SOFC Development at PNNL: Overview

May 30, 2020

Scope of Work

• Core Technology Program
  ▪ Materials Development
    ✓ Cathode materials and interactions
      • Effects of volatile species (Cr, Sr) on cell performance
      • Mitigation of Cr poisoning: Evaluation of Cr capture materials
      • Cathode contact materials: Enhancing reliability of cathode/contact materials interfaces
    ✓ Interconnects/BOP
      • Co-free protective coatings for metallic interconnects
  ▪ Modeling/Simulation
    ✓ SOFC Stack and System Modeling Tool Development
    ✓ Modeling of Stack Degradation and Reliability

• Small-Scale SOFC Test Platform
  ▪ Evaluation of performance and reliability of new stack technologies (1-10 kW)
Cr Poisoning

• Challenges
  ▪ Developing an understanding of the effects of Cr poisoning on phase formation in and atomic structure of SOFC cathodes
  ▪ Mitigation of effects of volatile Cr species on cathode performance

• Approaches
  ▪ In-operando XRD of LSM and LSCF-based cathodes with various Cr concentrations in the cathode air stream
    ▪ Evaluation/optimization of Cr “getter” materials intended to capture volatile Cr species
      ✓ May be located upstream of stack and/or within stack (“on-cell” capture)
      ✓ Possibly use upstream getter as primary, and “on-cell” getter as secondary (“polishing”)


Cr Poisoning: In-operando XRD

• Baseline test on LSCF cell in dry, clean air was recently completed – XRD analysis pending

• A hydrogen safety incident at PNNL prompted safety upgrades to all experiments using hydrogen.

• Safety upgrades for in-operando XRD of SOFCs were installed:
  - Metallic lines for flammable gases
  - Over temperature monitoring
  - Fume hood pressure monitoring
  - Flammable gas sensing
  - Automatic shut down
Cr Gettering Materials

• In previous work, LSCF perovskites with high Sr content were shown to be effective as upstream getters due to high reactivity with Cr vapor species (forming SrCrO$_4$ as reaction product).

• For on-cell applications, Cr-gettering material needs to have matched CTE, high electrical conductivity, chemical compatibility, and thermal stability.

• Approach: Evaluate LSCF/LSM and LSCF/LSCO mixtures as dual purpose cathode contact / Cr getter materials.
Cr Gettering Materials: LSCF/LSM Validation Testing

No Cr Getter:

80% LSCF / 20% LSM: On-cell Getter

PEN sealed on aluminized AISI441 WF

In test fixture
Cr Gettering Materials: LSCF/LSCO Characterization

Sintering Curves

Electrical Conductivity

Thermal Expansion
Vapor Transport of Species from LSCF Cathodes

- Early tests configured as above indicated transport of Sr and Co.

- Subsequent tests designed for long surface diffusion paths (above) between cathode material and substrate sink indicated no appreciable Sr and Co transport.

- Open geometry may have limited the concentration of vapor phases, thus new fixture was designed with long surface paths and enclosed chamber.

- Next tests are pending.
Cathode / Interconnect Contact Materials

• Challenge
  ▪ Electrical contact materials at cathode / interconnect interfaces in planar stacks tend to be mechanical “weak link,” especially during thermal cycling, due to brittle nature of ceramic materials and/or thermal expansion mismatch with adjacent components
    ✓ Low processing temperatures and constrained sintering conditions during stack fabrication lead to low intrinsic strength and low bonding strength of ceramic contact materials, especially at contact-to-cathode interface
    ✓ Use of metallic contact materials limited by cost, volatility, and/or electromigration

• Approach
  ▪ Use composite approach to develop ceramic-based contact materials having improved mechanical reliability by reducing thermal expansion mismatch and increasing contact strength/toughness
**LSCo / mullite / fiber composite contact materials**

- LSCo perovskite offers very high electrical conductivity but also has high CTE (~18x10^-6/°C) as cathode contact one needs to overcome the large residual stresses by:
  - Reduce thermal stresses by adding low CTE phase - mullite (~5.4x10^-6/°C)
  - Enhance the strength/toughness by reinforcement with strong short Al₂O₃ fibers with high elastic modulus

### Validation Testing

**Issues encountered with LSCo/mullite approach**

- Needs very high vol. fraction (~0.4) to match CTE in 12-13x10^-6/°C
- Poor densification by sintering with rigid inclusions
- Poor strength with mullite at high volume fractions
- Poor conductivity with mullite at high volume fractions
- Potential contamination by Si in presence of moisture?
- Adding 5-10v% Al₂O₃ improved strength and thermal cycle stability

