Ceramic Interconnects / Coatings

SECA Core Technology Program
SOFC Interconnection (IC) Technology Meeting
Argonne National Laboratory, Chicago IL
July 28-29, 2004
Interconnect Requirements

- Thermal expansion match with SOFC components
- Stability over operating pO$_2$ range (0.2 to 10$^{-18}$ atm)
- High electronic conductivity in air and fuel
- Gas impermeability
- Process compatibility
- Mechanical integrity
- Low material and fabrication costs
- Negligible non-electronic migration
Interconnect Materials

- **Two classes of interconnect materials**
  - **Ceramic**
    - suitable for high temp. operation (900 - 1000 C)
    - Electronic conductivity a strong function of temp.
  - **Metallic**
    - suitable for 650 - 800 C operation
    - Oxidation is a major problem at higher temp.
Introduction and Background

Typical Compositions of interest

- La(Sr)MnO$_3$ - Cathode
- La(Sr)CoO$_3$ - Cathode
- La(Sr)CrO$_3$ - Interconnect
- La(Sr)GaO$_3$ - Electrolyte

- Good Conductivity (ionic, electronic)
- OXYGEN NONSTOICHIOMETRY
- Good Catalytic Properties for Oxygen Exchange
- CTE flexibility (8.5 - 18.0 ppm / °C)
- Chemical Stability to Severe Conditions (LSCr)
Interconnect Requirements

• Thermal Expansion Match with SOFC components
• Stability over operating pO₂ range
• High electronic conductivity in air and fuel

LaCrO₃ meets the necessary electrochemical properties

• Gas Impermeability
• Process Compatibility
• Mechanical Integrity
Challenges & Options in Fabrication

• **Difficult to sinter due to**
  - High Temperature requirements - typically ~ 1700 C
  - control of CrO$_3$ volatilization - Air Sintering is the preferred option
  - capital and operational cost

• **Options**
  - Liquid Phase Sintering through addition of low melting eutectic
  - Transient liquid phase sintering in the chromite system
Lower Temperature Air Sintering

- Addition of Ca and Co promotes liquid phase sintering
- Lower Sintering Temperature ~ 1450°C
- High Conductivity > 30 S/cm compared 10 S/cm for Sr doped LCr
Sintering Characteristics of LaCrO$_3$

![Graph showing sintering characteristics of LaCrO$_3$.](image)
Evaluation of Interconnect Compositions

- Thermal Expansion Behavior
- Stability in Fuel Atmosphere
- Mechanical Properties
Thermal Expansion Behavior

La$_{0.79}$Ca$_{0.2}$Cr$_{0.9}$Co$_{0.1}$O$_3$, CTE = 10.7 ppm (°C)$^{-1}$

La$_{0.83}$Sr$_{0.16}$CrO$_3$, CTE = 10.3 ppm (°C)$^{-1}$

Thermal Event, ∼ 220°C
Stability in Fuel Atmosphere
Oxygen Non-stoichiometry
Stability in Fuel Atmosphere Conductivity

![Graph showing conductivity over time for different materials](image_url)
Mechanical Properties
Fracture Strength of La$_{0.89}$Ca$_{0.1}$Cr$_{0.9}$Co$_{0.1}$O$_3$ in Fuel

Weibull Modulus
- 0 time $m = 9.1$
- 30 sec $m = 11.5$
- 60 sec $m = 14.5$

Samples Crumbled
Mechanical Properties
Fracture Strength of La$_{83}$Sr$_{16}$CrO$_3$ in Fuel

![Graph showing fracture strength over time in fuel with data points and error bars for different time intervals. Weibull Modulus values are also provided for each interval: 0 time $m = 12.3$, 5 min $m = 11.2$, 18 hr $m = 8.5$, 24 hr $m = 10.4$, 72 hr $m = 12.4$, 1000 hr $m = 7.8$.}]
Comparison of compositions

- **LCCr**
  - Low sintering temp
  - High conductivity in air
  - Poor stability in fuel
  - Low mech. Properties

