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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College Park, MD, USA

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1:30 pm

NETL-1 Project Objectives

- **Purpose:** Develop high power density, intermediate temperature (600-650 ^{o}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)

REDOX

Project Team

REDOX

Project Partners:

calce®
Center for Advanced Life Cycle Engineering

University of Maryland 1856
ENERGY RESEARCH CENTER

Additional Redox Partners:

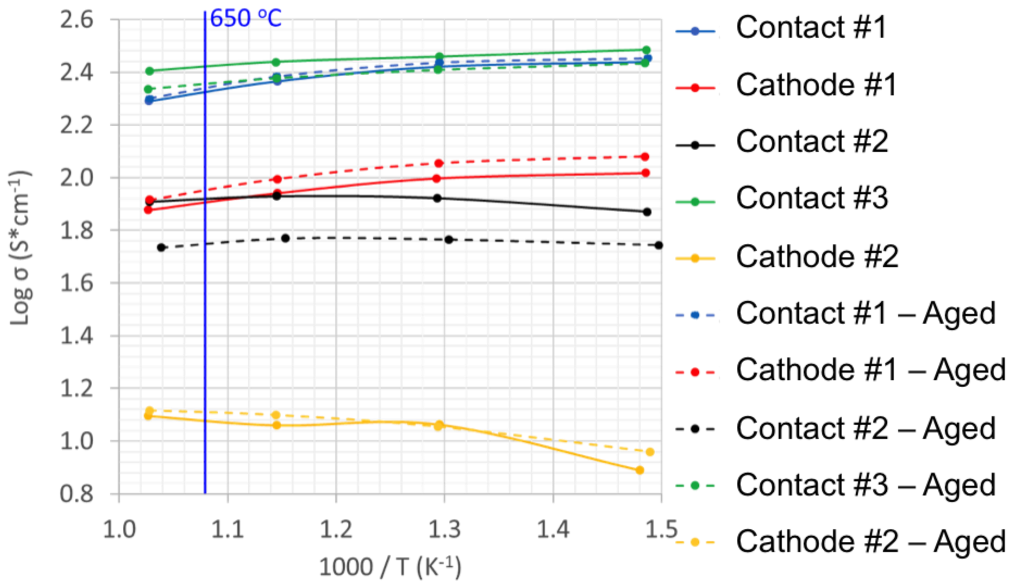
Trans-Tech™
Ceramics and Advanced Materials

SA™
STRATEGIC ANALYSIS INC

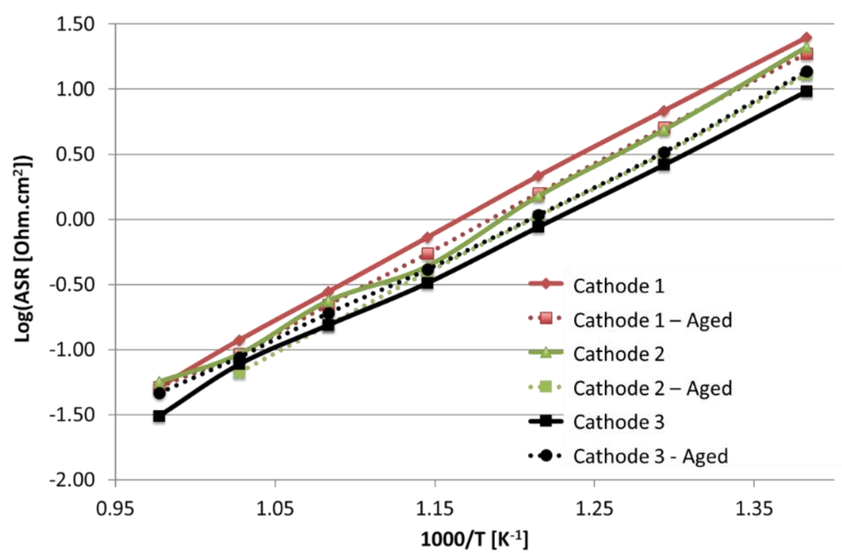
Electrode and Contact Degradation

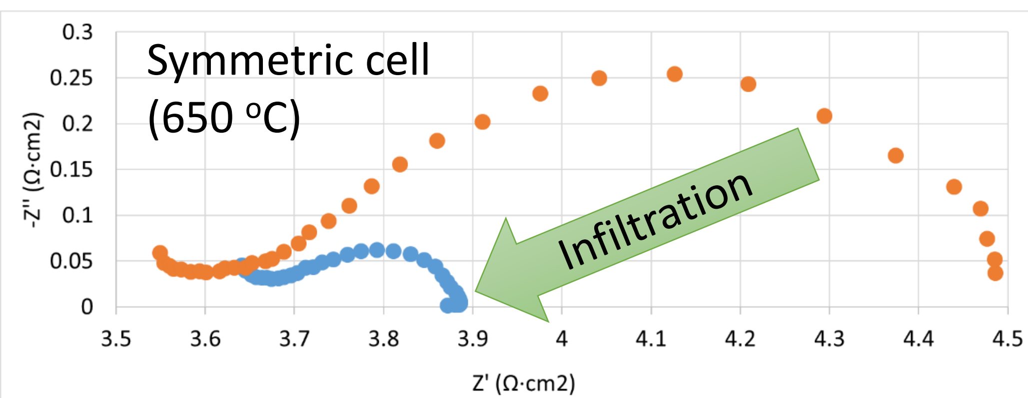
Screen printed electrodes before and after aging at 650 ºC for 100 h in air

Sheet resistance (Van der Pauw)



Polarization ASR of symmetric cells

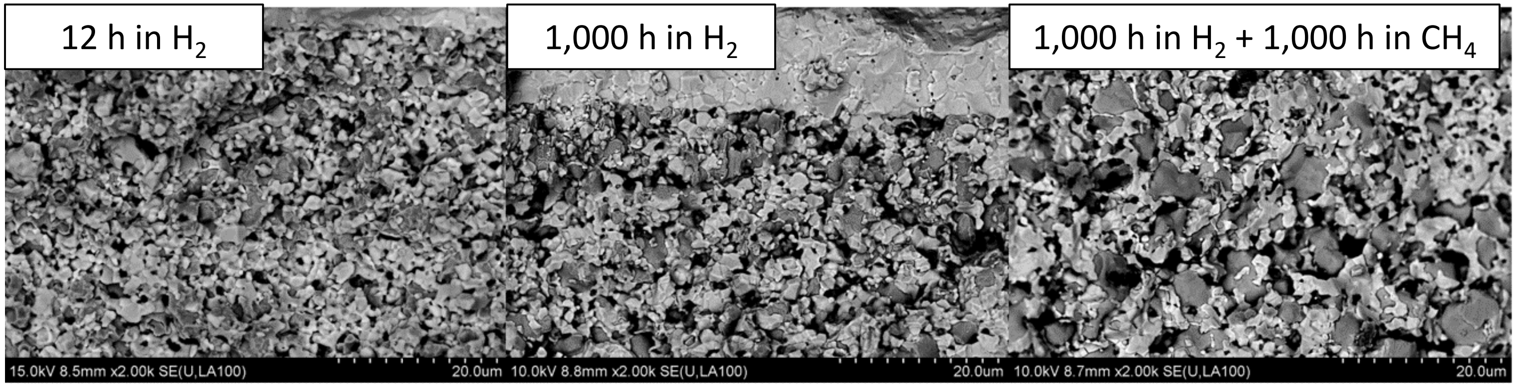


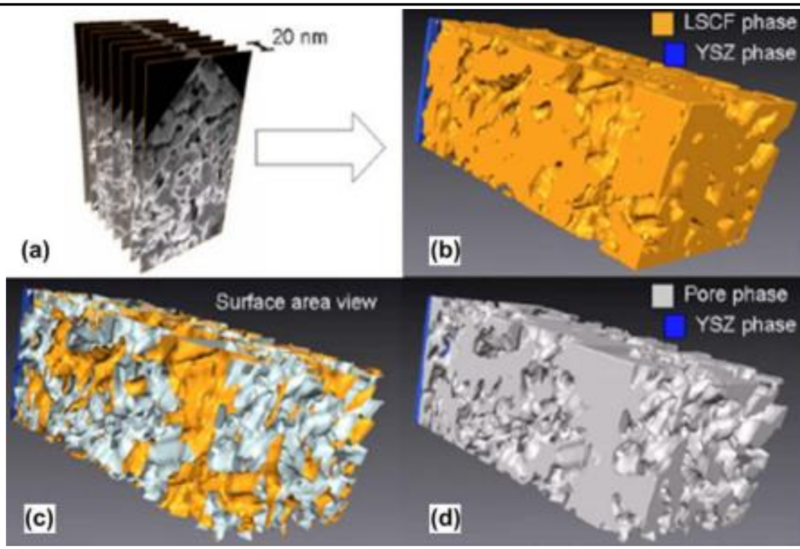


- Most cathodes and contacts show ~10% change after 100 h ("burn-in")
- Infiltration improves initial performance
- Test plan developed for >1000 h aging of cathodes and contacts of interest

Anode Morphology Degradation

Ni cermet anode aged for 1,000 h at 650 °C in humidified 3% H_2 , then 1000 h aged in humidified 3% CH_4,

