AN INTEGRATED APPROACH TO MODELING AND MITIGATING SOFC FAILURE

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Phase I is a one-year effort to investigate and evaluate the feasibility of the solution proposed and/or the merits of the scientific path of inquiry.

Phase II will seek to mature the science and technology developed to a sufficient level that it can be utilized by the SECA Industry Teams.
Technical Issues to be Addressed

Thermomechanical Damage and Failure
- Thermal stresses due to thermal mismatch
- Delamination and fracture due to thermal mismatch and thermal shock
- Warpage due to thermal mismatch
- Seal reliability

Thermal Transport
- Flow, heat and reagent species transport in porous media
- Thermal radiation heat transfer in porous media
- Coupling between radiation heat transfer and other modes of heat transfer
- Source/sink terms for transport equations due to electrochemical reactions

Electrochemistry
- Cell and stack level engineering models
- Interdependency between electrochemistry and thermal/mass transport
- Transient processes and failure modes
Electrochemistry
Model Objectives Achieved

- **Engineering Code**
  - Accurate and viable
  - Customized structural-language algorithms that are portable to software
  - Enhanced designer insight via graphically intuitive trends

- **Complement to SECA DOE National Labs’ Efforts**
  - Resolution of reformate stream analysis (NETL)
  - Automated convergence upon set fuel utilization (PNNL)
• Anode-supported cell
• Designs capable of 2 W/cm$^2$
• P-E-N dimensions from Kim, J., Virkar, A. V., Fung, K., Mehta, K., and Singhal, S., 1999
Planar SOFC Co-flow Model

Pressure\(n\) = \(f(x_i, P_o)\)
\(P_{O_2} \quad P_{N_2}\)
Flow rates\(n\) = \(f(NOS, N_{total})\)
\(N_{O_2} \quad N_{N_2}\)
Temperature\(n\) = \(f(Q(i))\)

Pressure\(n+1\) = \(f(x_i, P_o)\)
\(P_{O_2} \quad P_{N_2}\)
Flow rates\(n+1\) = \(f(NOS, N_{total})\)
\(N_{O_2} \quad N_{N_2}\)
Temperature\(n+1\) = \(f(Q(i))\)

Flow rates\(n\) = \(f(P_i, Q_{fuel}, i(n))\)
\(N_{H_2} \quad N_{H_2O} \quad N_{CO} \quad N_{CO2} \quad N_{CH4} \quad N_{total}\)

Flow rates\(n+1\) = \(f(P_i, Q_{fuel}, i(n))\)
\(N_{H_2} \quad N_{H_2O} \quad N_{CO} \quad N_{CO2} \quad N_{CH4} \quad N_{total}\)

\[ V(i) = E_o - iR_i - a - b \ln i + \frac{RT}{2F} \ln \left(1 - \frac{i}{i_{as}}\right) - \frac{RT}{2F} \ln \left(1 + \frac{p_{H_2} i}{p_{H_2,i} i_{as}}\right) \]

Electrochemical model is a combination of the polarization model of Kim et al. (1999) and Haynes’ slice technique (Haynes and Wepfer, 1999)
Planar SOFC Co-flow Model Validation

- Model agrees with experimental data
- Discrepancies, primarily differences in fuel utilization, caused by comparing a button cell to a much larger channel model
Thermal Model for Cells

- **Assumptions**
  - Isothermal channels as a design goal
  - Convection to air stream is the dominant form of cell thermal management
  - Laminar, hydrodynamically fully developed flow at the leading edge due to extensive manifolding

- **Methodology**
  - Use well-regarded laminar flow Nusselt correlations for airflow within rectangular ducts, to determine appropriate inlet air temperatures and resulting cell temperature profile
  - Vary parameters as required to determine impact
    - Voltage
    - Fuel utilization
    - *Fuel-based* inverse equivalence ratio / “number of stoichs” (NOS)
Promoting Isothermal Cells

Best Case

Fuel Utilization

↑ $V_{op}$

↑ NOS
Graphically Intuitive Design
Aids Development
Fuel Cell M&S Updates

Real-Time Visualization of Constraint Space

<table>
<thead>
<tr>
<th>Response</th>
<th>Contour</th>
<th>Current X</th>
<th>Current Y</th>
<th>Lo Limit</th>
<th>Hi Limit</th>
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Latter Phase I/ Phase II Developments

- Greater collaboration with SECA-affiliated national labs

- Mitigation of transient mode failure
  - Process optimization of transitional phase of SOFC start-up via modifications to fuel utilization, load allowance, etc.
  - Resolving mini thermal cycles due to load fluctuation
Latter Phase I / Phase II Developments

- Enhanced integration with colleagues for multi-physics simulation and mitigation of thermomechanical failure modes.

