Metal Interconnects for Solid Oxide Fuel Cell Power Systems

SECA Core Technology Program
Ceramatec, Inc.

Supported in part by
DOE-NETL

Presented at
Pacific Grove, CA
21 April 2005
Technical Issues Addressed

- **Technical Requirements for Metal Interconnects**
  - CTE match
  - No gas permeation
  - High temperature corrosion resistance
  - Scale conductivity
  - Scale adhesion
  - Stability in atmosphere (physical, chemical, microstructure, conductivity)
  - Stability against electrode/bond layer (poisoning effect)
  - Electrical contact with cells
  - Thermal cycle capability
Challenges

• Chromia formers preferred to provide a conductive scale
  - Continued scale growth during operation
    - Increased electrical resistance
    - Loss of adhesion
    - Porosity at interface
  - Chromium evaporation
    - Electrode Poisoning
  - Electrode compatibility
    - High resistance phase formation with electrode cations (spinel)
Approach

• Modify intrinsic scale
  ➢ surface treatment and thermal process
  ➢ Objective: Limit scale growth
• Apply extrinsic layer
  ➢ low Cr activity composition (~LaCrO$_3$)
  ➢ Objective: Limit Cr evaporation
• Combine the two layers
  ➢ graded composition
• Contact layer application
  ➢ Thermal Spray (Idaho National Lab.)
Approach

• **Alloy Selection** *(Fe-Cr based ferritic SS)*
  - CTE Match, Conductive scale (chromia former)
  - Choice of minor alloying elements

• **Surface Treatment & Oxidation**
  - Growth of selective oxide scale
    - Control P, T, X₁ and t
  - Scale characterization
Assessment Criteria

- Weight gain with time at temperature
- Scale thickness, morphology, composition
- Electrical resistance with thermal cycles
- Exposure to relevant atmospheres
- Reactivity with contact layer
- Chromium evaporation
## Experimental Arrangement

<table>
<thead>
<tr>
<th>TGA</th>
<th>Coupon Couples</th>
<th>Dual atm. couples</th>
<th>Stack</th>
</tr>
</thead>
</table>
| • Single atmosphere  
• No contact / electrode layers  
• No current  
• Isothermal | • Single atmosphere  
• Contact layer  
• Intermittent current  
• Isothermal | • Dual atmosphere  
• Contact layer  
• Isothermal | • Dual atmosphere  
• Continuous current  
• Contact/electrode layers  
• In-plane thermal, current density gradients |

![Diagram](image)
Weight Gain Measurements

- An order of magnitude reduction in scale growth rate constant with surface treatment
Conductivity Test Rig

- Coupon couple to provide symmetric arrangement
- Perovskite contact layer
Scale Resistance in Air (coupon couples)

Test temperature 750°C

Resistance (milliohm-cm²) vs. Time (hrs)

Sample 100H9-4
Sample 50N9-4

1st Thermal Cycle
2nd Thermal Cycle
3rd Thermal Cycle
4th Thermal Cycle
5th Thermal Cycle

Test temperature 750°C
Scale Resistance in H₂ - 3%H₂O
Dual atmosphere couples

- Dual atmosphere
- Contact layer
- Continuous load (constant current)
- Air atmosphere
- No contact layer
- No current

1x1 cm coupon on a larger (3.5x3.5 cm) blank
Identical treatment on mating surfaces
Contact layer: cobaltite
Rig Validation: Graded Coating in air

- Graded coating 750C
- Coupon couple in air using 'dual atm' set-up
- Coupon couple in air (includes two thermal cycles)
Graded Coating: Dual atmosphere

Graded coating
Air/H$_2$(H$_2$O) at 750C
Load=200mA/cm$^2$
Graded Coating

- Thin scale (1 µm) in both regions
- No Sr-Cr rich phase

200 mA/cm², ~300 hrs
7 milliohm.cm²
Graded coating - dual atm.

