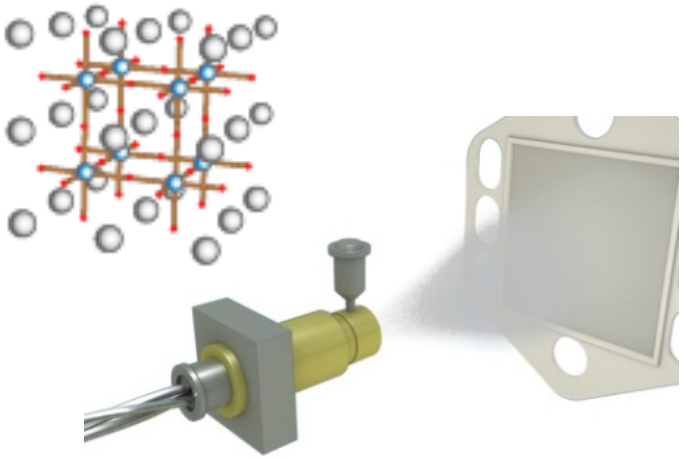
Development of a Thermal Spray, Redox Stable, Ceramic Anode for Metal Supported SOFC



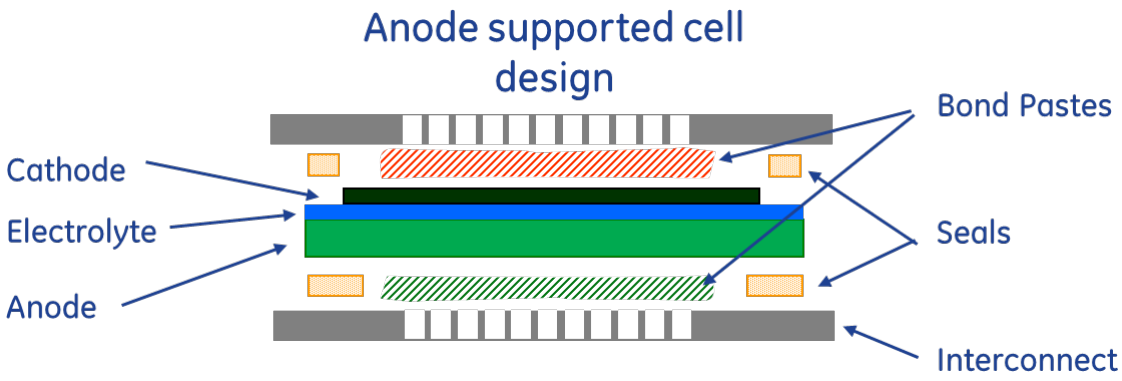
Richard Hart
GE Global Research
SOFC DOE Project Review June 14, 2018

Imagination at work.

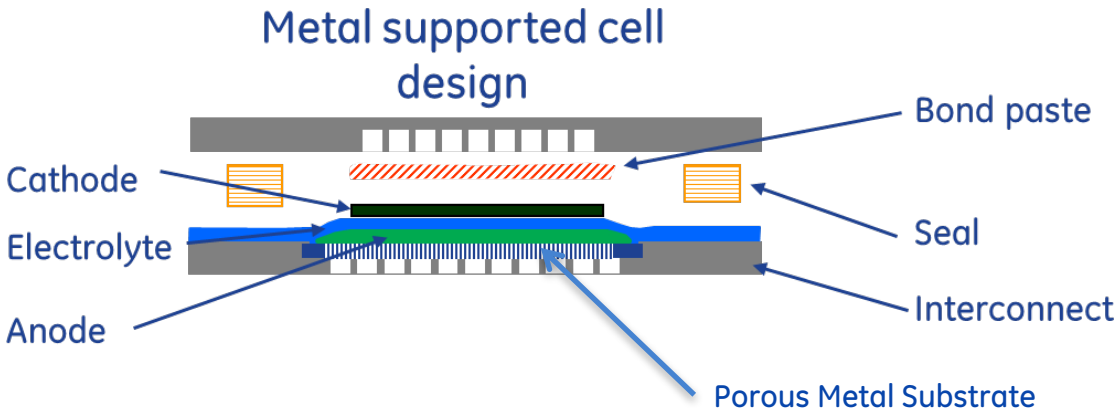
SOFC Innovative Concepts and Core Technology Research
DE-FOA-0001229 Award FE0026169

* Trademark of General Electric Company

Metal supported SOFC cells



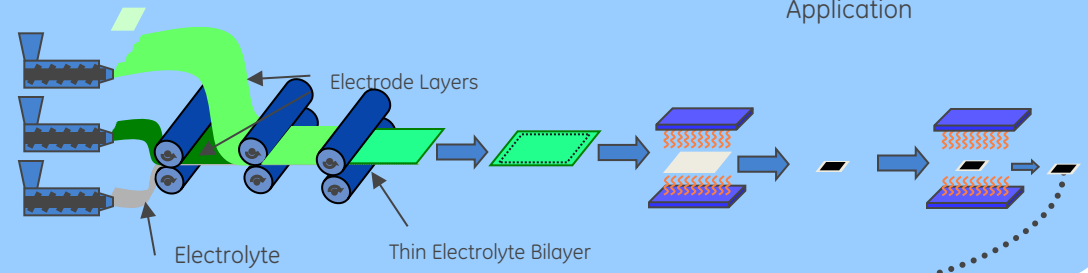
Advantages:
Integrated anode seal
Electrolyte in compression
Improved anode electrical contact
Increased active area
Lower anode polarization