Examples:

- Strength requirements for designated operating conditions
- Gleaning effective mass transport diffusivities for better characterizing concentration polarization

- Viable performance/reliability tools and training for industry
Thermal-Fluid Modeling of SOFC
Thermal-Fluid Modeling of SOFC

Focus of Thermal – Fluid Modeling Efforts

Porous Media Modeling

• Knudsen, dispersion, diffusion-thermo (Soret) and thermo-diffusion (Dufour) mass and heat transfer effects

• Non-equilibrium heat transfer in porous electrodes to account for unequal gas and solid matrix temperatures

• Effective thermal conductivity of solid matrix of porous electrodes

Radiation Modeling

• SOFC’s are high temperature systems – radiation modeling important

• Coupling between radiation and other modes of heat transfer affects reaction rates and cell output voltage

• Discrete Ordinate Method is computationally intensive – need for alternate modeling schemes
Radiation Modeling – Optical Properties

Wien’s law: \((\lambda n T)^\text{max} = 2898 \text{ µm}\).
\(n \sim 1.6; T = 700 ^\circ C = 973 \text{ K}; \lambda\text{max} = 1.86 \text{ µm}\)

80% of fractional emissive power is contained within \(1.4 \text{ µm} < \lambda < 6.1 \text{ µm}\)

**Electrolyte:** Weakly absorbing \((\kappa=496.2 \text{ m}^{-1})\) and optically thin \((\kappa L < 0.003)\)

**Electrodes:** Optically thick/opaque
Radiation Modeling – Discrete Ordinate Method

- Inclusion of radiation results in ~150 °K drop in the overall temperature level of the monolith type SOFC

- Coupled radiation effects result in increase of cell voltage from 0.65 V — 0.74V
### Methodology Cell Voltage (V) CPU time* (min)

<table>
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<th>Methodology</th>
<th>Cell Voltage (V)</th>
<th>CPU time* (min)</th>
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<tbody>
<tr>
<td>Discrete Ordinate Method</td>
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<tr>
<td>Two-Flux Approximation</td>
<td>0.731</td>
<td>76</td>
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*Based on time to convergence of Fluent simulations carried out on a 2.8 GHz pentium 4 personal computer*
Porous Media – Reagent Transport Modeling

Momentum Conservation - Forchheimer and Brinkman Model:

\[
\frac{1}{\varepsilon^2} \nabla \cdot \left( \rho \, \vec{V} \, \vec{V} \right) = -\nabla p + \nabla \cdot (\mu_e \nabla \vec{V}) - \frac{\mu}{K} \frac{\vec{V}}{\sqrt{K}} - \rho \, f \frac{\vec{V} | \vec{V}}{\sqrt{K}} + \rho \, \bar{g} \, \beta (T - T_\infty)
\]

\( \mu_e \) - effective viscosity 
\( \varepsilon \) - porosity 
\( K \) - permeability 
\( f \) - inertia coefficient

Species Conservation – Reagent and Intermediate Mole Fraction:

\[
\nabla \cdot \left( \rho \, \vec{V} \, Y_i \right) = \nabla \cdot \rho \left( D_i \nabla Y_i - D_{i,T} \frac{\nabla T}{T} \right) \pm S_i
\]

\( D_i \) - effective diffusion coefficient 
\( D_{i,T} \) - thermal diffusion coefficient 
\( S_i \) - species production / depletion rate

\[
D_i = \frac{\varepsilon}{\tau} \left( \frac{1 - \alpha_i \, x_i}{D_{i,m}} + \frac{1}{D_{i,k}} + \frac{1}{D_{i,d}} \right)^{-1}
\]

\( D_{i,m} \) - molecular diffusion 
\( D_{i,k} \) - Knudsen diffusion 
\( D_{i,d} \) - dispersion

\( \varepsilon \) - porosity 
\( \tau \) - tortuosity
Porous Media – Diffusion Modeling

Diffusion Coefficient for Species Conservation:

\[ D_i = \frac{\varepsilon}{\tau} \left( \frac{1 - \alpha_i}{D_{i,m}} + \frac{1}{D_{i,k}} + \frac{1}{D_{i,d}} \right)^{-1} \]

where \( \alpha_i = 1 - \left( \frac{M_i}{M_m} \right)^{1/2} \)

- \( M_i \) - molecular weight of component \( i \)
- \( M_m \) – average molecular weight

