Advanced Interconnect Development

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Pacific Northwest National Laboratory
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Interconnect Development

Objectives:

- Develop cost-effective, optimized materials for intermediate temperature SOFC interconnect and interconnect/electrode interface applications.
- Identify and understand degradation processes in interconnects and at their interfaces with electrodes.

Approaches:

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

Focus Areas & Progress

- Stainless steel interconnect with spinel protection layer
  - Thermally grown $(Mn,Co)_3O_4$ spinel protection layers on FSS;
  - Characterized thermally, electrically, and electrochemically.
- 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 a new electrical contact.
- 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.
- Degradation of metallic interconnects under SOFC operating conditions
  - Investigated oxidation behavior of Ni and Ni-base alloys under dual exposures;
  - Carried out advanced analyses to gain fundamental understanding.

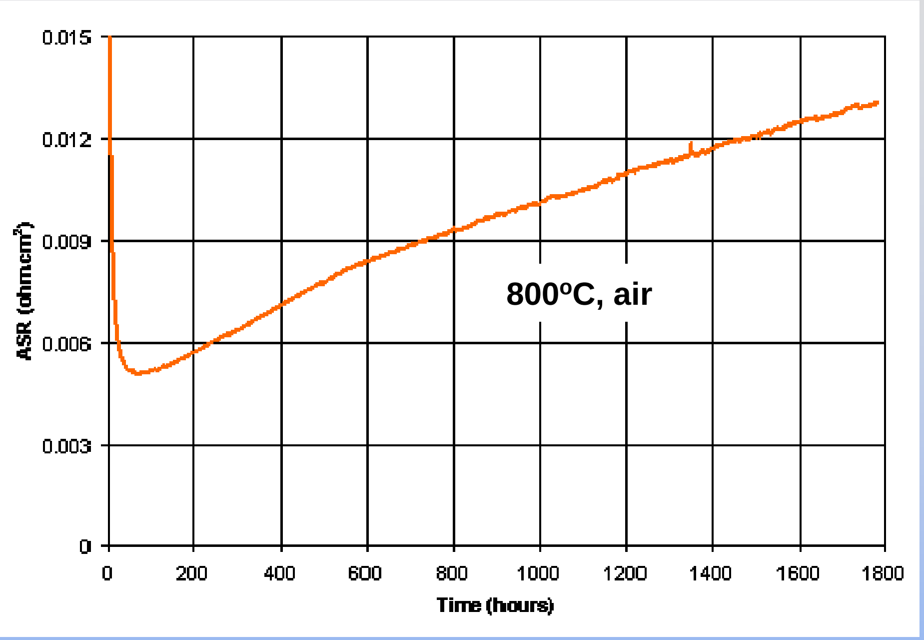
Focus Areas & Progress

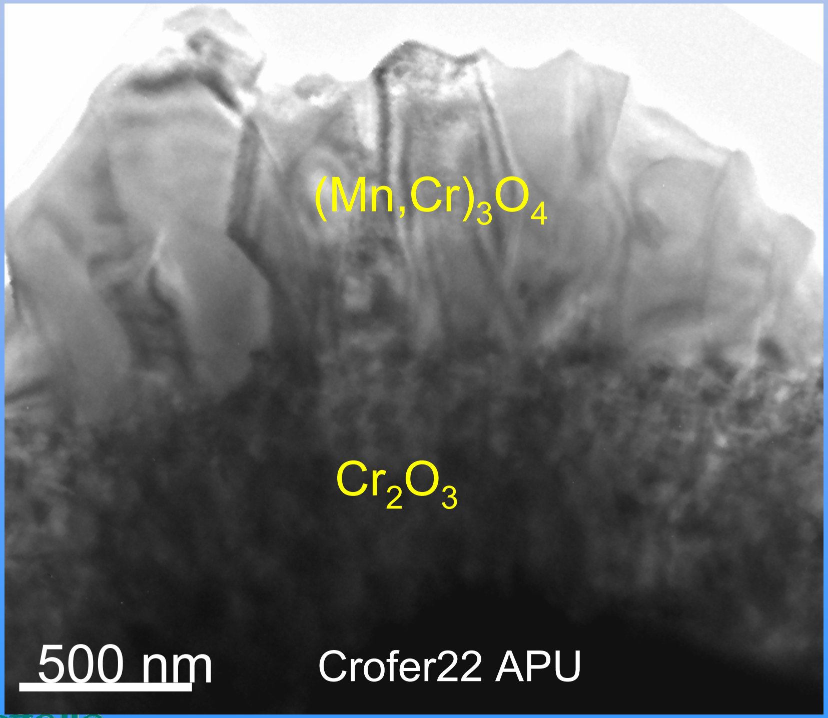
- Stainless steel interconnect with spinel protection layer
- Interactions and contact layer b/w cathode and interconnect
- Austenitic-base alloys, and laminated, composite interconnect structures
- Degradation of metallic interconnects under SOFC operating conditions

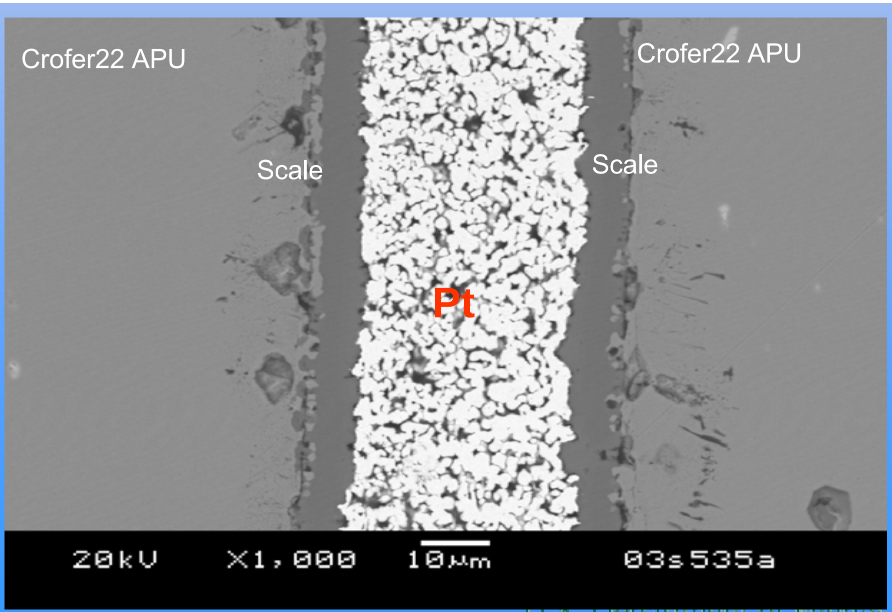
Protection Layer: The Need

Challenges and issues of newly developed alloys:

- Long term scale structural and electrical stability.





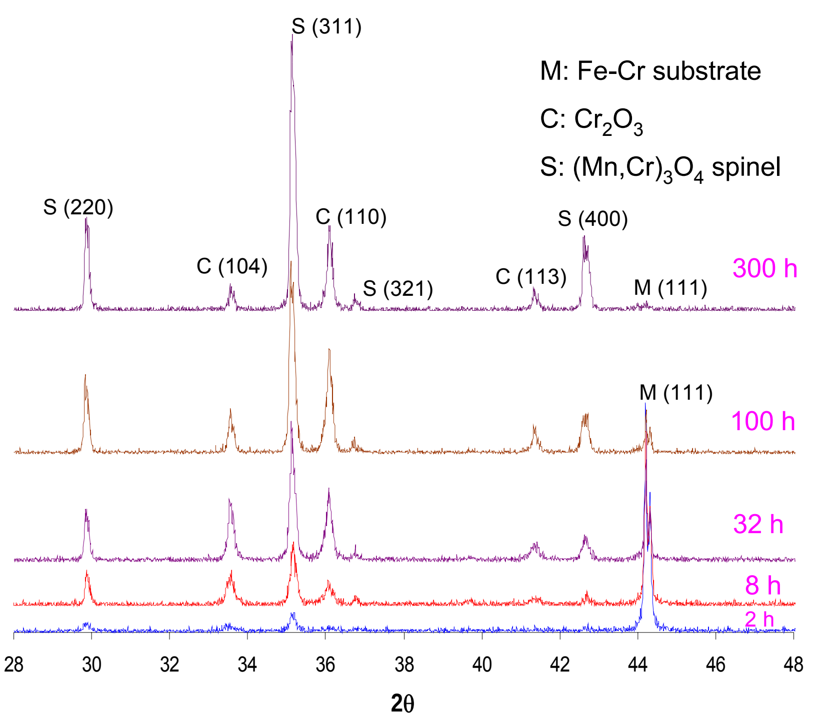


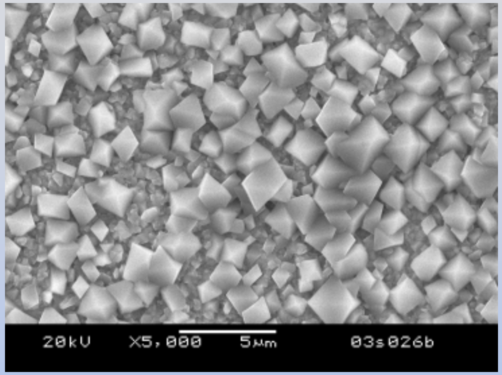
Protection Layer: The Need

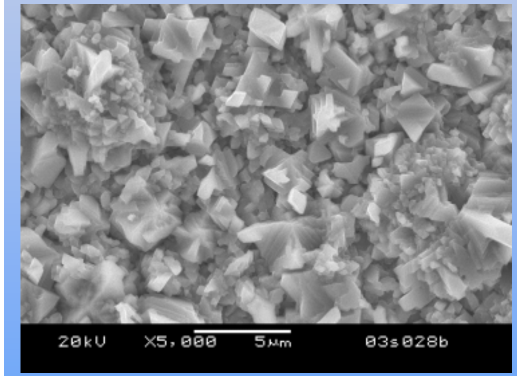
Challenges and issues of newly developed alloys:

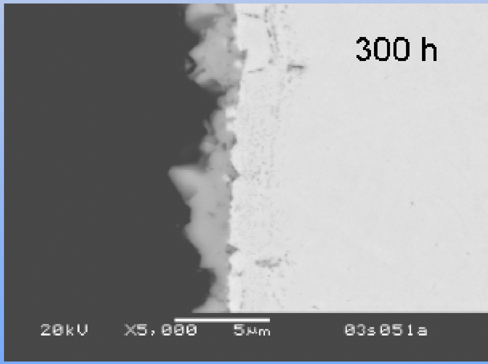
- Cr volatility

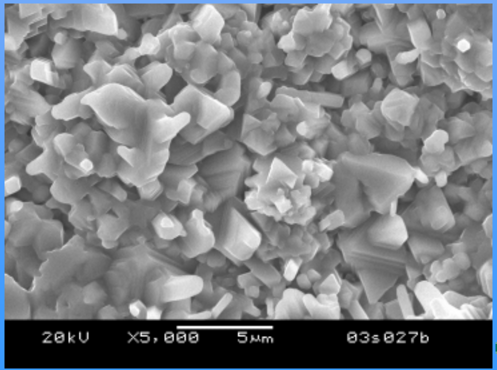
In-situ X-Ray Diffraction Analysis

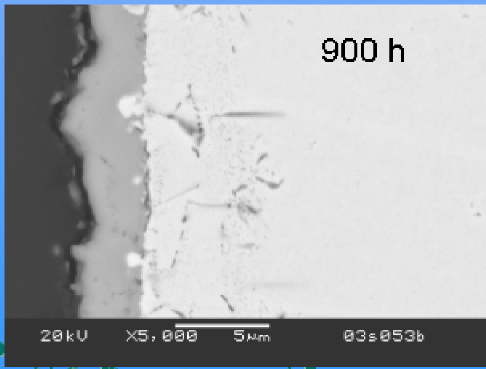












Why $(Mn,Co)_3O_4$ Spinel?

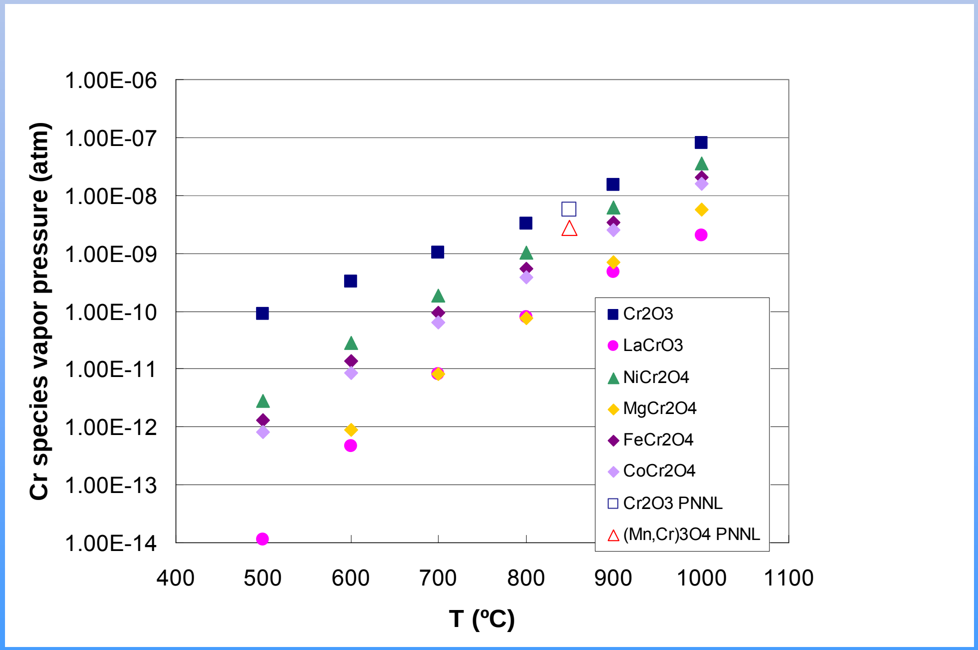
Non-Cr containing: Cr-containing oxides will release Cr

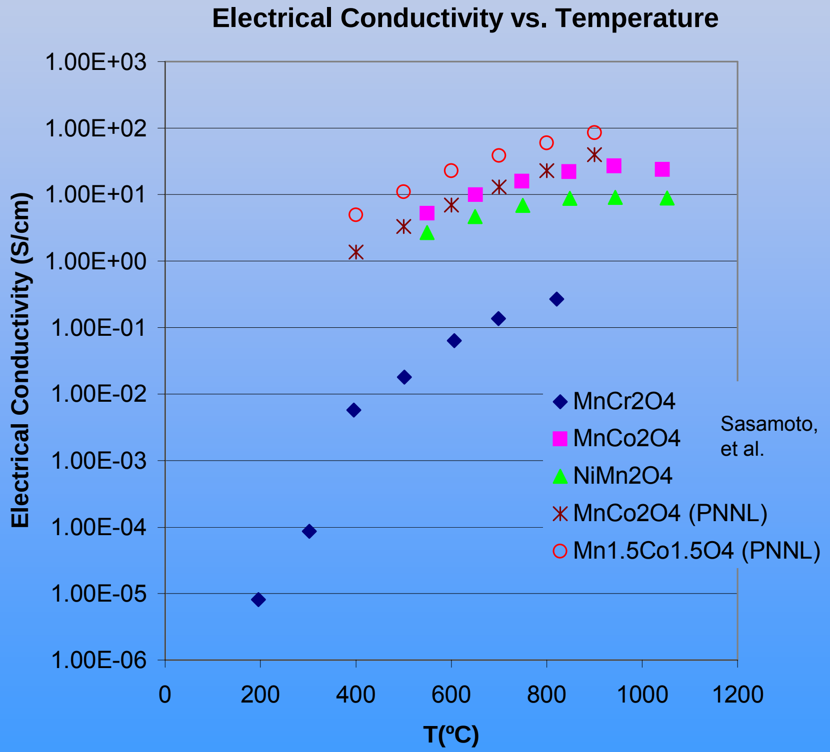
Electrical conductivity: $\sigma_{(Mn,Co)_3O_4} = 10^{3\sim4}\sigma_{Cr_2O_3} = 10^{2\sim3}\sigma_{MnCr_2O_4}$

Appropriate CTE: $CTE_{Mn_{1.5}Co_{1.5}O_4} = 11.5\times10^{-6}K^{-1}, 20-800^{o}C$

Flexibility of fabrication: THERMAL GROWTH

Cr volatility of chromium containing oxides



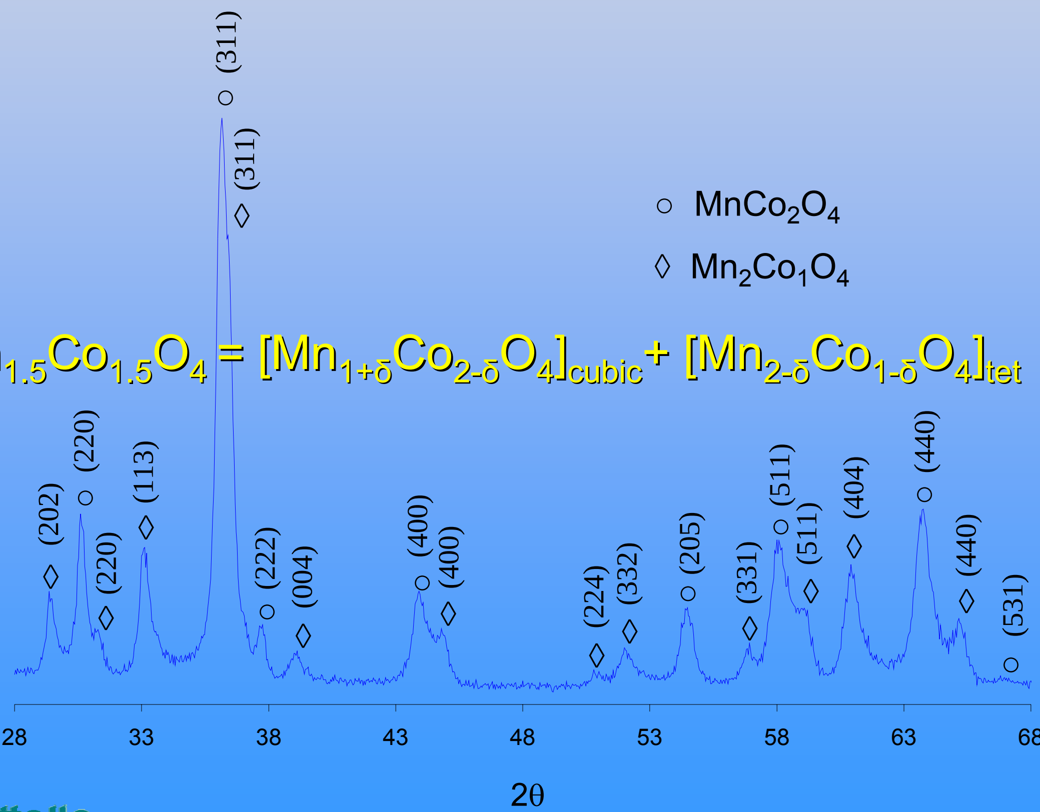


Thermal Growth of $Mn_{1.5}Co_{1.5}O_4$ Spinel Protection Layer

Why thermal growth?

