Modeling Tools for SOFC Design and Analysis: Recent PNNL Progress

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Modeling Objectives & Approach

**Objectives:** Develop stack modeling tools to:
- Evaluate the tightly coupled multi-physical phenomena in SOFCs
- Aid understanding of materials degradation issues
- Allow SOFC designers to perform numerical experiments for evaluation of electrochemical, thermal, and mechanical stack performance
- Provide wide applicability for industry teams to solve key design problems

**Approach:**
- SOFC-MP 2D/3D: Multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
- Stack reduced order model (ROM) creation for system-level studies
- Component and material models to improve stack mechanical reliability
- Micro/meso-scale models to evaluate electrode degradation mechanisms
- Experimental support to provide necessary material data for the models
Recent Progress

- **SOFC-MP Tools**
  - Modifications to the 3D tool for use in a more generic graphical user interface (GUI)
  - Development of the reduced order modeling (ROM) tool

- **Compliant Seals**
  - Constitutive model development and behavior of compliant seal materials in SOFC stacks

- **Metallic Interconnects**
  - Experimental and modeling approach for scale strength and prediction of interconnect lifetime using interfacial indentation tests

- **Electrochemical Degradation**
  - Models for cathode degradation under high humidity
Modeling Tools for SOFC Stack Analysis

**Challenge:**
- SOFC stacks must be designed for high electrochemical performance and mechanical reliability

**Goal:**
- Develop numerical modeling tools to aid the industry teams’ design and engineering efforts

**Technical Approach:**
- **SOFC-MP 3D** - Evaluates detailed 3D multi-cell stack structures for electrochemical, thermal, and mechanical stress analyses
- **SOFC-MP 2D** – Rapid engineering analysis of electrochemical and thermal performance of tall symmetric stacks
- **SOFC-ROM** – Creates reduced order models (ROMs) of SOFC stacks using response surface techniques for use in system modeling analyses
SOFC-MP 3D Recent Progress

- Construction of generic framework for SOFC-MP initiated
  - Replaces existing MSC MARC GUI for pre- and post-processing
  - Eliminates costly commercial license requirement
  - Unifies 3D and 2D packages under a common GUI for ease of use
- Pre- and post-processing for 2D tool completed
- Pre-processing for 3D model creation completed
  - Alternate model creation route beyond legacy Mentat-FC GUI
  - Implemented translators for ANSYS and ABAQUS FEA meshes
  - Fully integrated to the common GUI including assignment of operation and control parameters
Results post-processing for 3D tool started

- Linear plotting of distributions along the flow field for all physics properties completed:
  - Air and fuel temperature
  - Pressure
  - Current density
  - Species concentrations

- Multi-cell plotting and 3D contour plots using open-source software in progress

- Improved multi-physics solver performance for high methane (+20%) fuel compositions
SOFC-ROM Motivation

- More studies being performed for SOFC stack block integration and performance in large-scale demonstration systems
  - Understand performance and issues with BOP versus stand-alone testing
- Need a model to represent the stack in system models
  - Thermodynamic or 0-D models have no information about stack internal parameters such as temperature gradients, but such parameters may be critical for safe operation (e.g., maximum cell temperature)
  - Existing high fidelity SOFC-MP models have necessary information, but are too computationally expensive to run in system analyses
- Reduced order models (ROMs) provide approximate representations of such detailed models in O(1) time
- SOFC-ROM leveraged from the REVEAL framework at PNNL
  - REVEAL: a generic, automated framework for building ROMs for scientific simulations
SOFC-ROM Workflow

1. Identify Design Parameters: Stack Voltage, Fuel temperature, etc.
2. Sampling Method: LHS, Norm, QMC
3. Job Execution Infrastructure
4. Export ROM Plug-in for power system simulations
5. ROM Analysis Tools:
   - Visualization
   - Error Estimation
   - Predictive Analysis
6. Regression:
   - Kriging
   - ANN
   - SVM
7. Sensitivity Analysis:
   - ANOVA
   - SRC

