Advanced SOFC Development at Redox Power Systems

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1:45 pm
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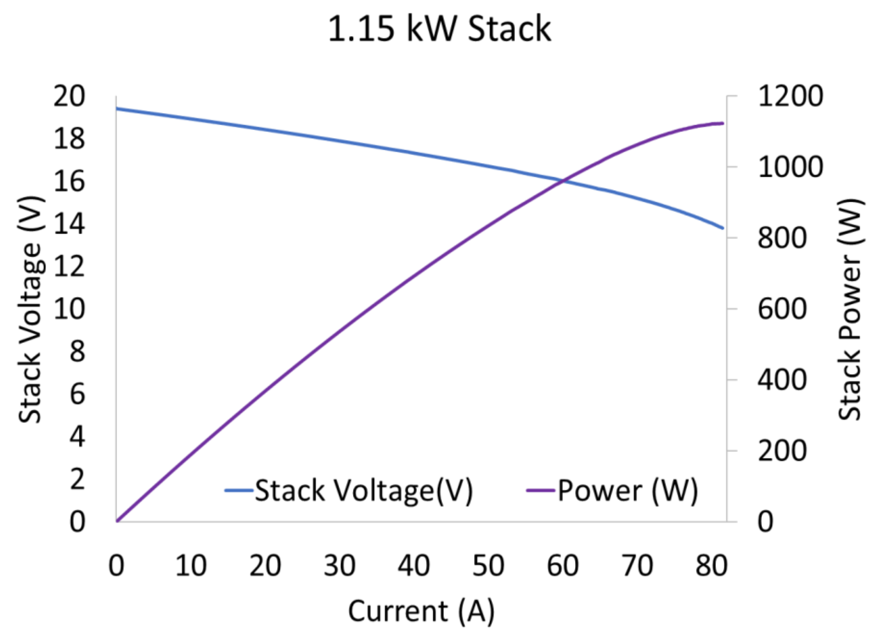
Outline

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

1. High Power SOFC Stacks



- We are currently working towards a 2.5 kW stack demo
- Two “lab reformers” qualified for > 2.5 kW

Natural Gas Test Facility (NGTF)

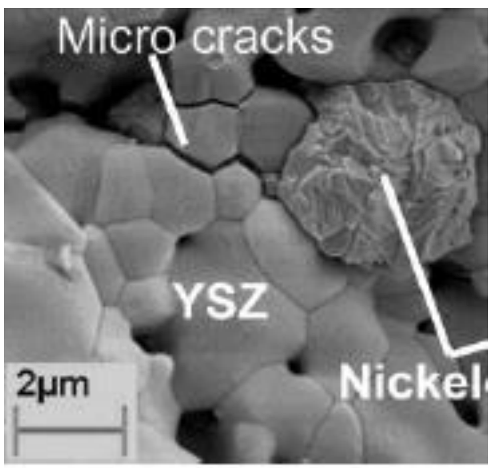
- Moved into new demo facility in early 2019 that is 3x larger than previous location
- Will allow additional stack and system testing
- Large natural gas feed capacity for a larger gas-powered reformer capable of supporting 5-6 kWe stacks and bringing the total reforming capacity to >15 kWe.
- Light manufacturing and engineering space as well

2. Red-ox Robust Stacks

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

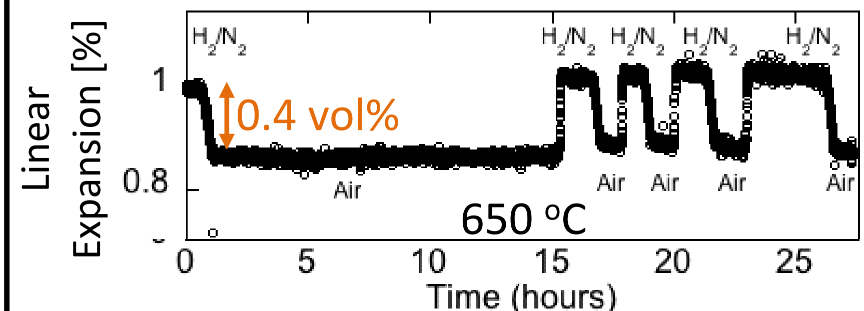


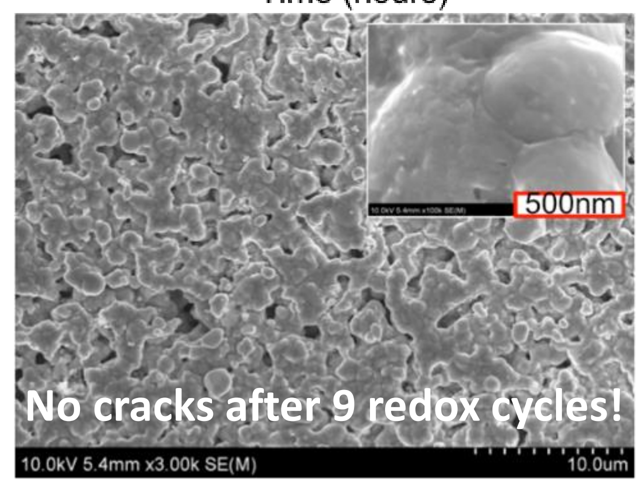
Journal of Power Sources 195 (2010) 5452–5467

~69 vol% expansion of Ni → NiO

Solution:

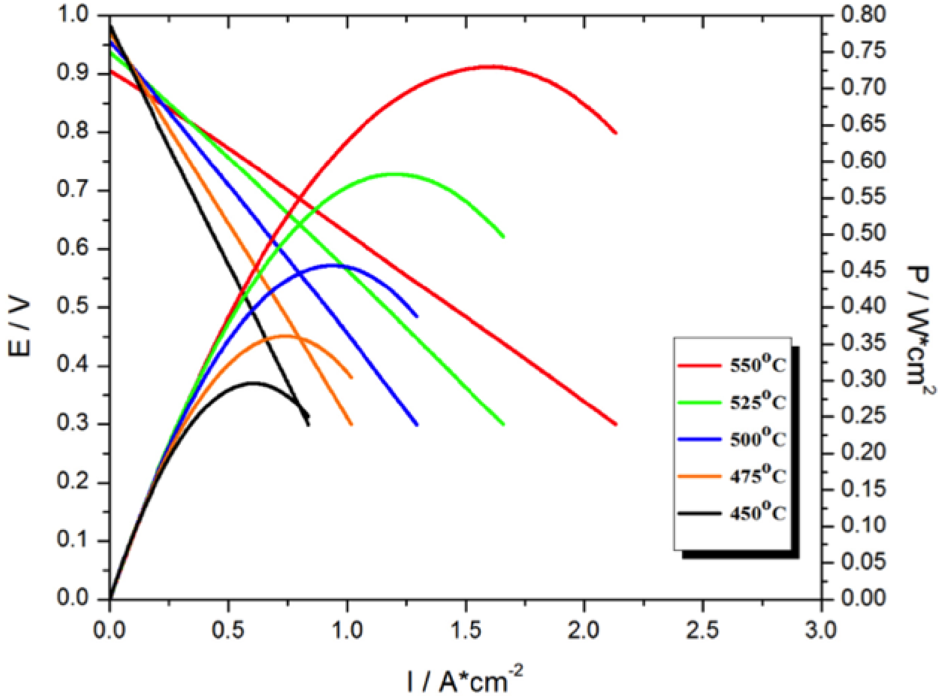
All ceramic anode → small Δoxygen = small dimensional change (0.4 vol%)



