SECA Core Program – Recent Development of Modeling Activities at PNNL

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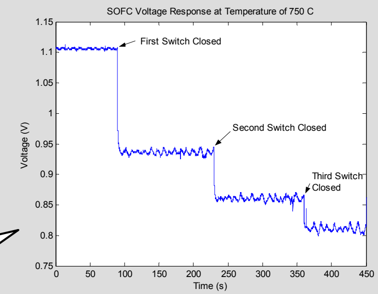
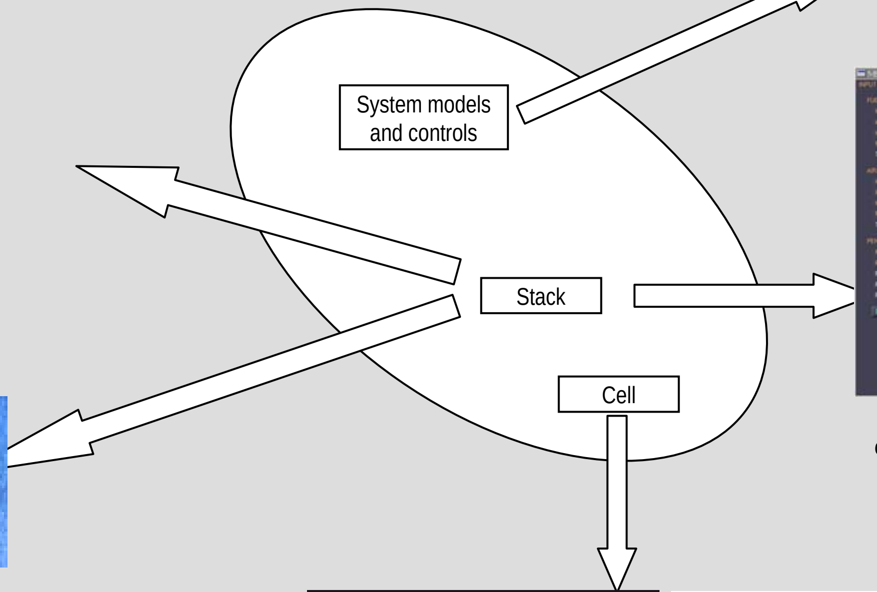
January 27, 2005

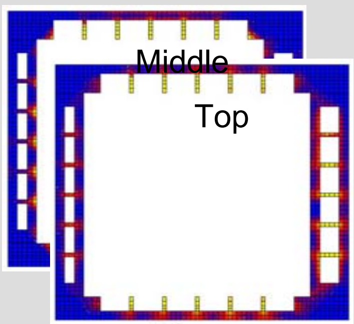
Integrated Modeling of Solid Oxide Fuel Cells

Consolidated Computational Modeling for SECA

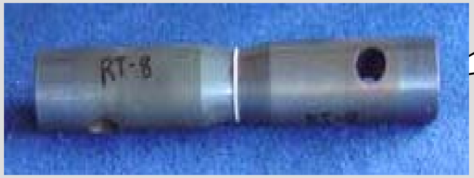
Training



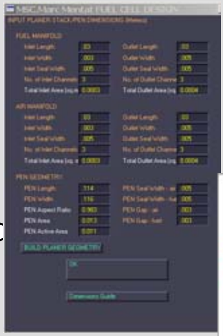




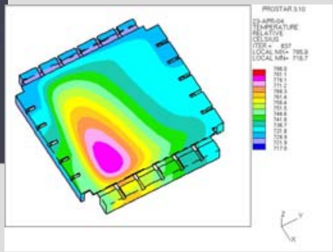
Thermo-mechanical cycling



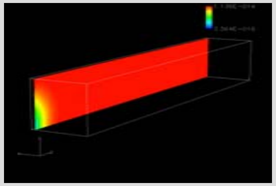
Experimental data for models (seals)



