SECA Core Program – Recent Development of Modeling Activities at PNNL

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January 27, 2005
Design Tool
Solid Modeling & Electrochemistry, Flow, Thermal & Stress Calculation

- **Mentat-FC**: Graphical User Interface for flexible finite element model generation.
- **PNNL-EC**: Finite element based electrochemistry, flow and heat transfer solution.
- **Marc**: Finite element stress analysis with temperatures from PNNL-EC.
CAD file specification menu

User Defines
Inlet and Outlet
Fuel and Air
Manifold Ports

Done in collaboration with Doug Malcolm
and Zach Pursell, MSC Software
**Mentat-FC: Comparison of the Phase 1 and Phase 2 Models**

**Phase 1 Model**
- Fixed SOFC design
- Meshed from dimensional parameters
- Compatible with *PNNL-EC* FE model
- Used for parametric design studies

**Phase 2 Model**
- Meshed from user CAD files
- Accepts existing FE meshes
- Compatible with *PNNL-EC* FE model
- Quick generation of very complex models
Mentat-FC: Model Generation from CAD Geometries

- Finite element grid directly from CAD geometry.
- Generic ACIS CAD format used.
- Layers identified by name.
- Material properties assigned to components from the database.
- Contact and boundary conditions are defined.
Mesh from CAD
67,919 Nodes
30,629 elements
**Mentat-FC Imports Existing Finite Element Grids**

- User provides meshes identified for individual components.
- Can mix and match with CAD generated components.
- Fuel and Air cavities must also be meshed.
- Incompatible meshes are allowed through contact.
- Finite element based.
- Fast 2-D flow and 1-D electrochemistry solver.
- Incompatible Meshes.
  - 67,919 Nodes.
  - 30,629 elements.
- 30 minute solution to Steady State on one processor.
- Algorithm works equally well in parallel.
Marc Stress Results

Electrolyte

Pen Seal

Principal Stress Max
The Goal of this model development work is to:

- Use what we know about steam-methane reformation (SMR) kinetics on Nickel anode materials
- Apply modeling tools capable of predicting fuel use and the distribution of temperature on an SOFC
- Provide direction - through simulations - for how to best control methane conversion to:
  - Minimize the endothermic impact of reformation
  - Optimize distribution of temperature
  - Minimize thermal stress
Modeling Subject: Typical Cross-Flow Cell Design

- 57,212 Computational Cells
- Cyclic Boundary Conditions Top & Bottom
- Natural Convection and Gap Radiation to containment walls
- Fixed Mass inflow conditions with adjustable temperature to enable control of average cell temperature to 750°C
- Fuel Composition (Baseline Case with No Methane):
  - 48.5%H₂, 3%H₂O, 1%CO, 1%CO₂, and 46.5%N₂
  - "Fuel Inflow" = 4.7E-4 mol/s (H₂)
- Fuel Composition (SMR Cases):
  - 13%H₂, 59%H₂O, 18%CH₄, 10%N₂
  - "Fuel Inflow" = 4.7E-4 mol/s
- Electrochemical Performance for 110.24 cm² Cell: 0.53 A/cm² (38.6 A) at 0.7 Volts at ~64% Fuel Utilization

\[
\begin{align*}
CH_4 + H_2O & \rightarrow 3H_2 + CO \\
CO + H_2O & \rightarrow H_2 + CO_2 \\
H_2 + 1/2O_2 & \rightarrow H_2O
\end{align*}
\]

1 mole of CH₄ => 4 moles of “fuel.” Also, inflowing CO converts to fuel.

3-D Model with fuel, air, and separator plates removed
Methane Reformation Kinetics

\[ (-r_{CH_4})(mol / g_{cat} / s) = 2.188 \times 10^8 e^{-\frac{94.95 \times 10^3}{RT}} C_{CH_4} C_{CO_2}^{-0.0134} \]

\{T, K\} \quad \{R, 8.314 \text{ J/mol-K}\} \quad \{C, \text{ mol/cc}\} \quad \{E, \text{ J/mol}\}

