IT-SOFCs: Overview of Stack Size Scaling Efforts and Red-Ox Robust All-Ceramic Anode Cell Based Stacks***

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06/14/2018

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*DE-FE0026189 (NETL-1)
**DE-FE0027897 (NETL-2)

AGENDA

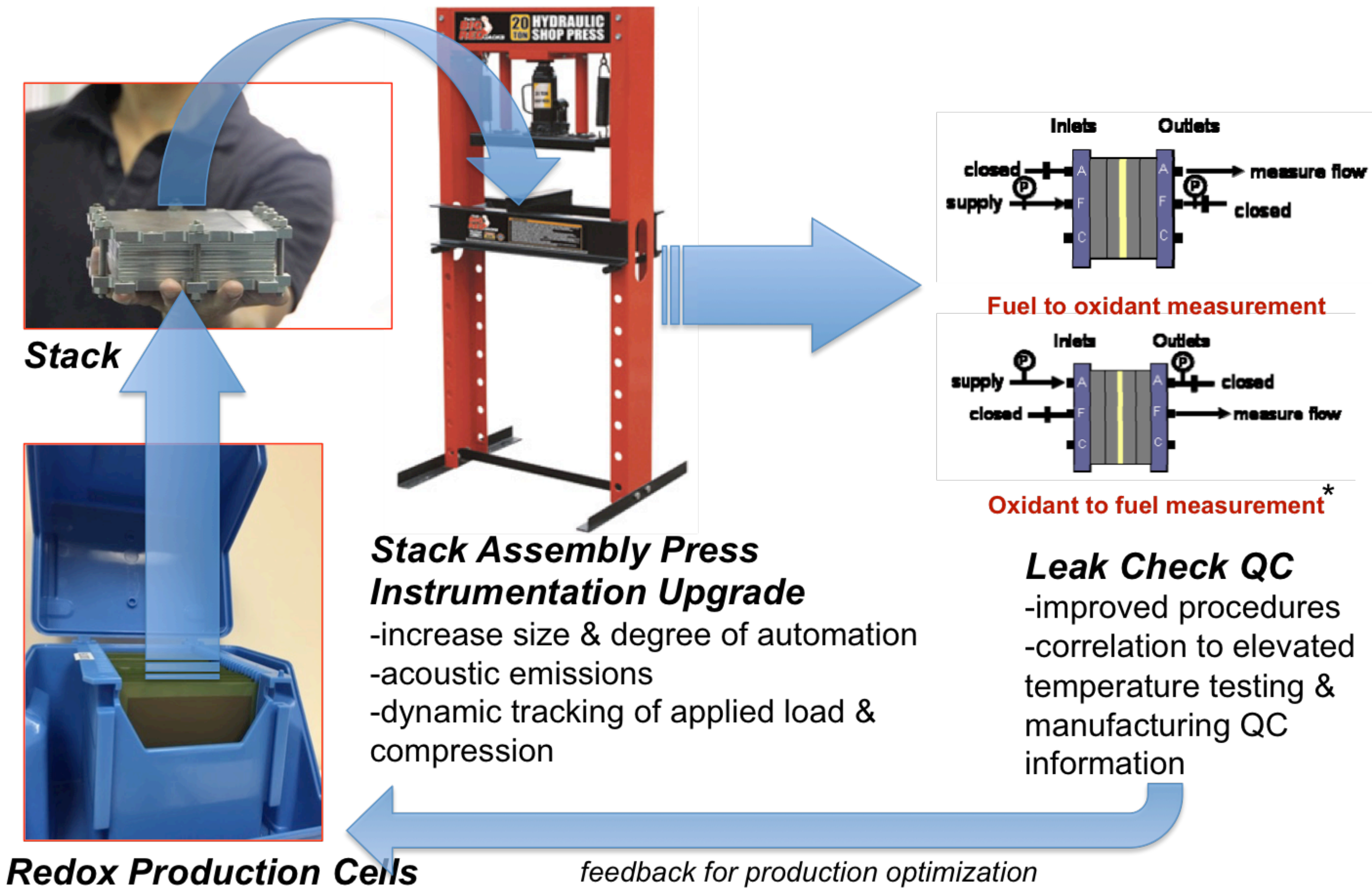
- NETL-1 Overview
  - Stack assembly improvements
  - Stack design updates
  - Results & Analysis
  - Plan moving forward
- NETL-2 Overview
  - All-ceramic anode
  - Materials characterization
  - Materials Scale-up (size and production quantity)
  - Red-Ox cycling of stack
  - Economics Analysis

HIGH POWER, LOW COST SOLID OXIDE FUEL CELL STACKS FOR ROBUST AND RELIABLE DISTRIBUTED GENERATION

(DE-FE0026189)

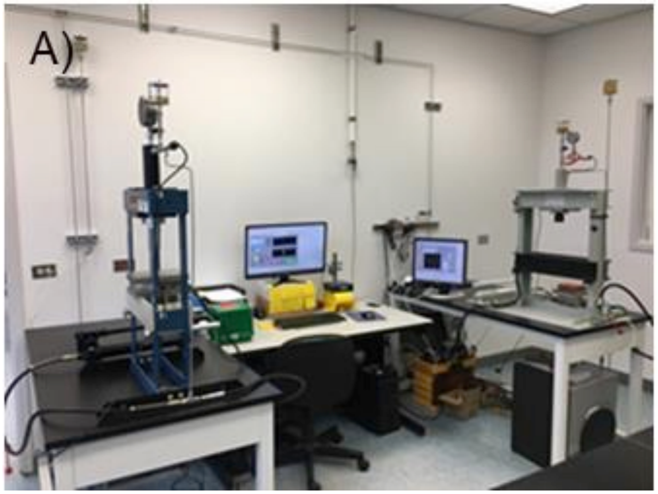
Stack Assembly Improvements

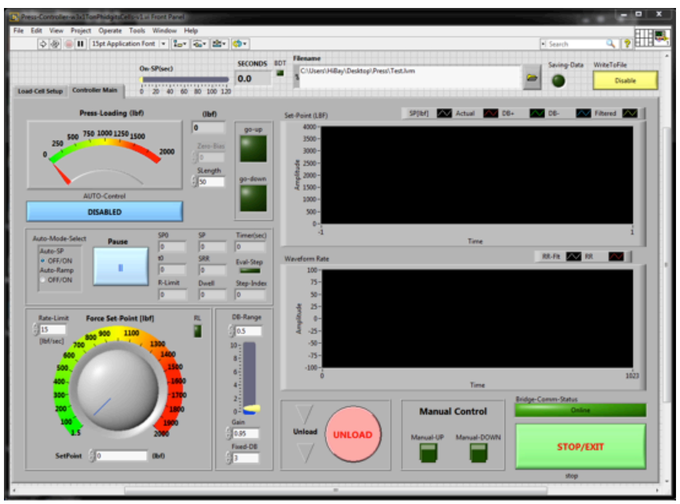
- Assembly gets much harder (and much more $$$) as stacks get bigger
- Need better automation to have repeatability in assembly process
- Need better metrology to ensure that quality control present



*Ref. US Fuel Cell Council, Document No. 04-070

Current Status: Stack Assembly Improvements





- Dedicated stack assembly, metrology, and post-test cataloging space
- Optical profilometry used as part of QC
- Expanded to multiple stack assembly stations and kit preparation areas
- Stack assembly uses fully integrated Controls Software
  - -Tracks uniformity of stack displacement during assembly
  - -Software integrated with other metrology (e.g., acoustic emission sensors)
- Database tracking of all relevant data

In situ stress monitoring of cells during stack assembly dev.

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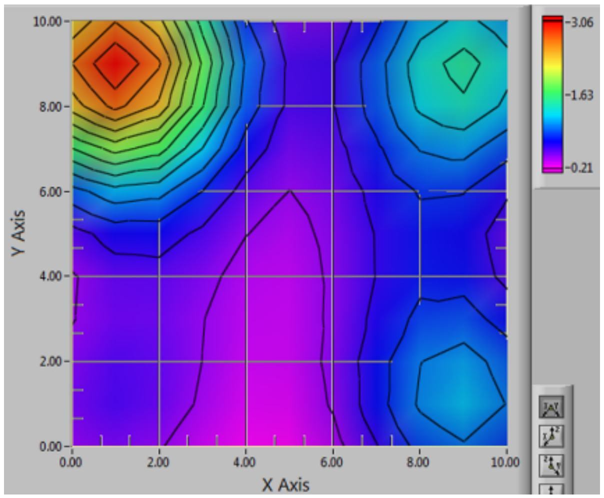

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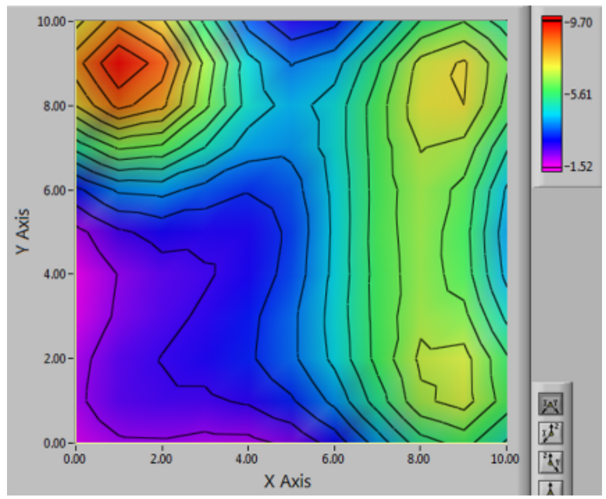

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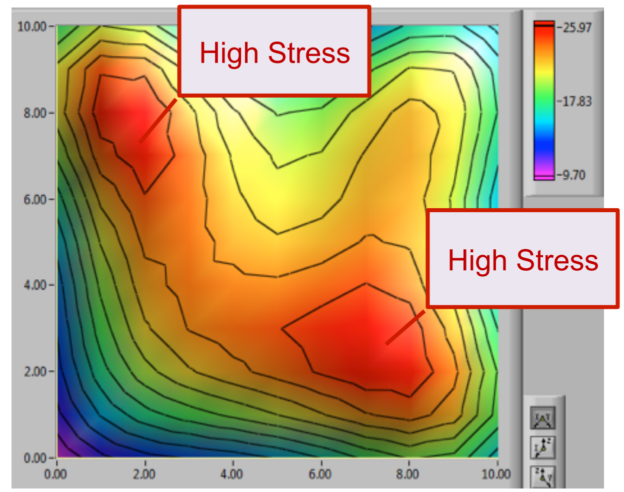
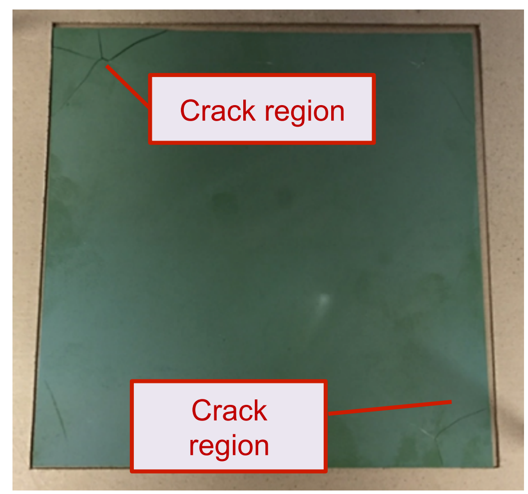




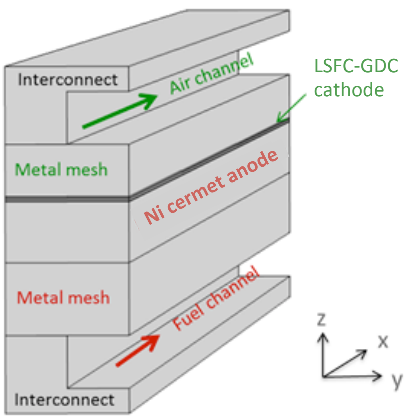
Distributed Force Sensing (DFS)