Therefore investigating LSCo/Alumina Fiber composites
LSCo/Al₂O₃ fiber composite contact materials characterization

Sintering Study

Thermal Expansion

Contact Strength

Bulk Strength
Interconnect / BOP Coatings

• Challenges
  ▪ Metallic interconnects susceptible to oxidation (leading to high electrical resistance), Cr volatilization (leading to Cr poisoning), and reactions with seals (leading to mechanical failure)
  ▪ Other metallic components susceptible to Cr volatilization

• Approaches
  ▪ Electrically conductive Mn-Co spinel coatings exhibit good performance; due to possible issues with Co cost and availability, developing Co-free alternatives
    ✓ Cu-Mn-O; Ni-Mn-O; Cu-Fe-O
  ▪ Reactive air aluminization for applications that don’t require electrical conductivity
    ✓ Simple slurry-based process
    ✓ Fabrication in air at temperatures as low as 900°C
Co-free Electrically Conductive Protective Coatings

$Cu_{1.3}Mn_{1.7}O_4$

$Ni_{1.5}Mn_{1.5}O_4$

$Cu_{1.5}Fe_{1.5}O_4$

$Cu_{1.5}Mn_{1.5}O_4$

$NiMn_2O_4$

$CuFe_2O_4$
Designed & Built Small-Scale SOFC Test Platform

• Purpose:
  ▪ Evaluate performance and reliability of emerging stack technologies (2-10 kW) under realistic operating conditions

• Test capabilities:
  ▪ Steam-reformed methane
  ▪ Steady-state isothermal tests
    ✓ Variables: temperature, current, voltage, fuel
  ▪ Thermal cycling
  ▪ E-stop cycles (redox tolerance)
  ▪ Variable anode recycle rates

• Validated the test platform in 500 hour test on reformed methane with 40% anode recycling – operated a 3.7 kW stack at 62% gross LHV efficiency

• Thereafter, various recycle rates were tested for effects on efficiency
Small-Scale SOFC Test Platform

Key features:
- Operation on methane via steam reforming
- Anode recirculation loop
- High efficiency microchannel heat exchangers for heat recuperation and anode/cathode stream temperature equalization
- Automated control system
Overview: Stack Modeling Tools

Technical Challenge
• SOFC stacks must be designed for high electrochemical performance and mechanical reliability

Modeling Objective
• Develop numerical modeling tools to aid the industry teams’ design and engineering efforts at the cell/stack scale

Technical Approach
• SOFC-MP 2D – Analysis of electrochemical and thermal performance of tall symmetric stacks
• SOFC-MP 3D - Detailed 3D multi-cell stack structures for electrochemical, thermal, and stress analyses
• SOFC-ROM – Reduced order models (ROMs) of SOFC stacks for use in system modeling analyses
• GUI – Common interface for the modeling tools with pre-processing and post-processing capabilities

Recent Accomplishments
• Implemented high-pressure operation in SOFC-MP
• Developed complete ROM generation tool
• Improved ROM exhaust species predictions through use of DNN and data normalization techniques
• Demonstrated dual mode degradation for prediction of end-of-life (EOL) performance
• Demonstration of SOFC tools for electrolysis mode
Program Modeling Objective: Linking Models Across Different Length Scales

- Recent modeling activity has focused on **linking model results across length scales**
  - Utilize a Reduced Order Model (ROM) approach to improve the accuracy of power system models

Micro/Meso-Scale Models
Cell/Stack Models
Response Surface Analysis
System Models

Property Data

I-V Performance

Performance: Electrical Thermal Mechanical

Reduced Order Model (ROM)
Overview: Reduced Order Model (ROM)

Technical Challenge
• SOFC systems must be designed for high efficiency and low capital costs

Modeling Objective
• Improve accuracy and capability of SOFC systems analyses used for design and cost of energy (COE) predictions

Technical Approach
• Integrate the PNNL SOFC-MP 2D model into NETL’s system model as a reduced-order model (ROM)
  ▪ Develop ROM that improves accuracy of the SOA SOFC analysis with reduced computational time and complexity
• Investigate machine learning (ML) approaches to improve accuracy and sensitivity of generated ROMs

Recent Accomplishments
• Delivered numerous ROMs for different power system architectures to NETL collaborators
• Developed automated ROM construction tool and GUI to support local and remote solution on HPC cluster
  ▪ Included error quantification for 95% confidence interval and sampling tool for high-dimensional parameter space
• Used machine learning methods to improve the prediction accuracy of stack exhaust species composition and classify case results
• Reviewed SOA electrochemical performance
ROM Generation