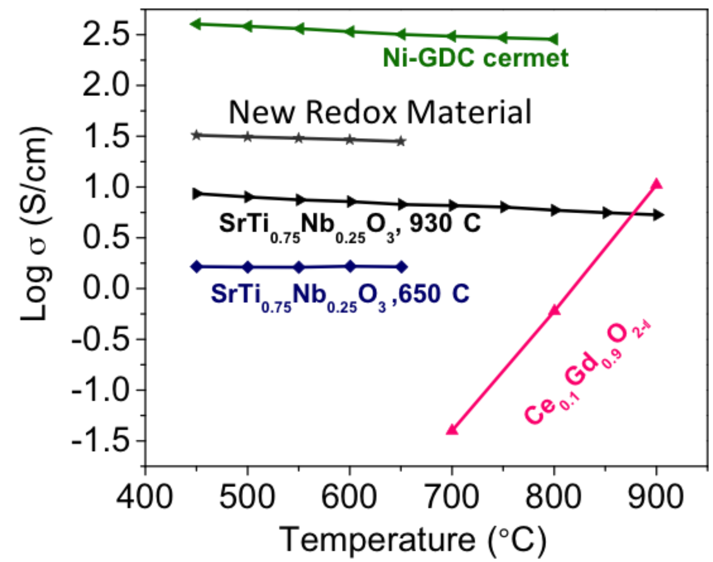


All-Ceramic Anode Performance

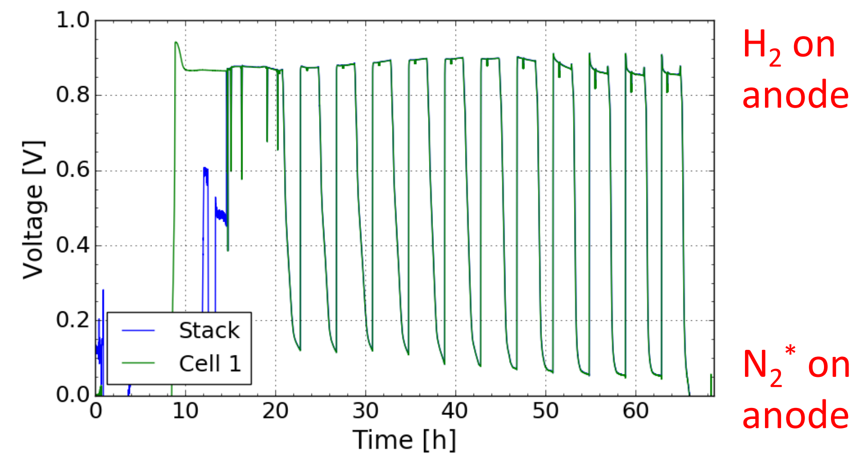
Button cell data



Anode electrical conductivity



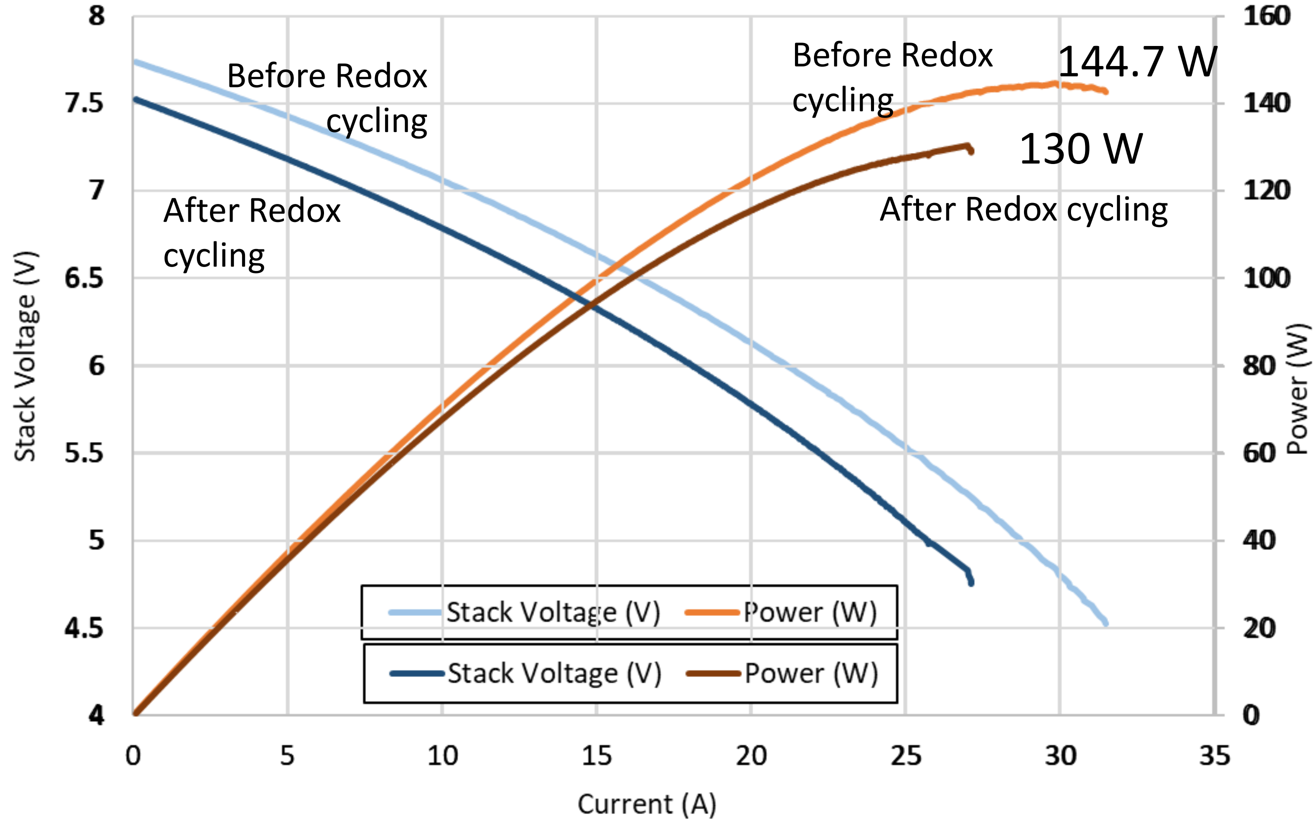
Red-ox Cycles: *5 cm by 5 cm cell (600 °C)*



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

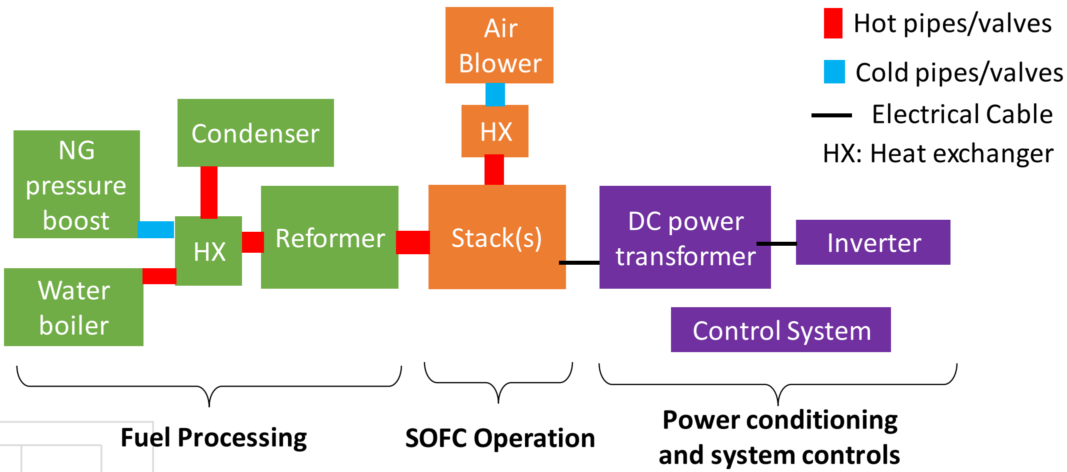


- Some degradation in performance after red-ox cycling
- Previous 5 cm x 5 cm tests showed 3 red-ox cycles with minimal ASR, OCV, and seal degradation, but more cycles led to degradation
- Future work includes continued anode structure modification

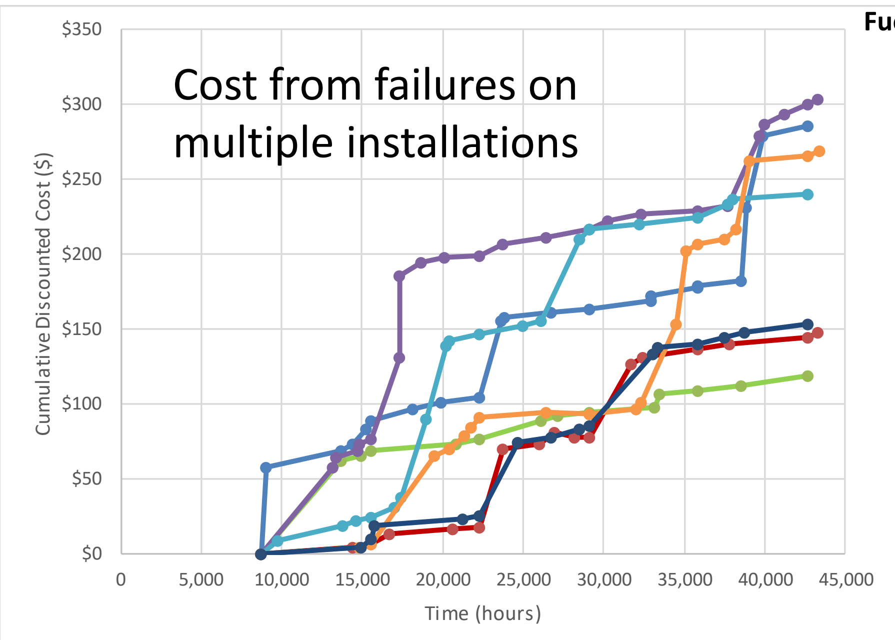
Redox can Cycle!

