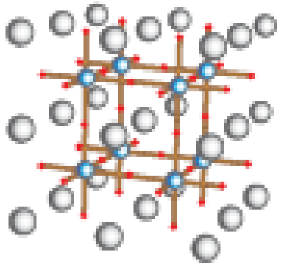
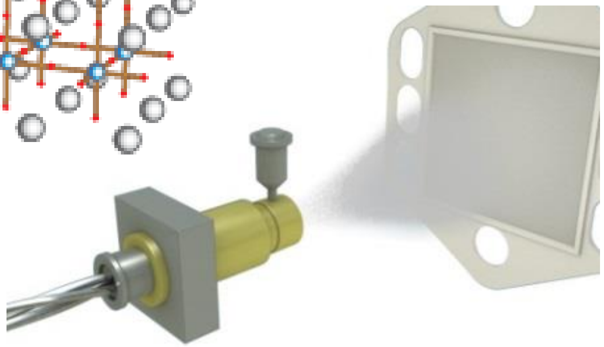
Development of a Thermal Spray, Redox Stable, Ceramic Anode for Metal Supported SOFC





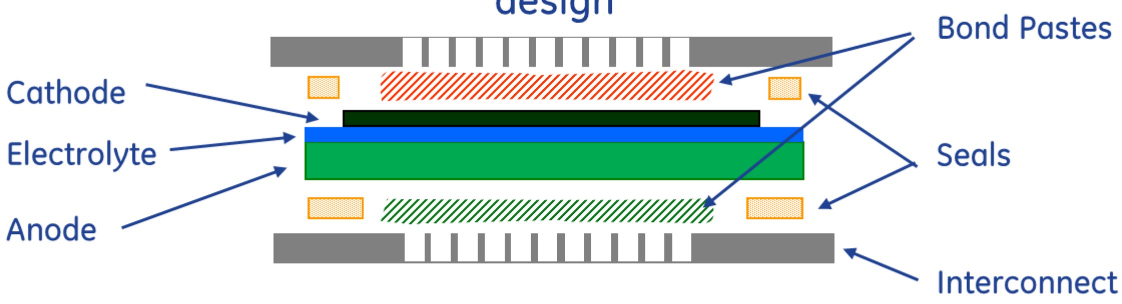
Richard Hart
GE Global Research
Pitt Review June 12, 2017

Imagination at work.

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

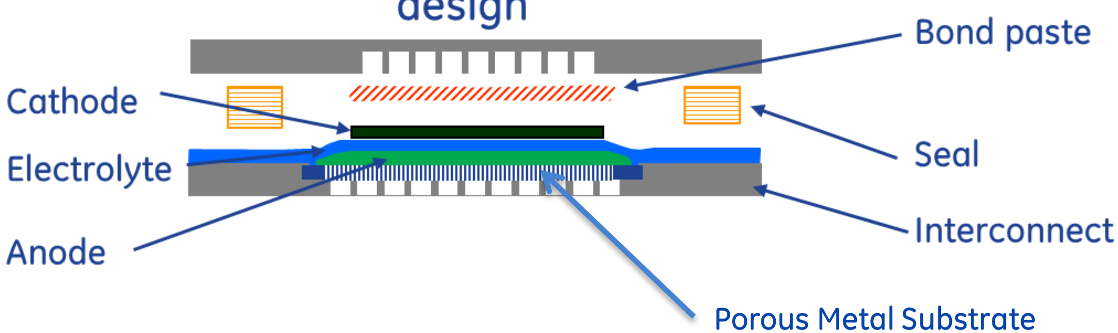
Metal supported SOFC cells

Anode supported cell design



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

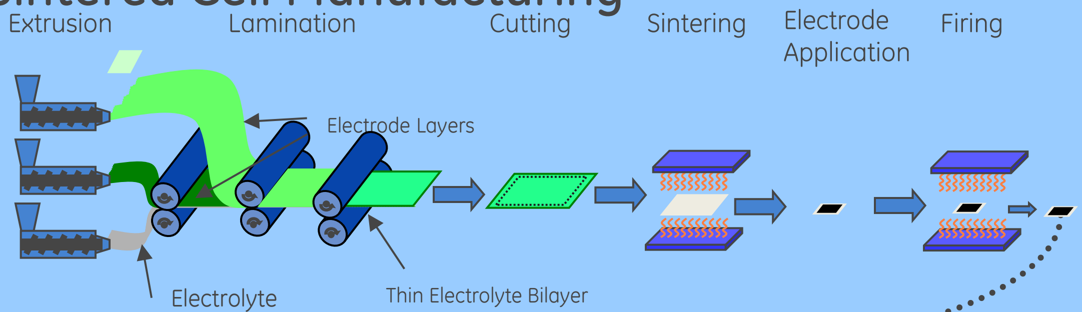
Metal supported cell design

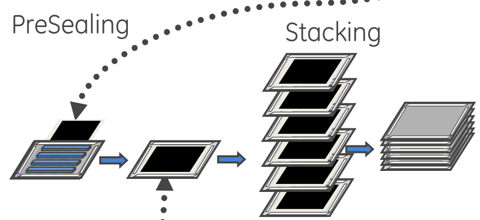


Challenges:
Dense / hermetic electrolyte
Porous metal substrate degradation

Low-cost manufacturing

Sintered Cell Manufacturing





Advantages

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

Thermal Spray

Leverage GE thermal spray expertise

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)

2017 Project Goals:

Transition WVU Set 2 Materials to GE Thermal Spray

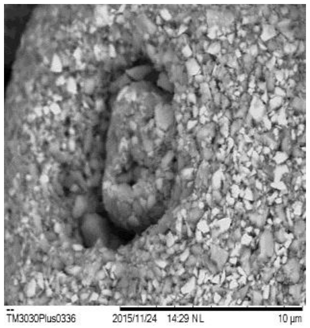
Metal Supported SOFC Cell (100cm^2) with:

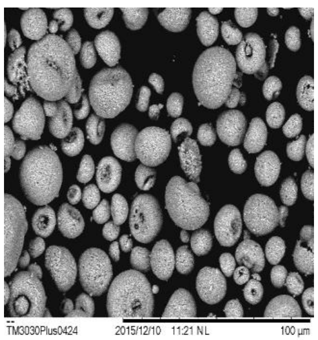
- >200 mW/cm2 on Reformate Fuel (>50%Uf, 0.7V)
- <10% Degradation after 1000h (or >180mW/cm2)
- >3 Redox Cycles
- ~Equivalent Materials Cost and Process vs. Baseline