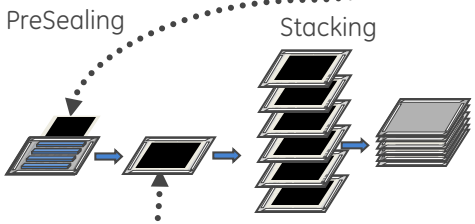


Challenges:
Dense / hermetic electrolyte
Porous metal substrate degradation

Low-cost manufacturing

Sintered Cell Manufacturing





Thermal Spray

Leverage GE thermal spray expertise

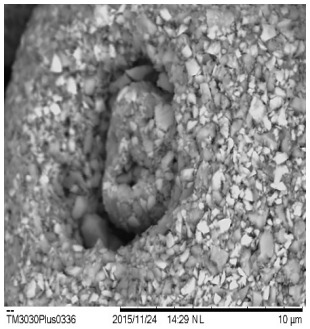
Advantages

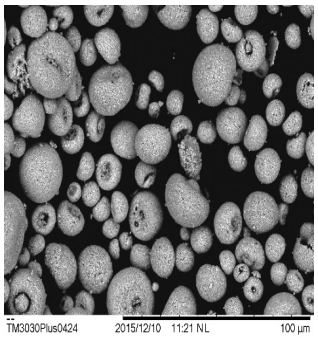
Larger area / Scalable
Simplified sealing
Low Capex / Modular
Lean Manufacturing

Traditional NiO(Ni)/YSZ anodes

- Advantages:
  - High initial electrochemical activity
  - Good electronic conductivity
  - Low cost
  - Well understood, wealth of data
- Disadvantages:
  - High redox Vol change (fuel↔air)
  - Ni particle ripening/poisoning
  - EHS concerns (NiO)
  - Sourcing concerns (REACH in Eu)

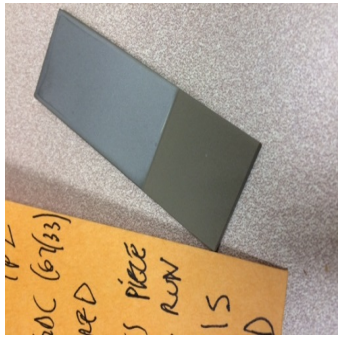
Task 2-4 Review – Metal Support Ceramic Anode Cells





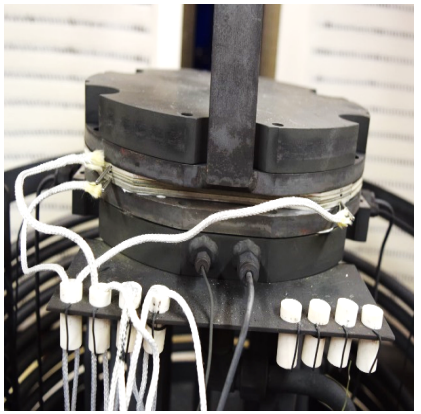
Materials Screening & Engineered Powder Prep.

LST ($La_{0.35}Sr_{0.65}TiO_3$) /GDC ($Gd_{0.2}Ce_{0.8}O_{\sim 1.9}$)



Coupon Screening Experiments (Thermal Spray)

XRD, SEM, Permeability, DE, Roughness, etc...



100cm^2 Cells

(2-6 cell stacks)

OCV, W/cm2
Redox Stability

2018 Project Goals:

Scale 3 Ceramic Anode Candidates:

- Powder Scale up: 10grams -> 17kg
- Thermal spray and Test at ~100cm^2
  - >200mW/cm2
  - >3 redox cycles
  - <10% Degradation over 1000h
  - Eqv materials cost and process vs. baseline

Task 2-4 Complete

GE + WVU

5kW Stack Testing:

- Repeat scale up 1-2 powders
- Demonstrate cell size scaling (100cm^2->400cm^2)
- Build and test 5kW stack

Task 5 ~9 months

Ceramic Anode Material Screening Test Results GE + WVU

Material Development Testing Plan

Synthesis

- XRD - impurities
- Particle Size

Conductivity Testing

- Screen w/ pressed pellets or free-standing films
- Electron Conductivity > 10S/cm (bulk), >5 S/cm (film)
- Ion Conductivity > 0.5×10^{-2} S/cm (film)

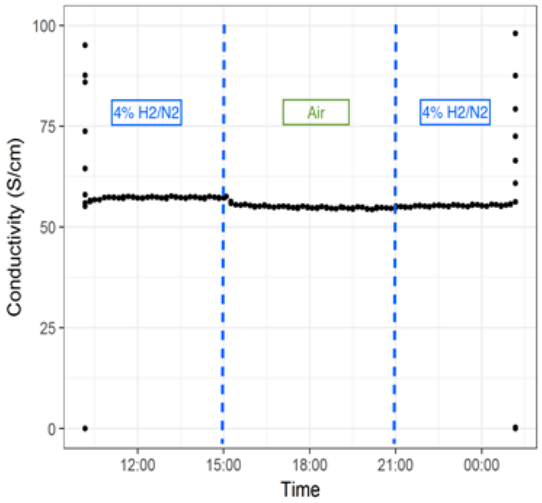
Mechanical Stability During Redox Cycling (800C)