- 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

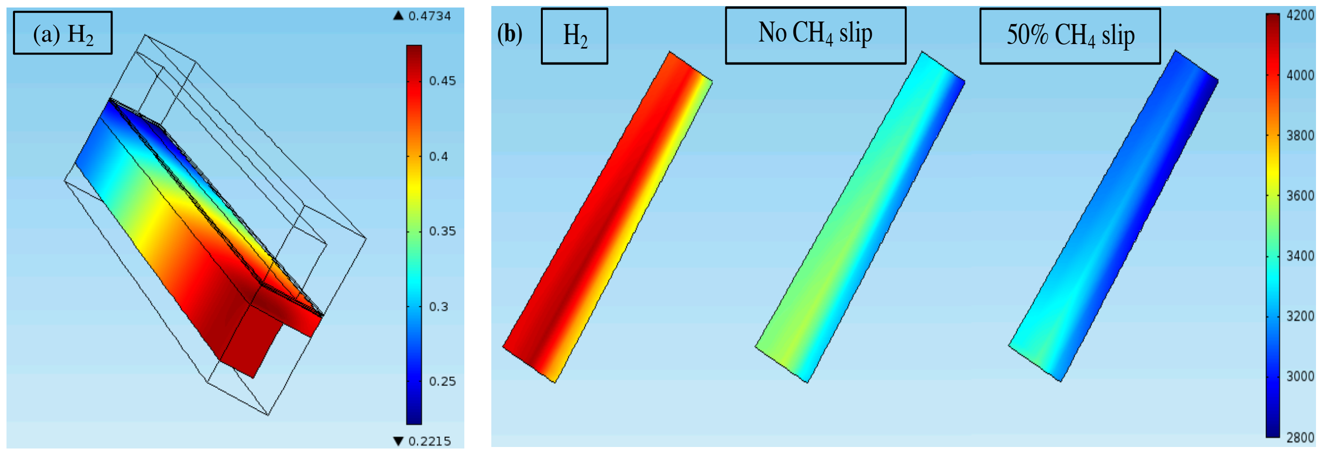
Multi-Physics Modeling Tool For Stack Improvements

- Custom 3D computational model takes into account the unique thermochemical and physical properties of the Redox materials as derived from more fundamental materials and electrochemical measurements
- Model considers impacts of leakage current (electron current) on the OCV drops from theoretical Nernst potential due to over-potentials associated with the electrolyte and electrodes
- Model also captures the kinetics of electrochemical and heterogeneous internal reforming reactions in the anode

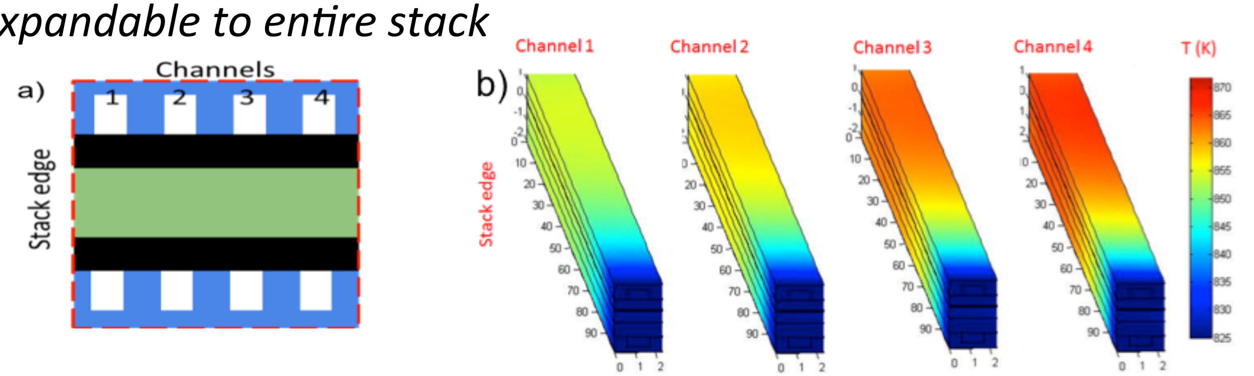
Detailed Single Channel Model



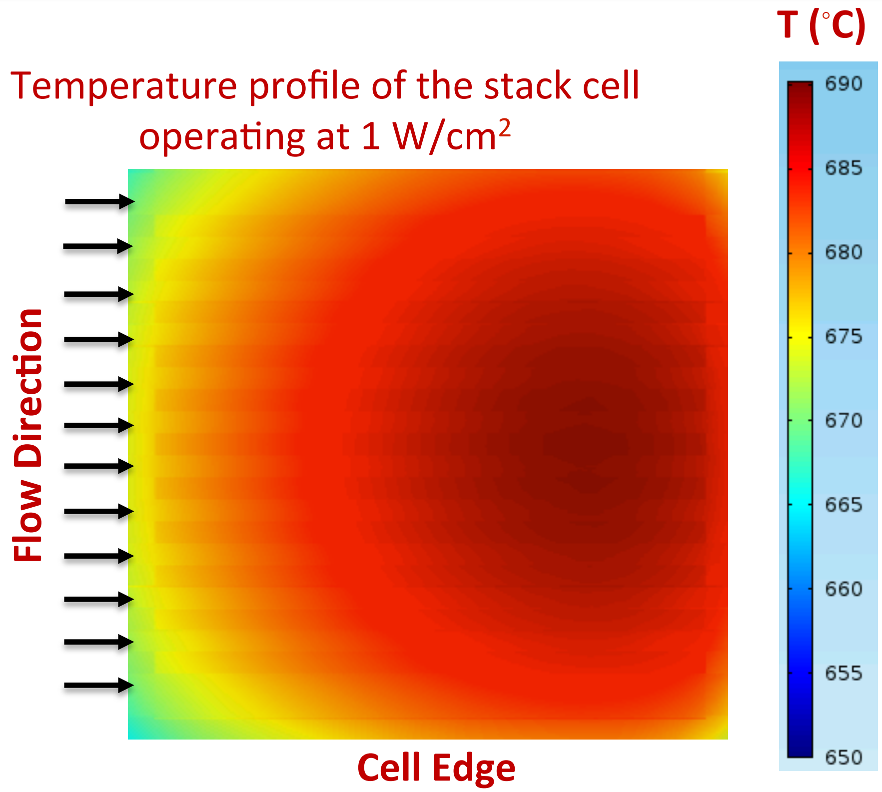
(a) Mole fraction of H_2 for 0.7V at standard fuel utilization for 0% CH_4 slip at 600°C inlet temp.
(b) 2D current distribution for 3 anode fuel feeds operating at 0.7 V and 600°C and a U_f of 80%

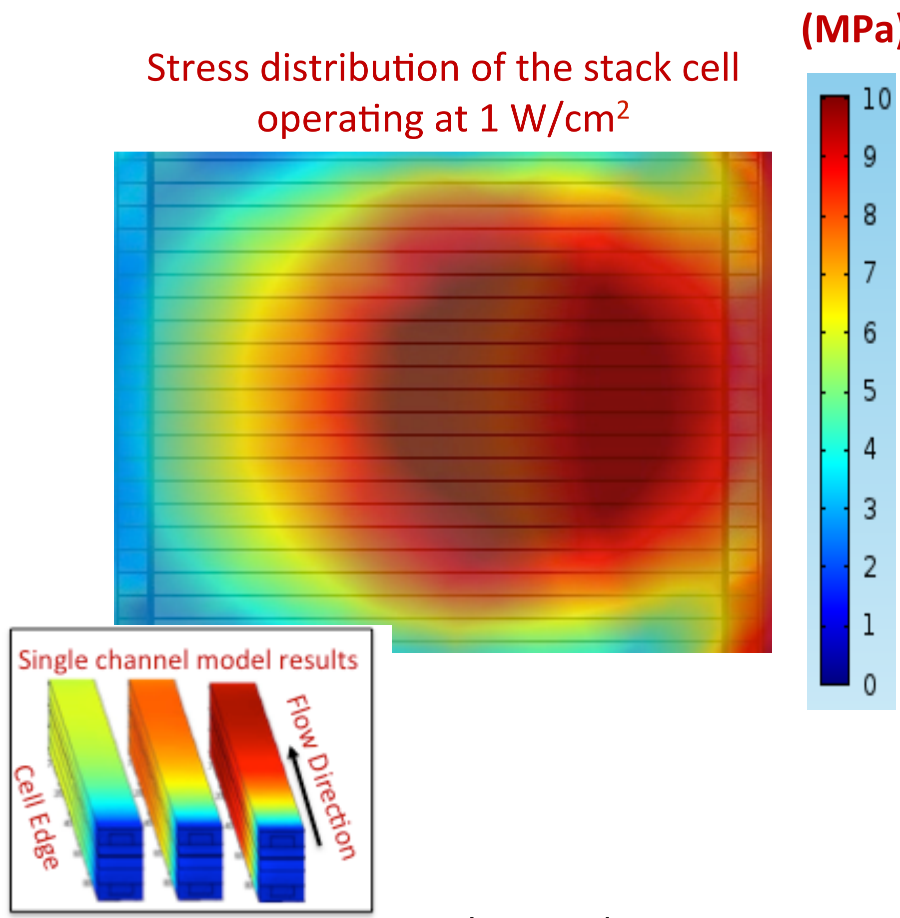


Expandable to entire stack



Example of Modeling Results





H_2 as fuel

- Integrated thermo-mechanical study based on temperature profile of stack is similar to iterative-solved single channel modeling results
- Stresses increase (up to 10 MPa) as temperatures rise in the center of the stack and concentrate mostly in the center and at end edge
- Model currently being used to evaluate enhancements for improved thermal management

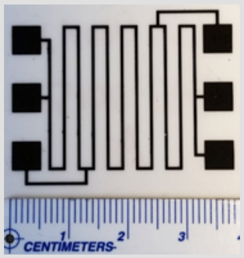
Stack Design Updates

- Tie Rod Holes, Endplate/IC Geometry
  - Optimized to minimize stress on cells and achieve lower cross-over leak rate
- Seal specifications
  - Minimum seal widths anywhere within stack
- Inlet/outlet specifications
  - Increased area to accommodate flows in larger stacks
- Plenum/Flowfield specifications
  - Based on other changes, modified to ensure uniform flow distribution from inlet to channels

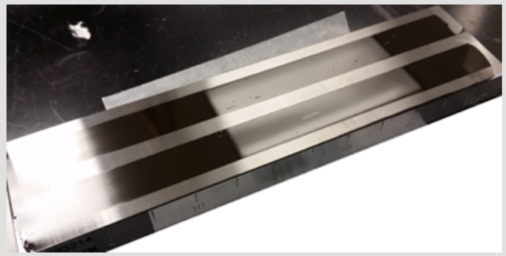
Cell Processing & Metrology Improvements

Cell and materials: Particle size analysis, bulk conductivity, XRD, etc.