5

Cell Testing & Thermal Spray Film Results

Y1 Review – Metal Supported Ceramic Anode Cells





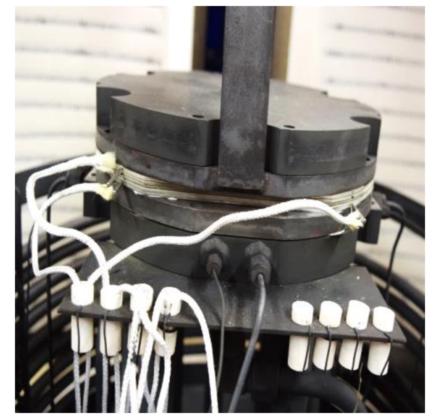
Sourced Engineered Powders

LST ($La_{0.35}Sr_{0.65}TiO_3$)

GDC ($Gd_{0.2}Ce_{0.8}O_{\sim1.9}$)

Coupon Screening Experiments (Thermal Spray)

XRD, SEM, Permeability,
DE, Roughness, etc…

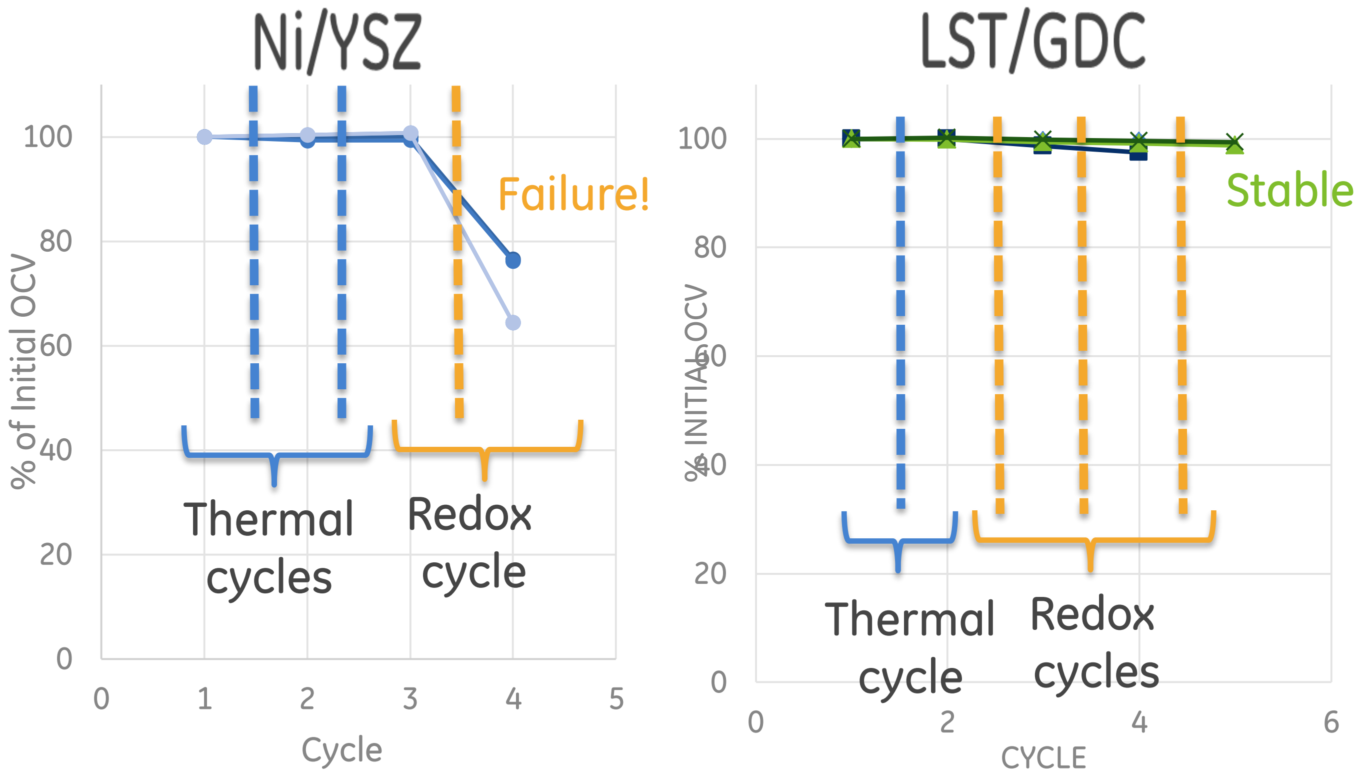


$100 cm^2$ Cells

(2-6 cell stacks)

OCV, W/cm2
Redox Stability

Redox Cycling – (2 cell stacks)

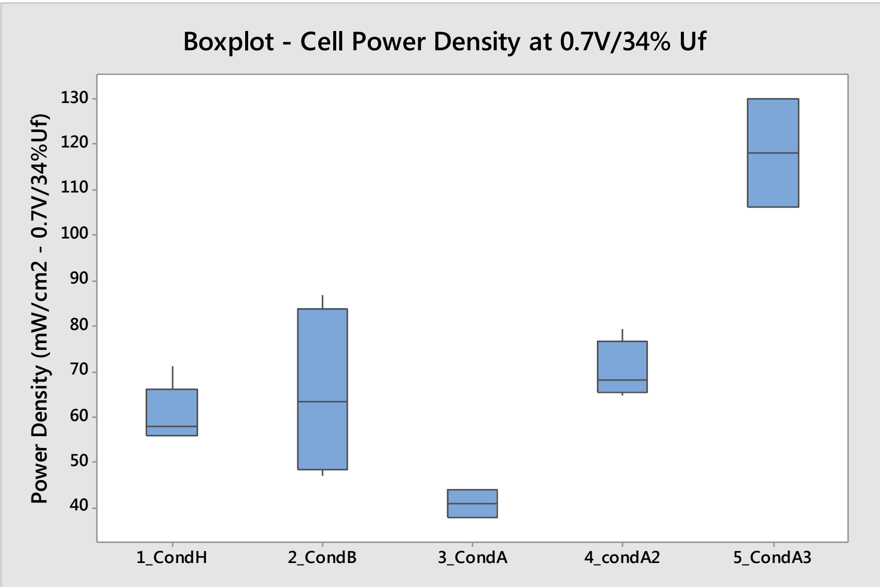


Ni/YSZ cells fail after a single redox cycle

Ceramic anode cells survive > 5 cycles

LST/GDC cells = Low power (55-130mW/cm2) –H2/N2 fuel
Inherently low material conductivities (e-)

