Development & Validation of Low-Cost, Highly-Durable, Spinel-Based Materials for SOFC Cathode-Side Contact

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Annual Solid Oxide Fuel Cell (SOFC) Project Review Presentation, 2020
Outline

• Introduction and Project Objectives

• Performance Evaluation of the Sintered Spinel Contact Thermally Converted from Pre-alloyed Precursors
  – Area Specific Resistance (ASR), Chemical Compatibility, etc.

• Initial Study on Reaction Layer Formation Kinetics/ Mechanism

• Reactive Sintering of Dense (Mn,Co)$_3$O$_4$ Coatings

• Co-sintering of Spinel-Based Coating/Contact Dual-Layer Structure between Full-sized Ferritic Alloy and LSM Plates

• Concluding Remarks

• Acknowledgments
Need of Contacting for Different SOFC Stacks

- In stacks with anode-supported cells (ASC-SOFC), the contact is required to minimize the cathode-interconnect interfacial resistance.

Cathode-Interconnect Interface in ASC SOFC Stacks

- In all-ceramic stacks, the contact is required to minimize the interfacial resistance between the current collector plate and cathode end plate.

Cathode-Current Collector Interface in All-Ceramic SOFC Stacks
Contact Material Requirements

- Requirements for contact materials in ASC-SOFC and all-ceramic SOFC stacks are generally similar, including:
  - Low material/processing cost
  - High electrical conductivity
  - Match in coefficient of thermal expansion (CTE)
  - Adequate stability and compatibility
  - Appropriate sinterability
  - Good bonding strength with adjacent stack components
  - Absence of volatile species

- Additionally, a reasonable porosity level in the cathode-side contact is needed in ASC stacks for maximizing the triple phase boundaries for cathodic reaction.
**Different Contact Materials**

- While various materials for ferritic alloy-cathode contacting have been studied, most developments have focused on \((\text{La, Sr})(\text{Mn, Co, Fe, Ni, Cu})\text{O}_3\):
  - Difficulty in balancing the electrical conductivity, CTE, sinterability and chemical compatibility of the perovskites.

<table>
<thead>
<tr>
<th>Material Type</th>
<th>Example</th>
<th>CTE (\times10^{-6}/\text{K}) (20–800°C)</th>
<th>Conductivity (\text{S}\cdot\text{cm}^{-1}, 800°C)</th>
<th>Main Concern</th>
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</thead>
<tbody>
<tr>
<td>Noble Metal</td>
<td>Pt</td>
<td>10.0</td>
<td>Metallic</td>
<td>High Cost</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>12.3</td>
<td>Metallic</td>
<td>High Cost</td>
</tr>
<tr>
<td></td>
<td>Au</td>
<td>16.6</td>
<td>Metallic</td>
<td>High Cost</td>
</tr>
<tr>
<td></td>
<td>Ag</td>
<td>22.0</td>
<td>Metallic</td>
<td>Volatility</td>
</tr>
<tr>
<td>Perovskite</td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})\text{CoO}_3) (\delta)</td>
<td>19.2 (20-1000°C)</td>
<td>1400</td>
<td>CTE Mismatch</td>
</tr>
<tr>
<td></td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})(\text{Co}<em>{0.5}\text{Fe}</em>{0.5})\text{O}_3) (\delta)</td>
<td>18.3 (20-1000°C)</td>
<td>340</td>
<td>CTE Mismatch</td>
</tr>
<tr>
<td></td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})(\text{Co}<em>{0.5}\text{Mn}</em>{0.5})\text{O}_3) (\delta)</td>
<td>15.0 (20-1000°C)</td>
<td>190</td>
<td>CTE Mismatch</td>
</tr>
<tr>
<td></td>
<td>((\text{La}<em>{0.8}\text{Sr}</em>{0.2})\text{MnO}_3)</td>
<td>11.7 (20-1000°C)</td>
<td>170</td>
<td>Sinterability</td>
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<tr>
<td></td>
<td>\text{LaMn}<em>{0.45}\text{Co}</em>{0.35}\text{Cu}_{0.2}\text{O}_3)</td>
<td>13.9</td>
<td>80</td>
<td>Mn/Cu Migration</td>
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<tr>
<td>Spinel</td>
<td>\text{MnCo}_2\text{O}_4)</td>
<td>9.7-14.4</td>
<td>24- 89</td>
<td>Sinterability</td>
</tr>
<tr>
<td></td>
<td>\text{Mn}<em>{1.5}\text{Co}</em>{1.5}\text{O}_4)</td>
<td>10.6-11.6</td>
<td>55-68</td>
<td>Sinterability</td>
</tr>
<tr>
<td></td>
<td>\text{NiCo}_2\text{O}_4)</td>
<td>12.1</td>
<td>0.93</td>
<td>Sinterability</td>
</tr>
<tr>
<td></td>
<td>\text{NiFe}_2\text{O}_4)</td>
<td>11.8</td>
<td>0.3, 6.8, 17.1</td>
<td>Sinterability</td>
</tr>
<tr>
<td></td>
<td>\text{Ni}<em>{0.85}\text{Fe}</em>{2.15}\text{O}_4)</td>
<td>12.1</td>
<td>15.4</td>
<td>Sinterability</td>
</tr>
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</table>
Why \((\text{Ni,Fe})_3\text{O}_4\)- and \((\text{Mn,Co})_3\text{O}_4\)-Based Spinels as Contact Material?

