Advanced Interconnect and Interconnect/Electrode Interfaces Development at PNNL


Pacific Northwest National Laboratory
Richland, WA 99352

8th Annual SECA Workshop and Peer Review
San Antonio, TX, August 6-9, 2007
Objectives and Approach

♦ Objectives
  • Develop cost-effective, optimized materials and fabrication approaches for SOFC interconnect and interconnect/electrode interface (i.e. contacts) applications
  • Identify and understand degradation processes in interconnects and interconnect/electrode interfaces

♦ Approach
  • Materials and process development
    ■ Cost-effective oxidation resistant alloys
    ■ Surface modification via coatings
    ■ Interconnect/electrode contact materials
  • Materials evaluation and degradation study
    ■ Screening study of alloys and ceramics for interconnect and interface applications, respectively
    ■ Investigation and understanding of oxidation/corrosion and interfacial reactions and stability under SOFC operating conditions.
Accomplishments in FY07

- Investigation and development of cost-effective ferritic stainless steels (In collaboration with Allegheny Ludlum Corp.)
  - Systematically investigated 430
  - Identified and evaluated 439 and 441, two modified versions of 430
  - Applied protection layers onto candidate alloys and evaluated their performance

- Development of protection layers and fabrication approaches
  - Completed long-term thermal stability and electrical performance evaluation
  - Initiated optimization of materials and fabrication for further cost-reduction

- Investigation and development of contact layers between metallic interconnects and electrodes
  - Screening-studied more than a dozen materials systems via different fabrication approaches
  - Identified two promising material groups and three approaches
  - Evaluated electrical performance of selected candidates
Investigation and Development of Novel Interconnect Alloys

**Goal**: Identify/develop a novel ferritic stainless steel (FSS) with an optimized alloy chemistry that offers comparable or improved performance relative to the state-of-the-art compositions such as Crofer 22 APU, while being more cost-effective.

**Approach**: To achieve the desired alloy chemistry or control residual alloy elements of Si, C, N, etc., via alloying, instead of extra refining that adds cost.

**Accomplishments**
- Investigated properties of 430 relevant to interconnect applications
- Identified potential candidates 441 and 439, two modified versions of 430
- Evaluated their properties relative to interconnect requirements
- Surface-modified the potential candidates with spinel protection layers and investigated their stability and electrical performance
Oxidation Kinetics of Bare and Coated 430

**Why 430:** cost reduction

- 430: 17% Cr, via conventional melting – more cost-effective
- Crofer 22 APU: 23%Cr, extra refining (e.g. vacuum refining) for cleaning residual elements, Si, C, N, etc.

- Bare 430 demonstrated a fairly low scale growth rate at early stages
- Leveling off of the weight gain indicated likely spallation
- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ (MC) spinel protection layers drastically mitigated the scale growth beneath the coating
Surface Stability of 430

- Unlike bare 430, no spallation observed on MC 430
- Fe transported through the coating, BUT not Cr
- No solubility of SiO₂ in Cr₂O₃
- Formation of continuous, insulating SiO₂ layer b/w scale and Fe-Cr substrate

Bare 430

1,200 hrs, air, 800°C

MC coated 430
Long-Term Performance of MC Coated 430

- The formation of a continuous insulating SiO$_2$ layer at the scale/metal interface led to a high ASR.
- The ASR became unstable after about 4,000 hours, likely due to detachment of scale from the metal substrate.

Area specific resistance (ASR) measurement:
IC/contact/cathode/LSM pellet/cathode/contact/IC
800°C, air

Cathode: La$_{0.8}$Sr$_{0.2}$MnO$_3$
IC: Mn$_{1.5}$Co$_{1.5}$O$_4$ coated 430
Contact: La$_{0.8}$Sr$_{0.2}$Co$_{0.5}$Mn$_{0.5}$O$_4$
Metallurgy of 441 and 439

