Oxidation Behavior and In-Cell Performance of Developmental SOFC Interconnect Alloys

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Materials Issues for Distributed Energy Resources
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Exploratory Effort

• Background - Key issues for metallic interconnects

• First Screening: Microalloyed Ni and ferritic alloy
  - Oxidation
  - Electrical Resistivity
  - In-Cell Performance

• Results on oxidation (volatility) and electrical resistivity studies for 2nd series of ferritic alloys

• Concluding remarks
Metallic Interconnects in SOFC Fuel Cells

Key Interconnect Functions are to Electrically Connect Series of Cells into Stacks and to Separate Fuel/Oxidant

• Environment: 700-850°C, Oxidizing/Reducing, Thermal expansion compatibility with ceramic cell components is important in some designs

• Benchmark: Coated Cr-5Fe-1Y$_2$O$_3$ or Doped Perovskite Ceramic ($, Brittle)
Advantages of Planar Metallic Interconnects

- Potentially Significantly Lower Cost Than Ceramics
  - Raw Materials and Processing/Machining

- Mechanical Integrity - Thinner Plates than Ceramics

- Dense (Important for Fuel/Oxidant Separation)

- Potential for Better Performance Due to High Electrical Conductivity
Major Issue for Metallic Interconnects is Maintenance of Electrical Conductivity

• Metals Oxidize in Fuel Cell Environments

• Oxidation Products Usually Electrically Resistive, Can Contaminate/Degrade Other Cell Components

• Manage Surface Chemistry via Alloy Design and Processing to Maintain Sufficient Electrical Conductivity
No Clear Choice for Metallic Interconnects

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Max Theoretical Scaling Limit</th>
<th>*Bulk Resistivity (ohm-cm)</th>
<th>*Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>1750°C</td>
<td>$7 \times 10^6$ 600°C</td>
<td>44th CRC</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1450°C</td>
<td>$5 \times 10^8$ 700°C</td>
<td>MSE CRC</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>1100°C</td>
<td>$1 \times 10^2$ 800°C</td>
<td>Holt+Kofstad</td>
</tr>
<tr>
<td>NiO</td>
<td>850°C</td>
<td>5-7 $\times 10^0$ 900°C</td>
<td>Nowotny + Sorrell</td>
</tr>
<tr>
<td>CoO</td>
<td>700°C</td>
<td>$1 \times 10^0$ 950°C</td>
<td>Nowotny +</td>
</tr>
</tbody>
</table>

- SiO₂, Al₂O₃ too insulating
- Cr₂O₃: high volatility-contaminates cell, borderline resistivity
- NiO, CoO: high CTE, sulfur, borderline scaling
Options are Limited

• No Uncoated, Non-Precious Metal Viable Above 850°C

• Ni/NiO has a Chance in Range of 700 to 850°C if Successfully Doped to Lower Scale Growth Rate
  - No volatility issues
  - Noble (won’t oxidize) in fuel-side environment
  - Fuel Sulfur Impurities May Lead to Low Melting Ni-S Compounds
  - CTE mismatch requires use as coating (substrate interdiffusion)

• Literature Data Suggests Conventional Cr₂O₃-Formers Not Viable Above ~700-800°C (possibly lower). Will need to:
  - Microalloy to reduce scale growth rate/increase scale conductivity
  - Reduce volatility
No One Alloy May be Able to Meet Conductivity and CTE Requirements

• Optimize for Scale Growth Rate and Conductivity
  - May require different alloy for anode/cathode environments
  - May not be possible to co-optimize for CTE compatibility

• Eventual Implementation as Cladding or Coating on CTE Optimized Alloy Substrate

• Investigate Microalloyed Ni and Microalloyed Ferritic
Candidate Alloys

• Microalloyed Ni
  - Hot-Pressed Ni-0.3Y2O3 Wt.%, Cast/Rolled Ni-0.15Y Wt.%
  - Hot-Pressed Li-Doped Ni-0.3Y2O3 (0.07 wt.%, 0.6 at.% Li)
  - Rationale:
    Y or Y2O3 to reduce NiO growth rate
    Li to reduce NiO growth rate, increase conductivity

• Microalloyed Ferritic (Based on Quadakkers et al.)
  - Cast and Rolled Fe-25Cr-1Mn-0.5Ti-0.4La wt.%
  - Rationale: reduced volatility, scale growth rate,
    and contact resistance reported with Mn, Ti, La additions
Screening Evaluation

• Air oxidation screening: 3, 1 week cycles at 850°C (500 h Total)

• Area specific resistance (ASR) measurements

• In-cell stack test: 400-800 h at 850°C (isothermal)
Adherent NiO Formed at 850°C in Air
(similar behavior for 0.15Y and 0.3Y₂O₃ doping)

SEM Cross-sections after 3, 1 week cycles (500 h), 850°C, Air
Ni-0.3Y₂O₃

• Li slowed NiO growth beyond that achieved with Y₂O₃
• NiO growth at 850°C in range of estimated growth rate for potentially acceptable resistivity (based on bulk NiO)
Duplex Scale Formed on Fe-25Cr-1Mn-0.5Ti-0.4La at 850°C in Air