- **LSCr**
  - Better stability in fuel

- **LMgCr**
  - Best stability
  - Low conductivity

Need to compare ionic transport
### Symptoms of Ionic Leakage

- **Low OCV**
- **Low Fuel Utilization**

### Prior Measurements:

<table>
<thead>
<tr>
<th>Source</th>
<th>Test Type</th>
<th>Doping</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>WE:</td>
<td>Differential $pO_2$</td>
<td>Mg doped</td>
<td>$&lt;10 \mu A/cm^2$</td>
</tr>
<tr>
<td></td>
<td>gas Analysis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tokyo Gas:</td>
<td>Conductivity</td>
<td>Sr, Ca doped</td>
<td>10-300 mA/ cm$^2$</td>
</tr>
<tr>
<td></td>
<td>Relaxation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NIMCR:</td>
<td>Limiting Current</td>
<td>Ca doped</td>
<td>1 mA/ cm$^2$</td>
</tr>
<tr>
<td>Ceramatec:</td>
<td>In-line Sensor</td>
<td>Sr doped</td>
<td>50 mA/ cm$^2$</td>
</tr>
</tbody>
</table>
Ionic Leakage Modeling*

- **3D stack model** - thermal, electrochemical, electrical
- **Input data:** Tokyo Gas (Yasuda et al.)
  
a) **La\(_{1-y}\)Ca\(_y\)CrO\(_3\)**

\[
j = \frac{1152 (-\log P_{O_2} - 12)}{L} \exp(18.72 Y_{Ca} - 16000/T)
\]

b) **La\(_{1-y}\)Sr\(_y\)CrO\(_3\)**

\[
j = \frac{2240 (-\log P_{O_2} - 12)}{L} \exp(16.1 Y_{Sr} - 21000/T)
\]

*work done at Institutt for energiteknikk, Norway
Geometry Consideration

Geometry 1
Thickness(t): 0.36 mm
Channel Depth(d): 0.71 mm
Channel Width(w): 1.7 mm

Geometry 2
Thickness(t): 0.86 mm
Channel Depth(d): 0.84 mm
Channel Width(w): 1.7 mm
Effects of Composition on Ionic Leak Current

Geometry 1  Inlet Temp. 1125K

Ca doping shows high leakage current
Effects of Geometry: OCV and Leakage Current

La$_{0.8}$Sr$_{0.2}$CrO$_3$  Inlet Temp: 1125K

Geometry 2 exhibits lower leakage
Geometry 1: Two solutions
Effects of Inlet Temperature: OCV

Geometry 1

La$_{0.8}$Sr$_{0.2}$CrO$_3$

Geometry 2

- OCV decreases with increasing temp
- OCV of geometry 2 is independent of Dp(air)
Effects of Inlet Temperature: Leakage Current

- Leakage current increases with increasing temp.
- Geometry 2 is insensitive to air pressure
Measurement Technique

- **Direct measurement of ionic current is cumbersome**
- **Need an indirect measurement technique**
  - Oxygen loss from the lattice causes lattice expansion
Lattice Expansion in Fuel

![Graph showing lattice expansion in fuel and air as a function of temperature.](image)
## Characterization of Lanthanum Chromite

<table>
<thead>
<tr>
<th>Composition</th>
<th>Conductivity in Air S/cm</th>
<th>Conductivity in Fuel S/cm</th>
<th>Thermal Expansion to 1000°C ppm/°</th>
<th>CCE at 1000°C in 3% H₂ - Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>La₉₈Sr₁₃Ca₆₃CrO₃</td>
<td>15 - 25</td>
<td>2 - 6</td>
<td>10.1</td>
<td>0.135%</td>
</tr>
<tr>
<td>La₈₃Sr₁₆Cr₉₈Fe₀₂O₃</td>
<td>~ 15</td>
<td>&lt;1</td>
<td>10.4</td>
<td>0.088%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₉O₃</td>
<td>8 - 10</td>
<td>1 - 2</td>
<td>8.9</td>
<td>0.05%</td>
</tr>
<tr>
<td>La₉₉Mg₂Cr₈O₃</td>
<td>4.44</td>
<td>0.45</td>
<td>9.5</td>
<td>0.077%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₈₅Fe₀₂O₃</td>
<td>5.86</td>
<td>1.01</td>
<td>9.23</td>
<td>0.035%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₈Fe₁O₃</td>
<td>4.02</td>
<td>0.61</td>
<td>9.32</td>
<td>0.044%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₈ₐ₈₁₀O₃</td>
<td>0.62</td>
<td>0.56</td>
<td>9.02</td>
<td>0.025%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₈₅₅Al₁₀O₃</td>
<td>5.33</td>
<td>0.73</td>
<td>9.40</td>
<td>0.050%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₈₈₅Al₁₁₀O₃</td>
<td>8.33</td>
<td>0.86</td>
<td>9.90</td>
<td>0.065%</td>
</tr>
<tr>
<td>La₉₉Mg₁Cr₆₅₅Al₃O₃</td>
<td>3.85</td>
<td>0.101</td>
<td>10.4</td>
<td>0.07%</td>
</tr>
<tr>
<td>La₆₃Gd₂Sr₁₆CrO₃</td>
<td>22.4</td>
<td>3.99</td>
<td>9.37</td>
<td>0.14%</td>
</tr>
</tbody>
</table>
Fuel Induced Warpage
Effect of fuel $pO_2$ on OCV
Ceramic Interconnect Stack Test