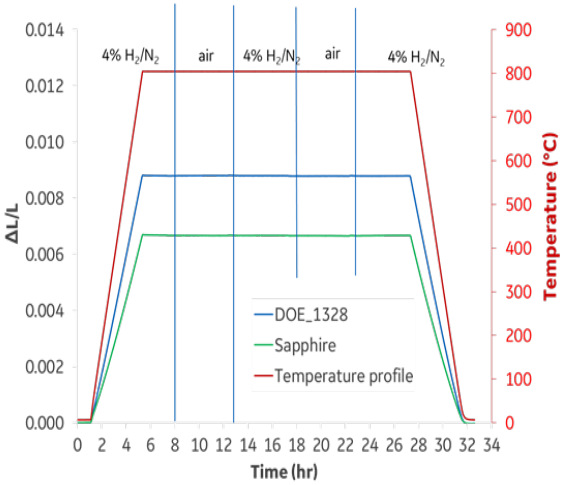
- Redox Vol. Change < 0.15% ΔV – redox dilatometry

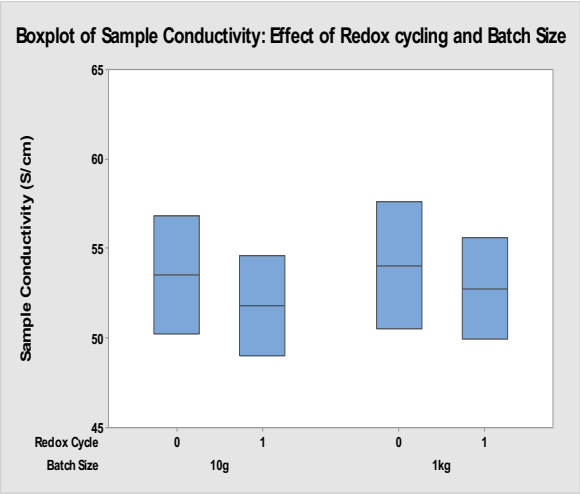
GE + WVU screened > 200 samples (chemistry + processing)

Down-selected 3 materials / process conditions for trial under GE Task 4

Alternately Doped SrTiO3







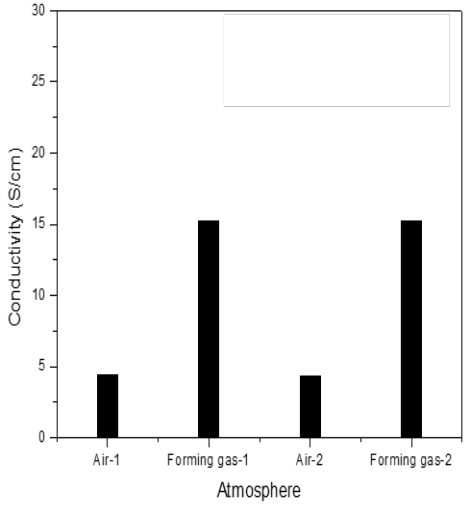
Redox Conductivity:
- -Excellent conductivity
- -Good redox stability

Redox Dilatometry:
- -Excellent mech redox properties

Scaling from 10g->1kg->17kg

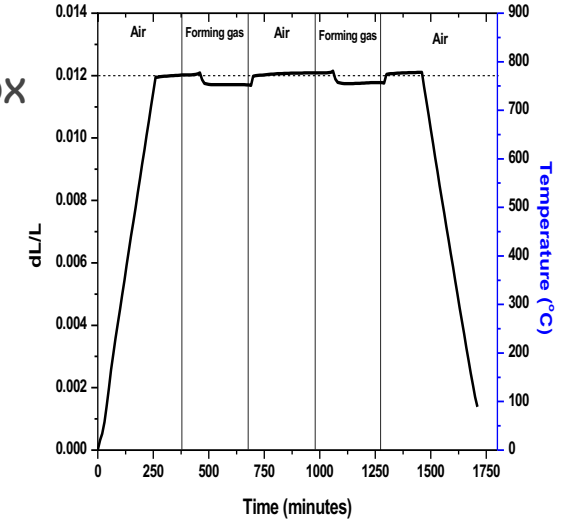
Scale up of WVU doped-SFM at GE:

