Summary of SOFC Development at Redox Power Systems

07/10/2020

U.S. Department of Energy, National Energy Technology Laboratory's (NETL) 21st Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting

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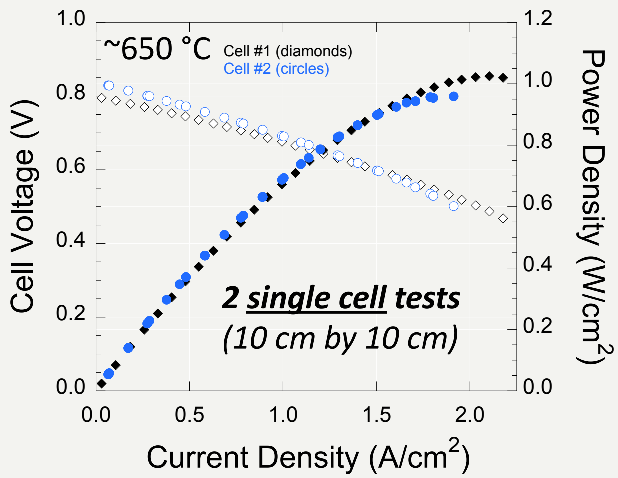
NETL Projects at Redox

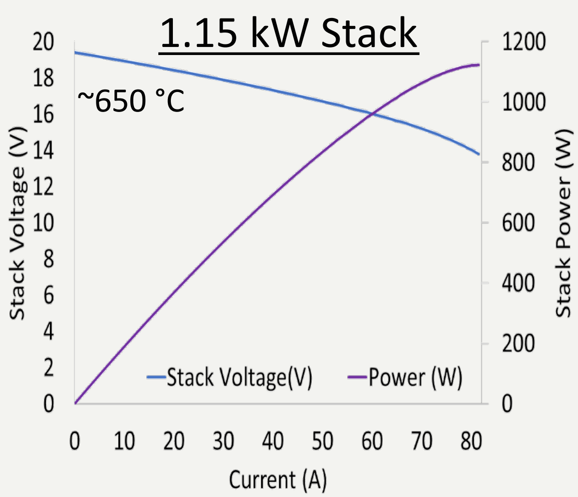
1. **FE0026189:** High power, low cost solid oxide fuel cell (SOFC) stacks for robust and reliable distributed generation
2. **FE0027897:** Red-ox robust SOFC stacks for affordable, reliable distributed generation power systems
3. **FE0031178:** High throughput, in-line coating metrology development for SOFC manufacturing
4. **FE0031656:** Sputtered thin films for very high power, efficient, and low-cost commercial SOFCs

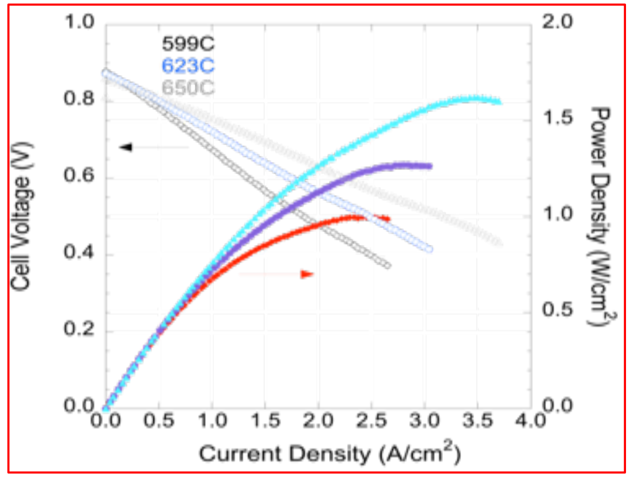
1. Redox Cells & Stacks

Gen-1 Cell

- GDC electrolyte cell shows good performance at lower operating temperatures
- Established manufacturing for 10 cm by 10 cm cells
- Gen-1 cell used in this project's larger stacks



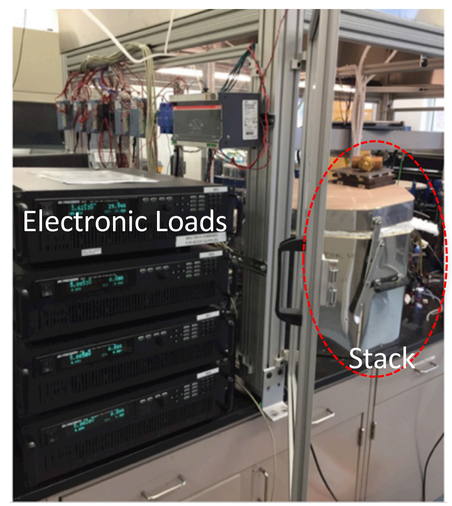




Gen-2 Cell

- Optimized anode offers higher performance over Gen-1 cell
  - >1.8 times higher power density
  - > 5% higher open circuit voltage
- Scaled to 10 cm by 10 cm
- Manufacturing optimization needed

- Lab-scale setup
- Wet H_2 fuel
- Relatively high concentration polarization
- Better performance possible with improved reactant distribution in stack



Stack Development & Natural Gas Test Facility

Summer 2019

Summer 2020

- 8+ test stations for cell/stack development testing
- 2 large stack test stations and bench top system equipment
- Systems development walk-in hood
- Large pipeline natural gas feed capacity can more than support current reformer equipment for >15 kWe.
- Light manufacturing and engineering space as well

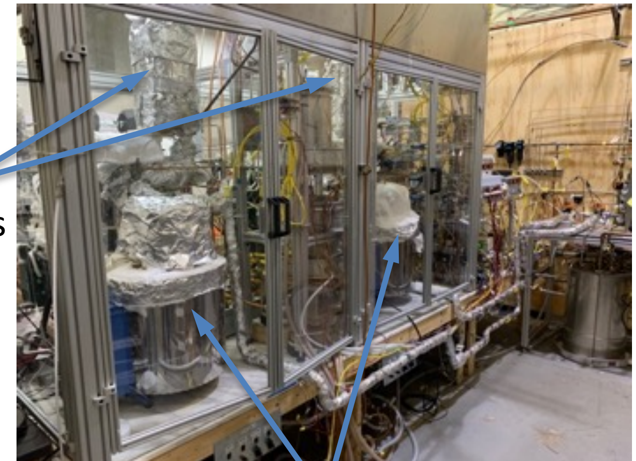
Large Stack Characterization & Bench Top System

Large size stack(s)

Individual or 2-Stack Module

Balance of Plant

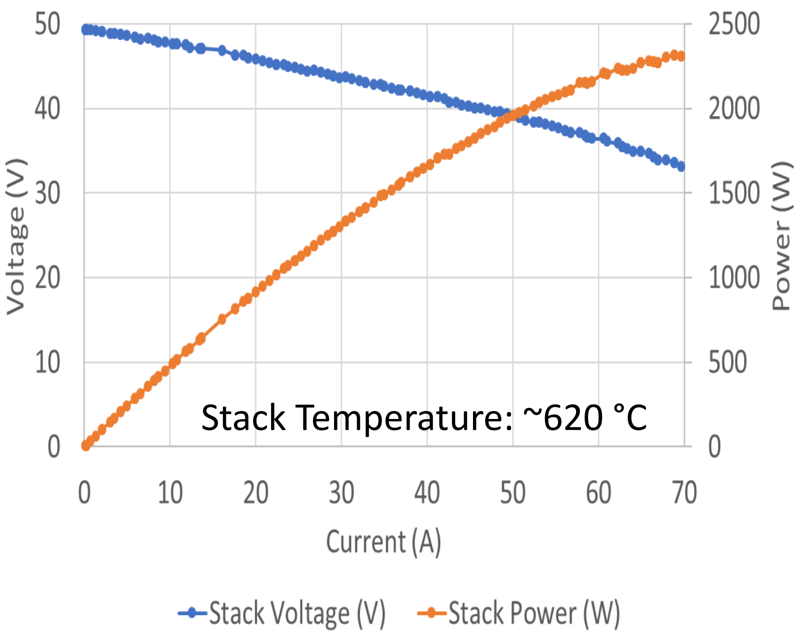
Cathode Recuperators



Steam Reformers

Individual, Large Stack (~2.4kW) Characterization

(reformed, pipeline natural gas fuel)

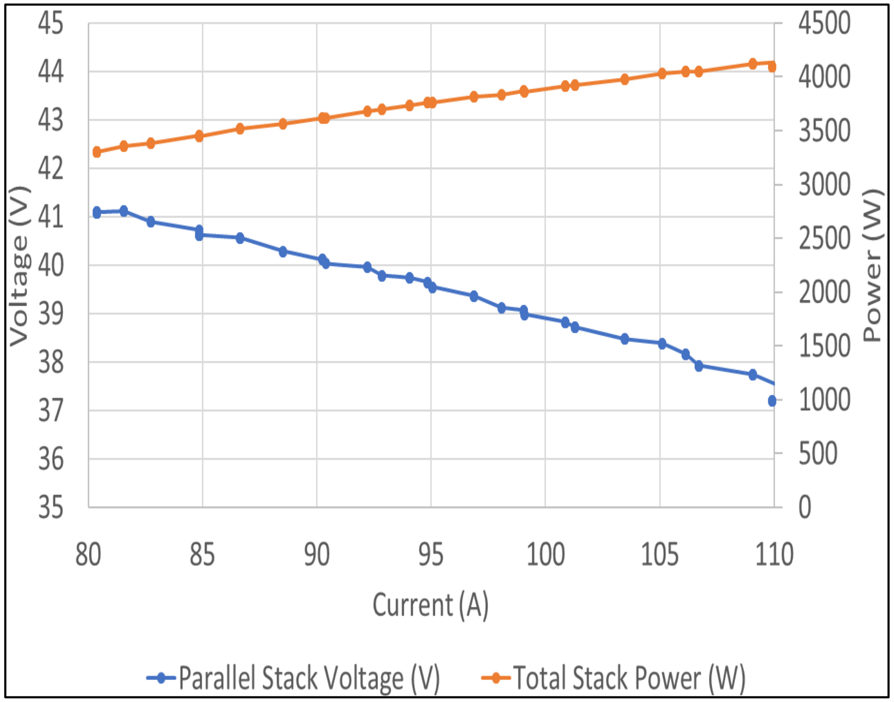


- Bench top system BOP is on opposite side of hood from stacks
  - Steam control
  - Steam reformers
  - Air delivery (shop compressor) with cathode recuperator heat exchangers
  - Electronic load bank: >12 kW
  - System instrumentation, control, and data logging