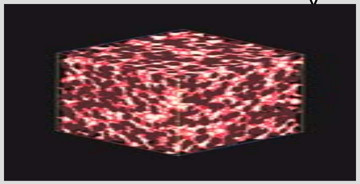
GUIs for continuum EC

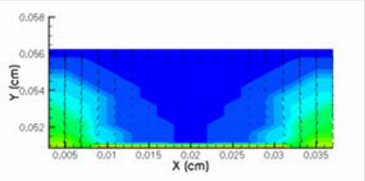


On Cell Reforming



Cr formation and transport



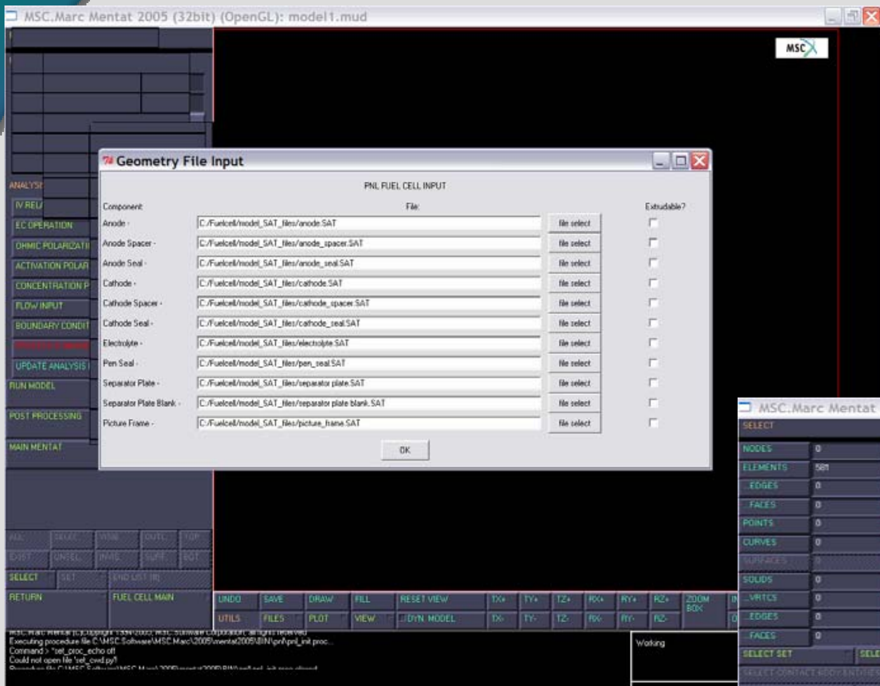


Microstructural electrochemistry
Fracture and Electrochemistry

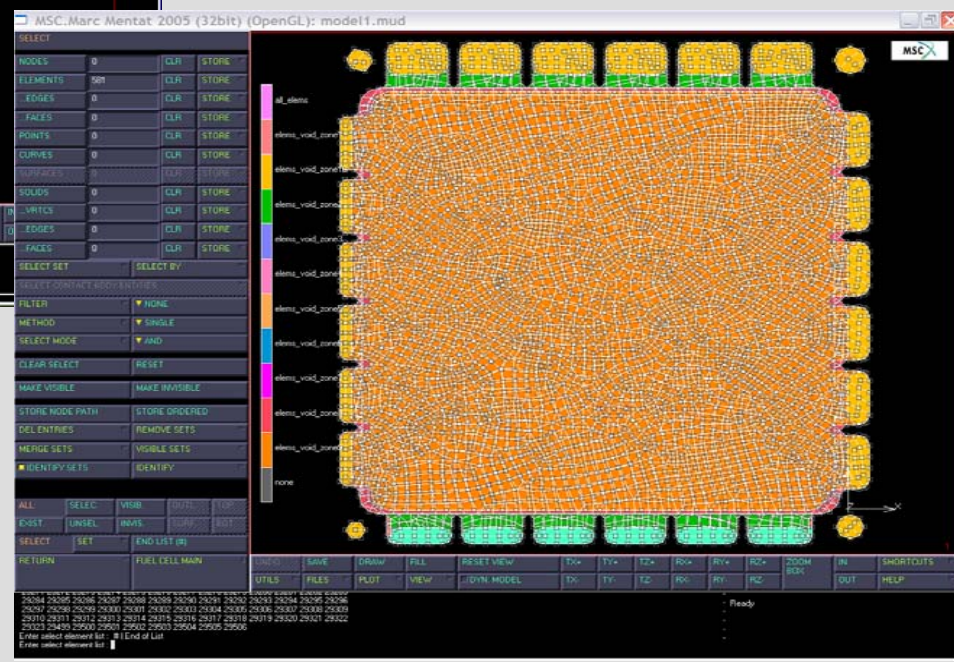
Design Tool
Solid Modeling & Electrochemistry, Flow, Thermal & Stress Calculation