Redox S/cm



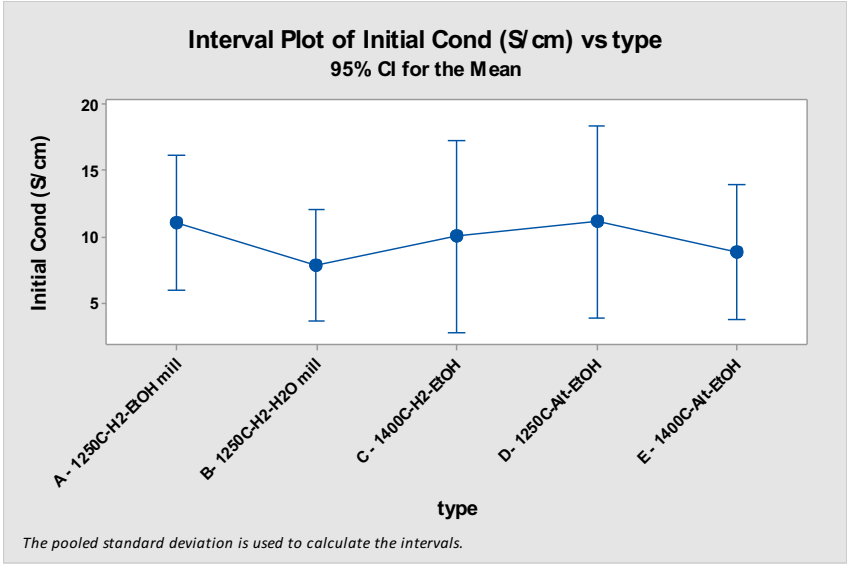
Doped SFM, solid state synthesis

Redox Dil



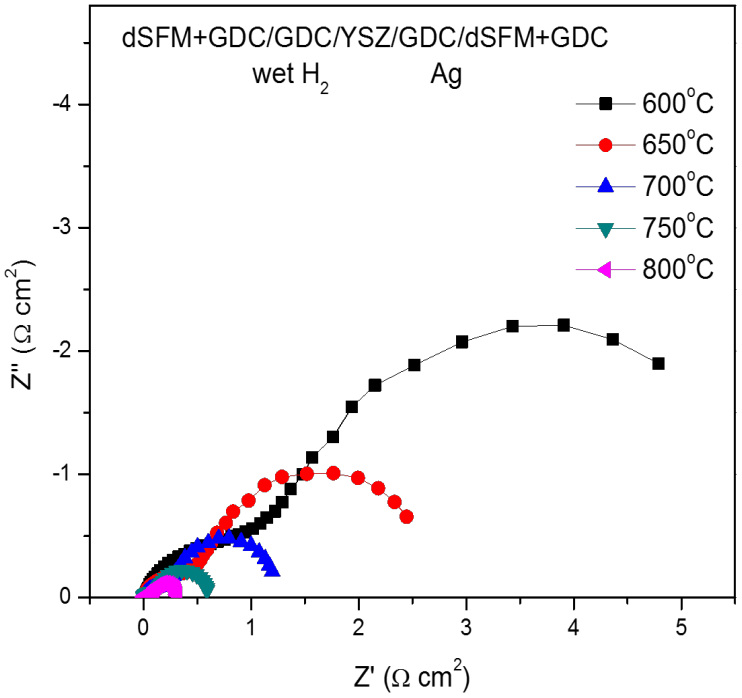
CTE in Air, 25-800°C = $15.31 \times 10^{-6}\ K^{-1}$

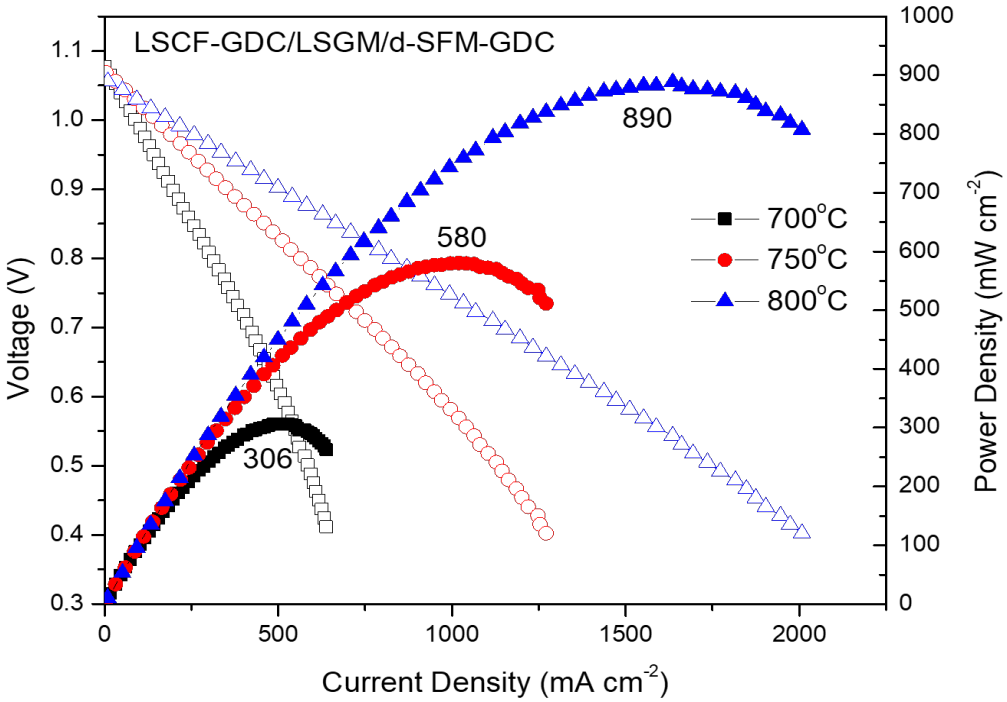
Scale up experiments at GE:
Calc Temp, Firing Atm, milling conditions, crucible sizes, etc...



GE Identified process to scale dSFM to 17kg quantities w/ similar electrical & mech properties!

Doped-SrFeMo Oxide 1” Button Tests- WVU





- High temperature sintering of dSFM-YSZ causes rxn
- Using GDC barrier layer or LSGM electrolyte, WVU demonstrated material entitlement for low ASR + high power density!!

GE Thermal Spray & Cell Testing Results

Task 4 – Ceramic Anode Candidate Testing

Experimental Process:

Scale to 15-20kg Batch → Spray Dry Agglomeration (slow!) → Coupon Tests (XRD, SEM, etc…) → Cell thermal Spray → Full Stack Testing (100cm2 cells)

1) LST + GDC with Modified Spray Process (July –Sept 2017)

2) $dSrTiO_3$ + GDC

3) Doped SFM + GDC

Dec 2017 – Apr 2018
Substantial delays with vendor spray drying!

All candidates used Modified T-Spray Process

Candidates 1 + 3 performed well.