2-Stack Module: ~4.2 kW

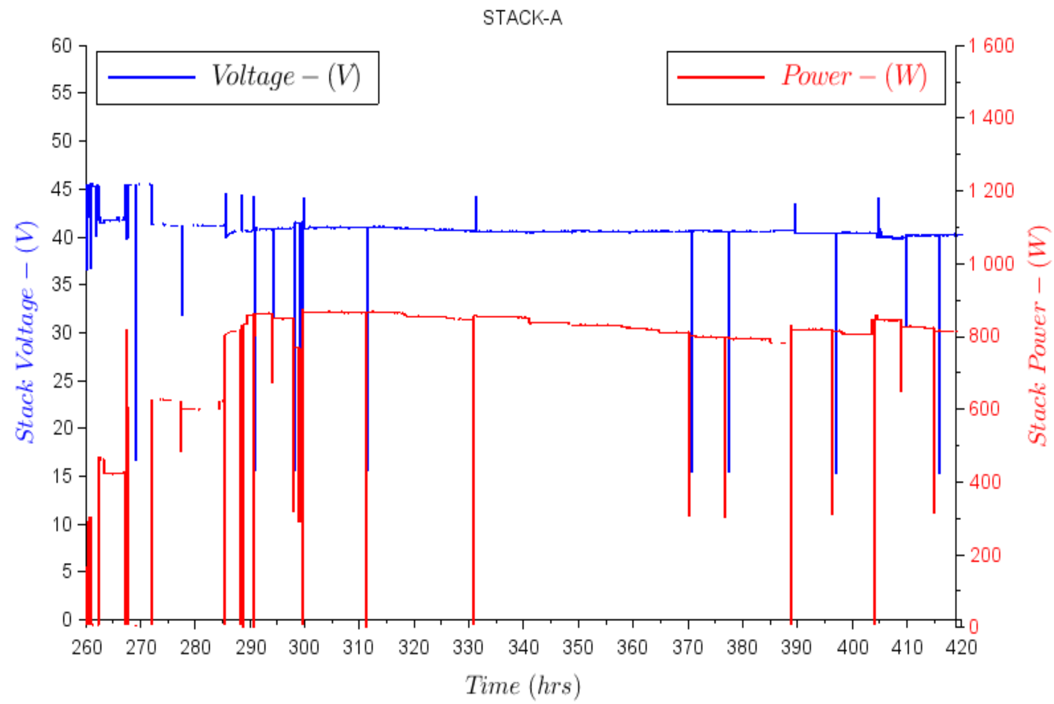
Reformed, pipeline natural gas fuel with stack operation at ~600 °C

Stack Module: Stack A & B (parallel)



- Current-voltage-power characteristic acquired from base constant current load of 80A
- Difference in current between stacks A & B of parallel-connected module: ~6 Amps

Stack-A Time Series



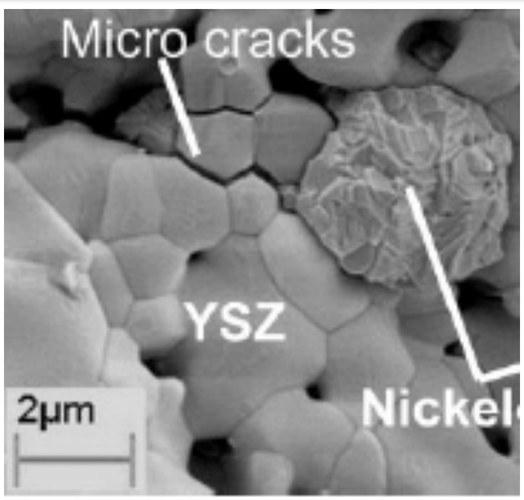
- From approximately 285-420 hours, relatively minor changes in current caused power levels to fluctuate slightly (~2.5%) around 0.8 kW
- This was traced to a problem with the system safety chain and had negligible impact on the stack operating voltage, which remained essentially unchanged during operation

2. Red-ox Robust Stacks

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

- Interruptions in fuel supply
- 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

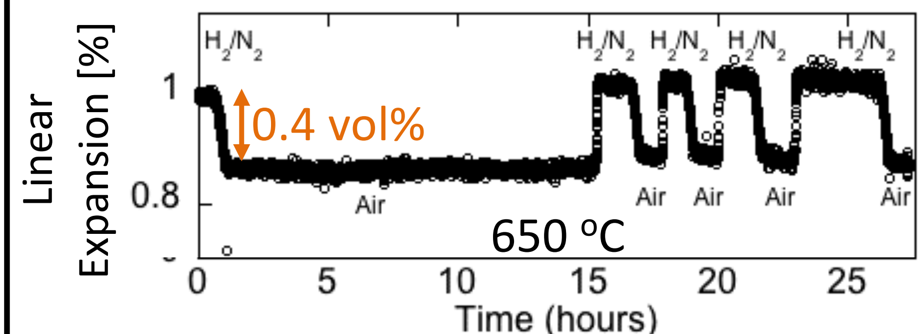


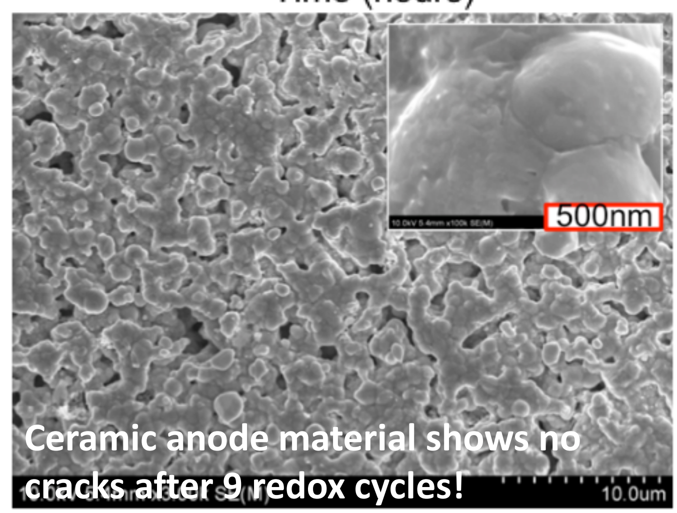
Journal of Power Sources 195 (2010) 5452–5467

~69 vol% expansion of Ni → NiO

Solution:

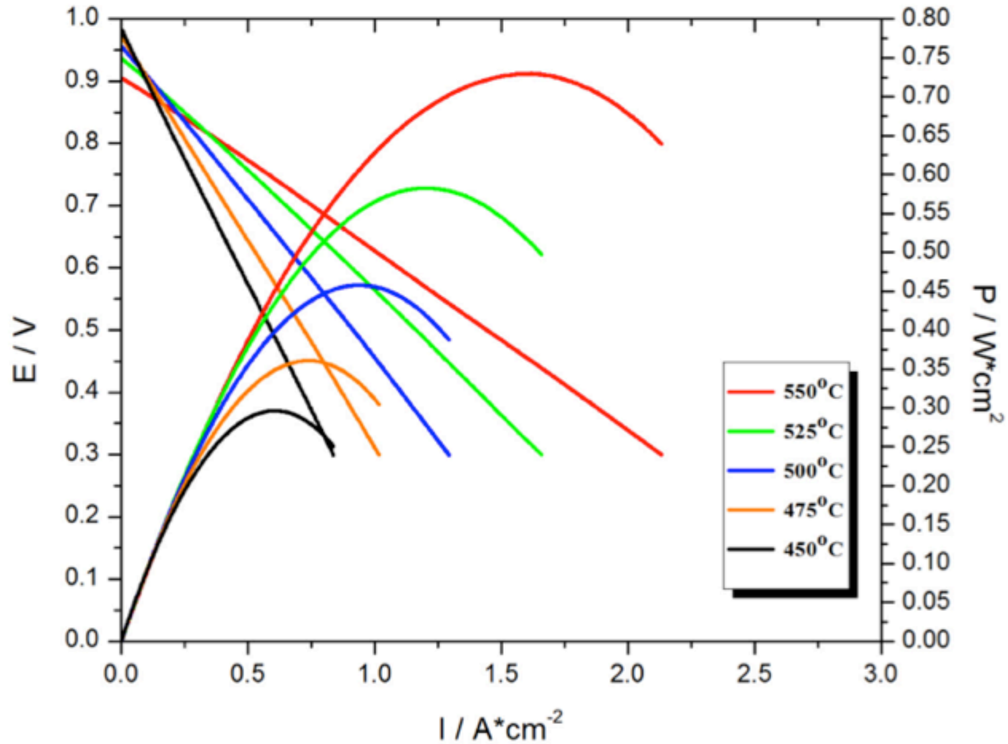
All ceramic anode → small Δoxygen = small dimensional change (0.4 vol%)