- *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

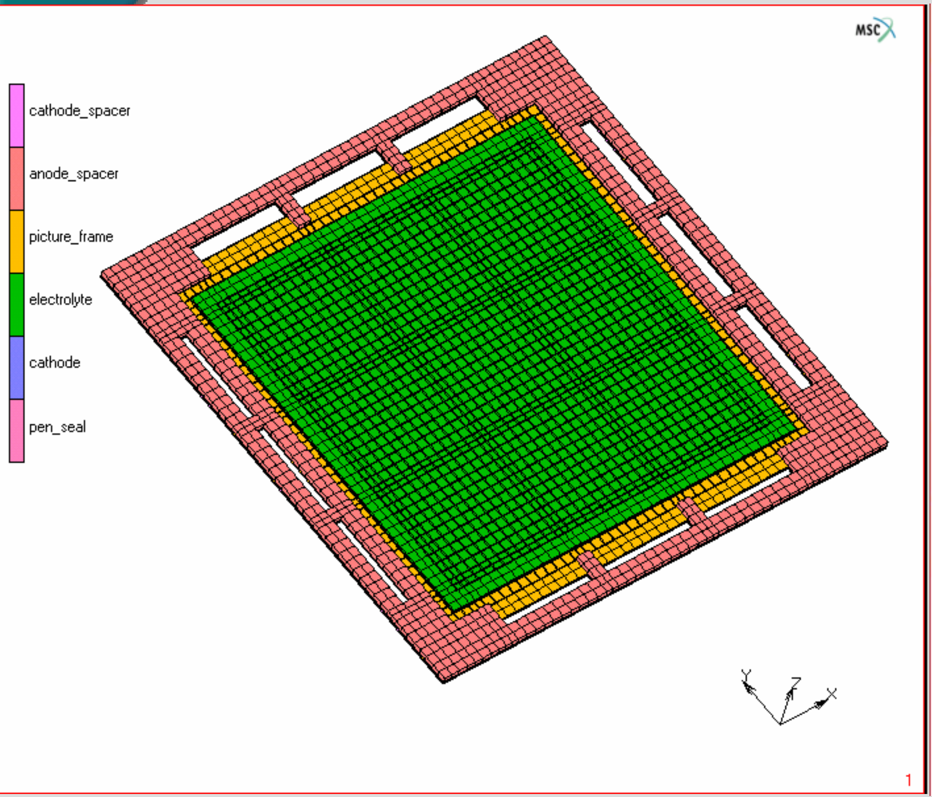


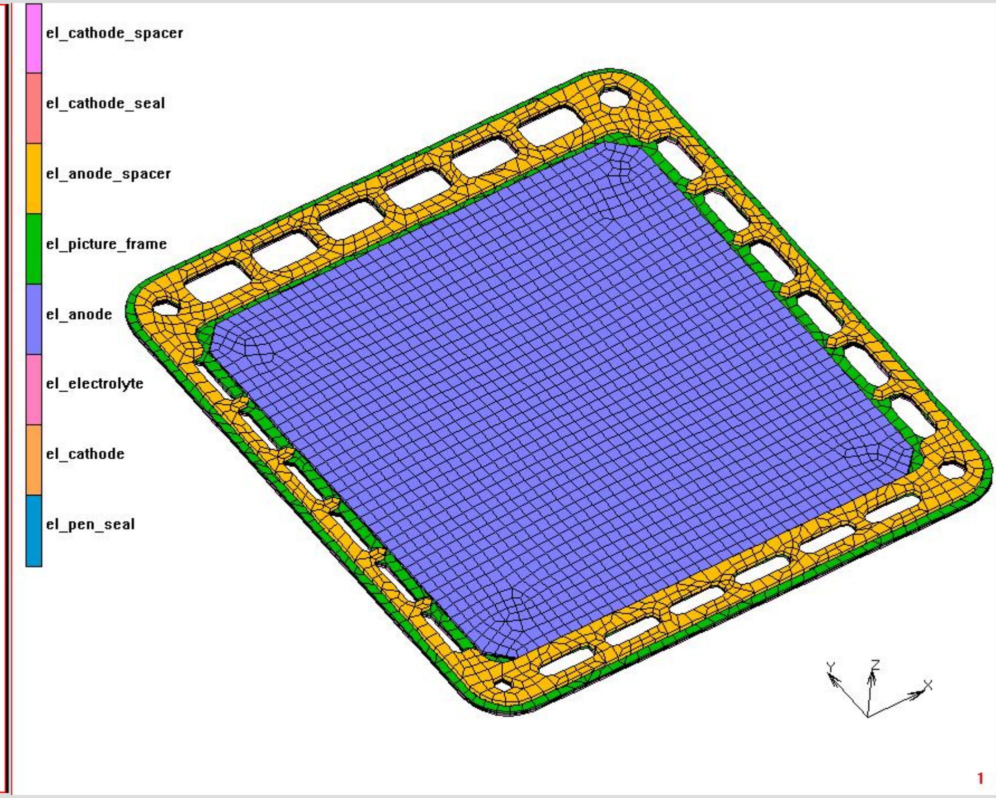
User Defines Inlet and Outlet Fuel and Air Manifold Ports



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

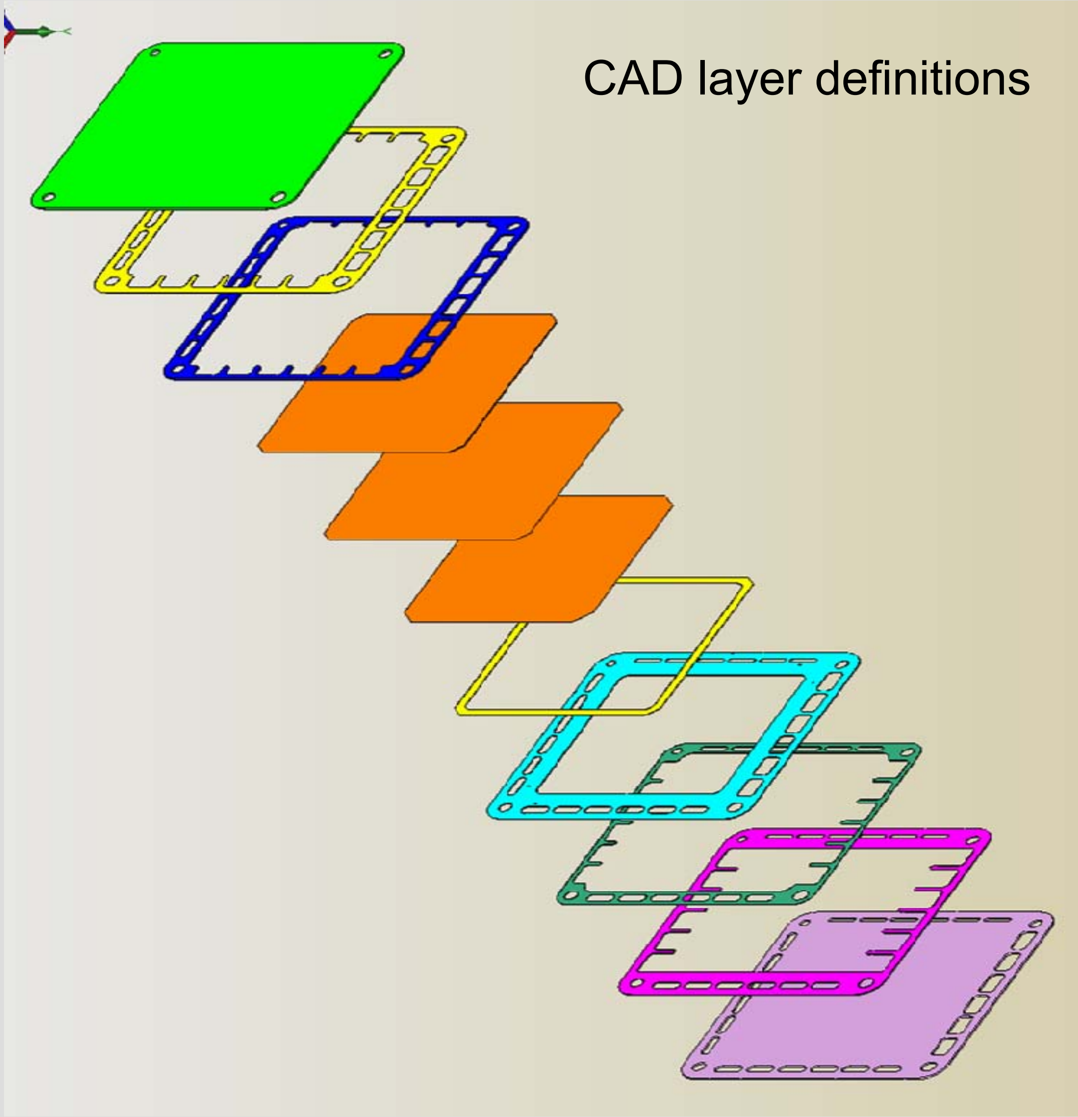
- Fixed SOFC design
- Meshed from dimensional parameters
- Compatible with *PNNL-EC* FE model
- Used for parametric design studies