SEM Cross-section after 3, 1 week cycles (500 h), 850°C, Air

- Mn, Cr-based oxide (likely spinel) above continuous Cr₂O₃
- Internal oxidation suggests overdoping of Ti, possibly La (levels not optimized)
Li-Doped Ni-0.3Y$_2$O$_3$ Exhibits Similar ASR to Fe-25Cr-1Mn-0.5Ti-0.4La wt.%

Arrhenius Plot of Area Specific Resistance vs. 1/T
3, 1 week cycles (500 h), 850°C, Air
(Pt Electrode, DC 4 point method)

- Cross-section analysis of scale thickness not yet performed
  (ASR trends for Ni-alloys consistent w/oxidation mass change data)
TMI’s Radial Flow Cell

**Component** | **Functional Requirement**
--- | ---
Interconnect | **Metal Alloy**  
<subject of tests>
Cathode with Seal | LaMnO$_3$-type Perovskite
Electrolyte (w / Primary Electrodes) | Yttria-Stabilized Zirconia
Anode with Seals | Metal/Ceramic Composite
Repeating Stack | 

- Cell Design Tolerates Some Metal CTE Mismatch-Ideal Test Bed for Candidate Interconnect Alloys
Cell Test Configuration

- 2-5 Cell Stacks Tested at ~ 850°C Run with Humidified H₂
Moderate Performance Improvement Over Conventional Cr₂O₃-Forming Alloys

850°C In-Cell Performance Relative to 100% Baseline for Commercial Cr₂O₃-Forming Alloys

- Ferritic 1.7X better than baseline, Ni 1.6X baseline
- Li doping effect in Ni did not translate to better performance
- Stack degradation rates 2-3X greater than long term target rates
**Ni-0.15Y Alloy Reacted with Cathode**
(similar behavior for Ni-0.3Y$_2$O$_3$)

SEM Cross-Section of Ni Interconnect/Cathode Interface after ~ 600 h in-cell at 850°C

- No Ni alloy oxidation or reaction at anode contact layer
- Preliminary analysis of Fe25Cr(Mn,Ti,La) alloy revealed thin dense scale at anode and cathode—not yet analyzed
Alloy Optimization Will Require Detailed Oxidation and Electrical Resistivity Studies

Ferritic Baseline Composition of Fe-18Cr-9W wt.% Selected for Study

• Ueda and Taimatsu, 2000 baseline composition for lower CTE (improved thermal compatibility with zirconia)

• Controlled levels of La, Mn, Ti (Quadakkers et al, 2000)

• Oxidation/Volatility Assessment in 10% H₂O, 800-900°C, 1h or 100h cycles, 500-1000+ total h

• Post-Oxidation Area Specific Resistance (ASR) Measurements
Performance of microalloyed Fe-18Cr-9W Laboratory oxidation testing at 800°C (1472°F)

Base alloy - protective scale in air
La - reduces scale growth rate (lower mass gain)
Add H₂O - mass loss due to volatilization of CrO₂(OH)₂

This volatilization causes a contamination problem in fuel cells!
Performance of microalloyed Fe-18Cr-9W Laboratory oxidation testing at 800°C (1472°F)

Try to minimize evaporation:
La+Ti - higher initial mass gain, but mass loss at later times
La+Mn - no mass loss detected, suggests reduction in volatility
Optimization of microalloyed Fe-18Cr-9W Laboratory oxidation testing at 800°C (1472°F)

Combination of La+Mn+Ti reported to have best performance

Adding more elements to alloy leads to higher mass gains due to internal oxidation of La, Mn and Ti
Optimization of microalloyed Fe-18Cr-9W
Laboratory oxidation testing at 800°C (1472°F)

First attempt at optimization:
By dropping La, Mn and Ti (at.%): cut mass gain by 50% (in cell test: attack 2-3X high) further optimization possible!
However, can’t rely only on mass change data alone...
Results Suggest Co-Doping of Mn and Ti Significantly Reduces Scale ASR

Arrhenius Plot of Area Specific Resistance vs. 1/T
Fe-18Cr-9W Base, 550 1h Cycles, 10% H₂O

- La,Mn,Ti synergistic trends consistent with Quadakkers et al.
- Need oxide thickness & chemistry to better assess results
Summary

Using commercial Cr₂O₃-forming interconnects as baseline:

• **Microalloyed Ferritic Cr₂O₃ Former up to 80% Performance Improvement Over Baseline Alloy**
  - In-cell degradation rate too high (2-3X long term target)
  - Series of Fe-Cr-W alloys indicated:
    La: reduce Cr₂O₃ growth rate
    La +Mn: reduce Cr₂O₃ evaporation (less cell contamination?)
    La+Mn+Ti: synergistic decrease in ASR (Pt electrode)
  - Further optimization of composition may be possible

• **Microalloyed Ni/NiO up to 60% Performance Improvement Over Baseline Alloy**
  - Comparable ASR to doped ferritic (Pt electrode)
  - Reactivity with cathode may limit performance
  - Degradation rate also too high (2-3X long term target)
  - Merits further investigation (possibility as cladding)