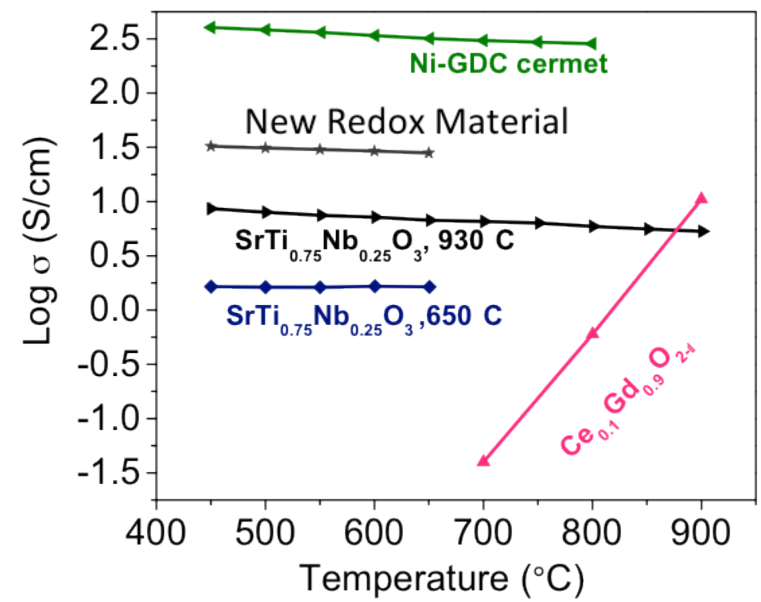


All-Ceramic Anode Performance

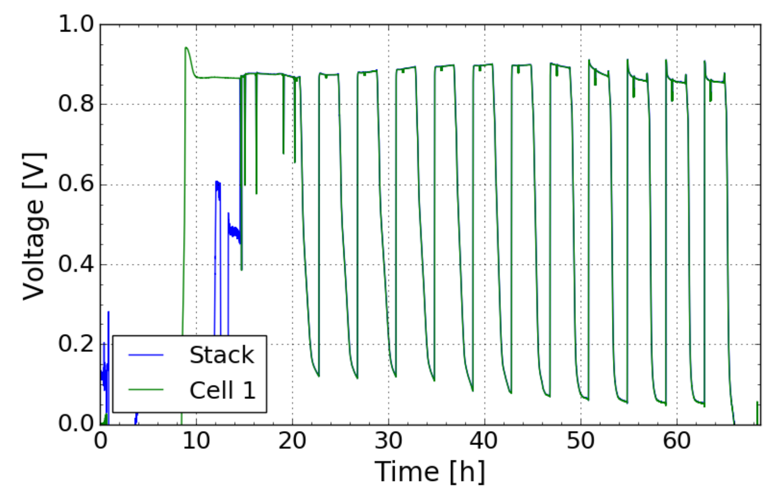
Button cell data



Anode electrical conductivity



Red-ox Cycles: *5 cm by 5 cm cell (600 °C)*



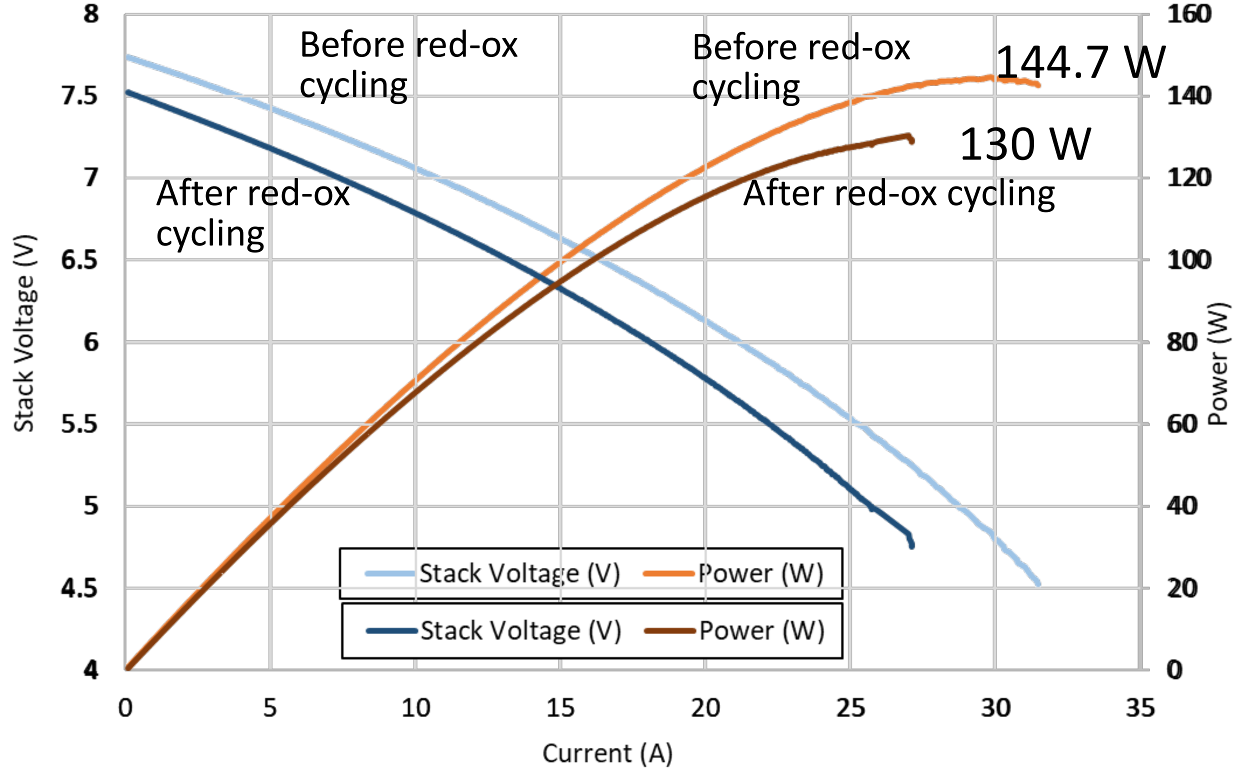
H_2 on anode

N_2 on anode

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

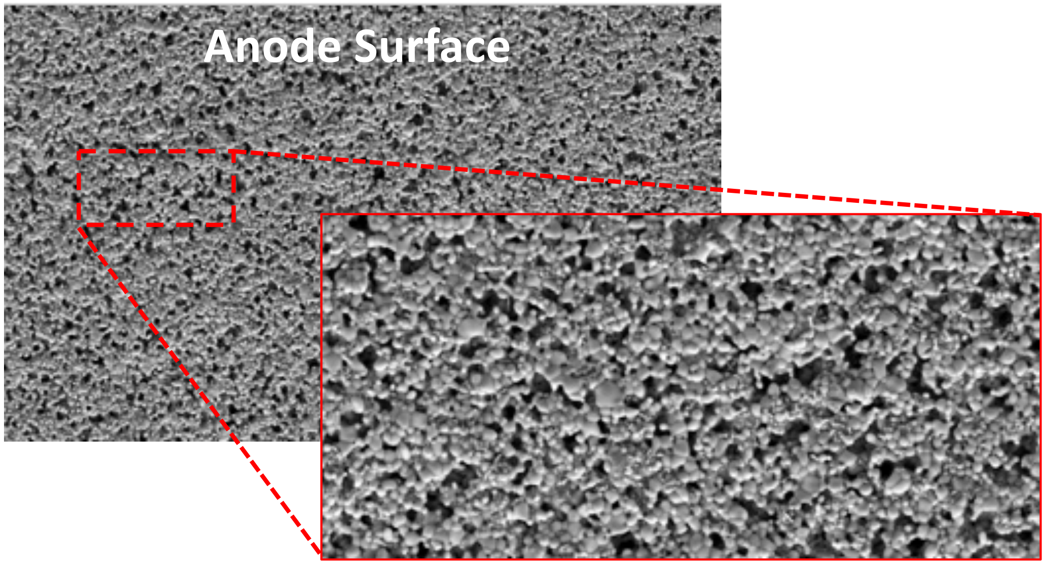
Red-Ox Cycling of Stack

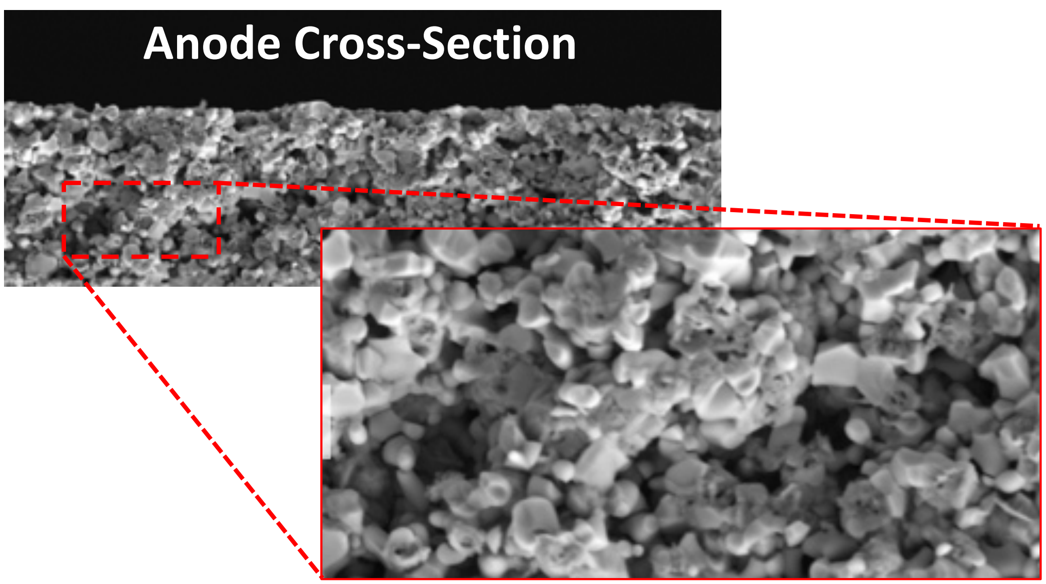
10 cm by 10 cm stack - cycling between hydrogen and nitrogen at 600 °C



