Engineering Innovations and Degradation Modeling in SOFC Cathodes

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Outline

• NETL-RUA
  – Description
  – Engagement

• Cathode Engineering
  – Infiltration
  – Microstructural Engineering

• Cathode Degradation
  – Degradation framework
  – Constitutive (ORR, Microstructure, ab initio)
  – Core (3D multi-physics, Cathode evolution)
  – Additive (Aging effects, Secondary phases / breakdown)

• Summary
NETL RUA

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Support Industrial Development

Operation of NETL Solid Oxide Fuel Cell Multi-Cell Array on direct, coal-derived synthesis gas at the National Carbon Capture Center at Wilsonville, AL in August/Sept 2009.

Collected 4,000 + cell-hours of data to support development of gas cleanup systems sufficient for gasifier / fuel cell integration.

Evaluate Advanced Concepts

Fundamental computations (3D multiphysics model, at left) inform modeling of advanced degradation, performance, and microstructural evolution at the cell and stack level.

Integrated gasifier / fuel cell / turbine systems (IGFT, at right) support advanced fuel cell demonstrations efforts (2013+). NETL operates a system hardware evaluation and controls development platform.

Innovate Technology

Cathode infiltration technology is being developed to enhance the SOFC operating performance. Initial results have demonstrated > 40% performance improvement and acceptable material stability.
Cathode Engineering

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- **Summary**
Infiltration concept

Cathode infiltrates
- Nano-scale electrocatalysts
- High-surface area (EISA)

Long-term stability verification
> Variation of $R_o$ and $R_p$ of selected baseline cell and infiltrated cell for 1,500 h

Short-term performance validation
Demonstrated statistically significant performance improvement for infiltrated cathodes in 200 hour tests
> 30% peak power density increase (average) observed

Industry Engagement
Unaltered industry cells + unmodified infiltrate: 200 hour tests
> 38% power density increase @ 0.7 V (average)

Verified stability of electrochemical performance in 1500 hour test, cell degradation not accelerated above baseline
Electrocatalytic Infiltration

- Focus on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3-\delta$
- Activity enhancement
  > 30% power output @ 0.7 V
- Stability
  No phase breakdown or interphase reaction
- Durability
  Equal or better than baseline @1500 hours
- Cost / Scalability
  Requires 6 wt% infiltrate (or less)
  Formula compatible w/ commercial cathode structures/materials
Cathode Infiltration

- Improved infiltration process to minimize total number of infiltration steps
- Developed EISA process to increase infiltrate surface area (mesopores) and enhance thermal stability
- Evidence for role of structural relationships between infiltrate and backbone
  - LSM infiltrated by LSM (top)
  - LSCF infiltrated by two morphologies of LSM (bottom)

Images and data: Shiwoo Lee, National Energy Technology Laboratory
Paul Salvador & Robin Chao, Carnegie Mellon University
Cathode Infiltration

- **Prior accomplishments**
  - Developed and demonstrated a functional infiltrate (LSC)

- **Recent progress**
  - Generated evidence of structure-dependent performance enhancements
  - Examined the role of infiltrate wetting in fabrication and infiltrate function

- **Continued research**
  - Examination of stability and improvements from infiltrates composed of doped and/or non-standard materials

**Infiltration Publications**

In-situ Foamed Cathode

- **In-situ foaming process**
  - One-step, functionally graded cathode microstructure
  - Enhanced receptiveness to infiltration

- **Electrolyte supported system development** → anode supported

- **Optimized formula decreases cathode polarization by > 50% over traditional microstructure**
FY12-FY13 Cathode Engineering

• NETL RUA
  – Increased engagements with SECA core
    • Argonne National Laboratory - initiated
    • Georgia Institute of Technology – executing
    • Additional partners arising from FY13 starts

  – Increased engagements with industrial teams
    • Primary demonstrations on unmodified MSRI button cells
    • FY12 demonstration with SECA industrial partner cell

  – Finalize cathode and extend effort to include anode
    • Anode – catalytic enhancement, chemical resistance, durability
Cathode Materials Testing

- MCA Video
Cathode/Electrode Engineering Beyond FY13

- **FY12**: Foundational Materials Development (Cathode Infiltration and Microstructural Engineering)
- **FY13**: Demonstration on Commercially Relevant Cell System (Cathode)
- **FY14**: Development of Anode Infiltrates and Initial Cathode Technology Transfer to Industry
- **FY15**: Co-Development of Industrial Processes, Infiltration / Microstructure, and Complete Technology Transfer / Industrial Adoption (Cathode & Anode)
Cathode Degradation