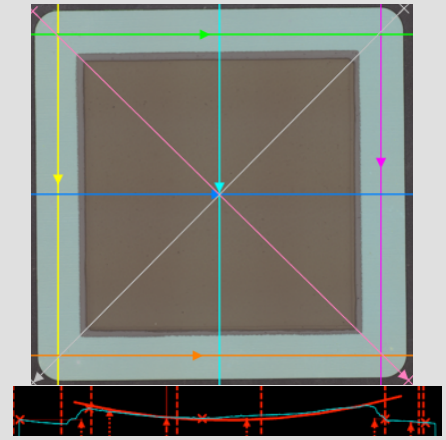
In-plane resistance



Paste uniformity
and viscosity

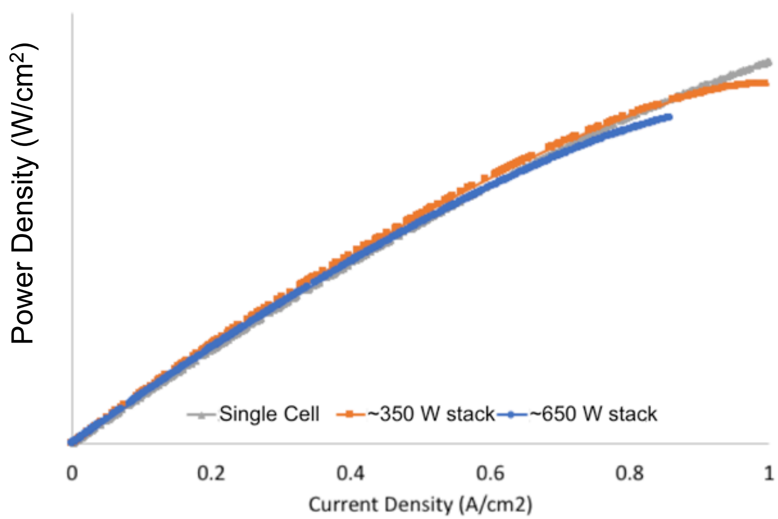


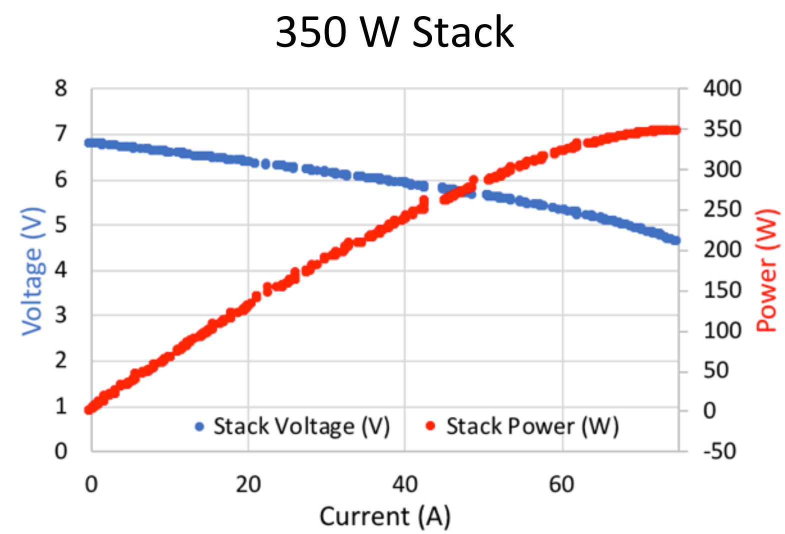
Optical profilometry



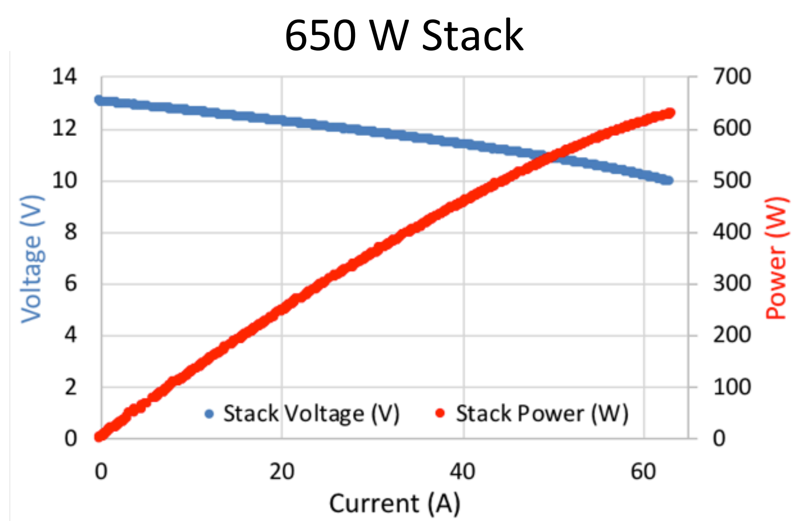
Fully qualified, semi-automatic screenprinting process for cathode and contacts

Scaling the updated stack design

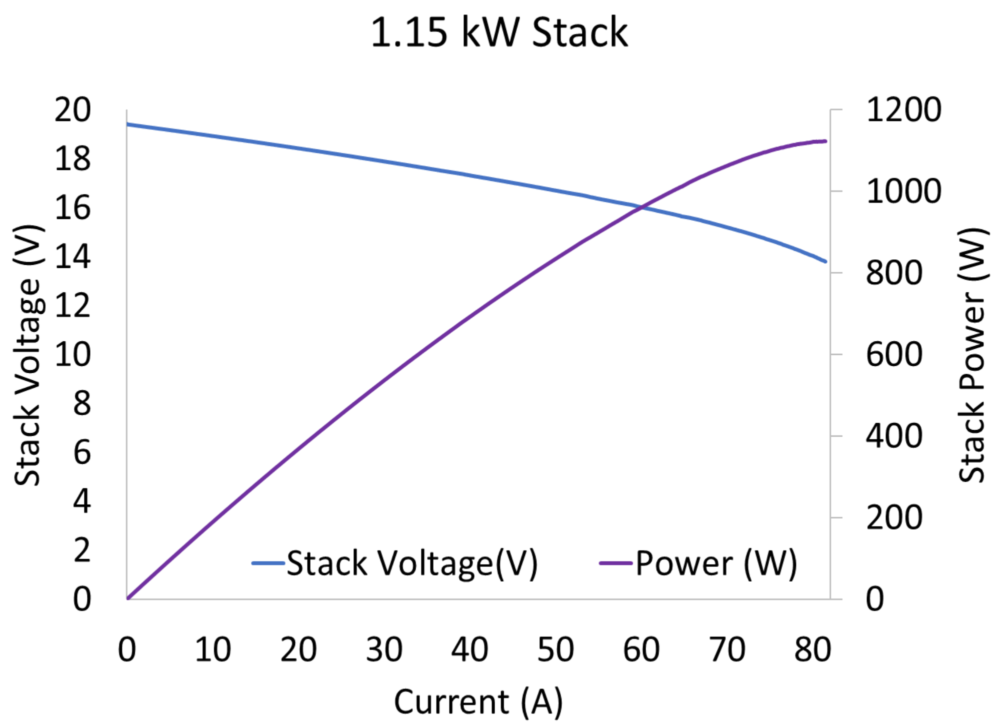




Stack Size	Anode -> Cathode X-Over	Cathode -> Anode X-Over
250 W	0.18%	0.21%
350 W	0.69%	0.29%
650 W	0.33%	0.46%
750 W	0.3%	0.29%



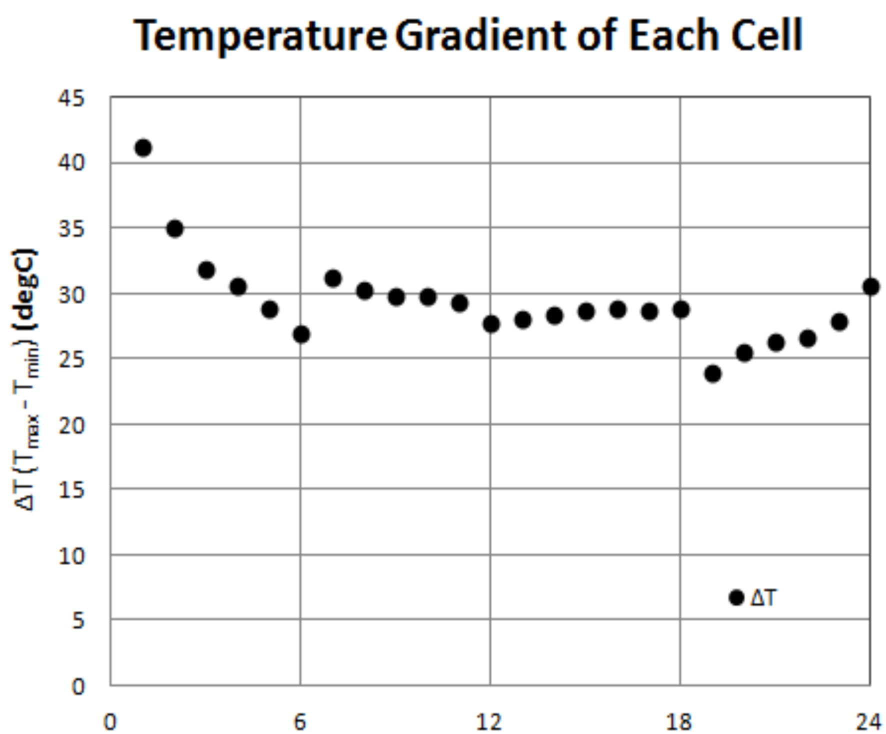
Stack Scale-up: 1.15 kW Stack



- >1.15 kW stack demonstrated
- Gas preheat with plate heat exchangers
- Additional performance anticipated with optimized thermal management
- Modeling predicts design should hold > 2.5kW
- New "lab reformer" just verified >2.5kW

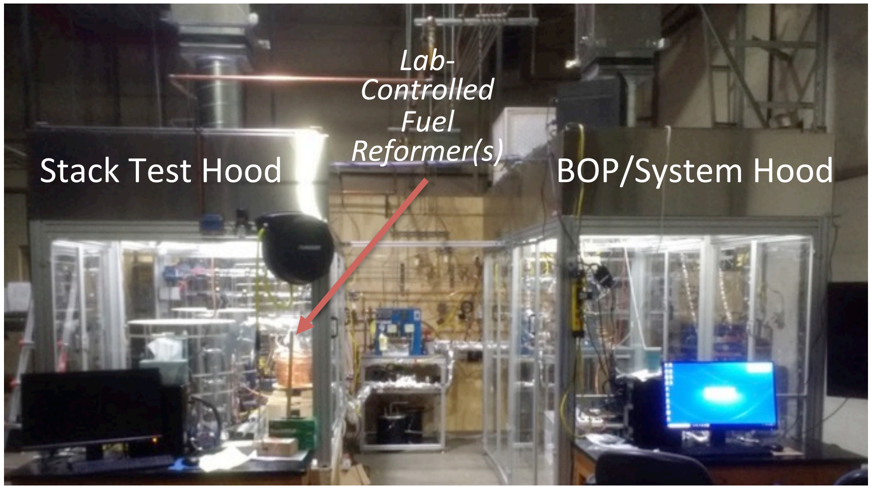
Data Analysis: Thermal Management

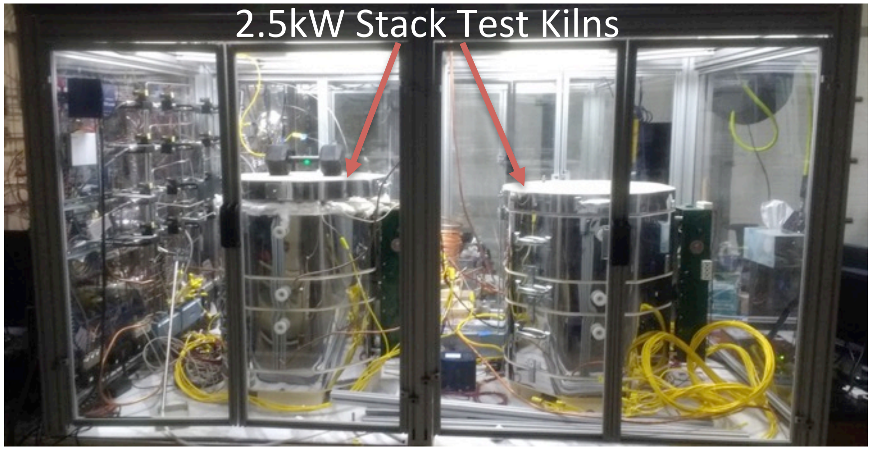
- Multi-physics modeling
  - Model validated using calculated cell temperatures from experimentally measured values
  - Model then used to probe ways to improve thermal management
- Temperature gradient across each cell within 1.15 kW stack
  - Largest gradients near gas manifold
  - Majority of the cells have gradient of ~25 °C to 30 °C



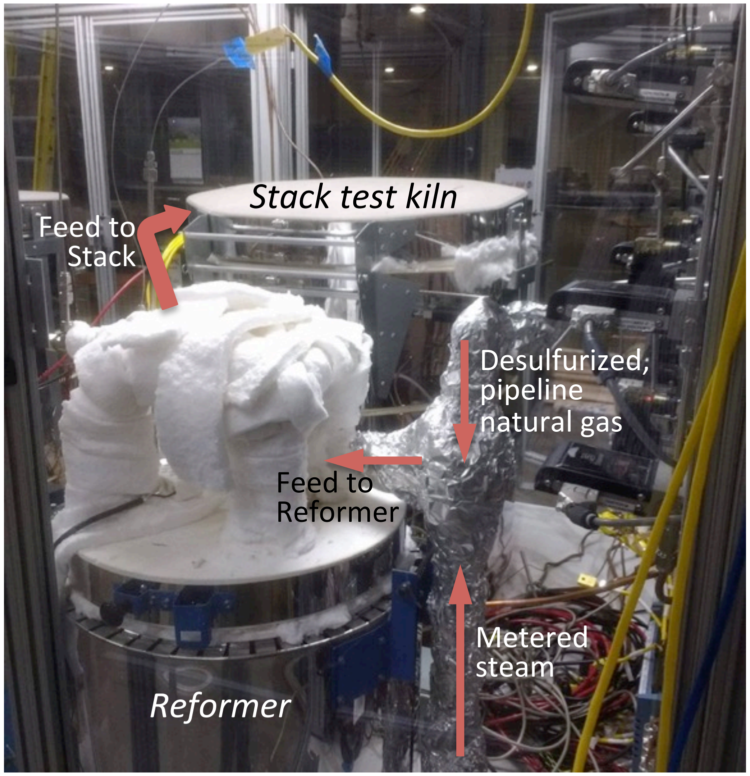
Redox's Natural Gas Test Facility (NGTF)