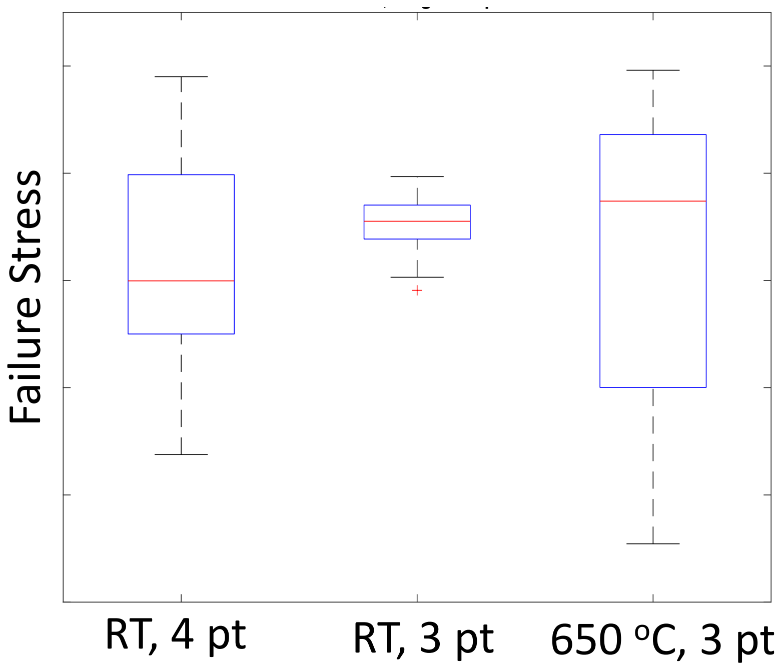


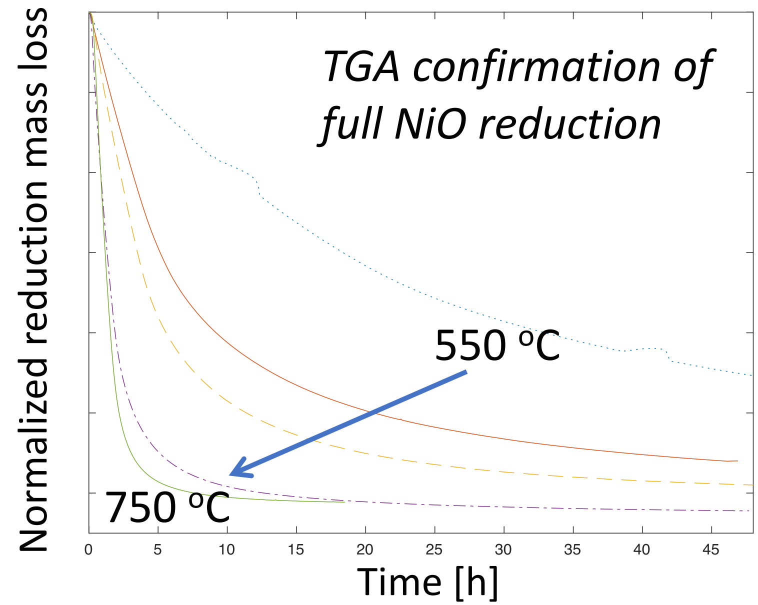


E.D. Wachsman et al., Electrochem. Solid-State Lett. 10, B214 (2007).

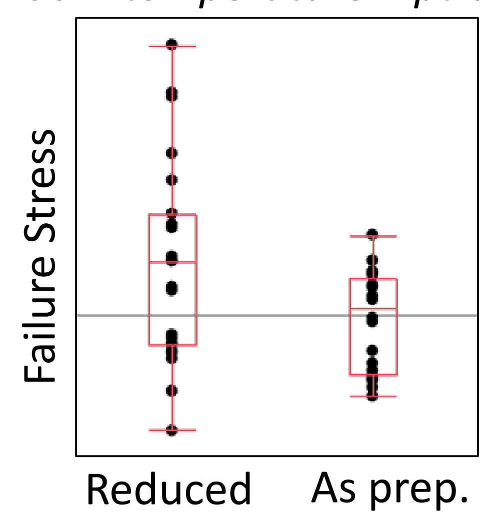
- Evidence for Ni coarsening in SEM cross-sections
- *Future work:*
  - Quantitative analysis with FIB/SEM planned
  - Evaluate role of high steam contents typical of reformate

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





Room temperature 4 pt bend

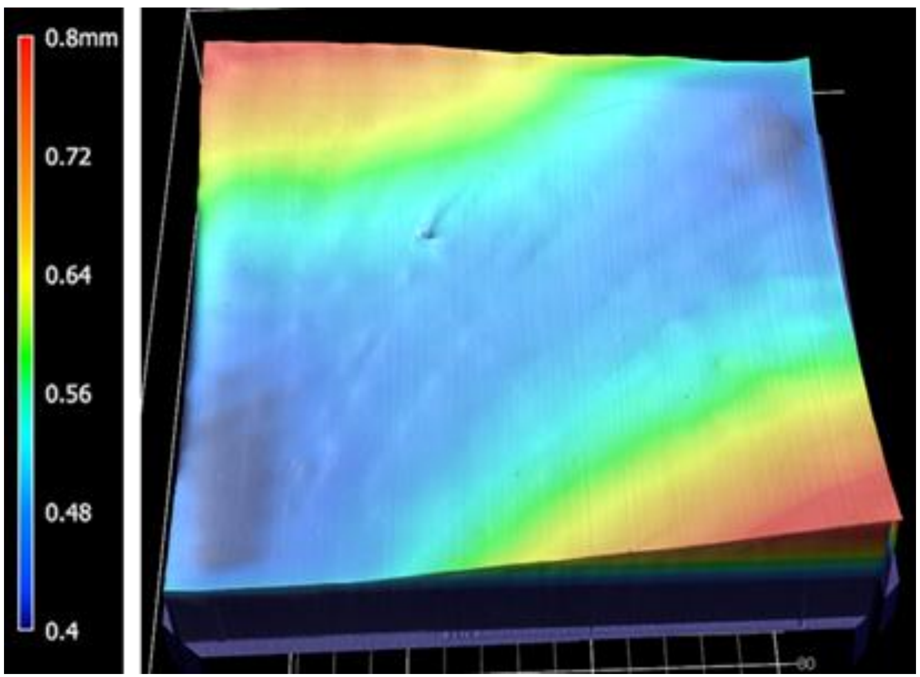


- Half-cell test coupons show reproducible strength values
- 650 °C and RT show similar strength
- Reduced and as prepared cells have similar strength (↓ strength from porosity, ↑ strength from Ni ductility*)
- Failure strength of half-cells after long-term aging planned

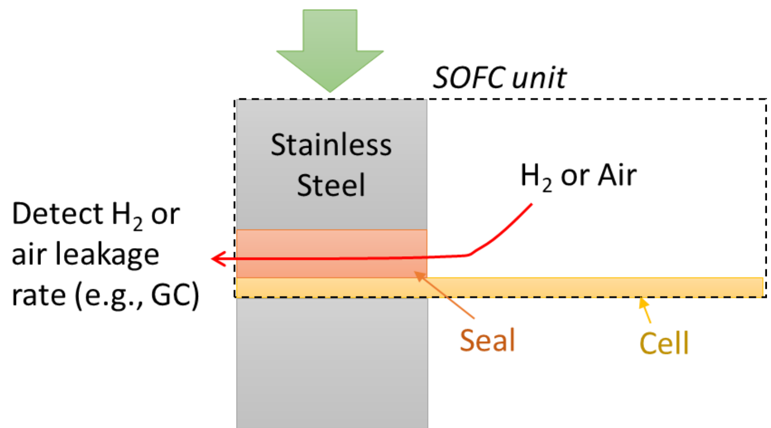
**Radovic and Lara-Curzio, Acta Materialia 52 (2004) 5747*

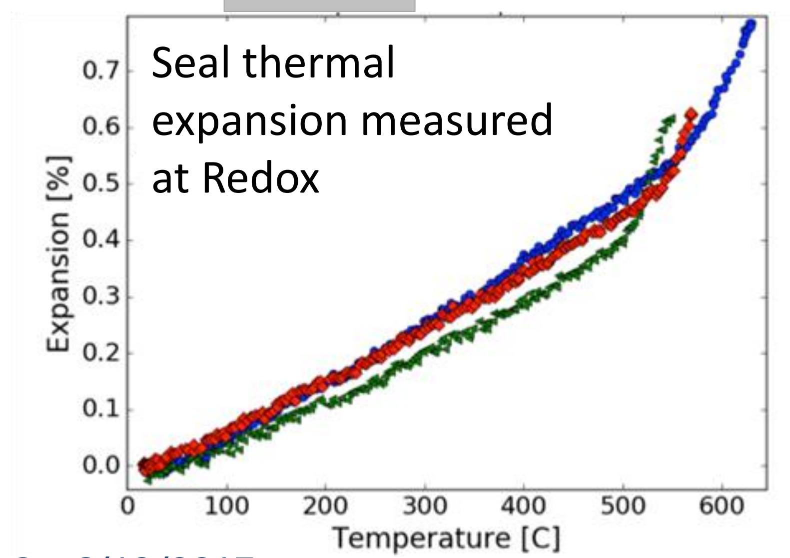
Future Work with UMD Collaborators

- 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)





