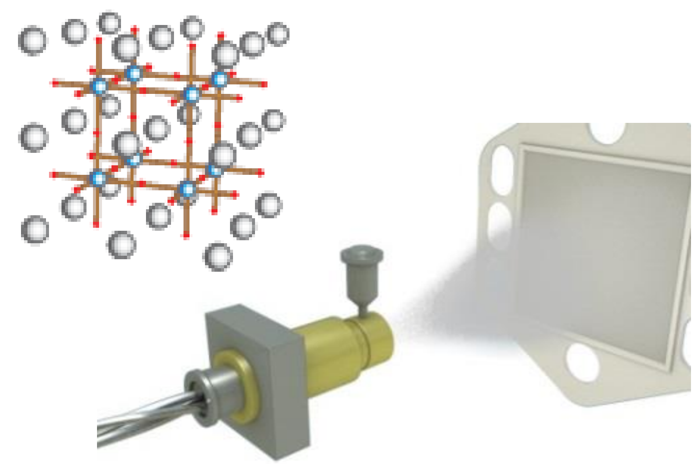


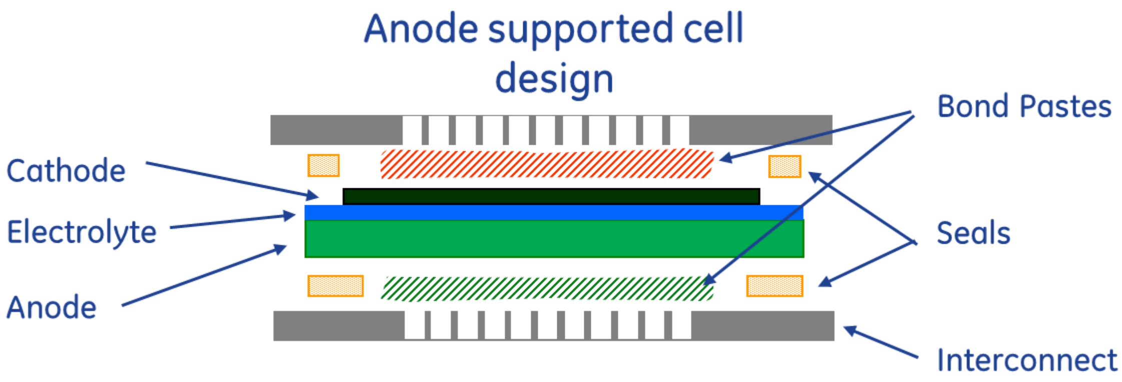
Development of a Thermal Spray, Redox Stable, Ceramic Anode for Metal Supported SOFC

Richard Hart
GE Global Research
Pitt Review July 20, 2016

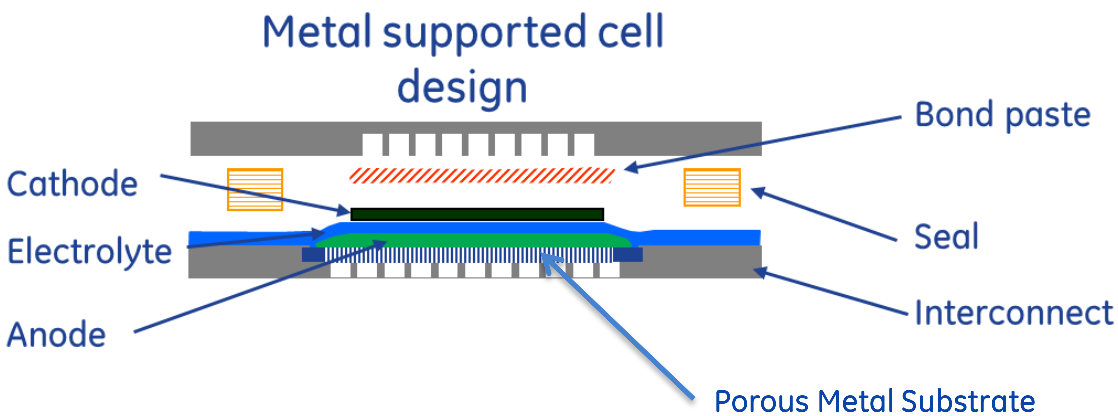
Imagination at work.

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

Metal supported SOFC cells



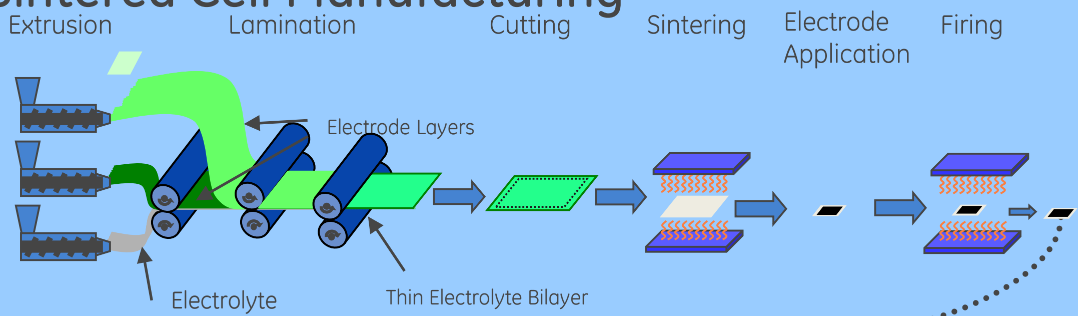
Advantages:
Integrated anode seal
Electrolyte in compression
Improved anode electrical contact
Increased active area
Lower anode polarization

