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

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GE Global Research
Pitt Review     June 12, 2017

Imagination at work.  SOFC Innovative Concepts and Core Technology Research
DE-FOA-0001229    Award FE0026169
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

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/cm$^2$ on Reformate Fuel ($>50\%$Uf, 0.7V)
- $<10\%$ Degradation after 1000h (or $>180$mW/cm$^2$)
- $>3$ Redox Cycles
- ~Equivalent Materials Cost and Process vs. Baseline
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 ($Gd_{0.2}Ce_{0.8}O_{1.9}$)

Coupon Screening Experiments (Thermal Spray)

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

100cm² 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-)

Failure!

Stable!
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

“Hotter”
“Cooler”

Porosity
TPB - m²/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, Vendor B

- 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*
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 > 0.5x10^{-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)
LST Conductivity – Effect of Sintering Atm, and Redox:

LST – 1450C sintered, effect of atm:

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

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
## Summary of doped Strontium Titanate Screening - GE

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

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 SrTiO3

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

Scale Up 2: Altered reducing gas environment

Boxplot of Sample Conductivity: Effect of Redox cycling and Batch Size

<table>
<thead>
<tr>
<th>Batch</th>
<th>Pressing Cond</th>
<th>Sintering Cond</th>
<th>Initial Cond (S/cm)</th>
<th>PostRedox1 (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC-0202-S1</td>
<td>Std</td>
<td>Std</td>
<td>41.2</td>
<td>38.7</td>
</tr>
<tr>
<td>FC-0202-S1</td>
<td>Std</td>
<td>Std</td>
<td>45.2</td>
<td>41.8</td>
</tr>
<tr>
<td>FC-0202-S2</td>
<td>Std</td>
<td>Std</td>
<td>52.1</td>
<td>45.5</td>
</tr>
<tr>
<td>FC-0202-S3</td>
<td>Std</td>
<td>Std</td>
<td>1.7</td>
<td>0.97</td>
</tr>
<tr>
<td>FC-0202-S4</td>
<td>Std</td>
<td>Std</td>
<td>18.1</td>
<td>12</td>
</tr>
<tr>
<td>FC-0202-S4</td>
<td>Std</td>
<td>Std</td>
<td>45.9</td>
<td>43.1</td>
</tr>
<tr>
<td>FC-0202-S5</td>
<td>Std</td>
<td>Std</td>
<td>55.3</td>
<td>51.4</td>
</tr>
</tbody>
</table>

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:

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

- Identified higher performing SMM formulations (only 1 variant shown)
- continuing optimization work & scale up

Baseline SMM

Baseline Sr₂MgMoO₆-δ

Comp B

Redox S/cm

Redox Dil
Redox Dilatometry and Conductivity of SFM vs doped-SFM

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

Initial scale up studies underway

CTE in Air, 25-800°C = 17.12x10⁻⁶ K⁻¹

CTE in Air, 25-800°C = 15.31x10⁻⁶ K⁻¹
Summary

- 100 cm² LST-GDC co-spray anodes: achieved redox stability but limited <130 W/cm²
  - 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 SrTiO₃ (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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