SOFC Development at PNNL: Overview


Pacific Northwest National Laboratory
Richland, WA 99354

July 20, 2016
17th Annual Solid Oxide Fuel Cell Project Review Meeting
Scope of Work

▲ Materials Development
- Cathode materials and interactions
  - Effects of volatile Cr compounds
    ◆ Poster: SOFC Testing in Cathode Air with Quantified Cr Concentration (John Hardy)
  - Improved density of ceria barrier layers
    ◆ Sintering aids, PVD
- Mitigation of Cr poisoning
  - Evaluation of Cr capture materials
    ◆ Poster: Evaluation of Cr-Gettering Material in a Generic Stack Test Fixture (Matt Chou)
- Cathode-to-interconnect contacts
  - Strengthening of cathode/contact materials interfaces (combined experimental/modeling approach)
    ◆ Poster: Effect on Sintering Aids on Densification and Contact Strength of SOFC (Matt Chou)
- Interconnects/BOP
  - Reactive air aluminization: Dip-coating and reduced fabrication temperatures
    ◆ Poster: Lower Temperature RAA Process for Planar SOFC Stacks (Jung Choi)

▲ Modeling/Simulation
- SOFC Stack Modeling Tools
  - SOFC-MP (2D and 3D) enhancements to support the Reduced Order Model (ROM) tool for improved system modeling
    ◆ Poster: Enhanced SOFC-MP Software Tool Set (Brian Koeppel)
- Modeling of Stack Degradation and Reliability
  - Reliability of cell and stack structures
    ◆ Poster: Structural Reliability Considerations for Planar SOFCs (Naveen Karri)
  - Integration of lower-scale degradation data
Cathode materials and interactions: Effects of volatile Cr compounds on cathode performance

Approach

- Button cell tests to quantitatively assess effects of Cr on cell performance as function of Cr concentration, temperature and time
  - Anode-supported button cells with LSM/YSZ cathodes
  - Correlate Cr dosing with cell performance (power density and stability) and cathode microstructure and chemistry.
- Constant current testing with I-V and EIS sweeps
- Post-test characterization: SEM/EDS/EBSD/XRD
PNNL Test Fixture Design (Not to scale)
Thermodynamic calculations show that sodium carbonate can reduce the concentration of Cr-species in the air by more than 8 orders of magnitude.

The Na$_2$CO$_3$ reacts with Cr-species to form water soluble Na$_2$CrO$_4$

\[
\text{CrO}_3(g) + \text{Na}_2\text{CO}_3(s) \rightarrow \text{Na}_2\text{CrO}_4(s) + \text{CO}_2(g)
\]

\[
\text{CrO}_2(\text{OH})_2(g) + \text{Na}_2\text{CO}_3(s) \rightarrow \text{Na}_2\text{CrO}_4(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)
\]
Assembled Cr Test Fixtures

Downstream Filter

Chromia Pellet
Validation Testing of Fixture for Cell Tests w/ Cr

1) Preliminary tests at 850ºC with no cell in air stream *(complete)*

<table>
<thead>
<tr>
<th>No. of Tests</th>
<th>Cr2O3 Source</th>
<th>Cr2O3 Temperature (°C)</th>
<th>Humidity Level</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>N/A</td>
<td>&lt;5 ppm</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>&lt;5 ppm</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>600</td>
<td>&lt;5 ppm</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>600</td>
<td>~3%</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Powder</td>
<td>800</td>
<td>~3%</td>
<td>200</td>
</tr>
</tbody>
</table>

- Cr2O3 Powder at 800°C 3% Water
  - Cr Mass (µg): 306.17
  - Cr Conc in Air: 2.20E-08
  - Theo. Eqm. Conc: 5.33E-07
  - Meas/Theo: 4.13E-02

- Cr2O3 pellet at 800°C 3% Water
  - Cr Mass (µg): 143.21
  - Cr Conc in Air: 1.05E-08
  - Theo. Eqm. Conc: 5.33E-07
  - Meas/Theo: 1.97E-02

- Cr2O3 pellet at 600°C 3% Water
  - Cr Mass (µg): 35.83
  - Cr Conc in Air: 2.59E-09
  - Theo. Eqm. Conc: 1.28E-07
  - Meas/Theo: 2.03E-02

- Cr2O3 pellet at 800°C Dry Air
  - Cr Mass (µg): 0.46
  - Cr Conc in Air: 3.41E-11
  - Theo. Eqm. Conc: 1.78E-09
  - Meas/Theo: 1.92E-02