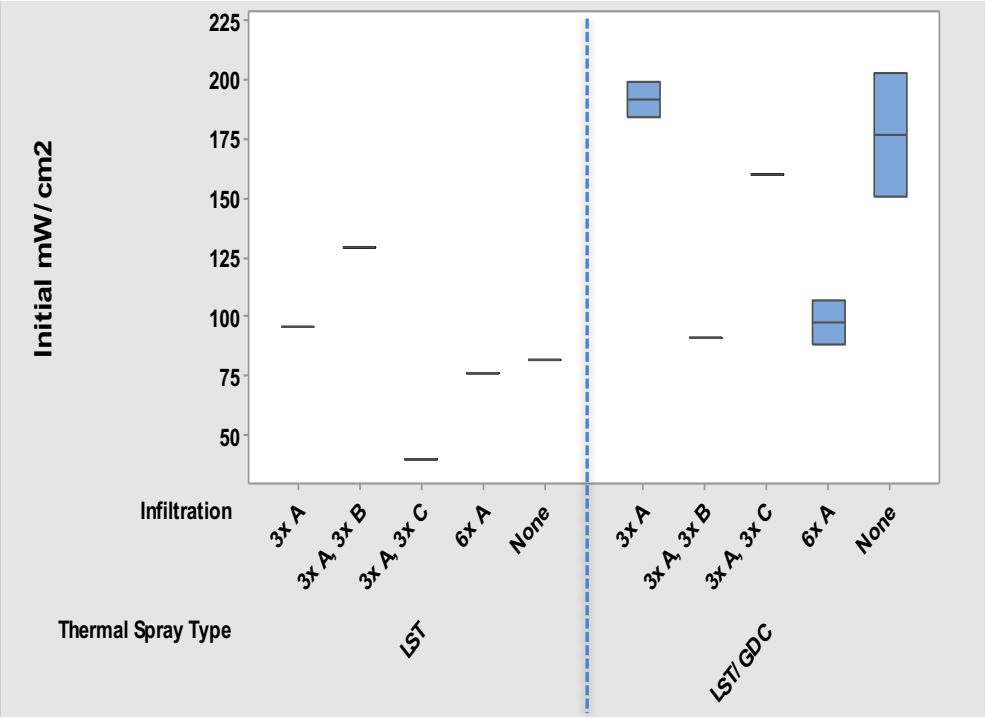
Candidate 2 underperformed wrt. Expectations (post mortem in progress)

Candidate 1
LST+ GDC
Modified Spray Process

LST-GDC with Modified Thermal Spray Process:

Multi-factor Designed Experiment:
-LST vs LST/GDC
-Anode Infiltration:
*3 materials (A, B, C)
*# infiltration cycles

Testing:
24 Total Cells ~100cm^2 cells
Cells were randomly mixed into stacks



Experiment Results:
-LST/GDC higher power vs. LST

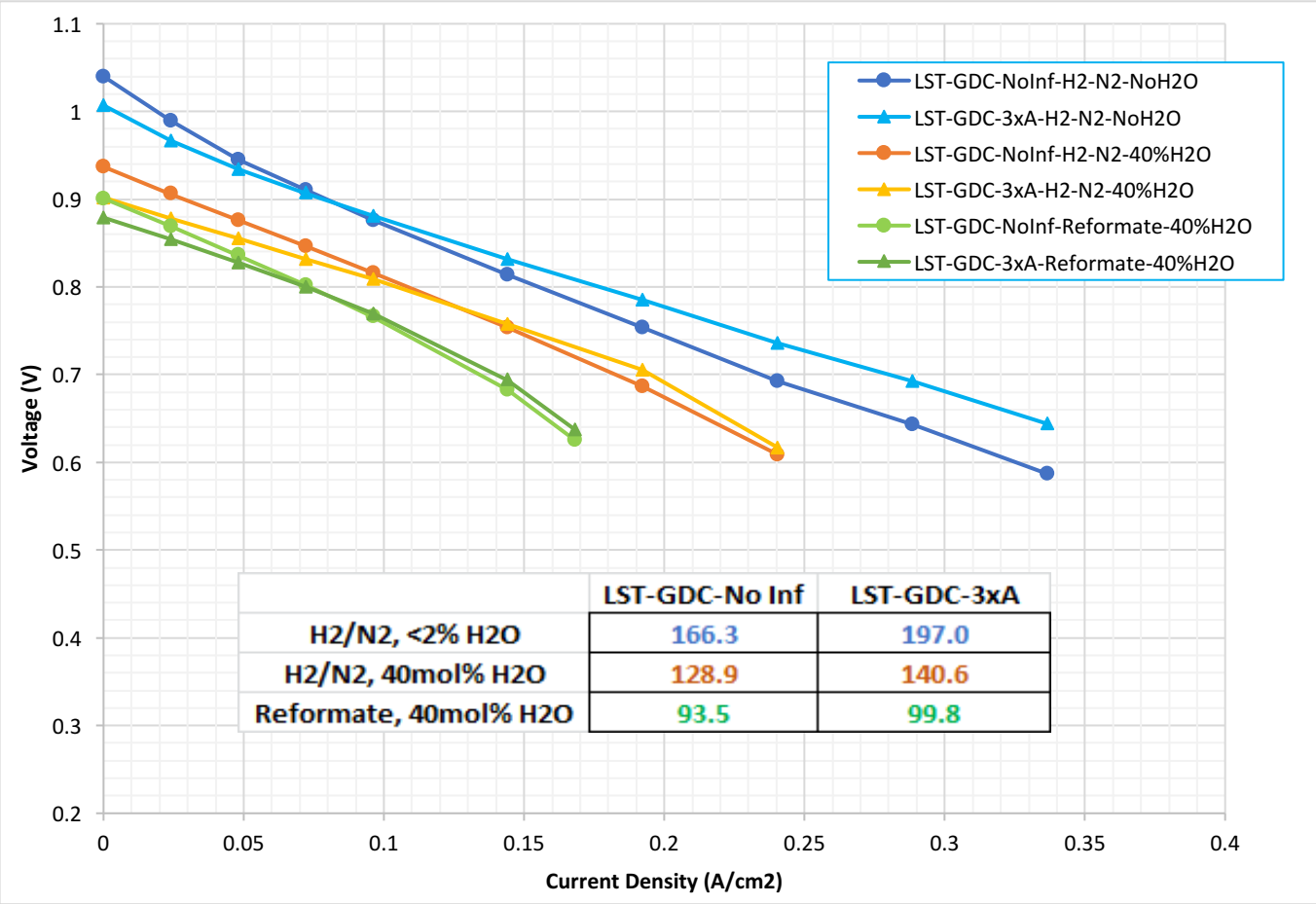
-Infiltration effects weren't consistent, no clear advantage over LST/GDC (may repeat Type A again)