<table>
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<tr>
<th>Designation</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>C</th>
<th>Al</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>Nb</th>
<th>Re</th>
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<tbody>
<tr>
<td>T-441</td>
<td>17.8</td>
<td>0.33</td>
<td>0.20</td>
<td>0.010</td>
<td>0.045</td>
<td>0.47</td>
<td>0.024</td>
<td>0.001</td>
<td>0.18</td>
<td>0.46</td>
<td></td>
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<tr>
<td>439 HP</td>
<td>17.5</td>
<td>0.44</td>
<td>0.20</td>
<td>0.012</td>
<td>0.040</td>
<td>0.73</td>
<td>0.016</td>
<td>0.0004</td>
<td>0.41</td>
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</tr>
<tr>
<td>AL 430</td>
<td>17.0</td>
<td>≤1.0</td>
<td>≤0.75</td>
<td>≤0.12</td>
<td>≤1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Crofer 22 APU</td>
<td>23.0</td>
<td>0.4-0.8</td>
<td>0.030</td>
<td>≤0.50</td>
<td>≤0.50</td>
<td>0.020</td>
<td>0.050</td>
<td>≤0.2</td>
<td>0.04-0.20</td>
<td></td>
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</tbody>
</table>

- Fractional % of Ti and Ti/Nb were added into Fe-17%Cr substrate for 439 and 441, respectively.
- Nb leads to laves phase (Fe$_2$Nb) precipitation along grain boundaries that significantly improves high temperature strength and creep resistance of the Fe-Cr substrate (double yield strength at 800ºC).
- As strong carbide/nitride formation elements, Ti and Nd lower interstitial elements C and N in the substrate.
- Can Nb (or Ti) tie up Si to prevent SiO$_2$ layer?
Electrical Evaluation of 441 and 439

La$_{0.8}$Sr$_{0.2}$MnO$_3$ cathode and contact, air, 800°C

Chipping

Crofer 22 APU (LSCM contact)

439

500 mA.cm$^2$

441

Scale
Effects of Minor Alloying Elements in 441

- There was Si buildup or silica layer formation between scale/metal interface, in spite of about 0.5% residual Si in the metal substrate.
- Nb tied up Si, preventing formation SiO$_2$ layer at the scale/metal interface.
Scale Structure and Compositions of 441

- Scale grown on 441 is mainly comprised of (Mn,Cr)$_3$O$_4$ and Cr$_2$O$_3$, similar to that of Crofer 22 APU
- Negligible Fe or iron oxides in the scale, different from that of 430

300 hours, 800°C, air
Kinetics of Scale Growth on 441

- Scale growth rate comparable to Crofer 22 APU, but with inferior scale adherence
  (Local spallation found occasionally after extensive oxidation)
- 2–3 times lower for MC coated specimens; no spallation

After 900 hours
Electrical Performance of Surface-Modified 441

- $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ spinel protection layers minimized area specific electrical resistance (ASR)
- ASR of coated sample increased little, if any, over the course of the test

*Graph*

- Bare T-441
- T-441 with $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$ protection

Conditions:
- Cathode: LSM
- Contact: LSM
- IC: bare 441 or MC coated 441
- Current: 500 mA.cm$^{-2}$
- Temperature: 800$^\circ$C, air
SEM Cross-Sections of ASR Samples

- Improved surface stability: no spallation or detachment observed
- No penetration of Cr through the protection layer, though there appeared Fe migration into the coating (similar to 430).

MC coated 441

BS image
Summary

- 441 exhibited promising alloy chemistry: addition of a small amount of Nb helps avoid formation of a continuous silica layer and promote desirable second phase precipitation, thus leading to a lower scale resistance and higher mechanical strength.

- The alloying approach eliminates the costly refining process that is currently employed for making Crofer 22 APU and other super-grade ferritic stainless steels for IC applications.

- Protection layers are required to further improve alloy surface stability and electrical performance, and seal off Cr.

Future Work

- Evaluate long-term thermal stability and electrical performance of bare and surface modified 441

- Further understand the alloy chemistry via advanced diagnostic study

- Investigate and optimize bulk alloy chemistry and surface modification for satisfactory long-term stability and performance. (In collaboration with Allegheny Ludlum Corp.)
**Protection Layer Development and Investigation**

- **Goal**: develop cost-effective, optimized protection layers that are effective barriers to both oxygen inward and chromium outward diffusion, while being stable over lifetime of SOFC operation.