- Cr2O3 pellet at 600°C Dry Air
  - Cr Mass (µg): 0.08
  - Cr Conc in Air: 5.95E-12
  - Meas/Theo: 2.27E-01

- No Cr Dry Air
  - Cr Mass (µg): 0.70
  - Cr Conc in Air: 5.13E-11
  - Theo. Eqm. Conc: 0
  - Meas/Theo: N/A

Some Chromia blew out of the container

Very similar ratios
Preliminary Testing of Cr Cell Test Apparatus

2) Determine time-to-saturation of Cr filters at high Cr concentration (in progress)

<table>
<thead>
<tr>
<th># of Tests</th>
<th>Cr2O3 Source</th>
<th>Cr2O3 Temperature (C)</th>
<th>Humidity Level</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>200</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>400</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>600</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>800</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>~3%</td>
<td>1000</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Cr Conc in Air</th>
<th>Meas/Theo Cr Conc</th>
</tr>
</thead>
<tbody>
<tr>
<td>195</td>
<td>7.08E-09</td>
<td>1.33E-02</td>
</tr>
<tr>
<td>312</td>
<td>7.17E-09</td>
<td>1.34E-02</td>
</tr>
<tr>
<td>602</td>
<td>1.15E-08</td>
<td>2.16E-02</td>
</tr>
</tbody>
</table>

~800 Test in Progress
~1000 Test in Progress

3) Determine time-to-detection for low Cr concentration exposures (in progress)

<table>
<thead>
<tr>
<th># of Tests</th>
<th>Cr2O3 Source</th>
<th>Cr2O3 Temperature (C)</th>
<th>Humidity Level</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>N/A</td>
<td>&lt;5 ppm</td>
<td>1000</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>600</td>
<td>&lt;5 ppm</td>
<td>1000</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>&lt;5 ppm</td>
<td>1000</td>
</tr>
<tr>
<td>1</td>
<td>None</td>
<td>N/A</td>
<td>&lt;5 ppm</td>
<td>2000</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>600</td>
<td>&lt;5 ppm</td>
<td>2000</td>
</tr>
<tr>
<td>1</td>
<td>Pellet</td>
<td>800</td>
<td>&lt;5 ppm</td>
<td>2000</td>
</tr>
</tbody>
</table>
Cr-contamination Button Cell Test Plan

1) Baseline Cr-contamination tests of LSM/YSZ cells *(Upcoming)*

<table>
<thead>
<tr>
<th># of Tests</th>
<th>Cr2O3 Source</th>
<th>Cr2O3 Temperature (C)</th>
<th>Humidity Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>No</td>
<td>N/A</td>
<td>&lt;5 ppm</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>800</td>
<td>&lt;5 ppm</td>
</tr>
</tbody>
</table>

2) LSM/YSZ cell tests with variable Cr dosing *(Upcoming)*

<table>
<thead>
<tr>
<th># of Tests</th>
<th>Cr2O3 Source</th>
<th>Cr2O3 Temperature (C)</th>
<th>Humidity Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>Yes</td>
<td>800</td>
<td>~3%</td>
</tr>
<tr>
<td>3</td>
<td>Yes</td>
<td>600</td>
<td>&lt;5 ppm</td>
</tr>
</tbody>
</table>

3) Seek Cr concentration threshold below which cell performance and stability is not significantly affected *(Upcoming)*

- 3 conditions with progressively lower Cr source temperatures in <5 ppm water
Mitigation of Cr Poisoning

- Objective: Evaluate/optimize novel Cr getter materials
  - Collaboration with P. Singh’s group at U. Conn.
  - Cell tests in Core Technology Program stack test fixture
    - Baseline 1: Cr-free; Baseline 2: Cr source, no getter
    - Evaluation of getter in upstream and/or on-cell configurations
Validation with Inlet and On-cell Cr-Gettering

- 2 pre-oxidized AISI 441 metal strips (~7 cm²)
- LSCF-based cell (2”x2”), spinel-coated and aluminized AISI 441 interconnect plates, humidified 50%H₂ vs. air, 800°C
- Inlet with both solid-state reaction pellets and chemically impregnated foam
- On-cell painted with LSCo ink (10% gettering material) on cathode
- Calculated Cr-gettering capacity about 15-20 times of available Cr volatile species
Validation with Inlet Cr-Gettering Only