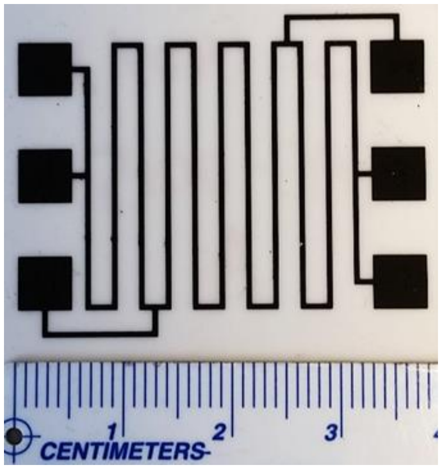
Modeling Effort

- 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

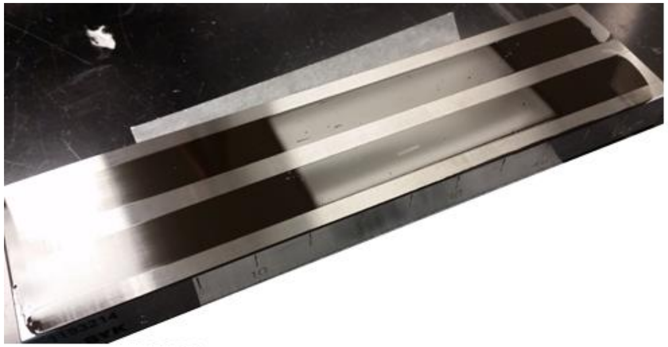
Quality Assurance Improvements

Cell and materials

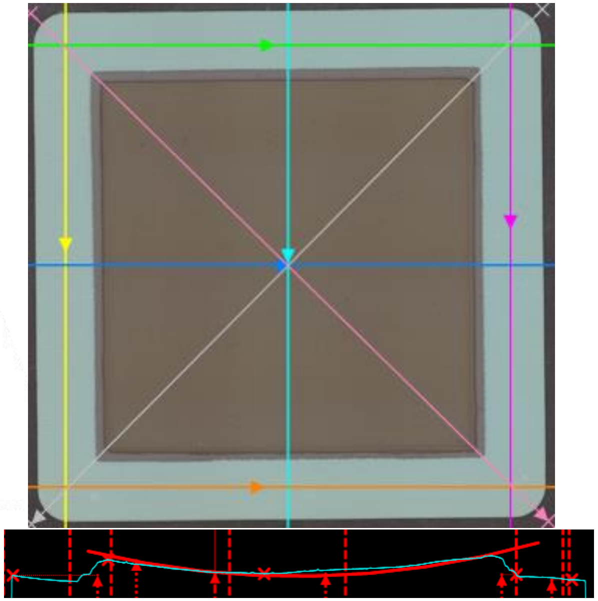
In-plane resistance



Paste uniformity and viscosity



Optical profilometry



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

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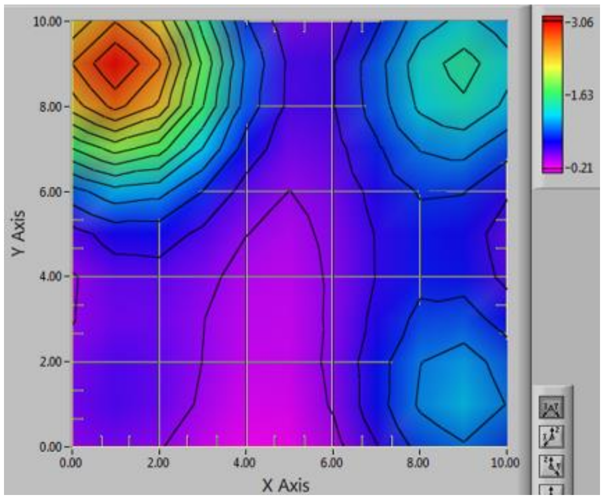

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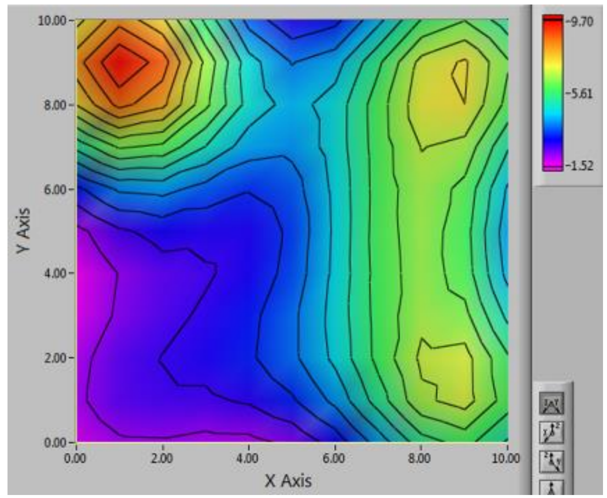

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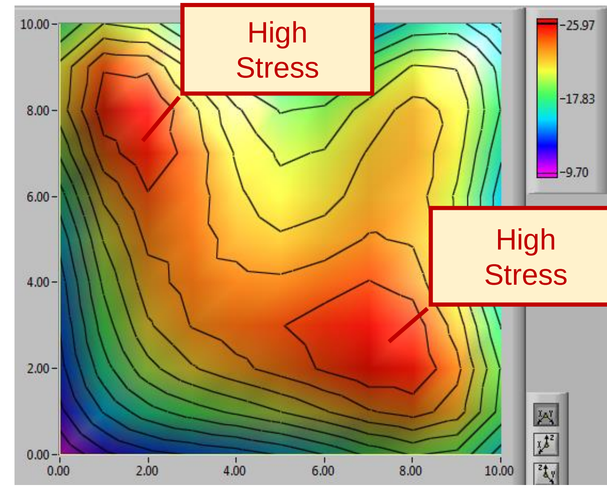
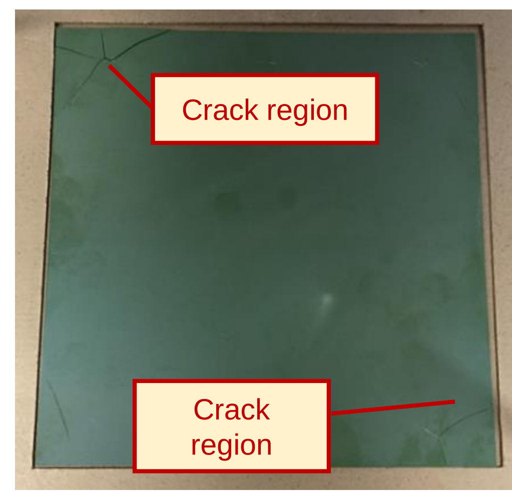
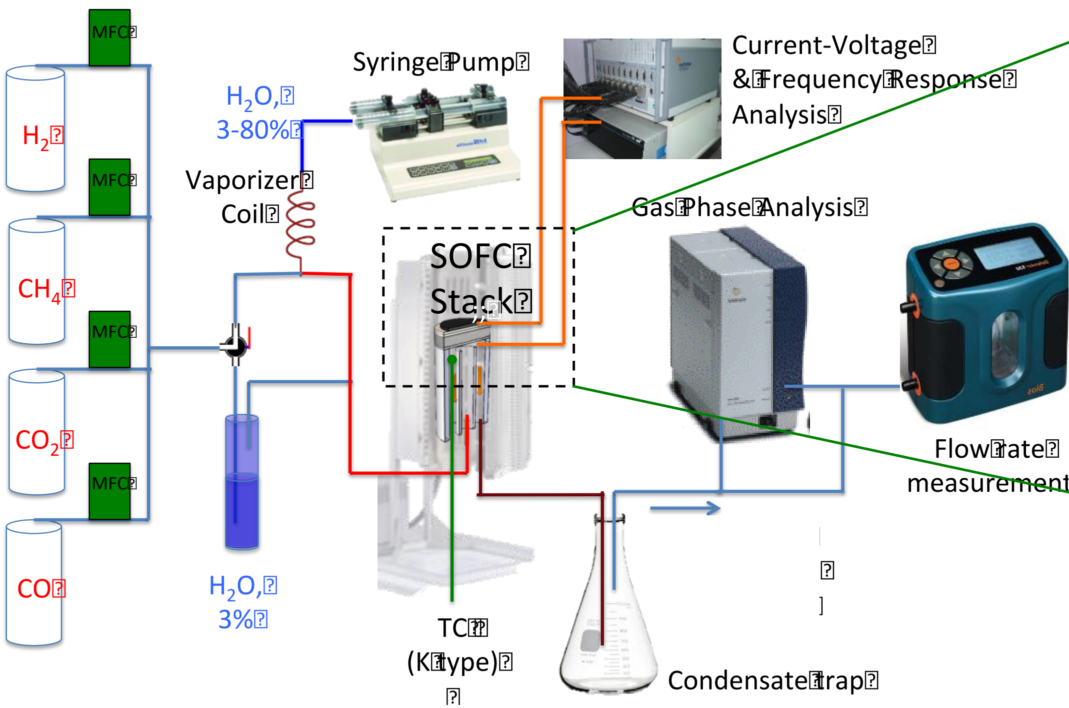