Discrete Event Simulator

Schematic of system design approximation



Model output

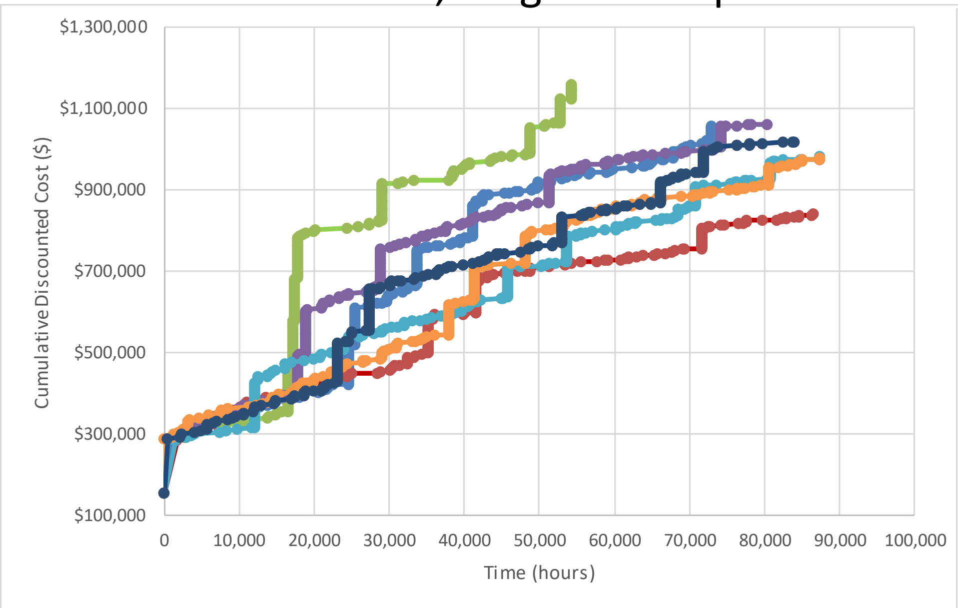


- *Initial deployment and stack replacements largest cost components in initial model*
- *Stack replacements include failure due to "critical events"*
- *Future work includes improving estimates of MTTFs, costs, and model utility*

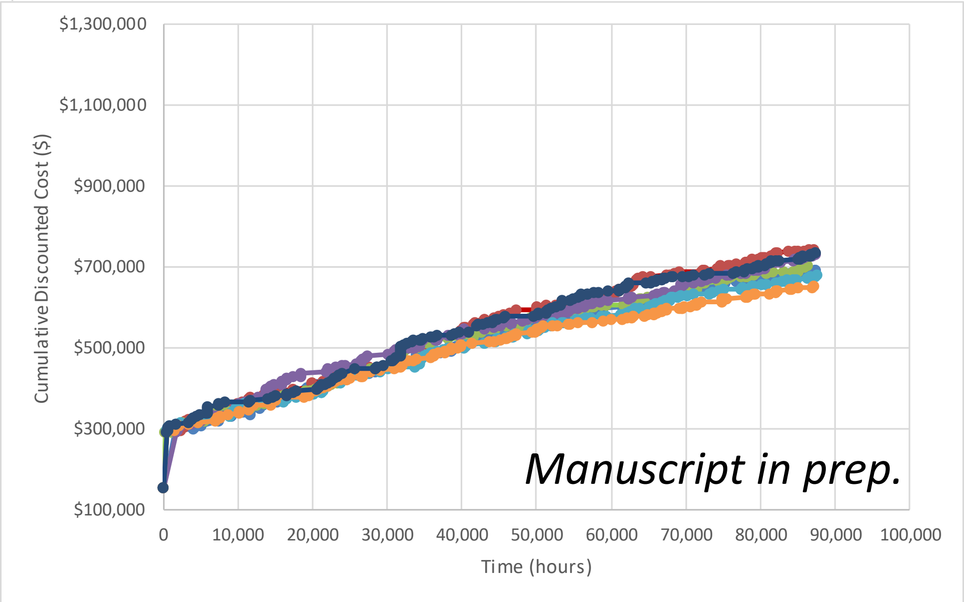
Discrete Event Simulator

Comparison of a back-up fuel gas system (standard system) and a red-ox tolerant system

Standard, no gas-backup



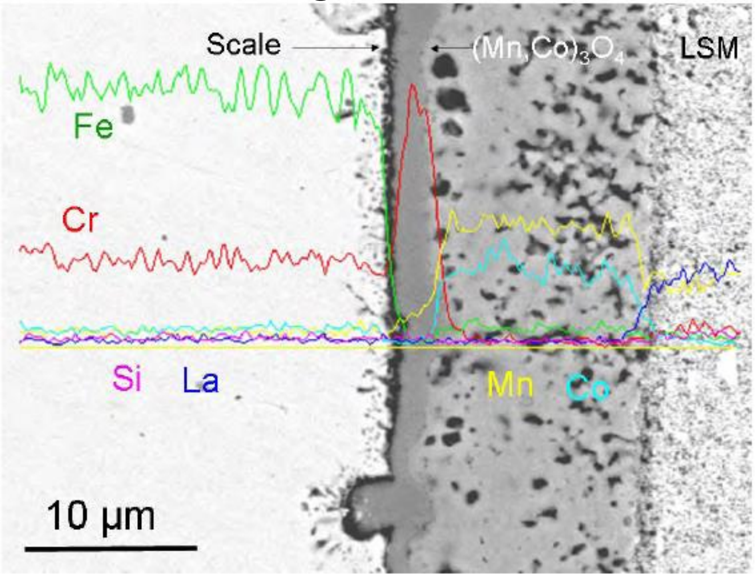
Red-ox tolerant or gas-backup



- Largest cost in lifetime ownership from replacing stacks every time gas emergency shut-down occurs (even though they are fairly rare)
- Red-ox tolerance or gas back-up system dramatically reduces lifetime cost

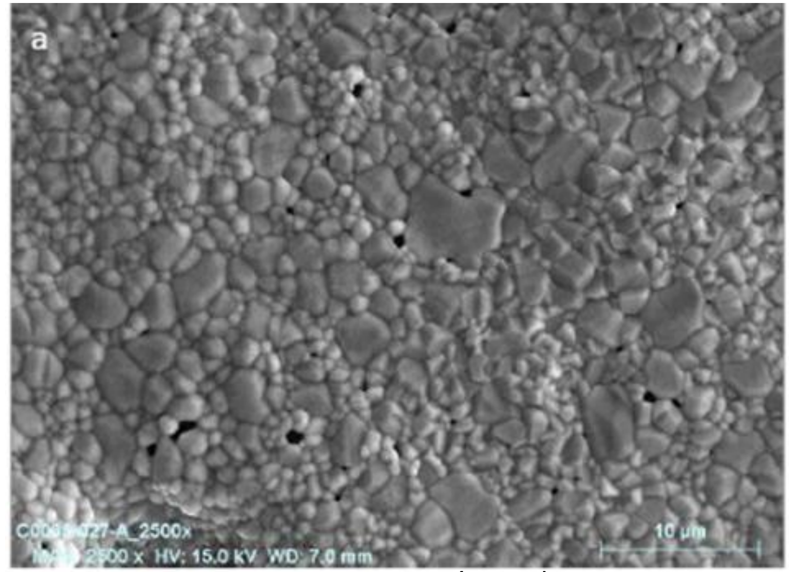
3. Metrology for SOFC Coating Manufacture

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

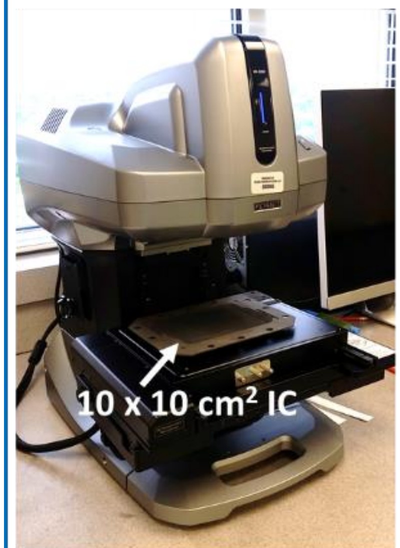
Defect	Challenges it presents	Likelihood of occurrence (1-5)	Severity (1-5)	Level of focus (1-5)
Surface dips and/or bumps	Could be high ASR spots, Cr volatility	5	3	5
Thickness non-uniformity, >50%	Large gradients --> variations in ASR and ability to block Cr transport, (growth of Cr oxide layer -> 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

REDOX Metrology of Key Defects Approach

Measurement methods

- Optical microscopy
- Optical profilometry
- Thermography

Optical profilometry capabilities at Redox (Keyence VR and VHX)



High throughput

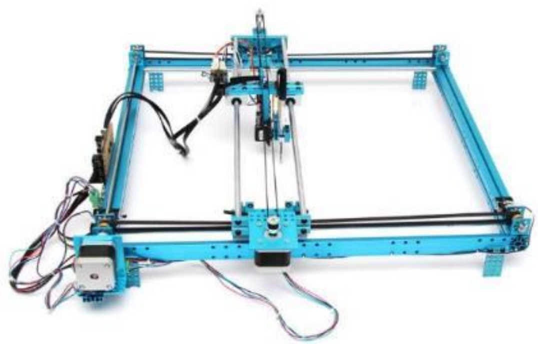
High resolution (1000x)

Thermography in collaboration with NREL
Derek Jacobsen, Peter Rupnowski, Brian Green, and Michael Ulsh

