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

Oxidation resistant alloys:

\[
\begin{align*}
\text{Alumina–forming alloys} & \quad \text{Chromia-forming alloys} \\
\text{Fe-Ni-base superalloys} & \\
\text{Face-centered-cubic (FCC)} & \quad \text{Body-centered-cubic (BCC)} \\
& \quad \text{e.g. austenitic Fe-Cr, Ni-Cr-base alloys}
\end{align*}
\]

- 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)$_3$O$_4$ 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.

Extrapolation of the 2,000 h test gives an ASR about 200 mΩ.cm² after 40,000 h.

After 6 months, 100 cycles, 800°C:


Protection Layer: The Need

To mitigate or prevent Cr migration and potential poisoning.

Crofer22 APU, 800°C, in air

In-situ X-Ray Diffraction Analysis

M: Fe-Cr substrate
C: Cr₂O₃
S: (Mn,Cr)₃O₄ spinel


Development of (Mn,Co)₃O₄ Spinel Protection Layer

Why (Mn,Co)₃O₄ spinel?
- Electrical conductivity:
  \[ \sigma_{(Mn,Co)₃O₄} = 10^{3-4} \sigma_{Cr₂O₃} = 10^{2-3} \sigma_{MnCr₂O₄} \]
- Appropriate CTE:
  \[ CTE_{Mn₃Co₃O₄} = 11.5 \times 10^{-6} K^{-1}, 20 – 800^\circ C \]
- 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.

Approach

Preparation of (Mn,Co)₃O₄:
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$_2$O, 800°C, 24h

\[
[MnCO_3O_4]_{cubic} + 3H_2 \uparrow \Rightarrow 2Co + MnO + 3H_2O \uparrow
\]

\[
[Mn_CoO_2]_{tet} + 2H_2 \uparrow \Rightarrow Co + 2MnO + 2H_2O \uparrow
\]

4Mn$_{1.5}$Co$_{1.5}$O$_4$ + 5H$_2$ $\uparrow$ $\Rightarrow$ 6Co + 6MnO + 5H$_2$O $\uparrow$

**Oxidation**

Air+3% H$_2$O, 800°C, 100h

4Co + 2MnO + 3O$_2$ $\uparrow$ $\Rightarrow$ 2[MnCO$_3$O$_4$]$_{cubic}$

2Co + 4MnO + 2O$_2$ $\uparrow$ $\Rightarrow$ 2[Mn$_2$Co$_3$O$_4$]$_{tet}$

6Co + 6MnO + 5O$_2$ $\uparrow$ $\Rightarrow$ 4Mn$_{1.5}$Co$_{1.5}$O$_4$
Contact ASR w & w/o Protection Layers

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

- **Crofer22 APU without spinel protection layer**
- **AISI430 with spinel protection layer**
- **Crofer22 APU with spinel protection layer**

**Graph:**
- Time (h) vs. ASR (mohm.cm²)

**Diagram:**
- Interconnect
- Screen-printed cathode
- Sintered, dense LSF
- Electrical contact
- Interconnect

- **6.5 PSI Load**
- **500mA.cm⁻²**
- **LSCM electrical contact, 800°C, air**

Pacific Northwest National Laboratory
U.S. Department of Energy
Six Month Thermal Cycling Test

IRU test: 800°C, air, cycling from 80-800°C, 125 cycles plus 4 times of power failure.

Test was started in an isothermal mode on May 24, 2004; cycling began 300 h later on June 6, 2004.

As of Nov. 24, 2004, ASR slowly dropped to 14.3 mohm.cm² after enduring four months testing and three power failures.
Improved Surface Stability

Crofer22 APU
Contact layer
LSF substrate
LSF cathode
Protection layer

[Images of microscopic sections showing layers and schematics of the Crofer22 APU structure.]
Effective Cr-Barrier

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

Summary

- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel protection layers can be thermally grown on ferritic stainless steel interconnects.

- The thermally grown $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ 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

#### Chemical Composition

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<td>W</td>
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*Alloys were made at Haynes International Inc.*
Scale structure similar to Crofer, i.e. $(\text{Mn,Cr})_3\text{O}_4 + \text{Cr}_2\text{O}_3$; Mn addition increased scale growth, but still better than Crofer; Superior oxidation resistance under dual environments.
Properties of M Alloys

- (Mn, Cr)\textsubscript{3}O\textsubscript{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

- After rolling
- After heat treating

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

\[
ASR_{contact} = \Phi \left( \begin{array}{l}
Scale: \text{conductivity, growth-rate;}
\text{contact: area, conductivity;}
\text{reactions: scale | contact | electrodes}
\end{array} \right)
\]

- SrCrO₄ can be formed via both solid-solid and solid–gas reactions.
- LSM and LSCM facilitate (Mn,Cr)₃O₄ 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

![Graphs showing ASR (ohm.cm²) over time for different conditions.](image-url)
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

Anomalous Oxidation of Alloys under Dual Exposures: A Summary

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.
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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