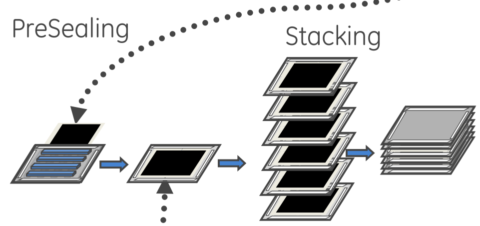


Challenges:
Dense / hermetic electrolyte
Porous metal substrate degradation

Low-cost manufacturing

Sintered Cell Manufacturing





Thermal Spray

Leverage GE thermal spray expertise

Advantages

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

Fuel Cell Pilot Facility – Malta NY

4

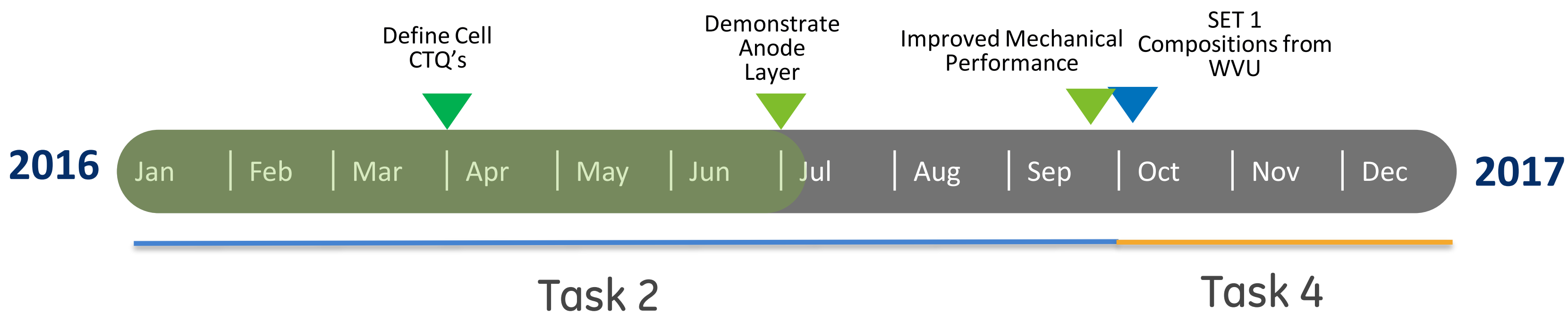
Traditional NiO(Ni)/YSZ anodes

- 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)

Project Plan & Deliverables (~$3.5M, 3 year, 25% cost share)

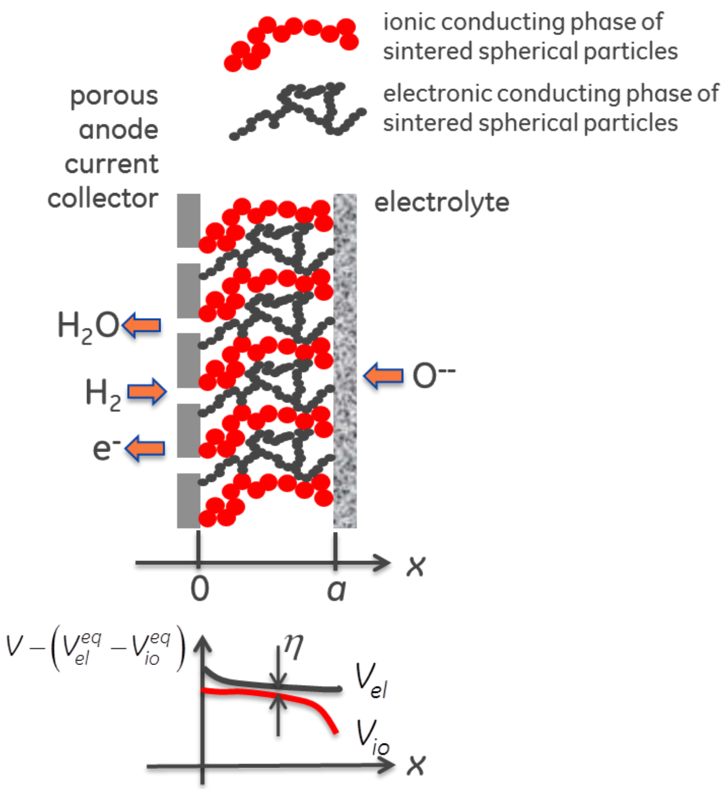
Task	Owner	Timing	Objectives
1	GE Global Research	Months 1-36	• Defined by DOE; risk management, coordination, reporting
2	GE Global Research GE–Fuel Cells	Months 1-12	• Derive anode layer requirements from existing systems models • Tailor Global Research thermal spray process using single baseline composition • Streamline (cost and lead time) powder engineering methods • Establish redox cycle cell test procedures
3	West Virginia University	Months 1-24	• Develop key materials properties measurements • Hand off to GRC SET1 and SET2 Anode Compositions
4	GE Global Research	Months 13-27	• Optimize thermal spray process for improved formulations • Go/No – Does single scaled cell (100-400cm^2) meet CTQs?
5	GE Global Research GE–Fuel Cells	Months 28-36	• Powder scale up, cell fabrication scale up. • Build and test, 5 kW SOFC stack for 1000 hr, Nat Gas/Sim Nat Gas fuel.



Define cell specifications for Go/No Go decision point (27months)	[March 31]
Demonstrate a working all ceramic anode layer (OCV on a cell)	[June 31]
Demonstrate improvement mechanical perf. (no failure @ 1 cycle)	[Sept 30]
Deliver SET 1 compositions (WVU-> GE)	[Oct 1]

Electrochemical Model

Electrochemical Model

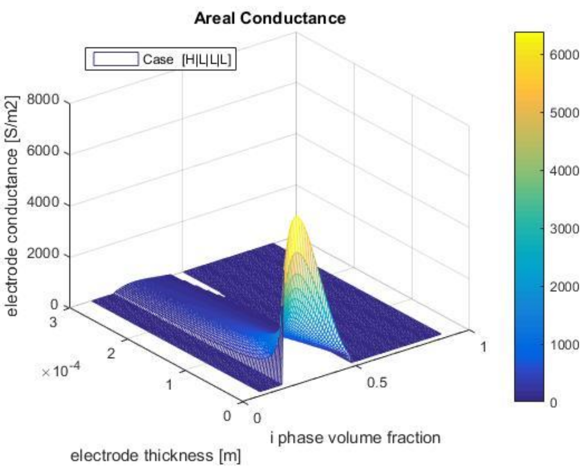


For our system:
Red = $Gd_{0.2}Ce_{0.8}O_{1.9}$
Black = $La_{0.35}Sr_{0.65}TiO_3$

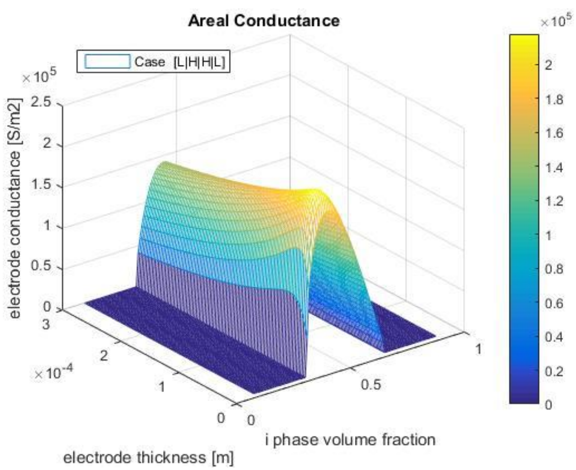
- Adapted simple Literature Model (Costamagna)
- Initial programming complete (Matlab)
- Completed 6 factor DOE exploring:
  - Electrode thickness
  - Particle size & ratio of particle sizes
  - Volume fraction of phases
  - Effective electron conductivity
  - Effective ion conductivity
- WVU performing screen printed electrode study for model validation/calibration (kinetics)

Mike Vallance, Badri R.