- 2 pre-oxidized AISI 441 metal strips (~7 cm²)
- LSCF-based cell (2”x2”), humidified 50%H₂ and air (~4.75% H₂O) @375mA/cm², 800°C
- Inlet with solid-state reaction pellets only
- Calculated Cr-gettering capacity about 15-20 times of available Cr volatile species

ASC4 with wet air 6A

- 12.1%/kh
- 15.3%/kh
- 56%/kh
Reactive Air Aluminization (RAA)

- Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., SrCrO$_4$), which degrade interfacial strength
- Cr volatility from alloys can poison cathodes
- Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects (and BOP components)

- Simple process (aluminum powder slurry, single heat treatment in air)
- PNNL has developed screen-printing, aerosol spray, and dip-coating fabrication processes
- Current emphasis: Reduction of heat treatment temperature to <1000ºC
Modeling of Rough Interfaces
Strength of Rough Bi-Material Interfaces

- Last year, demonstrated the DEM particle method could simulate effects of roughness on interfacial delamination of metallic interconnects.
- Apply to cathode contact materials under development.
  - Evaluate sinusoidal and random interface geometries.
Application to Cathode Materials

- Model development performed on interconnect materials (i.e. SS441)
- Apply to cathode contact materials (e.g. LSM20)
- Utilize test data from materials experiments

- Bulk strength of sintered paste from diametral compression test
- Elastic properties for sintered paste from acoustic test
- Interfacial strength of sintered paste from couple tensile test
- Elastic properties for cathode from acoustic test of fully sintered pellet and adjusted for porosity
Partially Sintered LSM20

- Evaluated mean and standard deviation for different surface roughness values (sinusoidal interface)
  - 2 hour 950°C heat treatment
- Little benefit for $A/\lambda < 0.2$
- Benefit begins to reduce for roughness ratios $A/\lambda > 0.8$
  - Fracture through the paste layer away from the interface favored for high roughness
  - 20% improvement
  - Consistent with observations using the interconnect data set
  - Use of a textured cathode surface is preferred

![Graph showing typical densification and increase in interface strength.](https://example.com/graph.png)
Fully Sintered LSM20

- Evaluated the strength improvement assuming full densification can be ultimately achieved due to further material enhancements.
- Little benefit for $A/\lambda < 0.2$
- Greater improvement (relative to a flat interface) compared to the partially dense material: 50% improvement.
- Use of sintering aids to increase densification in stack applications should exhibit greater benefit from interface roughness.
Comparison to Generated Topologies

- Semi-quantitative estimate of the $A/\lambda$ ratio for the different topologies obtained visually
  - Average number of peaks for a given path length
- All estimated roughness ratios are $A/\lambda < 0.3$
  - Less than the value at which strengthening was incurred
- The finest particle #100 mesh had the highest $A/\lambda$ ratio but only the second highest strength
- The largest particle #35 mesh had the next highest $A/\lambda$ ratio but overall highest strength
  - May be due to particle size and propensity for interlocking
The roughened interface exhibited two failure loads:
- Initiation of delamination
- Ultimate load for full separation
- Strengthening due to local stress state and particle orientation

Enhanced sintering will help delay the initial delamination, but the ultimate load capacity was almost unchanged
- Interface was the weak link for this material set
Variation of Interface Toughness with Roughness Value Ra

- Computed roughness for random interface geometries
- Strength enhancement of LSM20 interface for Ra > 3µm

Surface Roughness Produced by Common Production Methods

<table>
<thead>
<tr>
<th>Ra (µm)</th>
<th>50</th>
<th>25</th>
<th>12.5</th>
<th>6.3</th>
<th>3.2</th>
<th>1.6</th>
<th>.8</th>
<th>.4</th>
<th>.2</th>
<th>.1</th>
<th>.05</th>
<th>.025</th>
<th>.012</th>
</tr>
</thead>
<tbody>
<tr>
<td>Source</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

source: en.wikipedia.org
Reliability
Reliability of Ceramic Components

Weibull Statistics

1a. Specimen Testing
Fracture Strength Data, Fatigue Data

1b. Fractography
Identification of volume and surface flaw populations (optional)

2a. Specimen Stress State Characterization

2b. Weibull Statistics Processing

3. Component Design & Loading

4a. Component Stress Analysis
ANSYS
Finite element analysis

4b. Component Reliability Calculations
CARES
Ceramic reliability

Possible Redesign Iteration
Specimen-independent strength data

Stresses
Stack Contact Material Sintering

- Reliability of cathode contact materials formed in-stack by constrained sintering needed to optimize the density and strength of this structural ‘weak link’
- Used continuum sintering model to predict the temperature/stress-dependent densification and residual fabrication stresses in a planar 400 cm² SOFC stack with uniform cathode contact layer
- Characterized effect of material, geometry and heat treatment parameters on the maximum densification and subsequent risk of layer failure under stack operating/shutdown conditions
Cathode Contact Materials