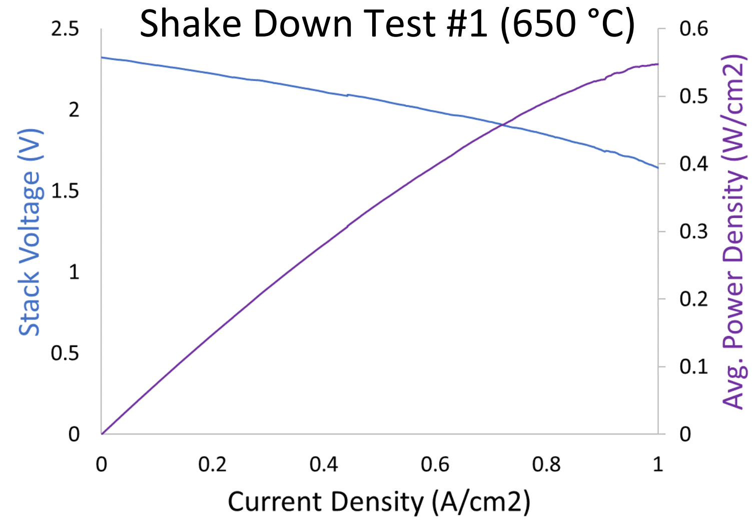
- Dedicated site for continuous NG use, no gas bottles required
  - Desulfurized and raw feeds available
- Presently can accommodate 2.5 kW stacks in each of 2 test stations
  - Test bench is designed for robust operation over long periods of time
- Several NG Reforming systems available, up to 9 kW stack feed
- Second test bench houses an islanded system prototype: only facility tie-in is NG

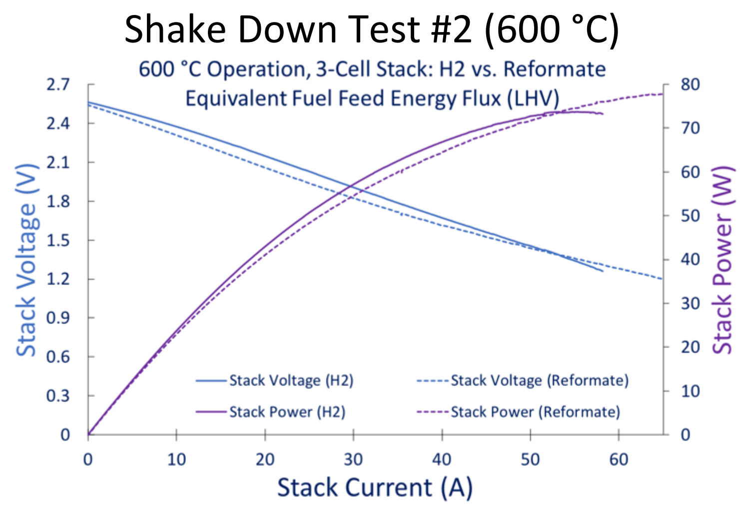




Lab-Controlled Pipeline NG Steam Reformer







Reformer capacity good for >2.5 kW stack

	H_2	CH_4	CO	CO_2	*H_2O*
Feed to Reformer	0%	100%	0%	0%	*5.6:1 S:C*
Feed to Stack (GC Measurement)	67.5%	10.1%	8.8%	13.2%	*Bal.*
Thermodynamic Equilibrium Values	78.1%	0.1%	7.8%	13.7%	*Bal.*

Red-Ox Robust SOFC Stacks for Affordable, Reliable Distributed Generation Power Systems

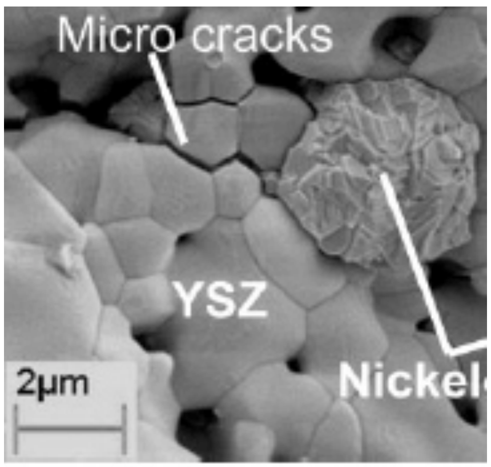
(DE-FE0027897)

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

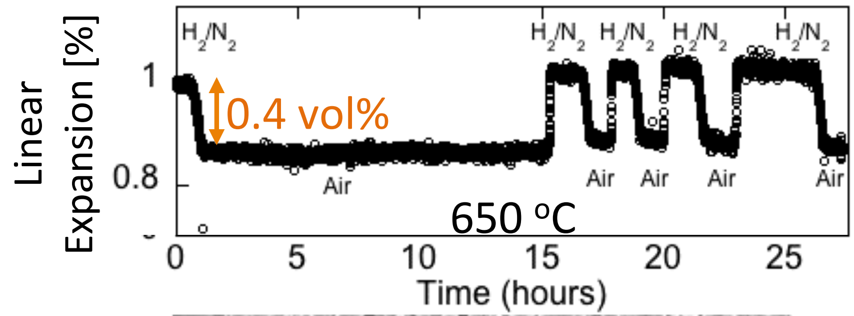


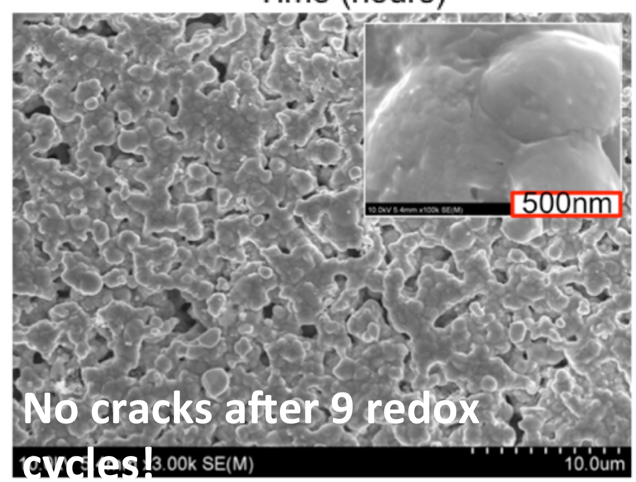
Journal of Power Sources 195 (2010) 5452–5467

~69 vol% expansion of Ni → NiO

Solution:

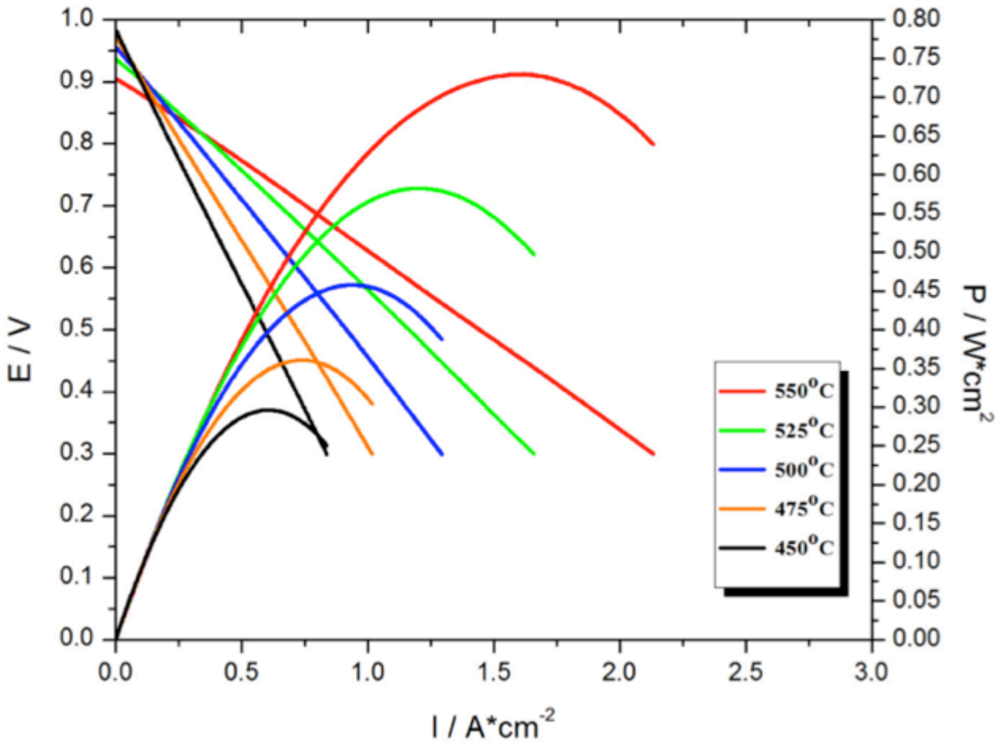
All ceramic anode → small Δoxygen = small dimensional change (0.4 vol%)