SOFC-ROM User Environment

- Base Fuel Cell Model
- Sampling Method Parameter Ranges Number of Samples
- Export ROM Plug-in for power system simulations
- Regression
- Sensitivity Analysis
- Automated Post processing Data Management

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SOFC-ROM Recent Progress

- SOFC-ROM workflow completed
  - SOFC-MP 2D tool integrated as stack input
  - Multiple sampling methods implemented (LHS, QMC, Gaussian)
  - Multiple methods for regression (Kriging, ANN, MARS, SVM) and sensitivity analysis (ANOVA, SRC, MARS) implemented
  - ROM output in ACM or CAPE-Open format added
  - Fuel/air composition added to parameter set
  - Constraints on fuel/air compositions and parameter dependencies added
  - Error handling added to trap and discard invalid or unconverged cases from the solution set
  - Installation and user manuals prepared
Ongoing and Future Work

► SOFC-MP 3D
  ■ Implement post-processing visualization of SOFC-MP 3D results contours in the common GUI
  ■ Implement FEA stress analysis routines

► SOFC-ROM
  ■ Evaluate ROM export capabilities and integration with commercial system modeling tools (e.g. ASPEN) for study of SOFC-based power generation systems.
  ■ Release ROM version with documentation and examples
Modeling of Compliant Seals

**Challenge:**
- SOFC stacks must have reliable hermetic seals under operating and thermal cycling loads

**Goal:**
- Develop constitutive and damage models to design and simulate robust compliant seal materials and concepts for stacks

**Technical Approach:**
- Understand the healing and damage mechanisms
- Combine different length-scale modeling approaches to establish quantitative relationships between material structure and its measured physical properties
- Perform stack-level thermo-mechanical simulations to determine the effects of material properties and operating conditions
- Validate the models through comparisons with experimental data
Constitutive Damage/Healing Model

- Continuum thermo-inelastic model for dynamic damage and healing of self-healing glass
  - Includes the crack evolution and internal pore propagation

\[ \dot{\sigma}_{ij}^M = (1 - \xi) \left( C_{ij}^{eq} \dot{\varepsilon}_{ij}^M + C_{ij}^{neq} \dot{\varepsilon}_{ij}^e \right) \]

\[ \dot{\xi} = \dot{\xi}_c + \dot{\xi}_p \]

- Consider different underpinning mechanisms
  - Pressure driven crack nucleation
  - Deformation energy driven crack growth
  - Thermal diffusional crack healing
  - Homogenous and heterogeneous pore nucleation
  - Inelastic flow induced pore growth

\[ \dot{\xi}_c = \dot{\xi}_{c_n} + \dot{\xi}_{c_g} + \dot{\xi}_{c_h} \]

\[ \dot{\xi}_p = \dot{\xi}_{p_n} + \dot{\xi}_{p_g} \]
SOFC single cell simulation predicts the seal mechanical response during rapid thermal cycling

- Realistic temperature profile from SOFC-MP analysis

- Cracking damage fully recovered during 30 min high temperature operation
- Pore damage not recovered (based on experimental observations to date)
Can simulate multiple cycles

Overall damage within the glass seal is still kept within tolerance (<2%)

Periodic maximum crack damage increases with loading cycles due to porosity accumulation and its effect on the elastic properties
Effect of Temperature Uniformity

- Effects of temperature uniformity in the cell
  - Uniform temperature takes the mean of the non-uniform temperature field
  - Very similar stress distributions in the seal
  - Slightly different damage evolution profiles
  - Temperature variation leads to more non-uniform damage distribution and low temperature regions show slower healing
Effect of Dominant Damage Sources

Depending on which damage sources are dominant, the effects of viscosity on seal glass material behavior may be different.

