High throughput, in-line coating metrology development for SOFC manufacturing (DE-FE0031178) – 24 month program

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Redox Power Systems, LLC, College Park, MD

Project Partner:
Mike Ulsh and Peter Rupnowski
NREL, Golden, CO

11/30/2017
Introduction to Redox Project Team

- **Sean Bishop (PI), Sr. Materials Engineer**
  - Expertise in materials characterization, processing, design and defect modeling
  - Expertise in thin film coatings and characterization
  - Project management experience for large R&D groups at MIT and Kyushu University (Japan) focused on SOFC and related materials characterization and development

- **Bryan Blackburn, CTO**
  - Expertise in SOFC materials /stack / reformer development, design/test of electrical and mechanical systems, and manufacturing
  - Currently PI on 3 large Dept. of Energy SOFC projects (NETL, ARPA-E)
  - Project management experience leading teams of dozens of engineers working on materials, subsystems, and systems development

- **Thomas Langdo, VP of R&D**
  - Expertise in the design, fabrication, and manufacturing of advanced materials, solid state devices, and microelectronics
  - Expertise in SOFC materials scale-up, techno-economic analyses, and stack development
Introduction to Partner

National Renewable Energy Laboratory (NREL)
• Mike Ulsh, Sr. Engineer and Fuel Cell Manufacturing Project Lead
  • Expertise in evaluating and developing diagnostics for in-line quality control for manufacturing of fuel cell component materials
  • Expertise in studying impact of manufacturing defects on durability and performance of components
  • Interacts with industry on understanding and addressing barriers to high-volume production of fuel cell materials and systems
• Peter Rupnowski, Materials Scientist
  • Expertise in manufacturing level metrology techniques for SOFCs, polymer electrolyte fuel cells, and solar cells
Relevance: Project Objectives

- **Purpose:** Lower cost and increase lifetime of SOFC stacks using high throughput, in-line, early defect detection techniques on protective interconnect coatings.

- **Objectives:**
  
  - *Identify key interconnect coating and substrate defects that lead to coating failure through the use of detailed characterization methods (e.g., microscopy, XRD, EDS, electrochemistry);*
  
  - *Assess capabilities of in-line metrology techniques, e.g., optical profilometry (Redox) and thermography (NREL), to probe these defects, or evidence thereof;*
  
  - *Demonstrate long-term performance of short stacks (1 to 3 cells) using coated interconnect having a low defect count, as identified by in-line metrology.*
Schematic of Objectives

1. ID key defects & metrology tools
2. Controlled process variation → seed defects
3. In-line Metrology
4. Coated sample test and detailed post-test analysis
5. Demonstrate technique in SOFCs
6. Fabricate full-size coated interconnects
7. Optimized In-line Metrology
8. SOFC testing & post-test analysis

Fast, automated, reliable, and non-destructive metrology!
The SOFC Interconnect

- Transfers current from cathode to anode
- Dense gas barrier between anode and cathode compartments
- May serve as a gas distribution layer
- High temperature stability typically requires use of Cr containing alloys (e.g., stainless steel and Crofer)
Role of the Interconnect Coating

Protective coating applied to the interconnect surface:
• Barrier to Cr transport from the interconnect to the electrode (prevent cathode poisoning)
• Barrier of inward oxygen migration to the interconnect (block resistive oxide film growth)

\[(\text{Mn,Co})\text{O}_4 \text{ (MCO) is a commonly used barrier coating layer}\]

Defects in coating (e.g., porosity, cracks) inhibit coating and SOFC performance
Cell Performance Degradation depends on Interconnect Coating Quality

(a) No Coating
(b) Commercial (Fiaxell) CuMn$_2$O$_4$ Spinel Coating
(c) BU CuMn$_{1.8}$O$_4$ Spinel Coating

Cell Performance (Potential at 0.5 A/cm$^2$) as a Function of Time:

- No observable degradation
- Degradation after Cr gettering capacity of coating exhausted
- Degradation was observed from the beginning

S. Gopalan, 18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting, June 2017, Pittsburgh, PA
### Key Coating Defects

<table>
<thead>
<tr>
<th>Defect</th>
<th>Impact on SOFC</th>
<th>Severity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Through thickness crack</td>
<td>Cr induced degradation</td>
<td>High</td>
</tr>
<tr>
<td>Delamination</td>
<td>Increased coating resistance</td>
<td>High</td>
</tr>
<tr>
<td>Spallation</td>
<td>Increased coating resistance and Cr induced degradation</td>
<td>High</td>
</tr>
<tr>
<td>Coating porosity</td>
<td>Increased coating resistance, decreased coating mech. integrity</td>
<td>Low-Medium</td>
</tr>
<tr>
<td>Coating-substrate interface porosity</td>
<td>Increased coating resistance, increased delamination risk</td>
<td>Medium</td>
</tr>
<tr>
<td>Inhomogeneous or out-of-spec. coating thickness</td>
<td>Non-uniform current distribution (hot spots), high coating resistance, and/or non-uniform layer stress</td>
<td>Low-Medium</td>
</tr>
<tr>
<td>Inhomogenous or incorrect coating composition</td>
<td>Incorrect electrical, mechanical, and materials compatibility properties</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Many defects exist
- Level of their impact on cell performance not well documented
- High throughput defect detection techniques not characterized or well-developed
# Coating Qualification State of the Art