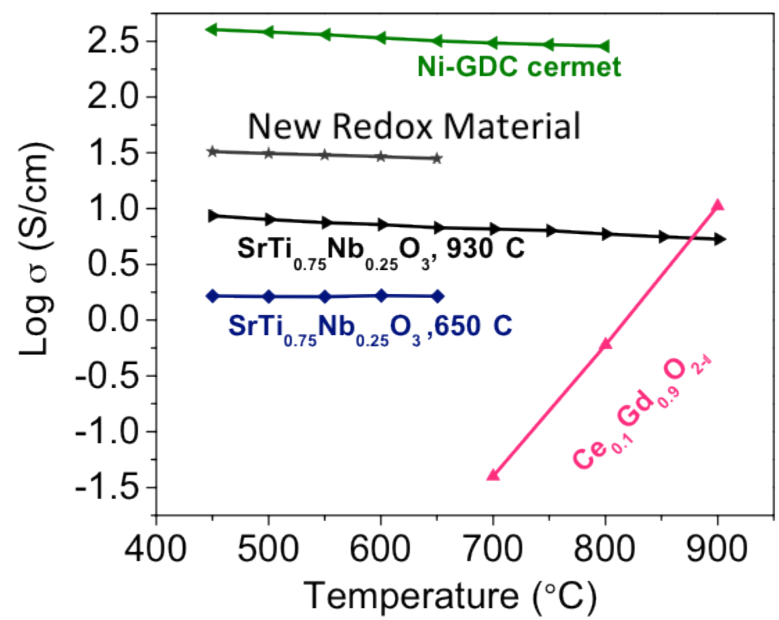


All-Ceramic Anode SOFC Performance

Button cell data



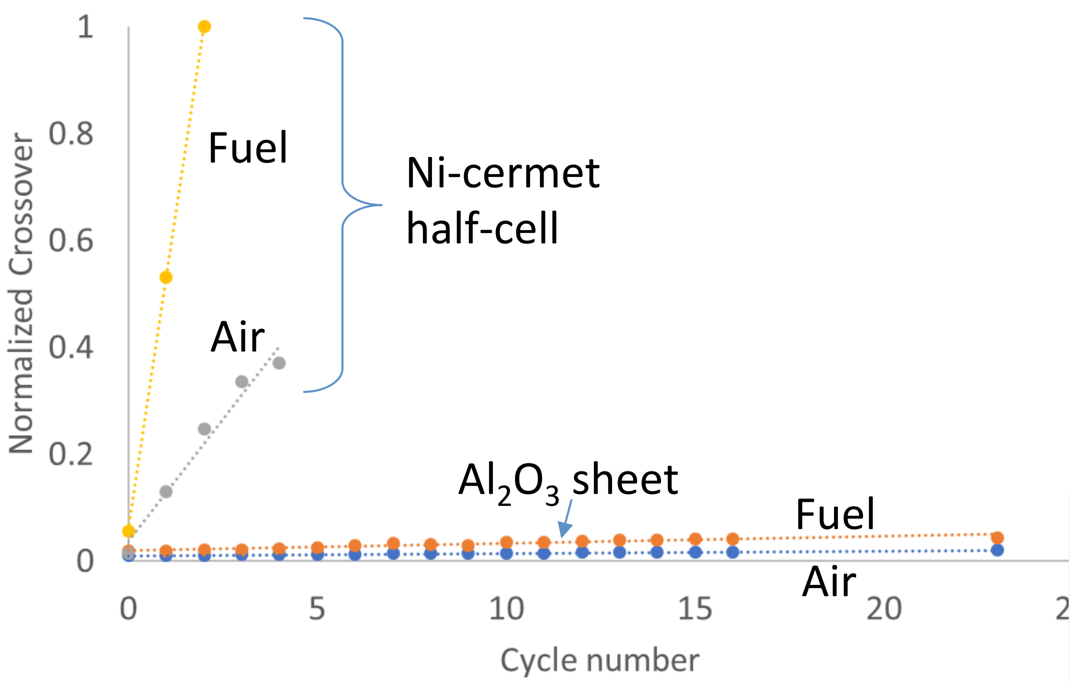
Anode electrical conductivity

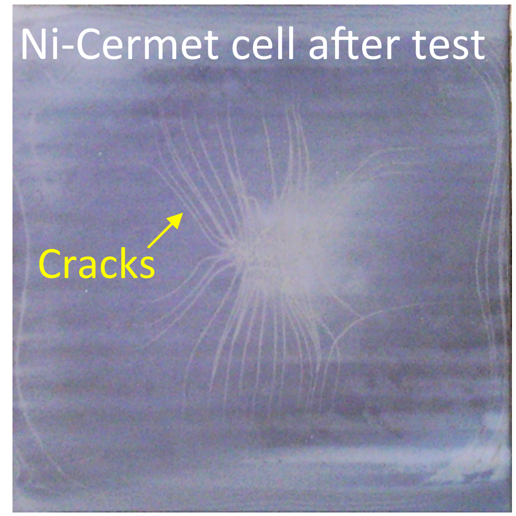


- High power densities
  - ~0.75 W/cm^2 @ 550°C
  - ~0.3 W/cm^2 @ 450 °C
- Acceptable electronic conductivity

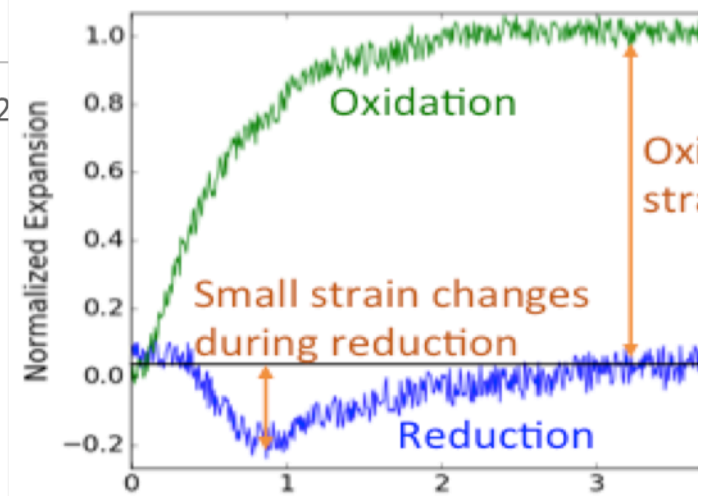
Seal and Gen.1 Cell (Ni-Cermet) Red-Ox Cycling Stability

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





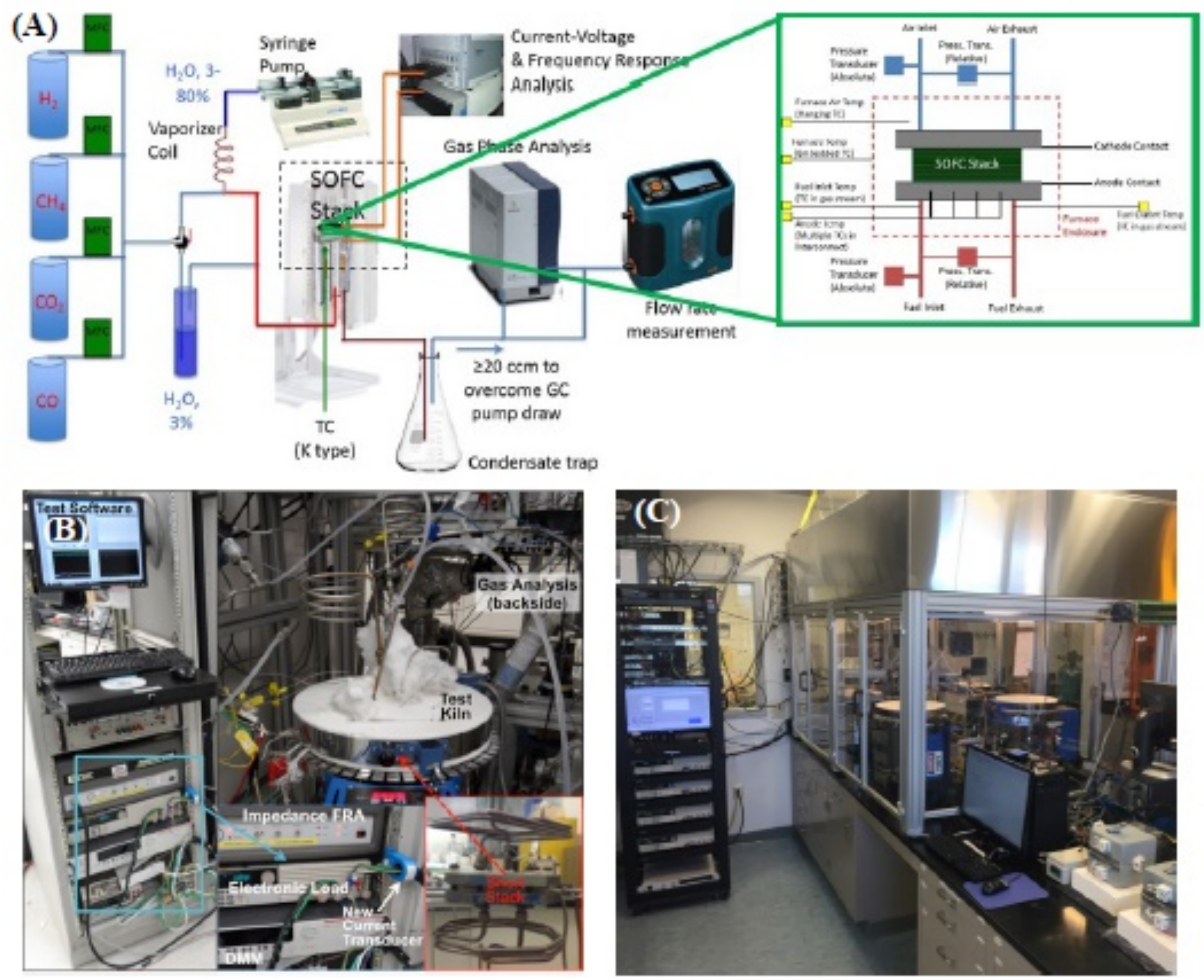
~1% half-cell expansion on oxidation



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), then fails catastrophically
- Seals with Al_2O_3 sheet "mock cell" show small increase in cross-over with cycling (H_2 ↔ air)
  - -Dilatometry: seal shrinks by ~2% after > 20 red-ox cycles

SOFC Testing Capabilities



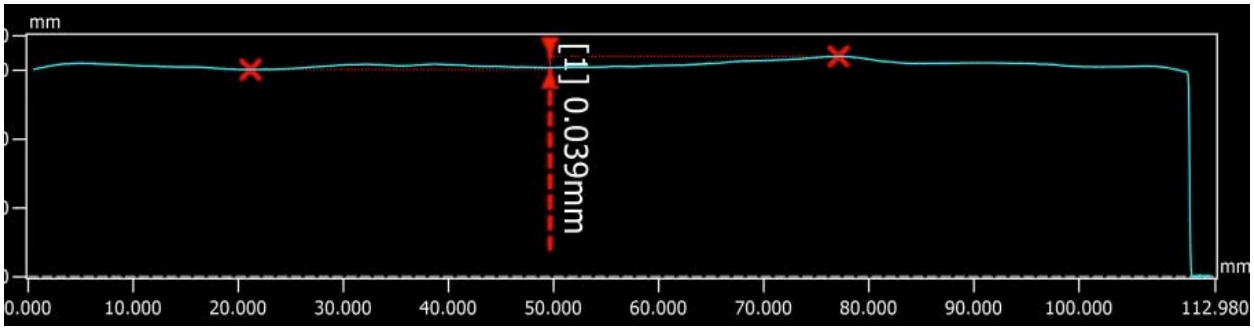
Biologic BCS-815

- 8-channel
- 15 A/channel
- Potentiostat
- Impedance analyzer
- →Mini-cell short stack and 5x5 stack testing

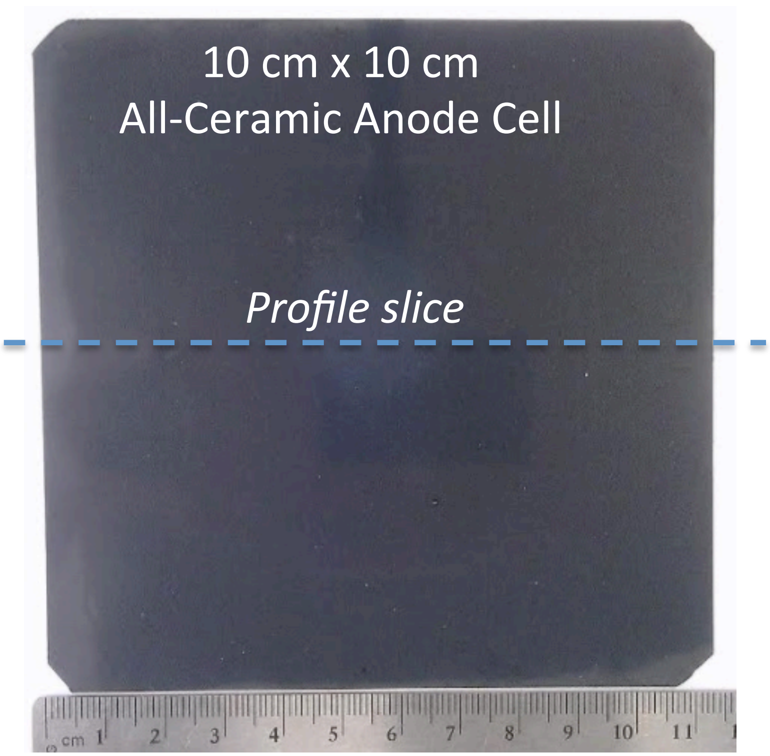
Scaling for All-Ceramic Anode Manufacturing

- Production-scale tape casting and laminate manufacture with production partners
- Production-scale cell firing with production partners
- Multiple commercial-scale casts of all-ceramic anode production tape
- Successfully fabricated and fired >30 10 cm by 10 cm laminates
- Production cast alternative electrolyte and anode functional layers tailored for all-ceramic anode cells
- Future work involves introducing modified anode structure in production runs and continued casting for large-scale stack needs