- **Pore dominates**
  - Viscosity \( \uparrow \) Leak Rate \( \downarrow \)
  - [Chou, PNNL]

- **Crack dominates**
  - Viscosity \( \uparrow \) Leak Rate \( \uparrow \)
Effect of Material Heterogeneity

- Reinforcement phases (fibers, particles) can introduce heterogeneity
  - Normal distribution is assumed for the viscosity within the seal geometry
  - Heterogeneous viscosity field greatly reduces the damages
  - Low viscosity regions provide local compliance and stress relief

Crack Evolution

Pore Propagation
Effect of Material Properties

- Material mechanical response in terms of characteristic material properties, i.e. elastic modulus and viscosity
  - 25 cases to establish the response surface: $\log(\eta/\eta_0)$: -2:1:2, $\log(E/E_0)$: -2:1:2
  - Cracking damage is highly sensitive to stiffness but less affected by viscosity
  - Pore growth is strongly influenced by both properties
  - High viscosity together with low stiffness would lead to the least damage
Ongoing and Future Work

- Evaluate the seal performance within multi-cell SOFC stacks
- Continue model development by including effects such as stress dependent viscosity and material stochastic behavior
- Examine different engineering seal designs to support the seal material development effort
Mechanical Reliability and Life Prediction of Coated Metallic Interconnects

**Challenge:**
- IC must meet SECA lifetime requirement

**Goal:**
- Use experiments and modeling to predict interconnect life for spinel-coated surface-modified specimens under isothermal cooling and thermal cycling

**Technical Approach:**
- Vickers pyramidal nano/micro-indentation performed at the substrate/oxide scale interface to assess apparent fracture toughness and spallation resistance of surface modifications
- Fracture mechanics and FEA modeling tools to evaluate driving force and energy release rate for spallation to determine the main factors influencing IC degradation
- Evaluation of IC candidate materials
Interfacial Indentation Testing

- Apparent interface fracture toughness \( (K_i) \) of bimaterial interface may be estimated as \([1, 2]\):

\[
K_{in} = 0.015 \left( \frac{P_c}{a_c^{3/2}} \right) \left( \frac{E}{H} \right)^{1/2}
\]

- Nano/micro indentation performed to propagate crack between substrate and scale to determine the critical load \( P_c \) and critical crack length \( a_c \)

- Intersection of the indentation data linear fit and the apparent hardness defines the critical load (adaptation of methodology)

Surface ground, 10,000 h, 800 °C

Interfacial Indentation Testing Results

- Data collection time intensive
- Initial results indicate indentation tests follow the expected response
- Average stress intensity factor:
  - 441 SB: $\sim 2.5 \text{ MPa}\cdot\text{m}^{0.5}$
  - 441 SG: $\sim 2.0 \text{ MPa}\cdot\text{m}^{0.5}$
Failure Modes for Coatings

Shear stress distribution

$$\sigma_{13}(x,0)$$

Edge delamination (Mode II dominant)

Compressive stress distribution

$$\sigma_{11}^{\text{ave}} = \frac{1}{h} \int_{0}^{h} \sigma_{11} \, dx_3$$

$$\sigma_R = \frac{E \Delta \alpha \Delta T}{1 - \nu}$$

Buckling delamination (Mixed mode I and II)
Failure Criteria for Critical Thickness $h_c$

Energy release rate:

$$G = \frac{(1 - \nu^2)ho^2}{2E} \left(1 - \frac{\sigma_c}{\sigma}\right) \left(1 + 3\frac{\sigma_c}{\sigma}\right)$$

Thermal stress:

$$\sigma = \frac{E\Delta\alpha\Delta T}{1 - \nu}$$

Critical buckling stress:

$$\sigma_c = \frac{\pi^2 E}{12(1 - \nu^2)} \left(\frac{h}{b}\right)^2$$

Fracture toughness:

$$\Gamma(\Psi) = \Gamma_I \left(1 + \tan^2 \left[(1 - \lambda)\Psi\right]\right)$$

$$\Gamma_I = \frac{1 - \nu^2}{E} K_i^2$$

From interface indentation experiment

Failure Criterion:  

$$G(h, \sigma, b) > \Gamma(\Psi(h))$$

If $h > h_c$: coating will fail under cooling  
If $h < h_c$: coating will survive cooling
Based on the measured stress intensity factor, a threshold blister size is predicted for which no buckling delamination failure is expected:

- $K_I = 1.8 \text{ MPa-m}^{0.5}, b=60 \mu m, h_c \sim 4.4 \mu m$
- $K_I = 2.9 \text{ MPa-m}^{0.5}, b=120 \mu m, h_c \sim 9.2 \mu m$
Failure Analysis Results (cont’d)

- For range of stress intensity factor of ~2-3 MPa-m^{0.5}, a critical thickness of 4-9 µm is predicted for SB/SG materials.