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

$Mn_{1.5}Co_{1.5}O_4 = [Mn_{1+\delta}Co_{2-\delta}O_4]_{cubic} + [Mn_{2-\delta}Co_{1-\delta}O_4]_{tet}$



Approach

Synthesis of $Mn_{1.5}Co_{1.5}O_4$: SS or GNP

↓

Preparation of paste and screen-printing

↓

Heat-treated in reducing environments

↓

Oxidation and reaction-sintering in oxidizing environments

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

Reduction

In H_2/Ar+3% H_2O

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

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

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

Oxidation and reaction sintering

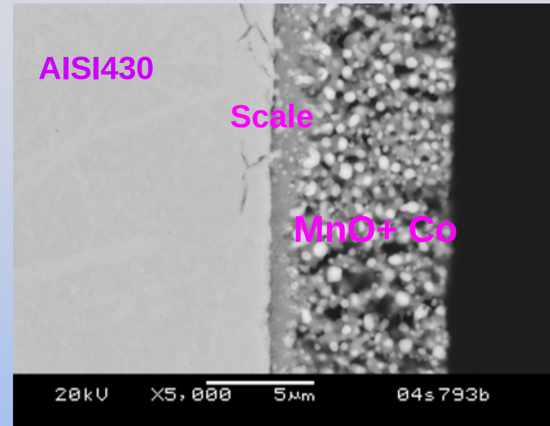
Air+3% H_2O

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

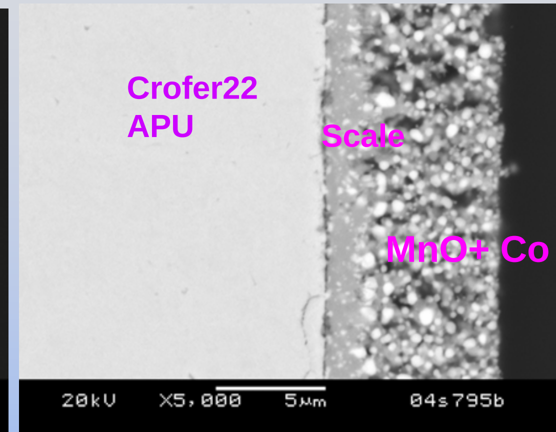
$$2Co + 4MnO + 2O_2 \uparrow \Rightarrow 2[Mn_2CoO_4]_{tet}$$

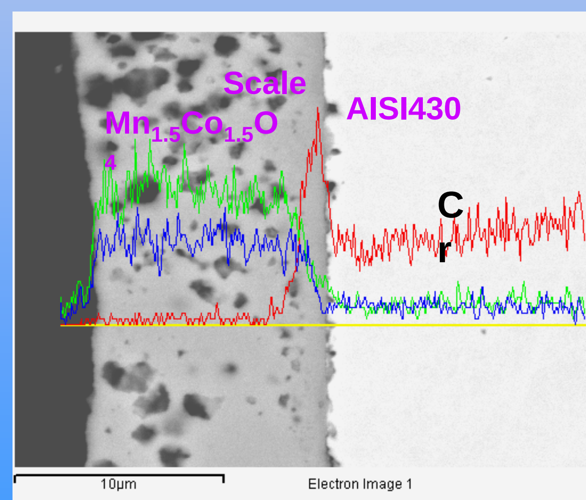
$$6Co + 6MnO + 5O_2 \uparrow \Rightarrow 4Mn_{1.5}Co_{1.5}O_4$$

