Summary of SOFC Development at Redox Power Systems for FE0027897 & FE0031656

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U.S. Department of Energy, National Energy Technology Laboratory’s (NETL) Solid Oxide Fuel Cell (SOFC) Project Review Meeting

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Redox Power Systems
1. **FE0027897**: *Red-ox robust SOFC stacks for affordable, reliable distributed generation power systems*
   - Background (ceramic anode cell with a GDC electrolyte)
   - Red-Ox cycling impact on material conductivity and cell OCV & Power
   - Challenges balancing cell size, strength, and power density

2. **FE0031656**: *Sputtered thin films for very high power, efficient, and low-cost commercial SOFCs*
   - Background (electron-blocking layer for GDC electrolyte SOFCs)
   - Problems/solutions for achieving high OCV
   - Problems/solutions for achieving low ASR
Red-ox cycles can be expected during long-term fuel cell operation

- Interruptions in fuel supply
- Impact of small seal leaks over the long-term
- Transient SOFC operation
  - System shutdown
  - Very high fuel utilization events (e.g., extreme load following)

Ni-cermet anodes prone to mechanical failure during redox cycling

Solution: 

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

![Graph showing linear expansion with 0.4 vol% increase at 650 °C](image)

Ceramic anode material shows no cracks after 9 redox cycles!

~69 vol% expansion of Ni → NiO

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All-Ceramic Anode Performance

Button cell data

- High power densities
  - \( \sim 0.75 \text{ W/cm}^2 \) @ 550°C
  - \( \sim 0.3 \text{ W/cm}^2 \) @ 450 °C
- Reasonably high (acceptable) electronic conductivity
- Conductivity and electrochemical activity further boosted using anode infiltration

Anode electrical conductivity

Ni-GDC cermet
New Redox Material
SrTi\(_{0.75}\)Nb\(_{0.25}\)O\(_3\) at 930 °C
SrTi\(_{0.75}\)Nb\(_{0.25}\)O\(_3\) at 650 °C

Good Long-term stability
\( \Delta V < 0.3\% \) per 1000 h

\( i = 0.2 \text{ A/cm}^2 \) at 500 °C
81% H\(_2\), 16% CH\(_4\), and 3% H\(_2\)O
Red-Ox Cycling

- Reduction-Oxidation cycles for ceramic anode material
- Single chamber environment, switching between H\textsubscript{2} and air (flush with N\textsubscript{2} first)

- Open Circuit Voltage during for 5 cm by 5 cm for 11 Red-Ox cycles (switching between H\textsubscript{2} and N\textsubscript{2})
- Industrial grade N\textsubscript{2} has some oxygen
- This was done primarily due to the test setup configuration and no difference was observed from when air is used instead of N\textsubscript{2}
Red-Ox Cycling of Stack

- Small performance drop after red-ox cycling
  - Possible small difference in operating temperature (thermal equilibrium not reached between cycles)
  - The ceramic anode may exhibit an initial decrease in conductivity after first cycle, followed by no changes (previous slide)
  - May also have been due to general long-term stability issues with large format cells
- Discovered problems with ceramic anode delamination during long-term operation in high humidity conditions experienced in large format cell operation and not observed in button cells
- Problem not in the ceramic-anode material itself (confirmed in 30% H₂O, balance H₂)
- Evidence that part of problem is due in part to bonding strength between layers
- To eliminate delamination, we explored modifications to the ceramic-anode configuration and processing conditions

Industrial grade N₂ has some oxygen
Competing Challenges for Ceramic-Anode SOFC

• Strength issues for large format cell
• Cell must be flat to prevent stress concentrators during stack assembly and operation
• Porosity must remain high for catalyst infiltration
• Shrinkage mismatch is challenging and normal methods for characterization (e.g., dilatometry) cannot always be relied upon to guide design and processing optimization
• Balance between pore-former size/amount, composite anode composition, layer thickness, and sintering process
Red-Ox Cycling: Improved Ceramic-Anode Config.

• Red-Ox cycle conditions
  – The sample was heated to 600 °C in air, held for 3 hours; reducing gas (3% H₂ / 97% N₂) was introduced and held for 3 hours; air was re-introduced

• 10 red-ox cycles

• After 10 red-ox cycles, no cracks are observed in anode surface or cross-section

• No delamination of any layers, or any other mechanical problem
Improved Ceramic-Anode Config. Performance

- 4 cm by 4 cm cell tested at 600 °C
- Better electrochemical performance compared to the original ceramic-anode configuration of the same size
  - > 5% increase in open circuit voltage
  - >35% increase in power density
  - Additional improvements possible

Ceramic Anode Cell I-V Curve

<table>
<thead>
<tr>
<th>Current Density [A/cm²]</th>
<th>Voltage [V]</th>
<th>Power Density [W/cm²]</th>
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<tr>
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<td>0.00</td>
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<tr>
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<td>0.30</td>
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<td>0.4</td>
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<tr>
<td>1.2</td>
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<td>1.20</td>
</tr>
<tr>
<td>1.4</td>
<td>0.30</td>
<td>1.40</td>
</tr>
</tbody>
</table>
1. Composition optimization to prevent delamination (5 cm by 5 cm and 10 cm by 10 cm)