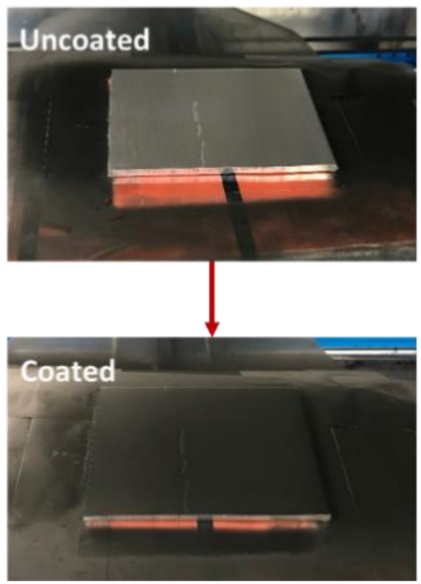
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Coating Fabrication at Redox

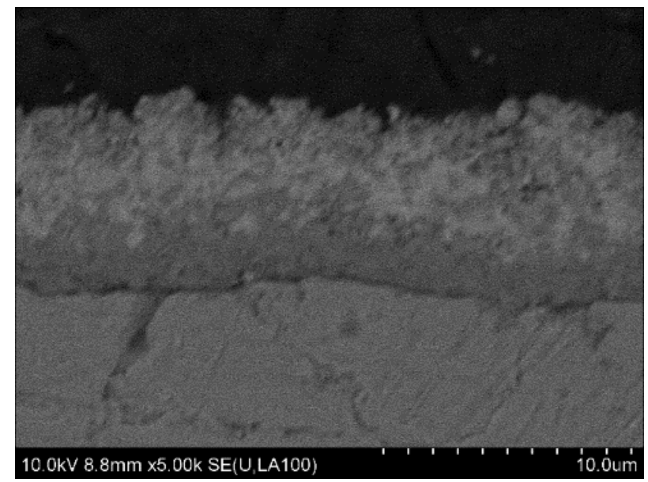
- Sprayed MCO coatings followed by typical annealing methods (reducing atmosphere followed by oxidation to achieve oxide coating)



10 cm x 12 cm metal substrate



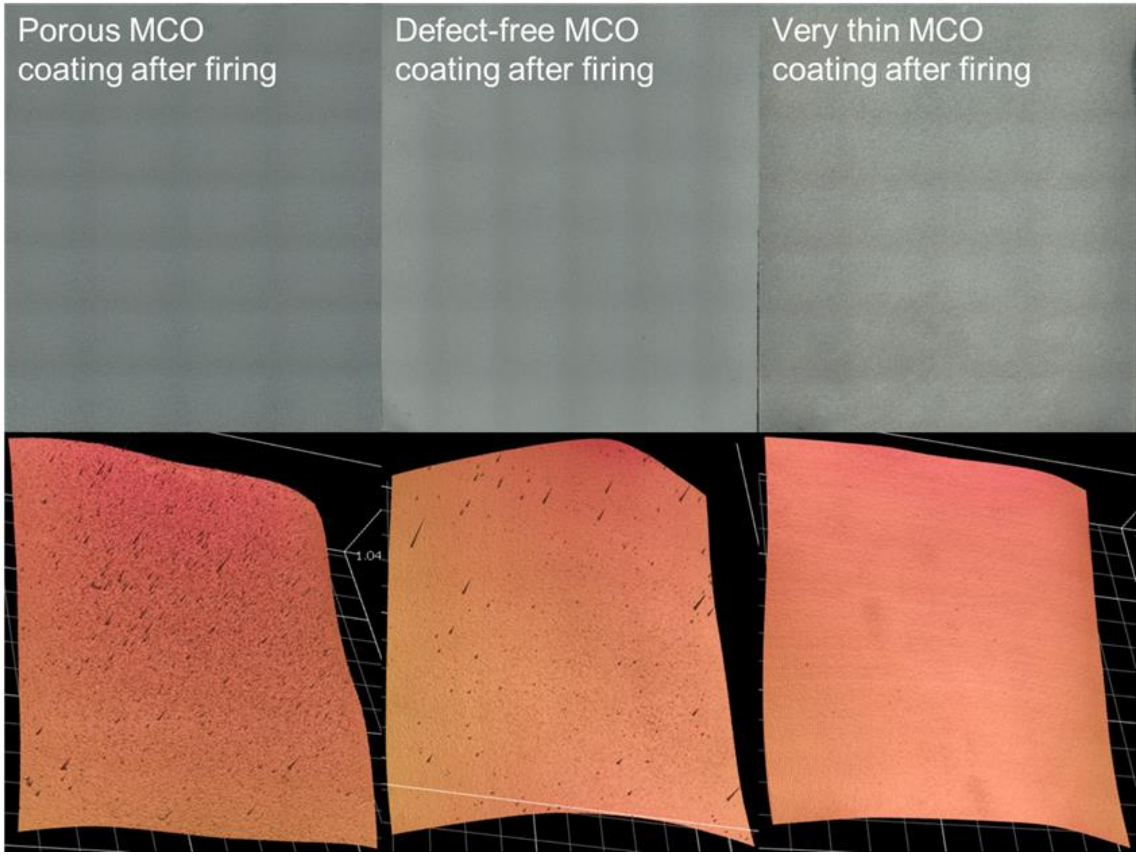
SEM cross-section of an MCO coating on stainless steel developed at Redox



Optical imaging detects porosity and thin intentional defects

Optical microscopy (grid is an image stitching artifact)