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

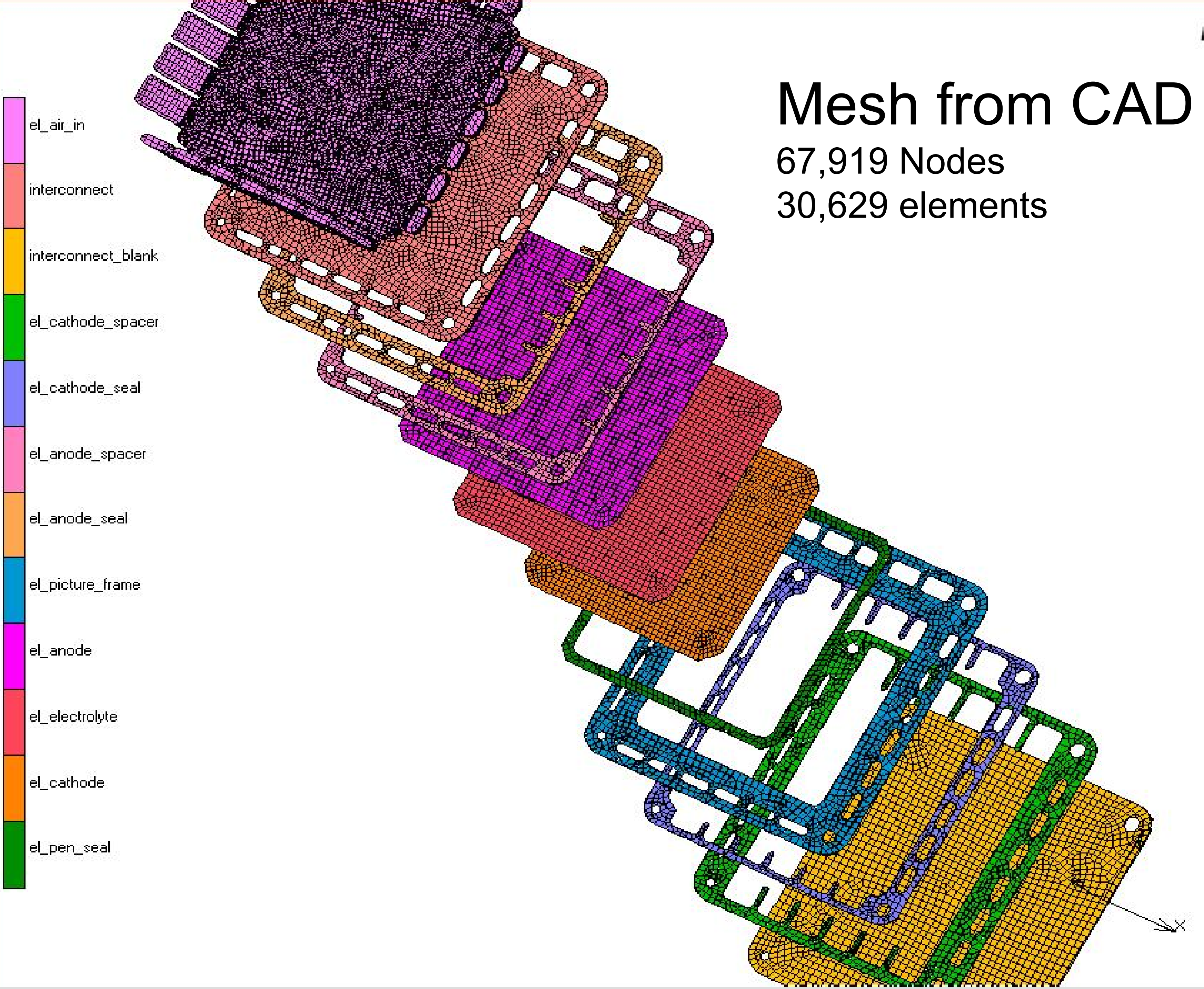
- Finite element grid directly from CAD geometry.
- Generic ACIS CAD format used.
- Layers identified by name.
- Material properties assigned to components from the database.
- Contact and boundary conditions are defined.