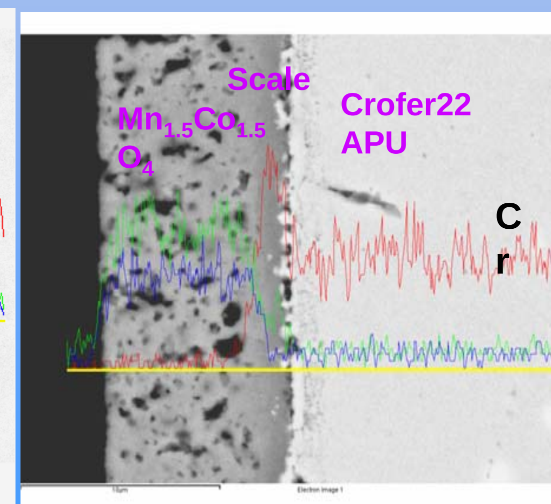
AISI430



Crofer22APU

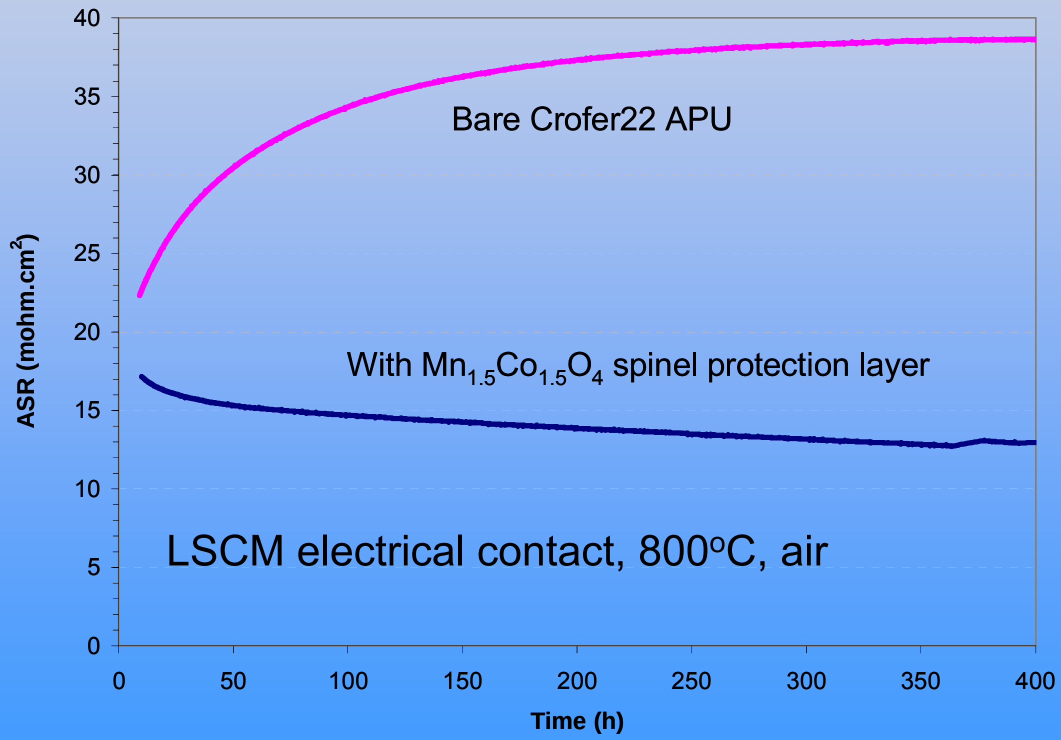


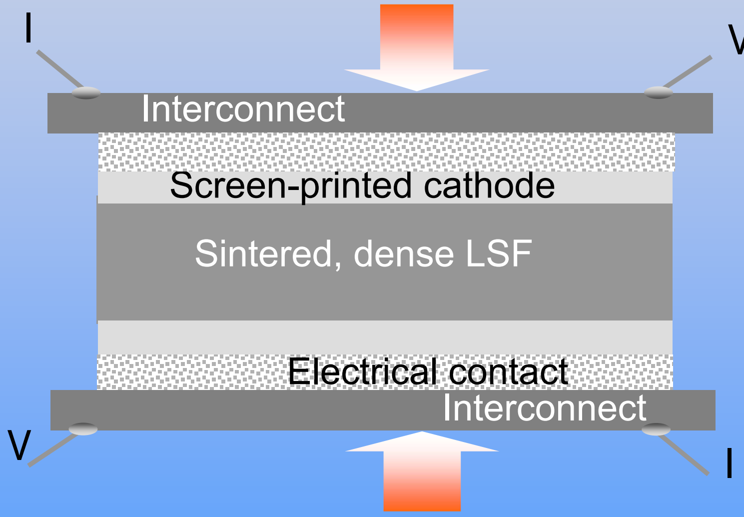




Contact ASR of Crofer22 APU: With and without $(Mn,Co)_3O_4$ Protection Layer

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





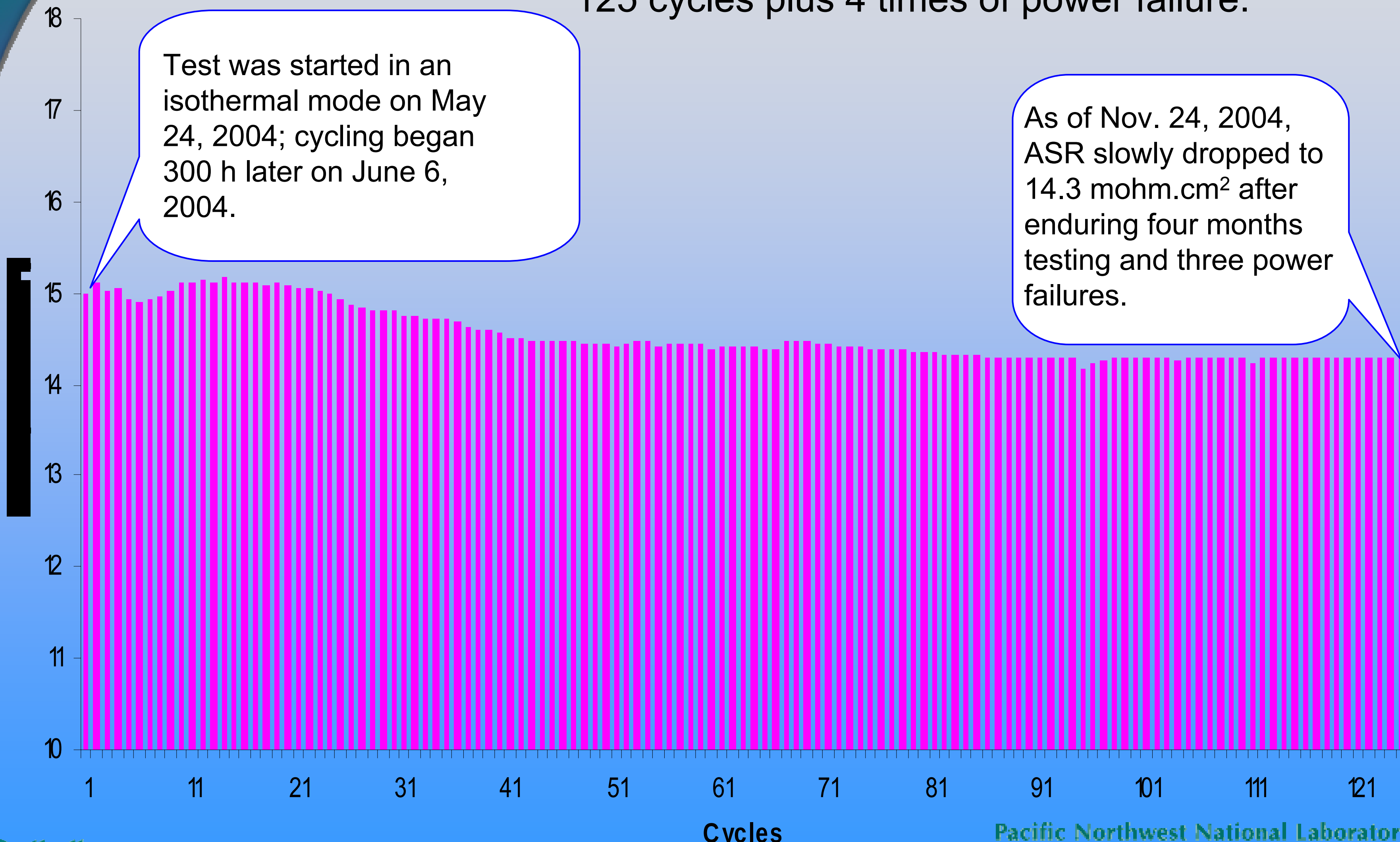
6.5 PSI Load

$500 mA.cm^{-2}$

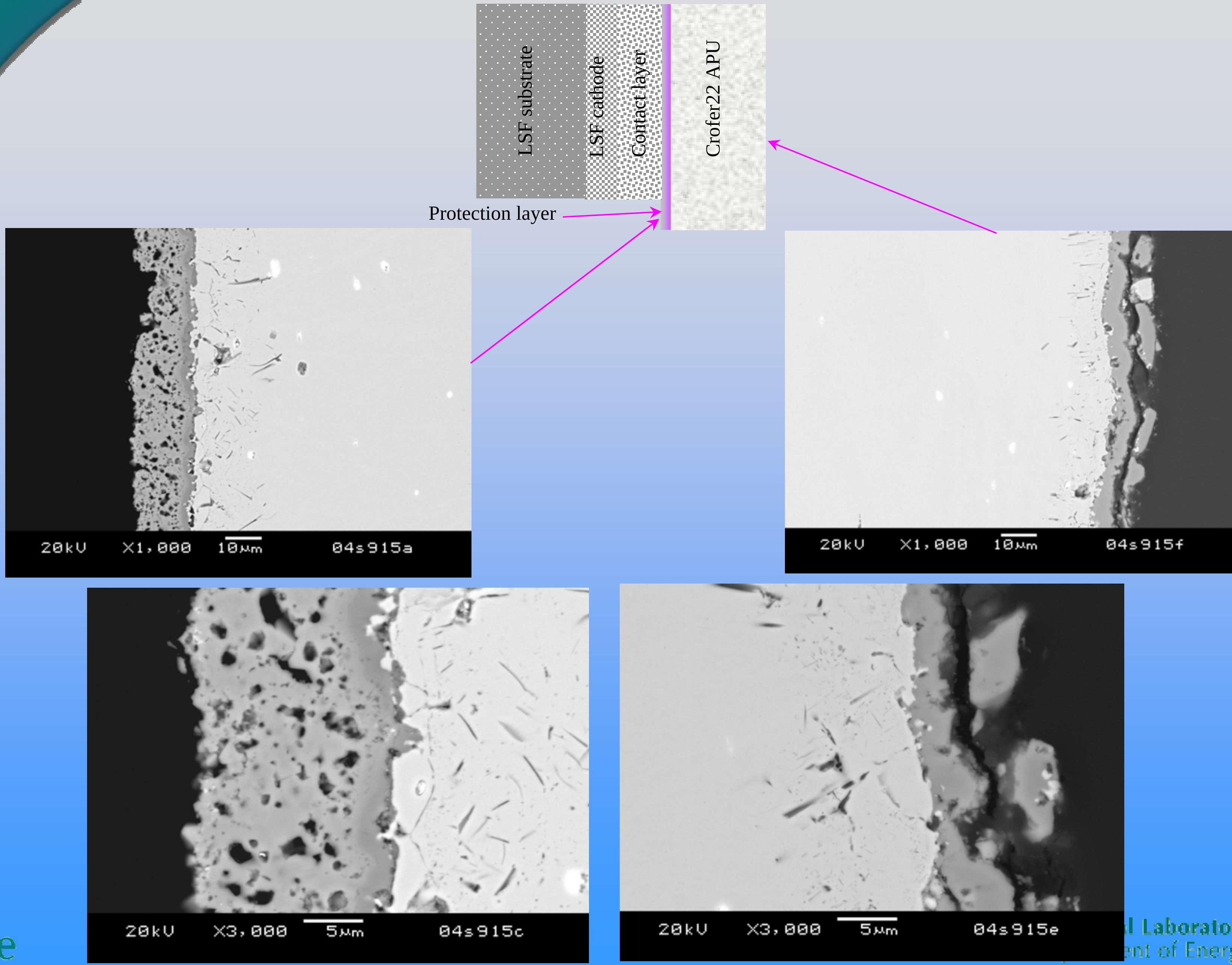
Six Month Thermal Cycling Test

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

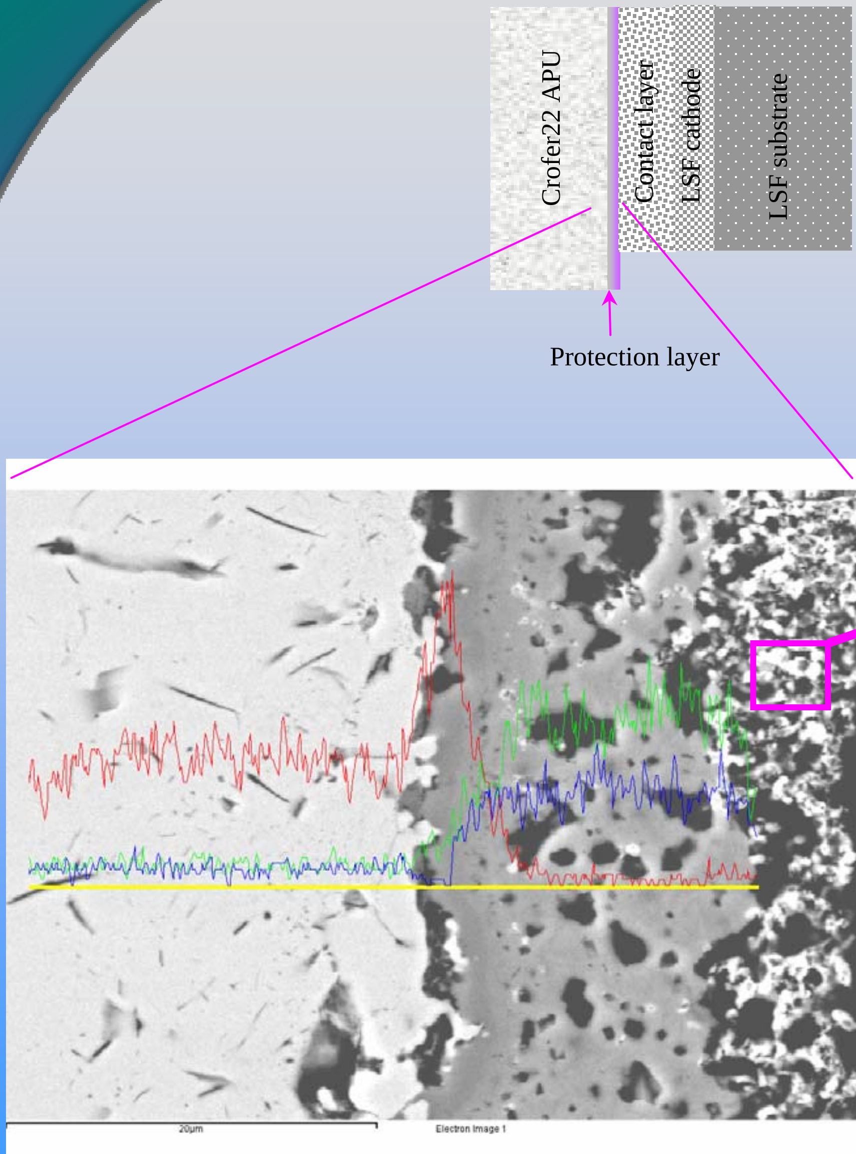
125 cycles plus 4 times of power failure.