Electrochemical Model - Example DOE Results



Quadrant 3: $P = 2$ and $\sigma_{0el} = 20$ S/m

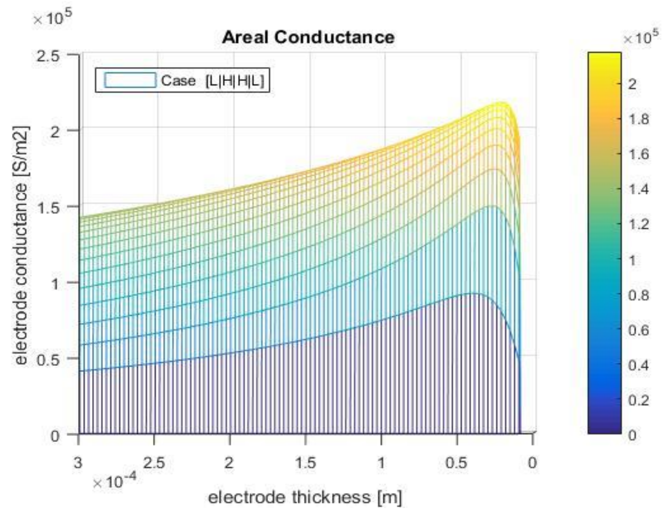


Quadrant 2: $P = 1$ and $\sigma_{0el} = 2000$ S/m

-Wide range of electrode area conductance (1/ASR)

-Model results match qualitative expectations

-Identified regions of performance near GE goals



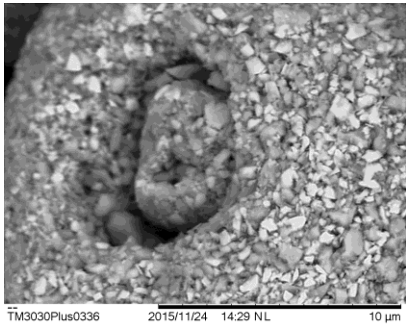
-Exchange current density for reactions largely unknown for these systems. Goal of WVU study.

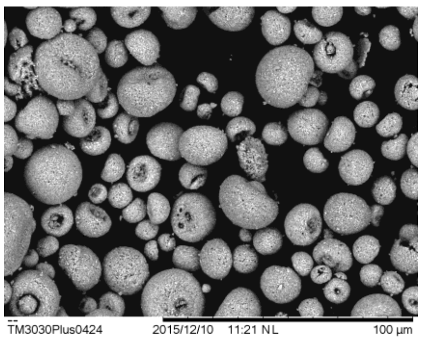
-Used model to aid material spec. definition

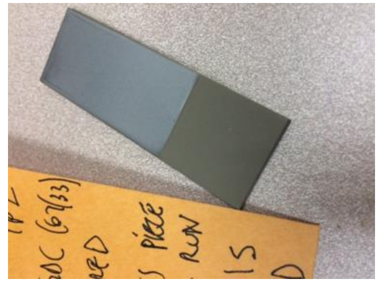
Mike Vallance, Badri R.

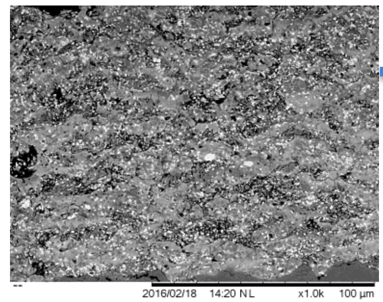
Cell Testing Results

Demonstrating Ceramic Anode Metal Supported Cells:









Sourced
Engineered Powders

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

GDC ($Gd_{0.2}Ce_{0.8}O_{\sim 1.9}$)