2. Fine tune composition / firing profile to reduce edge cracks

3. Optimize furnace temperature uniformity, tape caster thickness variation to increase yield in multi-level (4+) batch firing
**Sputtered Thin Film SOFCs**

- Thin electron-blocking layer expected to increase Redox Gen-1 Ni-cermet cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria-based Electrolyte-1 → as much as ~40% increase in open circuit voltage is possible
- Very thin, dense electron-blocking layer adds negligible resistance
- Takes advantage of high-performance Redox Gen-1 cell platform
- Potential for even more power using Redox Gen-2 cell platform with porous, infiltrated anode (3.2 W/cm² at 650°C)

*Note: Layers are not shown to scale*
GDC Buffer Layer Deposition

GDC deposited on Gen-1 SOFC sample with YSZ layer previously deposited using commercial sputtering equipment

- 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 subsequently optimized on commercial equipment to ensure dense, robust film with greater uniformity in larger size cells and faster deposition rates
Initial Cell Tests: Difficulties Achieving Target OCV

Two types of issues were observed during initial tests:

- **Stability Issues**
  - Typically observed higher OCV initially, followed by rapid voltage drop to low values (e.g., Cell 1)
  - Lower OCV or similar OCV as standard, non-sputtered cells (same GDC electrolyte thickness)
    - Typically observed to have considerably lower OCV (e.g., Cell 2)

Cell 1
4 cm by 4 cm

Cell 2
4 cm by 4 cm
Achieving ≥ 1V Open Circuit Voltage

- Optimized sputtering conditions and post-sputter processing conditions
- 2 cm by 2 cm (sputtered YSZ & GDC) cell tested with stainless steel stack components
- Gas chromatography of the exhaust streams verified good sealing
- Theoretical OCV is 1.135V at 650 °C with 97% H₂ / 3% H₂O at the anode and air at the cathode
- Therefore, the observed OCV was 99.6% of theoretical OCV, confirming an effective electron-blocking layer on the GDC electrolyte
- The OCV is stable and represents a > 30% increase over the baseline (same GDC electrolyte thickness)
Processing Improvements for Repeatable High OCV

- **Type A sputtered layers**
  - OCV: 1.13 V
  - Stable for > 100 hours before scheduled shutdown

- **Type B sputtered layers**
  - OCV: 0.95 V
  - Stable for ~400 hours before scheduled shutdown

- **Type C sputtered layers**
  - OCV: 1.10 V
  - Stable for ~400 hours before scheduled shutdown

*Made using production sputtering equipment*
Higher Than Anticipated ASR

- Sputtered cell tested between 550 °C and 700 °C
- High OCV: ~1.13 V
- ASR of sputtered cell at 650 °C is about 5X higher at 650 °C than the target ASR (Redox Gen-1, non-sputtered)
- ASR did not change at 33% O₂ or 55% O₂ (mixed with air) or flow rate, suggesting the cathode is not the problem
• Regular (non-sputtered) Gen-1 cell with same cathode/contact processing as sputtered cell
• Same ASR for the two cells at 650 °C and 700 °C
• Confirms the higher ASR is very likely due to cathode/contact processing
Contact Adhesion Issues

• We conducted several studies looking at cathode and contact adhesion at the various processing conditions used with sputtered cells
• Cathode/contact adhesion was found to be poor
• Adhesion of cathode (directly on GDC, without contact) was found to be sufficient
• Adhesion of standard contact (directly on GDC) was found to be poor
  – We therefore looked at some alternate contact materials
  – Several of the alternate contacts were found to have "good” adhesion
  – Adhesion remained "good" for the cathode/alternate contact
Higher Than Anticipated ASR

- Standard Gen-1 cell (no sputtered layers; standard cathode / alternate contact) with standard cathode + alternate contact ("good" adhesion)
- Much lower ASR: ~2x the target ASR at 650 °C
- This result combined with adhesion test results provide strong evidence that the high ASR is due to the contact
Next Steps for Sputtered Cells

• Repeat test with standard (non-sputtered cell)
  – fresh cathode paste to verify results
  – Standard contact & alternate contact
  – Use gold or silver contact

• Once the cathode and an alternate contact are found to match the target ASR, prepare additional sputtered cells

• Test these sputtered cells using the same procedures as the latest tests at several temperatures
Summary of FE0027897 & FE0031656

• **FE0027897: Red-Ox Robust SOFCs**
  – Red-Ox stability demonstrated
  – Improved performance demonstrated
  – Future room for improvement to balance strength and performance at large format cell size

• **FE0031656: High-Power Thin-Film SOFCs**
  – Optimized sputtering conditions to achieve dense YSZ electron-blocking layer and dense GDC buffer layer
  – Overcame low OCV issues and repeatably achieved theoretical OCV at 650 °C using target cell size
  – Demonstrated that the cathode contact is the cause for high ASR and that there is a path for reaching the target ASR with the sputtered cells
Acknowledgements

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- DE-FE0031656