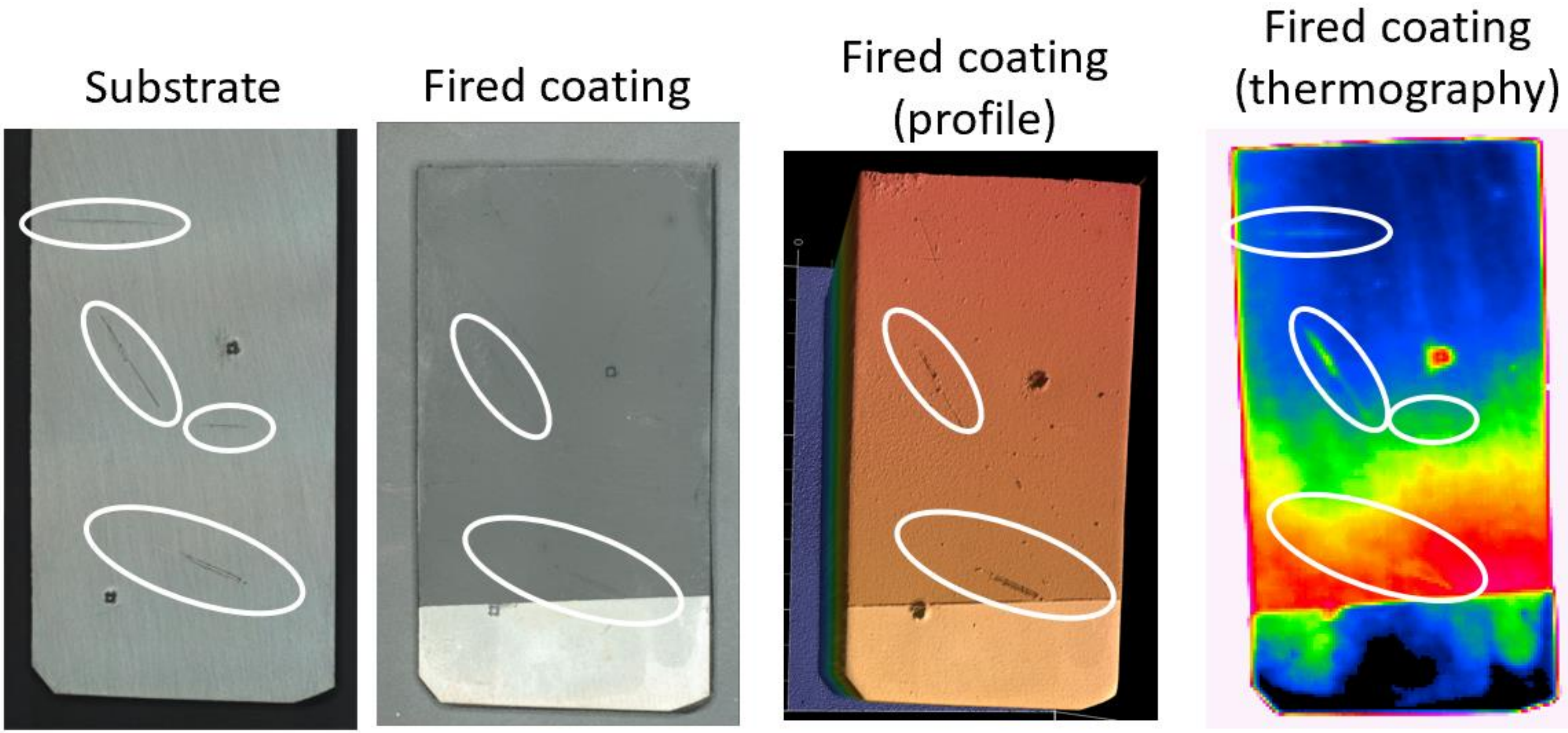
Optical profilometry



- 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

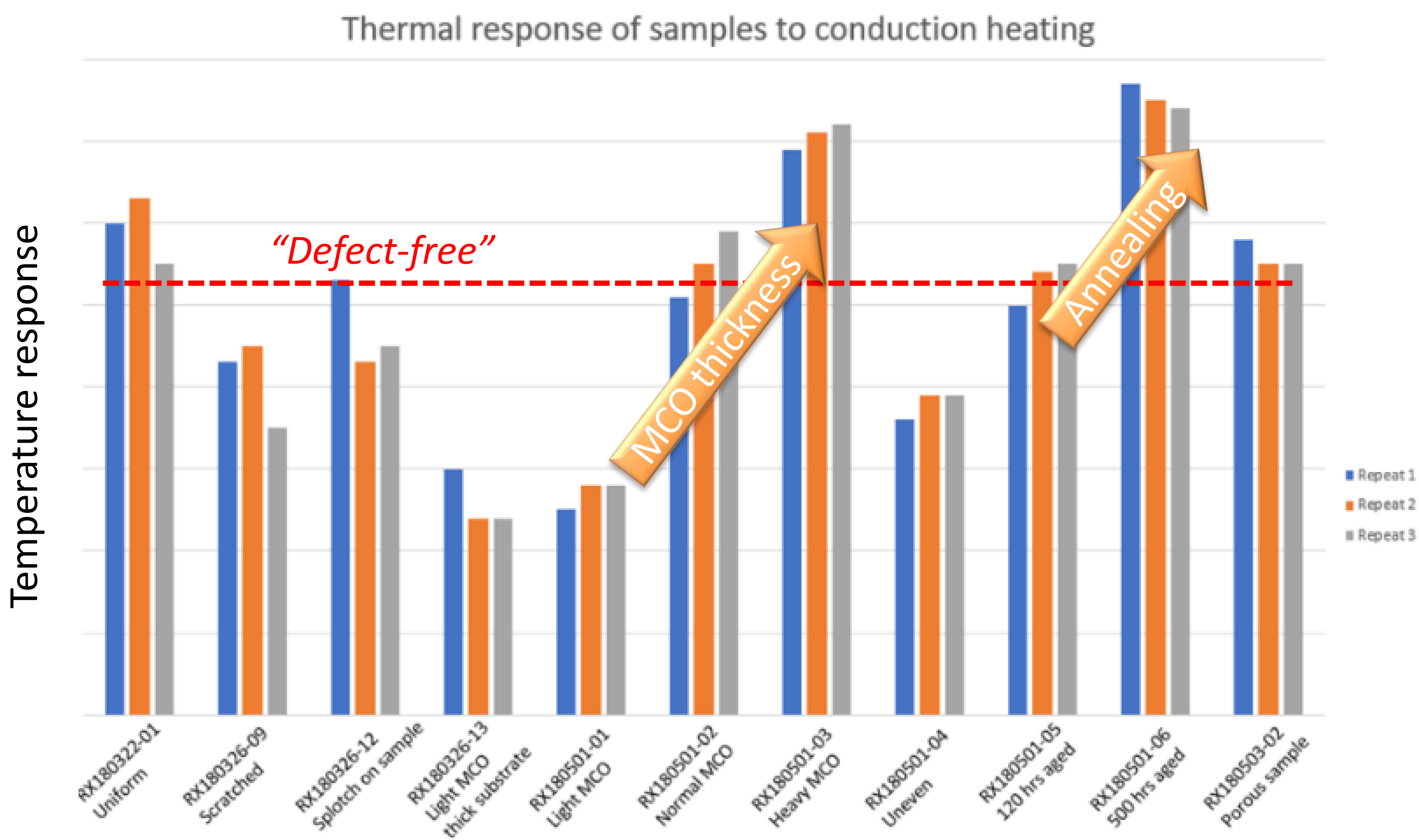
Thermography Detects Substrate Scratches

Intentionally scratched substrate with MCO coating



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

Trends observed in thermal responses



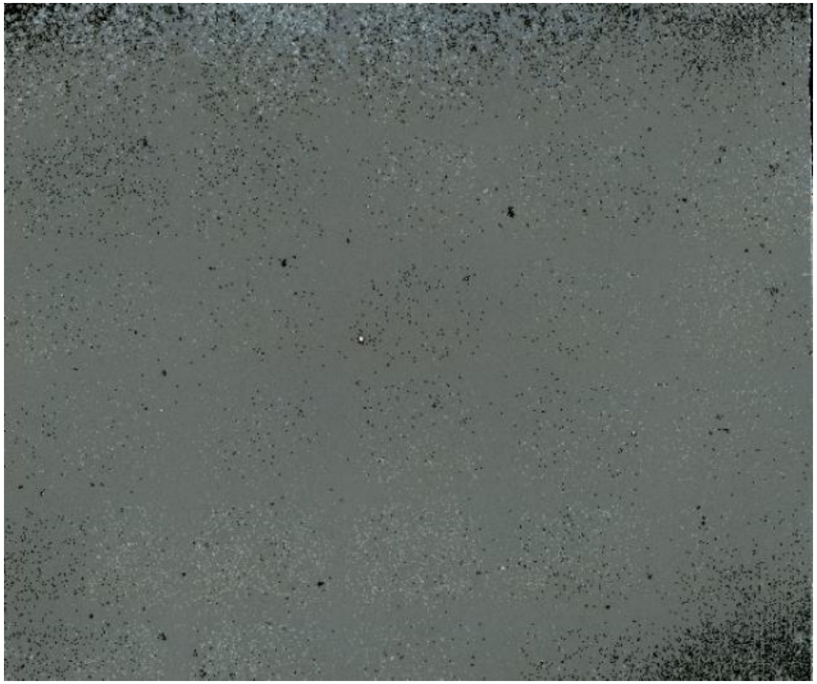
Redox currently performing microstructural and compositional analysis on NREL evaluated samples for feedback on thermography response origin and modeling

Image Processing – Raster Removal and Defect Detection of Optical Image

MCO coated sample (with lots of bump defects)

Optical Image as taken with macroscope

Processed image

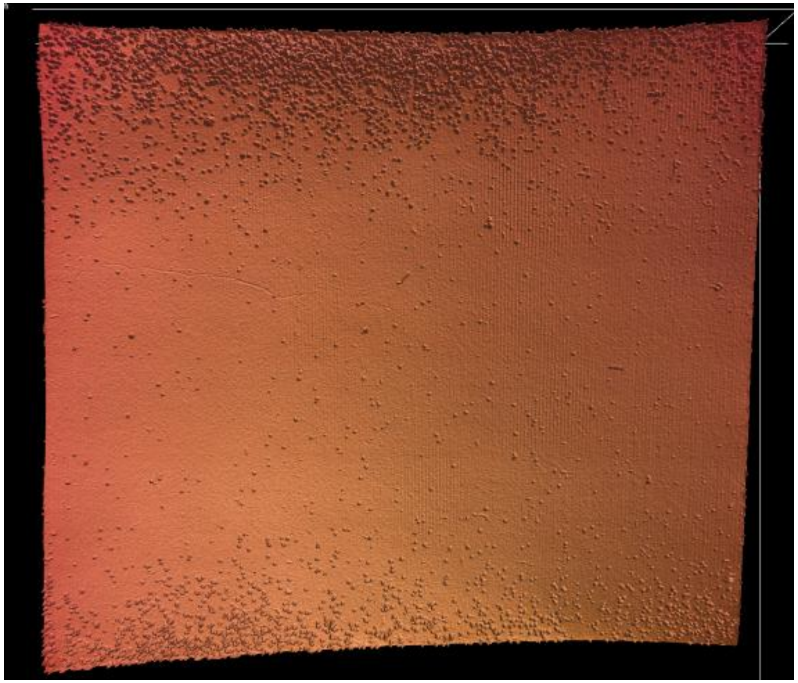


- Removal of raster pattern
- Image processing highlights defects using black lines based on a contrast or color difference
- Future capability to count defects and quantify size and shape

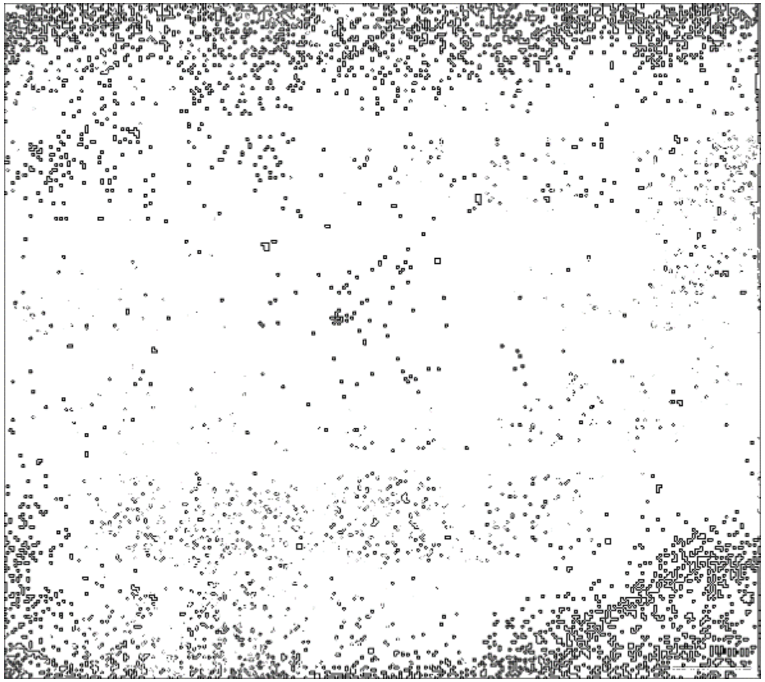
Image Processing: Defect Detection of Height Profile

