AN INTEGRATED APPROACH TO MODELING AND MITIGATING SOFC FAILURE

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Outline

• First Order Failure Criteria for SOFC PEN Structure
• Creep Modeling of YSZ/Ni Cermet
• Fracture Mechanics Analysis Tool
• Thermal Transient Modeling
First Order Failure Criteria for SOFC PEN Structure

- Objectives
- Local Failure Criteria
  - Failure Modes
  - Strength Failure Criteria
  - Fracture Failure Criteria
- Global Failure Criteria
- Analyses for Various Crack Cases
- Conclusion
Objectives

Develop first-order failure criteria to be used for the initial design, material selection and optimization against thermomechanical failure of the PEN structure in high temperature SOFCs.
Failure Modes

Material Characteristics

• Static Strength
• Fracture Toughness
• Fatigue Strength

Does a material contain flaws above certain threshold value?

No  -> Failure is strength-controlled

Yes -> Failure is fracture toughness-controlled
Strength-Based Failure Theory

Failure occurs when

\[ \bar{\sigma} = f(\sigma_1, \sigma_2, \sigma_3) = \sigma_f \]

where

\[ \bar{\sigma} = f(\sigma_1, \sigma_2, \sigma_3) \quad \text{Effective Stress} \]

\[ \sigma_1, \sigma_2, \sigma_3 \quad \text{Principle Stresses} \]

\[ \sigma_f \quad \text{Material Strength} \]
Fracture-Based Failure Theory

Fracture occurs when

\[ G = \frac{1 - \nu^2}{E} \left( K_I^2 + K_{II}^2 + \frac{K_{III}^2}{1 - \nu} \right) = G_c \]

where

- \( G \): Energy Release Rate
- \( K_I, K_{II}, K_{III} \): Stress Intensity Factors
- \( G_c \): Fracture Toughness
YSZ Electrolyte

Maximum Normal Stress Criterion \( \bar{\sigma} = \sigma_f \)

\[
\bar{\sigma} = f(\sigma_1, \sigma_2, \sigma_3) = \max \left\{ |\sigma_1|, |\sigma_2|, |\sigma_3| \right\}
\]

\( \sigma_f = 100 \sim 300 \text{ MPa} \)

Fracture Criterion \( G = \frac{1-v^2}{E} \left( K_I^2 + K_{II}^2 + \frac{K_{III}^2}{1-v} \right) = G_c \)

\( G_c = 7.8 \sim 13.7 \text{ J/m}^2 \)
YSZ/Ni Cermet

Von Mises Criterion (elevated temp) \( \bar{\sigma} = \sigma_f \)

\[
\bar{\sigma} = \sqrt{\left(\sigma_x - \sigma_y\right)^2 + \left(\sigma_y - \sigma_z\right)^2 + \left(\sigma_z - \sigma_x\right)^2 + 2\tau_{xy}^2 + 2\tau_{yz}^2 + 2\tau_{zx}^2}
\]

Maximum Normal Stress Criterion \( \bar{\sigma} = \sigma_f \)

\[
\bar{\sigma} = f(\sigma_1, \sigma_2, \sigma_3) = \max \left\{ |\sigma_1|, |\sigma_2|, |\sigma_3| \right\}
\]
\[ \sigma_f = \sigma_{YSZ} \left[ V_{YSZ} + \frac{E_{Ni}}{E_{YSZ}(1 - \nu_{Ni})} (1 - V_{YSZ} - V_{Void}) \right] \]

\( \sigma_{YSZ} = 100 \sim 300 \text{MPa} = \text{YSZ tensile strength} \)

\( E_{Ni} = \text{Ni Young's modulus} \)

\( E_{YSZ} = \text{YSZ Young's modulus} \)

\( \nu_{Ni} = \text{Ni Poisson's ratio} \)

\( V_{YSZ} = \text{YSZ Volume fraction} \)

\( V_{Void} = \text{Void Volume fraction} \)
Global Failure Criteria

Warpage Criterion

\[ W < W_c \]

Curvature Criterion

\[ \rho < \rho_c \]

\[ \rho = \frac{1}{R} \]
Implementation

- Based on material/geometry parameters to compute $W_c$ and $\rho_c$
- Measure $W$ or $\rho$ of each cell after sintering
- Compare the measured $W$ with $W_c$ or $\rho$ with $\rho_c$
Crack Types