Optimization Experiments: LST-GDC co-spray



- Co-Spray Experiments investigated:
  Plasma power
  Feedstock powder calcination
  Powder injection parameters

- Results limited to < 130 mW/cm2
  *Rxn to form new phase
  *Low film conductivity (LST)

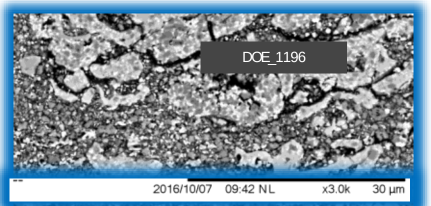
Film conductivity
Good Cohesion
Stiffness/Cracking
Rxn Phase formation

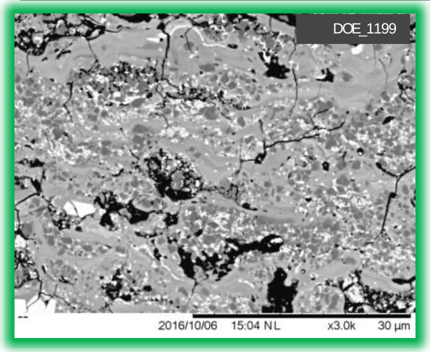
Porosity
TPB -m^2/g
Low Cohesion

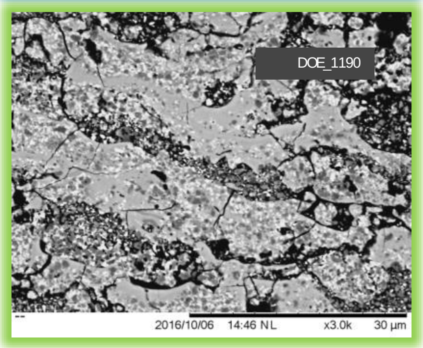
Need alternate formulation/method to achieve >200 mW/cm2

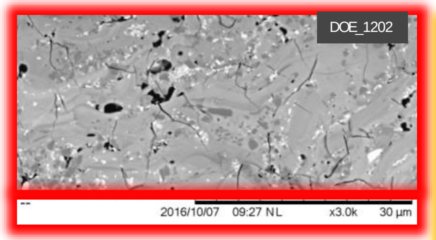
LST-GDC Electrodes: Microstructure, film XRD

Red = Hot, GRC
Orange = Hot, Vendor B
Dark Green = Cool, GRC
Light Green= Cool, Vendor B
Blue = coldest cond, VendorB

