High Power, Low Cost SOFC Stacks For Robust And Reliable Distributed Generation (DE-FE0026189)
and
Red-Ox Robust SOFC Stacks for Affordable, Reliable Distributed Generation Power Systems
(DE-FE0027897)

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NETL-1 Project Objectives

**Purpose:** Develop high power density, intermediate temperature (600-650 °C) SOFC stacks for reliable distributed generation.

**Objective:** Improve performance/durability of IT-SOFC stacks while reducing costs

- Scale-up of current stack module designs from 1 kW to 5 kW
- Determination of cell and stack degradation mechanisms
- Cell and stack optimization to improve long-term stability
- Cost analysis with a 20% manufacturing cost reduction
Project Approach

• Understand degradation under operating conditions, aided with accelerated test protocols

• Improve structure, manufacturing, and metrology for cells as well as stack assembly procedures for improved reliability

• Optimize stack designs with enhanced multi-physics model (e.g., reduce thermal gradients and mechanical stresses expected from increased stack size)
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Project Team

Project Partners:

Additional Redox Partners:
Electrode and Contact Degradation

Screen printed electrodes before and after aging at 650 °C for 100 h in air

Sheet resistance (Van der Pauw)

Polarization ASR of symmetric cells

- Most cathodes and contacts show ~10% change after 100 h (“burn-in”)
- Infiltration improves initial performance
- Test plan developed for >1000 h aging of cathodes and contacts of interest
Anode Morphology Degradation

Ni cermet anode aged for 1,000 h at 650 °C in humidified 3% H₂, then 1000 h aged in humidified 3% CH₄.

- Evidence for Ni coarsening in SEM cross-sections
- **Future work:**  
  - Quantitative analysis with FIB/SEM planned  
  - Evaluate role of high steam contents typical of reformate

Gen. 1 (Ni-Cermet) Half-Cell Strength

- Half-cell test coupons show reproducible strength values
- 650 °C and RT show similar strength
- Reduced and as prepared cells have similar strength (↓ strength from porosity, ↑ strength from Ni ductility*)
- Failure strength of half-cells after long-term aging planned


Future Work with UMD Collaborators

- Identification of critical processing defects (UMERC+CALCE)
  - Metrology (Optical profilometry)
  - Mechanics (Bend bars, indentation)
  - Quality assurance purposes

Evaluation of in and out of plane thermo-chemical stresses in seal region (CALCE)

Detect H₂ or air leakage rate (e.g., GC)

Seal thermal expansion measured at Redox
Modeling Effort

• Add ability to assess mechanical stress due to thermal gradients and phenomena such as creep at elevated temperatures

• Optimize stack design through parametric studies
  • modify cell geometry/composition and interconnect flow field geometry)
    • minimize pressure drops
    • improve flow distribution
    • minimize thermal gradients
Quality Assurance Improvements

Cell and materials

In-plane resistance

Paste uniformity and viscosity

Particle size analysis, bulk conductivity, XRD, etc.

Stack assembly

• Documentation
• Acoustic emissions and Distributed Force Sensing (DFS) during assembly
• Gas leak check before and after testing
In situ stress monitoring of cells during stack assembly

**Distributed Force Sensing (DFS)**
- Spatial stress monitoring real-time during stack assembly
- Correlation of regions of high stress with mechanical failure
- Acoustic emissions also monitored spatially for mechanical failure location identification
Suite of tools for evaluation of stack performance, such as:

- GC for mass balance and leakage evaluation
- Impedance spectroscopy electrochemical characterization
- Individual cell voltage monitoring
- Inlet and outlet cathode and anode temperature

→ Identification of key areas limiting initial and long-term performance
Independent 3rd Party Evaluation

3 separate 3-cell 10 cm x 10 cm stacks fabricated by Redox

- Demonstrated reproducible power densities
- 4% higher performance in 3rd party test

600 °C
½ kW Performance

- Compressive stack design
- Extensive multi-physics modeling (e.g., structural, sealing, and fluidic flow field design changes)
- Improvements to assembly process and initial results from modeling efforts $\rightarrow$ next iteration $= \uparrow$ performance

Gen. 1 stack
500 W 10 cm x 10 cm
~625 °C
Long-Term Cell Performance

Gen. 2 - porous anode SOFC (*development sponsored by DOE-EERE*)

- Operating temperature: 600 °C
- Current density: 1.3 A/cm²
- Power density: 0.8 W/cm²

*Good voltage stability during 250 h operation*
Summary of NETL-1 Efforts

• Investigations into degradation mechanisms
  • Electrical and electrochemical performance of aged electrodes and contacts
  • Morphology changes in anode

• Stack assembly, testing, and design upgrades
  • Distributed force sensing (DFS) in addition to previous sensing capabilities
  • Suite of stack evaluation tools

• Cell process improvements
  • Manufacturing quality assurance protocols and documentation
  • Metrology for critical process defect identification

• Demonstrated stack reproducibility and 0.5 kW power

• Achieved good long-term (250 h) cell voltage stability
NETL-2 Project Objectives

- **Purpose:** Develop a high power density, reduction-oxidation (red-ox) stable SOFC for lower cost distributed generation.

