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

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GE Global Research
Pitt Review    July 20, 2016

Imagination at work.

SOFI 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

Electrode Layers

Thin Electrolyte Bilayer

Electrolyte

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

Thermal Spray

Leverage GE thermal spray expertise
Fuel Cell Pilot Facility – Malta NY
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~~)

<table>
<thead>
<tr>
<th>Task</th>
<th>Owner</th>
<th>Timing</th>
<th>Objectives</th>
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<tbody>
<tr>
<td>1</td>
<td>GE Global Research</td>
<td>Months 1-36</td>
<td>• Defined by DOE; risk management, coordination, reporting</td>
</tr>
</tbody>
</table>
| 2    | GE Global Research | Months 1-12 | GE–Fuel Cells  
* 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 (100-400cm²) meet CTQs? |
| 5    | GE Global Research | Months 28-36 | GE–Fuel Cells  
* Powder scale up, cell fabrication scale up.  
* Build and test, 5 kW SOFC stack for 1000 hr, Nat Gas/Sim Nat Gas fuel. |

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**2016**

- **Jan**: Define Cell CTQ's
- **Mar**: Demonstrate Anode Layer
- **Jun**: Improved Mechanical Performance
- **Oct**: SET 1 Compositions from WVU

**2017**

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

- 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)

For our system:
Red = Gd$_{0.2}$Ce$_{0.8}$O$_{1.9}$
Black = La$_{0.35}$Sr$_{0.65}$TiO$_3$
Example DOE Results

- Wide range of electrode area conductance (1/ASR)
- Model results match qualitative expectations
- Identified regions of performance near GE goals

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

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

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

- Used model to aid material spec. definition
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$_{~1.9}$)

Coupon Screening Experiments

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

100cm$^2$ Cells

(2 cell stacks)

OCV, W/cm$^2$

Redox Stability

Hart, Rosenzweig, Thomas, Northey, Bancheri, Leblanc
Stack Redox Cycling – Ni/YSZ vs. Alt Anode Stacks

Ni/YSZ

Orange = Standard Thermal Cycle w/ H2 Flow (we did two of these, to check cell health)
Red = Redox Thermal Cycle (no protective flow)

Failure!

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)

Agglomerated, Uncalcined, LST/GDC - Cond H Results

- Cond H – Std Substrate Prep
- Cond H – Alt Substrate Prep

- 56-88mW/cm²
- 2.5-4.1 Ω/cm²

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

Freestanding Electrode “Colder” Condition, 4%H2/N2

Average @ 800°C:
\[ \sigma = 0.7 \text{ S/cm} \]
SD = 0.2

Freestanding Electrode “Colder” Condition, Air

Average @ 800°C:
\[ \sigma = 0.0003 \text{ S/cm} \]
SD = 0.0001

Solatron 1287/1260, 4pt, AC impedance, ~1kHz
LST Conductivity – Effect of Sintering Atm, and Redox:

LST – 1450C sintered, effect of atm:

LST 1450C, H2 sintering
LST 1450C, Air sintering

LST Pellet Conductivity – Redox Cycling

H2, AIR, N2, H2

Conductivity during Redox
Solatron 1287/1260, 1kHz, 4pt

E-chem Model -> need to identify materials w/ >10-20S/cm after redox
WVU & GE Anode Material Development
Material Development Testing Plan

Conductivity Testing

• Screen with 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

<table>
<thead>
<tr>
<th>Structure</th>
<th>Performance Attributes</th>
<th>Examples</th>
<th>Research Level Required (RLR)</th>
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<tbody>
<tr>
<td>Perovskite</td>
<td>Good/excellent e- or hole-conductor, low catalysis of HCs</td>
<td>LST, YST, LSCM</td>
<td>Low</td>
</tr>
<tr>
<td>Layered-Perovskite</td>
<td>Good e- conductor (very slight ionic), some catalysis of HCs</td>
<td>Sr$<em>2$MgMoO$</em>{6-x}$</td>
<td>Low</td>
</tr>
<tr>
<td>Fluorite</td>
<td>Ionic conductor (very slight electronic), low/high catalysis</td>
<td>doped-CeO$_2$</td>
<td>High</td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>Low e- conductor, some catalysis of HCs, high redox stability</td>
<td>doped-Gd$_2$Ti$_2$O$_7$</td>
<td>High</td>
</tr>
<tr>
<td>Ruddlesden-Popper</td>
<td>Low e- conductor, high redox stability (for Ti or Nb-oxides)</td>
<td>(Sr,La)$_3$(Mg,Nb)$_2$O$_7$</td>
<td>High</td>
</tr>
<tr>
<td>Tungsten-Bronzes</td>
<td>Good/low e- conductor, redox stable, chemical stability issues</td>
<td>Sr$<em>{0.2}$Ba$</em>{0.4}$Ti$<em>{0.2}$Nb$</em>{0.8}$O$_3$</td>
<td>High</td>
</tr>
</tbody>
</table>
Redox Dilatometry

- 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 \(~13.23\times10^{-6}\)

\(~0.2\%\) volume changes due to redox

G Mogensen, M. Mogensen|Thermochim Acta 214 (1993) 47-50
Redox Dilatometry (LST and GDC)

GDC (GRC Supplied)

CTE in Air between 25-800°C is $\sim 13.23 \times 10^{-6}$

$\sim 0.2\%$ volume changes due to redox

LST (GRC Supplied)

CTE in Air between 25-800°C is $12.51 \times 10^{-6}$

$\sim 0.02\%$ 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
GE Fuel Cells, scale up Thermal Spray Systems Support

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