- Methane conversion rate for Ni-YSZ anode determined experimentally at PNNL
- Rate is 1st order with CH\(_4\) concentration.
- CO\(_2\) has slight hindering effect
- Activation Energy (E) = 94.95E3 J/mol (Baseline)
- Leading coefficient with units of moles per gram catalyst per second
  - Coefficient could also be considered in terms of exposed area of Nickel catalyst per gram bulk catalyst (cm\(^2\)/gm\(_{\text{cat}}\))
- On-Cell SMR [or Direct Internal Reformation (DIR)] can be slowed by:
  - Increase of the activation energy by some interfering reaction or other mechanism
  - Decrease of the exposed catalyst area by some form of surface masking
- The following example cases were simulated by artificially adjusting the catalyst (Ni-YSZ anode) activation energy
Results: Temperature Distributions

**Case 1:**
Baseline Case: No Methane

- **T(cell)= 750°C**
- **Range = 671 to 788°C**
- **I(cell)= 0.5302 A/cm² (58.45 A)** (64.3% utilization of 4.7mol/s)
- **V(cell) = 0.7 Volts**
- **Power = 40.9 Watts**
- **T(inflow) = 651.3°C**

**Case 2:**
Baseline SMR Activation Energy

- **T(cell)= 750°C**
- **Range = 636 to 817°C**
- **I(cell)= 0.519 A/cm² (57.22 A)** (63.5% utilization of 4.7mol/s)
- **V(cell) = 0.695 Volts** (decr V to incr i)
- **Power = 39.8 Watts**
- **T(inflow) = 735.8°C**

**Case 2a:**
SMR, E<sub>act</sub> up 20.6%

- **T(cell)= 750°C**
- **Range = 718 to 781°C**
- **I(cell)= 0.4466 A/cm² (49.23 A)** (lower utilization)
- **V(cell) = 0.695 Volts**
- **Power = 34.2 Watts**
- **T(inflow) = 744.0°C**

**Note:** Diminished ∆T

All cases are plotted at same temperature scale. Cases with temperatures in RED and or BLUE range indicate large ∆T and are not desirable.
Results: Temperature Distributions

**Case 3** (Case 2a with voltage decreased to boost current):
- $T(\text{cell}) = 750^\circ C$
- Range = 712 to 787°C
- $I(\text{cell}) = 0.52984$ A/cm² (58.41 A) (64% utilization of 4.7mol/s)
- $V(\text{cell}) = 0.641$ Volts
- Power = 37.44 Watts
- $T(\text{inflow}) = 714.9^\circ C$

**DIR case with “smoothed” temperatures**

**Case 2d:**
- SMR, Variable E.1
- $T(\text{cell}) = 750^\circ C$
- Range = 690 to 810°C
- $I(\text{cell}) = 0.4972$ A/cm² (54.81 A) (lower utilization)
- $V(\text{cell}) = 0.695$ Volts
- Power = 38.1 Watts
- $T(\text{inflow}) = 746.6^\circ C$

Gradation Case 3a

Baseline Activation Energy ($E=94950$)

+10%

+20.6%
CASE HIGHLIGHTS

Case 1:
Baseline
H₂ only
No CH₄

Case 2:
With CH₄
& Baseline
SMR activity

Case 3:
Uniformly
Decreased
Activity

<table>
<thead>
<tr>
<th>Case</th>
<th>Temperature, C</th>
<th>S₁ max, MPA Anode</th>
<th>S₁ max, MPA Seal</th>
<th>S₁ max, MPA Picture Frame</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Minimum</td>
<td>Maximum</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>671</td>
<td>788</td>
<td>25.0</td>
<td>10.1</td>
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<tr>
<td>2</td>
<td>636</td>
<td>817</td>
<td>40.0</td>
<td>10.9</td>
</tr>
<tr>
<td>3</td>
<td>712</td>
<td>787</td>
<td>11.8</td>
<td>5.9</td>
</tr>
</tbody>
</table>
Materials Testing in Support of Modeling

- Information needed to calibrate models
- Materials Database at NETL to provide information on materials properties to the SECA team
- PNNL currently concentrating on seal materials
  - G18 Glass-bulk properties, “thin film” properties
  - Mica-strength, deformation behavior, leak rates
- Additional data provided on CTE and properties of many SOFC materials
Materials Database

Solid State Energy Conversion Alliance (SECA)

Physical and Mechanical Properties of SOFC Materials & Structures
- Elastic Properties
- Monotonic Strength
- Fracture Toughness
- Residual Stresses
- High-Temperature Alloy Material Property Database
- Thermal Conductivity
- Thermal Cycling
- Thermal Shock
- Creep Deformation
- NO Reduction
- Thermal Expansion
- Links