<table>
<thead>
<tr>
<th>Technique</th>
<th>Measured parameter</th>
<th>Automation for interconnect</th>
<th>Speed for large area scan</th>
<th>Non-destructive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape peel test</td>
<td>Film adhesion</td>
<td>Yes</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>Mass</td>
<td>Film thickness</td>
<td>Yes</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>Scratch test</td>
<td>Film adhesion</td>
<td>Yes</td>
<td>Slow</td>
<td>Yes</td>
</tr>
<tr>
<td>SEM/EDS/TEM</td>
<td>Cracks, pores, film uniformity, subsurface defects/composition</td>
<td>No</td>
<td>Slow</td>
<td>No</td>
</tr>
<tr>
<td>XRF</td>
<td>Composition</td>
<td>Yes</td>
<td>Slow-Medium</td>
<td>Yes</td>
</tr>
<tr>
<td>Indentation</td>
<td>Mechanical properties</td>
<td>Yes</td>
<td>Slow</td>
<td>Possibly</td>
</tr>
<tr>
<td>Ellipsometry</td>
<td>Film thickness</td>
<td>No, requires uniform substrate</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>X-ray tomography</td>
<td>Microstructure</td>
<td>Yes</td>
<td>Slow</td>
<td>Yes</td>
</tr>
<tr>
<td>X-ray diffraction</td>
<td>Composition</td>
<td>Yes</td>
<td>Slow</td>
<td>Yes</td>
</tr>
<tr>
<td>Raman Spectroscopy</td>
<td>Local atomic arrangement</td>
<td>Yes</td>
<td>Slow</td>
<td>Yes</td>
</tr>
</tbody>
</table>

- Fast techniques yield only limited information (only rough estimate of coating thickness and adhesion)
- Other common measurements are labor intensive, destructive, and typically only evaluate a small part of the specimen
- Less common measurements are too slow for rapid evaluation or only for featureless substrates
## Redox Approach

<table>
<thead>
<tr>
<th>Technique</th>
<th>Measured parameter</th>
<th>Automation interconnect</th>
<th>Speed for large area scan</th>
<th>Non-destructive</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical Profilometry</td>
<td>Cracks, pores, film uniformity</td>
<td>Yes</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>Optical Reflectance</td>
<td>Cracks, pores, film uniformity</td>
<td>Yes</td>
<td>Fast</td>
<td>Yes</td>
</tr>
<tr>
<td>Thermography</td>
<td>Cracks, pores, film uniformity, subsurface defects</td>
<td>Yes</td>
<td>Fast</td>
<td>Yes</td>
</tr>
</tbody>
</table>

High-throughput, in-line techniques for manufacturing-scale defect identification
Coating Fabrication at Redox

- Sprayed MCO coatings followed by standard annealing methods (reducing atmosphere followed by oxidation to achieve, dense oxide coating)

- Obtain commercial coatings for comparison (e.g., Fiaxell)
1. Identify key interconnect coating and substrate defects that lead to coating failure through the use of detailed characterization methods (e.g., microscopy, XRD, EDS, electrochemistry);

2. Assess capabilities of in-line metrology techniques, e.g., optical profilometry (Redox) and thermography (NREL), to probe these defects, or evidence thereof;

3. Demonstrate long-term performance of short stacks (1 to 3 cells) using coated interconnect having a low defect count, as identified by in-line metrology.
1. Identify Key Interconnect Coating and Substrate Defects

- Deposition of coatings on interconnect test coupons and full-size (~10 cm x 10 cm) interconnects.
- Procurement of commercially coated substrates for tests and benchmarking of Redox coatings.
- ASR Testing of coupons in SOFC-like environments (e.g., annealing in air at 650 °C)
- Detailed post-test characterization of coatings, including morphology and compositional characterization with SEM and EDS of cross-sections and phase purity with XRD
- Intentional introduction of defects (e.g., cracks, porosity) in coatings by control of processing parameters (e.g., deposition rate, particle fraction, temperature of thermal treatment).
- Identification of key coating-related defects that lead to degradation of SOFC performance (e.g., increase in coating resistance, Cr contamination of cathode).
1. Coating Evaluation at Redox

- Optical profilometry at Redox
- SEM, EDS, and XRD available to Redox through UMD
1. Optical Profile of Coated Interconnect

Develop methods to rapidly identify defective coatings
1. Coating Electrical Evaluation


Setup at Redox to evaluate area-specific-resistance (ASR)
2. Assess Capabilities of In-Line Metrology Techniques

- Evaluation of high throughput optical profilometry techniques at Redox, and optical and thermography techniques at NREL to identify inhomogeneities (i.e., defects) in interconnect test coupons before and after coating.
- Optimization of in-line metrology (e.g., down-select available techniques, improve data analysis methods, optimize metrology hardware parameters) to demonstrate that key coating-related defects or evidence of their existence can be identified.
- Screening MCO coated full-sized interconnects for key defects with in-line metrology techniques to identify defect-free and defective components.
2. In-Line Metrology at NREL

Thermography at NREL

(a) in-plane measurement of a crack on the surface of a GDL, (b) through-plane measurement of shorts in a PEM cell caused by GDL fibers penetrating the membrane during hot-pressing, (c) electrical short identified as hot spot in a tubular SOFC.