A – crack in the cathode
B – crack in the anode
C – delamination crack between the cathode and electrolyte
D – delamination crack between the anode and the electrolyte
E – blister crack on the anode/electrolyte interface
F – crack in the electrolyte
Max. Allowable Warpage

\[ \frac{W_c}{L} = Y \sqrt[2]{\frac{G_c}{h_e E_e}} \left( \frac{L}{h_e} \right) \]

- \( G_c \) = fracture toughness
- \( h_e \) = electrolyte thickness
- \( E_e \) = modulus of electrolyte

<table>
<thead>
<tr>
<th>Crack</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crack A</td>
<td>( Y = \left( \frac{h_2^3 E_2}{16 H^2 E_3} \right)^{1/2} \left[ \left( \frac{\Delta \alpha}{Q(1 - \nu_3)} \right)^2 + \left( \frac{t_4 - a}{2} \right)^2 \right]^{-1/2} )</td>
</tr>
<tr>
<td>Crack C</td>
<td>( Y = \left( \frac{h_2^3 E_2}{16} \right)^{1/2} \left( \frac{c_3 F_2}{16 h_3^3} Q_1^{-2} + \frac{4 h_3 (\Delta \alpha_2)^2 F_1}{c_3} Q^{-2} \right)^{-1/2} )</td>
</tr>
<tr>
<td>Crack D</td>
<td>( Y = \left( \frac{h_2^3}{16 \pi a E_2} \right)^{1/2} \left[ \left( \frac{\Delta \alpha}{Q(1 - \nu_2)} \right)^2 + \left( \frac{h_1 - h_3}{2} \right)^2 \right]^{-1/2} )</td>
</tr>
<tr>
<td>Crack E</td>
<td>( Y = \left( \frac{h_2^3 E_2}{16 h_2} \right)^{1/2} \left( \frac{c_{ee} F_2}{16 h_{ee}^3} Q_1^{-2} \rho^2 + \frac{4 h_{ee} (\Delta \alpha)^2 F_1}{c_{ee}} Q^{-2} \right)^{-1/2} )</td>
</tr>
<tr>
<td>Crack F</td>
<td>( Y = \frac{Q h_2 \sqrt{h_2 E_2}}{4 \Delta \alpha} \sqrt{\left( \frac{1}{P_1} + \frac{P_1 P_2^2}{G_c} \right)} )</td>
</tr>
</tbody>
</table>
Implementation

Definition of Variables:

✓ See our monthly report or e-mail jianmin.qu@me.gatech.edu

Basic Assumptions:

✓ Linear elastic fracture mechanics

Implementation:

✓ A FORTRAN code

Material Properties Needed:

✓ Elastic moduli
✓ Coefficient of thermal expansion
✓ Fracture toughness

Other Parameters needed:

✓ Layer thickness
✓ Warpage (curvature)
Materials Properties

<table>
<thead>
<tr>
<th></th>
<th>Young’s Modulus (GPa)</th>
<th>Poisson’s Ratio</th>
<th>CTE(10^-6/°C)</th>
<th>Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode</td>
<td>90</td>
<td>0.3</td>
<td>11.7</td>
<td>75</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>200</td>
<td>0.3</td>
<td>10.8</td>
<td>15</td>
</tr>
<tr>
<td>Anode</td>
<td>96</td>
<td>0.3</td>
<td>11.2</td>
<td>500</td>
</tr>
</tbody>
</table>

Considering sintering process, the set of materials in table will result in

- tensile stress in cathode;
- compressive stress in electrolyte;
- compressive stress in anode;
Average in-Plane Stress in the PEN Layers

- Stress free at 800°C
- No-creep
- NiO reduction results in 0.1% vol. shrinkage
Numerical Examples of Max. Allowable Warpage

<table>
<thead>
<tr>
<th></th>
<th>Crack A</th>
<th>Crack C</th>
<th>Crack D</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a = 0.01h_3)</td>
<td>4.63e-3</td>
<td>3.87e-3</td>
<td>2.01e-3</td>
</tr>
<tr>
<td>(a = 0.05h_3)</td>
<td>2.08e-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a = 0.1h_3)</td>
<td>1.48e-3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a = 0.2h_3)</td>
<td>1.06e-3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Crack C is the limiting factor, unless crack A is larger than 5% of the cathode thickness.
Statistical Consideration

Failure theories have the following form:

Failure occurs when $\Sigma > \Sigma_f$

where $\Sigma$ is the “stress” (e.g., max. normal stress, Mises stress, or SIFs, max. warpage, etc.) and $\Sigma_f$ is the “strength” (e.g., yield strength, fracture toughness, etc.)