- Present long-term experiments with average thickness of almost 8 µm for SB/SG materials are still running.
Proposed Predictive Methodology

- Use short duration oxidized specimens for long-term predictions
- Validate on modified and unmodified specimens
- Identify possible standard materials

Oxidize Specimen for Short Duration

Perform Indentation on Cross-Section

Calculate $K_{IC}$

Calculate Minimum Thickness

Projected Time to Initial Spall Failure

Theory of Interfacial Toughness

Bi-Layer Fracture Mechanics and Isothermal Cooling

Materials Testing

Oxide Growth Kinetics

Modeling
Ongoing and Future Work

- Indentation measurements on 850°C specimens
- Evaluation of experimental/analytical methodology as screening method for life-prediction
  - Life predictions of surface modified specimens exposed to 800°C
  - Determine $K_{in}$ for 2000 h, 800°C, unmodified, coated 441 specimens
  - Benchmarking of methodology with known standards if available
  - Effect of surface roughness on methodology and data scatter
Electrochemical Degradation Under High Cathode Humidity Conditions

Challenge:
- Long-term electrochemical performance degradation must be low

Goal:
- Use modeling to identify cathode degradation mechanisms and characterize electrochemical impact for high humidity conditions

Technical Approach:
- Micro-scale – Investigate the surface level kinetics and thermodynamics of $\text{H}_2\text{O}$ with LSM using molecular dynamics modeling of $\text{H}_2\text{O}$, $\text{O}_2$ and LSM in the presence of an applied field
- Meso-scale – Resolve the reactive transport in the cathode and at the cathode-electrolyte interface using SPH porous media model
- Macro-scale – Cell and stack level modeling of the effects of degradation on stack performance using SOFC-MP
Micro-Scale Modeling Results

- Want to evaluate O₂ and H₂O competitive adsorption and diffusion on LSM
- La₀.₈Sr₀.₂MnO₃ periodic solid structure model built (density, cohesion energy, and O₂ adsorption activation energy) consistent with experiment
- H₂O adsorption activation energy predicted and passed up to the meso-scale model

<table>
<thead>
<tr>
<th>Property</th>
<th>Calculated</th>
<th>Experiment</th>
</tr>
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<tbody>
<tr>
<td>density at 1000 K (g/mL)</td>
<td>5.77</td>
<td>5.99[2]</td>
</tr>
<tr>
<td>cohesion energy at 1000 K (eV)</td>
<td>26.55</td>
<td>31.0 [3]</td>
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<tr>
<td>O₂ adsorption activation energy (eV)</td>
<td>0.97±0.02</td>
<td>1.09±0.01 [1]</td>
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<tr>
<td>H₂O adsorption activation energy (eV)</td>
<td>1.32±0.07</td>
<td>n/a</td>
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</tbody>
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Meso/Macro-Scale Modeling Results

- SPH model for 2D porous cathode structure created
- Langmuir model for competitive adsorption
- Simulated accelerated testing with higher humidity levels (10%, 20%, 40%) for 100 hr to accelerate rate of degradation
  - Adsorption site competition alone cannot explain the degradation results of PNNL or Nielsen (2011)
- Electrochemical degradation captured as damage factor and applied to the cathode exchange current density in the macro-scale I-V curve
Ongoing and Future Work

- Expand micro-scale model to consider possible reactions with Mn or Sr
- Evaluation of PNNL long-term test data for identification of possible mechanisms at low humidity
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