- Slightly lower performance after red-ox cycling
    - But this may have had more to do with general long-term stability
- Discovered problems with ceramic anode delamination in high humidity conditions experienced in large format cell operation
- Extensive investigations to obtain ground truth understanding of the problem
- Problem not in the ceramic-anode material itself (confirmed in 30% H_2O, balance H_2)
- Modified ceramic-anode configuration eliminates delamination

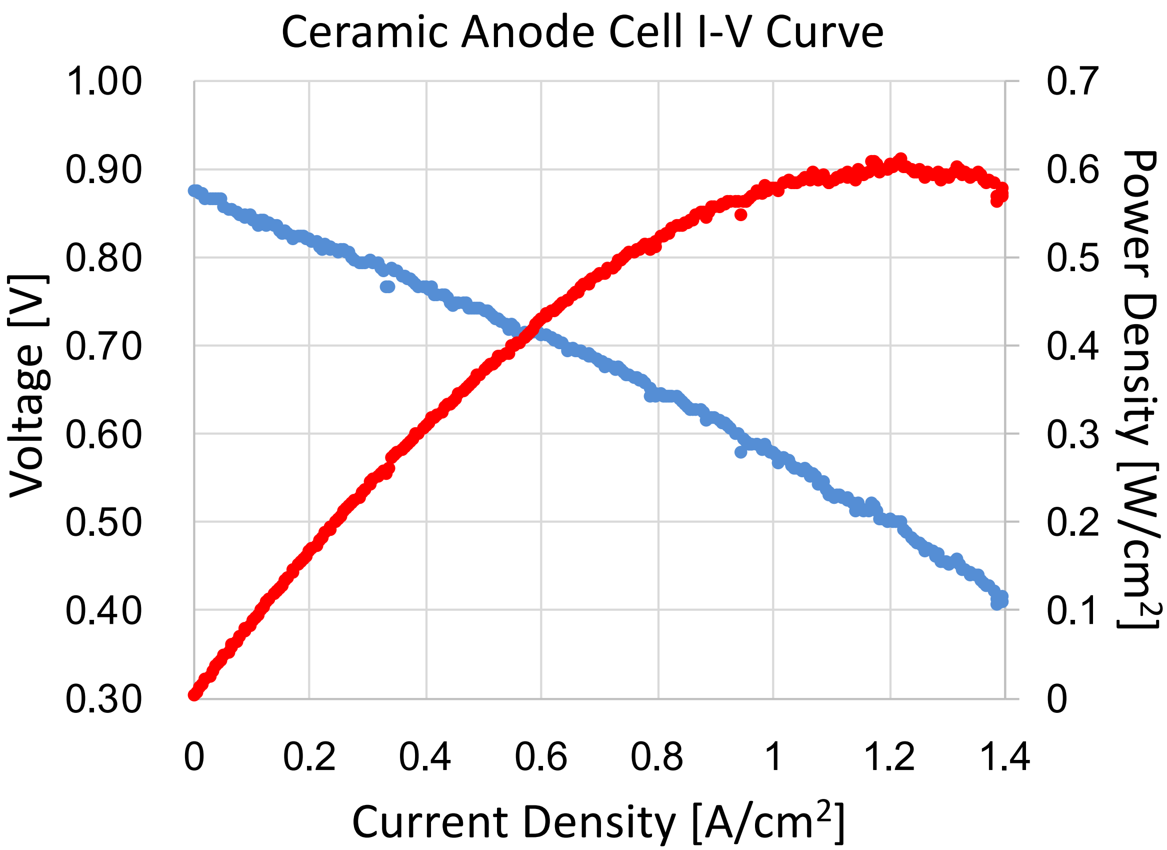
Red-Ox Cycling: Improved Ceramic-Anode Config.





- Red-ox cycle conditions
  - The sample was heated to 600 °C in air, held for 3 hours; reducing gas (3% H_2 / 97% N_2) 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

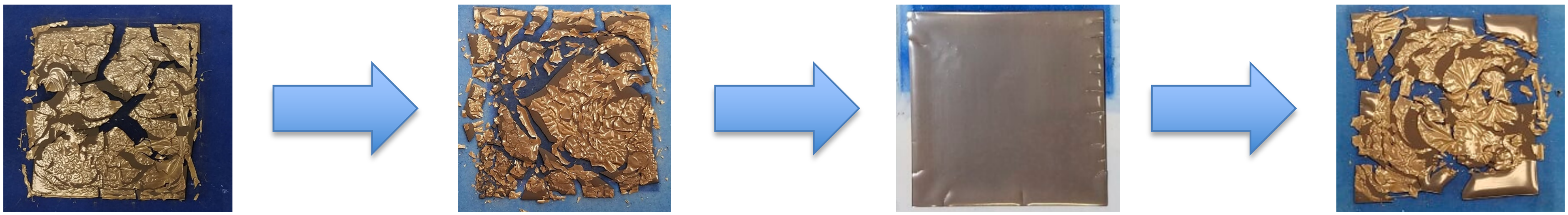
Improved Ceramic-Anode Config. Performance



- 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 likely during final size scale-up

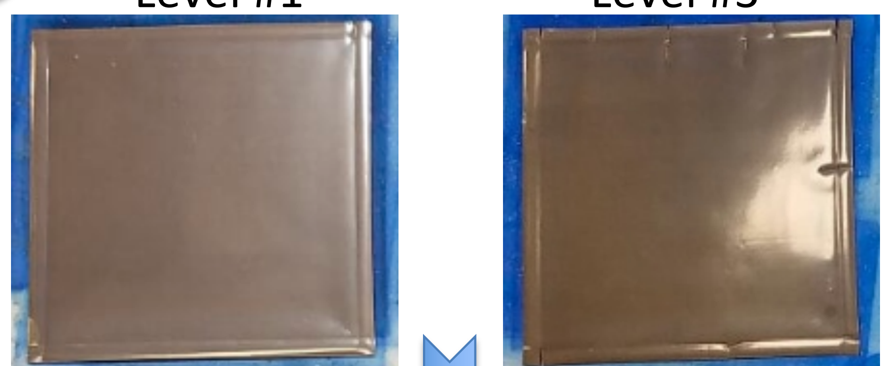
Cell Size & Batch Size Scaleup

Improved ceramic-anode cell config.



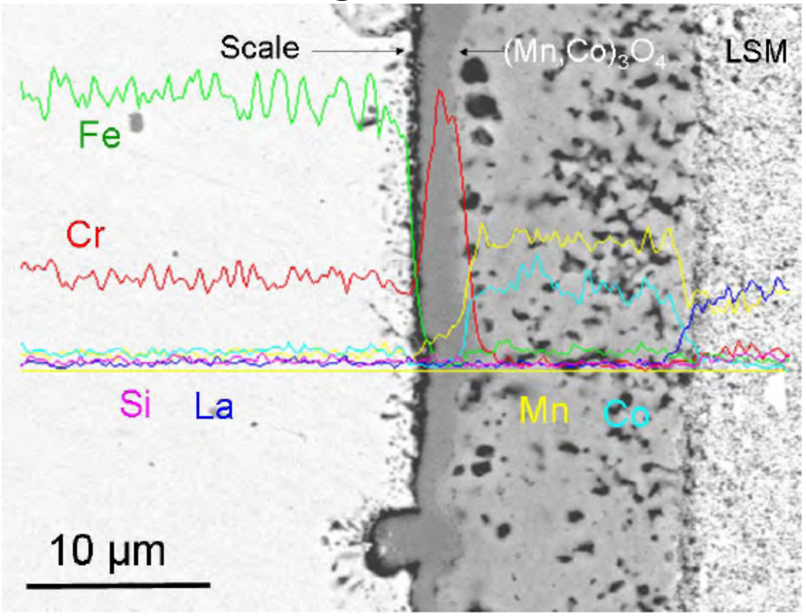
1. Composition optimization to prevent delamination (5 cm by 5 cm)
2. Fine tune composition / firing profile to reduce edge cracks
3. Optimize furnace temperature uniformity, tape caster thickness variation to increase yield in multi-level (4+) batch firing
4. Increase cell size to 10 cm by 10 cm and build up inventory for stack testing