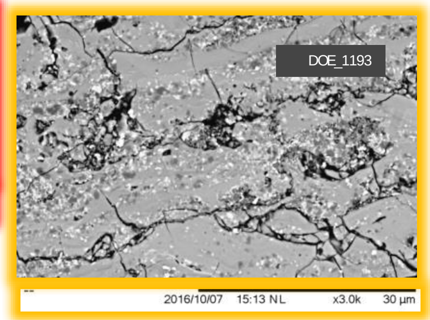




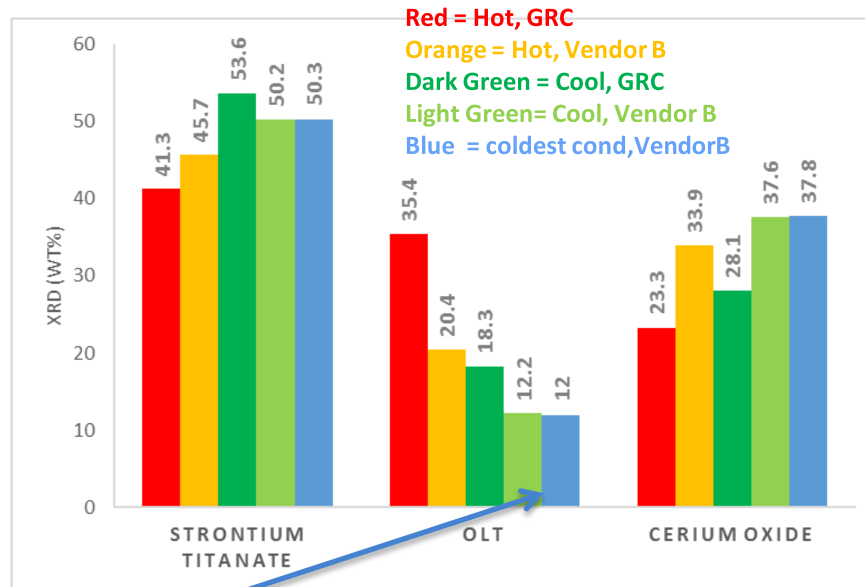




GRC Pilot Batch



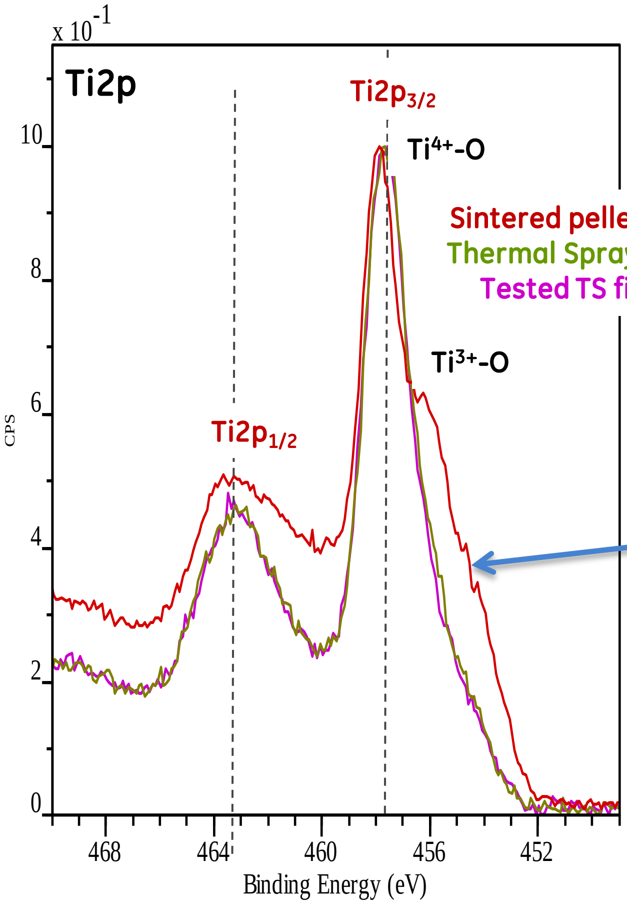
Vendor Batch



-Process opt minimized LST+GDC Reaction
*3Q-4Q: alternate methods of GDC/YSZ integration: infiltration/co-feed

Variation in feedstock agglomerate size → variation in microstructure/phase/cond
-Confirmed this is a key factor to control
-2nd Learning: use larger scale up batches (less re-optimization needed)

Deactivation of doped SrTiO3 (no GDC) in Thermal Spray

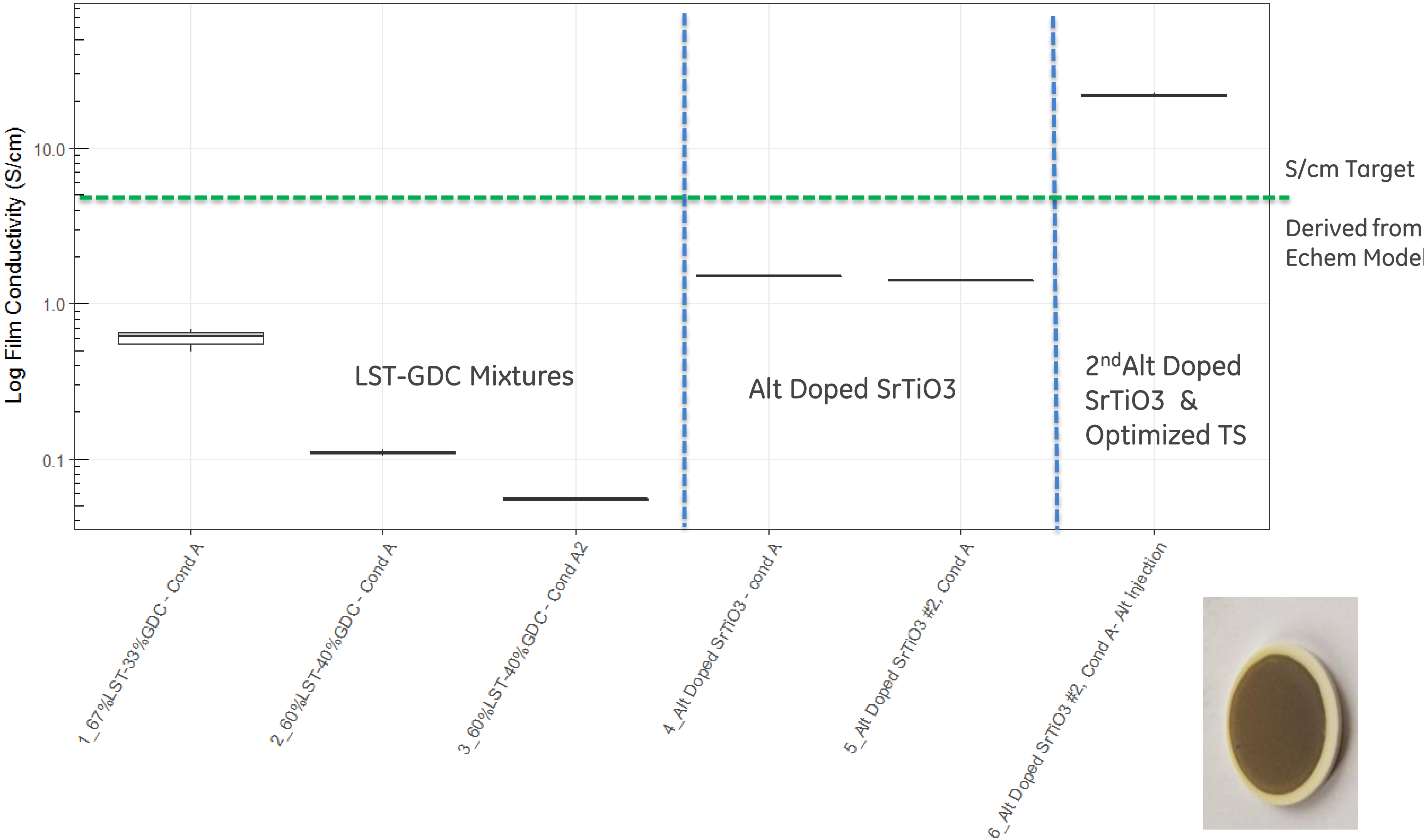


XPS High Resolution Spectra
after 1um etching– Chemical Bonding

- Chemically deactivation of doped SrTiO3!
- 2017 Q1-Q2 – noted process changes can be made to reduce/eliminate this effect

*Improved thermal spray film S/cm ~40-100x

Thermal Spray Anode Film Conductivity Screening



Achieved sufficient film S/cm (anode chemistry & thermal spray conditions)
Next step: focus/balance electrode microstructure +catalyst prop

GE Ceramic Anode Material Screening Test Results

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)