- Evaluated experimental data for 3 candidate contact materials
  - Diametral compression tests
- Calculated Weibull statistics
  - Assume single flaw population
  - Highest reported strength from LSC
  - LSC also had most scatter though
  - LSCF more uniform properties, so has highest scale parameter

<table>
<thead>
<tr>
<th>Material</th>
<th>Characteristic Strength (Pa)</th>
<th>Weibull Modulus</th>
<th>Scale Parameter (Pa-m$^{3/\alpha}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM20</td>
<td>3,817,690</td>
<td>4.57</td>
<td>113,052</td>
</tr>
<tr>
<td>LSC20</td>
<td>6,551,610</td>
<td>4.27</td>
<td>151,928</td>
</tr>
<tr>
<td>LSCF6428</td>
<td>6,388,830</td>
<td>4.93</td>
<td>240,953</td>
</tr>
</tbody>
</table>
Contact Material Stresses

- Stresses due to constrained sintering are small but non-zero
- Thermal stress increases during stack operation
  - Stresses increase as the cell thermal gradient increases
  - Magnitude comparable to strength of partially sintered contact materials
- Shutdown has highest stresses

<table>
<thead>
<tr>
<th>Condition</th>
<th>End of Sintering</th>
<th>Isothermal operating condition - 750°C</th>
<th>Realistic operating condition - 750°C avg</th>
<th>Shutdown Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4 MPa</td>
<td></td>
<td>1.7 MPa</td>
<td>2.5 MPa</td>
<td>16 MPa</td>
</tr>
<tr>
<td>( \Delta T = 0 )</td>
<td></td>
<td>( \Delta T = 0 )</td>
<td>( \Delta T \neq 0 )</td>
<td></td>
</tr>
</tbody>
</table>

*Graphical representation of stresses in various conditions.*

[Image of graphical representation of stresses in various conditions.]
Contact Material Reliability

- Calculated reliability based on the experimentally measured material properties for the 3 candidate materials
  - The LSM showed the lowest reliability at shutdown (29%) while the LSCF showed the highest reliability (90%)
  - Enhanced densification using sintering aids and strength improvement would still be highly advantageous

- Reliability of the electrolyte and cathode layers were also low in the generated stack design

<table>
<thead>
<tr>
<th>Loading Condition</th>
<th>Anode</th>
<th>Electrolyte</th>
<th>Cathode</th>
<th>Paste</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress Free</td>
<td>100 / 100 / 100</td>
<td>100 / 100 / 100</td>
<td>100 / 100 / 100</td>
<td>100 / 100 / 100</td>
</tr>
<tr>
<td>Compression</td>
<td>100 / 100 / 100</td>
<td>100 / 100 / 100</td>
<td>100 / 100 / 100</td>
<td>99.9 / 99.9 / 99.9</td>
</tr>
<tr>
<td>Isothermal Operation</td>
<td>100 / 100 / 100</td>
<td>96.0 / 96.0 / 96.1</td>
<td>99.0 / 99.9 / 99.9</td>
<td>99.9 / 99.8 / 99.9</td>
</tr>
<tr>
<td>Actual Operating State</td>
<td>100 / 100 / 100</td>
<td>11.2 / 11.2 / 11.2</td>
<td>29.8 / 29.8 / 29.8</td>
<td>93.1 / 99.1 / 99.6</td>
</tr>
<tr>
<td>Shutdown state</td>
<td>100 / 100 / 100</td>
<td>86.3 / 86.3 / 86.3</td>
<td>99.9 / 99.9 / 99.9</td>
<td>28.9 / 88.7 / 90.5</td>
</tr>
</tbody>
</table>

NOTE: xxx / xxx / xxx indicate the %Reliability when evaluated with LSM20/LSC20/LSCF6428 Weibull data respectively
Risk of Rupture

- The risk of rupture plots indicate the potential locations of failure initiation (cracking) within the ceramic contact material layers.
- The low reliability estimates for the contact layer and cell components arise from very localized regions due to mechanical interaction with the frame.
  - Emphasizes the extremely high importance of integrated mechanical design to avoid initiation of damage in the ceramic components.
Alternate Stack Designs