Molecular Diffusion Coefficient:

\[ D_{i,m} = \frac{1 - x_i}{\sum_{k \neq i} \frac{x_k}{D_{ik}}} \]

- \( x_i \) - molar fraction
- \( D_{ik} \) - binary diffusion coefficient

Knudsen Diffusion Coefficient:

\[ D_{i,k} = \frac{2}{3} \left( \frac{8RT}{\pi M_i} \right)^{1/2} R \text{ - gas constant} \]
\[ T \text{ - fluid temperature} \]
\[ r \text{ - pore radius} \]

Thermal Diffusion Coefficient:

\[ D_{i,T} = -2.59 \times 10^{-7} T^{0.659} \left[ \frac{M_i^{0.511} x_i}{\sum_{i=1}^{N} M_i^{0.511} x_i} - Y_i \right] \]

\[ D_{i,d} = f(Pe, \varepsilon) \]

- \( Pe = uR/D_{i,m} \) (Peclet #)
- \( Y_i \) - mass fraction of \( i \)
Porous Media – Energy Conservation Modeling

Energy Conservation: Non-Equilibrium Thermal Model:

\[
\nabla \cdot \left( \rho \bar{V} c_p T_g \right) = \nabla \cdot \left( k_{g,\text{eff}} \nabla T_g \right) - h_v \left( T_g - T_s \right) + \sum S_i \Delta H_i \quad \text{(Gas phase)}
\]

\[
0 = \nabla \cdot \left( k_{s,\text{eff}} \nabla T_s \right) + h_v \left( T_g - T_s \right) \quad \text{(Solid phase)}
\]

- \( k_{g,\text{eff}} \) - gas phase thermal conductivity
- \( k_{s,\text{eff}} \) - solid phase thermal conductivity
- \( h_v \) - volumetric heat transfer coefficient
- \( \Delta H_i \) - enthalpy of reaction species

Non-equilibrium thermal model necessary when:

a) Difference in solid and fluid thermal properties is non-negligible
b) Significant generation in porous media – existence of hot spots
c) Low Reynolds number or flow velocities through porous media
Research Tasks – Accomplishments & Future Work

- Thermal radiation effects were investigated by coupling of radiative heat transfer and other modes of heat transfer → significant effects on the temperature and cell voltage were found warranting more detailed analysis, including experiments.

- Accurate models of species transport physics and the effective properties for reagent transport in the porous electrodes are currently being developed.

<table>
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<th>March ‘03</th>
<th>May ‘03</th>
<th>July ‘03</th>
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<tbody>
<tr>
<td>Develop and validate radiation models for different fuel cell configurations</td>
<td>Develop porous media transport models</td>
<td>Implement porous media modeling schemes</td>
<td>Linking of Fluent, ANSYS &amp; Electrochemical models</td>
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Thermomechanical Failure Analysis
Major Thermomechanical Failure Modes and Mechanism

- Warpage
- Cracks in seal
- Cracks in electrodes
- Cracks in electrolyte
- Delamination of interfaces
- Creep/fatigue of interconnects
- ?? (industry inputs)

- Thermal mismatch
- Thermal gradient (spatial)
- Thermal shock (temporal)
- Thermal diffusion
- Mass diffusion
Modeling Methodologies

**Cell Structure**

\( L > 10^{-3} \text{ m} \)

- Warpage
- Seal failure
- Seal design
- Residual stresses
- *Plate and laminate theories*

**PEN Structure**

\( 10^{-5} \text{ m} < L < 10^{-3} \text{ m} \)

- Cracks growth
- Delamination
- Spalling
- *Fracture mechanics*
- *Finite element method*

**Material Structure**

\( L < 10^{-5} \text{ m} \)

- Crack initiation
- Plasticity
- Creep
- *Micromechanics*
- *Damage mechanics*
Warpage and Stress Analysis

\[ \Delta T = -500^\circ C \]

Deflection due to temperature change

\[ w_0(x) = \frac{(A_{11} + E_s h)M_0 - B_{11}N_0}{2[B_{11} - (D_{11} + aE_s h^2)(A_{11} + E_s h)]}(a^2 - x^2) \]

Max. deflection vs. seal stiffness

Max. cell stress vs. seal stiffness
Effect of Graded Anode

Porosity in anode
- 10%
- 50%

Max. cell stress vs. seal stiffness

Max. deflection vs. seal stiffness

- Uniform anode
- Graded anode
Finite Element Analysis

Finite element mesh

Deformed shape

In-plane normal stress ($\sigma_x$)

Out-of-plane normal stress ($\sigma_y$)