Both $\Sigma$ and $\Sigma_f$ can be random variables with certain distributions, such normal distribution, Weibull distribution, etc.
Assume:

\[ g(\sigma) = \text{distribution of stress}; \quad g_f(\sigma) = \text{distribution of strength} \]

The probability of failure at a given stress \( \sigma \) is

\[ \int_{-\infty}^{\sigma} g_f(x) dx \]

The probability of failure for a given stress distribution \( g(\sigma) \) is

\[ p_f = \int_{-\infty}^{\infty} g(\sigma) \left[ \int_{-\infty}^{\sigma} g_f(x) dx \right] d\sigma \]
Example (Normal Distributions)

Strength distribution

\[
g_f(\sigma) = \frac{1}{s_f \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\sigma - \bar{\sigma}_f}{s_f} \right)^2 \right]
\]

Stress distribution

\[
g(\sigma) = \frac{1}{s \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{\sigma - \bar{\sigma}}{s} \right)^2 \right]
\]

\(s = \text{Standard deviation}\)

\(\bar{\sigma} = \text{Mean value}\)

\[
\int_{-\infty}^{\infty} g(\sigma)d\sigma = 1
\]

\[
p_f = \frac{1}{2s \sqrt{2\pi}} \int_{-\infty}^{\infty} \text{Exp} \left[ -\left( \frac{\sigma - \bar{\sigma}}{s \sqrt{2}} \right)^2 \right] \text{Erfc} \left[ \frac{\bar{\sigma}_f - \sigma}{s_f \sqrt{2}} \right] d\sigma
\]
# Failure Probability

<table>
<thead>
<tr>
<th>$\bar{\sigma}_f / \bar{\sigma}$</th>
<th>$s / \bar{\sigma}_f = s_f / \bar{\sigma}_f$</th>
<th>$p_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor of Safety</td>
<td>Deviation</td>
<td>Failure Probability</td>
</tr>
<tr>
<td>1.0</td>
<td>any value</td>
<td>0.5</td>
</tr>
<tr>
<td>2.0</td>
<td>0.2</td>
<td>$3.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>5.0</td>
<td>0.2</td>
<td>$2.3 \times 10^{-4}$</td>
</tr>
<tr>
<td>10.0</td>
<td>0.2</td>
<td>$7.3 \times 10^{-5}$</td>
</tr>
<tr>
<td>1.5</td>
<td>0.1</td>
<td>$9.2 \times 10^{-3}$</td>
</tr>
<tr>
<td>2.0</td>
<td>0.1</td>
<td>$2.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>3.0</td>
<td>0.1</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>4.0</td>
<td>0.1</td>
<td>$5.7 \times 10^{-8}$</td>
</tr>
<tr>
<td>1.5</td>
<td>0.05</td>
<td>$1.2 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>0.05</td>
<td>$7.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>1.5</td>
<td>0.02</td>
<td>$2.3 \times 10^{-32}$</td>
</tr>
</tbody>
</table>
\[ S = S_f \]
Summary
- First Order Failure Criteria

• Local and global failure criterion were established. These criterion may be easily used to aid the initial design, material selection and optimization of SOFCs.
• Using the local failure criteria, the user can predict (estimate) the potential material failure
• Using the global failure criteria, the user can predict whether a cell can survive the stacking assembly process
A Numerical Simulation Tool for Fracture Analysis in Solid Oxide Fuel Cells

\[ K = K_I + iK_{II} \equiv (\text{applied stress}) \times FL^{1/2-i\varepsilon} \]
Significance of SIFs

1. Will the crack grow?

\[ \frac{1}{E^*} \frac{K \bar{K}}{\cosh^2 (\pi \epsilon)} + \frac{K_{II}^2}{2 \mu^*} = G_{ic} \]

2. In what direction? (What is mode mixity?)

\[ \psi = \tan^{-1} \left[ \frac{\text{Im}[K L_i^e]}{\text{Re}[K L_i^e]} \right] \]
Computing Fracture Parameters Using Volume Integrals

\[
I = G_{\text{int}} = -\int_V \left( P_{jk}^\text{int} \frac{\partial q_j}{\partial x_k} + \frac{\partial P_{kj}^\text{int}}{\partial x_k} q_j \right) dV
\]