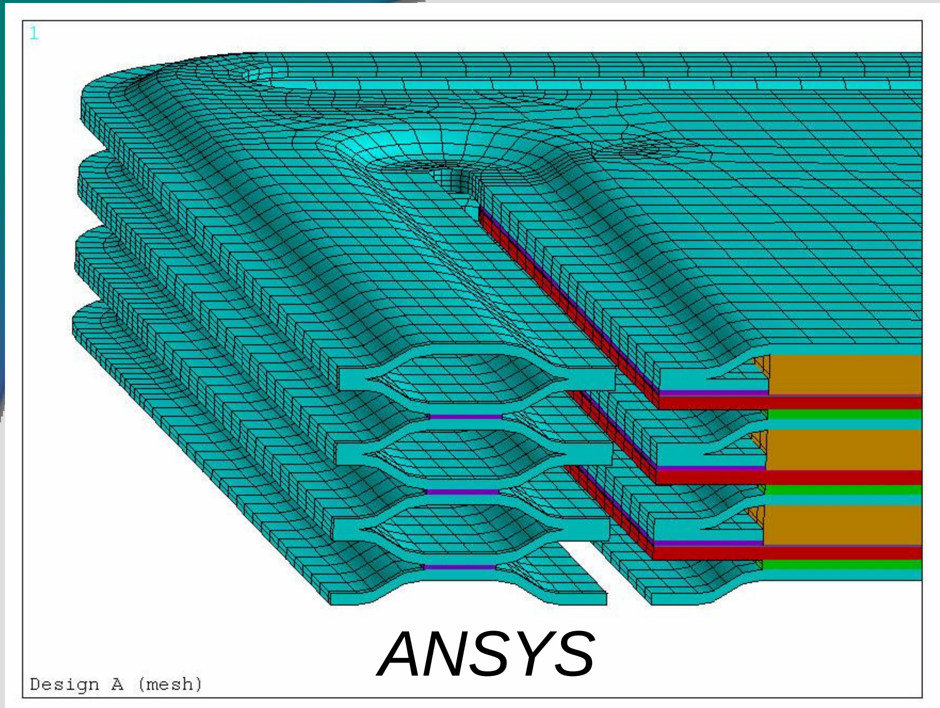
Mesh from CAD

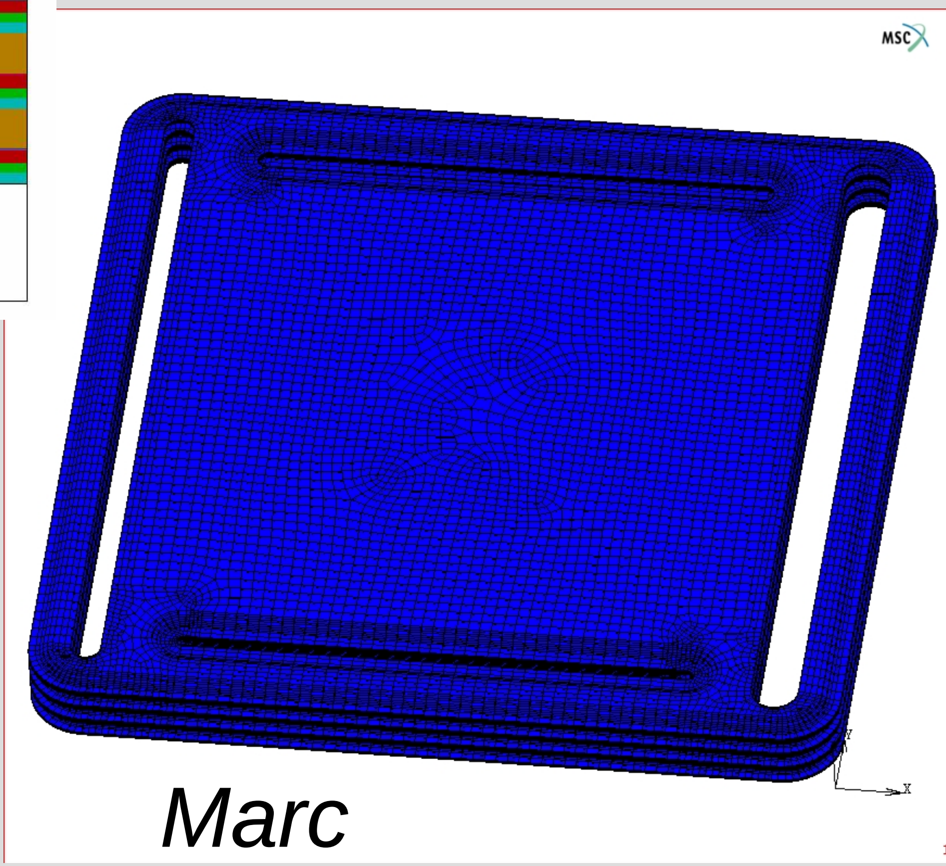
67,919 Nodes

30,629 elements



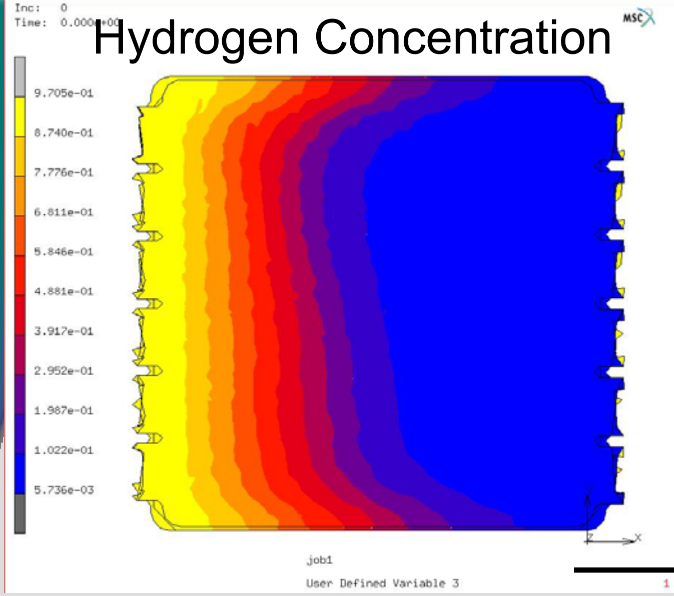
Mentat-FC Imports Existing Finite Element Grids