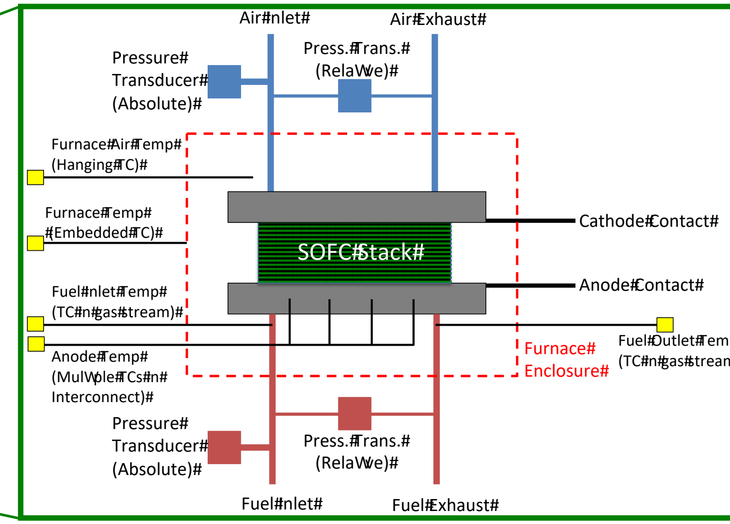


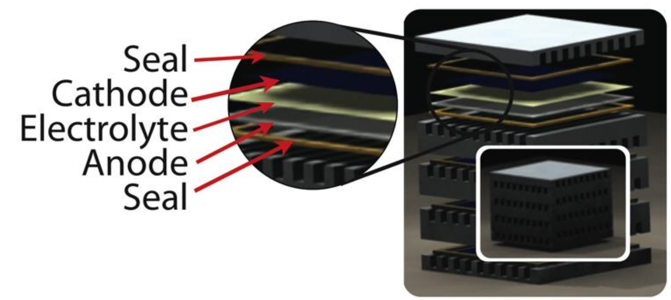
Distributed Force Sensing (DFS)

- 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

Stack Evaluation Instrumentation







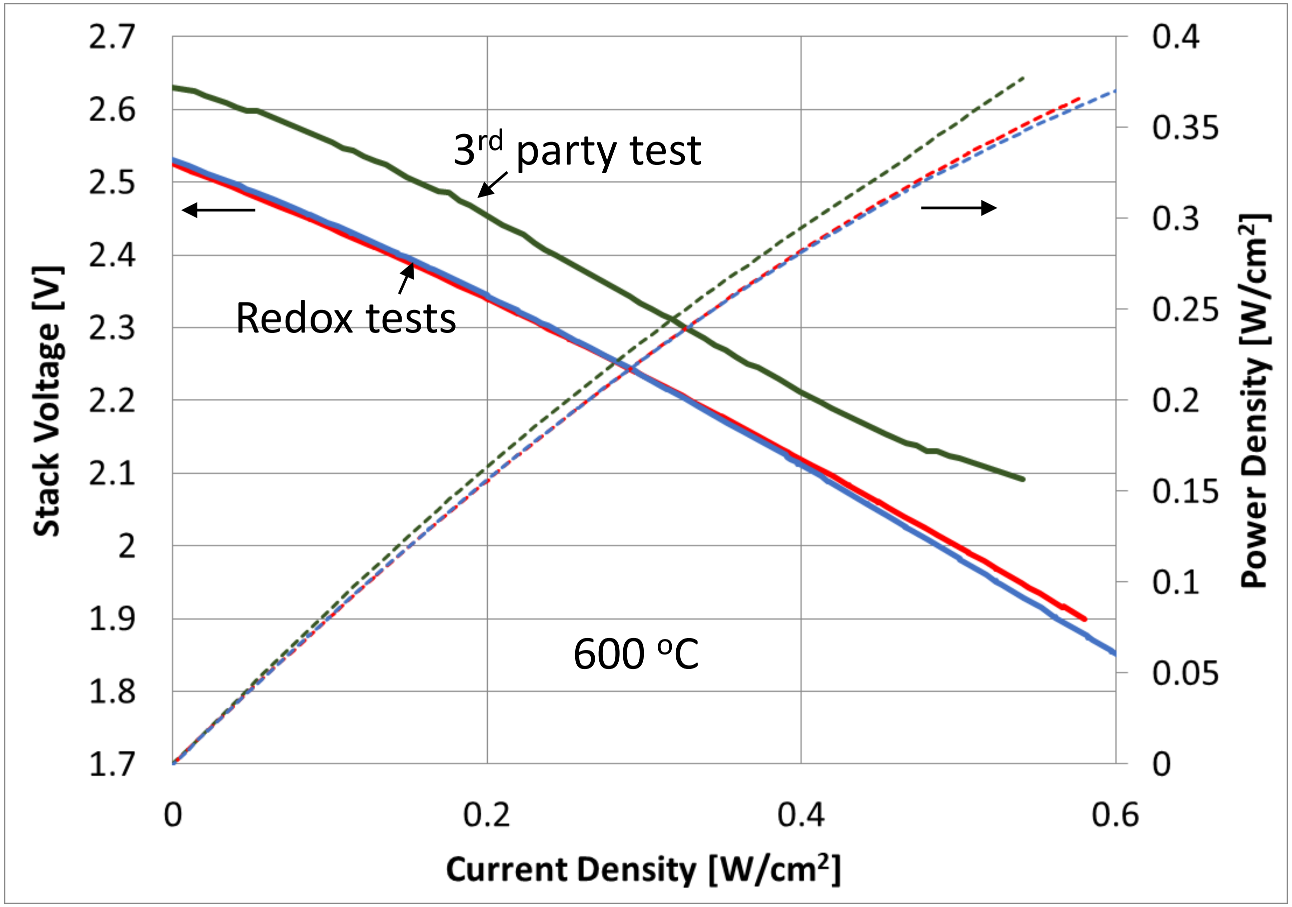
Suite of tools for evaluation of stack performance, such as:

- 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

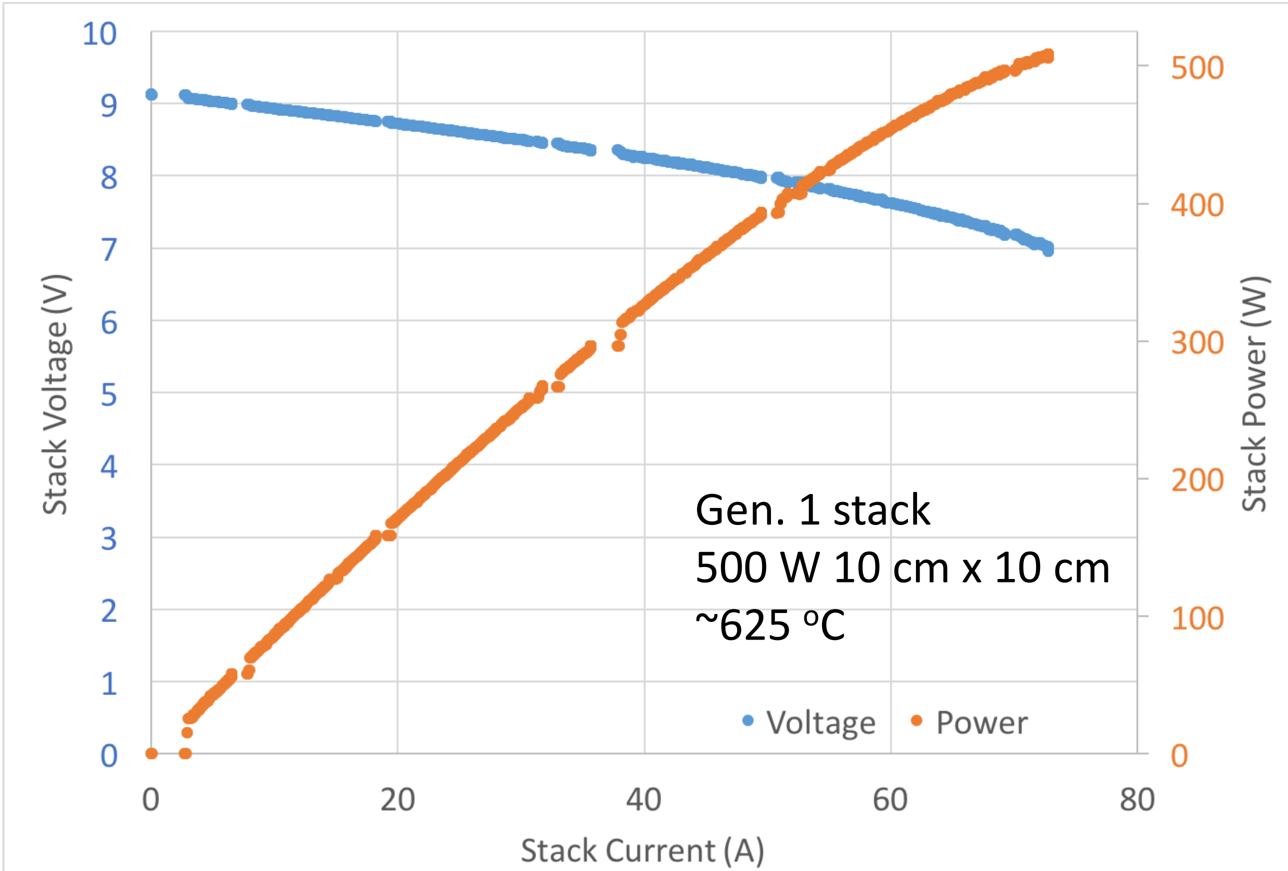
Independent 3rd Party Evaluation

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



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

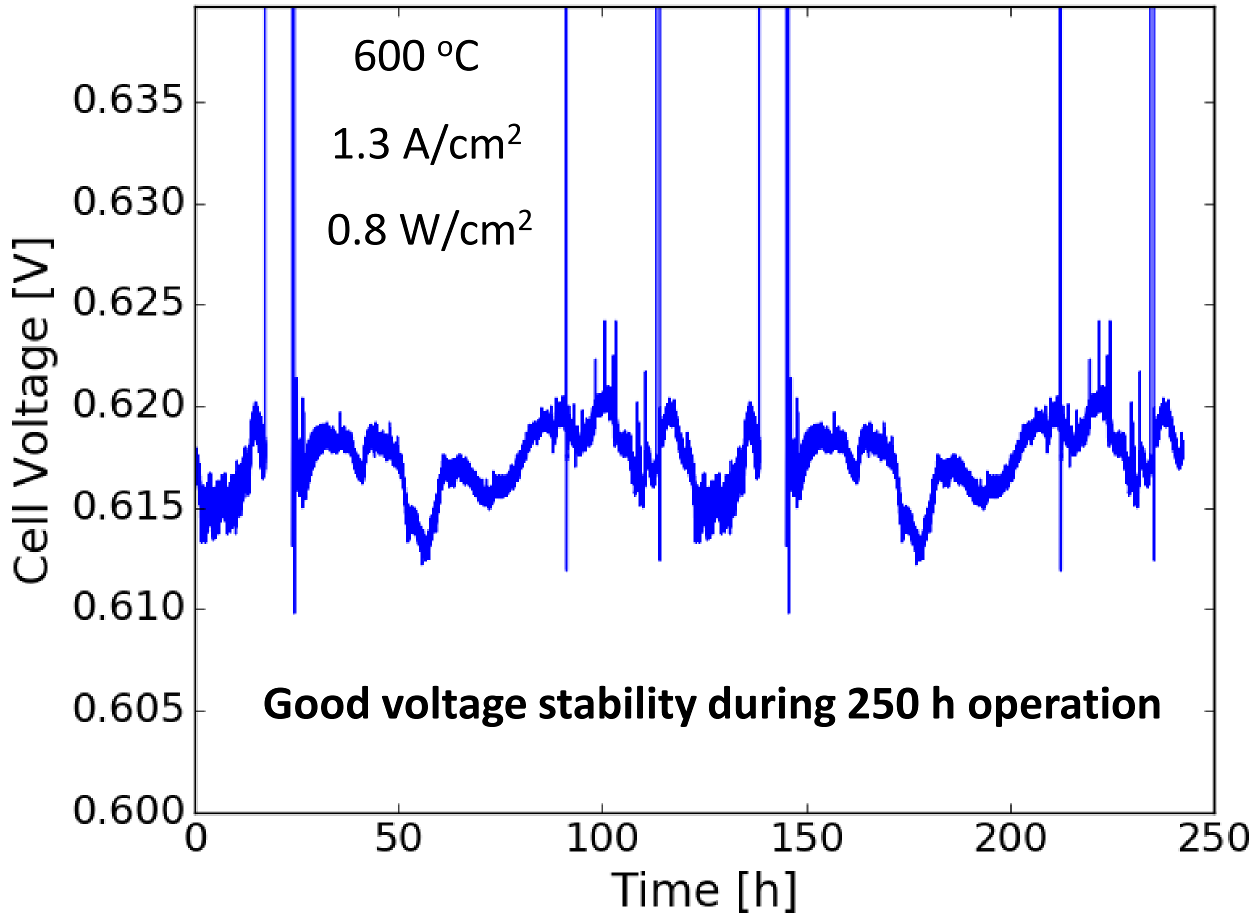
½ kW Performance



- 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 → next iteration = ↑ performance

Long-Term Cell Performance

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



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, **red**uction-**ox**idation (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

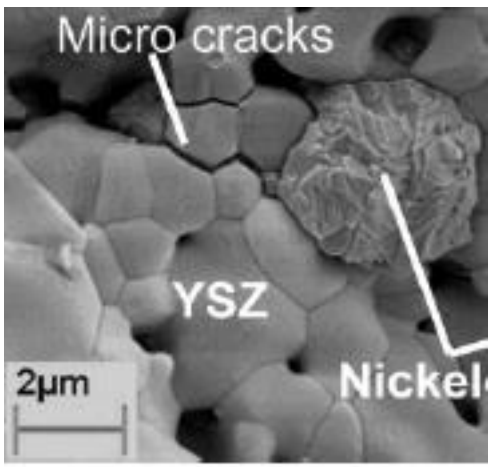
verbose

REDOX 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

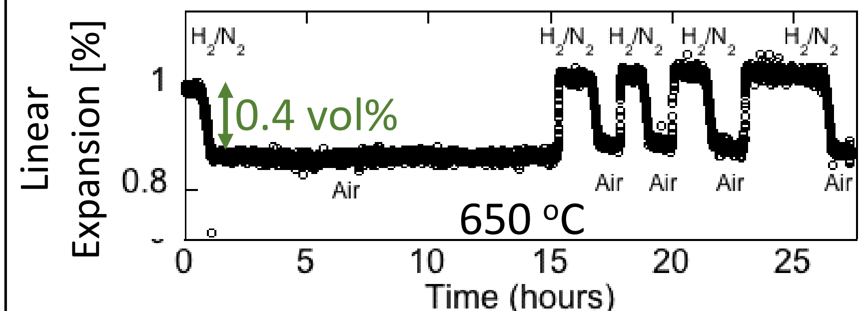


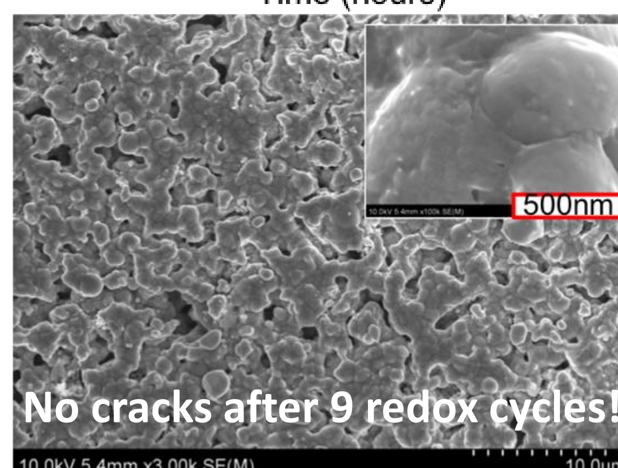
Journal of Power Sources 195 (2010) 5452–5467

~69 vol% expansion of Ni → NiO

Solution:

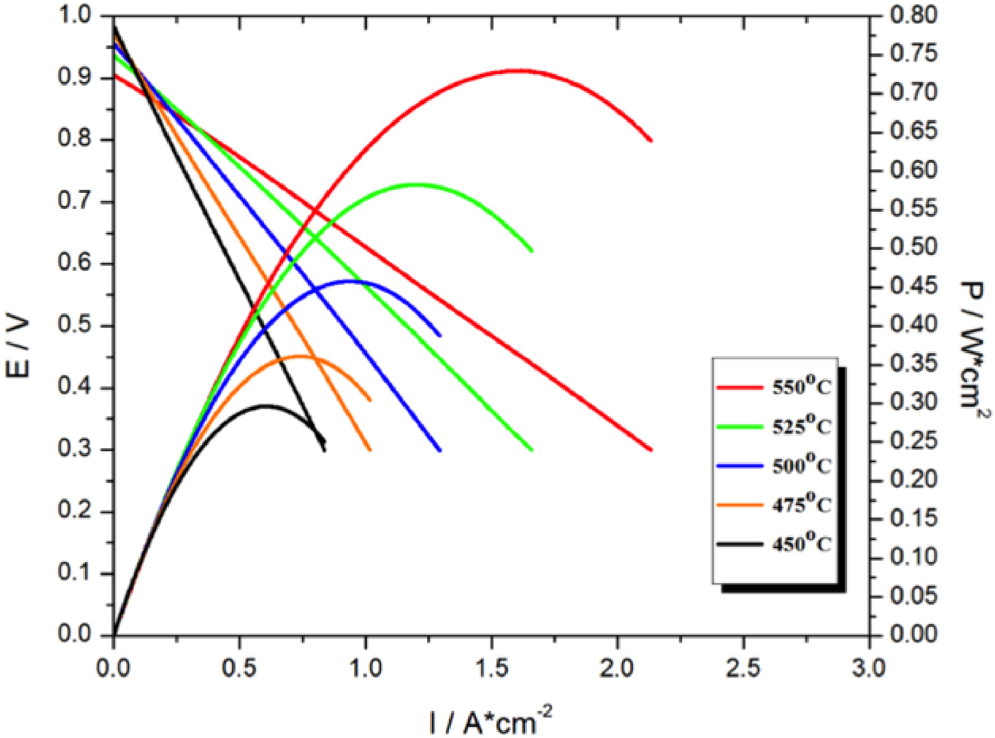
All ceramic anode → small Δoxygen = small dimensional change (0.4 vol%)