Virtual crack growth (Q)

\[
P_{jk}^\text{int} = \sigma_{mn} \varepsilon_{mn}^{\text{aux}} \delta_{jk} - \sigma_{ik} \frac{\partial u_i^{\text{aux}}}{\partial x_j} - \sigma_{ik}^{\text{aux}} \frac{\partial u_i}{\partial x_j}
\]

Strain Energy

Stress and spatial derivatives of displacements

\[
P_{kj}^\text{int} \frac{\partial}{\partial x_j} = \sigma_{ij} \varepsilon_{ij,k}^{\text{aux}} - \sigma_{ij} u_{j,ik}^{\text{aux}} - \sigma_{ij}^{\text{aux}} u_{j,k} - \alpha \sigma_{ii}^{\text{aux}} \theta_{,k}
\]

Curvilinear

Temperature

\[u, \sigma, \text{ and } \varepsilon \text{ from FEM}
\]

\[u^{\text{aux}}, \sigma^{\text{aux}}, \text{ and } \varepsilon^{\text{aux}} \text{ analytical} \]
• Pointwise Value

\[ I(s) = \frac{\bar{I}}{\int_{L_c} \Delta a(s) ds} \]

\[ I(s) = \frac{2}{E^* \cosh^2 (\pi \epsilon)} \left[ K_I K_I^{\text{aux}} + K_{II} K_{II}^{\text{aux}} \right] + \frac{1}{\mu^*} K_{III} K_{III}^{\text{aux}} \]

• To find \( K_I \) by setting
  
  • \( K_I^{\text{aux}} = 1 \)
  
  • \( K_{II}^{\text{aux}} = K_{III}^{\text{aux}} = 0 \)

\[ K_I = \frac{I(s)}{2} E^* \cosh^2 (\pi \epsilon) \]
**A Penny-Shaped Crack on Electrolyte/Anode Interface**

**Half Model - Interface Penny Crack**

Temperature gradient parallel to crack plane
Temperature Gradient Parallel to the Crack Plane

ANSYS Model

FMA Volume

Anode

Electrolyte

\[ T_{\text{max}} \]

\[ T = 0^\circ C \]

\( \sigma_y \) (MPa)

Full Sized Penny Shaped Crack
$K_I$, $K_{II}$, $K_{III}$ Variation Along Crack Front
Summary
-- Fracture Mechanics Analysis Tool

Fracture Mechanics Analysis Tool:
• Based on volume integral (requires less mesh density)
• Written in MatLab language (run on both Window and Unix)
• Add-on to any commercial FEM codes (requires less processing time)

Capabilities:
• Calculate energy release rate and individual stress intensity factors
• 2D and 3D planar cracks of arbitrary shapes
• Homogeneous and interfacial cracks
• Arbitrary mechanical and thermal loading
Transient Heat Transfer Analysis:
Convective-Conductive Heating of SOFC
SOFC unit cell Transient Thermal Modeling

Key Question/Focus: Provide model-based design tool(s) to assess how quickly a cell/stack can be heated without excessive (damaging) thermomechanical gradients?

**Design/Model Outputs:**
- total time required for heating
- max temperature spatial gradient
- max temperature time-derivative

**Model Inputs:**
- size of components; thickness of layers
- thermal properties of components
- boundary conditions; heating strategies

**Multi-Level Methodology:**
- 3-D CFD modeling (e.g. FLUENT)
- Reduced order numerical modeling
- Simplified order analytical modeling
Simplified Analytical Model/Design Tool: Key Ideas & Assumptions

Heating by hot air supplied at prescribed time-dependent inlet temperature

- 1-D temperature profile in each component $T_{layer} = f(z,t)$ only
- Constant velocity plug flow in channel
- Constant properties
- Radiation neglected (to be included later)
- Adiabatic boundaries (no heat losses)
1st order 1-D Purely Convective Heating Model

Key Assumptions:
- thermally thin cell materials (i.e. no energy storage)
- thermal equilibrium between air and channel walls

Governing Equation

\[
\frac{\delta T}{\delta t} + u \frac{\delta T}{\delta z} = 0
\]

B.C. & I.C.

\[
T(z = 0, t) = f(t) \\
T(z, t = 0) = T_o
\]

Closed-form analytical solution:

\[
T(z, t) = \begin{cases} 
T_o & \text{for } z > ut \\
 f\left(t - \frac{z}{u}\right) & \text{for } z \leq ut
\end{cases}
\]
2\textsuperscript{nd} Order Convective-Conductive Heating Model