- Conductive spinels based on \((\text{Ni,Fe})_3\text{O}_4\) and \((\text{Mn,Co})_3\text{O}_4\), which have been extensively evaluated as interconnect coating, are also promising for contact application, based on electrical conductivity, CTE, chemical compatibility, etc.

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<th>Material Type</th>
<th>Example</th>
<th>CTE ((\times 10^{-6} /\text{K})) ((20-800,^\circ\text{C}))</th>
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<th>Main Concern</th>
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<tr>
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<td>(\text{MnCo}_2\text{O}_4)</td>
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<td>24- 89</td>
<td>Sinterability</td>
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<tr>
<td></td>
<td>(\text{Mn}<em>{1.5}\text{Co}</em>{1.5}\text{O}_4)</td>
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<td>12.1</td>
<td>15.4</td>
<td>Sinterability</td>
</tr>
</tbody>
</table>

- Unfortunately, the sinterability of spinels is very poor (typically \(\geq 1000\,^\circ\text{C}\)), if metal oxides are used as the starting powders.

- Employment of metallic powders (instead of oxide powders) as the starting precursor will lower the sintering temperature via a reactive sintering mechanism called \textit{environmentally-assisted reactive sintering (EARS)}. 
In EARS, with the participation of oxygen from air, the **metallic powder precursor** will be oxidized and reacted to form a well-sintered spinel at a reduced temperature (e.g., $900^\circ C$):

(b): $A_O_x + 2B_O_y + (2-\frac{1}{2}x-y)O_2(g) = AB_2O_4 + \Delta H_1$

(c): $A + 2B_O_y + (2-y)O_2(g) = AB_2O_4 + \Delta H_2$

(d) & (e): $A + 2B + 2O_2(g) = AB_2O_4 + \Delta H_3$

$\Delta H_3 > \Delta H_2 >> \Delta H_1$

Enhanced sintering via EARS is likely due to:
- Heat released during the reaction;
- Volume expansion upon conversion of metal to metal oxide;
- Formation of highly-active surface nano-oxides;
- Shorter diffusion distance when a pre-alloyed powder is employed.

Zhu et al., IJHE, 2018
Project Objectives

• **Optimization of the multi-component alloy precursor composition as contact material.** The alloy compositions will be optimized via composition screening in the \((\text{Ni},\text{Fe},\text{Co},X)\text{O}_4\) and \((\text{Mn},\text{Co},X)\text{O}_4\) system, alloy design using physical metallurgy principles, and cost considerations. The desired alloy powders will be manufactured & characterized in detail.

• **Demonstration/validation of the contact layer performance in relevant SOFC stack environments.** Long-term ASR behavior and in-stack performance of the contact layer in relevant stack operating environments, its microstructure, chemical compatibility & Cr-retaining capability will be evaluated.

• **Further cost reduction and commercialization assessment.** Approaches to further reducing the stack cost will be explored, such as co-sintering of the interconnect coating and contact layer. Cost analysis and scale-up assessment will be conducted for potential commercialization.
Compositional Design for Co-Mn Based Alloy Precursor

- Co-31.76 wt.%Mn was selected as the baseline composition, which after thermal conversion would lead to the MnCo$_2$O$_4$ spinel formation:
  - The Co-31.76 wt.%Mn alloy has the single-phase fcc structure at 900°C;
  - MnCo$_2$O$_4$ has a cubic structure at both 800 and 20°C
Compositional Design for Co-Mn Based Alloy Precursor

- Fe addition to the binary Co-Mn alloy for reducing the reaction layer growth;
- Ce doping for slowing down the Cr$_2$O$_3$ scale growth on the alloy and improving the scale adhesion via “reactive-element effect”.