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Degradation framework

• Degradation
  – Topic too vast to cover in industrial report (as collection of relevant observations or description of applied heuristic approaches)
  – Too many combinations of materials, too many operating states

• Framework organization
  – Attempt to generalize/categorize degradation
  – Provide a simple framework based on *degradation source* and *mechanistic complexity*
  – *Intrinsic* v. *extrinsic*; and *primary* v. *secondary*

<table>
<thead>
<tr>
<th></th>
<th>Intrinsic</th>
<th>Extrinsic</th>
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<tr>
<td>Primary (direct or single step)</td>
<td>Best Engineering Practices</td>
<td>i) Best Engineering Practices</td>
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• *Integrated modeling and experimental* efforts to quantify degradation
• Model validation – ongoing validation using literature and direct experimental sources

**3D multi-physics** (Celik – WVU)

**3D reconstructions** (Salvador – CMU)

**ORR model** (Liu – WVU; Gemmen – NETL)

**ab intio model** (Mantz – NETL)

**Constitutive**

FY10-FY12

**Integrated, Domain scale**

FY11-FY12

**Additive**

FY11-FY12

**700°C**

**800°C**

**Aging**

(Finklea – WVU; Abernathy – NETL)

**Phase breakdown**

(X Song – WVU)

**Secondary phases**

(X Song – WVU; Gerdes/Hackett – NETL)
Constitutive Models and Reconstructions

- **Oxygen Reduction Reaction (ORR)**
  - Treats parallel pathway (2PB v. 3PB)
  - Assumes surface potential separation

- **ab initio simulations** – LSZ → LSM

- **FIB-SEM reconstructions, FIB-OIM**

M.Gong, R. Gemmen, X. Liu, “Modeling of oxygen reduction mechanism for 3PB and 2PB pathways at solid oxide fuel cell cathode from multi-step charge transfer” *Journal of Power Sources* 201 (2012) 204–218

Integrated, domain scale models

- **3D multi-physics model (space domain, 10’s cm)**
  - Powerful dynamic model predicts full 3D multi-physics (e.g. T, species, η, impedance response)
  - Informed by ORR and full 3D reconstructions
  - Validated by parametric analysis and comparison to independently published data

[Image of a 3D model with color legend showing temperature variations]


- **Microstructural evolution model (time domain, 1000’s hrs)**
  - Describes evolution of 3-phase microstructure subject to thermodynamic and kinetic drivers
  - Predicts geometric and topological parameters relevant to fuel cell reaction and transport

[Graph showing TPB fraction over time steps]

Additive degradation phenomena

- **Cathode – Aging**
  - \( R_p \) of LSM symmetric cell held at OCV and cycled between 700°C and 800°C changes between two steady states requiring 10’s hrs to acquire
  - Believed attributable to cation diffusion

  H. Abernathy, H.O. Finklea, D.S. Mebane, X. Chen, K. Gerdes, M.D. Salazar-Villalpando, “Reversible aging behavior of \( \text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3 \) electrodes at open circuit” *Journal of Power Sources* 216 (2012) p11-14

- **Anode - Direct syngas exposure**
  - Direct syngas produces only minor secondary phases
  - Degradation of seal and mechanical obstruction of pores


- **Electrolyte - YSZ attack by phosphine**
  - Stable Y-P-O phase is generated at electrolyte in \( \text{PH}_3^- \)-exposed anode

FY12-FY13 Degradation Modeling

• NETL RUA
  – Increased engagements with SECA core
    • Argonne National Laboratory - initiated
    • Boston University - discussions
    • Additional partners arising from FY13 starts
  – Initiate engagements with SECA industry teams
    • Information sharing and stack analysis
  – Continue cathode and extend effort to include anode
    • Principal modes of degradation must be considered
Degradation Modeling Beyond FY13

- Foundational Operation and Evolution Modeling (Anode / Electrolyte / Cathode)
- Quantitative Analysis of Specific Degradation Modes (Anode / Electrolyte / Cathode)
- Quantitative Evaluation of Model Uncertainty Statistical Approach
- Integrated Predictions of Performance and Degradation (Long-term (40 khr +) Creation of industry accessible modeling tool)
- Real-time Performance Tracking and Forecasting Industry tool

- FY12
- FY13
- FY14
- FY15
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• NETL RUA has developed significant expertise and demonstrated maturity in two principal areas
  – Materials development, infiltration, and testing
  – Cell degradation modeling and testing

• NETL RUA supports industrial development
  – Direct R&D engagements with SECA industry teams
  – Analytical support and diagnostics

• NETL RUA collaborates with SECA core
  – Intensification of depth of understanding
  – Facilitate transfer of fundamental knowledge to applied cell development
Questions

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