Level #1 Level #3



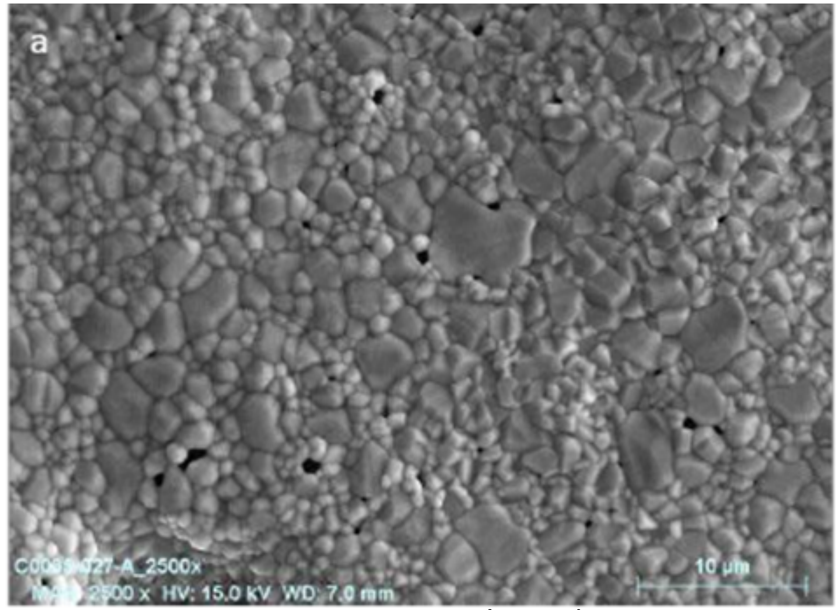
3. Metrology for SOFC Coating Manufacture

Coating cross-section



PNNL report ID: PNNL- 17568, May 2008

Coating surface



ECS Transactions, v. 68, i. 1 (2015) 1569

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)

$(Mn,Co)O_4$ (MCO) is a commonly used barrier coating layer

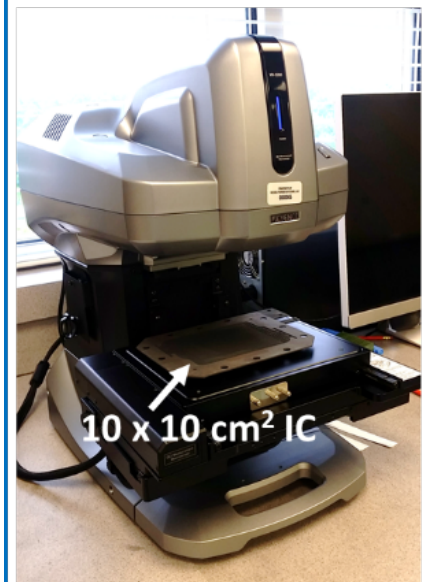
Defects in coating (e.g., porosity, cracks) inhibit coating and SOFC performance

Key Defects of Interest Rating

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

Metrology of Key Defects Approach

Optical profilometry capabilities at Redox (Keyence VR and VHX)



High throughput

High resolution (1000x)

Measurement methods

- Optical microscopy
- Optical profilometry
- Thermography

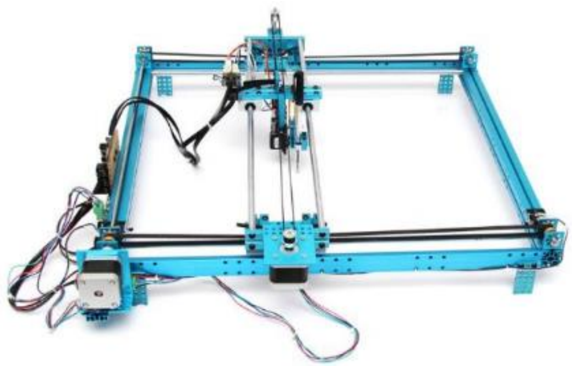
Thermography in collaboration with NREL

Derek Jacobsen, Peter Rupnowski, Brian Green, and Michael Ulsh

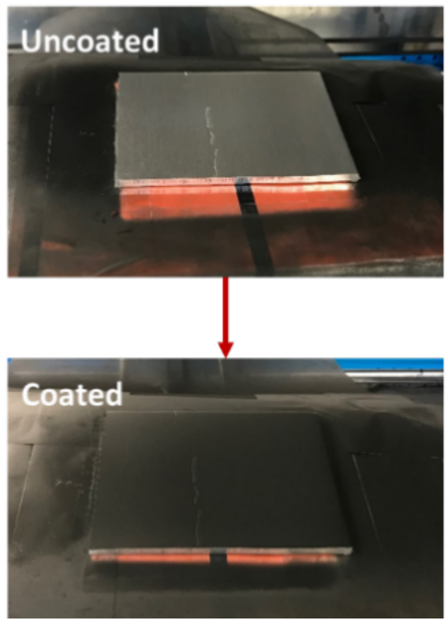
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Coating Fabrication at Redox

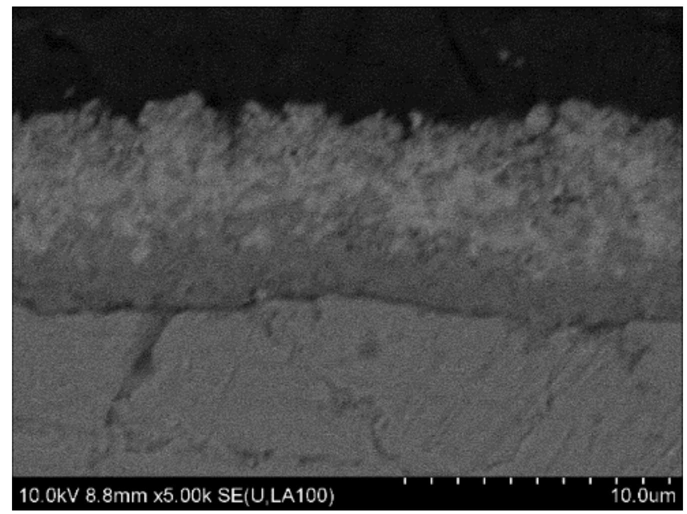
- Sprayed MCO coatings followed by typical annealing methods (reducing atmosphere followed by oxidation to achieve oxide coating)



10 cm x 12 cm metal substrate



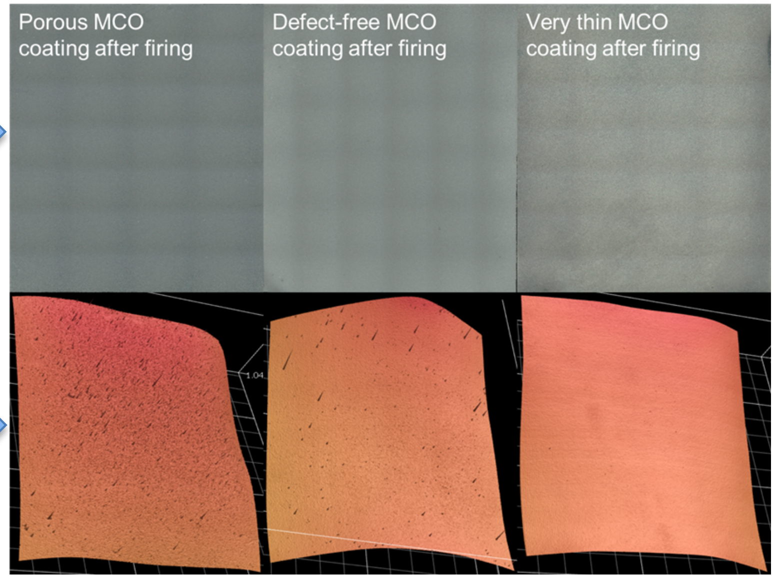
SEM cross-section of an MCO coating on stainless steel developed at Redox



Thermography Detects Substrate Scratches

Optical microscopy*

Optical profilometry



- 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

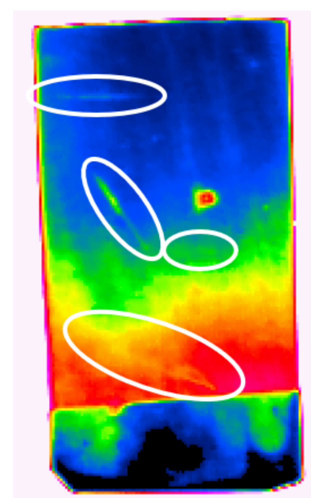
"Seeded" (scratch) defect

Substrate

Fired coating

Fired coating (profile)

Fired coating (thermography)

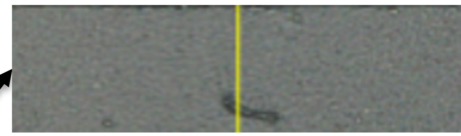


- 4 scratches in stainless steel substrate
- Optical and height profile mapping can only detect two scratches in fired film
- *Thermography detects all 4 scratches!*

**grid is an image stitching artifact*

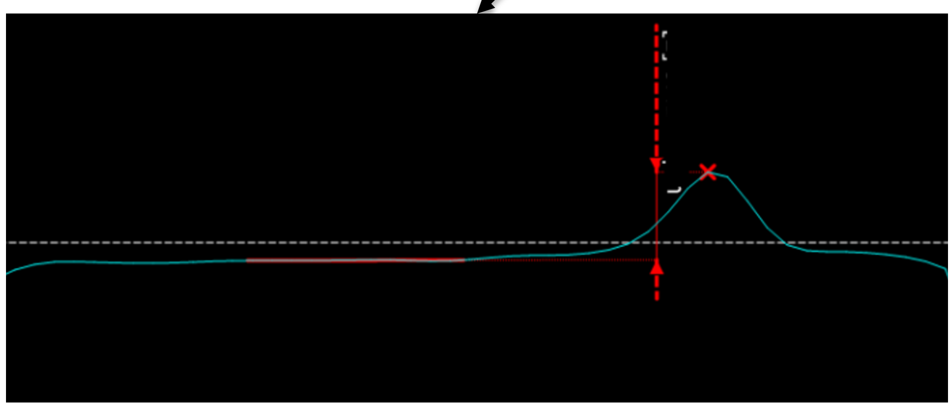
Example: Quantitative Analysis of Surface Defects