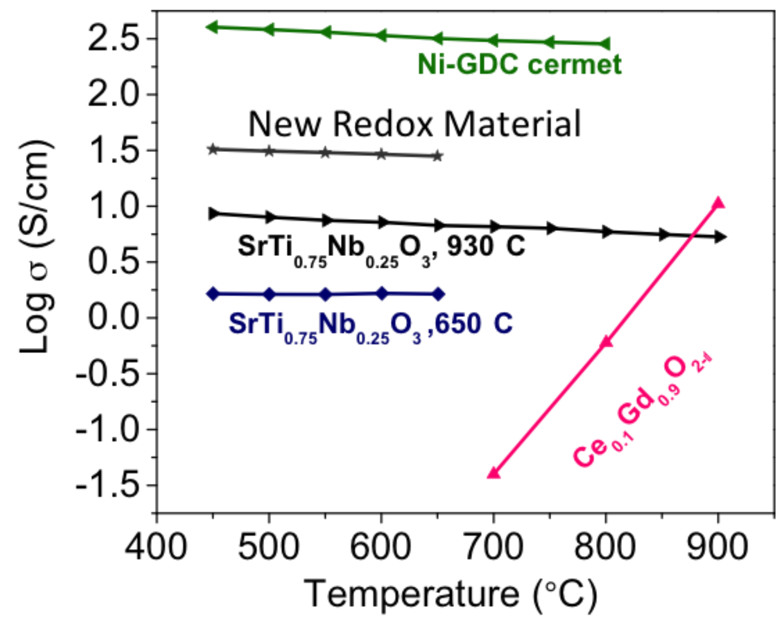


All Ceramic Anode SOFC Performance

Button cell data



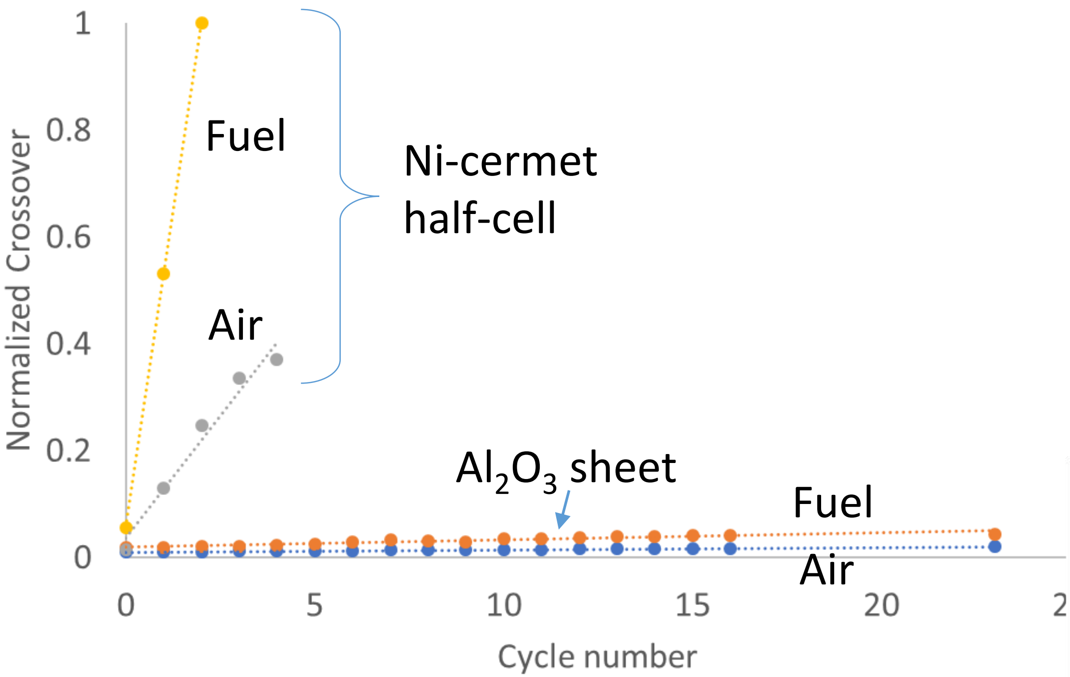
Anode electrical conductivity

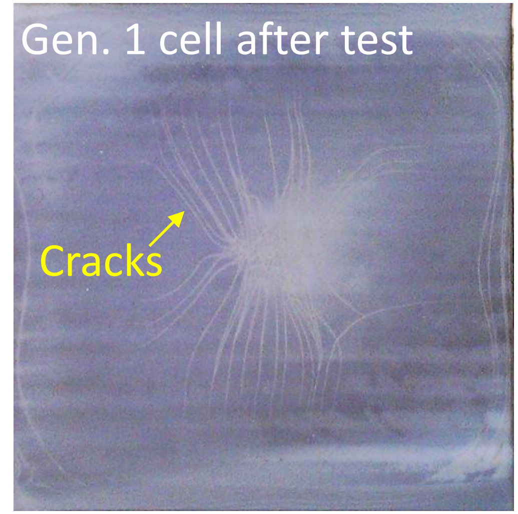


- High power densities
  - ~0.75 W/cm^2 @ 550°C
  - ~0.3 W/cm^2 @ 450 °C
- Acceptable electronic conductivity

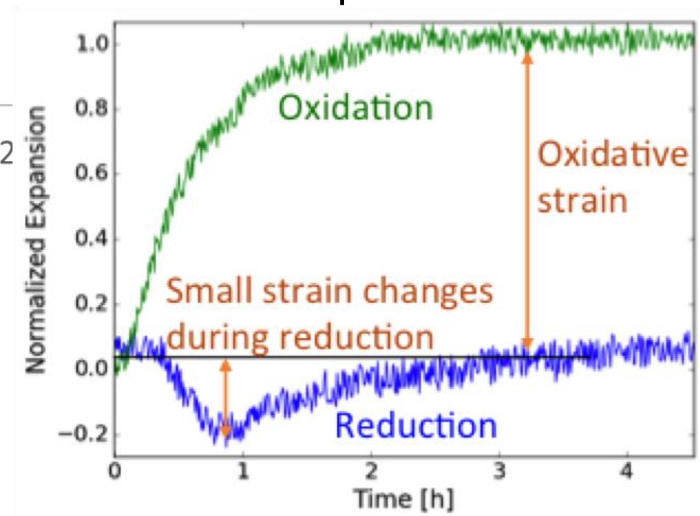
Seal and Gen.1 Cell (Ni-Cermet) Red-Ox Cycling Stability

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





~1% half-cell expansion on oxidation

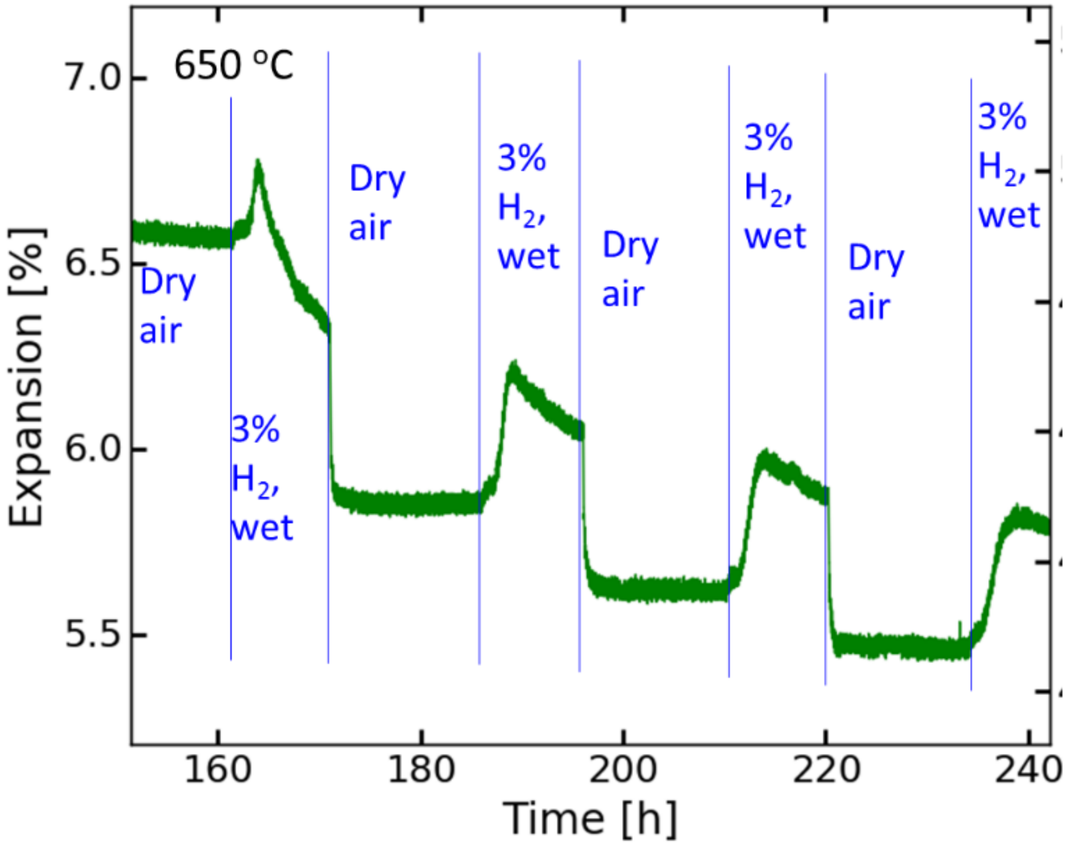


Linear dilatometry at 650 °C

- Ni-cermet half-cell → large crossover even after 3 cycles of only H_2 ↔ N_2 (<0.02% O_2)
- Cracking of Ni-cermet → red-ox cycling instability
- Seals with Al_2O_3 sheet "mock cell" show small increase in cross-over with cycling (H_2 ↔ air) → ***seals are robust***