Monotonic Strength

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Environment</th>
<th>Aging Treatment</th>
<th>Mean strength</th>
<th>Flexural Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-800</td>
<td>air</td>
<td>4 hr @ 750°C</td>
<td>data</td>
<td>data</td>
</tr>
<tr>
<td>25-800</td>
<td>air</td>
<td>1000 hr @ 750°C</td>
<td>data</td>
<td>data</td>
</tr>
</tbody>
</table>

Material: G18 glass (bulk)

Material: G18 glass (thin film)

Glass-Ceramics for Sealing Solid Oxide Fuel Cells (PDF 4.6MB)

Patents: 6,430,966 & 6,532,769

Contact: John Vettering, PNLL, (509) 372-0724
# Data Collected on Bulk G18 Glass

<table>
<thead>
<tr>
<th>Test Temperature (°C)</th>
<th>Flexural Modulus (GPa)</th>
<th>Mean Strength (MPa)</th>
<th>Std Dev Strength (MPa)</th>
<th>Maximum Strain</th>
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</thead>
<tbody>
<tr>
<td>25 (4 hr)</td>
<td>89</td>
<td>80</td>
<td>10</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>600 (4 hr)</td>
<td>26</td>
<td>83</td>
<td>15</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>700 (4 hr)</td>
<td>30</td>
<td>64</td>
<td>10</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>800 (4 hr)</td>
<td>12</td>
<td>39</td>
<td>4</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>25 (1000 hr)</td>
<td>64</td>
<td>43</td>
<td>3</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>600 1000 hr)</td>
<td>56</td>
<td>42</td>
<td>6</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>700 (1000 hr)</td>
<td>33</td>
<td>35</td>
<td>2</td>
<td>0.30-0.60%</td>
</tr>
<tr>
<td>800 (1000 hr)</td>
<td>20</td>
<td>31</td>
<td>2</td>
<td>0.30-0.60%</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Test Temperature (°C)</th>
<th>Condition (aging time @ 750 °C)</th>
<th>Elastic Modulus (GPa)</th>
<th>Shear Modulus (GPa)</th>
<th>Flexural Modulus (GPa)</th>
<th>Poisson Ratio</th>
<th>Number of tests</th>
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<td>4 hr.</td>
<td>80.5</td>
<td>31</td>
<td>89</td>
<td>0.3</td>
<td>4</td>
</tr>
<tr>
<td>25</td>
<td>1000 hr.</td>
<td>80.2</td>
<td>30.6</td>
<td>64</td>
<td>0.31</td>
<td>5</td>
</tr>
<tr>
<td>600</td>
<td>4 hr.</td>
<td></td>
<td></td>
<td>26</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>700</td>
<td>4 hr.</td>
<td></td>
<td></td>
<td>30</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>800</td>
<td>4 hr.</td>
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<td></td>
<td>12</td>
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<tr>
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<td>1000 hr.</td>
<td></td>
<td></td>
<td>56</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>700</td>
<td>1000 hr.</td>
<td></td>
<td></td>
<td>33</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>800</td>
<td>1000 hr.</td>
<td></td>
<td></td>
<td>20</td>
<td></td>
<td>6</td>
</tr>
</tbody>
</table>
Data From Seal Assembly Analogs

0.020” Crofer 22 washer (Ni brazed to 430) on both sides
Dispensed Glass

<table>
<thead>
<tr>
<th>Testing Method</th>
<th>Test Temperature (°C)</th>
<th>Mean Failure Stress (MPa)</th>
<th>Number of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tension</td>
<td>25</td>
<td>22.8</td>
<td>2</td>
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<tr>
<td></td>
<td>700</td>
<td>23.2</td>
<td>2</td>
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<tr>
<td></td>
<td>750</td>
<td>16.5</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>5.3</td>
<td>3</td>
</tr>
<tr>
<td>Torsion</td>
<td>25</td>
<td>46.7</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>50.9</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>22.8</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>11</td>
<td>6</td>
</tr>
</tbody>
</table>

Thin-film analogs to test the entire seal assembly
Failure is generally interfacial rather than in the glass itself
Mica Seal Testing

8 mil thick phlogopite mica sheets with binder; cut to fit the torsion holders. 100 psi compressive force and 0.2 psig He pressure utilized during torsion testing.
Initial Results on Mica Seals

