Mitigation of Chromium Impurity Effects and Degradation in Solid Oxide Fuel Cells

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• Summary of Test Conditions
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Introduction

• **Background**
  
  – Chromium (Cr) poisoning of cathode in solid oxide fuel cells (SOFCs) is considered to be one of the major reasons for performance degradation
  
  – For different cathode materials, the mechanisms of Cr-poisoning are complex.

• **Project Goals**
  
  – Compare the degradation phenomena in LSM, LSF, and LNO (La$_2$NiO$_4$) - based cathodes caused by Cr-poisoning
  
  – Through the comparative study, investigate the mechanisms of Cr-poisoning in these three types of cathodes in realistic full cell operating conditions
  
  – Design mitigating strategies based on applying protective coatings to ferritic stainless steel interconnects
Cell Fabrication

LSM: \((\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-x}\)
LSF: \((\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{FeO}_{3-x}\)
GDC: \((\text{Gd}_{0.10}\text{Ce}_{0.90})\text{O}_{2-x}\)
Summary of Test Conditions

- **General test conditions:**
  - Fuel: 98% H₂ + 2% H₂O (300 cc/min): Fixed
  - Oxidant: Air (1000 cc/min)
  - Interconnect: Crofer 22 H mesh (used as cathodic current collector in cell tests)

- **Conditions varied in the study:**

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Cathode Atmosphere</th>
<th>Current Condition</th>
<th>Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Dry Air</td>
<td>Open Circuit</td>
<td>LSM-1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>LSF-1</td>
</tr>
<tr>
<td>2</td>
<td>Humidified Air (10% H₂O)</td>
<td>Open Circuit</td>
<td>LSM-2</td>
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<tr>
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<td></td>
<td></td>
<td>LSF-2</td>
</tr>
<tr>
<td>3</td>
<td>Dry Air</td>
<td>Galvanostatic (0.5 A/cm²)</td>
<td>LSM-3</td>
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<td>LSF-3</td>
</tr>
<tr>
<td>4</td>
<td>Humidified Air (10% H₂O)</td>
<td>Galvanostatic (0.5 A/cm²)</td>
<td>LSM-4</td>
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<td></td>
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<td>LSF-4</td>
</tr>
</tbody>
</table>
Electrochemical Degradation: V-i

<table>
<thead>
<tr>
<th>Condition 1: Dried Air + OCV</th>
<th>Condition 2: 10% Humidified Air + OCV</th>
<th>Condition 3: Dried Air + 0.5 A/cm²</th>
<th>Condition 4: 10% Humidified Air + 0.5 A/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM-Based cells</td>
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</tr>
<tr>
<td>LSM-1</td>
<td>LSM-2</td>
<td>LSM-3</td>
<td>LSM-4</td>
</tr>
<tr>
<td>Voltage (V)</td>
<td>Voltage (V)</td>
<td>Voltage (V)</td>
<td>Voltage (V)</td>
</tr>
<tr>
<td>Power Density (W/m²)</td>
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<td>Power Density (W/m²)</td>
</tr>
</tbody>
</table>

LSM-Based cells:
- LSM-1
- LSM-2
- LSM-3
- LSM-4

LSF-Based cells:
- LSF-1
- LSF-2
- LSF-3
- LSF-4
Electrochemical Degradation: V-i

- **Cr-poisoning** is more deleterious in LSM-based cell than that in LSF-based cell.
  - In the case of **LSM-based** cell:
    - Current load (0.5 A/cm²) accelerates the degradation
    - Presence of humidity in air promotes degradation under current load
  - In the case of **LSF-based** cell:
    - Current load (0.5 A/cm²) slightly improved the cell performance (presumably due to cell break-in)
    - In humidified air, performance deteriorated under OCV condition but improved under current load
## Electrochemical Degradation: EIS