Flat All-Ceramic Anode Cells

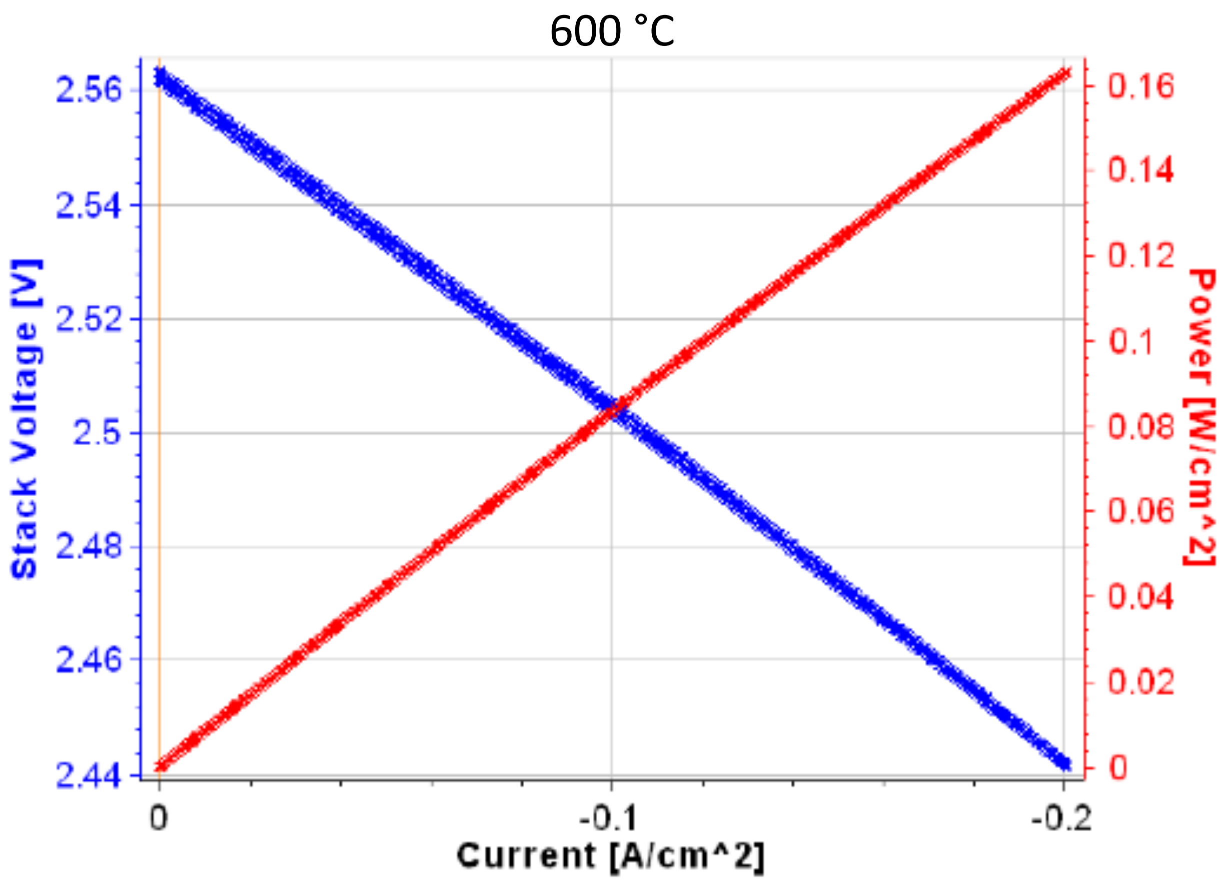


Cell Profile
Only 0.039 µm variation (max − min)



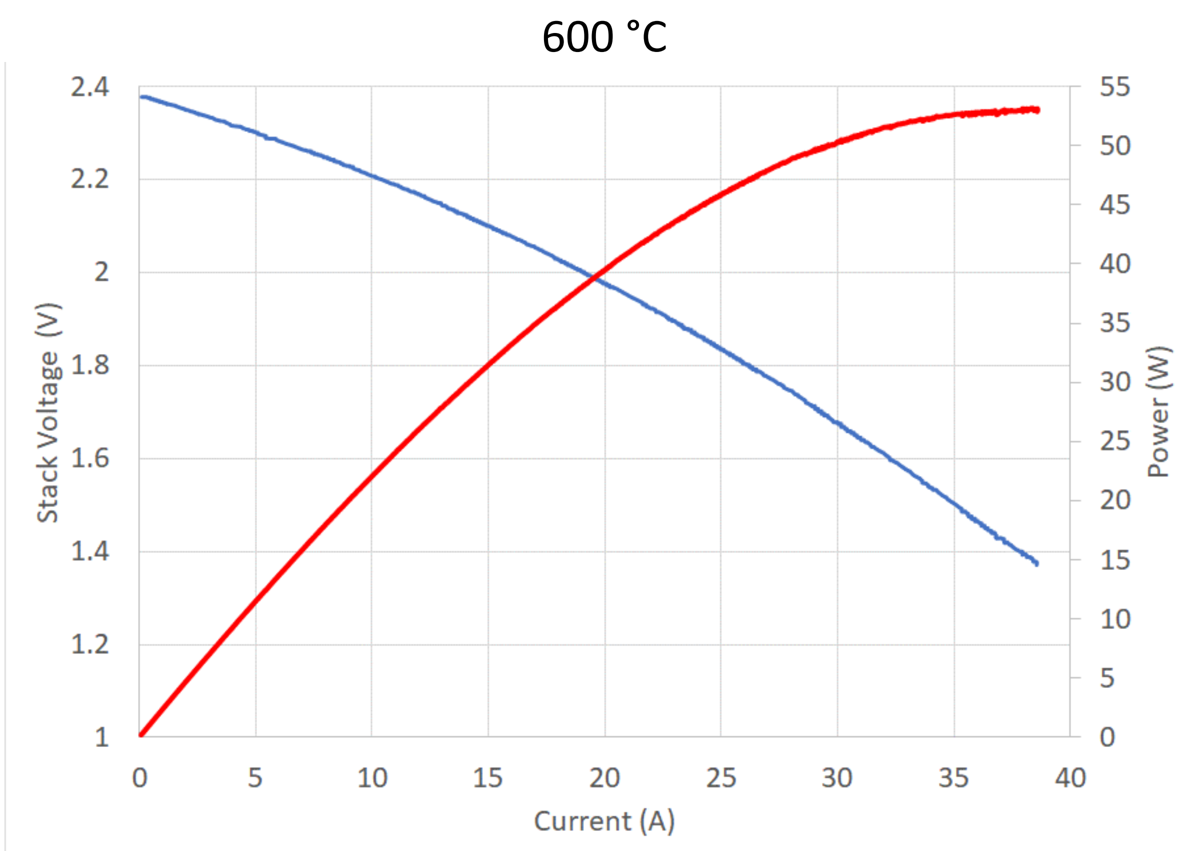
- *Achieved very flat all-ceramic anode cells fabricated at R&D, and "production" scale*
- *Demonstrated firing in large "production" kilns*

3-cell 5 cm x 5 cm All-Ceramic Anode Stack



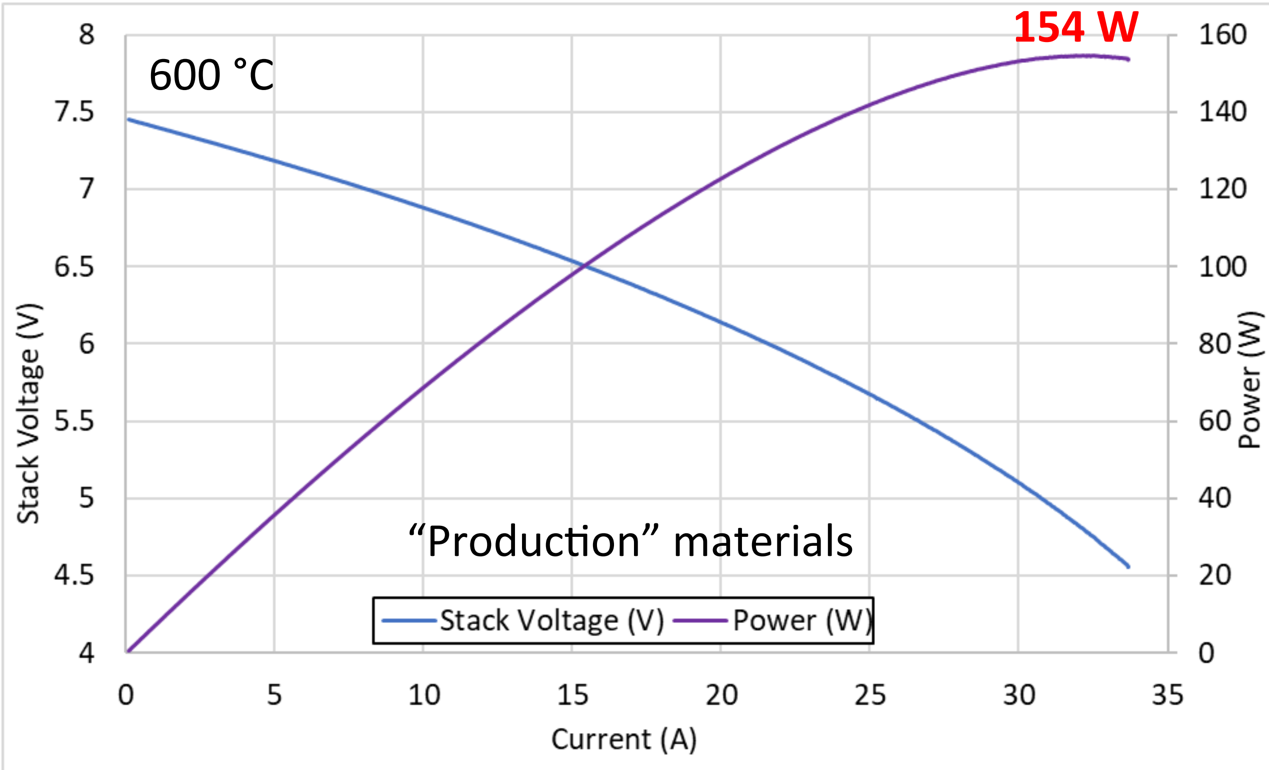
- *First stack demonstration of R&D-scale fabricated cells*
- *Low ASR ~0.19 Ω-cm² at 600 °C*

3-cell 10 cm x 10 cm All-Ceramic Anode Stack

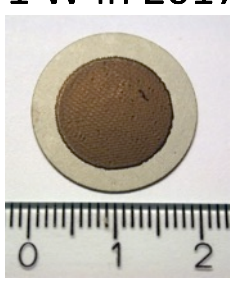


1st stack demonstration of "production" cast and laminated Gen-3 cells

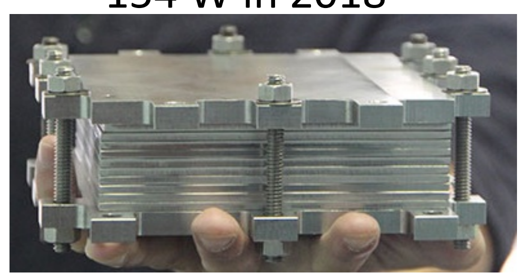
10-cell 10 cm x 10 cm All-Ceramic Anode Stack



< 1 W in 2017



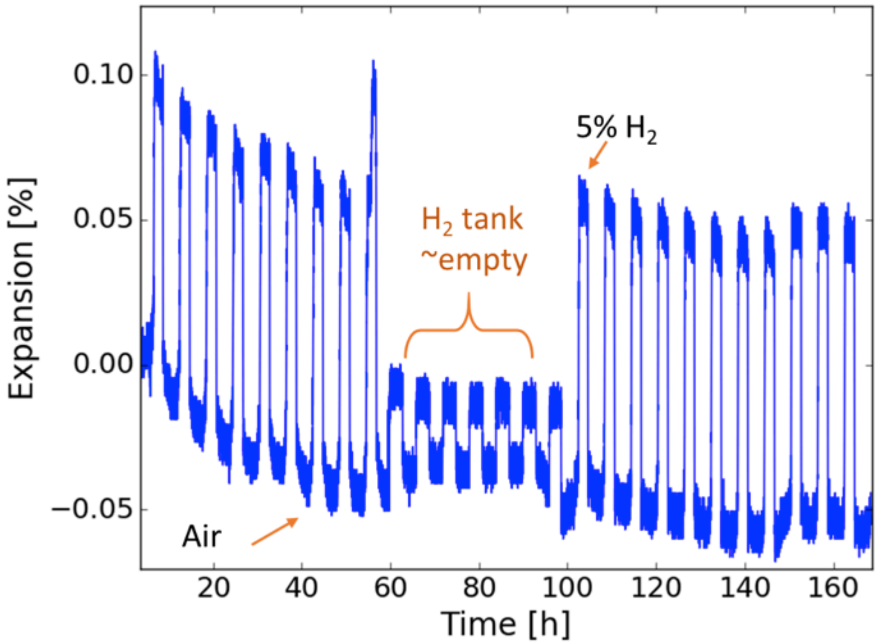
154 W in 2018

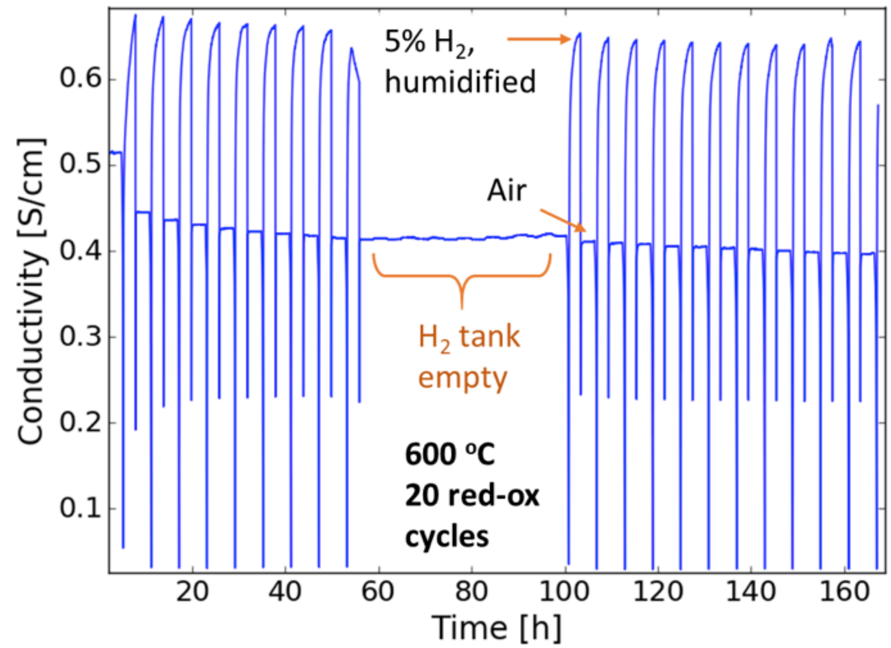


*Note: Cell performance not fully optimized. Additional power out of same size stack by end of project.