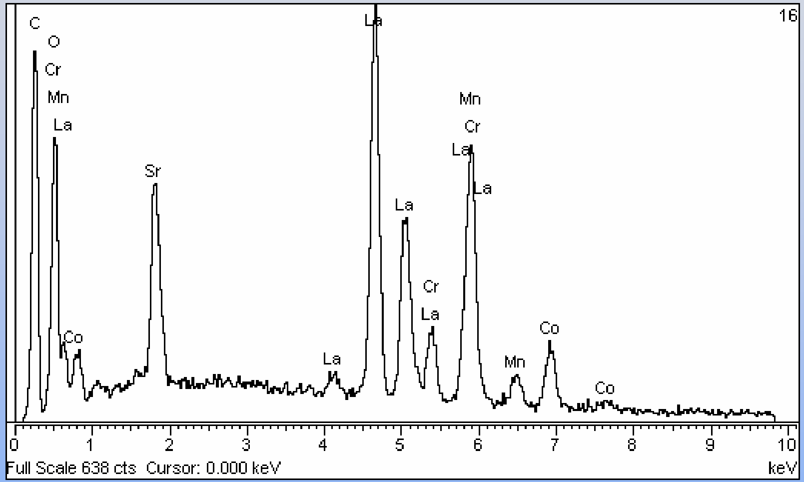
Improved Surface Stability



Effective Cr-Barrier



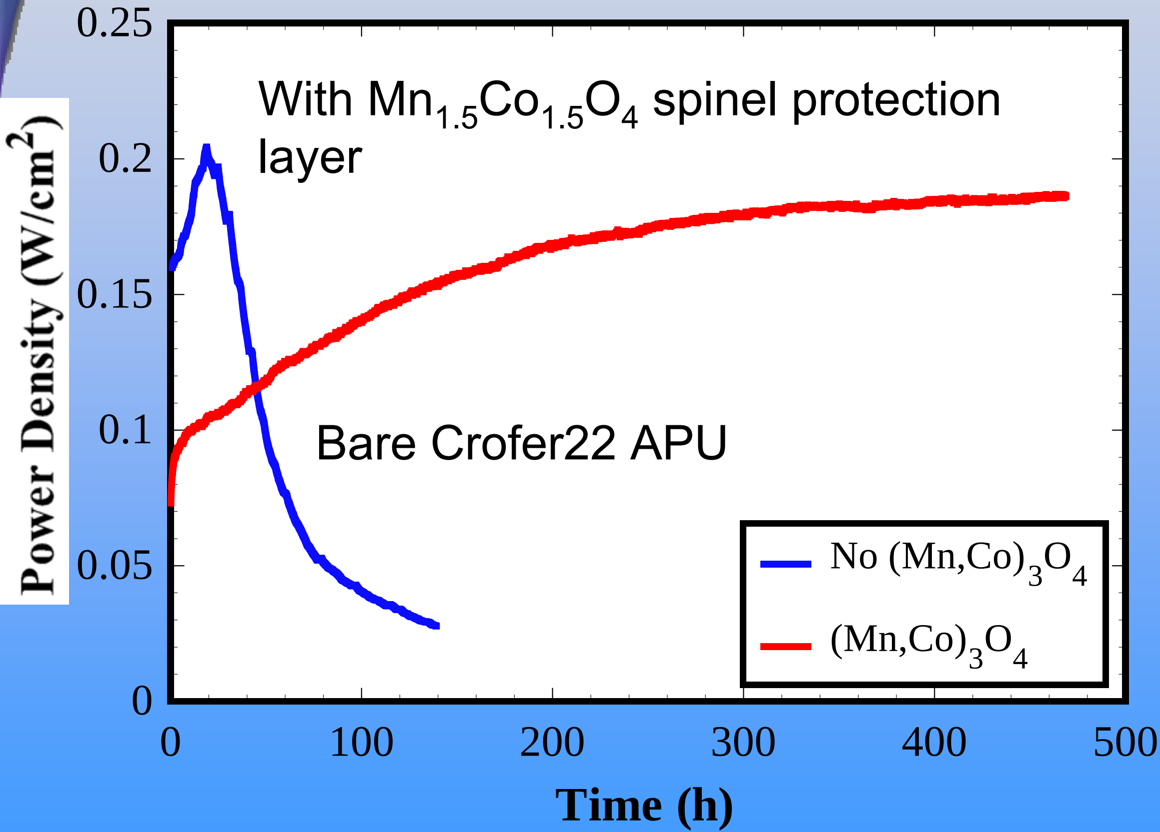
No Cr migration across the spinel protection layer after six months of heating and cycling.

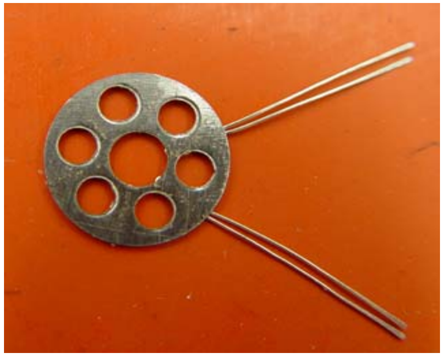


Element	App Conc.	Intensity Corrn.	Weight%	Weight% Sigma	Atomic%
O K	11.20	1.1185	16.01	0.63	51.91
Cr K	0.00	1.0284	0.00	0.00	0.00
Mn K	10.78	0.9163	18.79	0.46	17.74
Co K	3.77	0.9180	6.56	0.36	5.77
Sr L	4.64	0.6073	12.20	0.56	7.23
La L	29.51	1.0148	46.45	0.68	17.35

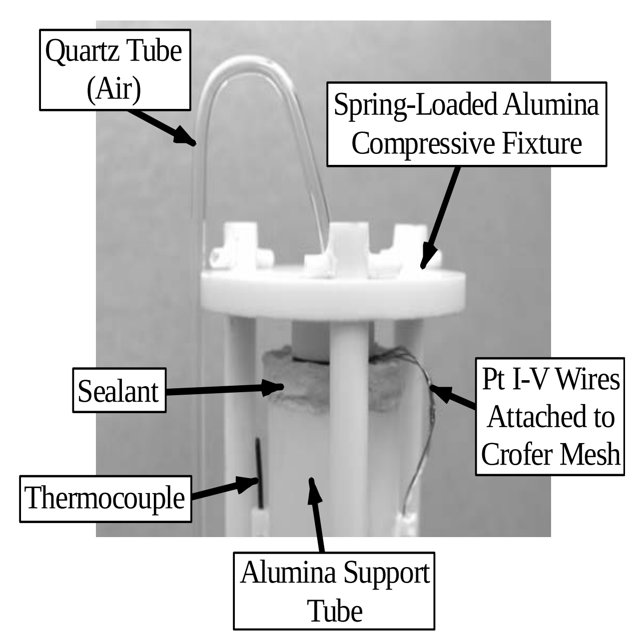
Electrochemical Investigation

Cell: LSM cathode, YSZ electrolyte, Ni/YSZ anode
Interconnect: Crofer22 APU with or without $Mn_{1.5}Co_{1.5}O_4$ protection layer
Contact: LSM
Temperature: 750°C





Crofer22 APU current collector for compressive button cell tests (~20mm diameter)



No Cr migration was observed on the cross-section.

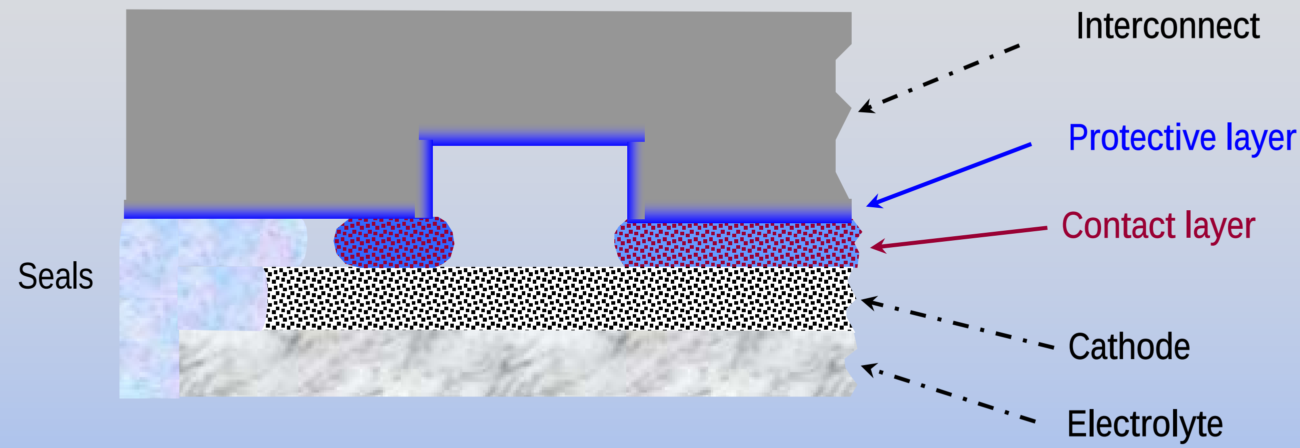
Summary

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

Focus Areas & Progress

- Stainless steel interconnect with spinel protection layer
- Interactions and contact layer b/w cathode and interconnect
- Austenitic-base alloys, and laminated, composite interconnect structures
- 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

