Advanced SOFC Development at Redox Power Systems

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1. High power, low cost solid oxide fuel cell (SOFC) stacks for robust and reliable distributed generation

2. Red-ox robust SOFC stacks for affordable, reliable distributed generation power systems

3. High throughput, in-line coating metrology development for SOFC manufacturing

4. Sputtered thin films for very high power, efficient, and low-cost commercial SOFCs
1. High Power SOFC Stacks

- We are currently working towards a 2.5 kW stack demo
- Two “lab reformers” qualified for > 2.5 kW
Natural Gas Test Facility (NGTF)

- Moved into new demo facility in early 2019 that is 3x larger than previous location
- Will allow additional stack and system testing
- Large natural gas feed capacity for a larger gas-powered reformer capable of supporting 5-6 kWe stacks and bringing the total reforming capacity to >15 kWe.
- Light manufacturing and engineering space as well
2. Red-ox Robust Stacks

Red-ox cycles can be expected during long-term fuel cell operation

- Interruptions in fuel supply
- Transient SOFC operation (e.g., shutdown)

*Ni-cermet anodes prone to mechanical failure during redox cycling*

~69 vol% expansion of Ni → NiO

Solution:

*All ceramic anode* → small Δoxygen = small dimensional change (0.4 vol%)

No cracks after 9 redox cycles!
• High power densities
  • ~0.75 W/cm² @ 550°C
  • ~0.3 W/cm² @ 450 °C
• Acceptable electronic conductivity
Before Redox cycling

10 cm x 10 cm stack - cycling between hydrogen and nitrogen at 600 °C

• Some degradation in performance after red-ox cycling
• Previous 5 cm x 5 cm tests showed 3 red-ox cycles with minimal ASR, OCV, and seal degradation, but more cycles led to degradation
• Future work includes continued anode structure modification
Redox can Cycle!
Cost from failures on multiple installations

- Initial deployment and stack replacements largest cost components in initial model
- Stack replacements include failure due to “critical events”
- Future work includes improving estimates of MTTFs, costs, and model utility
Discrete Event Simulator

Comparison of a back-up fuel gas system (standard system) and a red-ox tolerant system

- Largest cost in lifetime ownership from replacing stacks every time gas emergency shut-down occurs (even though they are fairly rare)
- Red-ox tolerance or gas back-up system dramatically reduces lifetime cost

Manuscript in prep.
3. Metrology for SOFC Coating Manufacture

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)

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

Defects in coating (e.g., porosity, cracks) inhibit coating and SOFC performance
## Key Defects of Interest Rating

<table>
<thead>
<tr>
<th>Defect</th>
<th>Challenges it presents</th>
<th>Likelihood of occurrence (1-5)</th>
<th>Severity (1-5)</th>
<th>Level of focus (1-5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface dips and/or bumps</td>
<td>Could be high ASR spots, Cr volatility</td>
<td>5</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Thickness non-uniformity, &gt;50%</td>
<td>Large gradients --&gt; variations in ASR and ability to block Cr transport, (growth of Cr oxide layer -&gt; ASR)</td>
<td>4</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Sample-to-sample loading variations</td>
<td>Similar to thickness non-uniformity above (measurable by mass gain)</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Variations in film porosity</td>
<td>Same as above</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Film delamination (initial)</td>
<td>Huge ASR, Increase in Cr volatility</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Film delamination (during operation)</td>
<td>Huge increase in ASR, Increase in Cr volatility</td>
<td>1</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Small Roughness, bumps, dips, scratches in substrate</td>
<td>possible non-uniform coatings</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Large roughness/defects in substrate</td>
<td>non-uniform coating</td>
<td>1</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Small scratches in film due to handling</td>
<td>breaches in film (most likely to occur in green film)</td>
<td>2</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>mud-cracks in film</td>
<td>breaches in film</td>
<td>2</td>
<td>4</td>
<td>3</td>
</tr>
</tbody>
</table>
Metrology of Key Defects Approach

Measurement methods
• Optical microscopy
• Optical profilometry
• Thermography

Optical profilometry capabilities at Redox (Keyence VR and VHX)

Thermography in collaboration with NREL
Derek Jacobsen, Peter Rupnowski, Brian Green, and Michael Ulsh
Coating Fabrication at Redox

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

*SEM cross-section of an MCO coating on stainless steel developed at Redox*
Optical imaging detects porosity and thin intentional defects