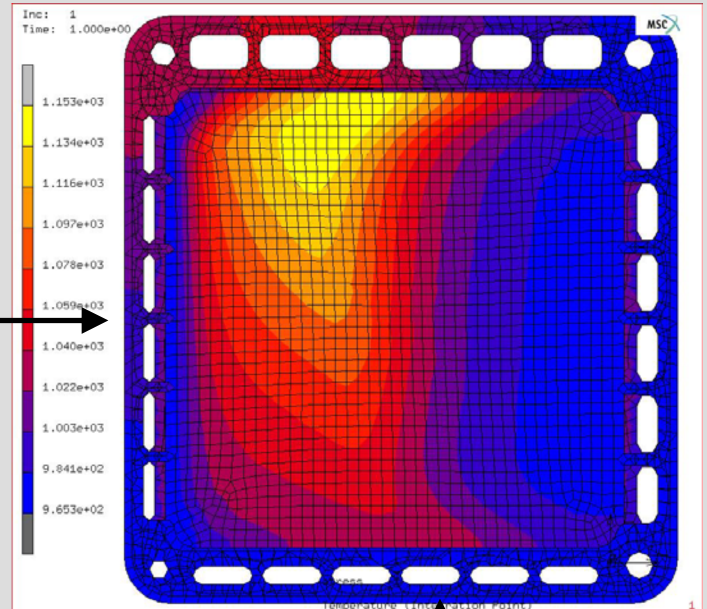


- User provides meshes identified for individual components.
- Can mix and match with CAD generated components.
- Fuel and Air cavities must also be meshed.
- Incompatible meshes are allowed through contact.

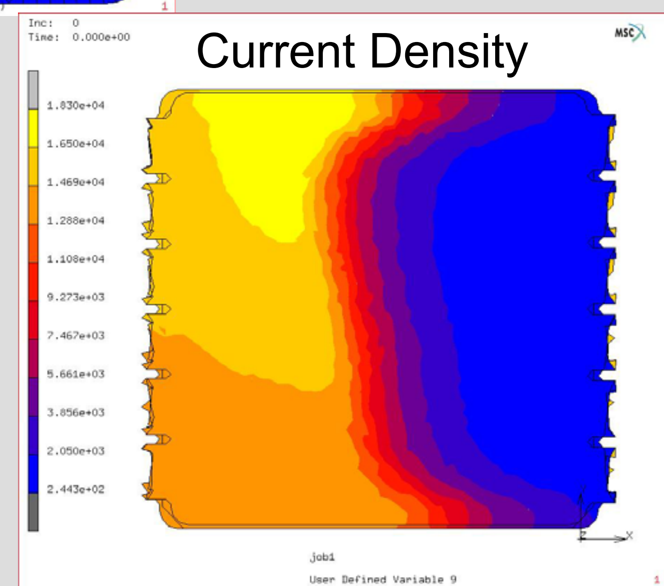
PNNL-EC Electrochemistry and Thermal Results



Fuel



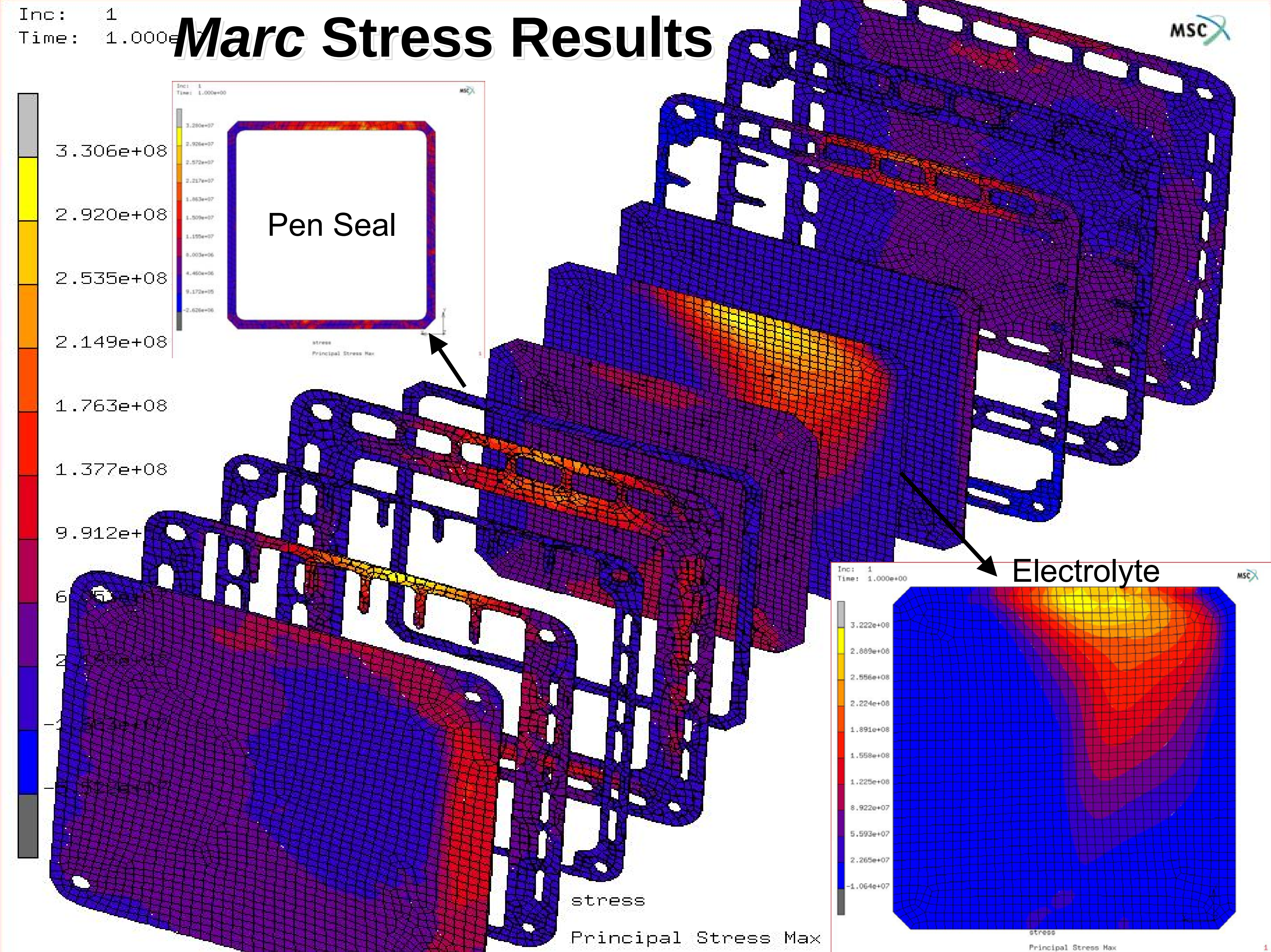
Air



- 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.