Temp: 850 - 900°C
H₂+3%H₂O vs Air
Load: 100 mA/cm²
Summary - Ceramic ICs

- Ionic leakage of chromite interconnects must be considered in the selection of material composition
- Global optimization of properties necessary
- Stack endurance demonstrated using this approach
- Materials and fabrication costs need to be addressed
Metal Interconnects

- **Additional Requirements**
  - High temperature corrosion resistance
  - Scale conductivity
  - Scale adhesion
  - Stability against electrode/bond layer (poisoning effect)
  - Thermal cycle capability
Approach

- **Controlled growth of conductive scale to achieve**
  - Electronic conductivity in scale
  - Low cation (metal) and anion (oxygen) diffusivity
  - Good adhesion (‘native’ scale)
Approach

- **Alloy Selection (Fe-Cr based ferritic SS)**
  - CTE Match, Conductive scale (chromia former)
  - Choice of minor alloying elements
  - < 30% Cr to avoid brittle sigma phase formation
    - Slow cooling to be avoided below 650°C
    - > 12% for Cr₂O₃ formation

- **Surface Treatment & Oxidation**
  - Growth of selective oxide scale
  - Control P, T, Xi and t
  - Scale characterization
Scale Resistance in Air (coupon couples)

Test temperature 750°C

Resistance (milliohm-cm²)

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/H₂O

![Graph showing scale resistance over time for three thermal cycles.](image)
Scale Morphology

Untreated dry air
750°C 200 hours

Untreated wet air
750°C 500 hours

Treated dry air
750°C 500 hours

Treated dry air of dual atm.
750°C 500 hours

Treated wet air
750°C 500 hours
Stack Evaluation (SBIR Project)

- A treatment process with low resistance in coupon tests evaluated (screen printed contact layer)
- Post-test: Sr-Cr rich phase on La(Sr)CoO$_3$ cathode
Phase II Evaluations

• **Approaches to surface treatment optimization**
  - 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
TGA

- 50C940: oxide scale modification
- MI2: Graded coating
Elemental Map: Graded coating
Post-TGA

SEM

Cr

Fe

La
Dual atmosphere couples

- Dual atmosphere
- Contact layer
- Continuous load (constant current)

1x1 cm coupon on a larger (3.5x3.5 cm) blank
Identical treatment on mating surfaces
Contact layer: cobaltite
LaCrO$_3$ - Dual atmosphere

Extrinsic Layer
Air/H$_2$(H$_2$O) at 750C
Load ~ 200mA/cm$^2$
Graded Coating: Dual atmosphere

Graded coating
Air/H₂(H₂O) at 750°C
Load=200mA/cm²
**LaCrO₃ layer**

- Thick scale
- Poor adhesion

- 200 mA/cm², ~350 hrs
- 140 milliohm.cm²

- Thin scale
  - Scale loss?

- Thick scale under contact layer
  - Sr-Cr rich interface
Graded coating - dual atm.

- 200 mA/cm², ~400 hrs
- 15 milliohm.cm²

6 µm scale
Influence of dual atm. away from the region?

Thin scale
Flaky?

Thin scale under contact layer
No Sr-Cr phase at the scale

IC Workshop
July 28 - 29, 2004
Summary - Metal IC

- **New test arrangement**
  - Allows resistance measurement in dual atm. exposure
  - Allows continuous load

- **Graded coating provides low resistance and thinner oxide scale in initial tests**

- **Additional work planned**
  - Effect of coating variations
  - Effect of current density

- **Stack test validation in parallel programs**
Acknowledgement

- GRI
- Ceramatec
- Norcell
- SOFCo
- DOE SECA CTP