<table>
<thead>
<tr>
<th>Conditions</th>
<th>LSM-Based</th>
<th>LSF-Based</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition 1: Dried Air + OCV</td>
<td><img src="image1.png" alt="Graph" /></td>
<td><img src="image2.png" alt="Graph" /></td>
</tr>
<tr>
<td>Condition 2: Humidified Air + OCV</td>
<td><img src="image3.png" alt="Graph" /></td>
<td><img src="image4.png" alt="Graph" /></td>
</tr>
<tr>
<td>Condition 3: Dried Air + 0.5 A/cm²</td>
<td><img src="image5.png" alt="Graph" /></td>
<td><img src="image6.png" alt="Graph" /></td>
</tr>
<tr>
<td>Condition 4: Humidified Air + 0.5 A/cm²</td>
<td><img src="image7.png" alt="Graph" /></td>
<td><img src="image8.png" alt="Graph" /></td>
</tr>
</tbody>
</table>
EIS consistent with the V-i results. In 10% humidified air, it shows increasing polarization of LSM-based cell and decreasing polarization of LSF-based cell.
Microstructural Evolution: LSM-Based

**LSM-1**: Dry Air + OCV

**LSM-2**: Humidified Air + OCV

**LSM-3**: Dry Air + Current

**LSM-4**: Humidified Air + Current

Cr-containing deposits are Cr,Mn-rich, suggesting (Cr,Mn)$_3$O$_4$ spinel phases.
Microstructural Evolution: LSM-Based

- Cr intensity at cathode/electrolyte interface: LSM-4 > LSM-3 > LSM-2 ≈ LSM-1
- Cr deposition was promoted by current and extended to TPB’s away from the cathode/electrolyte interface.

Microstructural Evolution: LSF-Based

**OCV condition:**
Cr distribution is homogeneous in the bulk of cathode

Most of Cr is distributed at the surface of cathode

Cr is distributed at the surface of cathode and also cathode/electrolyte interface
Microstructural Evolution: LSF-Based

LSF-1: Dried Air + OCV

Cr Line Scan
Sr Line Scan

LSF-2: 10% Humidified Air + OCV

Cr Line Scan
Sr Line Scan

LSF-3: Dried Air + 0.5 A/cm²

Cr Line Scan
Sr Line Scan

LSF-4: 10% Humidified Air + 0.5 A/cm²

Cr Line Scan
Sr Line Scan

Cr and Sr profiles do not match at the cathode/electrolyte interface
Microstructural Evolution: LSF-Based

**LSF-1: Dried Air + OCV**
- LSF Paste
- LSF
- LSF-GDC
- GDC

**LSF-2: 10% Humidified Air + OCV**
- LSF Paste
- LSF
- LSF-GDC
- GDC

**LSF-3: Dried Air + 0.5 A/cm²**
- LSF Paste
- LSF
- LSF-GDC
- GDC

**LSF-4: 10% Humidified Air + 0.5 A/cm²**
- LSF Paste
- LSF
- LSF-GDC
- GDC

**LSF contact paste**

**LSF current collective layer**

**Dense Sr-Cr-O phase**

Sr:Cr ≈ 1:2 (At%)

**LSF contact paste**

**LSF current collective layer**

**Dense Sr-Cr-O phase**

Sr:Cr ≈ 1:1 (At%)
Microstructural Evolution: LSF-Based

- LSF-1: Dried Air + OCV
- LSF-2: 10% Humidified Air + OCV
- LSF-3: Dried Air + 0.5 A/cm²
- LSF-4: 10% Humidified Air + 0.5 A/cm²

Major amount Cr₂O₃
Minor amount Sr,Cr-containing deposits

Major amount Cr₂O₃
Minor amount Sr,Cr-containing deposits
Degradation in LNO Cathodes
Degradation Mechanisms

- Effect of humidity on Cr evaporation:

  Equilibrium Partial Pressure of Cr in Dry Air

  Equilibrium Partial Pressure of Cr in 10% Humidified Air

  Equilibrium Partial Pressure of Cr vapor species over Cr₂O₃ scale

- Cr vapor pressure in 10% humidified air is ~2-order-of-magnitude higher than that in dry air*.