InterConnect$_1$: \[
\left(\rho c_p A\right)_{IC1} \frac{\partial T_{IC1}}{\partial t} = (kA)_{IC1} \frac{\partial^2 T_{IC1}}{\partial z^2} + h P_{g-IC1} \left( T_g - T_{IC1} \right) - \frac{P_{IC1-C}}{R_{IC1-C}} \left( T_{IC1} - T_C \right)
\]

Air Channel (gas): \[
\left(\rho c_p A\right)_{g} \left[ \frac{\partial T_g}{\partial t} + u \frac{\partial T_g}{\partial z} \right] = (kA)_{g} \frac{\partial^2 T_g}{\partial z^2} - h P_{g-C} \left( T_g - T_C \right) - h P_{g-IC1} \left( T_g - T_{IC1} \right)
\]

Cathode: \[
\left(\rho c_p A\right)_{C} \frac{\partial T_C}{\partial t} = (kA)_{C} \frac{\partial^2 T_C}{\partial z^2} + h P_{g-C} \left( T_g - T_C \right) + \frac{P_{IC1-C}}{R_{IC1-C}} \left( T_{IC1} - T_C \right) - \frac{P_{C-E}}{R_{C-E}} \left( T_C - T_E \right)
\]

Electrolyte: \[
\left(\rho c_p A\right)_{E} \frac{\partial T_E}{\partial t} = (kA)_{E} \frac{\partial^2 T_E}{\partial z^2} + \frac{P_{C-E}}{R_{C-E}} \left( T_C - T_E \right) - \frac{P_{E-A}}{R_{E-A}} \left( T_E - T_A \right)
\]

Anode: \[
\left(\rho c_p A\right)_{A} \frac{\partial T_A}{\partial t} = (kA)_{A} \frac{\partial^2 T_A}{\partial z^2} + \frac{P_{E-A}}{R_{E-A}} \left( T_E - T_A \right) - h P_{f-A} \left( T_f - T_A \right) - \frac{P_{A-IC2}}{R_{A-IC2}} \left( T_A - T_{IC2} \right)
\]

FuelChannel: \[
\left(\rho c_p A\right)_{fuel} \frac{\partial T_{fuel}}{\partial t} = (kA)_{fuel} \frac{\partial^2 T_{fuel}}{\partial z^2} + h P_{f-A} \left( T_f - T_A \right) + h P_{f-IC2} \left( T_f - T_{IC2} \right)
\]

Applying thermal equilibrium between flow channels and components; model reduces to a single equation dependent only on effective Peclet number and inlet temperature function!

\[
\frac{\partial T}{\partial t} + \frac{\partial T}{\partial z} = \frac{1}{Pe} \frac{\partial^2 T}{\partial z^2}
\]

\[
Pe = \frac{u_{eff} L}{\alpha_{eff}} = \frac{\text{advection}}{\text{conduction}}
\]

\[
B.C. & I.C.: \ T(0,t) - Pe \frac{\partial T}{\partial z}(0,t) = F(t); \quad \frac{\partial T}{\partial z}(1,t) = 0; \quad T(z,0) = 1
\]

\textbf{Closed-form analytical solution has been obtained!!!}
Results: Comparison of 1\textsuperscript{st} and 2\textsuperscript{nd} order models

Key advantages demonstrated:

- Computationally efficient, analytical models capture key physics of heating process!
- 1\textsuperscript{st} order model is the limiting case of 2\textsuperscript{nd} order model ( Pe \rightarrow large ) provided it is properly re-scaled. The guidelines for re-scaling have been developed!

**Design Maps:** Dimensionless plots of temperature gradient and time-derivative vs. total heating time for various rates of inlet temperature rise (K) and Peclet numbers (Pe).
Summary
-- Convective-Conductive Heating of SOFC

- Developed reduced order solutions for transient thermal analysis.
- Obtained closed-form analytical solutions that provide a relationship between heating rate and the spatial temperature gradient.
- Obtained closed-form analytical solutions that provide a relationship between rate and the temporal temperature gradient.
Future Work

- Refine and validate the first order failure criteria
- Develop and implement the global-local computational algorithm in MARC
- Validate and implement a suitable FEA tool for analysis of fracture failure in the context of various pre-existing flaws within SOFC cells under various operating conditions.
- Validate and implement a computationally-efficient transient thermal model.