MCO coated sample (with lots of bump defects)

Profilometry as taken with macroscope



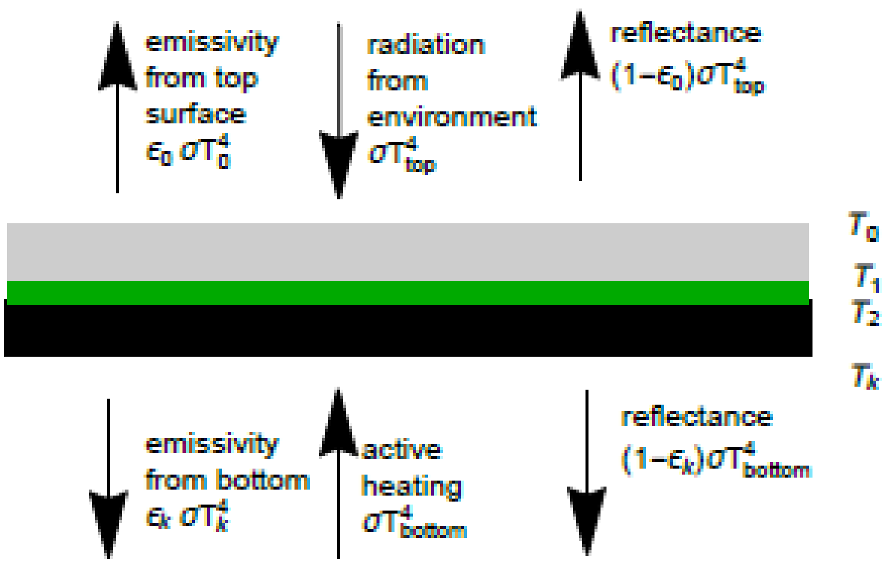
Processed image



- Similar set of defects as observed in original optical profilometry image (left), but defects are more pronounced after image processing (right)

Thermal transport modeling

Thermal transfer parameters model



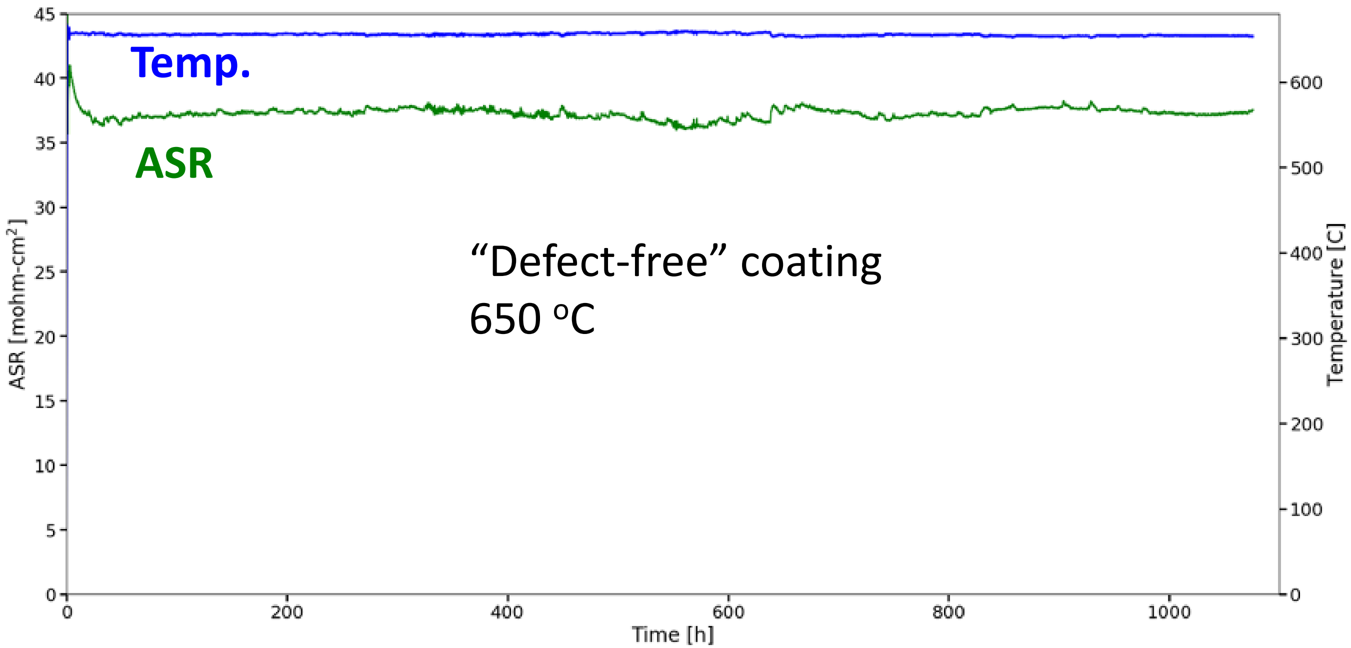
Key observations:

- Spatial variation in IR images even when there is no excitation
- Thermal map "reversal" when a specimen is excited vs. non-excited

Recent Progress:

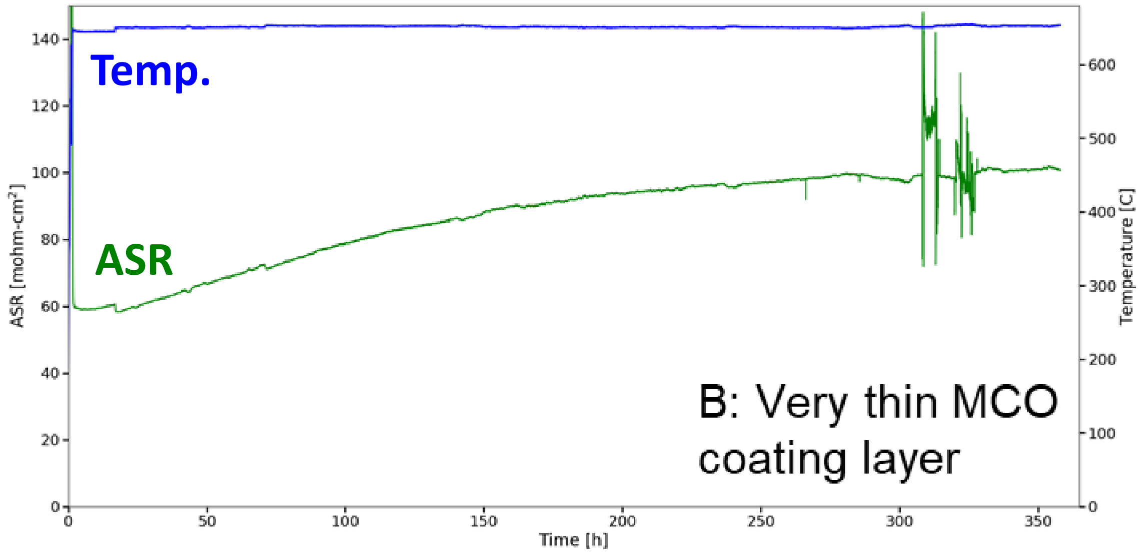
- Concept of model defined (see left image)
- Coating and substrate properties (e.g, thermal conductivity, heat capacity, and density) collected and/or predicted (includes coating porosity function)

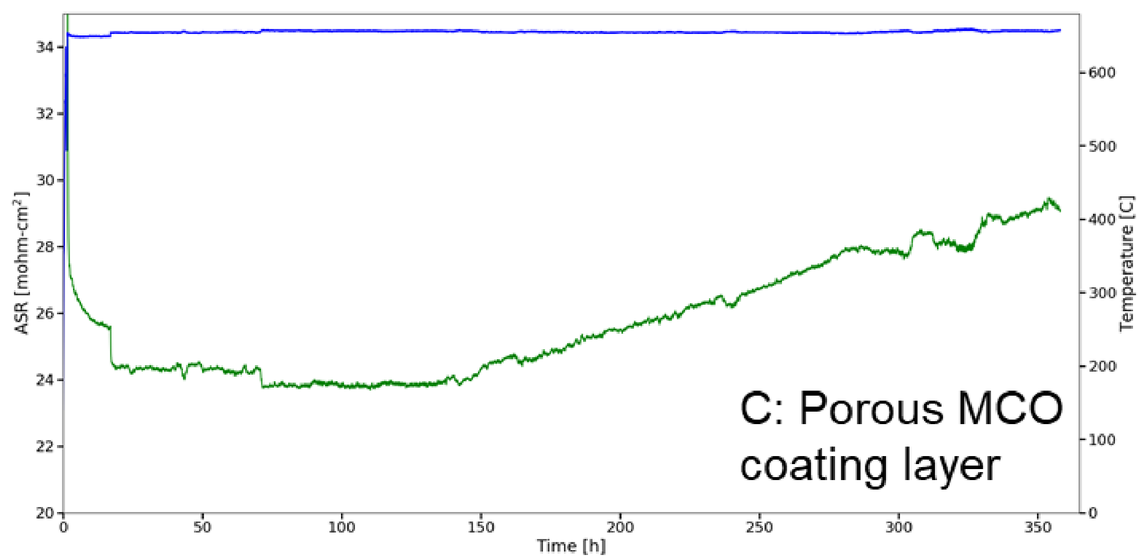
Long-term ASR of "defect-free" coating exhibits reasonable performance