Battelle

Marc Stress Results

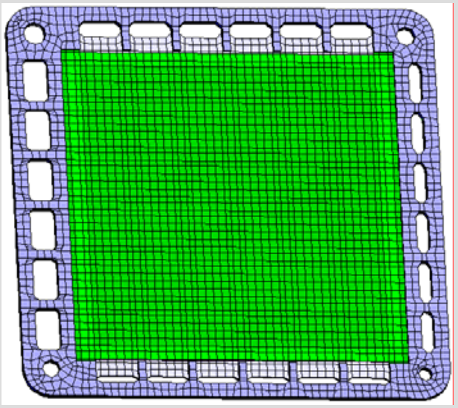


ON-CELL REFORMATION

- 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**
    (H2+CO+4CH4)
- Electrochemical Performance for 110.24 cm2 Cell: 0.53 A/cm2 (38.6 A) at 0.7 Volts at ~64% Fuel Utilization



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

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

$$CH_4 + H_2O \longrightarrow 3H_2 + CO$$

$$CO + H_2O \longleftrightarrow H_2 + CO_2$$

$$H_2 + 1/2O_2 \longleftrightarrow H_2O$$

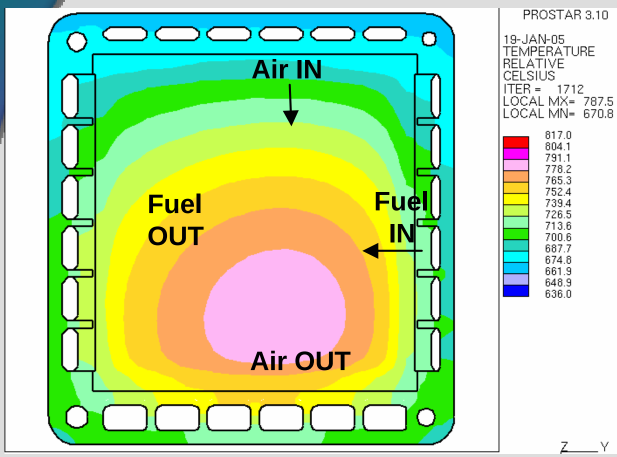
Methane Reformation Kinetics

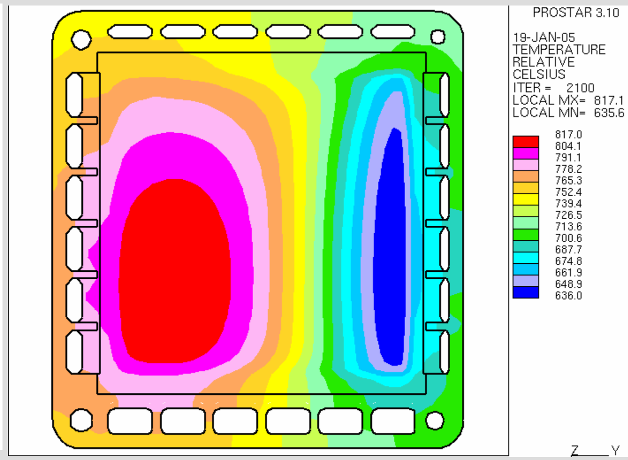
$$(-r_{CH_4})(mol/g_{cat}/s) = 2.188\times 10^{8} e^{-\frac{94.95\times 10^{3}}{RT}} C_{CH_4} C_{CO_2}^{-0.0134}$$

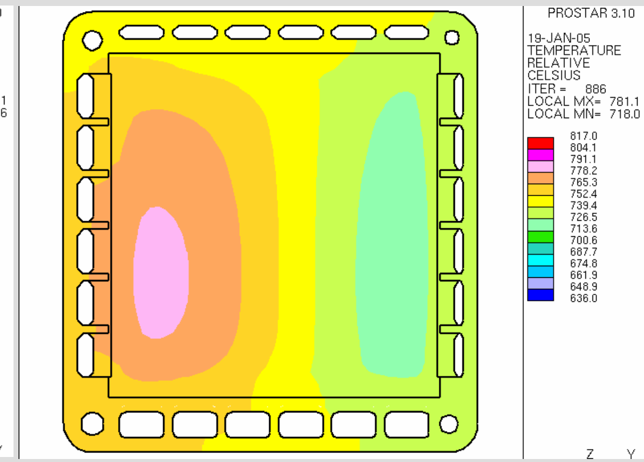
{T, K} {R, 8.314 J/mol-K} {C, mol/cc} {E, J/mol}

- 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_{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_{act} 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