- Stainless steel substrate with intentionally added porosity or thin coating deposition
- Optical imaging detects more inhomogeneities in thin as compared to “defect-free” coating
- Optical profile detects roughness change of porous > ”defect-free” > thin coatings

Optical microscopy (grid is an image stitching artifact)

Optical profilometry
Thermography Detects Substrate Scratches

Intentionally scratched substrate with MCO coating

- 4 scratches in stainless steel substrate
- Optical and height profile mapping can only detect two scratches in fired film
- Thermography detects all 4 scratches!
Trends observed in thermal responses

Redox currently performing microstructural and compositional analysis on NREL evaluated samples for feedback on thermography response origin and modeling
Image Processing – Raster Removal and Defect Detection of Optical Image

MCO coated sample (with lots of bump defects)

Optical Image as taken with macroscope

Processed image

- Removal of raster pattern
- Image processing highlights defects using black lines based on a contrast or color difference
- Future capability to count defects and quantify size and shape
MCO coated sample (with lots of bump defects)

- Similar set of defects as observed in original optical profilometry image (left), but defects are more pronounced after image processing (right)
Thermal transport modeling

Key observations:
- Spatial variation in IR images even when there is no excitation
- Thermal map “reversal” when a specimen is excited vs. non-excited

Recent Progress:
- Concept of model defined (see left image)
- Coating and substrate properties (e.g., thermal conductivity, heat capacity, and density) collected and/or predicted (includes coating porosity function)
Long-term ASR of “defect-free” coating exhibits reasonable performance

- ASR at ~0.037 $\Omega \text{cm}^2$ for 1000 h (a 2$^{nd}$ measurement resulted in ASR ~0.048 $\Omega \text{cm}^2$ for 350 h)
- Achieved M2.2 (<0.05 $\Omega \text{cm}^2$ for 1000 h at 650 °C)
Long-term ASR of intentionally defective coatings

- Thin coating exhibits high ASR that increases from 0.06 $\Omega\text{cm}^2$ to 0.1 $\Omega\text{cm}^2$ (66%) with time
- Porous coating has low ASR, which also increases with time from 0.024 $\Omega\text{cm}^2$ to 0.029 $\Omega\text{cm}^2$ (21%)
- Porous coating exhibits a promising initial ASR, though high porosity may lead to more Cr volatilization
4. Sputtered Thin Film SOFCs

- Thin electron-blocking layer expected to increase Redox GEN1 Ni-cermet cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria based electrolyte → ~40% increase in open circuit voltage
- Thin-ness of electron-blocking layer adds negligible resistance
- Takes advantage of high performance Redox GEN1 cell platform
GDC Buffer Layer Deposition

GDC deposited on GEN1 SOFC sample with YSZ layer previously deposited by KDF

- Successful deposition of GDC buffer layer with over 1 μm/hour deposition rate on lab-scale system
- Required development of pre-sputter parameters and improvement of deposition conditions (e.g., Ar and O₂ pressure and sputtering power)
- GDC film deposition still being developed to ensure deposition of dense, robust film (see next slides on oxidative stress)
Buffer Layer Annealing in Air

• GDC film cracked substantially after annealing
• YSZ layer appears to retain integrity

As deposited

After 600 °C 1 h anneal

Surface

Surface

Cross-section

GDC film
YSZ film
GDC electrolyte
**Source of Film Fracture**

**Color lightening after annealing**

As-deposited  
Annealed

Consistent with loss of oxygen vacancy color centers

**XRD spectra peak shift**

- Alumina substrate peak
- GDC peak shift after annealing

- Film fracture after annealing most likely due to oxidation driven stress
- Deposition parameters being tuned accordingly

This is a 0.19% chemical expansion
\[ \Delta \text{stress} \approx 0.0019 \times 250 \text{ GPa} = 0.5 \text{ GPa} \]
\[ \delta \approx 0.015 \] (from graph at left)
Scale-Up Sputtering Process

High Rate!
Summary

- Good progress toward 2.5 kW stack demonstration
- Expanded capabilities in new, larger natural gas test facility
- Fabricated large format cells and all-ceramic anode stack with promising red-ox stability
- Cost modeling predicts significant decrease in lifetime cost for red-ox tolerant stacks
- Optical, height profile, and thermography metrology techniques shown to detect key defects in MCO coatings
- Thermal modeling and image analysis software in development to aid in defect detection
- Successfully deposited GDC buffer layer with sputtering, identified significant chemical expansion effect to be mitigated with process optimization
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