Coupon Screening
Experiments

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

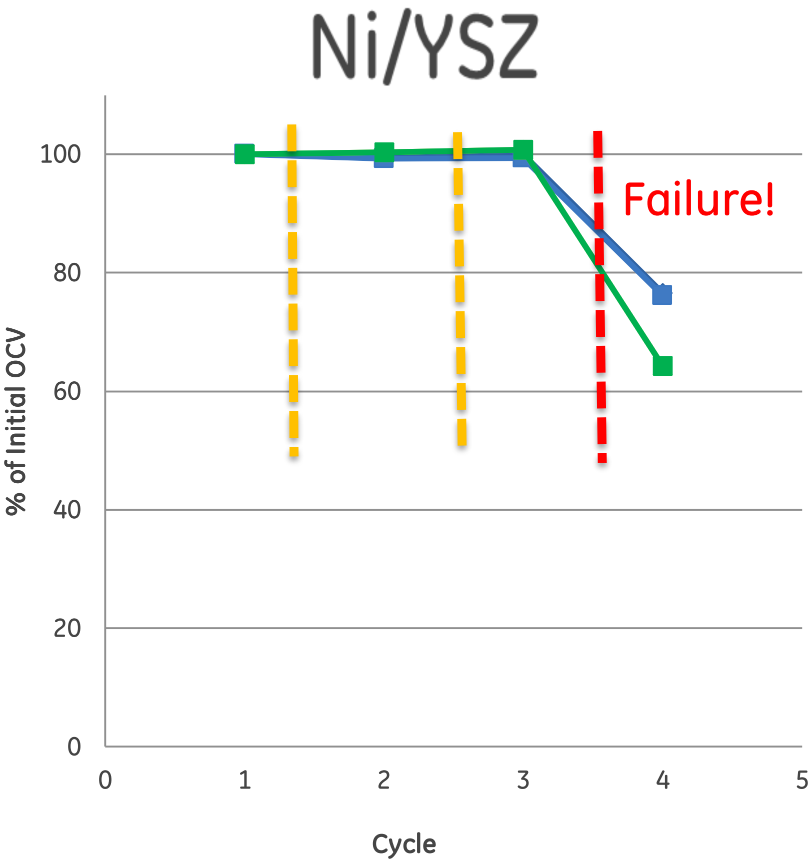
$100cm^2$ Cells

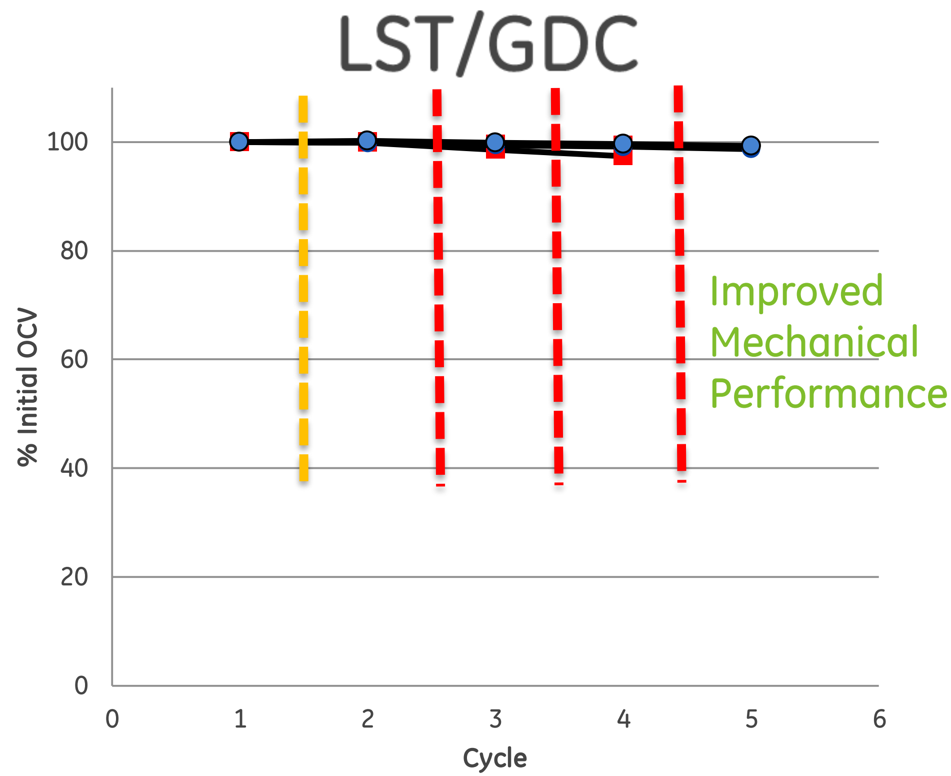
(2 cell stacks)

OCV, W/cm2
Redox Stability

Hart, Rosenzweig, Thomas, Northey, Bancheri, Leblanc

Stack Redox Cycling – Ni/YSZ vs. Alt Anode Stacks





Orange = Standard Thermal Cycle w/ H_2 Flow (we did two of these, to check cell health)

Red = Redox Thermal Cycle (no protective flow)

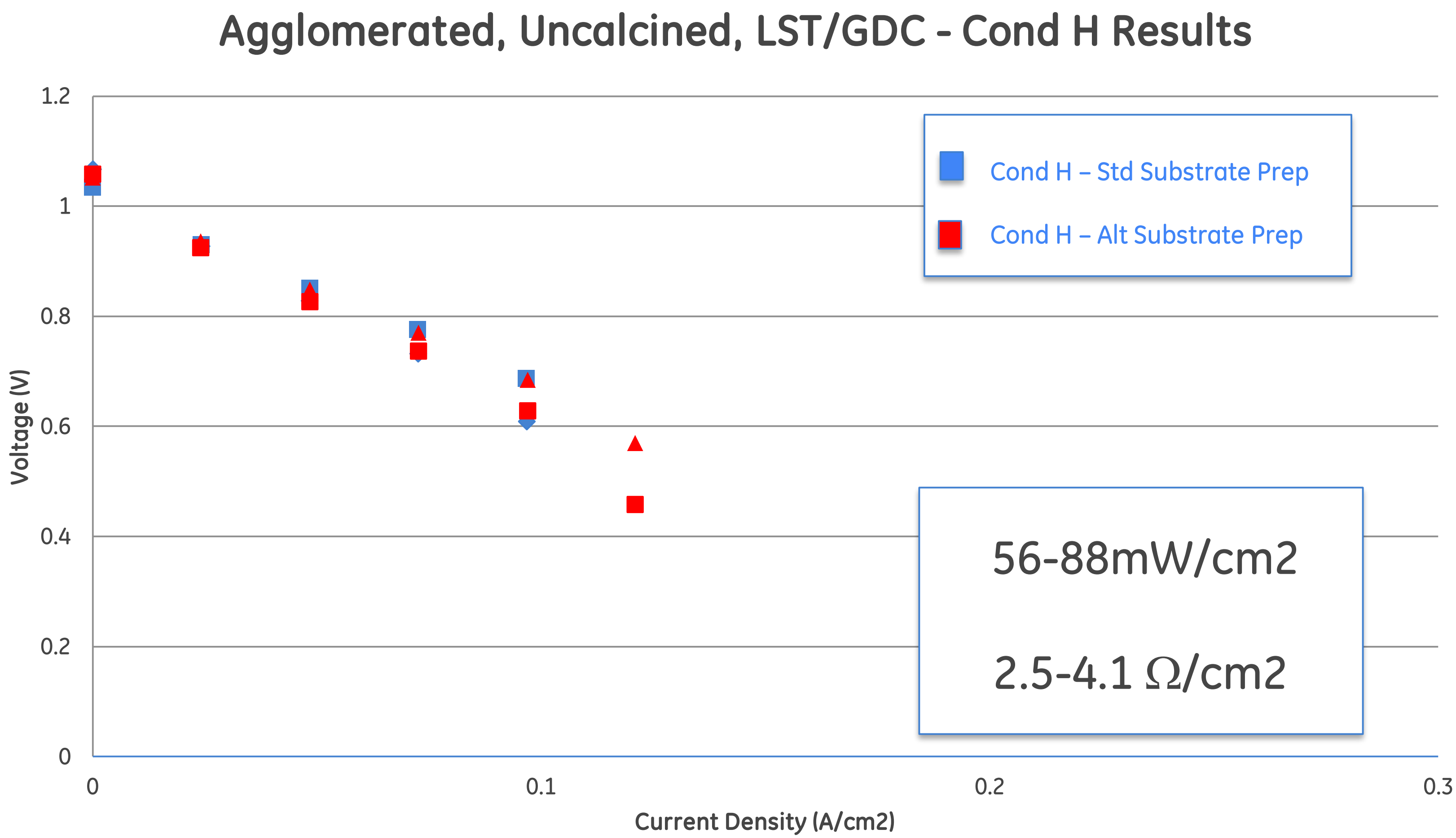
Ni/YSZ cells fail after a single redox cycle