Torsion-Leak test of Mica seals revealed that as the mica slides it may show slip-stick behavior and during the “stick” phase there might be some leakage. Preliminary tests show only small leaks.
Thermal-Mechanical Seal Damage
SOFC Rigid Seals

- Glass-ceramic materials provide cheap, hermetic sealing option
- Cracks problematic for structural integrity and leak
- Reactions can make the interfaces weak
- Seal fractures
  - Through glass layer
  - Between glass layer and scale
  - Between scale and metal interconnect
- Need predictive modeling tools
  - Begin with bulk G18
Thermal-Mechanical Seal Damage G18 Continuum Damage Model

Damage and deformation mechanisms of G18 glass

- **Behavior at T < 710°C**
  - Existence of voids
  - Linear stress/strain responses until failure
  - Failure due to growth and coalescence of a critical void

- **Behavior at T > 710°C**
  - Considerable void formation at high temp
  - Heat treatment increases void fraction
  - Imperfect bonding leading to sliding between phases
  - Visco-elastic deformation of non-crystallized phase
  - Microcracking

- **Nonlinear stress/strain responses until failure**

- **A thermodynamics-based formulation**
  - Define a damage variable that is related to the reduction of elastic modulus:
    \[ E(T, d) = E^0(T)(1 - d) \]
  - Temperature-dependent material properties are accounted for
  - The elastic deformation energy is defined as the thermodynamic potential
  - Derive the potential with respect to the strains for constitutive relations
  - Derive the potential with respect to the damage variable for the thermodynamic force
  - Dissipation criterion (Clausius-Duhem’s inequality) assumes decoupled thermal and intrinsic dissipations.
  - Damage criterion depends on a damage threshold function
  - Damage evolution law from the damage criterion and consistency conditions

- **Model Implementation**
  - A program to determine the damage threshold function using the experimental stress/strain curves
  - Implement the model into MARC via the user subroutines
  - Material input data were prepared and included into data file
Damage and failure progressions at the maximum applied displacement for a G18 glass sample subjected to 4-point bending at 800°C. Damage is more important on the top and bottom surfaces of the beam as expected. Macro cracks initiate within the loading span and near the locations where the displacement is applied. The prediction of the fracture locations has been confirmed experimentally.
Thermal-Mechanical Seal Damage Multi-Cell Stack Model

- 3-cell planar stack built by the MARC GUI
- Thermal cycle loading
  - Transient thermal response of stack using heat generated from electrochemical reactions for fuel composition and gas flow rates
  - Convective and radiation heat exchange from stack exterior
  - Thermal boundary condition histories create cyclic loading
  - Quasi-static structural solution using results of thermal solution
- Seal damage model
  - Interconnect/metal frame seals
  - Electrolyte/metal frame seals

PEN ΔT max: 150°C at steady state
PEN ΔT of 40°C occurs on shutdown
Thermal-Mechanical Seal Damage
Thermal Cycling Results

Operating Temperature

- **Bottom Seal**
  - External Leak
  - Internal Leak

- **Middle**
- **Top**

- **PEN seal** doesn’t fail
  - No leak!

Room Temperature

- **Damage accumulates**
- **Bottom seal fails due to influence of hearth and leaks expected**
- **Consistent with experiments**

**Graphs**:
- **Principal Stress (Pa)**
  - Bottom Electrolyte
  - Middle Electrolyte
  - Top Electrolyte
- **Max Normal Stress**

Pacific Northwest National Laboratory
U.S. Department of Energy
Thermal-Mechanical Seal Damage
Leak Rate Estimate Based on Damaged State

**Damage mechanisms causing leak**
- Transverse cracking → damage model
- Layer delamination → interface model

**Interface model**
- Delamination predicted by maximum normal stress criterion or critical stress criterion accounting for shears
- Interface modeled by thin layer having zero Poisson’s ratio and elastic moduli averaged from constituent layers

**Leak through seal (damage model)**
- Occurs when damage variable attains critical value, $D_{\text{crit}}$
- Maximum leak rate, $\mu_{\text{max}}$ attained at seal failure ($D = D_{\text{sat}}$)
- $\mu_{\text{max}}$ computed from pressure differences

**Leak via delamination (interface model)**
- Leak occurs when the delamination criterion is satisfied
  \[ f(\sigma_n, \tau) = \sqrt{\left(\frac{\sigma_n}{\sigma_f}\right)^2 + \left(\frac{\tau}{\tau_f}\right)^2} \]
- Rate computed from pressure differences and crack opening area