• General process diagram for NGFC or IGFC power system
• Evaluated stack performance and thermal gradient for wide range of potential operating conditions
• Provided NETL collaborators with 27 ROMs for various configurations to support pathway studies
  - NGFC
  - IGFC (conventional, enhanced, catalytic)
  - SOA and future stack performance
  - System w/ or w/o carbon capture
  - System w/ or w/o vent gas recirculation concept

### Input parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average current density (A/m²)</td>
<td>2000-6000</td>
</tr>
<tr>
<td>Fuel temperature (C)</td>
<td>15-600</td>
</tr>
<tr>
<td>Internal reforming (NA) *</td>
<td>0-1</td>
</tr>
<tr>
<td>Oxidant temperature (C)</td>
<td>550-800</td>
</tr>
<tr>
<td>Oxidant recirculation (NA)</td>
<td>0-0.8</td>
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<tr>
<td>Oxygen to carbon ratio (NA)</td>
<td>1.5-3</td>
</tr>
<tr>
<td>Stack fuel utilization (NA)</td>
<td>0.4-0.95</td>
</tr>
<tr>
<td>Stack oxidant utilization (NA)</td>
<td>0.0833-0.833</td>
</tr>
<tr>
<td>System pressure (ATM)</td>
<td>1-5</td>
</tr>
<tr>
<td>VGR temperature (C) **</td>
<td>15-204</td>
</tr>
<tr>
<td>VGR rate (NA) **</td>
<td>0.3-0.97</td>
</tr>
</tbody>
</table>

* Only available in NGFC
** Only available in VGR
ROM Graphical User Interface (GUI)

• Created a graphical user interface (GUI) and manual to allow a general user to more easily create a ROM using SOFC-MP stack results

1. Sampling
2. Create Cases and Solve
3. Build Kriging ROM
4. ROM Prediction
ROM GUI Features

- Simplified creation of ROMs for different NGFC and IGFC system configurations w/ or w/o carbon capture and storage (CCS) and vent gas recirculation (VGR) options
- Smart sampling of more cases in regions of high mean square error
  - Local solution on PC
  - Remote solution on high performance computer (HPC)
- Cross validation of results to determine confidence interval of prediction
- Deep neural network (DNN) prediction option in addition to the standard Kriging prediction
ROM w/ Machine Learning: Result Classification

• Not all input parameter combinations are physically viable for the system
  • Developed classifier network to identify physically operational cases
  • Deep neural network (DNN) regression + DNN classifier + mass balance model (MBM) to improve prediction accuracy and reduce RMS error by 2-3X
Stack State-of-Art Electrochemical Performance

• Reviewed voltage-current density (V-J) data within and outside the DOE SOFC program to ensure the best state-of-art (SOA) performance is being used for modeling simulations

• Challenges
  ▪ Teams often report performance but do not provide enough data (i.e., stack details, conditions) to fully identify the V-J curve
  ▪ Difficult to make ‘apples-to-apples’ comparisons

• Observations
  ▪ Multi-cell stacks not as good as single cells due to ohmic losses
  ▪ All-ceramic cells not as good as planar anode-supported cells
  ▪ For the SOFC program, FCE and Delphi stacks are top performers
  ▪ Wide range of activation losses due different material sets
  ▪ The best metal-supported cells are approaching performance of best anode-supported cells, so purported advantages in lower temperature operation and higher durability may drive it to be the prominent architecture
  ▪ V-J data used for ROM activity is representative of current stacks
Overview: Short Term Reliability

Technical Challenge
• Stack operating stresses dependent on design, flow configuration, operating conditions and affect reliability

Modeling Objective
• Investigate influence of stack design, geometry, fuel composition and identify conditions for high reliability

Technical Approach
• Predict stack temperature distribution with different designs, geometry, flow configuration, and fuel compositions for NGFC systems using SOFC-MP
• Perform FEA stress analysis to predict operating and shutdown stresses and evaluate mechanical reliability
• Identify optimal operating conditions using design-of-experiments approach with desirability function

Recent Accomplishments
• Evaluated electrochemical/thermal performance and mechanical reliability of co- and counter-flow configurations for multi-cell stacks under similar operating conditions
Beginning of Life (BOL) 3D Stack Evaluations

- Evaluated 15 and 45 cell large area stacks to understand the benefits of flow configuration and operating conditions on the relative performance at beginning of life (BOL)