Shear stress ($\sigma_{xy}$)
Blister vs. Edge Delamination

\[ \sigma_c = 1.2235 \frac{E}{1-\nu^2} \left( \frac{h}{a} \right)^2 \]

\[ G = \frac{(\Delta T \Delta \alpha)^2 Eh}{(1-\nu)[1 + 0.9021(1-\nu)]} \left[ 1 - \frac{1.2235}{\Delta T \Delta \alpha (1+\nu) \left( \frac{h}{a} \right)^2} \right]^2 \]

- Relationships between processing temperature, electrolyte layer thickness and critical flaw size
- Comparison of energy release rate between edge and blister delamination
Effective Properties of Porous Electrodes

\[
E = \frac{2(1-c)(5v_0 - 7)E_0}{2(5v_0 - 7) + c(13 - 2v_0 - 15v_0^2)} \\
E_0 = \frac{9K_0}{1 + 3K_0/\mu_0} \\
\nu = \frac{2(10v_0^2 - 9v_0 - 7) + c(25v_0^2 + 6v_0 - 19)}{2(5v_0 - 7) + c(15v_0^2 + 2v_0 - 13)} \\
\nu_0 = \frac{1 - 2\mu_0/3K_0}{2 + 2\mu_0/3K_0}
\]

Input:
Properties and volume fractions of Ni, LSM and YSZ and porosity

Output:
Effective properties of Ni/YSZ and LSM/YSZ

Model prediction

Experimental data (E. Lara-Curzio from ORNL)
Thermal Shock Induced Microcrack Initiation

Heating Source

\[ f(r) = \frac{q}{\rho c \left( \sqrt{\pi} r_0 \right)} \exp \left( -\frac{r^2}{r_0^2} \right) \]

Temp Distribution

\[ T(r, t) = \frac{q}{4\pi rk} \left[ \text{erf} \left( \frac{r}{r_0} \right) - \text{erf} \left( \frac{r}{\sqrt{r_0^2 + 4\kappa t}} \right) \right] + T_0 \]

\[ \dot{T} = \frac{\partial T(x, t)}{\partial t} = \frac{q}{\rho c \pi^{3/2} (r_0^2 + 4\kappa t)^{3/2}} \exp \left( -\frac{r^2}{r_0^2 + 4\kappa t} \right) \]

Strain Energy

\[ U_b = \frac{q^2 \alpha^2 E(1-2\nu)}{6k^2(1-\nu)^2 \pi^3 r_0^2} \]

Surface Energy

\[ U_s = 2\pi Nb^2 \gamma \]

Griffith Fracture Criterion

\[ \frac{d(U_s + U_b)}{da} = 0 \]

\[ q = \frac{3\pi^2 kr_0}{2\alpha} \left[ 1 + \frac{16(1-\nu^2)Nb^3}{9(1-2\nu)} \right] \sqrt{\frac{G_c \pi (1-\nu)}{E_0 b(1+\nu)}} \]

\[ q = \text{rate of heat generation (J/sec)} \]

\[ G_c = \text{Fracture toughness of the material} \]

\[ b = \text{crack size} \]

\[ N = \text{number of cracks per unit volume} \]

\[ k = \text{Thermal conductivity} \]

\[ \alpha = \text{Coefficient of linear thermal expansion} \]

\[ r_0 = \text{A length parameter characterizes the spatial non-uniformity of the heat source.} \]
Failure Analysis Activities for the Next 6 Months

1.1 Obtain fracture mechanics parameters for cohesive, interfacial and impinging cracks.

1.2 Model spalling phenomenon and thermal expansion induced stress during thermal transients and shock.

1.3 Identify and quantify crack path selection and crack propagation.

1.4 Implement temperature gradient as driving force for cracking. Investigate the individual and combined influences of electrochemical and mechanical load stress, as well as temperature gradients on crack initiation and propagation. Review and utilize/adapt, where appropriate, existing, available fracture mechanics models in order to advance the state-of-the-art.

1.5 Evaluate and validate the accuracy of developed fracture mechanics models using either experimental data or modeling results from PNNL/NETL/ORNL or other SECA members.
GT Project Summary

Major Accomplishments of the First 4 months
- “Slice technique” model/code to simulate the polarization curve, and reformate stream analysis model.
- Radiation models and porous models for thermal/fluid analysis.
- Models for cell deflection, thermal stresses, buckling induced delamination and thermal shock induced microcracking.

Focus for the Next 6 Months
- Enhance, improve, test and validate the models developed during the first 4 months.
- Integrate these models into a common computational testbed vehicle (a model cell) for validation.
- Transfer GT’s modeling modules to the PNNL/NETL simulation platform.