**Application to stack in progress**
Coarse Design Methodology

Provide probabilistic-based design tool for fuel cell designers:

- Utilize design software developed: PNNL-EC + MARC
- Achieve consistent failure probability levels for various fuel cell components
  - Eliminate design redundancy

Provide designers with directions for design improvement

Provide directions for experimental material property measurement activities:

- Critical properties
- Non-critical properties
Approach

Step 1: Component level design sensitivity study
- Pick nominal design parameters-current design
- Small perturbation or range of uncertainty (as in the case of electrochemical performance)
- Generate small scale finite element models using the design tool developed
- Run sensitivity study
- Rank sensitivity results and identify critical parameters for each component

Step 2: Characterization of probability distributions on critical component level variables:
- Material strength
- Manufacturing tolerance
Technical Approach-Cont’d

- **Step 3:** Characterization of probability distributions on loads
  - Thermal
  - Electrochemistry
  - Boundary conditions

- **Step 4:** Component-based reliability analyses and model calibration:
  - Construct response surfaces for each component:
    - PEN, Seal, Interconnect, etc…
  - Determine the failure probability of current design
  - Determine the appropriate resistance and load factors to achieve design with a desired reliability level

\[
\beta = \frac{\bar{R}_i - \bar{S}_i}{\sqrt{\sigma^2_{R_i} + \sigma^2_{S_i}}}
\]
Results: Evaluation of Current Design under Steady State Operating Condition

<table>
<thead>
<tr>
<th>Anode Thickness (microns)</th>
<th>Load: Fuel flow rate (gmol/sec)</th>
<th>Failure Probability (Pf)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Electrolyte</td>
<td>Seal</td>
</tr>
<tr>
<td>600</td>
<td>0.00272</td>
<td>&lt;1.0E-5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.067</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.955</td>
</tr>
<tr>
<td>0.00068</td>
<td>&lt;1.0E-6</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0002</td>
</tr>
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</table>
Results: Design Look-up Table – Steady State Operation

Design target: safe index $\beta=3$, failure probability $P_f=0.0014$

\[ \text{stress} < \alpha \times \text{strength} \]

<table>
<thead>
<tr>
<th>Anode Thickness (microns)</th>
<th>Load: Fuel flow rate (gmol/sec)</th>
<th>Strength Reduction Factor $\alpha$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Anode</td>
<td>Electrolyte</td>
</tr>
<tr>
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<td>0.59</td>
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<td>0.64</td>
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<tr>
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<td>0.00272</td>
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<td>0.000907</td>
<td>0.60</td>
<td>0.32</td>
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<tr>
<td></td>
<td>0.00068</td>
<td>0.65</td>
<td>0.3</td>
</tr>
</tbody>
</table>
Coarse Design Methodology

- This methodology utilizes the developed FEM tool
- This methodology uses much of the “Isolated” test data that has been generated
  - Bulk glass properties, thin seal properties
  - Anode, cathode, electrolyte
- The coarse design method will guide the experimental work on instrumented stacks
- It provides one fuel cell design that leads to compatible level of failure probabilities for various fuel cell components:
  - Improve reliability
  - Reduce weight
  - Eliminate design redundancy
- Provides directions for design improvement and material property improvement
Summary

GUI Development

- Using Mentat-FC, PNNL-EC and Marc, an example SOFC has been analyzed starting with CAD files directly through to stress analysis.
- Algorithms are efficient for rapid analysis and extension to transient thermal-mechanical analysis.
  - Mesh generation \(\sim 1.5\) hours
  - PNNL-EC solution = 30 min.
  - Marc stress solution = 3 min.
- We are ready to work with industry designs.

On-Cell Reforming

- Implementation uses latest Methane Reformation Kinetics Model
Summary

- Demonstrated capability to arbitrarily adjust conversion activity within multiple zones on a single cell
- Results show less stress in Case 3 with uniformly decreased reformation activity (remove this bullet if previous slide is removed)
- Capability enables prediction of optimal activity with focus on achieving:
  - Controlled temperature distribution
  - Diminished thermal stresses

► Completed studies on glass seals and the experimental data is available on the website.

► Thermal Cycling and Failure Analysis
  - Complete for G18 seals

► Coarse Design Methodology