Electrodeposited Mn-Co Alloy Coating for SOFC Interconnects

H.A. McCrabb¹, B. Kagajwala¹ T.D. Hall¹, H. Zhang², X. Liu², S. Snyder¹ E.J. Taylor¹

¹Faraday Technology, Inc. 315 Huls Dr., Clayton, OH 45315
²West Virginia University, Dept. of Mechanical Aerospace Eng. ESB, Morgantown, WV 26506

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July 25, 2012
Faraday Technology, Inc.

- Faraday Technology specializes in electrochemical engineering
  - www.faradaytechnology.com
- Faraday is a wholly-owned subsidiary of Physical Sciences, Inc. (Boston, MA)
  - www.psicorp.com
- Collectively, the company staffs ~185 employees - ~100 with PhDs
- Annual revenue of ~ $50M
**Faraday Technology, Inc.**

**Platform Technology:**
- Pulse/Pulse Reverse Processing

**Core Competency:**
- Design and Engineer of Novel Electrochemical Hardware

**Total Manufacturing Solution**

- Enables uniform processing
- Applicable for additive or subtractive electrochemical processes
- Uniform processing is achieved over entire substrate, improving end product reliability

**Total Manufacturing Solution**

- Either may be applied independently to improve current industrial practices or may be combined for a total manufacturing solution

**Services**
- Electronics
- Edge and Surface Finishing
- Engineered Coatings
- Battery and Fuel Cell Power
- Environmental Systems
- Corrosion and Monitoring Services
Achievements

- Continued optimization of FARADAYIC℠ Electrodeposition Process parameters in order to optimize coating thickness, coating composition and coating adhesion
- Improved coating uniformity across T441 planar interconnects at the 100 cm² scale
- Demonstrated coating process for 25 cm² 430 stainless steel interconnect containing gas flow fields
- Continued refinement of economic analysis to assess economic viability of FARADAYIC℠ Electrodeposition Process for high volume batch manufacturing
**Conventional (DC) Electrodeposition**

- Fast deposition rates
- Simple deposition equipment
- Non-line-of-sight deposition
- Industrially scalable

**FARADAYIC\textsuperscript{SM} Process**

- Improved electric field control
  - Enhanced control of coating thickness uniformity
  - Enhanced control of alloy composition
- Improved coating of “hidden surfaces”

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Coating Process

• Surface pretreatment to remove oxide and enhance coating adhesion

• Electrodeposition to coat interconnects with Mn-Co alloy
  – Pulse and pulse reverse electric fields to control deposit properties

• Elevated thermal treatment to convert alloy to spinel
Phase I Hull Cell Experiments

Enables investigation into the effect of various parameters on deposit properties during a single experiment

- Current density
- Temperature
- Electrolyte composition
- Additives
Phase I Hull Cell Experiments

Electrolyte with NaC$_6$H$_{11}$O$_7$

- Electrolyte without NaC$_6$H$_{11}$O$_7$ was selected for Phase I work on 5 cm x 5 cm T441 planar substrates because at reasonable current densities and metal ion concentrations results suggested
  - Potential for higher Mn content in coating
  - Less microcracking
  - Higher current efficiency
  - Faster coating deposition rates
Phase I Cr Diffusion and Coating Porosity

- Cross-sections of samples that underwent a soak treatment at 800°C for 500 hrs.
  - Coating thickness was as deposited
  - Indicates that the 3 micron layer has low Cr diffusion and the 10 micron coating has negligible Cr diffusion into coating
  - 3 micron coating appears more porous than 7 and 10 micron film
Phase I Coating Crystal Structure

Crystal Structure after 500 hrs. at 800 °C

40%Co 3µm
40%Co 7µm
40%Co 10µm

2 theta (degrees)
Intensity (a.u.)
Phase I Effect of Thickness and Composition on Performance

The ASR is $\leq 60 \text{ m}\Omega \text{ cm}^2$ in most cases regardless of compositions and thickness after 500 hrs. at 800°C

<table>
<thead>
<tr>
<th>Thickness (μm)</th>
<th>Composition</th>
<th>100 hr</th>
<th>500 hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>40% Co</td>
<td>35</td>
<td>49</td>
</tr>
<tr>
<td>7</td>
<td>40% Co</td>
<td>62</td>
<td>32</td>
</tr>
<tr>
<td>10</td>
<td>40% Co</td>
<td>22</td>
<td>36</td>
</tr>
<tr>
<td>3</td>
<td>85% Co</td>
<td>31</td>
<td>20</td>
</tr>
<tr>
<td>7</td>
<td>85% Co</td>
<td>59</td>
<td>54</td>
</tr>
<tr>
<td>10</td>
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<td>37</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>57% Co</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>57% Co</td>
<td>-</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>57% Co</td>
<td>-</td>
<td>12</td>
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</tbody>
</table>
### Phase III Program Management Plan

#### Milestones

<table>
<thead>
<tr>
<th>Fiscal Year</th>
<th>Title</th>
<th>Planned Completion</th>
<th>Percent Complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>1. Design/modification of 10” x 10” electrodeposition cell</td>
<td>May 2011</td>
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</tr>
<tr>
<td>2012</td>
<td>2. Long-term high temperature, thermal evaluation</td>
<td>August 2012</td>
<td>70%</td>
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<tr>
<td>2012</td>
<td>3. Process development for 4”x4” planar interconnects</td>
<td>May 2012</td>
<td>100%</td>
</tr>
<tr>
<td>2012</td>
<td>4. Process development for 4”x4” pattern interconnects</td>
<td>June 2012</td>
<td>10%</td>
</tr>
<tr>
<td>2012</td>
<td>5. Long-term on-cell performance evaluation</td>
<td>August 2012</td>
<td>10%</td>
</tr>
<tr>
<td>2012</td>
<td>6. Qualification/demonstration of IC in single cell test rig</td>
<td>September 2012</td>
<td>0%</td>
</tr>
</tbody>
</table>