The interface of (a) MnCo$_2$O$_4$ (MC)/Cr$_2$O$_3$ & (b) MnCo$_{1.7}$Fe$_{0.3}$O$_4$ (MCF)/Cr$_2$O$_3$ diffusion couple after 900°C for 300 h

### Alloy Compositions & Corresponding Spinels after Thermal Conversion

<table>
<thead>
<tr>
<th>(in wt.%)</th>
<th>Co</th>
<th>Mn</th>
<th>Fe</th>
<th>Ce</th>
<th>Spinel Composition</th>
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</thead>
<tbody>
<tr>
<td>Alloy 1</td>
<td>68.21</td>
<td>31.79</td>
<td></td>
<td>—</td>
<td>MnCo$_2$O$_4$</td>
</tr>
<tr>
<td>Alloy 2</td>
<td>64.72</td>
<td>31.80</td>
<td>3.23</td>
<td>—</td>
<td>MnCo$<em>{1.9}$Fe$</em>{0.1}$O$_4$</td>
</tr>
<tr>
<td>Alloy 3</td>
<td>64.72</td>
<td>31.77</td>
<td>3.23</td>
<td>0.41</td>
<td>MnCo$<em>{1.895}$Fe$</em>{0.1}$Ce$_{0.005}$O$_4$</td>
</tr>
</tbody>
</table>
Gas Atomization of Selected Alloys

- A number of Co-Mn based compositions were selected for the powder preparation.
- The powders with the desired composition and particle size were manufactured using a semi-industrial gas atomizer.
- Chemical analysis of the collected powders was conducted at Dirats Lab – a close match with the targeted compositions was achieved.

A lab-scale gas atomizer is currently being installed at TTU under a DoD DURIP project.
Thermal Conversion of Alloy Precursors

- Three alloy powders and a Co+MnO$_2$ mixture were used as the precursor for synthesis of the desired spinel layer.
- After screen printing, the precursor layer was sintered at 900°C for 2 h in air to convert it to the spinel layer.
- A single-phase (Mn,Co)$_3$O$_4$ (MCO) spinel layer was formed for all the precursors.
- The alloy precursors led to narrower peaks, indicating a more homogeneous composition.
The MCO layer formed with the alloy powders was more dense, compared to that with Co+MnO₂. This is a result of more volume expansion with the alloy precursor.
Area-Specific Resistance (ASR) Measurement

• A number of test cells were constructed, with the spinel-forming contact precursor layer sandwiched between the ferritic alloy Crofer 22 APU and the LSM cathode.

• The test cells were spring-loaded and heated to and held at 900°C for 2 h; after cooling down to 800°C, the cell ASR change during isothermal exposure at 800°C in air was monitored using a special 6-cell test rig.
Cell ASR with Different Metallic Contact Precursors

• The ASR for Crofer/contact/LSM cells with the alloy precursors was much lower than that with the Co+MnO$_2$ precursor over the duration of the test.

• The higher cell ASR with the Co+MnO$_2$ precursor is partially due to the higher porosities in the contact layer.

Cross Sections of Crofer/Contact/LSM cells with Different Contact Precursors

(a) Alloy 1  (b) Co+MnO$_2$

Cell ASR vs. Time at 800°C in Air
Crofer-Contact Interface: Formation of Cr$_2$O$_3$ Scale and (Mn,Co,Cr)$_3$O$_4$ Reaction Layer

- A Cr$_2$O$_3$ scale on Crofer 22 APU surface and a reaction layer (RL) between the Cr$_2$O$_3$ scale and the MCO contact were formed after testing.
- Alloy contact precursor composition had a significant effect on the thicknesses of these two layers.

Cross-sectional views of the ASR-tested cells with different contact precursors: (a) Alloy #1; (b) Alloy #2; (c) Alloy #3; and (d) Co+MnO$_2$. Images were taken near the Crofer-contact interface with the superimposed EDS line scans.
While Fe addition into the Co-Mn alloy powder had no beneficial effect on the cell electrical performance, Ce doping (in Alloy #3) led to the lowest cell ASR and ASR degradation rate as a result of slower \(\text{Cr}_2\text{O}_3\) scale/RL growth and better scale adhesion.