- Modified spray process eliminates Phase impurities → high initial perf!

120mW/cm2* → >200mW/cm2*

* 0.7V, 33.4% Uf, 800C

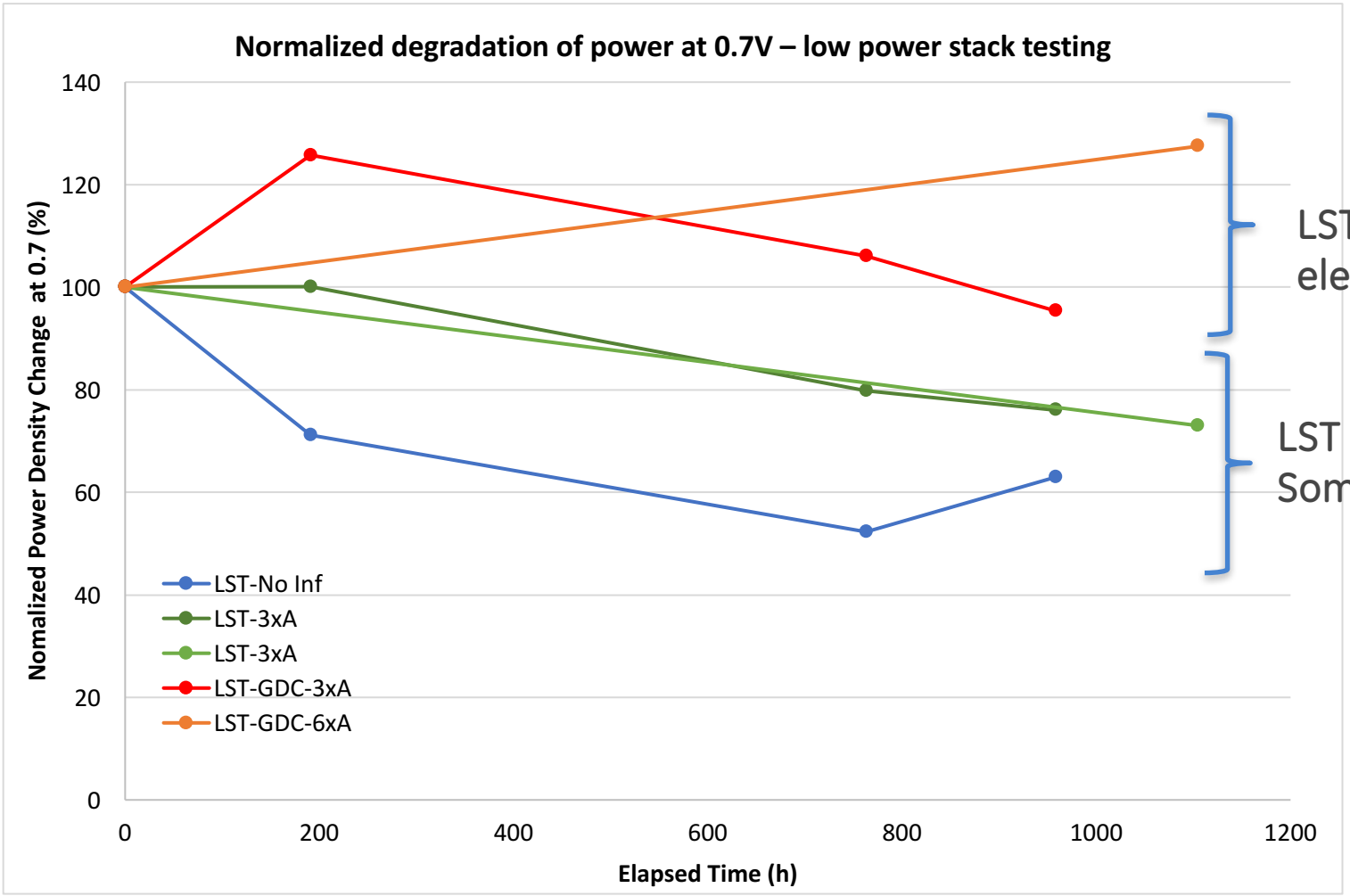
LST-GDC w/ Alt T-Spray – Reformate Testing