Ceramic anode cells survive up to 5 cycles

Confirmation of damage mechanism! (similar to mechanism previously reported for sintered Cells)

Hart, Renko, Northey

LST/GDC Anodes– Power curves (low Uf)

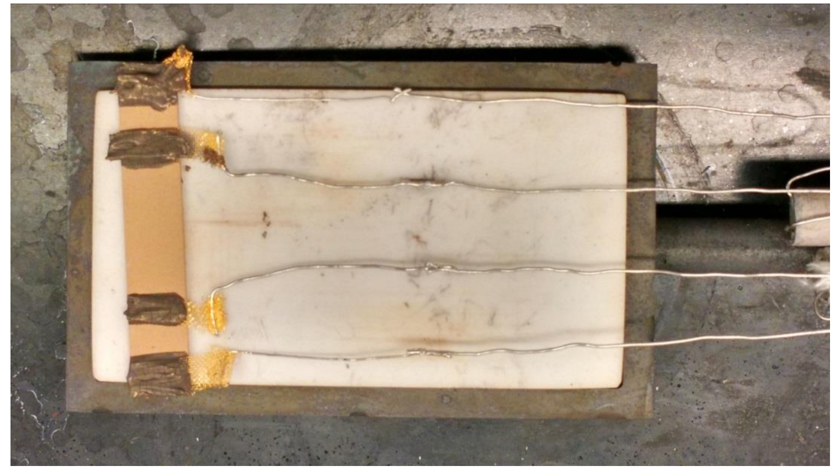


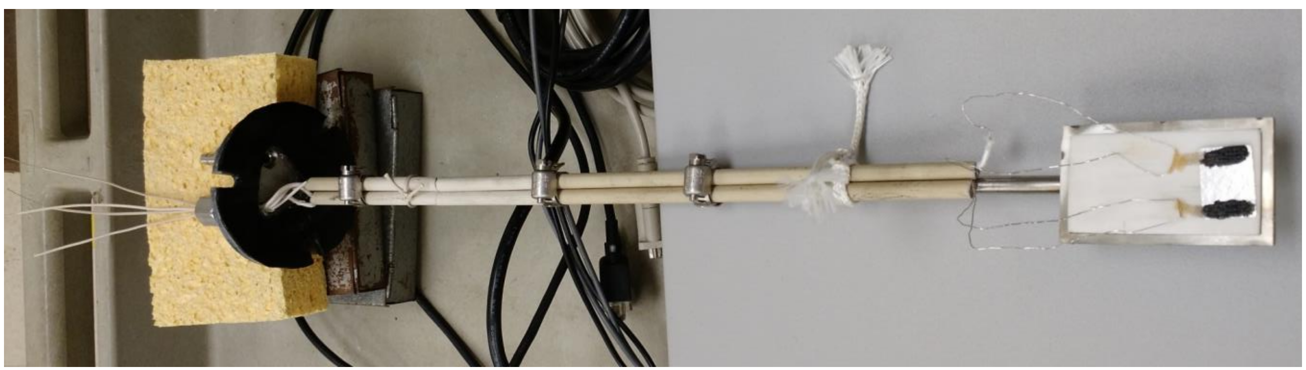
Demonstrated working ceramic anode cells (June 31 + Sept 30 Milestones)

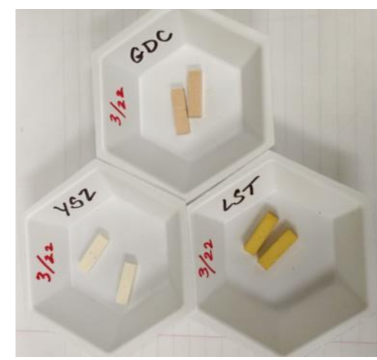
Next step: improve upon extreme low power density! (improve microstructure & test new formulations)

Material Conductivity Testing Results

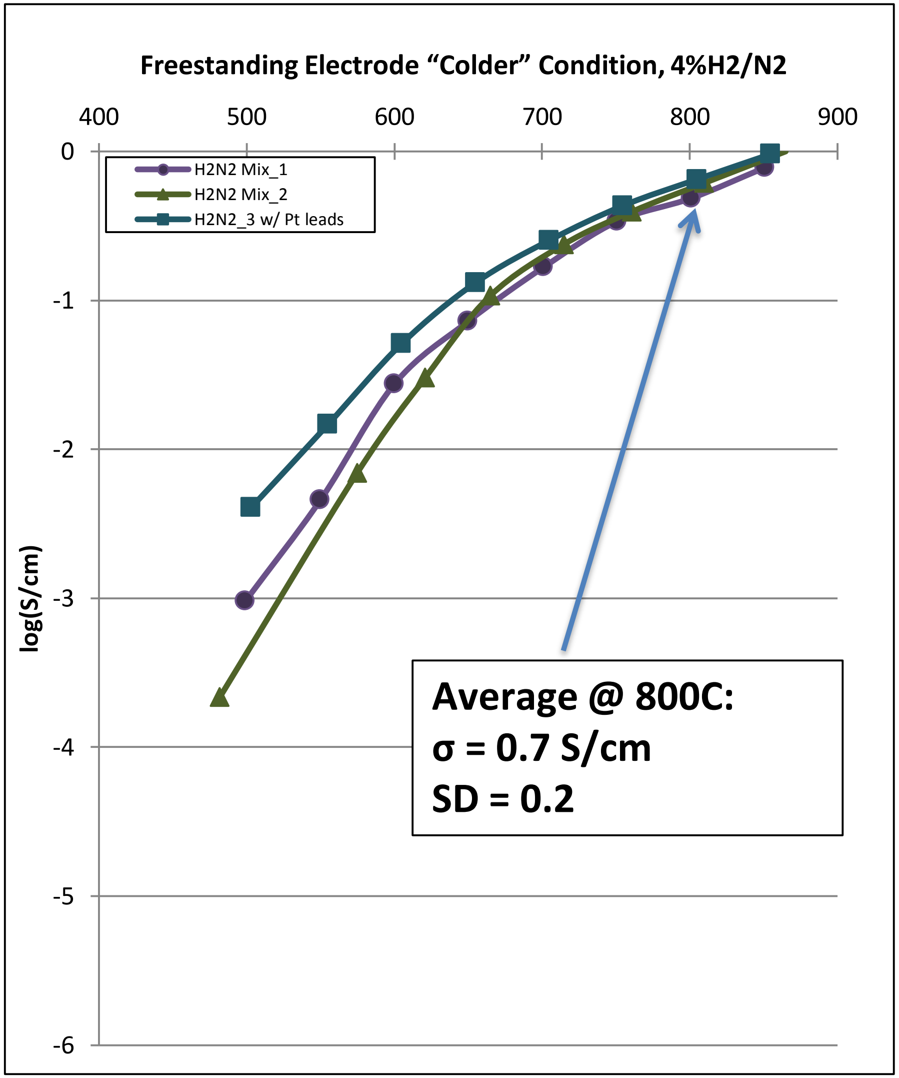
Conductivity Test Setup (GE-GRC)