**Initial ASR (\(R_o\)), Final ASR after 1000-h Testing (\(R_f\)), ASR Degradation Rate during Initial 50 h (\(D\text{R}_o\)), ASR Degradation rate during Final 50 h (\(D\text{R}_f\)), and Thicknesses of the \(\text{Cr}_2\text{O}_3\) Scale and RL after ASR Testing**

<table>
<thead>
<tr>
<th></th>
<th>Alloy 1</th>
<th>Alloy 2</th>
<th>Alloy 3</th>
<th>Co+MnO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R_o) (mΩ·cm(^2))</td>
<td>1.8</td>
<td>2.2</td>
<td>2.0</td>
<td>4.6</td>
</tr>
<tr>
<td>(R_f) (mΩ·cm(^2))</td>
<td>4.0</td>
<td>4.6</td>
<td>3.1</td>
<td>7.0</td>
</tr>
<tr>
<td>(D\text{R}_o) (µΩ·cm(^2)/h)</td>
<td>3.3</td>
<td>3.5</td>
<td>1.5</td>
<td>11.1</td>
</tr>
<tr>
<td>(D\text{R}_f) (µΩ·cm(^2)/h)</td>
<td>1.4</td>
<td>1.3</td>
<td>1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>(\text{Cr}_2\text{O}_3) scale (µm)</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td>0.6</td>
</tr>
<tr>
<td>RL (µm)</td>
<td>1.4</td>
<td>2.2</td>
<td>1.4</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Effectiveness of the Contact Layer in Mitigating Cr Migration

Cross-sectional View of Tested Cells near the LSM-Contact Interface with Different Contact Precursors: (a) Alloy 1 and (b) Co+MnO₂

- Minimal interdiffusion was observed between the contact layer and cathode for all tested cells.
- No Cr was detected in the LSM cathode for the cells with the alloy contact precursors, while for the cell with the Co+MnO₂ precursor the Cr level in the porous LSM cathode fluctuated noticeably.
Preliminary Study on Reaction Layer Formation Kinetics/Mechanism

Since a RL was formed between the MCO layer and the Cr$_2$O$_3$ scale, it is critical to study the effect of the MCO stoichiometry and additional doping on the LR formation kinetics/mechanism:

- Contacting faces of MCO/Cr$_2$O$_3$ pellets were ground to 800-grit;
- Pt particles were applied to contacting face of MCO pellet to mark the original interface;
- The couple was loaded into a vertical furnace and then diffusion annealed at 900°C for different times,
- The annealed couples were cross-sectioned and examined with SEM/EDS.
A minimum in RL thickness was observed when $x = 1.2$ in Mn$_x$Co$_{3-x}$O$_4$.

Pt marks were always observed near the MCO/RL interface, indicating the RL formation was via Co/Mn diffusion into Cr$_2$O$_3$.

The RL growth kinetics is being determined.
EARS Processing of Dense MCO Coatings

- Reactive sintering of a dense MCO coating via EARS has been explored and promising results were obtained:
  - By controlling the composition/shape/size/size distribution/initial packing density of the metallic precursor powders, a dense spinel layer was obtained after thermal conversion at 900°C for 2 h in air.

- The EARS-derived coating does not require a reduction treatment or a sintering temperature higher than 900°C, and potentially offers a better MCO coating quality.
By optimizing the metallic spinel-forming precursor and thermal conversion conditions, a dense MCO coating was achieved, which was quite uniform in thickness and density throughout the alloy plate surfaces.

The overall quality of the coating on the full-size alloy plate was comparable to that achieved on the small coupons.
Co-sintering of Coating/Contact Dual-Layer Structure: Further Cost Reduction and Performance Improvement

• To lower the interfacial ASR at the alloy/contact interface, improve the contact quality, and reduce the coating and contact processing cost, co-sintering of the coating and the contact layer during initial stack firing/operation is also explored, utilizing two different metallic precursors:
  
  – Two spinel-forming precursors (Type #1 – for the contact layer and Type #2 – for the dense MCO coating) will be employed;
  
  – Reactive co-sintering in air at a sintering temperature of 900°C will be utilized for simultaneous formation of the dual-layer structure.
Co-sintering of Coating/Contact Layers between Full-Size Ferritic ZMG 232G10 Alloy and LSM Plates

- Using full-sized alloy and LSM plates supplied by our industrial collaborator, a full-size alloy/coating/contact/LSM assembly with two metallic precursors for the coating and contact layer formation was prepared by co-sintering at 900°C.