► Working with E. Lara-Curzio at Oak Ridge National Laboratory (ORNL) on alternative stack design topologies that may be able to improve the mechanical reliability of SOFC stacks

► Investigated different stack tapers in an effort to increase the velocity and convection heat transfer of planar co-flow stacks to reduce the thermal gradient at the stack outlet

► Only minor improvements due to the low flow rates and total thermal capacity of the fuel and oxidant flows

See Poster: Structural Reliability Considerations for Planar SOFCs: Cathode Contact, Cell Thermal Gradients & Alternate Geometries
SOFC Stack Modeling Tools
SOFC Stack Modeling Tools

- Last year, successfully demonstrated ROM approach to simulate stack performance in system modeling tools
  - Accuracy for key parameters and metrics of interest greater than ~98%

Based on the demonstration, several improvements were identified to improve the ROM/SOFC-MP tools and implementation:

- Application to other NG compositions
- Recirculation capability for the fuel and oxidant recycling loops
- Pressurized electrochemistry
- Use of 3D SOFC-MP models
- Calculation of the pressure drop in 2D SOFC-MP
- Variable pre-reformer fraction in the NGFC material flow balance
- Simplified Aspen Plus integration
- Application to IGFC

See Poster: Enhanced SOFC-MP Software Tool Set
ROM Creation From 3D Model

- ROM demonstration originally used SOFC-MP 2D tool
- Added ability to use detailed SOFC-MP 3D solver in the ROM tool
- Demonstrated with a large area co-flow single cell stack
- Two parameter ROM creation
  - Inlet fuel/oxidant temperature: 700-800°C
  - Cell voltage: 0.8-0.85V
Fuel/Oxidant Recirculation

- ROM integration to the NGFC system model can be improved by including the fuel and oxidant recirculation loops directly
  - Includes mixing and heat exchanger functions
  - Implemented in the 3D SOFC-MP model
- Recirculation under fixed fuel utilization and maximum cell temperature constraint provides a more uniform temperature, smaller cell thermal gradient, and more uniform current distribution
Pre-Reformer Fraction

- External pre-reformer in the fuel recycle loop controls the amount of CH₄ sent to the stack for on-cell steam reformation to control cell temperature gradient
  - Capability was added to the ROM tool and successfully tested
  - Stack hotter with more external reforming
  - Cell thermal gradient lower with more external reforming

### NGFC Material Flow

![Diagram of material flow with components including NG, reformer, stack, anode recycle loop, cathode recycle loop, std air, and separator.]

### Average Cell Temperature (°C)

- Pre-Reform Fraction
- Average Current Density (A/m²)

<table>
<thead>
<tr>
<th>Pre-Reform Fraction</th>
<th>Average Cell Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>780</td>
</tr>
<tr>
<td>0.5</td>
<td>778</td>
</tr>
<tr>
<td>1.0</td>
<td>773</td>
</tr>
</tbody>
</table>

### Cell Temperature Difference

- Chart showing temperature difference across different pre-reform fractions.
High Pressure Operation

- Pressurized cell operation needed to reduce future SOFC COE
  - Capability added to SOFC-MP/ROM tools
  - Reduction in activation and concentration losses most significant at pressures near atmospheric condition with small additional benefits beyond ~5 atm
  - For fixed fuel utilization and maximum cell temperature, high pressure operation also decreases the cell temperature gradient
Summary

- PNNL is using experimental and computational capabilities to accelerate the commercialization of SOFC power systems.
- For more information at this meeting, contact the poster presenters:
  - **SOFC Testing in Cathode Air with Quantified Cr Concentration** (John Hardy)
  - **Evaluation of Cr-Gettering Material in a Generic Stack Test Fixture** (Matt Chou)
  - **Effect on Sintering Aids on Densification and Contact Strength of SOFC** (Matt Chou)
  - **Lower Temperature RAA Process for Planar SOFC Stacks** (Jung-Pyung Choi)
  - **Enhanced SOFC-MP Software Tool Set** (Naveen Karri)
  - **Structural Reliability Considerations for Planar SOFCs** (Brian Koeppel)
The work summarized in this paper was funded by the U.S. Department of Energy’s Solid Oxide Fuel Cell Program.

- NETL: Shailesh Vora, Joseph Stoffa, Patcharin Burke, Steven Markovich, Greg Hackett, and Heather Quedenfeld
- University of Connecticut: Prabhakar Singh
- ORNL: Edgar Lara-Curzio