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Based upon Faraday’s electrochemical cell design that facilitates uniform flow across the surface of a flat substrate (US patent #7,553,401)
Pilot Scale Experiments

- After several tests, issues were noticed with coatings
  - Non-uniform current density on front and back of sample during plating
    - Poor chemical composition control
    - Coating thickness non-uniformity
    - Poor coating adhesion
- Anodes removed from system
  - Mn fouling
    - High surface resistivity
      - In the megaohm range after only a few tests
    - Can be removed with 30% (v/v) sulfuric acid
Addition of NaC$_6$H$_{11}$O$_7$ to electrolyte

- Observed benefits
  - Boric acid dissolves completely
  - Complexing metal ions prevents hydroxide formation
  - Improved buffer capacity
  - Anode fouling eliminated
  - Improved coating adhesion in as-deposited state
  - Coating deposition rate appears linear
  - Maintain coating thickness upon spinel conversion

~ 20 μm coating

~ 21 μm coating

~3 μm Cr$_2$O$_3$
Varying Coating Thickness

~ 10 μm coating
~ 2 μm Cr\(_2\)O\(_3\)

~ 21 μm coating
~ 3 μm Cr\(_2\)O\(_3\)

~ 33 μm coating
~ 3 μm Cr\(_2\)O\(_3\)
Varying Cobalt Concentration

- 4:1 Co:Mn
  - ~ 10 µm coating
  - ~ 2 µm Cr$_2$O$_3$

- 6:1 Co:Mn
  - ~ 13 µm coating
  - ~ 4 µm Cr$_2$O$_3$

- 20:1 Co:Mn
  - ~ 8 µm coating
  - ~ 4 µm Cr$_2$O$_3$

- Negligible Cr diffusion
- Fairly significant Fe diffusion
- Minor Cr diffusion
- Some Fe diffusion
- Minor Cr diffusion
- Minor Fe diffusion
- Negligible Cr diffusion
- Fairly significant Fe diffusion
750 Hour Thermal Soak at 800 °C

2 hr. thermal treatment in air atm prior to thermal soak

After 750 hr. thermal soak

2 hr. thermal treatment in H₂ atm prior to thermal soak

After 750 hr. thermal soak
750 Hour Thermal Soak at 800 °C

2 hr. thermal treatment in air atm prior to thermal soak

2 hr. thermal treatment in H₂ atm prior to thermal soak
750 Hour Thermal Soak Testing

The ASR is ≤ 20 mΩ cm² after 750 hrs. at 800 °C

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Thickness (μm)</th>
<th>Atomic%</th>
<th>ASR (mΩ·cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Co</td>
<td>Mn</td>
</tr>
<tr>
<td>H₂ atm exposure for 2 hours followed by thermal soak for 750 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1132</td>
<td>7.5</td>
<td>89</td>
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<td>1136</td>
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<tr>
<td>Air atm exposure for 2 hours followed by thermal soak for 750 h</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1133</td>
<td>12</td>
<td>85</td>
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<tr>
<td>1135</td>
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</tr>
<tr>
<td>1137</td>
<td>14</td>
<td>85</td>
<td>15</td>
</tr>
</tbody>
</table>
750 Hour Thermal Soak

800 °C

850 °C

800 C

850 C

1137

SE1 1123D

5 µm

Electron Image 1

C, O, Al, Cr, Mn, Fe, Co

0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36

Distance (microns)
Process Scale-up from 25 cm² to 100 cm²

Coating thickness and compositional uniformity at the 100 cm² scale
- 6:1 Co:Mn
- ~12 μm coating
- ~4 μm Cr₂O₃ scale

As-deposited
MnCo coating

Post-thermal treatment
MnCo coating

T441 substrate

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Process Scale-up from 25 cm² to 100 cm²

B

MnCo coating

T441 substrate

A

MnCo coating

T441 substrate

Counts
Distance (microns)

C K O K AlK CrK MnK FeK CoK
25 cm² 430 Stainless Steel Interconnect With Gas Flow Fields

- 3 channel serpentine pattern
- Channel width ~ 0.9 mm
- Rib width ~ 0.8 mm
- Channel depth ~ 0.45 mm
25 cm² 430 SS Interconnect With Gas Flow Fields

Top left of channel

Bottom left of channel
25 cm² 430 SS Interconnect With Gas Flow Fields

Bottom of channel

Bottom right of channel
Future Work

• Complete thermal soak to 2000 hours for existing samples
• Development, optimization and validation of the FARADAYIC\textsuperscript{SM} Electrodeposition Process for 100 cm\textsuperscript{2} interconnects with gas flow field features
• Long-term on-cell performance evaluation of button cells
• Qualification/Demonstration of Interconnect Coating in Single Cell Test Rig under ideal SOFC operating conditions by potential commercial partners
• Continued development of a more comprehensive economic assessment of the electrodeposition coating process as it relates to interconnect manufacturing.
Acknowledgments

• Briggs White and the entire NETL SECA team

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• Contact Information:
  Heather McCrabb
  Ph: 937-836-7749
  Email: heathermccrabb@faradaytechnology.com