A) MCO coating on a stainless-steel coupon with ribs and channels



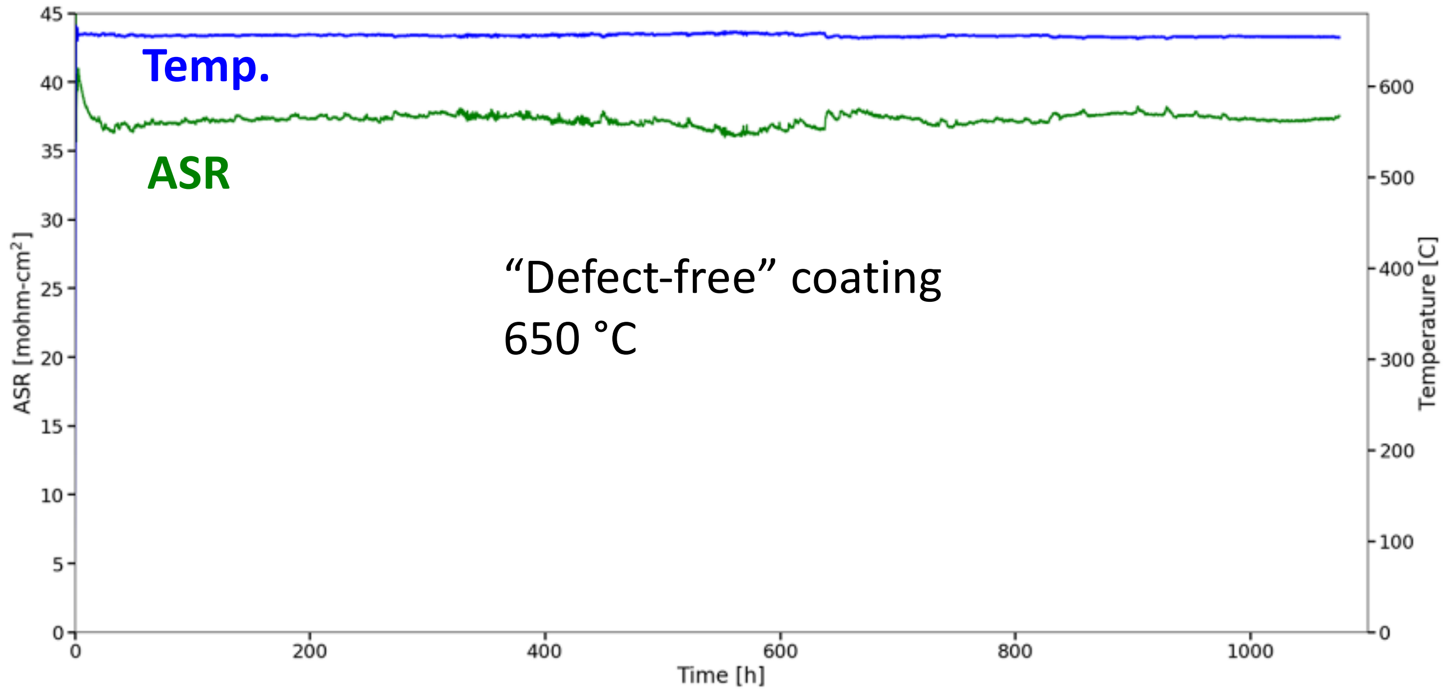
B) Expanded view of a selected area (coated rib) with defect

C) 3D height image of the selected area with defect



D) Cross section height profile that can be quantitatively analyzed, corelated to performance, and used during manufacturing QC

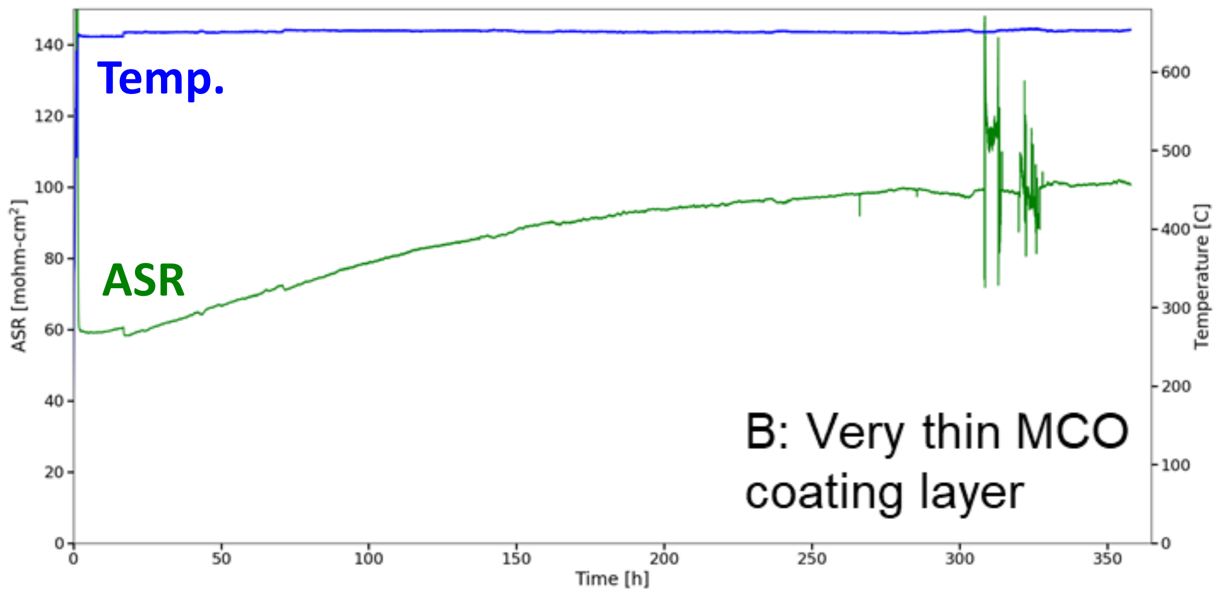
Long-term ASR of "defect-free" coating exhibits reasonable performance

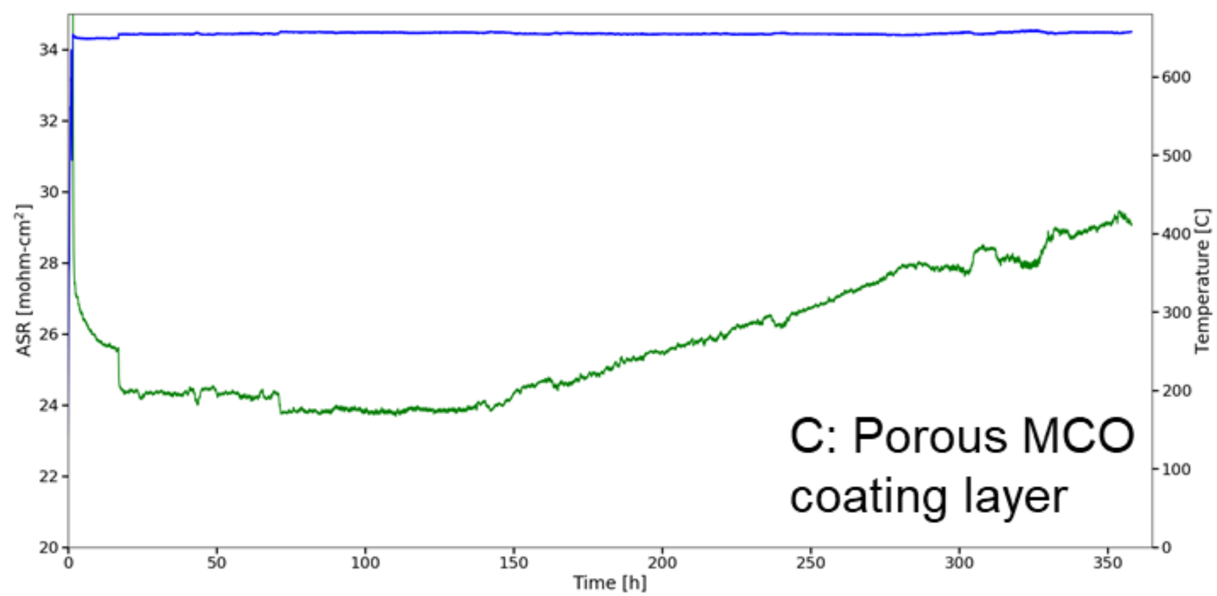


- ASR at ~0.037 Ω-cm^2 for 1000 hours (a 2nd measurement resulted in ASR ~0.048 Ω-cm^2 for 350 hours)
- Achieved M2.2 (<0.05 Ω-cm^2 for 1000 hours at 650 °C)