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

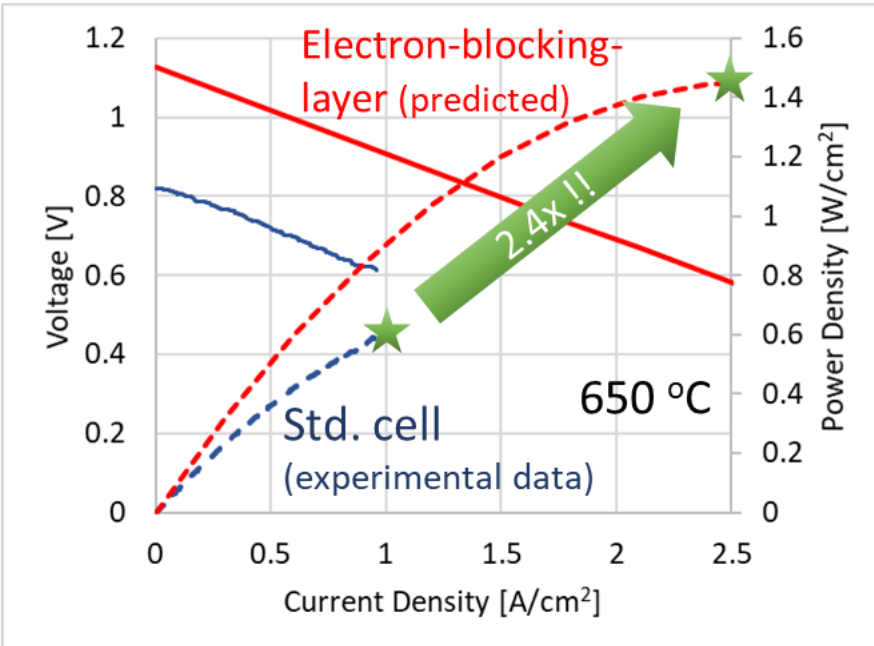
Long-term ASR of intentionally defective coatings

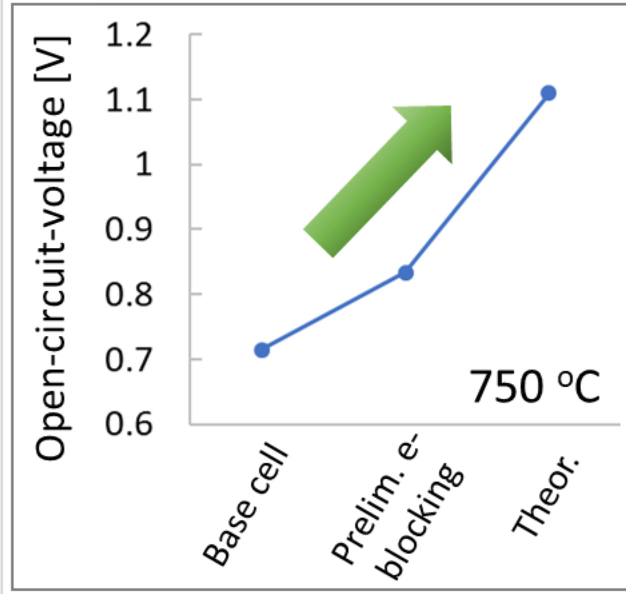




- Thin coating exhibits high ASR that increases from 0.06 Ωcm^2 to 0.1 Ωcm^2 (66%) with time
- Porous coating has low ASR, which also increases with time from 0.024 Ωcm^2 to 0.029 Ωcm^2 (21%)
- Porous coating exhibits a promising initial ASR, though high porosity may lead to more Cr volatilization

4. Sputtered Thin Film SOFCs

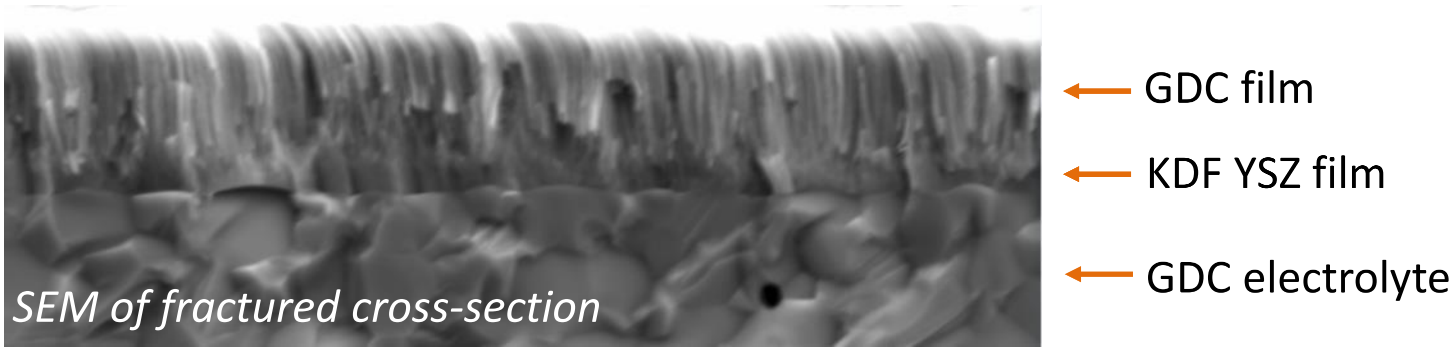




- Thin electron-blocking layer expected to increase Redox GEN1 Ni-cermet cell power density by >2x
- Electron-blocking layer eliminates electronic leakage through ceria based electrolyte → ~40% increase in open circuit voltage
- Thin-ness of electron-blocking layer adds negligible resistance
- Takes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

GDC Buffer Layer Deposition

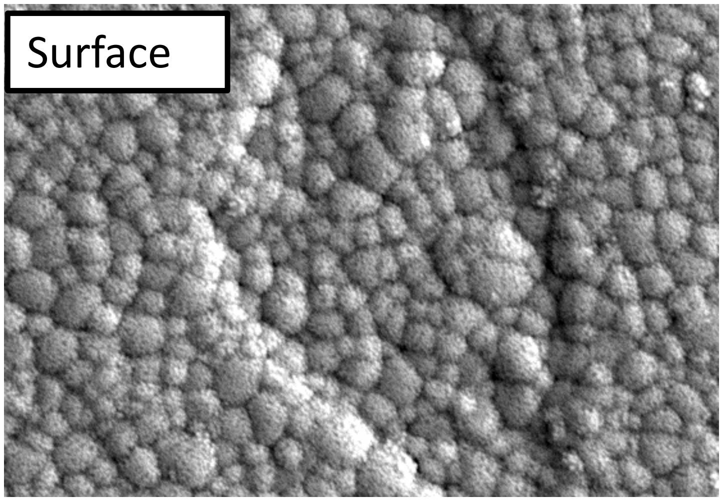
GDC deposited on GEN1 SOFC sample with YSZ layer previously deposited by KDF



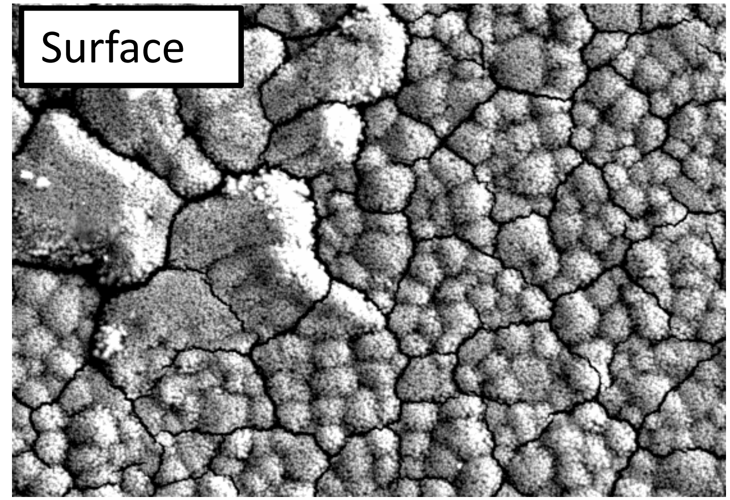
- Successful deposition of GDC buffer layer with over 1 μm/hour deposition rate on lab-scale system
- Required development of pre-sputter parameters and improvement of deposition conditions (e.g., Ar and O_2 pressure and sputtering power)
- GDC film deposition still being developed to ensure deposition of dense, robust film (see next slides on oxidative stress)