- 6 µm scale
- Influence of dual atm. away from the region?
- Thin scale
- Chromia nodules
- Thin scale under contact layer
- No Sr-Cr phase at the scale

200 mA/cm², ~400 hrs
15 milliohm.cm²
Dual Atmosphere Test - improved Coating Process

- Low ASR from the start
- Degradation after thermal cycle
1000 hr test microstructure

- Coupon sandwich area (current flow)
- 1000 hrs in dual atm.

- Away from sandwich area
- 1000 hrs in dual atm.
Coupon Test: Graded Coating + LSCo
Thermal Sprayed

- Test condition: 750°C in Air
Dual Atmosphere Test: Graded Coating + LSCo
Thermal Sprayed

- 750°C, 0.2 A/cm²

Resistence, milliohm-cm² vs. Time (hrs)
Reaction Study: Untreated SS Powder + Perovskite

- Stainless Steel Powder (Untreated) + Perovskite Mixture
  200 hrs in air
- Formation of (Fe,Cr)$_2$O$_3$

Stainless Steel powder from Hoeganaes Corporation
Bottom pattern - as mixed powders; Top Pattern - after heat treatment
Reaction Study: Untreated SS Powder + Perovskite

- Stainless Steel Powder (Untreated) + Perovskite Mixture
- 200 hrs in air
- Formation of $(\text{Fe,Cr})_2\text{O}_3$
Reaction Study: Coated SS Powder + Perovskite

- Stainless Steel Powder (Graded Coating) + Perovskite Mixture
- 300 hours in air
- No significant reaction product
Reaction Study: Coated SS Powder + Perovskite

- Stainless Steel Powder (Graded Coating) + Perovskite Mixture
- 300 hours in air
- No significant reaction product
Chromium Evaporation Test Rig

- MgO used as Cr getter

Diagram:
- Metal coupon
- Powder chamber (zirconia ring and disk)
- Zirconia tube
- Thermocouple
- Metal coupon
- Powder chamber (zirconia ring and disk)
- Zirconia tube
- Thermocouple

• MgO used as Cr getter
# Cr Evaporation Test Summary

<table>
<thead>
<tr>
<th></th>
<th>Baseline powder</th>
<th>Powder exposed to untreated coupon</th>
<th>Powder exposed to treated coupon</th>
<th>Powder exposed to treated and LSCo thermal sprayed coupon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>&lt; 0.5</td>
<td>250</td>
<td>140</td>
<td>4.1</td>
</tr>
<tr>
<td>Mn</td>
<td>&lt; 0.25</td>
<td>3.4</td>
<td>&lt; 2.5</td>
<td>0.74</td>
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<tr>
<td>Sr</td>
<td></td>
<td></td>
<td></td>
<td>1.8</td>
</tr>
<tr>
<td>Co</td>
<td></td>
<td></td>
<td></td>
<td>&lt;10</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td></td>
<td></td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>

- **Cr content in ppm by weight in MgO**
Reactivity of Contact Paste (300 hrs)

air

contact paste

Fuel
(H₂/H₂O)

treated coupon
Contact Paste Interaction

- Treated surface shows good adhesion with LSCo
- Cr diffusion into LSCo layer (due to porosity?)
Fuel Exposure

Syngas Exposure
750°C - 250 hrs

Syngas + H₂S Exposure
750°C - 250 hrs
Resistance Stack

- Repeat Unit
  - Interconnect + ‘pseudo cell’ made of separator plate

- Voltage probes to monitor resistance of interfaces

- Dual atmosphere

- Initial Data:
  - Air interface ~ 100 milliohm-cm²
  - Fuel interface ~ 50 milliohm-cm²
  - Scatter in data due to inconsistent contact
Summary

• **Commercial stainless steel with graded coating shows**
  - Low, stable interface resistance through several thermal cycles
  - Low air-side resistance in dual atmosphere
  - Modified treatment process provides stable microstructure on the air-side in dual atmosphere exposure
  - Powder mixture heat treatment shows no observable reactivity with potential contact materials (perovskites)
  - Limits chromium evaporation
  - Sulfur tolerance needs further investigation
  - Resistance stack provides resistance information in a stack arrangement
Acknowledgement

- Ceramatec team
- DOE-SECA project managers
  Project Manager: Lane Wilson
- CTP teams
- SECA industrial teams