	LST-GDC-No Inf	LST-GDC-3xA
H2/N2, <2% H2O	166.3	197.0
H2/N2, 40mol% H2O	128.9	140.6
Reformate, 40mol% H2O	93.5	99.8

- Much of the voltage/power loss on reformate testing came from Lower fuel content (effect on OCV & diffusion pol)
- No sign of kinetics issues or rapid degradation acceleration

LST-GDCw/ Alt T-Spray – Degradation

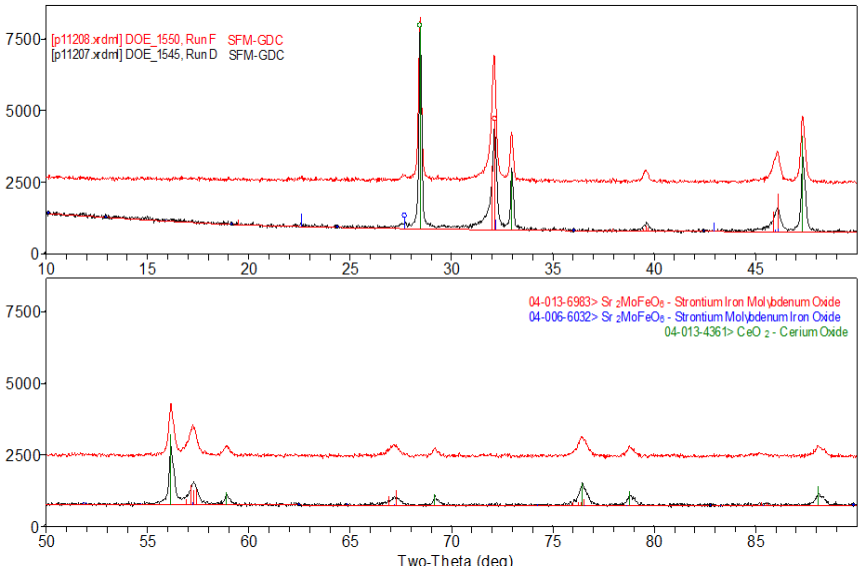


- LST+GDC electrodes showed <10 % degradation over 1000h
- Infiltration with various catalysts didn't statistically improve W/cm2 or deg rate!

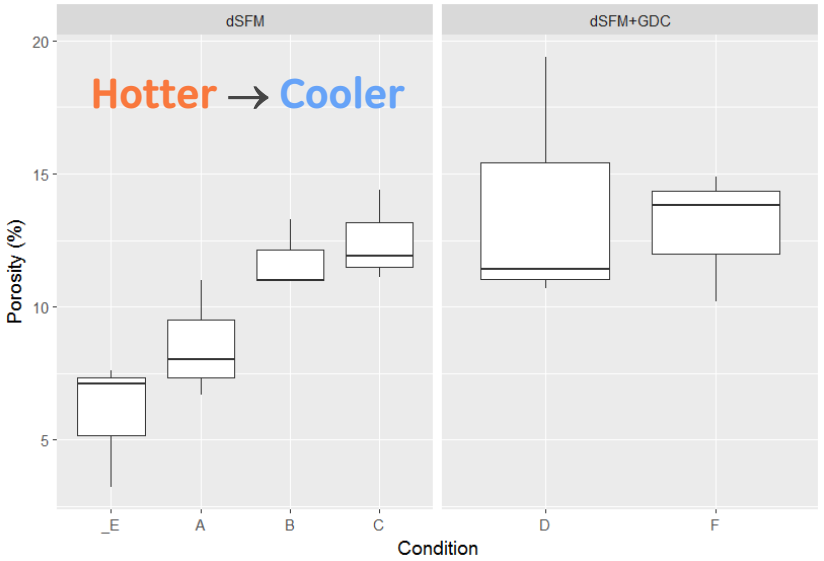
Candidate 3
dSFM + GDC

dSFM-GDCw/ Alt T-Spray – Coupon Experiment

XRD – Thermal Spray Film



SEM Analysis – Film X-Sections



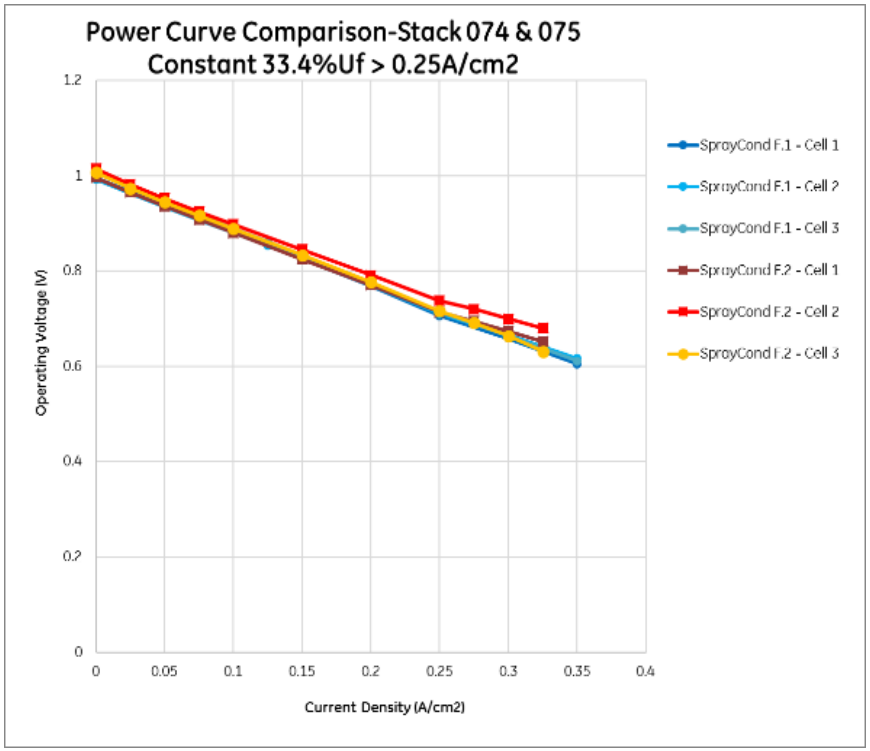
Modified T-Spray Process:
-eliminated impurity phase formation
-no evidence of chemistry degradation
-decent crystallinity (narrow peaks)