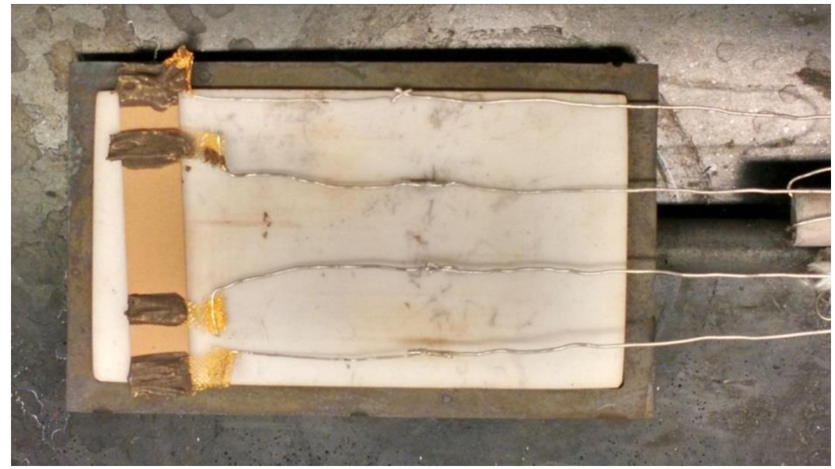
Mechanical Stability During Redox Cycling (800C)

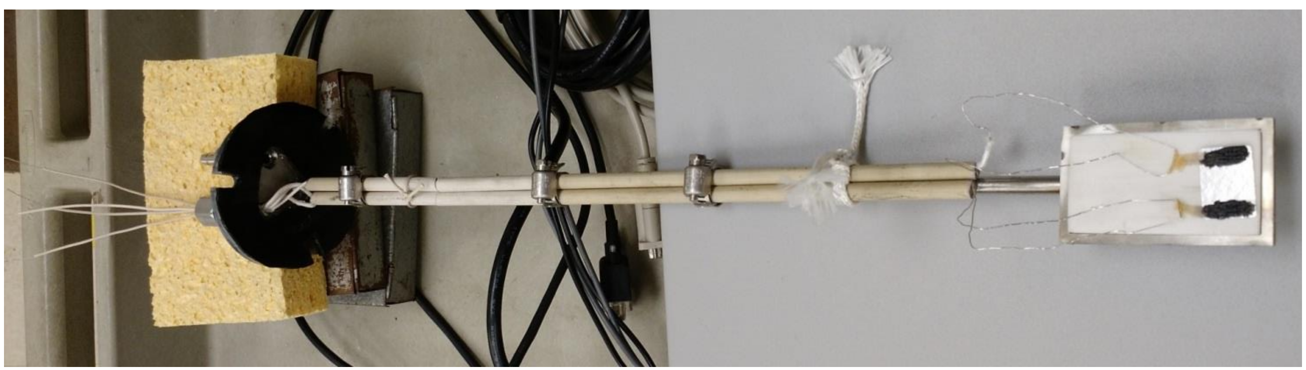
- Redox Vol. Change < 0.15% ΔV – redox dilatometry

SOFC Cell Testing

- GRC – thermal spray 100cm2 metal supported cells (2-6 cell stacks)

Conductivity Test Setup (GE-GRC)

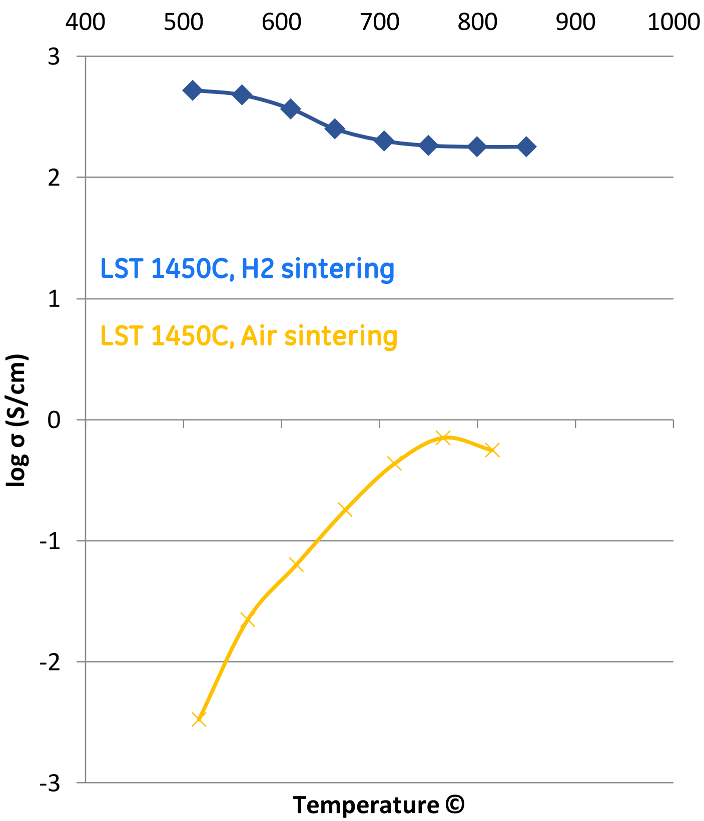




Jezek, Hart

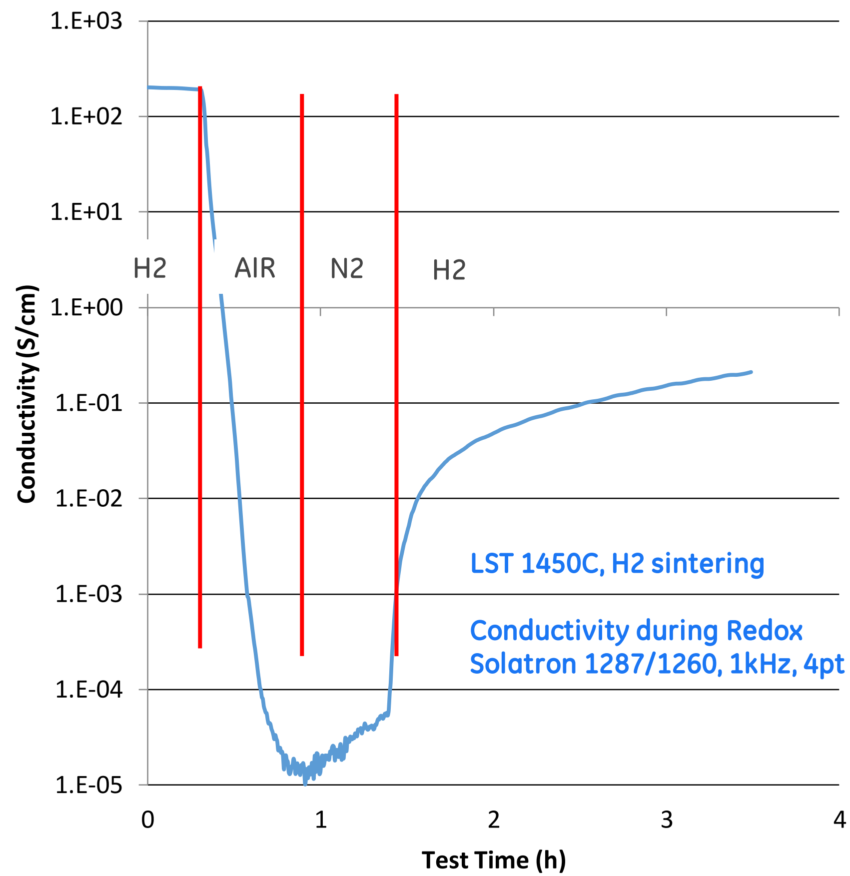
LST Conductivity – Effect of Sintering Atm, and Redox:

LST – 1450C sintered, effect of atm:



Solatron 1287/1260, 4pt, AC impedance, ~1kHz

LST Pellet Conductivity – Redox Cycling



E-chem Model -> need to identify materials w/ >10-20S/cm after redox

Jezek, Hart

Summary of doped Strontium Titanate Screening - GE

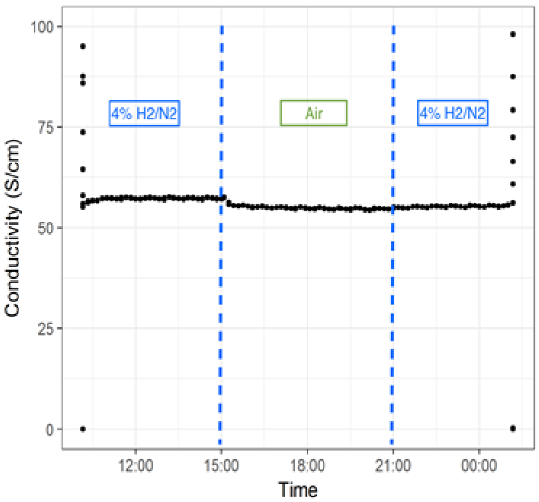
Factor:	Conditions/Ranges:
A dopant	RE (La, Y, Yb, Lu, Gd, etc...) [0.01>x>0.4]
A-site Def	0-10%
B dopant	Fe, Nb, Ga, etc.. [0.02>y>0.1]
Firing Temp	1200C-1500C
Firing Steps	1-4
Milling	Water/EtOH, time
Firing Batch	Qty/vessel (g), Crucibles vs. Tray
Gas	Air, different Reducing Gases
Precursors	oxides, carbonates, other salts

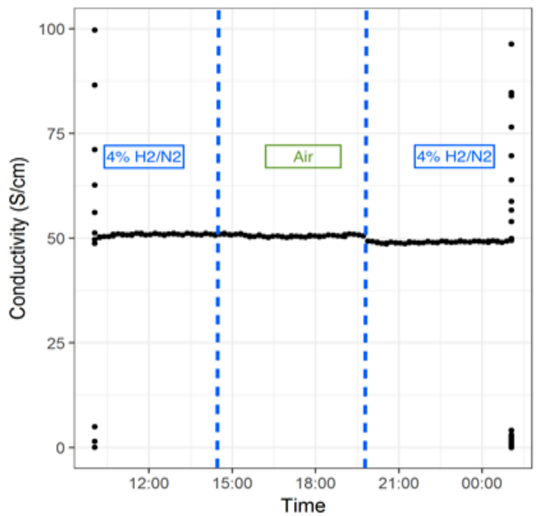
Over 100 tested batches @ GE!
(~10g size)

XRD and Redox S/cm

Identified several Promising leads!

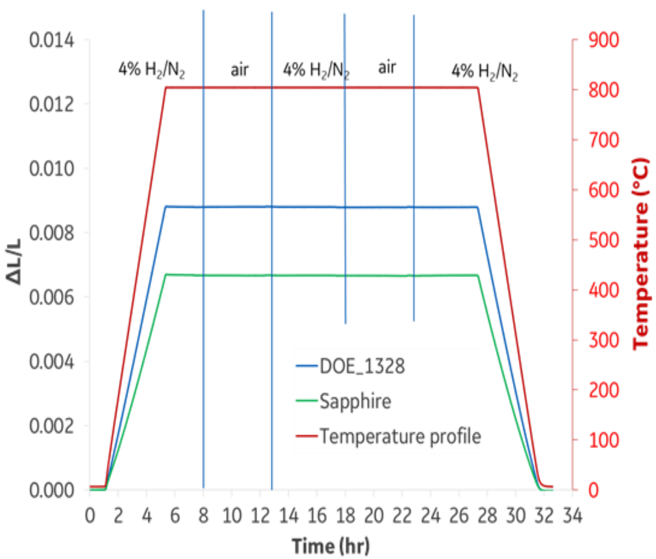
Alternately Doped SrTiO3 – leading candidate





Redox Conductivity:

- -Excellent conductivity
- -Good redox stability

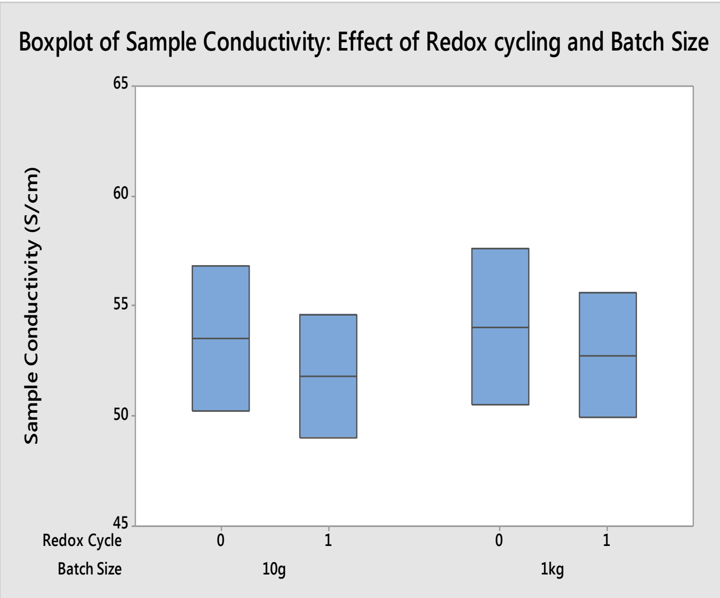


Redox Dilatometry:

- -Excellent mechanical redox properties
- -Material was selected for scale up to larger batch sizes

Scale up of Alternately Doped $SrTiO_3$

Scale Up 1: 10g->1kg std gas env



Scale Up 2: Altered reducing gas environment

Batch	Pressing Cond	Sintering Conds	Initial Cond (S/cm)	PostRedox1 (S/cm)
FC-0202-S1	Std	Std	41.2	38.7
FC-0202-S1	Std	Std	45.2	41.8
FC-0202-S2	Std	Std	52.1	45.5
FC-0202-S3	Std	Std	1.7	0.97
FC-0202-S4	Std	Std	18.1	12
FC-0202-S4	Std	Std	45.9	43.1
FC-0202-S5	Std	Std	55.3	51.4

May: Produced 17kg batch, Thermal Spray in July

1st compound scaled from 10g→ 1000g→17000g!

Factors: tray type, gas environment/flow, mixing & milling methods, precursors , etc..

Goal: Scale up ~2-3 more down-selected candidates by Fall 2017

GE currently has 2 formulations in the beginning stages of Scale Up

WVU & GE
Layered Perovskite
Development

Formulation Development Summary:

GE Global Research:

- -Pivot: added on ceramic synthesis efforts:
  - * Studied doped $SrTiO_3$
  - * Scale up of WVU formulations -> Vendor Transition

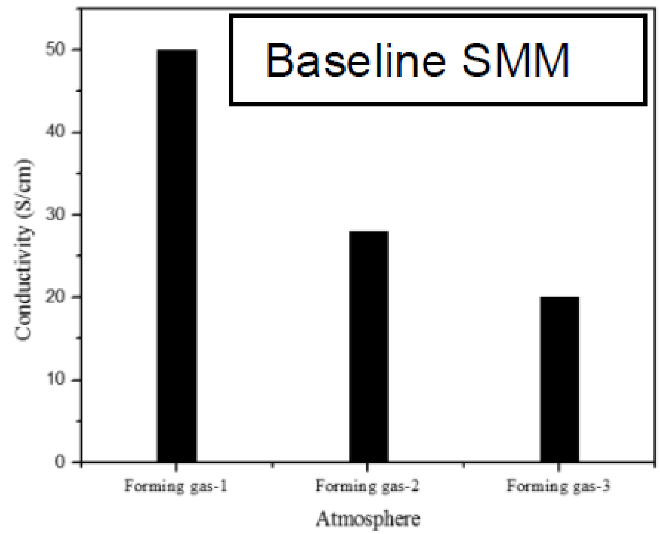
WVU:

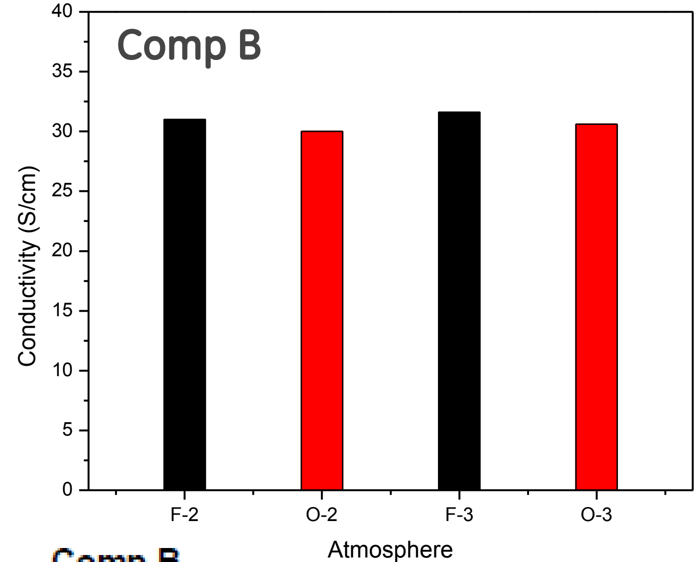
- -Higher Risk formulations:
  - * Scheelites – showed low S/cm or mech instability
  - * Layered perovskites – $SrMoO_3$
    - -Current focus of WVU research.
    - -GE currently trying to scale 2 formulations

Summary of Layered Perovskite Development:

Comp	Cond (S/cm)	Mech Redox (dV)	CTE (ppm/C)	Notes
SrMgMo	50	+	14.78	S/cm reduces with redox cycling
SrFeMo	20-148	--	NA	Poor redox stability
SrFeCoMo	7.4	-	20.39	Higher S/cm in air
SrMgMo (2)	~30	++	15.6	Improved Redox Stability vs baseline SMM
Doped - SrFeMo	15-22	+++	15.01	Mech and S/cm redox stability

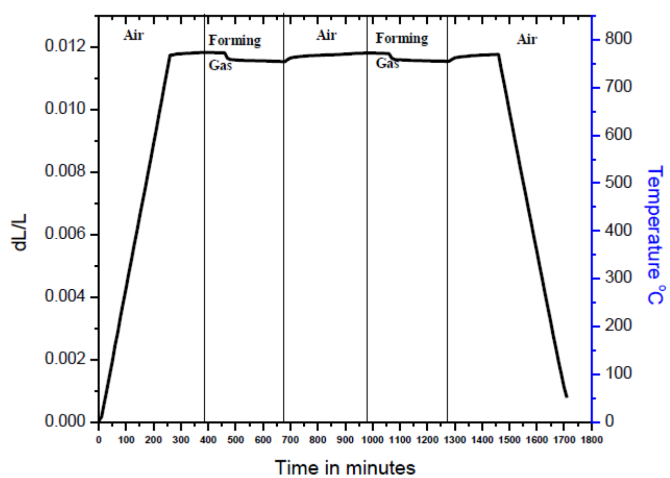
SMM Formulation Variation Study:



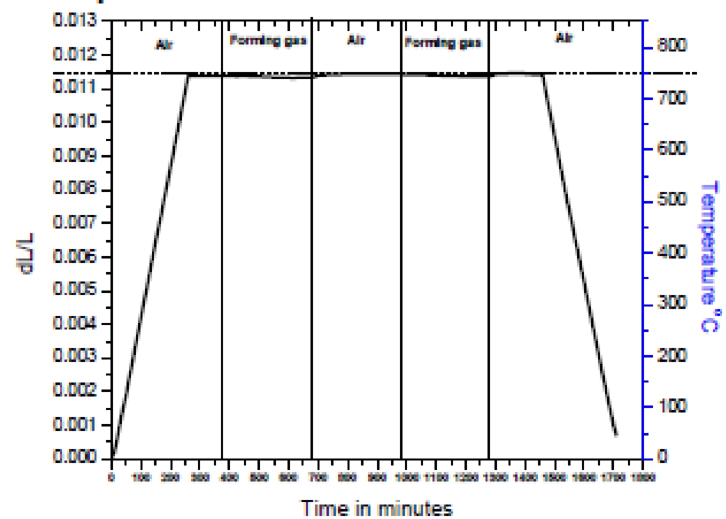


Redox S/cm

Baseline $Sr_2MgMoO_{6-\delta}$



Comp B



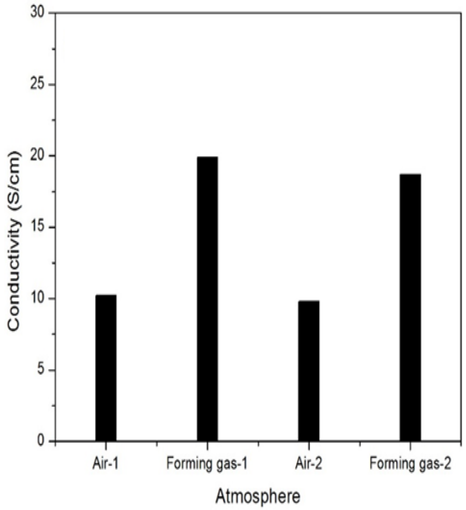
Redox Dil

-Identified higher performing SMM formulations (only 1 variant shown)

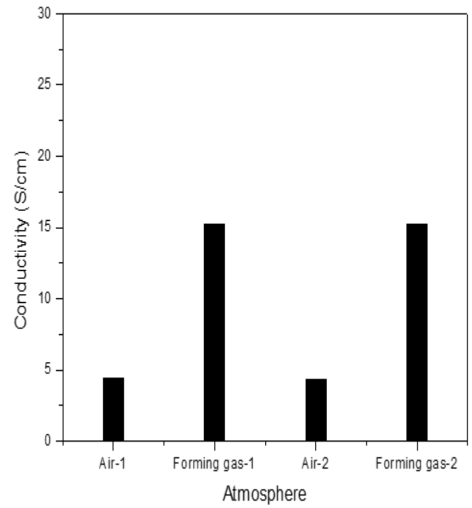
-continuing optimization work & scale up

Redox Dilatometry and Conductivity of SFM vs doped-SFM

Redox S/cm

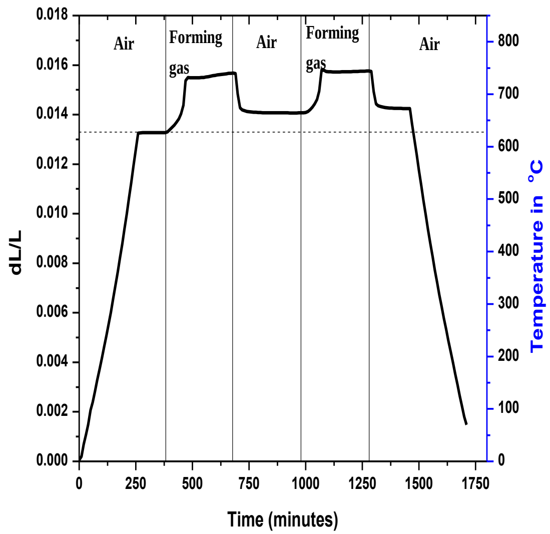


$Sr_2Fe_{1.5}Mo_{0.5}O_{6-\delta}$

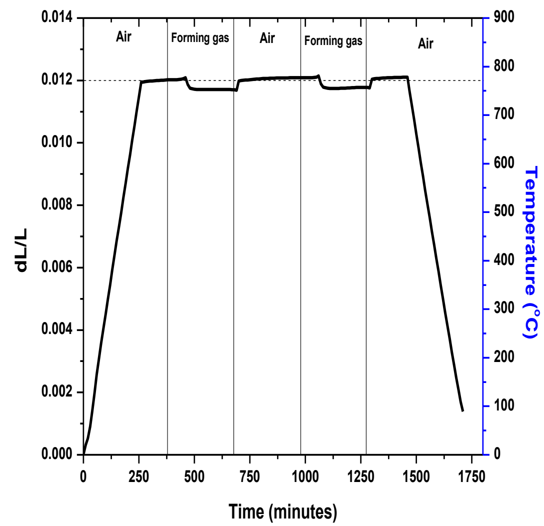


Doped SFM, solid state synthesis

Redox Dil



CTE in Air, 25-800°C = 17.12×10^{-6} K^{-1}



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

Doping Improved redox S/cm stability, Mechanical stability, And lowered CTE

Initial scale up studies underway

Summary

- 100 cm^2 LST-GDC co-spray anodes: achieved redox stability but limited <130 W/cm^2
  - -Reactive phase formation, limited film conductivity (SrTiO3 deactivation)
- GE identified methods to improve film conductivity through process opt
  - -Thermal spray focus shifting to microstructure optimization
- Identified several candidates for scale up: (1) doped $SrTiO_3$ (2) doped SFM
- Goal – scale up 3-4 promising down-selected candidates by Fall

Demonstrate higher power, ceramic anode, metal supported SOFC cells

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Dayna Kinsey, Luc Leblanc, Matt Alinger Todd Striker, Andy Shapiro, Simon Gaunt	GE Fuel Cells, scale up Thermal Spray Systems Support
Mike Vallance	Echem Model
Jae Hyuk Her, Erik Telfeyan, Matt Ravalli	Analytical Support
Johanna Wellington, Steve Duclos, Katharine Dovidenko, Wei Cai	GE Management Support

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