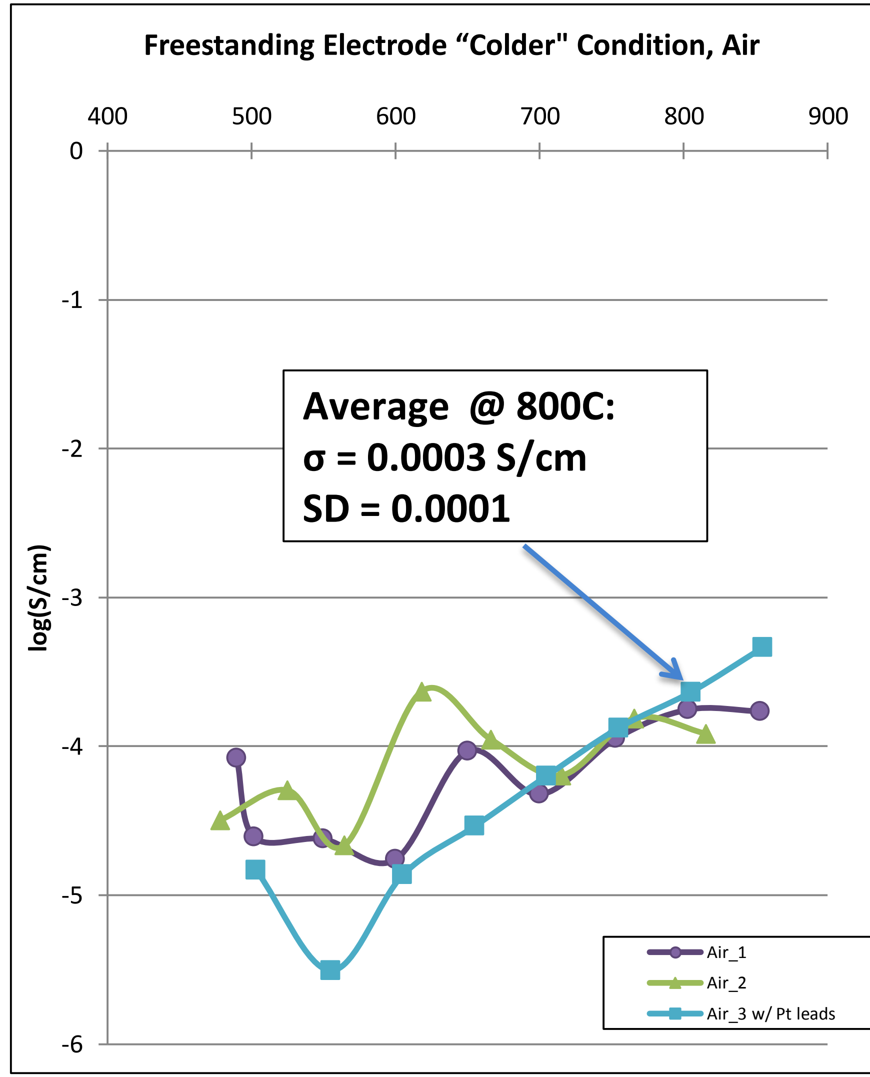






Conductivity Results – Replicate Measurements
Free Standing LST/GDC thermal spray films



