NETL Office of Research & Development

Solid Oxide Fuel Cell Team

Kirk Gerdes
Lead Engineer – Thermal Sciences Division
Research Group Leader – Fuel Cells
Outline

• NETL ORD research in context of SECA program
• Domain of expertise; Broad overview / approach
• Developments
  – Interfacial cation diffusion
  – Electrocatalysts to mitigate degradation
• Applications / Impacts
  – Cathode infiltration
• FY16 Research Portfolio / Conclusions
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Techno-Economic Analysis

Exhibit ES-12 Comparison of IGFC COE (without CO₂ T&S)

IGFC Case

COE (excl. T&S) (2011$/(MWh))

Atmospheric SOFC

Pressurized SOFC

Atmospheric SOFC

Pressurized SOFC

Capital Charges

Fixed O&M

Variable O&M

Fuel

20 percent reduction in COE (Reference IGCC with CCS)

NETL ORD domain of interest today & tomorrow

Baseline SOFC Parameters

Overpotential (mV) 140
Degrad. (%/1000 h) 1.5
Inverter Effy. (%) 97
Stack Cost ($/kW) 225
CF (%) 80

Dry Syn Gas CH₄ -10.0%

Stack Cost $200/kW

98% Inverter Effy. 90% CF

Pressurized (Case 1-5 Basis)

98% Inverter Effy. 90% CF

Pressurized (Case 1-5 Basis)

98% Inverter Effy. 90% CF

Catalytic Gasifier Baseline

Catalytic Gasifier

Conventional Gasifier

Enhanced Conventional Gasifier

Source: NETL

Enhance Fuel Cell Performance for the Fossil Energy Fuel Cell Program

- NETL ORD Fuel Cell Team supports SECA program
  - **Reduce** cell production / operation costs
  - **Enhance** cell activity / efficiency
  - **Improve** cell lifetime (40+ khr)

- Major research tasks
  - **Cell performance and degradation**
    - Complete 3D multi-physics informed with actual electrode microstructures
    - Evolution of grains and appearance of secondary phases
  - **Electrode engineering**
    - Cathode infiltration
      - Efficient oxygen reduction
    - Anode infiltration
      - Enhanced fuel reforming
Program requests → ORD deliverables

**Pre-FY16**
1) LSM + LSCF ORR
2) Nano-CT (AEC)
3) 3D multi-physics
4) Phase-field model
5) Cathode infiltration
6) Anode infiltration
7) ECR + Ionic Cond + Aging + UQ

**FY16**
1) Infiltrate ORR
2) Structural analysis
3) On-cell CH4
4) PF + ab initio
5) CI for H2O + CO2
6) AI commercial
7) ECR + Ionic Cond + Aging + UQ

**Post-FY16**
1) Scale-bridging
2) In-situ methods
3) MP Cell → System
4) PF Atoms → Cells
5) 2nd Gen CI, AI
6) Fundamental examinations
7) UQ

**SOFC Hurricane Model Components**

**Application**
1) ORR tool deployed to high power computing env
2) Impedance tool and diagnostic methodologies
3) Cathode infiltration @ TRL 6

1) Microstructural evolution tool deployed to SBEUC
2) Structural analysis tools on SBEUC + visualization
3) Anode infiltration @ TRL 5

1) Integrated tool coupling domains (atoms to systems)
2) Complete physics and structural visualization tools
3) CI, AI Gen 2 @ TRL 6

Lifetime operational performance tool, variable materials, structure, operating conditions → 40 khr performance analysis and predictions

**Impact**
- Cathode infiltration adopted by industry, 5% improved power density, 30% improved lifetime
- Anode infiltration adopted by industry.
- Impedance tools accel diagnostics. Vis tool accessed by more than 100 users.
- NETL FC Team: Decr system cost 10%
  - Improve power 30%
  - Increase lifetime 50%
  - Accel innovation

**Lower cost of electricity**
**Improved durability**
**Accelerate innovation**
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Interfacial Cation Diffusion

Modeled and experimentally validated descriptions of interfacial cation diffusion via Phase Field Model

Model system describes cation diffusion across YSZ/LSM interface at 1000°C held for 1000 hours

**Original model:**
Cation Chemical Diffusion only

**Updated model:**
Vacancies Included with Electrostatic Potential

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Interfacial cation diffusion