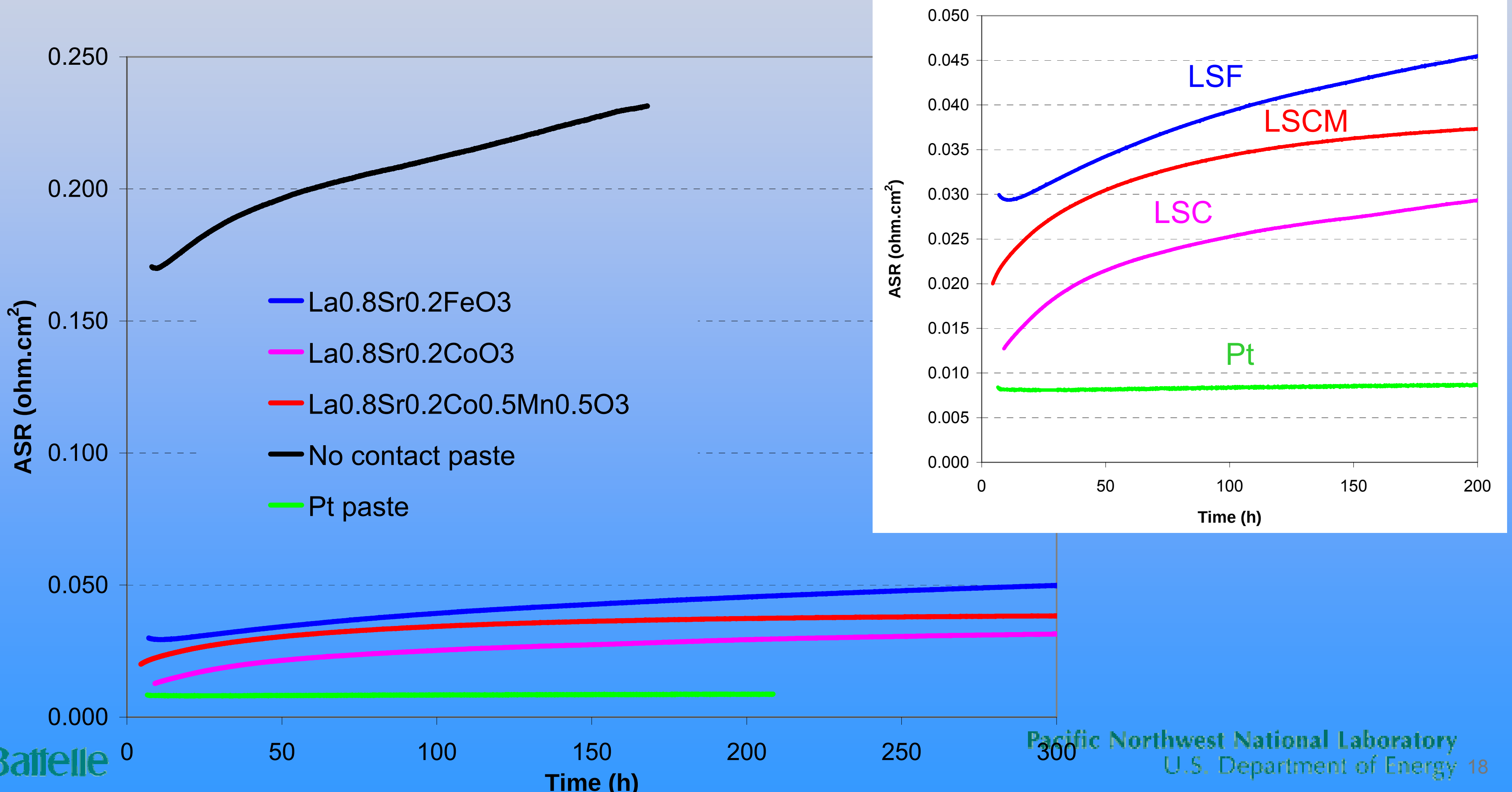
Materials requirements

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

Contact Resistance

$$ASR_{contact} = \Phi(scale, contacts, reactions)$$

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

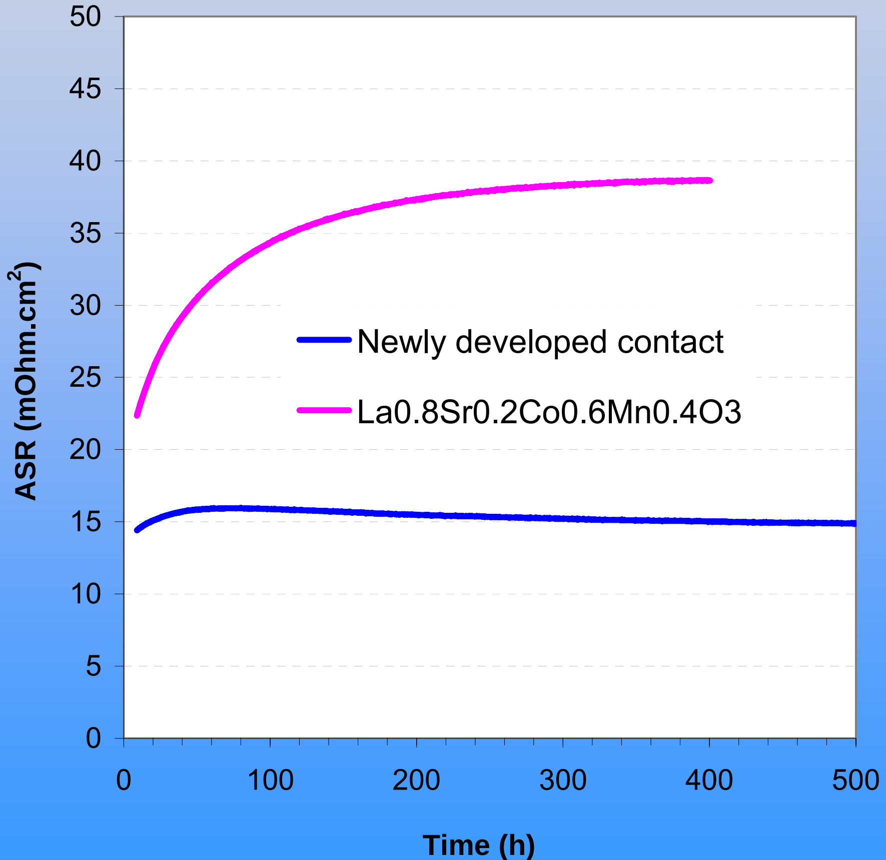


Performance of Newly Developed Contacts

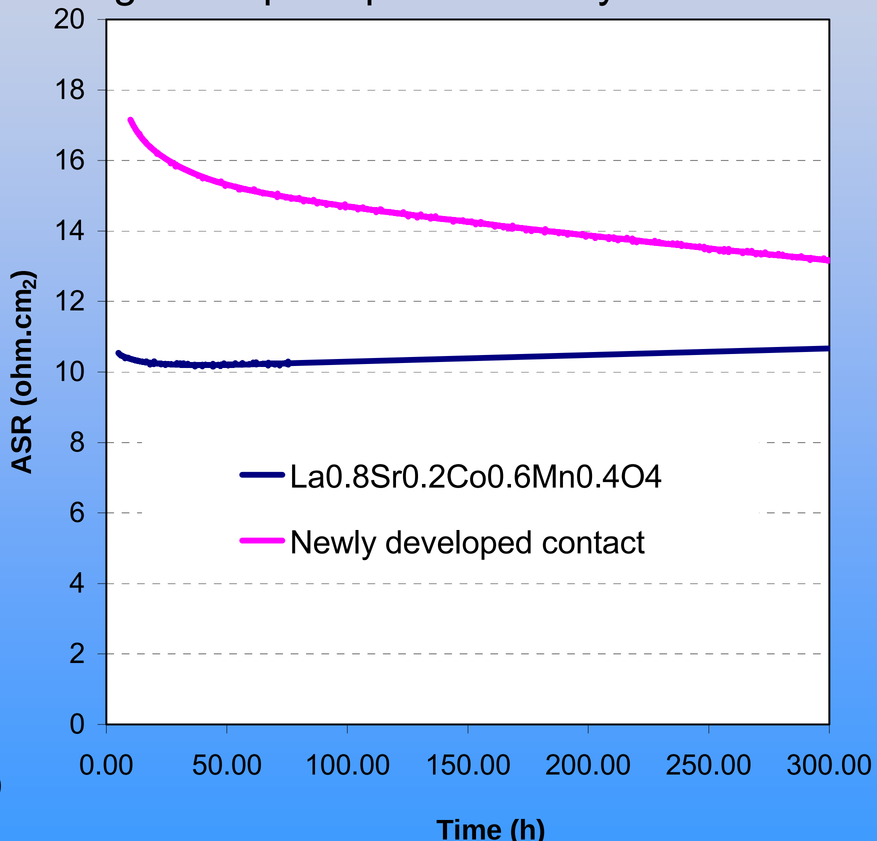
- **Combination of the spinel protection layer and a newly developed contact led to a significantly minimized contact ASR.**

IRU test: LSF cathode; Temperature: 800ºC

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 & Progress

- Stainless steel interconnect with spinel protection layer
- Interactions and contact layer b/w cathode and interconnect
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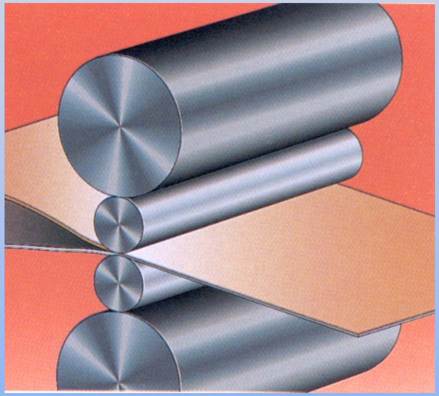
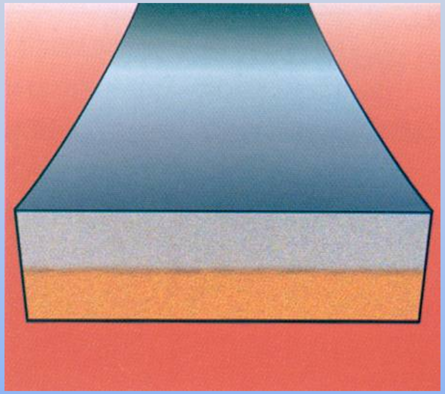
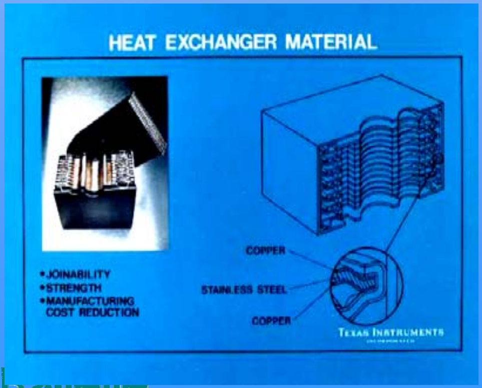
Laminated, Composite Interconnect Structures via Cladding