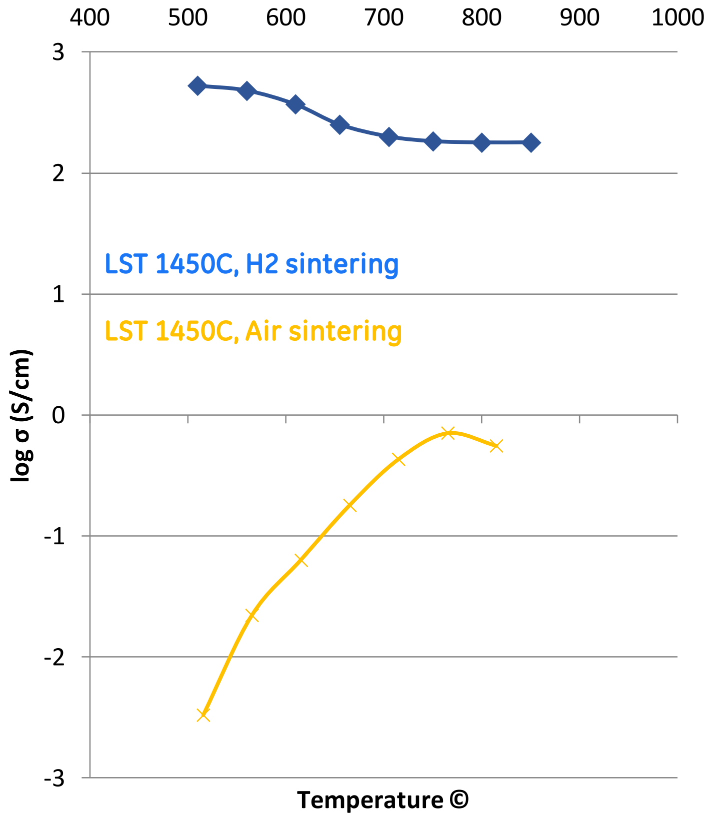


Solatron 1287/1260, 4pt, AC impedance, ~1kHz

Jezek, Hart

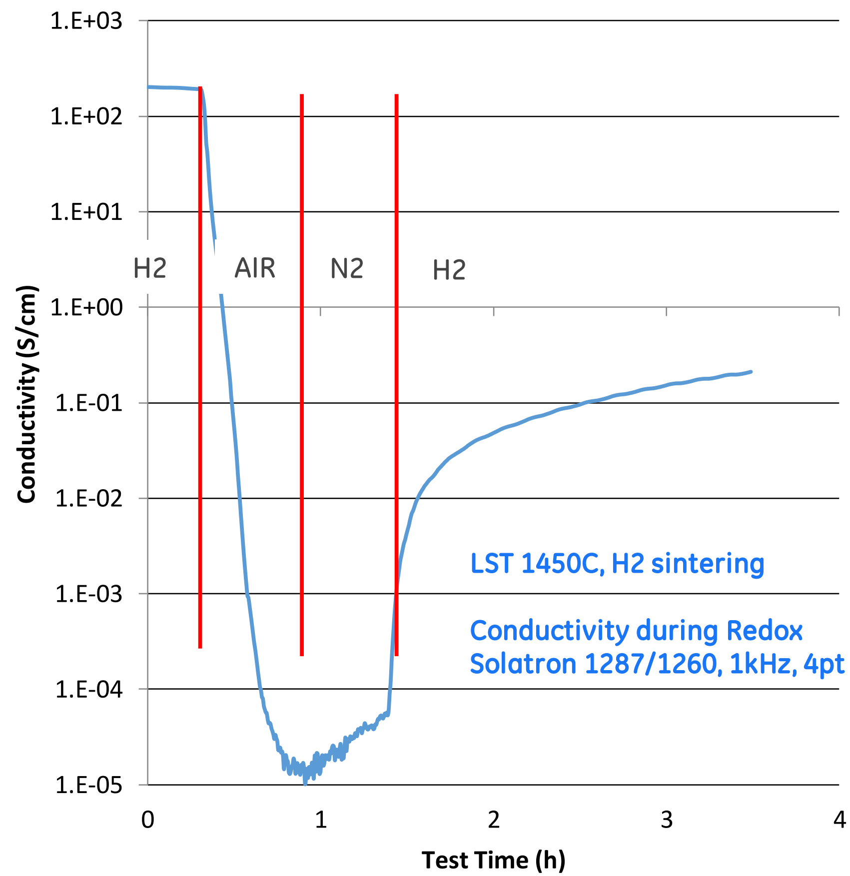
LST Conductivity – Effect of Sintering Atm, and Redox:

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

WVU & GE
Anode Material Development

Material Development Testing Plan

Conductivity Testing

- Screen w/ pressed pellets or free-standing films
- Electron Conductivity > 20S/cm (~30x improvement)
- Ion Conductivity > $1x10^{-2}$ S/cm (~100x improvement)

Mechanical Stability During Redox Cycling (800C)

- Redox Vol. Change target still in progress (Mech E) < GDC soft target
- Measuring vol change w/ redox dilatometry (good baseline)

SOFC Cell Testing

- WVU using 1" button testing
- GRC using 100cm2 metal supported cells (2-6 cell stacks)

Formulation Development Plan:

GE Global Research:

- -Pivot: added on ceramic synthesis efforts
  - -GE Targeting lower risk/reward candidates
- -Pivot: Testing GE lab scale spray dry (schedule risk abatement)

WVU:

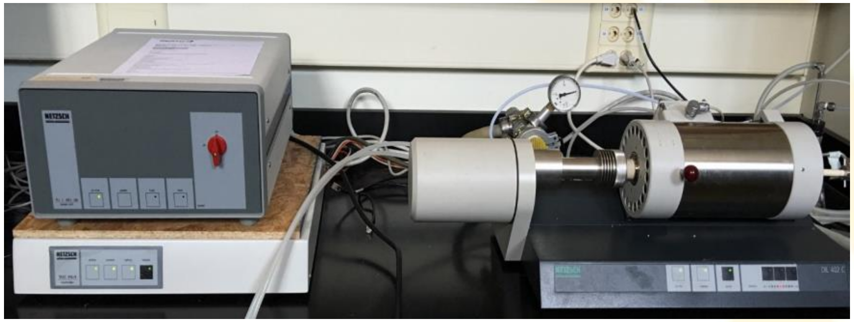
- -Starting from WVU's previous Anode Composition work
- -Developed Redox Dilatometry methods
- -Using 1" SOFC test bed: model validation & comp screening

Goal: thermal spray 1st new ceramic formulation by Oct 1

Lit Overview Alternative Ceramic Anodes

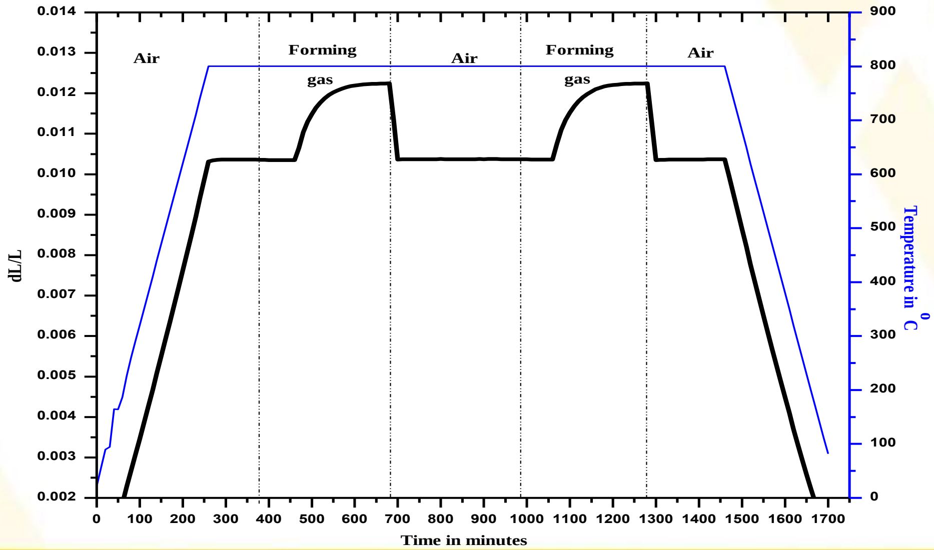
Structure	Performance Attributes	Examples	Research Level Required (RLR)
Perovskite	Good/excellent e- or hole-conductor, low catalysis of HCs	LST, YST, LSCM	Low
Layered-Perovskite	Good e- conductor (very slight ionic), some catalysis of HCs	Sr_2MgMoO_{6-x}	Low
Fluorite	Ionic conductor (very slight electronic), low/high catalysis	doped-CeO_2	High
Pyrochlore	Low e- conductor, some catalysis of HCs, high redox stability	doped-$Gd_2Ti_2O_7$	High
Ruddlesden-Popper	Low e- conductor, high redox stability (for Ti or Nb-oxides)	$(Sr,La)_3(Mg,Nb)_2O_7$	High
Tungsten-Bronzes	Good/low e- conductor, redox stable, chemical stability issues	$Sr_{0.2}Ba_{0.4}Ti_{0.2}Nb_{0.8}O_3$	High