Model created to represent diffusion immediately at 3PB

Interfacial Oxygen Exchange
\[ \frac{1}{2} \, \text{O}_2 + 2e^\prime + V_{\text{O}, \text{YSZ}} \rightarrow O_{\text{O}, \text{LSM}}^x \]

Electrolyte Vacancy Formation (Extrinsic Defect)
\[ Y_{\text{Zr}}^x + 2Zr_{\text{LSM}}^\times + \text{O}_\text{O}^x \rightarrow 2Y_{\text{Zr}}^\prime + V_{\text{O}} + 2ZrO_2 \]

The electrochemical potential of a species \( i \) is expressed as,
\[ \bar{\mu}_i = \mu_i^0 + k_B T \ln a_i + z_i e \varphi, \quad i \in \{ \text{O}_\text{O}^\prime, e^\prime, Y_{\text{Zr}}^\prime \} \]  
\[ (2) \]

\[ \frac{\partial c_i(x, t)}{\partial t} = -\nabla \cdot J_i - R_{3\text{PB}}^{\text{C}} K A_C = \nabla \cdot \frac{D_i c_i}{k_B T} \mu_i^0 + \nabla \cdot D_i \nabla c_i(x, t) \]
\[ + \nabla \cdot \frac{D_i z_i e c_i}{k_B T} \nabla \varphi - R_{3\text{PB}}^{\text{C}} K A_C, \]  
\[ (4) \]

Interfacial cation diffusion

- Oxygen vacancies and electrons equilibrate rapidly
- Oxygen vacancy profile minimum at 3PB results from model assumptions
- I/V relationship well-matched to linear (pure resistor) model at low voltages
Next Steps (FY16)

- Replace simple vacancy exchange reaction model with real 3PB ORR model
- Add vacancy and lattice oxygen transport across 2PB
- Update interface (e.g. $D_v$) according to interface function or actual compositional variations and compare results to static property case

Tool

- Accurately describe cation evolution in critical interfaces of cathode and anode
- Establish composition predictions to be used as basis for comp chem
- Predict and measure evolved interface properties

Impact: Approach provides fundamental basis for performance evolution predictions that address reliability
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Electrocatalysts to mitigate degradation

Examine infiltrate stability in SDC/LSCF cathode backbone

- **Controlled Systems**
  - Base SDC/LSCF backbone with LSC infiltration (as fabricated)
  - Same system thermally aged 1500 hours in air
  - Same system operated 1500 hours in conventional state

- **TEM analysis revealed significant structural differences**

![Image showing TEM analysis results](image)

Xueyan Song, Shiwoo Lee, Yun Chen, Kirk Gerdes. “Electrochemically influenced cation interdiffusion and Co$_3$O$_4$ formation on La$_{0.6}$Sr$_{0.4}$CoO$_3$ infiltrated into SOFC cathodes” Solid State Ionics 278 (2015) p91.
Electrocatalysts to mitigate degradation

Hypothesis: Operation forces Co$_3$O$_4$ formation owing to local charge balancing

- Cartoon illustrates driving forces for degradation

Conclusions
- LSC decomposition is not detrimental to infiltrated cell performance
- Hypothesis is testable with computational chemistry methods
- LSC infiltration could be used as a chemical marker for cathode activity

Xueyan Song, Shiwoo Lee, Yun Chen, Kirk Gerdes. “Electrochemically influenced cation interdiffusion and Co$_3$O$_4$ formation on La$_{0.6}$Sr$_{0.4}$CoO$_3$ infiltrated into SOFC cathodes” Solid State Ionics 278 (2015) p91.
Electrocatalysts to mitigate degradation

Examine mitigation of water-induced degradation via electrocatalyst

• Prior analysis of LSM system indicated accelerated degradation when exposed to water at high current density