Seal Expansion During Red-Ox Cycling

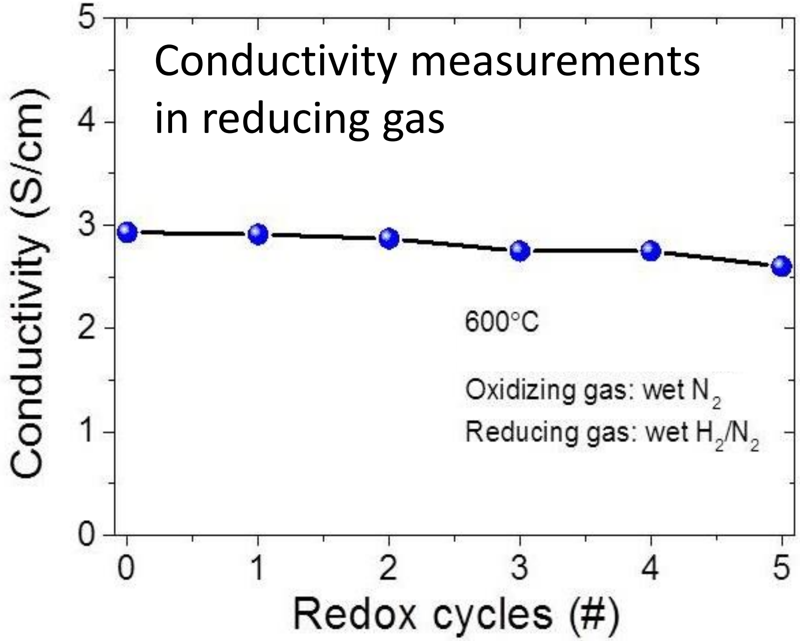
Seal material exposed to red-ox cycling in a dilatometer



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

All-ceramic anode redox cycling

UMERC porous anode support



Redox half-cell conductivity measurements at 650 °C

Step	Log(pO_2 [atm])	Gas	Sample 1 σ [S/cm]	Sample 2 σ [S/cm]
1	**-0.68**	**Dry air**	**1.3**	**1.5**
2	Undef.	Dry 5% H_2	5.2	skipped
3	**-0.68**	**Dry air**	**1.3**	skipped
4	Undef.	Dry 5% H_2	5.6	skipped
5	-22.7	Wet 5% H_2	3.0	2.8
6	-25.3	Wet 100% H_2	6.4	6.3
7	**-0.68**	**Dry air**	**1.2**	**1.3**

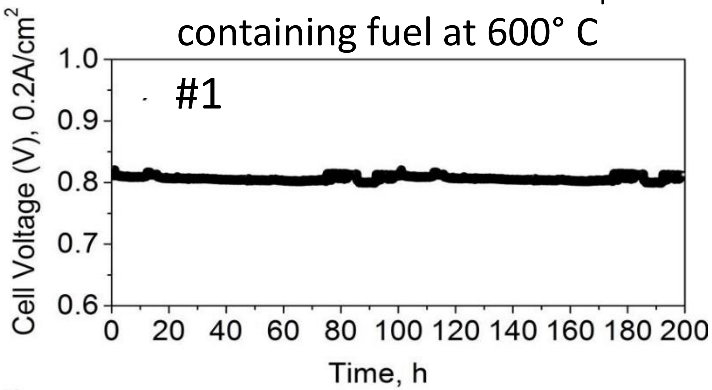
Electrolyte Side

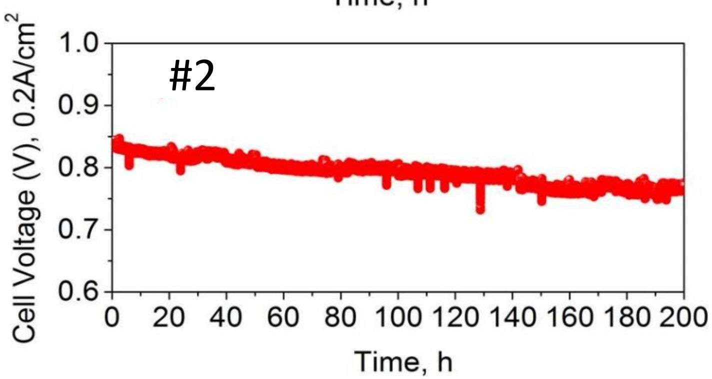
Anode Side

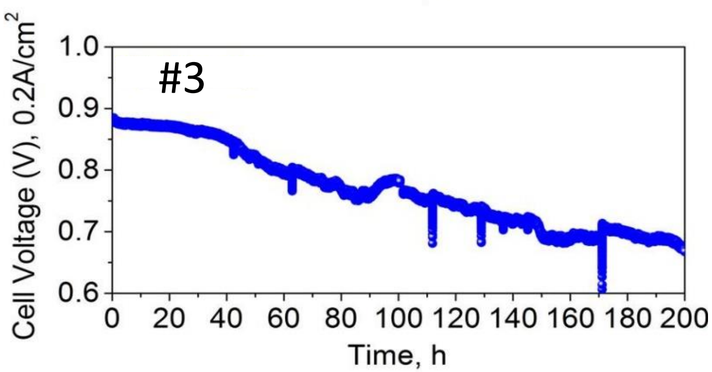
Conductivity stable over multiple red-ox cycles in H_2 and N_2, and H_2 and air

Long-Term All Ceramic SOFC Performance

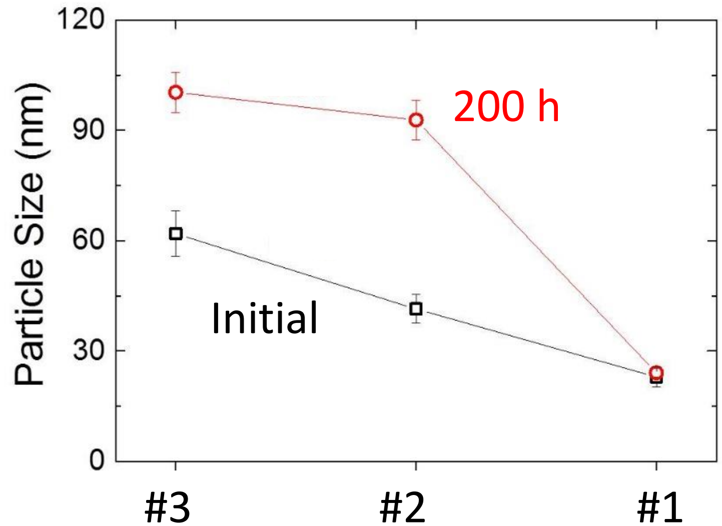
0.2A/cm² humidified CH_4-containing fuel at 600° C

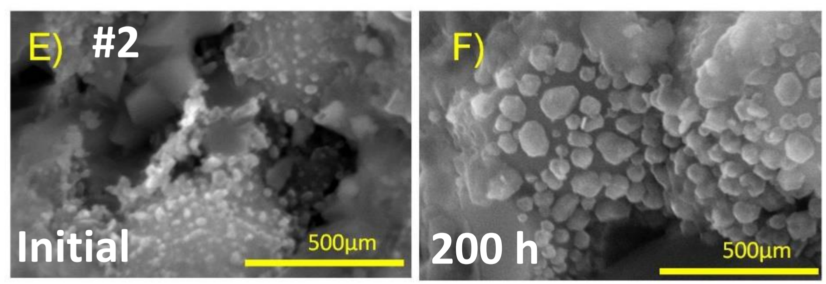






- Performance stable with Ni-GDC anode infiltrate composition
- Degradation rate dependence with Ni-GDC ratios
- Coarsening of Ni → degradation