Red-Ox Cycling of Half-Cells

Dilatometry and conductivity measurement of all-ceramic anode half-cell sample





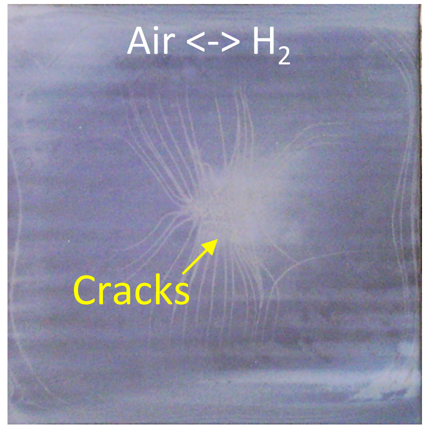
- *Cell expands during reduction and shrinks reversibly during oxidation*
- *Likewise, conductivity increases in H_2 and decreases, reversibly, in air*

Microstructure After Red-Ox Cycling

Optical microscope images of electrolyte side

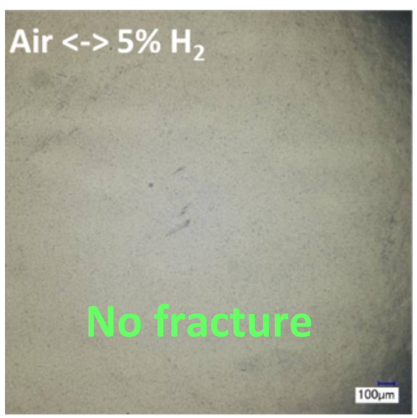
Ni-Cermet Cell

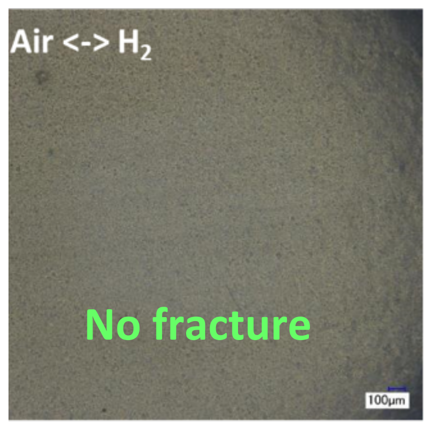
After <u>1-2</u> red-ox cycles

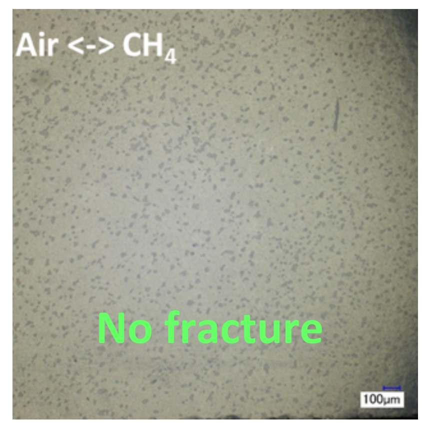


All-Ceramic Anode Cell

After ~<u>10-20</u> red-ox cycles

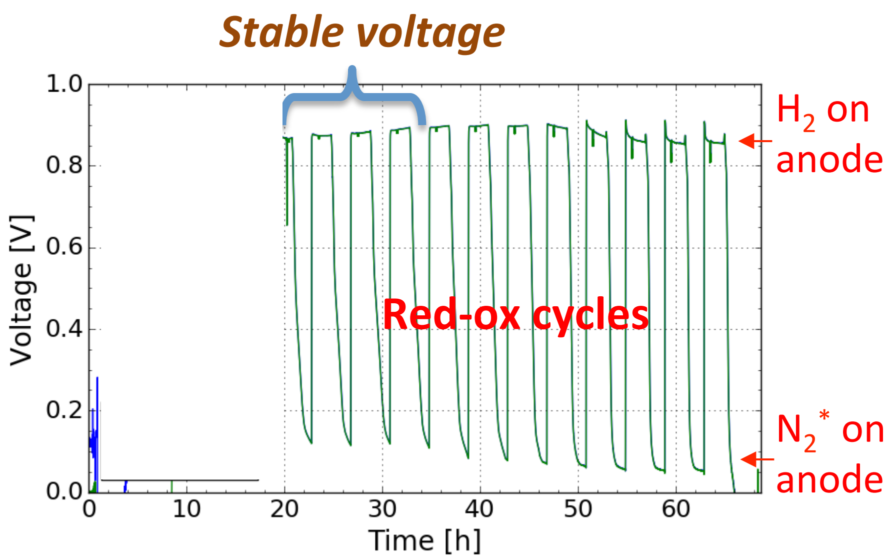


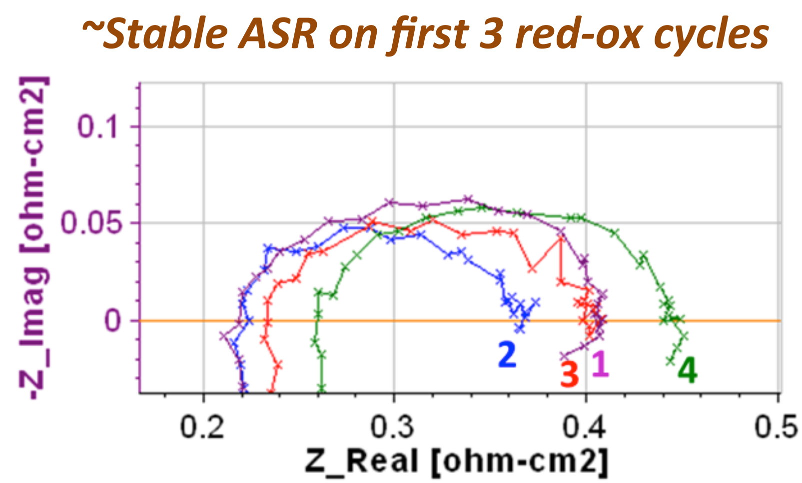


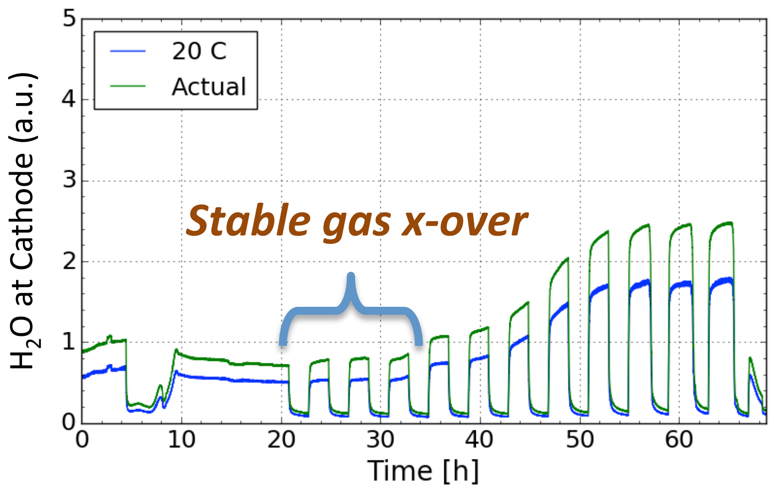


Red-Ox Cycling 5x5 SOFCs

Improvements to anode structure of 5x5 cells enables improved red-ox cycling @ 600 °C





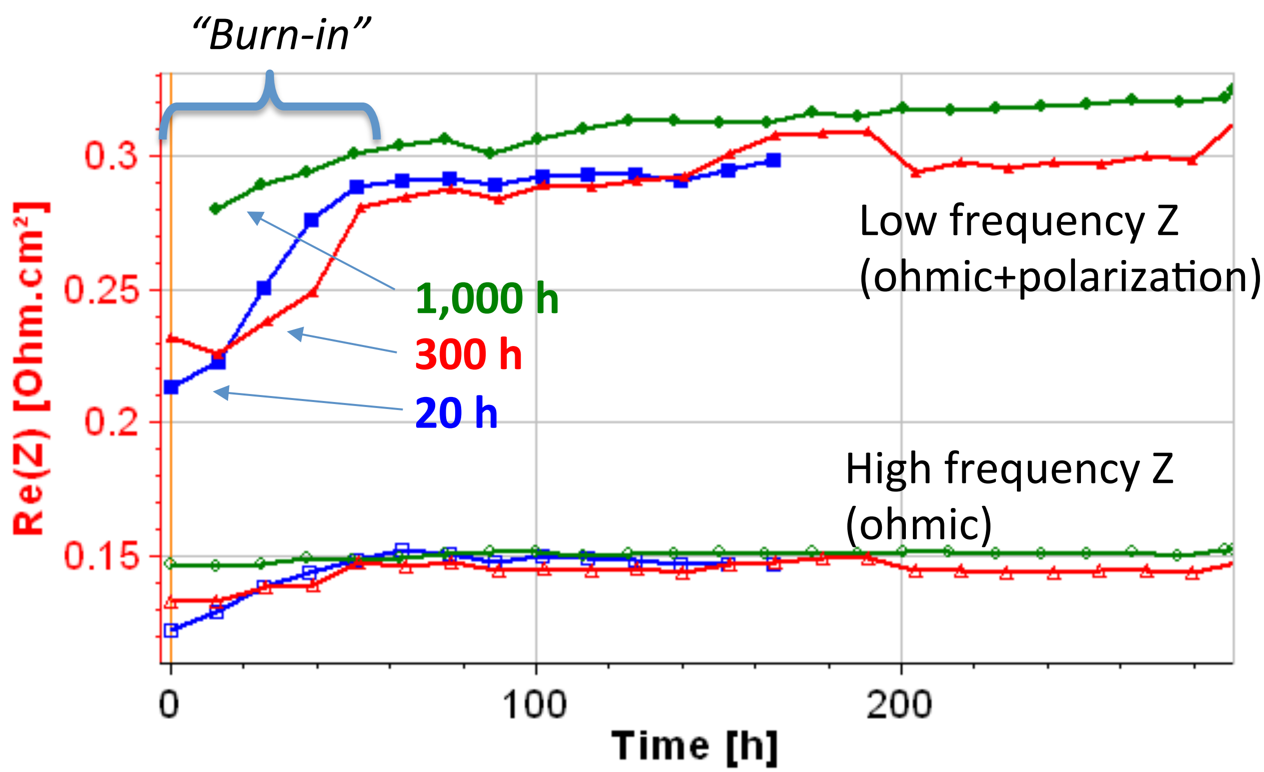


- 3 red-ox cycles with minimal ASR and OCV degradation
- Further cycling → increase in gas cross-over indicating cell fracture
- Future work includes continued anode structure modification