✓ A dense coating and a porous contact layer between the ZMG alloy and LSM plates were achieved after co-sintering, via the utilization of two individually-optimized metallic precursors.

✓ The thicknesses of the coating and the contact layer were 10-15 and 100-120 µm, respectively.

✓ ASR testing of the sintered assembly is underway.
# Project Milestones

<table>
<thead>
<tr>
<th>Milestone Title/Description</th>
<th>Planned Start Date</th>
<th>Planned Completion Date</th>
<th>Actual Completion Date</th>
<th>Verification Method</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Revised PMP</td>
<td>10/10/2017</td>
<td>10/30/2017</td>
<td>10/23/2017</td>
<td>PMP file</td>
<td>Completed</td>
</tr>
<tr>
<td>Kickoff Meeting</td>
<td>10/30/2017</td>
<td>12/29/2017</td>
<td>11/29/2017</td>
<td>Presentation file</td>
<td>Completed</td>
</tr>
<tr>
<td>Compositional optimization of Precursor alloy</td>
<td>11/01/2017</td>
<td>06/30/2018</td>
<td>06/28/2018</td>
<td>Optimal Fe/Ni/Co and other alloy additions are identified.</td>
<td>Completed</td>
</tr>
<tr>
<td>Preparation of the alloy powder</td>
<td>11/15/2017</td>
<td>09/31/2018</td>
<td>09/20/2018</td>
<td>Atomization of one alloy powder is completed.</td>
<td>Completed</td>
</tr>
<tr>
<td>Demonstration of ASR stability with the new contact</td>
<td>01/01/2018</td>
<td>06/30/2019</td>
<td>02/20/2019</td>
<td>The ASR stability is demonstrated successfully for about 5,000 h.</td>
<td>Completed</td>
</tr>
<tr>
<td>Demonstration of stack performance stability with 1-cell stack testing</td>
<td>04/02/2018</td>
<td>09/30/2019</td>
<td>09/27/2019</td>
<td>Stack performance stability testing for $\geq$ 1,000 h is completed at industrial site.</td>
<td>Completed</td>
</tr>
<tr>
<td>Synthesis of dense coating on full-size current collector</td>
<td>10/20/2019</td>
<td>02/29/2020</td>
<td>12/25/2019</td>
<td>Dense coating on full-size current collector plate is achieved.</td>
<td>Completed</td>
</tr>
<tr>
<td>In-stack evaluation with co-sintered coating/contact structure</td>
<td>01/20/2020</td>
<td>08/20/2020</td>
<td></td>
<td>Stack power output stability testing for over 500 h is completed at Saint Gobain.</td>
<td>In progress</td>
</tr>
<tr>
<td>Cost analysis and feasibility assess.</td>
<td>06/30/2020</td>
<td>09/30/2020</td>
<td></td>
<td>Cost analysis and scale-up assessment are completed.</td>
<td>No started</td>
</tr>
</tbody>
</table>
Concluding Remarks

- The spinel contact-forming alloy precursor composition had a significant effect on the Cr$_2$O$_3$ scale thickness/quality, reaction layer thickness between the spinel and Cr$_2$O$_3$, and cell ASR.

- The MCO spinel stoichiometry drastically affected the thickness of the reaction layer formed between MCO and Cr$_2$O$_3$, with the Mn$_{1.2}$Co$_{1.8}$O$_4$ spinel leading to the thinnest reaction layer.

- By controlling the metallic precursor powder composition, size, size distribution, and initial powder packing density, a dense MCO coating has been synthesized on large-size ferritic alloy plate.

- Co-sintering of a dual-layer structure with a dense spinel layer as coating and a porous layer as contact can be achieved by utilizing two tailored metallic precursors between large-size alloy and LSM plates.
Acknowledgments

• U. S. Department of Energy - National Energy Technology Laboratory, Solid Oxide Fuel Cell Prototype System Testing and Core Technology Development Program, Award No. DE-FE0031187; Project Manager: Dr. Patcharin Burke

• Allen Yu, Jacob Hayes, David Chesson, and Brian Bates, TTU

• Dr. Hossein Ghezel-Ayagh, FuelCell Energy, Inc.

• Dr. John Pietras and his team at Saint Gobain