- **Objectives:** Improve the red-ox stability of Redox stacks while reducing costs
  - Scale-up and optimization of all-ceramic anode material processing and cell fabrication for lower cost manufacturing
  - Determine all-ceramic anode degradation mechanisms and optimize anode compositions/geometries for enhanced red-ox stability
  - Demonstration of a 1-2 kW, robust for red-ox cycling stack
  - Demonstration >10% reduction in system cost and >30% reduction in O&M costs compared to a system without a red-ox stable stack
Red-Ox Stability Needed in SOFCs

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

\[ \text{Ni} \rightarrow \text{NiO} \]

\[ \text{~69 vol\% expansion of Ni} \rightarrow \text{NiO} \]

Solution:
All ceramic anode \( \rightarrow \) small \( \Delta \) oxygen = small dimensional change (0.4 vol\%)

Linear Expansion [%]

\[ \begin{array}{c}
0.8 \\
0.6 \\
0.4 \\
0.2 \\
0 \\
1 \\
\end{array} \]

Time (hours)

650 °C

No cracks after 9 redox cycles!
All Ceramic Anode SOFC Performance

- High power densities
  - ~0.75 W/cm² @ 550°C
  - ~0.3 W/cm² @ 450 °C
- Acceptable electronic conductivity
Seal and Gen.1 Cell (Ni-Cermet) Red-Ox Cycling Stability

Gas crossover (anode ↔ cathode) measured during Red-Ox cycling (650 °C)

- Ni-cermet half-cell → large crossover even after 3 cycles of only H₂ ↔ N₂ (<0.02% O₂)
- Cracking of Ni-cermet → red-ox cycling instability
- Seals with Al₂O₃ sheet “mock cell” show small increase in cross-over with cycling (H₂ ↔ air) → seals are robust

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Seal material exposed to red-ox cycling in a dilatometer

~1% non-recoverable linear expansion after 3 red-ox cycles → possible source of small increase in cross-over
All-ceramic anode redox cycling

Conductivity measurements in reducing gas

UMERC porous anode support

Redox half-cell conductivity measurements at 650 °C

<table>
<thead>
<tr>
<th>Step</th>
<th>Log(pO₂ [atm])</th>
<th>Gas</th>
<th>Sample 1 σ [S/cm]</th>
<th>Sample 2 σ [S/cm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.68</td>
<td>Dry air</td>
<td>1.3</td>
<td>1.5</td>
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<tr>
<td>2</td>
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<td>Dry 5% H₂</td>
<td>5.2</td>
<td>skipped</td>
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<tr>
<td>3</td>
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<td>skipped</td>
</tr>
<tr>
<td>4</td>
<td>Undef.</td>
<td>Dry 5% H₂</td>
<td>5.6</td>
<td>skipped</td>
</tr>
<tr>
<td>5</td>
<td>-22.7</td>
<td>Wet 5% H₂</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>6</td>
<td>-25.3</td>
<td>Wet 100% H₂</td>
<td>6.4</td>
<td>6.3</td>
</tr>
<tr>
<td>7</td>
<td>-0.68</td>
<td>Dry air</td>
<td>1.2</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Conductivity stable over multiple red-ox cycles in H₂ and N₂, and H₂ and air

No cracking observed in half-cell electrolyte after cycling!

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Long-Term All Ceramic SOFC Performance

- Performance stable with Ni-GDC anode infiltrate composition
- Degradation rate dependence with Ni-GDC ratios
- Coarsening of Ni → degradation

0.2A/cm² humidified CH₄-containing fuel at 600°C

Initial 200 h

#1

#2

#3

Initial 200 h
10 cm x 10 cm half cell

50% fracture strength of Gen. 1 (Ni-cermet) half-cells (4 pt. bend) → strong enough for handling and SOFC testing

*In situ* bend bar test rig (UMERC)
Cost Modeling

- Process flow model with associated costs
- Monte Carlo simulation (output of model will be a probability distribution of costs)
- Discrete event simulator
  - Evaluate impact of component failures over system lifetime
  - Aid in development of warranty and related business model
  - Estimates of natural gas disruptions
Identification of All-Ceramic Failure Modes

Ishikawa, or fish-bone, diagram (CALCE)

Environment

- Exposure to corrosive atmosphere
- Humidity

Corrosion

- Decomposition (surface chemistry) change
- Presence of sulfur impurities in fuel

Fuel

Operation

- System shutdown and startup without using protective gas
- Fuel supply shortage
- High load conditions
- Temperature cycling
- Change in metal catalyst surface morphology
- Outward metal diffusion
- Inward oxygen transport
- Particle agglomeration

Material

- Change in metal catalyst particle size

- Increase in porosity

- Redox Cycling (Reversible/irreversible volume expansion of anode)
- Air leakage near seals
- Increase in oxygen partial pressure

Material

- Decrease in catalytic activity
- Decrease in porosity
- Decrease in degradation

- Anode failure (performance degradation)
NETL-2 Summary

- Identified stability of all-ceramic anode cell components stability in red-ox cycles
  - All-ceramic half-cell exhibits minimal in-plane conductivity degradation after multiple red-ox cycles
  - Cell seal shows low increase in leakage with 20 red-ox cycles
  - Conventional Ni-cermet cell cracks and leaks in less than 3 red-ox cycles
- Key all-ceramic anode degradation modes identified and under evaluation
  - Ishikawa diagram maps out key degradation modes
  - Metal catalyst infiltrate coarsening Ni:GDC ratio change
- Demonstrated capability to fabricate 10 cm x 10 cm all-ceramic anode half-cell
  - Strength half of Gen. 1 Ni-cermet cells, sufficient for SOFC testing
- Cost model for all-ceramic anode under development
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