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





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

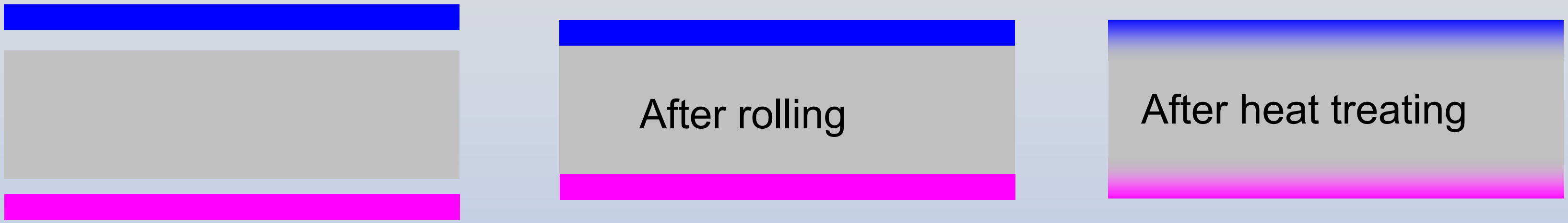


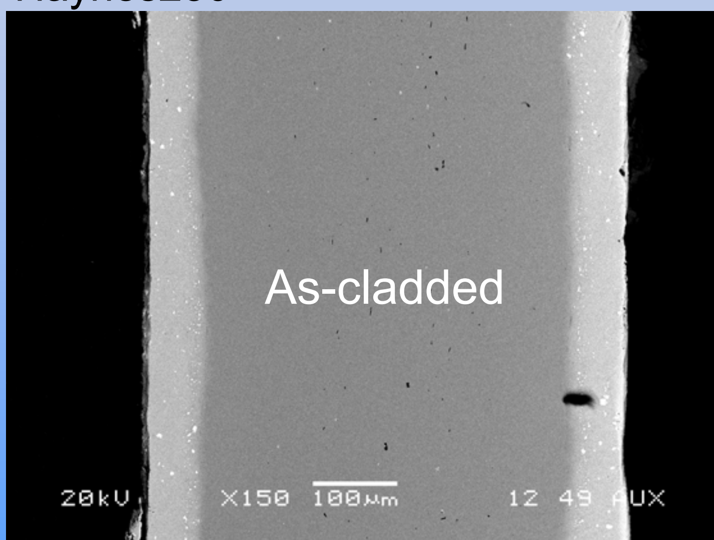
- **Clad Metal for interconnect applications**

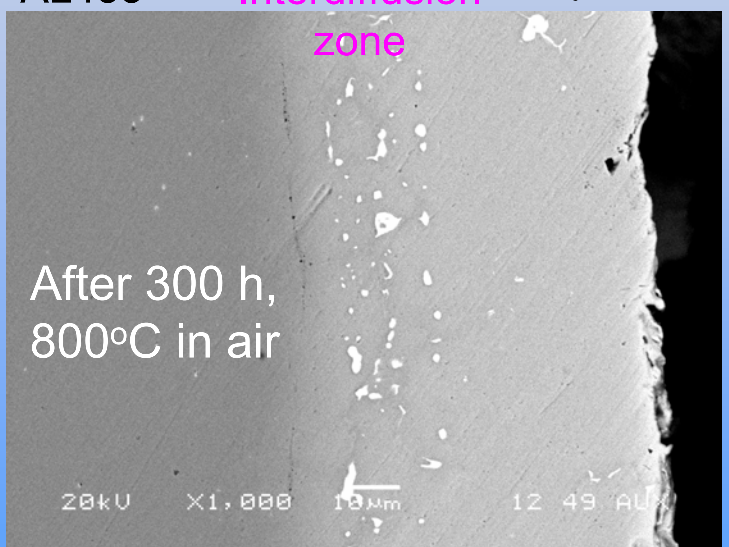
  - Integrate advantages of different alloys, while avoiding disadvantages.
    - ❖ Solve the issue of thermal expansion mismatch;
    - ❖ Optimize the interconnect mechanical and structural stability;
    - ❖ Make more cost-effective.
  - Allow to address cathode- and anode-side issues separately;
  -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

Collaboration with Leigh Chen, Engineered Materials Solutions Inc.

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



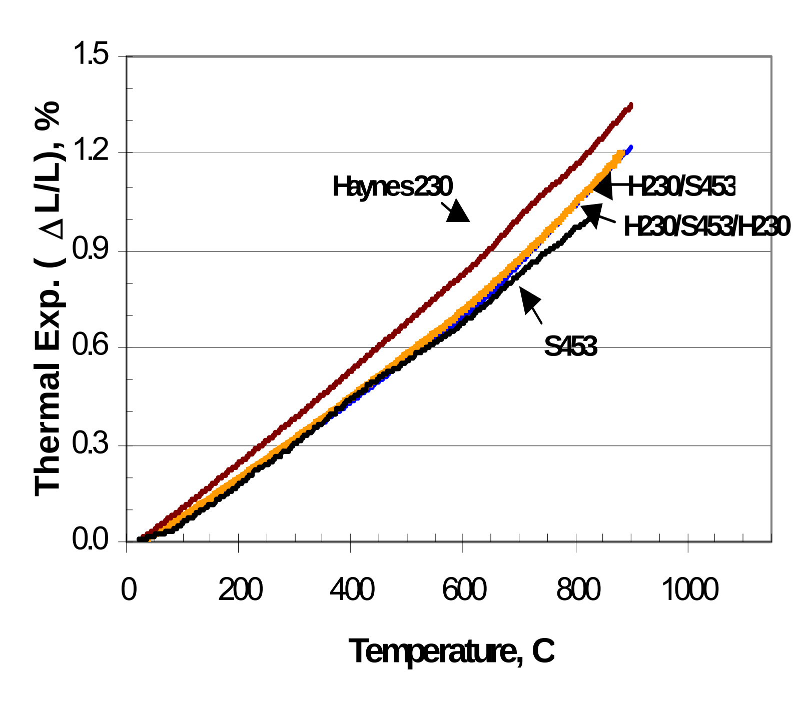




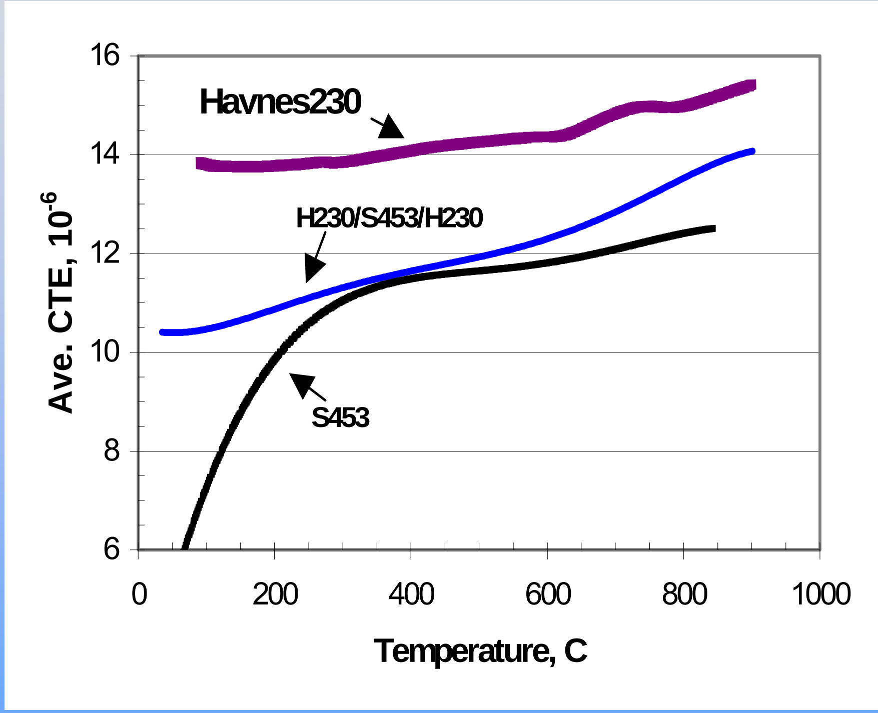
- The proof of concept work proved the viability of cladding FSS with Ni-based alloys and another piece of FSS;
- The cladded structures were stable during a subsequent heat treatment.

Thermal Expansion of Clad Metals

Thermal expansion of clad metals, compared to Haynes 230 and S453



CTE of the clad metal in comparison with that of Haynes230 and S453



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

CTE measured by EMS.

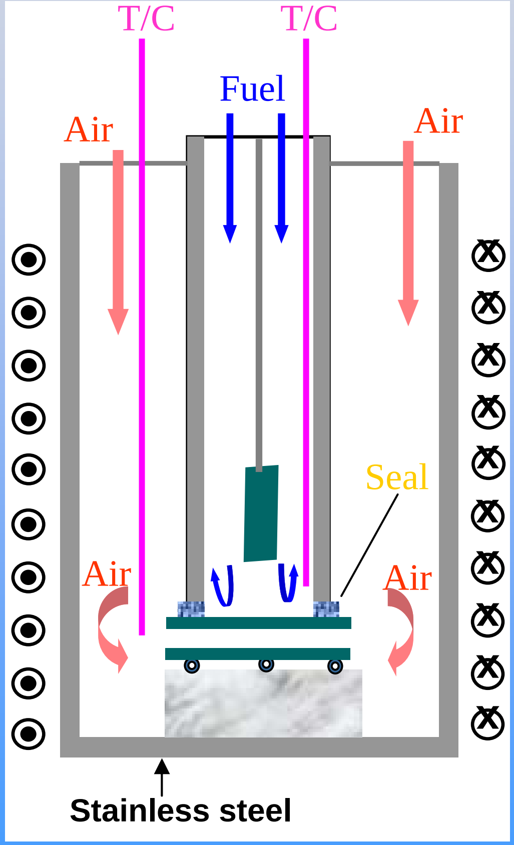
Summary

- The proof-of-concept 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 & Progress

- Stainless steel interconnect with spinel protection layer
- Interactions and contact layer b/w cathode and interconnect
- Laminated, composite interconnect structures
- Degradation of metallic interconnects under SOFC operating conditions