<table>
<thead>
<tr>
<th>Test</th>
<th>Degradation rate at 100 h [per 1000 h]</th>
<th>Degradation rate at 1000 h [per 1000 h]</th>
<th>$R_p$ at $t=0$ [$\Omega \times \text{cm}^2$]</th>
<th>$R_p$ at $t_F$ [$\Omega \times \text{cm}^2$]</th>
<th>Current [A/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Steam 500 h</td>
<td>1.8%</td>
<td>1.8%</td>
<td>0.22</td>
<td>0.15</td>
<td>0.75</td>
</tr>
<tr>
<td>10% Steam 200 h</td>
<td>0.1%</td>
<td>0.1%</td>
<td>0.32</td>
<td>0.32</td>
<td>0.25</td>
</tr>
<tr>
<td>10% Steam 500 h (1)</td>
<td>9.6%</td>
<td>9.6%</td>
<td>0.17</td>
<td>0.19</td>
<td>0.75</td>
</tr>
<tr>
<td>10% Steam 500 h (2)</td>
<td>9.9%</td>
<td>9.9%</td>
<td>0.22</td>
<td>0.20</td>
<td>0.75</td>
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<tr>
<td>10% Steam 500 h (3)</td>
<td>11.7%</td>
<td>11.7%</td>
<td>0.22</td>
<td>0.20</td>
<td>0.75</td>
</tr>
<tr>
<td>20% Steam 100 h</td>
<td>20.2%</td>
<td>20.2%*</td>
<td>0.21</td>
<td>0.23</td>
<td>0.75</td>
</tr>
<tr>
<td>20% Steam 500 h</td>
<td>25.0%</td>
<td>4.6%</td>
<td>0.34</td>
<td>0.50</td>
<td>0.25</td>
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</tbody>
</table>

**Operating conditions:**
hydrogen on anode;
air + 10% steam on cathode;
elevated current density;
750C;

**Results:**
Degradation rates exceeding 9% / 1000 hours were measured in repeat testing

Electrocatalysts to mitigate degradation

Simple electrocatalyst is deposited using conventional methods.

Degradation rate drops from greater than 9% / khr to less than 3% / khr

Analyses are preliminary and must tests must be repeated for validation

Will examine for overall stabilization of cathode structure and enhanced stability owing to decreased electric overpotential

Lynn Fan, April-July 2015 (NETL ORD internal communications)
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# Cathode Infiltration

## Concept to commercial

<table>
<thead>
<tr>
<th>Year</th>
<th>Stage</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Pre-) 2010</td>
<td>Laboratory activity, button cells</td>
<td>TRL 2-3</td>
</tr>
<tr>
<td>2012</td>
<td>Manf. component in simulated environment</td>
<td>TRL 3-4</td>
</tr>
<tr>
<td>2014</td>
<td>Prototype, manf. env. (short-stack test)</td>
<td>TRL 5</td>
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</tbody>
</table>

### Delphi’s button cells

<table>
<thead>
<tr>
<th>Program</th>
<th>Result: ↑10% peak power, 33% ↓relative degradation, &gt; 200% ↑ lifetime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Research</td>
<td>22% ASR decrease</td>
</tr>
</tbody>
</table>

### Commercial cells, 100% scale

- Manf. component in simulated environment: TRL 3-4
- Prototype, manf. env. (short-stack test): TRL 5

(b) Average Rp after 24 h operation (MCA)
Baseline cell = 0.21 ± 0.014 Ωcm²
Infiltrated cell = 0.15 ± 0.010 Ωcm²
Cathode Infiltration: Impact

- Complete manufacturer-specific infiltrate development
- Submitted ROI and patent application for graded infiltration concept
- Submitted ROI and provisional patent for scalable manufacturing process
- Continued pursuit of manufacturing scale-up with industrial collaborator(s)

On-going 10-cell stack test
- 6 infiltrated cells, 4 base cells
- 1200 hours reported (above)
- > 2000 hours operated
  “Conventional” operating mode
Mature ORD Program: Impact

Commercially scalable process available

ORD can infiltrate 1000+ cells annually at less than $0.006/cm² via advanced manufacturing

NETL has provided more than 7000 cm² of infiltrated cells to industry partners for evaluation at no cost to evaluator

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Continued research correlating structural features and cell performance

Especial focus on examination of critical interfaces and scale-bridging from atoms to particles to predict performance evolution

Ultimate goal: High fidelity predictive models intended for accelerated materials development and operational diagnostics
Thank you for your time and attention.

Contact:
Kirk Gerdes
DOE-NETL
Lead Engineer – Thermal Sciences
Office: (304)285-4342
EM: Kirk.Gerdes@NETL.DOE.GOV