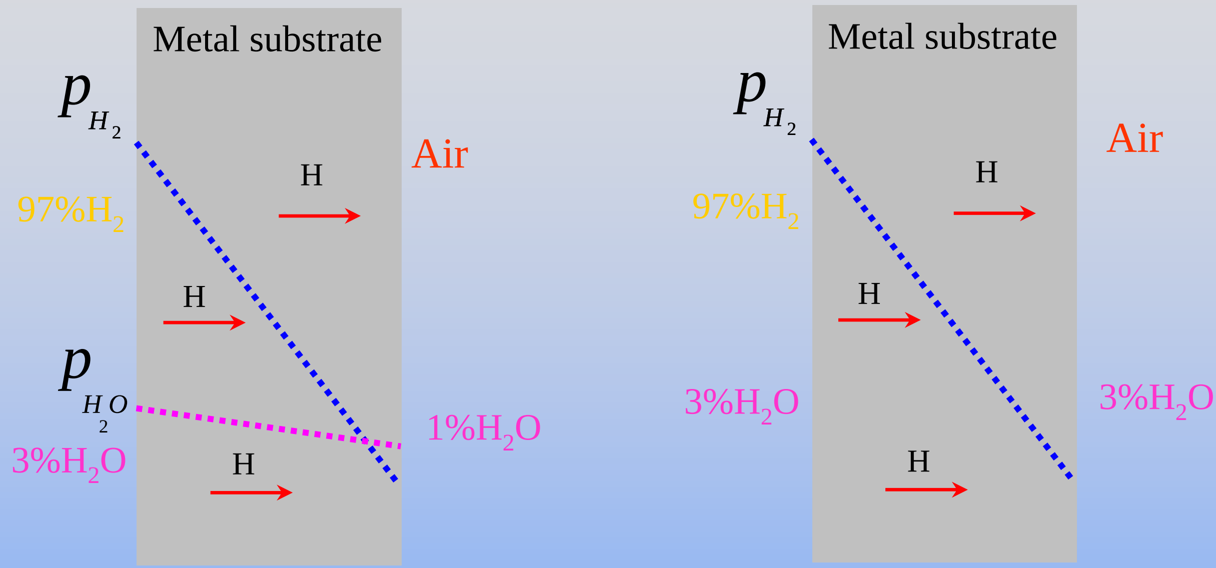
Crofer22 APU



M1 alloy



H/H+ Induced Anomalous Oxidation



- The anomalous oxidation of metals or alloys under dual exposures is due to the hydrogen transport from the fuel side to the airside.
- Both a hydrogen and a water vapor gradient can contribute to the hydrogen flux and affect the scale growth at the airside.
- Mechanistic understanding is an ongoing work: how the hydrogen/proton interacts with scale oxides and affects the scale composition, structure and its properties.

Future Work:

Surface modification of metallic interconnects

- Study spinel materials to optimize protection layers for best performance;
- Explore different approaches and search more economic ways for mass production.

Development of electrical contact layers

- Continue to study interfacial interactions and ASR;
- Develop and optimize contact layer materials for further improved performance.

Alloy development and optimization of clad interconnect structures

- Continue to develop and optimize bulk alloys for improved scale properties.
- Optimize laminate, composite interconnect structure and compositions.
- Study interdiffusion and predict life via modeling.

Study of oxidation behavior and scale properties under dual exposures

- Mechanistic understanding: Interaction and transport of H/H^+ at the metal/oxide interface and in the oxide scale; their effects on defect structure, transport properties, scale growth.
- Oxidation behavior of alloys under the reforming gas/air dual exposures.
- Study effects of dual exposure and electrical field on scale properties.

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