Oxidation Behavior of Alloys under Interconnect Dual Exposures



Motivation:

- **Dual exposures are commonly found in SOFC stacks and BOP, as well as other systems.**
- **Oxidation study has been a common area of interest, but typically 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

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

Variables:

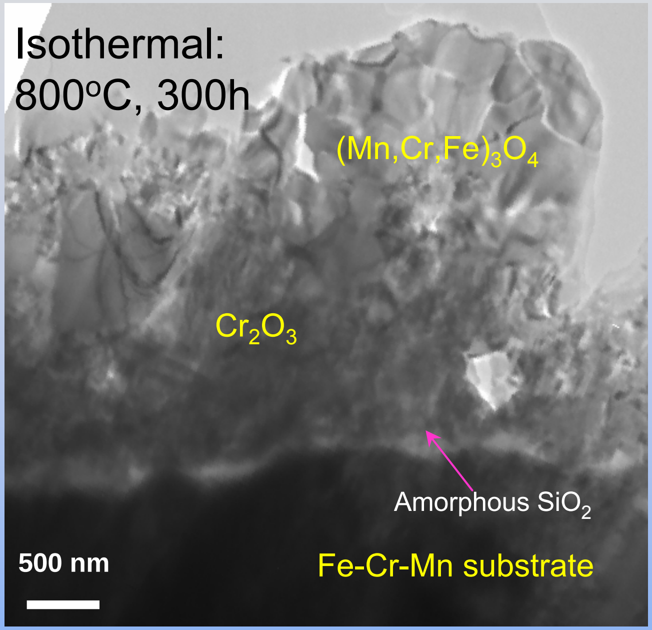
- Alloy composition
- Isothermal vs. cycling
- Hydrogen & Reformates

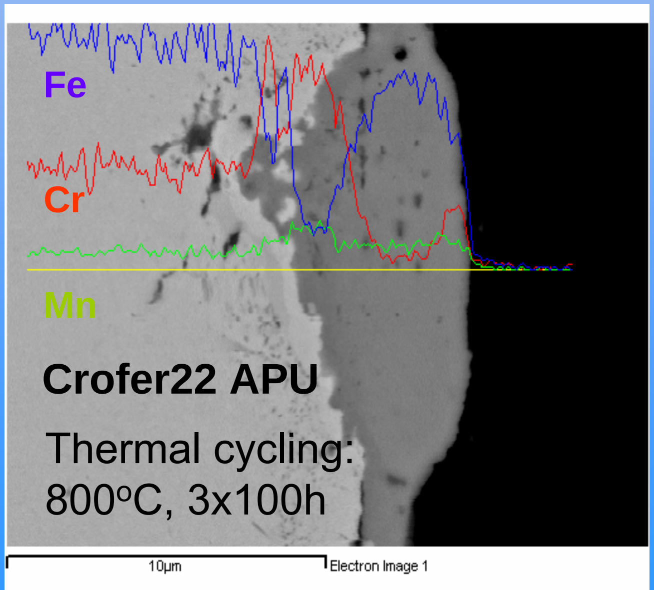
Anomalous Oxidation of FSS under Dual Exposures: A Summary

Under DUAL exposures, FSS demonstrate anomalous oxidation behavior, which can lead to a localized attack by formation of hematite nodules.

The anomalous oxidation of FSS is a function of alloy composition, thermal history and surrounding environment, e.g. water vapor level:

- For **ferritic stainless steels** with >22% Cr, dual exposure enhances the iron transport in scale on the airside, potentially leading to hematite formation and localized attack.
- No localized attack was observed in E-brite (27%Cr).
- The presence of moisture, thermal cycling, and higher temperatures further accelerate the anomalous oxidation.





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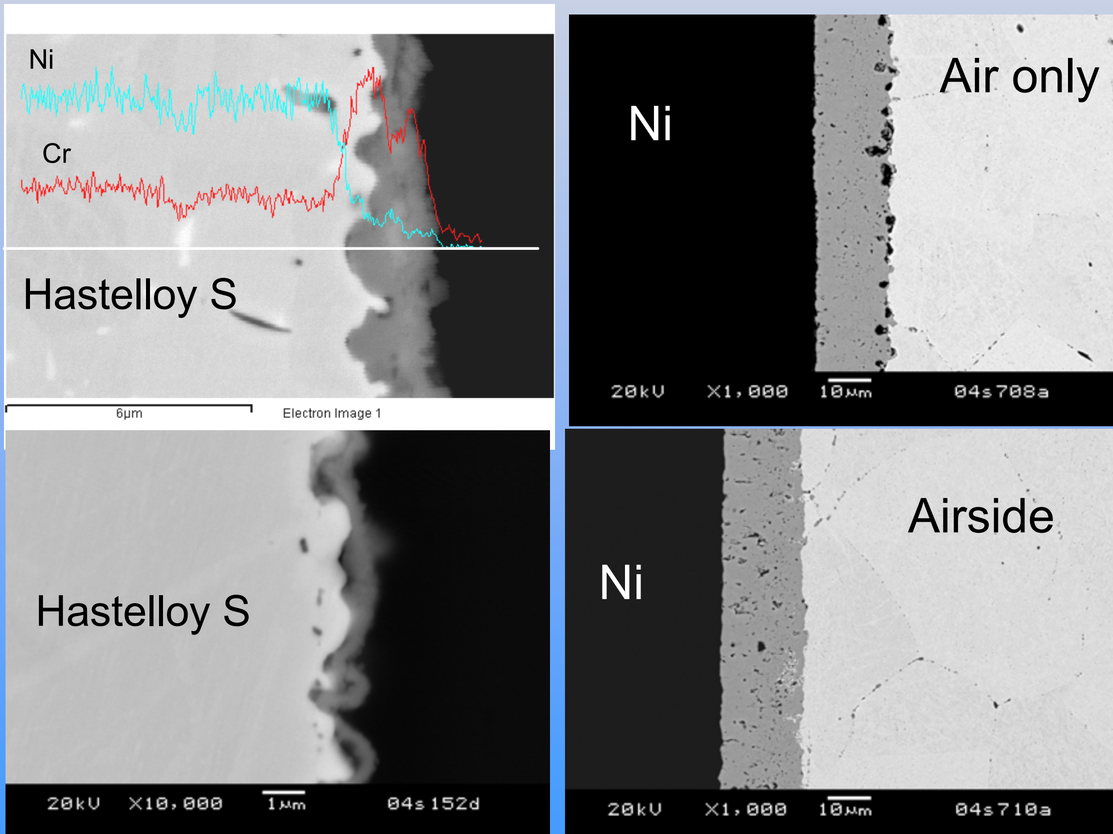
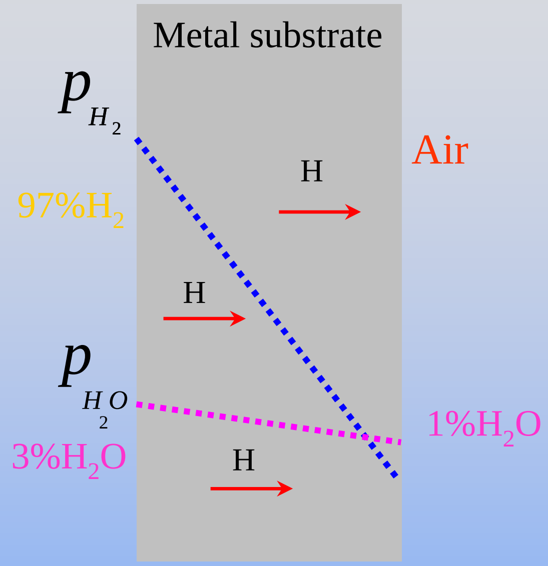
Oxidation Behavior of Ni and Ni-Based Alloys under Dual Exposures: A Summary

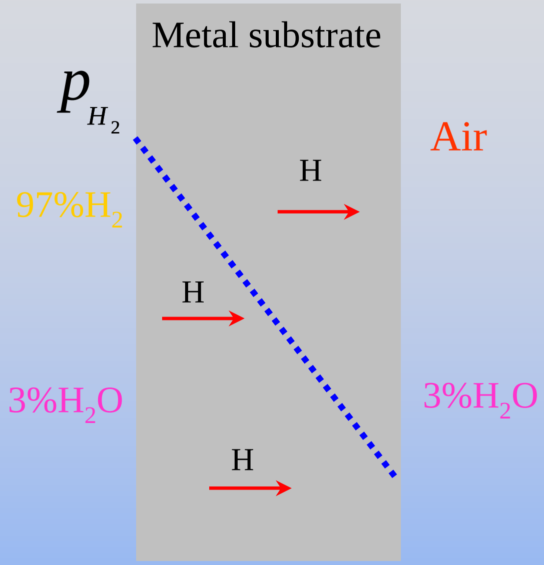
Under dual exposures, Ni-base alloys also demonstrate anomalous oxidation behavior, which however does not lead to a localized attack as observed in FSS.



- For Ni-based alloys; dual exposure tends to reduce NiO formation, and to facilitate the formation of a uniform chromia/spinel dominated scale.
- For pure Ni, dual exposures help eliminated porosity along scale/metal interface, while increasing NiO scale growth rate.

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.
- However, it is sill not clear how the hydrogen/proton interacts with scale oxides and affects the scale composition, structure and its properties.

Future Work:

Investigate and develop cathode-side functional interfaces

- Spinel protection layers: Explore different approaches and optimize processing and materials for further improved stability and performance.
- Electrical contact layers: Continue to study the interactions between conductive oxides and candidate alloys; investigate the interfacial ASR and develop contact composition for a minimized interfacial resistance.

Develop and investigate composite-structure interconnects

- Design alloys and engineering surface scale.
- Optimize structure and compositions.
- Study interdiffusion and predict life via modeling.

Study oxidation behavior 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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