Optical Diagnostic Platform at NREL

(a) electrolyte-layer scratch in a fired planar SOFC sub-assembly, (b) electrolyte-layer flaws in a tube SOFC cell.

And macroscope at Redox
3. Long-Term Performance of Short Stacks with Low Defect Interconnect Coatings

Demonstration that optimized in-line metrology methodology can successfully detect coating-related defects in full-size interconnects and extend operational lifetime of SOFC stacks.
Project Schedule

Task 1.0: Project Management and Planning
- Subtask 1.0

Task 2.0: Coating Fabrication and Testing
- Subtask 2.1: Fabricate MCO coating with hand-spray method
- Subtask 2.2: Build automated coater
- Subtask 2.3: Fabricate MCO coatings with automated coater
- Subtask 2.5: Relate key defects with testable parameters in coated test specimens
- Subtask 2.6: Evaluate SOFC performance with coated interconnects

Task 3.0: Coating Metrology Development
- Subtask 3.1: Evaluate metrology techniques to identify defects of interest in as prepared and commercial coatings
- Subtask 3.2: Develop in-line coating metrology techniques
- Subtask 3.3: Identify key defects in coatings leading to poor SOFC initial and long-term performance

Milestone 1.1
Milestone 2.1
Milestone 3.1
Milestone 2.2
Milestone 2.3
Milestone 3.2
Milestone 3.3

Key Dates:
- 10/31
- 3/30
- 6/29
- 12/31
- 3/29
- 6/28
- 9/26
<table>
<thead>
<tr>
<th>Milestone</th>
<th>Project Accomplishment</th>
<th>Due</th>
<th>Success Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Hold a kick-off meeting with NREL and Redox</td>
<td>Q1 (12/17)</td>
<td>Review overall project plan and scope. Formulate more detailed near term plan.</td>
</tr>
<tr>
<td>2.1</td>
<td>Demonstrate uniform coatings achievable with automated coater</td>
<td>Q2 (3/18)</td>
<td>Fabricated automated coater system, demonstration of uniform coatings with SEM.</td>
</tr>
<tr>
<td>2.2</td>
<td>Demonstrate high stability and low ASR with low defect (determined by in-line metrology) interconnect samples</td>
<td>Q5 (12/18)</td>
<td>Demonstrate ASR of &lt; 0.05 ohm-cm² at 650 °C for 1,000 hours</td>
</tr>
<tr>
<td>2.3</td>
<td>Demonstrate that low defect coatings on interconnects (screened using in-line metrology) have low volatilization of chromium</td>
<td>Q6 (3/19)</td>
<td>Demonstrate Cr volatization at 650 °C for 1,000 hours as detected using Cr-getter material is &lt; 5 at% increase above baseline.</td>
</tr>
<tr>
<td>3.1</td>
<td>Use in-line metrology to identify initial key defects of interest</td>
<td>Q3 (6/18)</td>
<td>Demonstrate capability to identify initial key defects of interest with in-line metrology</td>
</tr>
<tr>
<td>3.2</td>
<td>Demonstrate capability to identify as determined in this program key defects of interest with in-line metrology</td>
<td>Q7 (6/19)</td>
<td>Down-selection of initial key defects of interest to defects demonstrated to increase ASR or Cr volatility. Identification of these defects with in-line metrology.</td>
</tr>
<tr>
<td>3.3</td>
<td>Demonstrate low cell power degradation per 1,000 hours of low-defect interconnects in SOFCs</td>
<td>Q8 (9/19)</td>
<td>Demonstrate &lt; 0.4% cell power degradation per 1,000 hours of low-defect interconnects used in SOFC short stack (1 to 3 cells) test at a single fixed load at 650 °C</td>
</tr>
</tbody>
</table>
## Risk Management

<table>
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</thead>
<tbody>
<tr>
<td><strong>Technical Risks:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cannot detect defects with in-line metrology</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Multiple in-line metrology studies are being evaluated. Experts in metrology are subcontracted in the program.</td>
</tr>
<tr>
<td>Automated coater does not provide uniform coatings</td>
<td>Medium</td>
<td>High</td>
<td>Medium</td>
<td>Redox has previously demonstrated ability to achieve uniform, dense coatings. A range of processing conditions will be utilized to optimize coating process, but will extend time for task.</td>
</tr>
<tr>
<td>ASR and Cr volatility may be excessive</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Excessive Cr volatility and ASR may be corrected through coating optimization. Despite issue, does not take away from key outcome of project: identification of defects.</td>
</tr>
<tr>
<td>SOFC cell and stack may degrade too fast</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
<td>Degradation related to Cr will be alleviated as performed in above risk. Despite issue, does not take away from key outcome of project: identification of defects.</td>
</tr>
</tbody>
</table>