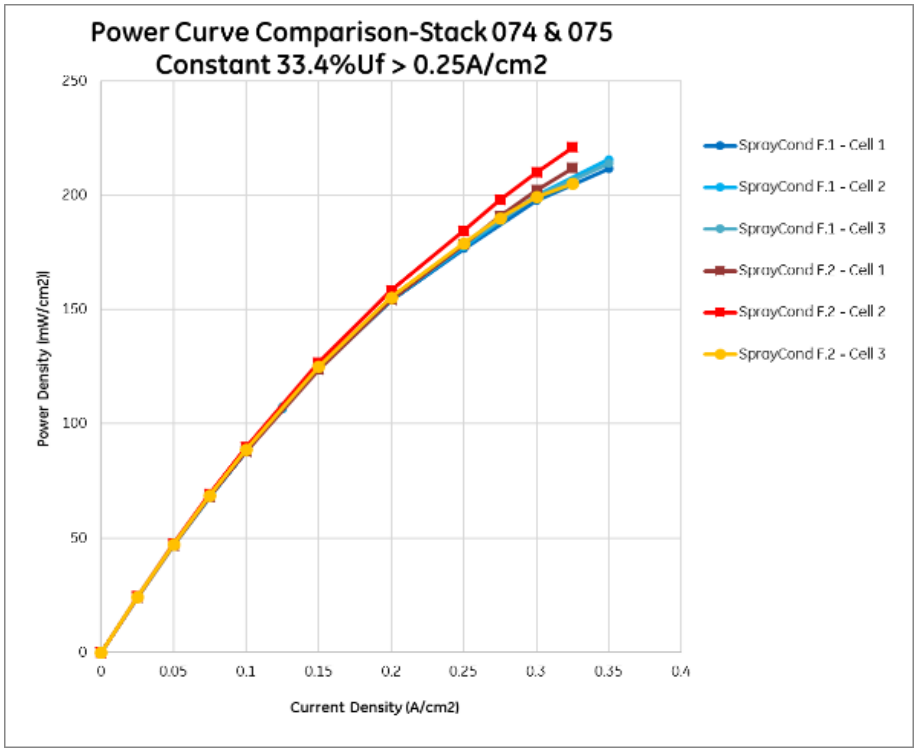
Microstructure:
-Identified process w/ acceptable porosity
-Likely still room for microstructure improvement! (best LST+GDC cells showed higher SA and porosity %)

100 cm^2 cell experiment centered on Conditions D/F

dSFM-GDCw/ Alt T-Spray – Cell Experiment

3 cell stacks – 2 spray conditions (minor differences)





Repeatable cell performance: >200mW/cm2 at 0.7V/33.4Uf
SEM analysis of microstructure suggests further W/cm2 increase possible

Ceramic Anode Chemistries – Stack Test Highlights

Property:	LST/GDC w/ Alt T-Spray	Alt $dSrTiO_3$ + GDC	dSFM + GDC
Redox Conductivity	-	+	+
Mechanical Stability	+	+	+
Power Density (mW/cm2) @ 0.7V & low Uf 100cm^2 size	163-203	30-80	200-245
Degradation @1000 h	<10%	NA	> 10%
Stack Redox	+	NA	+
Estimated Porosity (%)	12-25	NA	11-17
Notes	Candidate for 5kW stack build	Post Mortem & RCA in Progress	Candidate for 5kW stack build & Further dev work!

Final Summary

- GE identified modified thermal spray method
  Removed phase impurities + improved W/cm2 (doubling power output!)

- 100cm^2 Stack Testing:
  Large scale demo of ceramic anodes in metal supported stack tests
  Exceeded project power density targets
  Conducted multiple >1000h degradation stack tests

- Final Project Goal -
Deliver 5kW metal supported SOFC stack build with ceramic anodes

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GE Team:

Rich Hart	PI, testing & direction
Luc LeBlanc (GE Fuel Cells)	Thermal Spray
Holly Comanzo, Chris Hill	Powder dev & synthesis
Jim Gardner, Jon Klopman	Materials + Cell testing
Matt Alinger, Todd Striker, Andy Shapiro, Simon Gaunt	GE Fuel Cells, Systems Support
Jae Hyuk Her, Yan Gao, Vince Smentkowski	Analytical Support
John Freer, Dan Hancu, Wei Cai, Dave Moore	GE Management Support

WVU Team

Principle Investigators:

Dr. Xingbo Liu[a]

Dr. Edward M. Sabolsky[a]

Dr. John Zondlo[b]

Research Assistants:

Dr. Tony Thomas[a]

Laura (He Qi)[a]

[a]Department of Mechanical and Aerospace Engineering

[b]Department of Chemical Engineering

West Virginia University