REDOX

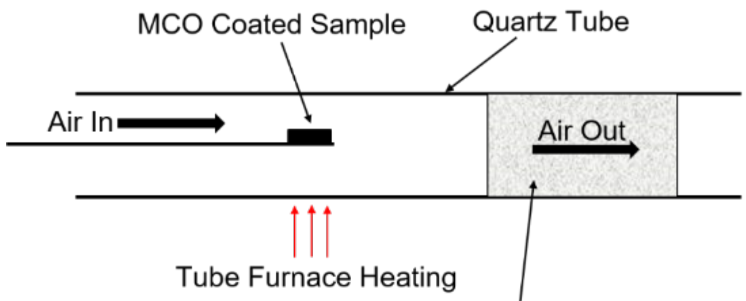
Long-term ASR of intentionally defective coatings



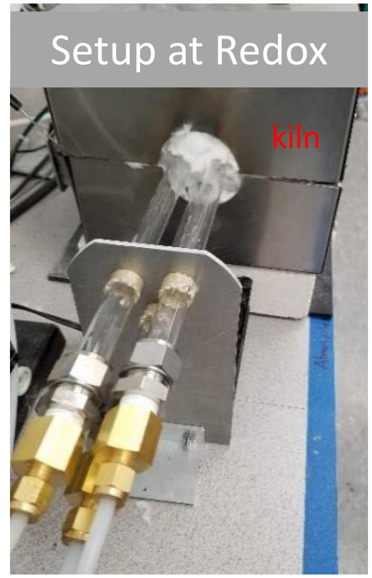


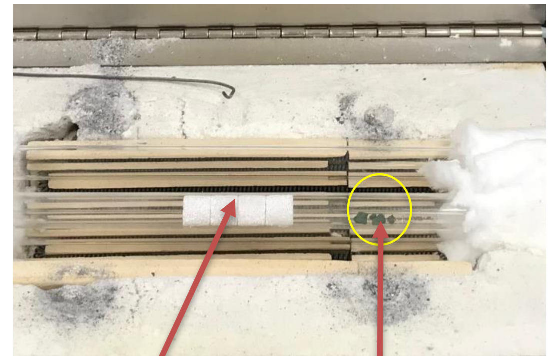
- Thin coating exhibits high ASR that increases from 0.06 Ω-cm^2 to 0.1 Ω-cm^2 (66%) with time
- Porous coating has low ASR, which also increases with time from 0.024 Ω-cm^2 to 0.029 Ω-cm^2 (21%)
- Porous coating exhibits a promising initial ASR, though high porosity may lead to more Cr volatilization

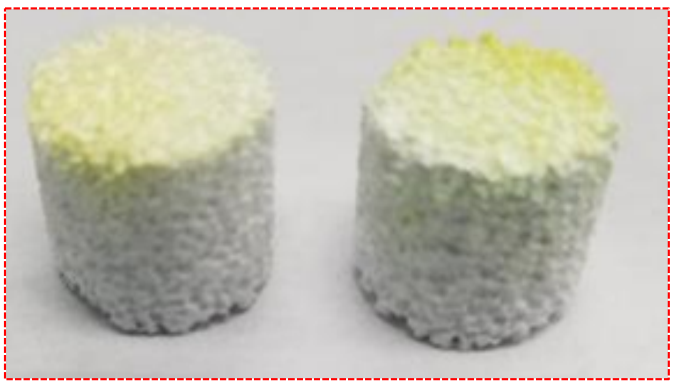
Evaluation of Cr Volatilization from Defective / Non-Defective MCO coatings



Gaseous Cr species released from the samples were captured using Na-carbonate coated alumina filters placed downstream from the samples*





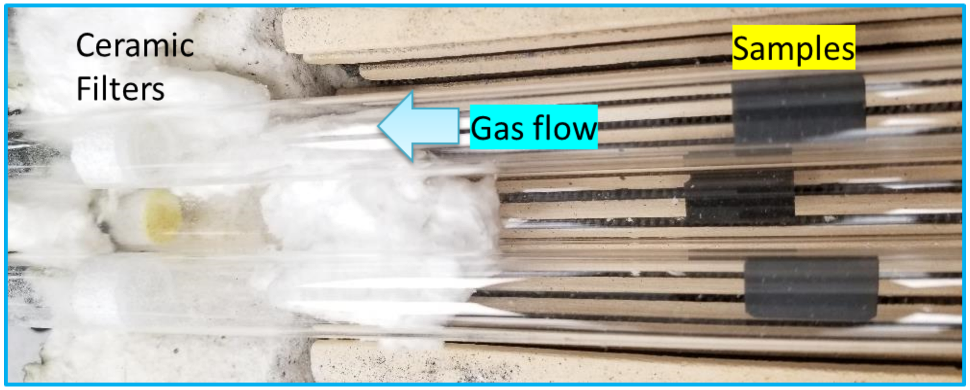


Filter after 500 h test with flowing humidified air over stainless steel (left) and Cr_2O_3 (right) at 750°C.

- The filters were washed with water
- The resulting color intensity was compared with the stock solutions (conc. verified via UV-Vis) to determine Cr in solution

* following methods developed by Chalmers Univ. and PNNL

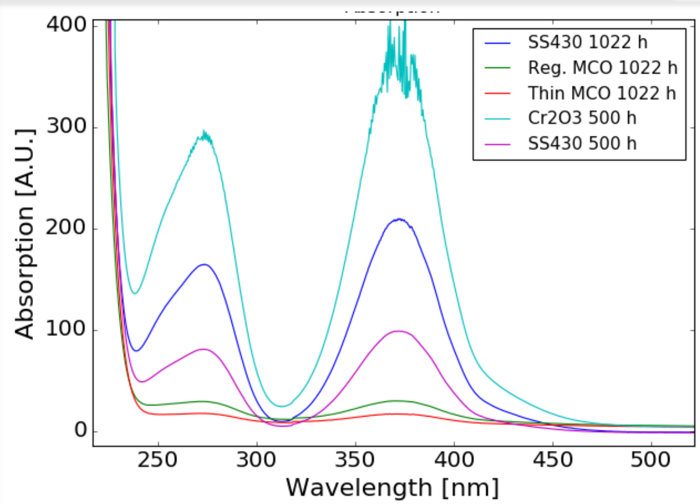
Long-term Cr-Volatilization Tests



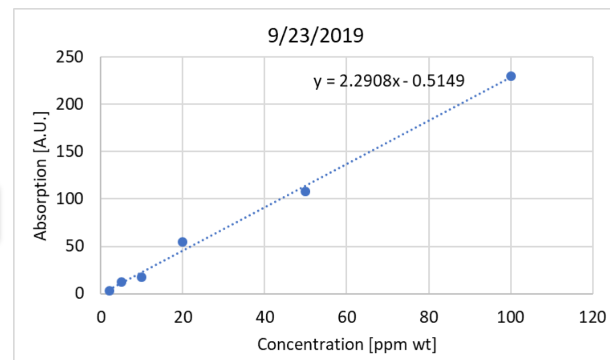
- 1022-hour anneals were performed for uncoated 400-series stainless steel samples and MCO coated 400-series stainless steel samples
- 500-hour anneals were performed for chromia and uncoated samples

Sample (750 °C)	Cr evap. rate (mg/cm^2-h)	Cr evap. rate x 8‡ (mg/cm^2-h)
400-Series SS, 1022 hours	4.6×10^{-5}	3.7×10^{-4}
MCO, 1022 hours	6.4×10^{-6}	5.1×10^{-5}
Cr_2O_3, 500 hours	8.4×10^{-5}	6.7×10^{-4}
400-Series SS, 500 hours	6.2×10^{-5}	5×10^{-4}

- While MCO reduces the amount of Cr released at 750 °C, coating defects that expose the underlying stainless steel need to be caught during QC steps in manufacturing to prevent Cr poisoning of the cathode in long-term SOFC operation.



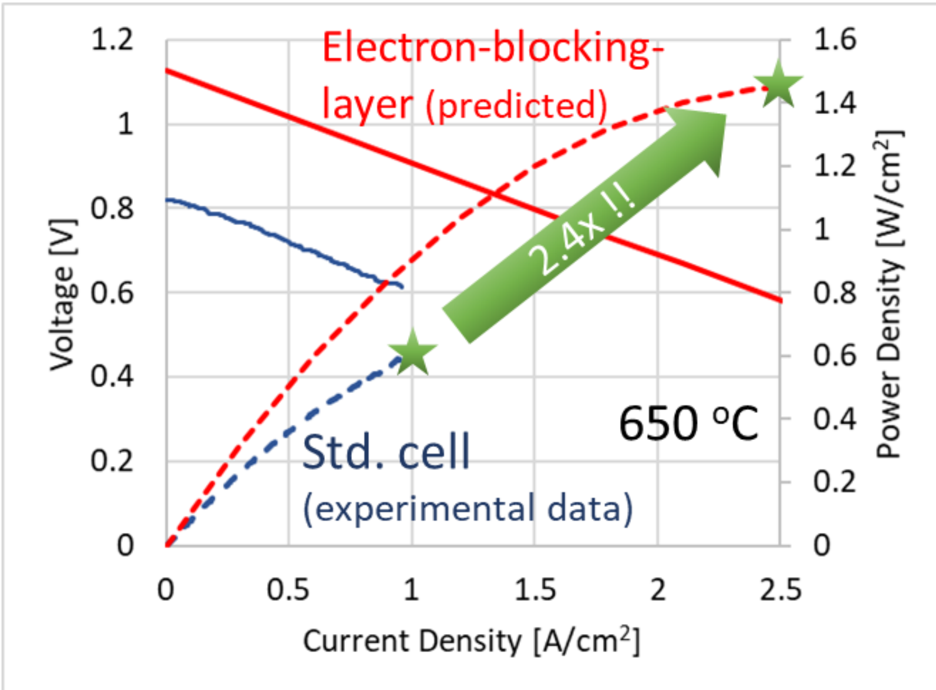
UV-vis measurements for chromia, uncoated sample and multiple types of MCO coated samples