*N_2 has ~0.1% O_2 impurity

Accelerated Testing: Cathode Degradation

GEN1 mini-cells aged ex situ at 650 °C in air for indicated time, then tested

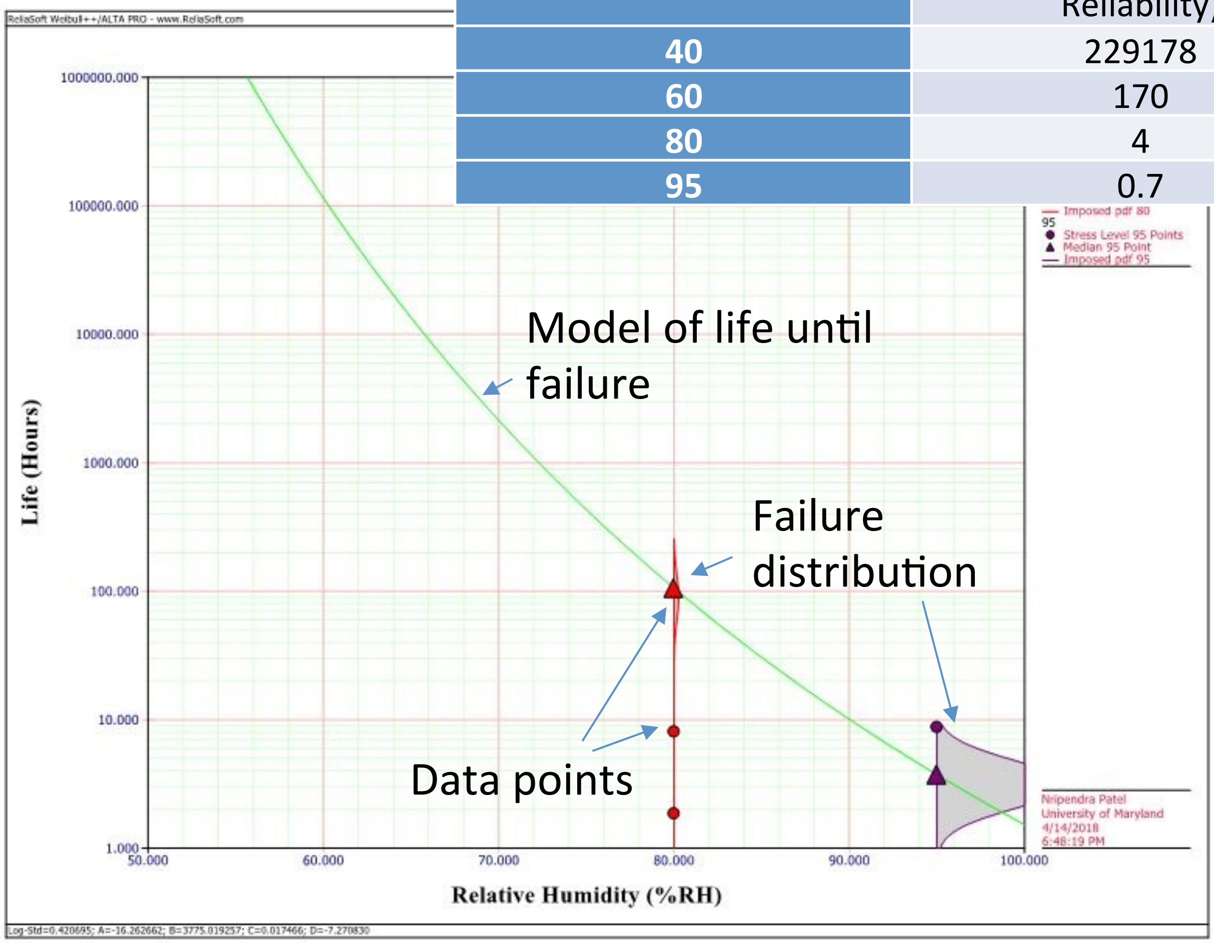


- *Increased ex situ aging results in less Initial ohmic burn-in (<60 h) → ohmic burn-in takes place during ex situ aging, likely cathode/contact related*
- *Similarly, polarization burn-in annealed into ex situ aged samples*
- *Long-term increase in total Z expected in SOFC test appears to be "added" to 1,000 h ex situ annealed sample*

Accelerated Testing: Storage Conditions

Measurement of all-ceramic anode test specimen. Similar behavior found on LSCF and LSC.

Effect of RH on Life at 25⁰C	100% Increase in Resistance	1500% Increase in Resistance
% RH	Life in Hours (95% Reliability)	Life in Hours (95% Reliability)
40	229178	$5.71*10^{10}$
60	170	57584
80	4	53
95	0.7	2

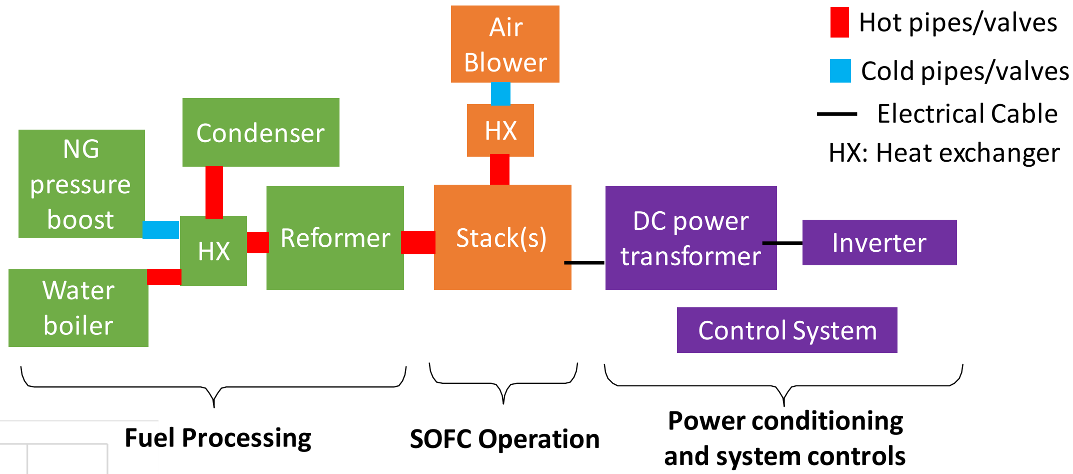


- *Device lifetime depends significantly on failure threshold criteria*
- *Lifetime is dramatically shorter at very high humidity (≥60%) at 25 °C*
- *Future work includes additional RH-T studies to refine model for all-ceramic anode and cathode materials*

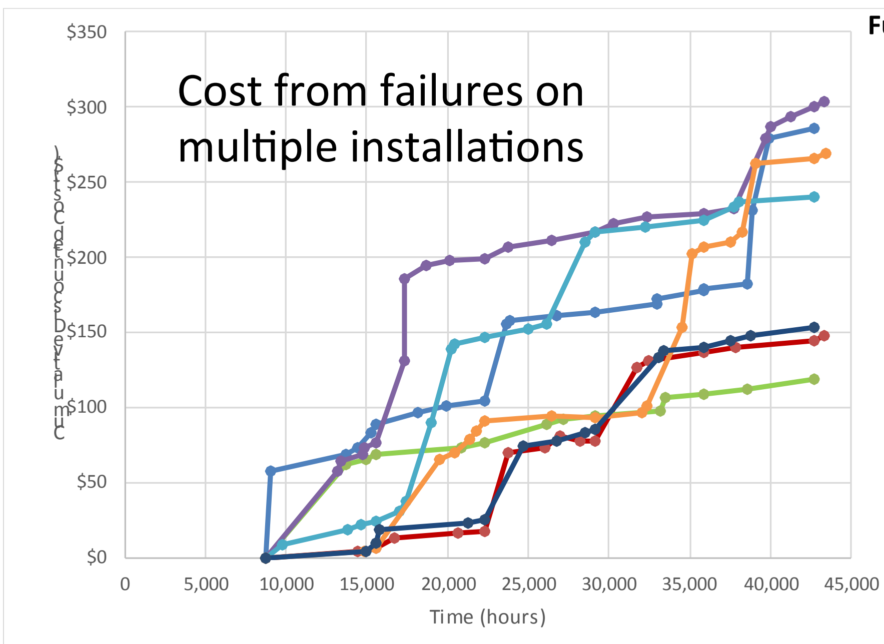
Discrete Event Simulator

- Simulates cost of system over lifetime of warranty
- Includes estimates of mean-time-to-failure (MTTF) of system components

Schematic of system design approximation



Model output

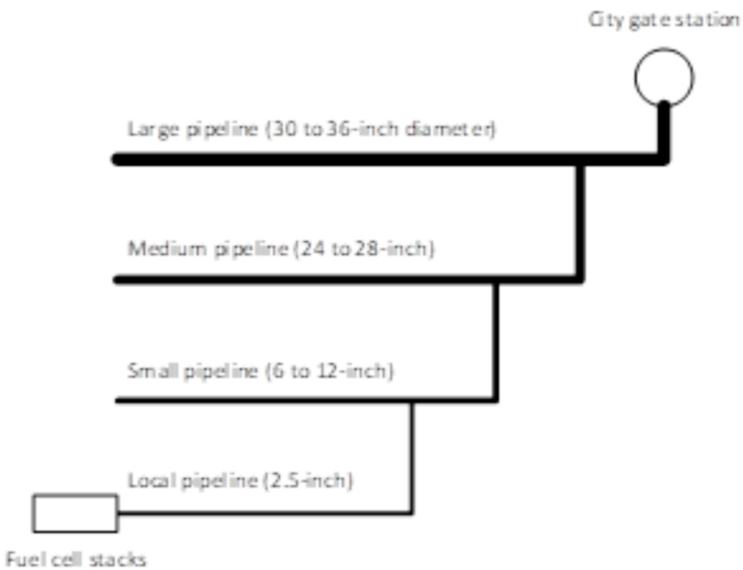


- *Initial deployment and stack replacements largest cost components in initial model*
- *Stack replacements include failure due to "critical events"*
- *Future work includes improving estimates of MTTFs, costs, and model utility*

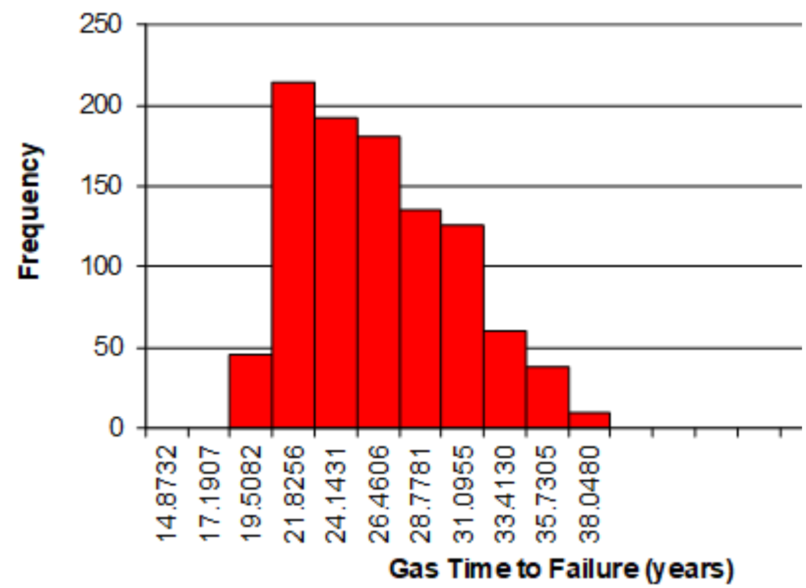
Natural Gas Pipeline Failures

(Monte Carlo based on pipeline model)

Pipeline model



Failure frequency prediction



- *Includes estimates from literature on failure frequency of different pipe sizes[1] – most failures originate from "dig-ins"*
- *Natural gas pipelines estimated to not fail for >20 years*

[1]J House Environmental, Pipeline Risk Analysis - Mountain House Specific Plan III, 2004. http://www.sjgov.org/commdev/cgi-bin/cdyn.exe/handouts-mtnhouse_EIR_Appendix_K_Pipeline_R?grp=handouts-mtnhouse&obj=EIR_Appendix_K_Pipeline_R (accessed October 16, 2017).

Projects Summary

DE-FE0026189 (NETL-1)

- Improved stack assembly and QC procedures
- Stack scale-up for improved design: 1.15 kW stack demonstrated
- >2.5 kW lab reformer verified along with rest of setup for testing 2.5 kW stack
- Cell production ramped up to begin moving toward 2.5 kW stack

DE-FE0027897 (NETL-2)

- Improved flatness of fired all-ceramic anode half-cells
- Scaled up all-ceramic anode production with tape casts, lamination, and firing
- Successfully tested 10-cell 10x10 all-ceramic anode stack
- Manufacturing cost and discrete event simulator models in workable state, refining with improved parameters

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  - Energy Research Center (fundamental R&D)