Degradation Mechanisms

- **Effect of humidity on Cr distributions:**

\[ 2\text{SrCr}_2\text{O}_4(s) + 2\text{H}_2\text{O}(g) + 3\text{O}_2(g) = 2\text{SrCr}_2\text{O}_4(s) + 2\text{CrO}_2\text{(OH)}_2(g) \]  
\[ \text{(1)} \]

\[ \text{SrCr}_2\text{O}_4(s) + 4\text{H}_2\text{O}(g) + 2\text{O}_2(g) = \text{Sr(OH)}_4(s) + 2\text{CrO}_2\text{(OH)}_2(g) \]  
\[ \text{(2)} \]

Evaporation of Cr-deposits on the LSF surface:
Oxide Protective Coatings
XRD: a) CuMn$_{1.8}$O$_4$ powders  
b) after reduction anneal  
c) after 1h oxidation anneal

EPD Coating of CuMn$_{1.8}$O$_4$

Cr Diffusion and Microstructure Evolution

- **750 °C 100 h**
  - Cr at%: ~<1 μm

- **750 °C 950 h**
  - Cr at%: ~2.1 μm

- **850 °C 100 h**
  - Crofer 22 APU: ~7.1 μm

- **850 °C 100h + 800 °C 400h**
  - Crofer 22 APU: ~13.5 μm

**Taxon:**

- Particle
- Needle structures
TEM Analysis of Protective Coatings

Needle structures: Mn$_3$O$_4$ particles in dense layer: Cr$_2$O$_3$
Solubility of \( \text{Cr}_2\text{O}_3 \) in \( \text{CuMn}_{1.8}\text{O}_4 \)

Reaction between \( \text{Cr}_2\text{O}_3 \) and \( \text{CuMn}_{1.8}\text{O}_4 \) powders (800 °C, 10 h, in air)
Electrical Conductivity of \((\text{Cu,Mn,Cr})_3\text{O}_4\)

![Graph showing electrical conductivity vs temperature for different compositions of \((\text{Cu,Mn,Cr})_3\text{O}_4\).](image)

- \((\text{Cu,1.8Mn})_{1.3}\text{Cr}1.7\text{O}_4\)
- \((\text{Cu,1.8Mn})_{1.8}\text{Cr}1.2\text{O}_4\)
- \((\text{Cu,1.8Mn})_{2.4}\text{Cr}0.6\text{O}_4\)

Coating on complex geometry (mesh) and Electrochemical tests – LSM cells

- Commercial CuMn2O4
- Uncoated interconnect
- Bare
- BU Coating

Graph showing potential over time (days) for BU Coating, Commercial coating, and Bare conditions.
Summary

- LSM, LSF-GDC, and LNO-based cathodes have been tested against chromium poisoning under load, and in the presence of 10% humidity
  - LSF-GDC and LNO cathodes show excellent tolerance towards chromium poisoning compared to LSM
  - The differences in the mechanisms of degradation are still being worked out

- High quality CuMn spinels have been applied using EPD to complex geometries of ferritic stainless steel interconnects.
  - The coatings are very effective in providing a barrier to Cr attack on LSM cathodes
  - The combination of LSF-GDC or LNO with CuMn protective coatings should provide excellent long term stability against Cr poisoning
Publications

- Effect of Humidity and Cathodic Current on Chromium Poisoning of Sr-Doped LaMnO3-Based Cathode in Anode-Supported Solid Oxide Fuel Cells, R Wang, M Würth, B Mo, UB Pal, S Gopalan, SN Basu, ECS Transactions 75 (42), 61-67
- Chromium Poisoning of Cathodes in Solid Oxide Fuel Cells and its Mitigation Employing CuMn1.8O4 Spinel Coatings on InterconnectsR Wang, Z Sun, Y Lu, UB Pal, SN Basu, S Gopalan, ECS Transactions 78 (1), 1665-1674
- Mitigation of chromium poisoning of cathodes in solid oxide fuel cells employing CuMn1.8O4 spinel coating on metallic interconnect, R Wang, Z Sun, UB Pal, S Gopalan, SN Basu, Journal of Power Sources 376, 100-110
- CuMn1.8O4 protective coatings on metallic interconnects for prevention of Cr-poisoning in solid oxide fuel cells, Z Sun, R Wang, AY Nikiforov, S Gopalan, UB Pal, SN Basu, Journal of Power Sources 378, 125-133
Acknowledgement

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Thank you! Questions?