**Previous work:**
- Developed spinel protection layers with a nominal composition \( \text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4 \)
- Systematically studied \((\text{Mn,Co})_3\text{O}_4\) spinel materials
- Developed slurry-based approaches for fabrication of the spinel protection layers
- Evaluated kinetics of scale growth, stability under thermal cycling, electrical and electrochemical performance, chromia volatility, etc., of coated Crofer 22 APU
- Completed one year thermal stability evaluation of coated Crofer 22 APU

**Recent Accomplishments:**
- Completed half year electrical evaluation of MC coated Crofer 22 APU and 430 (with LSM cathode & contact paste)
- Investigated suitability and performance of the spinel protection layers on 430 and 441 (see previous slides)
- Started developing alternative fabrication approaches, e.g. electrochemical deposition
Summary and Future Work

- Spinel protection layers with a nominal composition Mn$_{1.5}$Co$_{1.5}$O$_4$ and fabricated with slurry coating approaches are an effective oxygen inward and chromium outward diffusion barrier, mitigating scale growth and sealing off chromium.

- Interconnect FSS, e.g. Crofer 22 APU, with the spinel protection layers demonstrated excellent long-term stability and electrical performance.

- Developing cost-effective approaches compatible with mass production and practical shapes of interconnect:
  - Electroplating, electrophoresis, etc., in addition to spray process.
Contact Layer Investigation and Development

**Goal:** develop cost-effective, optimized contact layers between metallic interconnects and electrodes.

- **Functions**
  - Promote electrical contact
  - Facilitate stack assembling
  - Act as a potential buffer zone to prevent unwanted reactions and transport, such as Cr volatility

- **Challenges**
  - A metallurgical bond can be built between a metallic interconnect and Ni-YSZ anode, providing a low resistance path for electrons.
  - Oxide-metal interfaces are present between metallic interconnects and cathodes, increasing electrical resistance and thus causing power loss.
Previous Work and Current Strategy

Previous work and accomplishments:

- Evaluated metals and varied conductive oxides, including LSM, LSCo, LSCM, MC, etc.
- Investigated interfacial interactions
- Initiated enhanced sintering approaches for LSM and MC

Challenges of current materials:

- Precious metals demonstrate suitable properties, but too expensive (Ag, a possible exception).
- Conductive oxides of high sintering activity, e.g. superconductors, usually too reactive, negatively affecting the stack and interface stability
- Conductive oxides, e.g. LSM, that are typically used as cathode compositions demonstrated good compatibility, but need improvement in sintering activity at 800-900°C and thus better electrical contact

Approach: improve sintering activity via reaction sintering, addition of sintering agents or chemical modification
Fabrication of Contact Layers via Reaction Sintering

Paste of metals and/or oxides mixture

During first stack heating or sealing

Conductive oxide contact layer

Reactions assisted sintering

Conductive oxides

MC layer

Crofer 22 APU

After reaction sintering

Without sintering

5 μm

40 μm

Electron Image 1
Contac Layers via Adding Sintering Agents

- Among studied, CuO and Bi$_2$O$_3$ more effective for LSM
- To be effective needs 4–5%
Electrical Performance and Stability Evaluation

Interfacial resistance evaluation unit (IRU)

- LSM+1%CuO
- LSM+2%CuO
- LSM+4%Bi₂O₃

Time (hours)
- 0
- 100
- 200
- 300
- 400
- 500

Temperature (°C)
- 0
- 100
- 200
- 300
- 400
- 500
- 600
- 700
- 800
- 900

ASR, mΩ.cm²
- 0
- 5.0
- 10.0
- 15.0
- 20.0
- 25.0
Enhanced Sintering via Chemical Modifications

% Shrinkage vs. Temperature, °C
Summary

+ Reaction sintering appears to be a promising approach to fabricate contact layers between perovskite cathodes and metallic interconnects.
+ Addition of sintering aids and chemistry modifications also help improve sintering activity of conductive oxides.

Future work

- Continue to search and optimize contact materials and processing approaches
- Systematically evaluate candidate systems: dilatometry, IRU (ASR), SEM, XRD.
- Evaluate long term electrical performance and interface stability under isothermal and thermal cycling
The work summarized in this paper was funded under the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program.

The authors wish to thank the SECA management team at NETL for their helpful discussions regarding this work.

Metallographic preparation and SEM: Jim Coleman, Shelley Carlson, Nat Saenz