Buffer Layer Annealing in Air

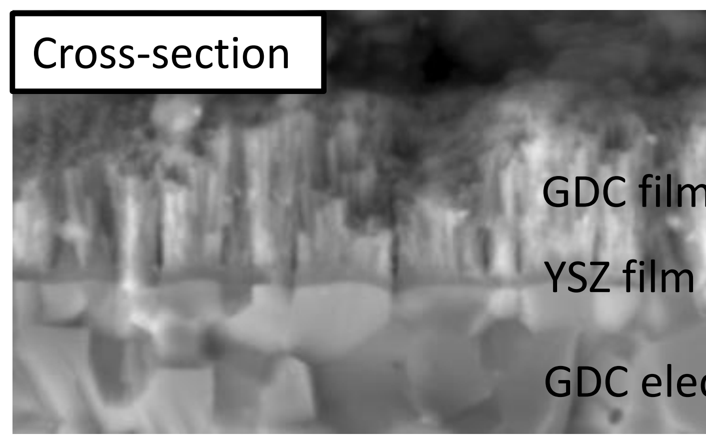
As deposited



After 600 °C 1 h anneal

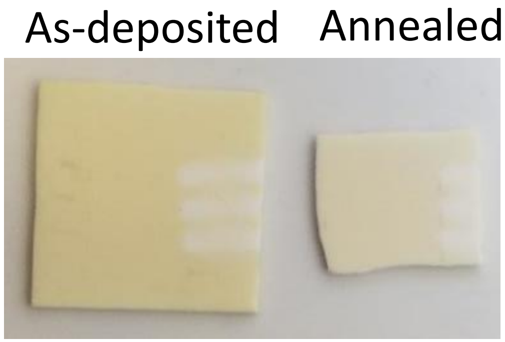


- GDC film cracked substantially after annealing
- YSZ layer appears to retain integrity

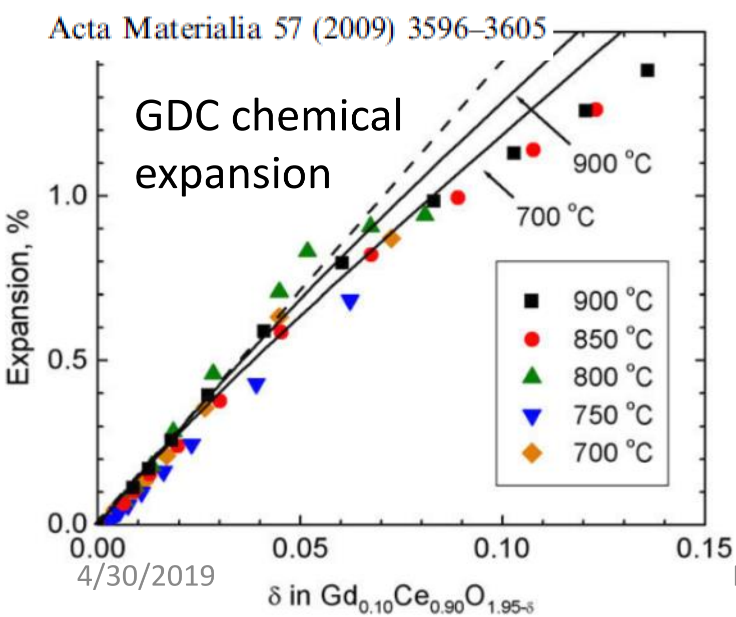


Source of Film Fracture

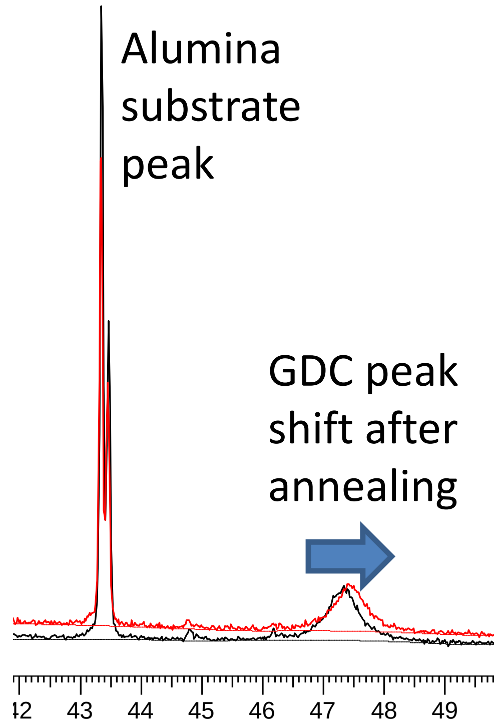
Color lightening after annealing



Consistent with loss of oxygen vacancy color centers



XRD spectra peak shift



- **Film fracture after annealing most likely due to oxidation driven stress**
- **Deposition parameters being tuned accordingly**

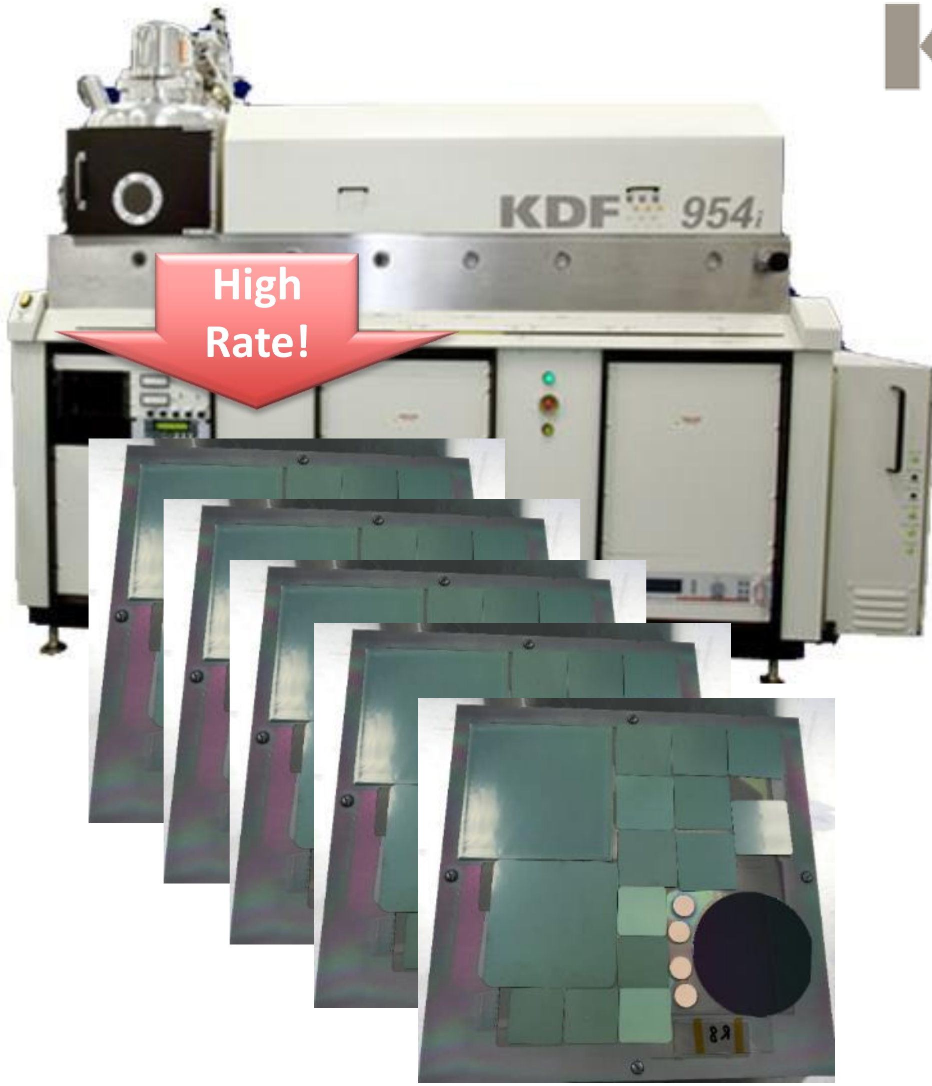
<u>This is a 0.19% chemical expansion</u>

→Δstress ~ 0.0019 * 250 GPa = 0.5 GPa

→δ ~ 0.015 (from graph at left)

Scale-Up Sputtering Process

KDF
in line with your process



Summary

- Good progress toward 2.5 kW stack demonstration
- Expanded capabilities in new, larger natural gas test facility
- Fabricated large format cells and all-ceramic anode stack with promising red-ox stability
- Cost modeling predicts significant decrease in lifetime cost for red-ox tolerant stacks
- Optical, height profile, and thermography metrology techniques shown to detect key defects in MCO coatings
- Thermal modeling and image analysis software in development to aid in defect detection
- Successfully deposited GDC buffer layer with sputtering, identified significant chemical expansion effect to be mitigated with process optimization

Acknowledgements

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- **DE-FE0031656**