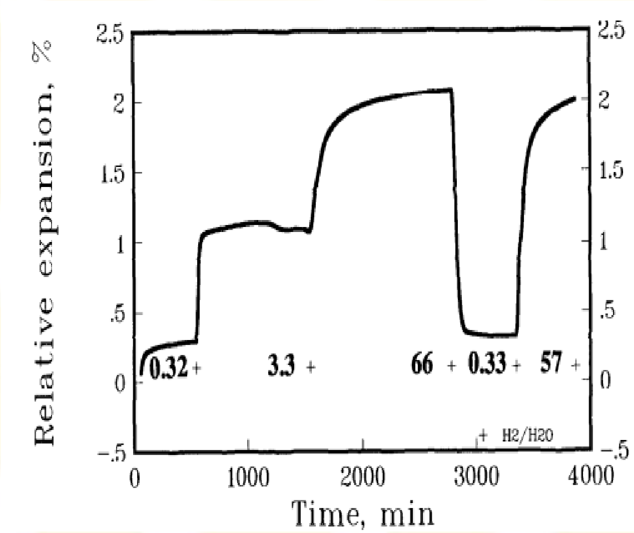
Redox Dilatometry



NETZSCH dilatometry setup in WVU for thermomechanical analysis

- Change in protocol was necessary (longer dwell times)
- Redox behavior for GDC now matches lit data shapes:



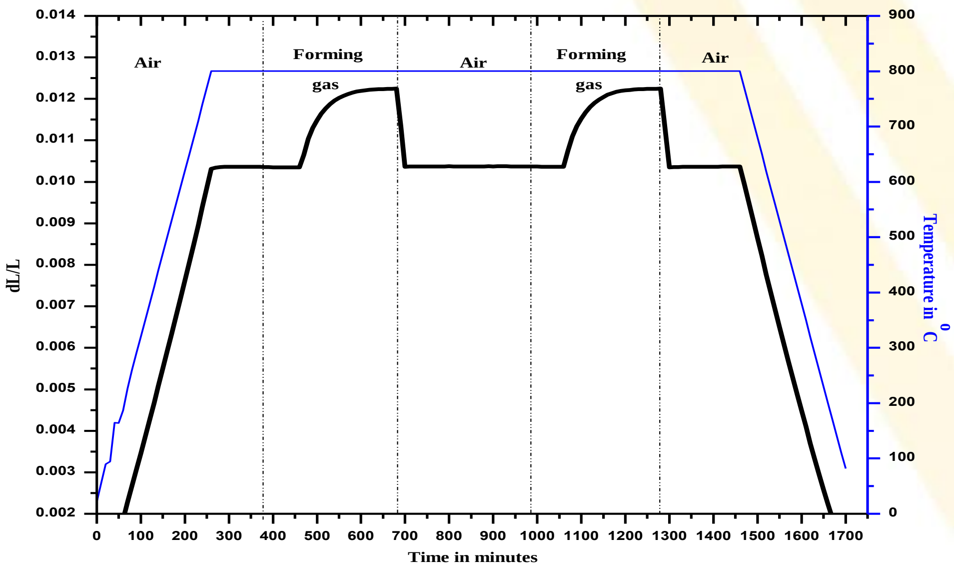


CTE in Air between 25-800°C is ~13.23x10^{-6}
~0.2% volume changes due to redox

G Mogensen, M. MogensenlThermochlm Acta 214 (1993) 47-50

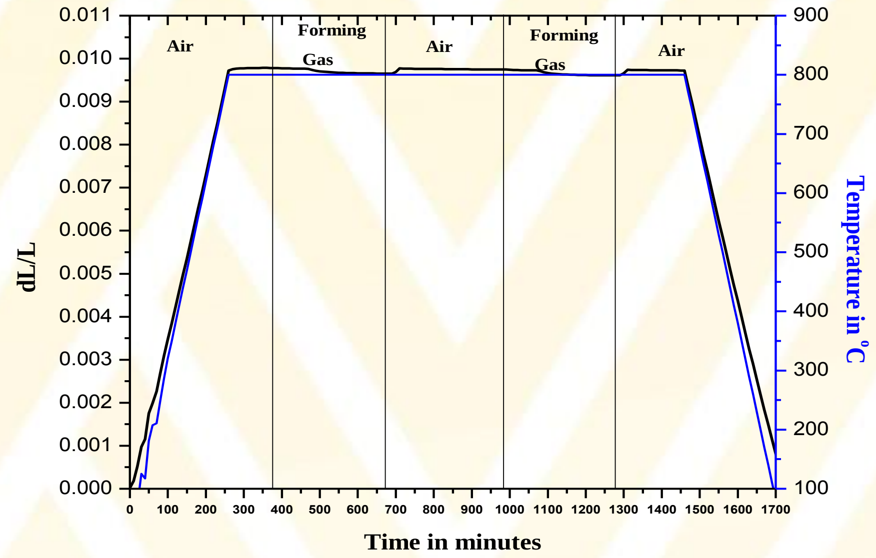
Sabolsky, Zondlo, Liu, Thomas, Qi

Redox Dilatometry (LST and GDC)



GDC (GRC Supplied)

CTE in Air between 25-800°C is ~13.23x10^{-6}
~0.2% volume changes due to redox



LST (GRC Supplied)

CTE in Air between 25-800°C is 12.51x10^{-6}
~0.02% volume changes due to redox?

Summary

- Demonstrated working ceramic anode cells
  - Improved mechanical performance vs. NiO/YSZ anodes
  - Very low power density (formulation + microstructure)
- Redox conductivity tests identified insufficient materials properties for baseline composition (LST)
  - Short term microstructure optimization delayed temporarily
- Formulation development in progress and additional resources at GE added to help accelerate

GE Team:

Rich Hart	PI, testing & direction
Larry Rosenzweig, Bastiann Korevaar, Paul Thomas	Thermal Spray GRC
Stephen Bancheri, Susan Corah	Powder development
Erik Jezek, Becky Northey	Materials testing, microstructure & degradation
Dayna Kinsey, Luc Leblanc, Matt Alinger Todd Striker, Andy Shapiro	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, Vanita Mani	GE Management Support

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West Virginia University

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- GE Global Research Team
- WVU (Dr. Sabolsky, Dr. Liu, Dr. Zondlo, & team)
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