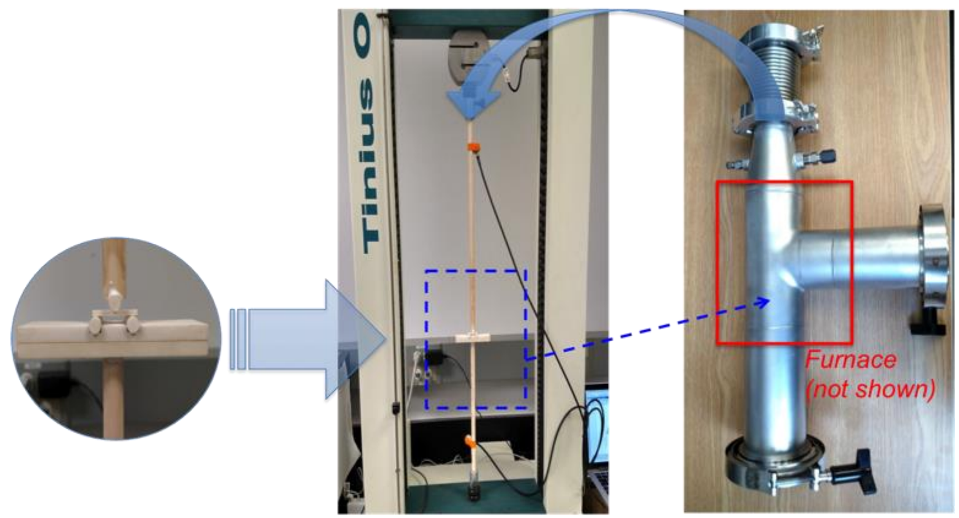


All-Ceramic Half-Cell Scale-Up

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)

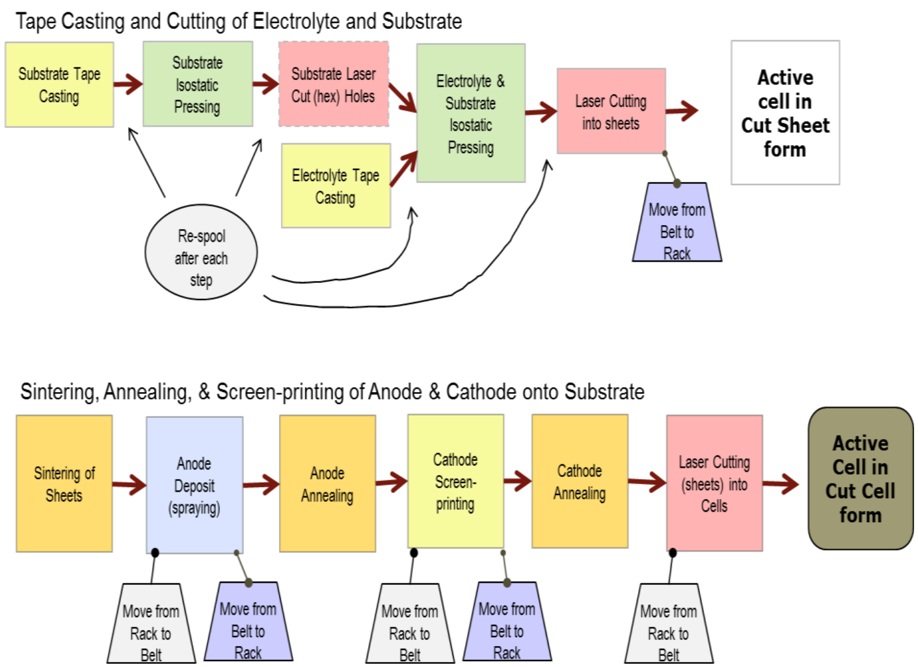


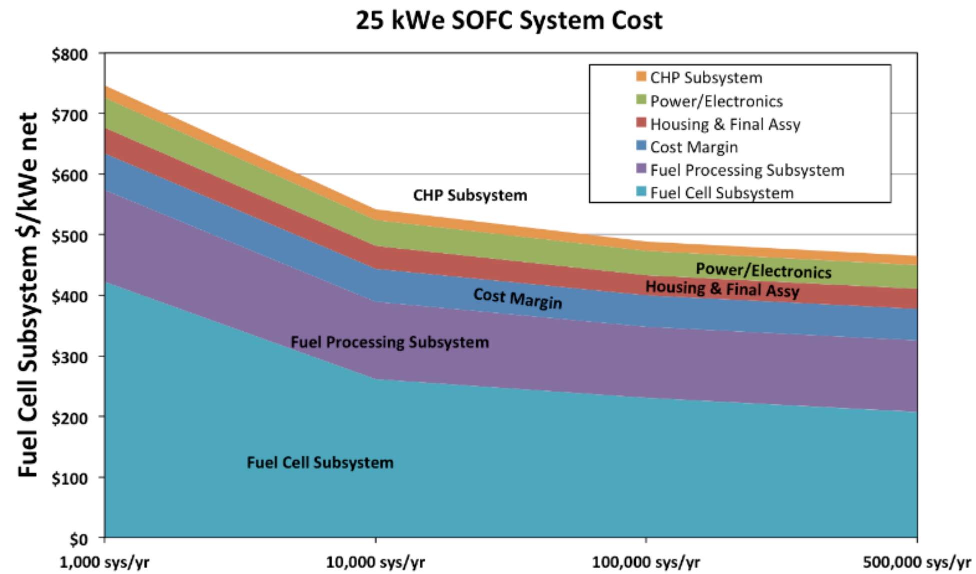
Alumina 3-point bend fixture

Universal Test Machine

Atmosphere/ temperature control for mechanical tester

Cost Modeling



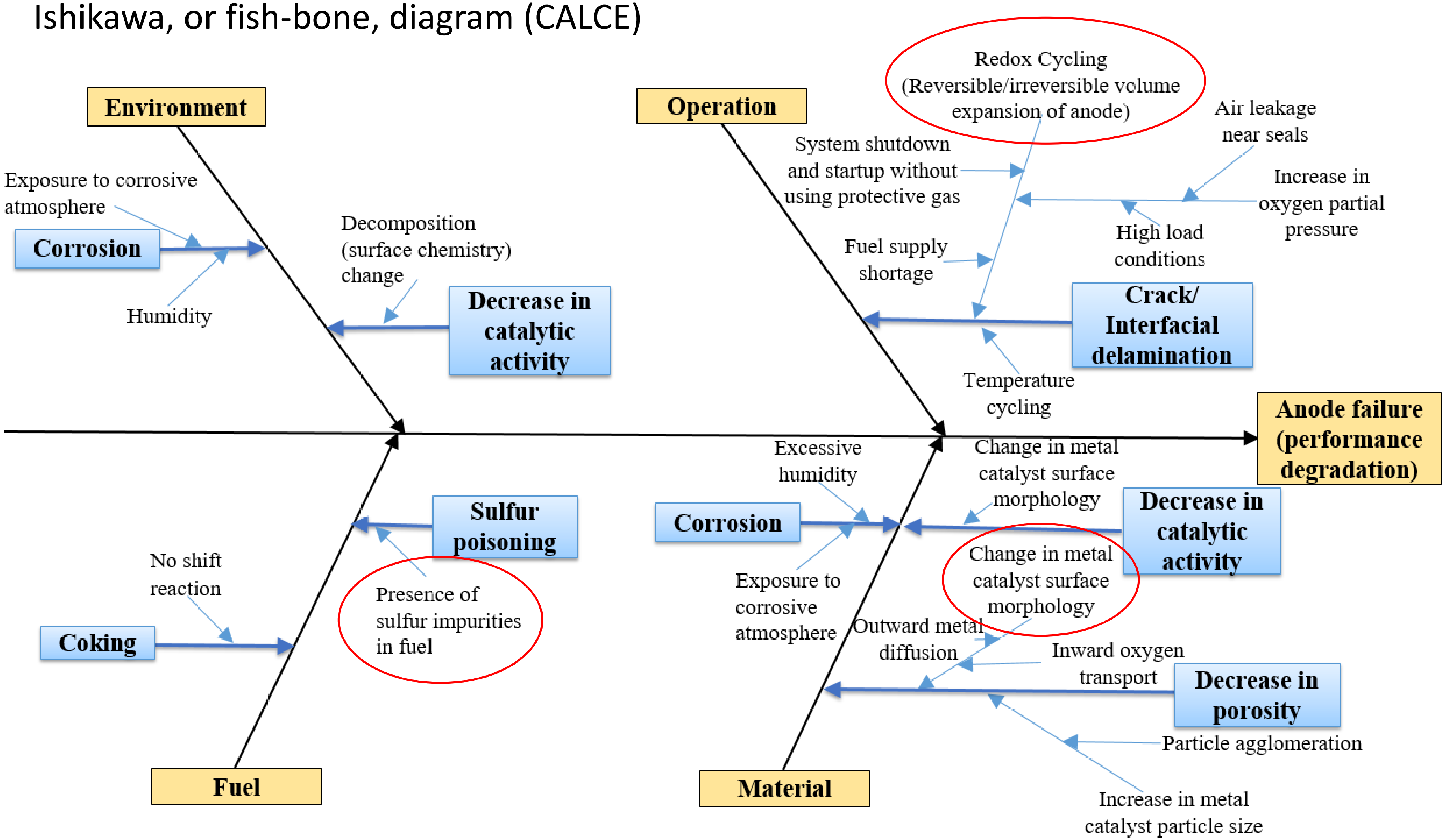


Manufacturing Cost Analysis of Stationary Fuel Cells, Strategic Analysis

- 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)



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

Acknowledgements

- NETL Project Manager
  - Seth Lawson

- University of Maryland
  - Energy Research Center (fundamental R&D) – Prof. Wachsman
    - Dr. Mohammed Hussain, Dr. Chris Pellegrinelli, Ian Robinson, Albert Painter, Patrick Stanley, Thomas Hays, and Dr. Abhishek Jaiswal
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    - Nripendra Patel, Robert Gutter, and Dr. Diganta Das