- Counter-flow stacks generally had higher power and peak temperature but also higher temperature difference for similar operating states and average cell temperature

- Local peak temperatures at corners induced high stresses and predicted high local failure probability

- This was more influential than the actual flow configuration effect
  - Reinforces importance of the sensitivity to realistic geometries and adequate fuel/oxidant manifold design
Overview: Long Term Degradation

Technical Challenge

• Bridge scales of degradation from microstructure to stack
• Understand effect of creep

Modeling Objective

• Identify operating conditions for optimal initial performance and minimal degradation
• Investigate effect of creep on SOFC mechanical reliability

Technical Approach

• Evaluate stack performance with multiple degradation mechanisms acting independently and simultaneously
  ▪ E.g., grain coarsening, Cr poisoning, scale growth, mechanical creep
• Evaluate BOL and long-term reliability of single and multicell stacks under realistic operating conditions.

Recent Accomplishments

• Evaluated the performance and reliability of single and multi-cell SOFCs stacks under one or more degradation mechanisms
• Material creep model parameters were identified for the SOFC operational range (700 – 800°C)
• Evaluated influence of creep on stresses and reliability of generic multi-cell stack designs for realistic operating temperatures
End of Life (EOL) 3D Stack Evaluations

- Evaluated 40k hour end of life (EOL) condition and mechanical reliability of 15 cell co- and counter-flow stacks experiencing mechanical creep
- Creep relaxation caused redistribution of stresses for both flow configurations that increased failure probabilities at the bottom cells of the stack
  - Potential for long-term damage in end cells nearest the load frame

![Co-Flow vs Counter Flow Operational Reliability](image)

**Co-Flow**
- Cell #1: Bottom
- Cell #8: Middle
- Cell #15: Top

**Counter-Flow**
- Cell #1: Bottom
- Cell #8: Middle
- Cell #15: Top

Legend:
- CoFlow BOL
- CoFlow 40k hrs
- Counter BOL
- Counter 40k hrs

![Failure Probability vs Cell Number](image)
Overview: Damage Progression

Technical Challenge
• Weibull analysis predicts 100% failure probability for components with localized (corner, edge) rupture. A better evaluation is needed for reliability predictions

Modeling Objective
• Predict progressive damage of SOFC electrode and evaluate long-term reliability

Technical Approach
• Investigate progressive damage models in literature and commercial FEA
• Develop and implement a continuum brittle damage mechanics constitutive model and validate with literature or experimental data.
• Evaluate progressive damage of electrodes in single and multicell stacks for reliability

Recent Accomplishments
• Reviewed literature damage models for SOFC materials
• Implemented prediction of mechanical properties as a function of porosity
• Implemented a continuum damage mechanics model in FEA to evaluate damage evolution in the anode
• Implemented a smeared crack model in FEA to evaluate damage evolution in the anode
Damage Models for SOFC Cell Materials

• Continuum Damage Mechanics (CDM)
  ▪ Constitutive theory that describes the progressive loss of material integrity due to the propagation and coalescence of micro-cracks, micro-voids, and similar defects
  ▪ Voids, microcacks and pores are modeled as ellipsoidal inclusions and negligible stiffness in an Eshelby-Mori-Tanaka approach (EMTA) formulation averaged over all possible orientations
  ▪ Typically phenomenological but focusing on mechanistic approach

• Smeared Crack Model (SCM)
  ▪ Accounts for highly oriented nature of cracking (anisotropic nature of the damaged stiffness and compliance matrices)
  ▪ Considers both Mode-I (normal) and Mode-II (shear) resistances
  ▪ Appropriate for quasi-brittle materials such as concrete or rock under predominantly tensile loading
  ▪ Typical crack initiation based on maximum principal stress
Continuum Damage Mechanics (CDM) Model

- Stiffness reduction law as a function of the void volume for porous material
- Develop constitutive relations and damage evolution laws
- Implement in FEA with stiffness reduction technique at a critical damage level

Porosity Effect on Elastic Moduli

Strength Reduction Due to Damage

\[ p_c = 0.11 \]

\[ \text{Elastic Moduli vs Porosity (Void Volume Fraction)} \]

\[ \text{Stress vs Strain} \]

\[ \text{Void Volume Fraction vs Applied Stress (MPa)} \]
Smeared Crack Model (SCM)

- Degradation due to cracking represented without discrete crack modeling
- Considers reduced strengths in compression, tension and shear after cracking
- Easy to implement with fewer material parameters than the CDM model, this model is used often for modeling brittle damage in concrete structures

Predicted Temperature

Anode Crack Density
Thank you