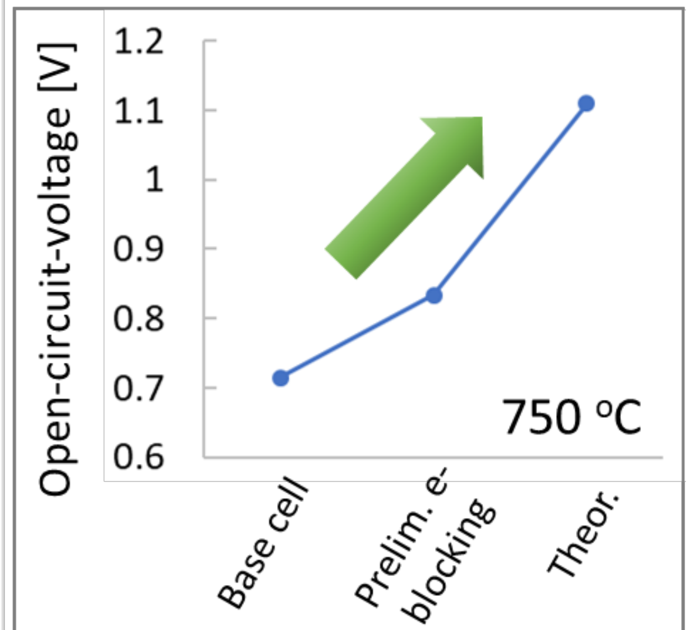


Calibration curve for UV-vis measurements on standard chromate concentrations

‡ factor of 8 applied due to lower flow rate used (Chalmers 2017: Journal of Power Sources 343 (2017) 1; DOI: 10.1016/j.jpowsour.2017.01.045)

4. Sputtered Thin Film SOFCs

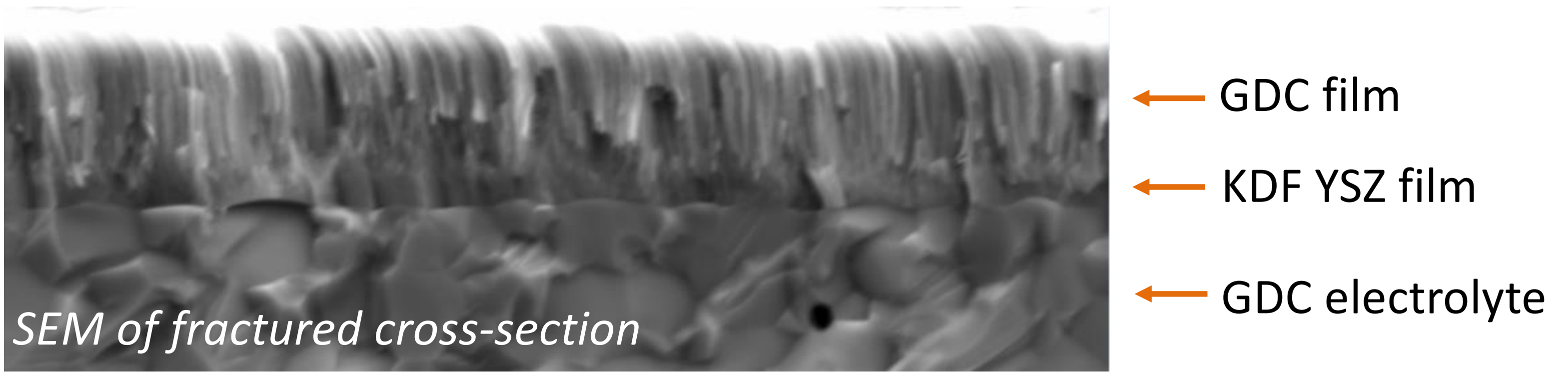




- Thin electron-blocking layer expected to increase Redox GEN1 Ni-cermet cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria based electrolyte → ~40% increase in open circuit voltage
- Thin-ness of electron-blocking layer adds negligible resistance
- Takes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

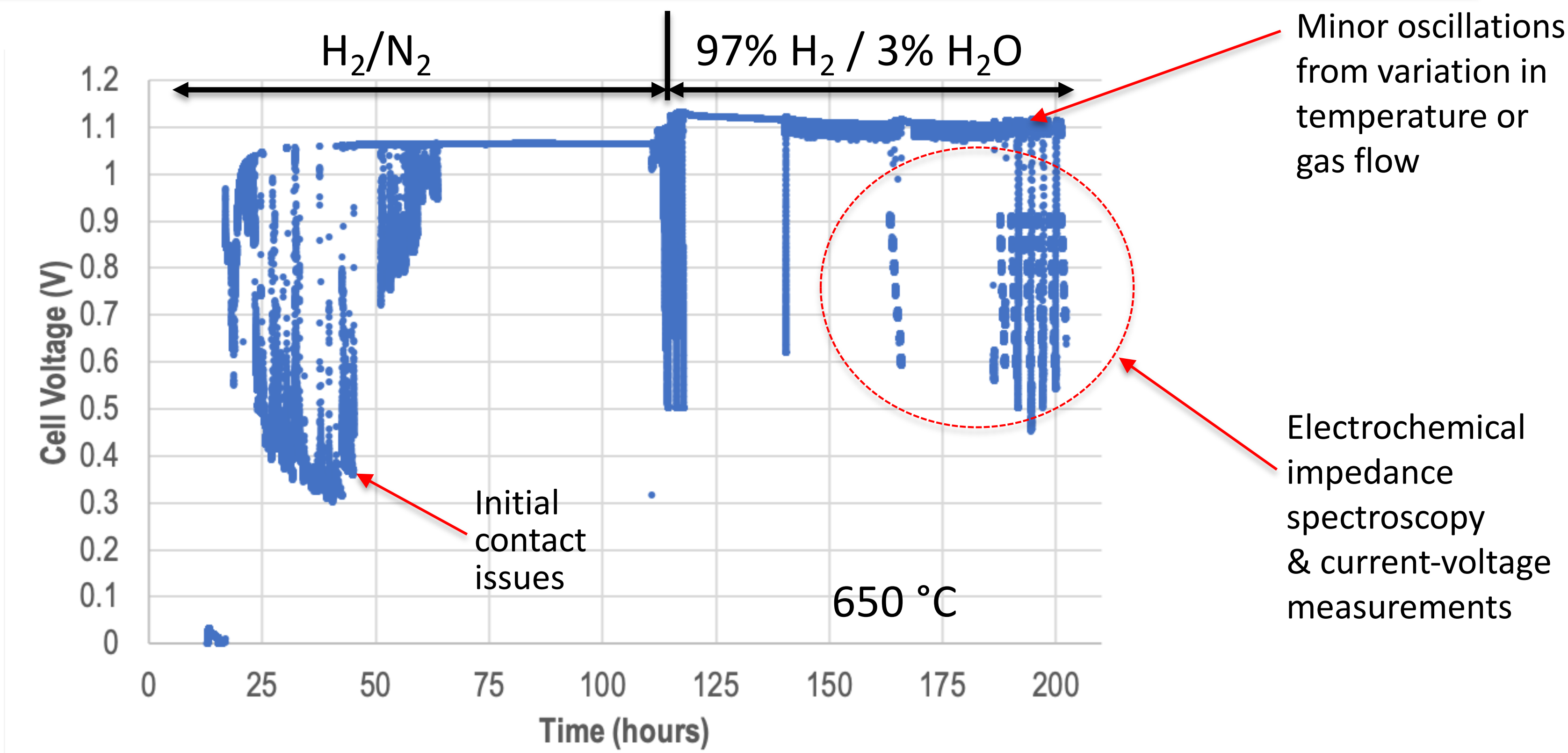
GDC Buffer Layer Deposition

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 O_2 pressure and sputtering power)
- GDC film deposition still being developed to ensure deposition of dense, robust film (see next slides on oxidative stress)

Achieving ≥ 1V Open Circuit Voltage



- 2 cm by 2 cm (sputtered YSZ & GDC) cell tested with stainless steel stack components
- Gas chromatography of the exhaust gas verified good sealing
- The theoretical OCV is 1.135V at 650 °C with 3% H_2O/97% H_2 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 GDC
- The OCV is stable and represents a > 30% increase over the baseline
- ASR and cell size enhancements are now being made by tuning the cell annealing and contact fabrication methods

Summary

- Individual stack of 2.4 kW and two-stack module for 4.2 kW using steam-reformed, pipeline natural gas
- Expanded Redox's capabilities of cell manufacturing, stack development and testing, fuel processing, and system integration in the new, larger natural gas test facility
- Increased quality and batch-firing yield of large format, all-ceramic anode cells
- Demonstrated red-ox stability of all-ceramic anode cells and optimized anode-configuration for improved long-term stability and performance
- Developed optical and thermographic defect detection approaches and methods to quantify key defects on coatings for SOFC stack components (e.g. interconnect)
- Successfully demonstrated sputtered thin-film SOFC, effectively blocking electron (leakage) current, to achieve 99.6% of theoretical OCV with GDC electrolyte cell
- Continue to optimize pre-sputter parameters, deposition conditions, annealing, and contact fabrication of large-scale cells

Acknowledgements

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