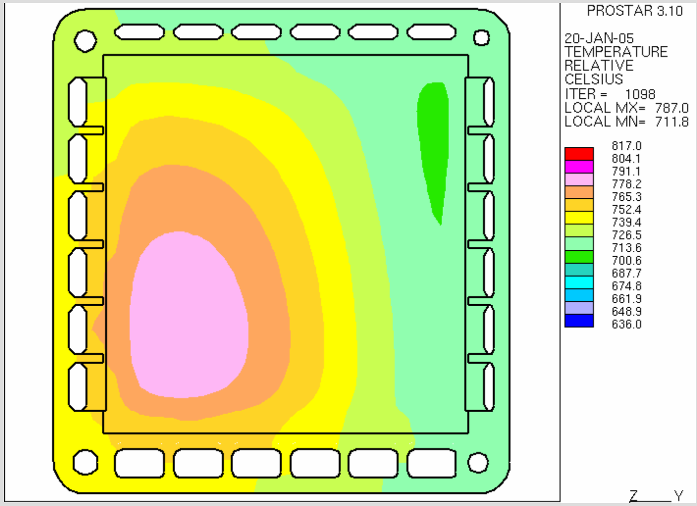
Power = 34.2 Watts

T(inflow) = 744.0°C

Note: Diminished ΔT

All cases are plotted at same temperature scale. Cases with temperatures in RED and or BLUE range indicate large ΔT and are not desirable

Results: Temperature Distributions



Case 3 (Case 2a with voltage decreased to boost current):

T(cell)= 750°C

Range = 712 to 787°C

I(cell)= 0.52984 A/cm2 (58.41 A)

(64% utilization of 4.7mol/s)

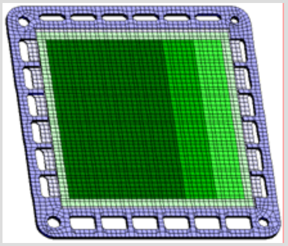
V(cell) = 0.641 Volts

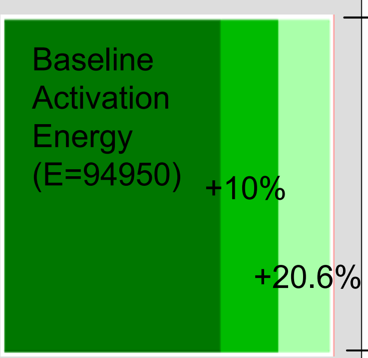
Power = 37.44 Watts

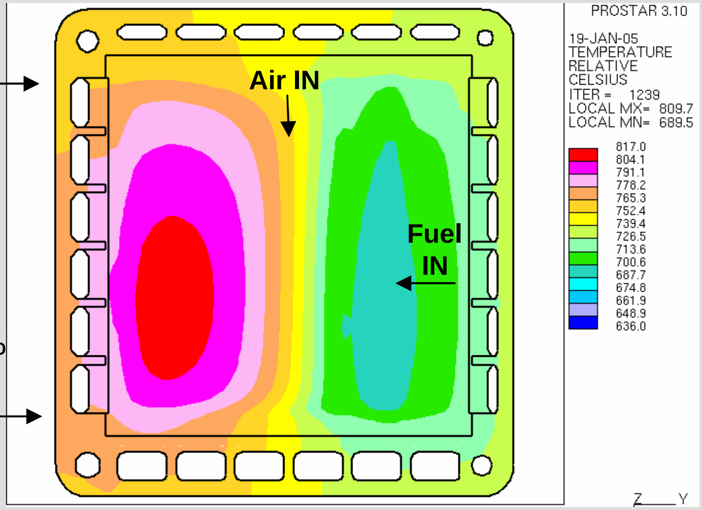
T(inflow) = 714.9°C

DIR case with "smoothed" temperatures

Model Configuration







Case 2d:

SMR, Variable E.1

T(cell)= 750°C

Range = 690 to 810°C

I(cell)= 0.4972 A/cm2 (54.81 A)

(lower utilization)

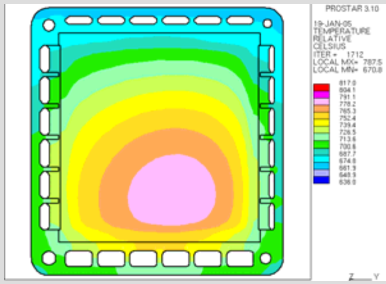
V(cell) = 0.695 Volts

Power = 38.1 Watts

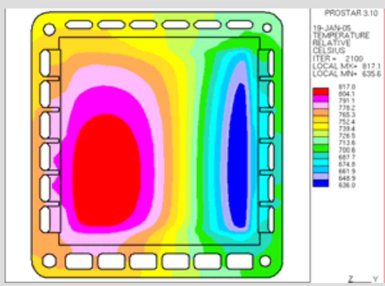
T(inflow) = 746.6°C

CASE HIGHLIGHTS

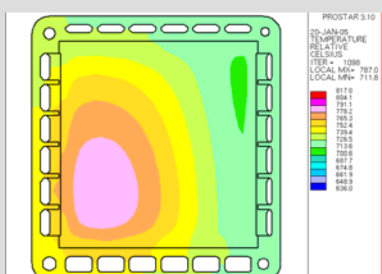
Case 1:
Baseline
H_2 only
No CH_4



Case 2:
With CH_4
& Baseline
SMR activity



Case 3:
Uniformly
Decreased
Activity



Case	Temperature, C		S1max, Mpa Anode	S1max, MPa Seal	S1max, MPa Picture Frame
	Minimum	Maximum			
1	671	788	25.0	10.1	141.1
2	636	817	40.0	10.9	109.6
3	712	787	11.8	5.9	59.5

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

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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
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Solid State Energy Conversion Alliance (SECA)

Monotonic Strength

Material: G18 glass (bulk)

Temperature (°C)	Environment	Aging Treatment	Mean strength	Flexural Strength
25-800	air	4 hr @ 750C	data	data
25-800	air	1000 hr @ 750C	data	data

Material: G18 glass (thin film)

Temperature	Environment	Testing Method	Strength
25-800	Air	Torsion	Data
25-800	Air	Tension	Data

- Glass-Ceramics for Sealing Solid Oxide Fuel Cells (PDF-4.4MB)
- Patents: 6,430,966 & 6,532,769

Contact: John Vetrano, PNNL, (509) 372-0724

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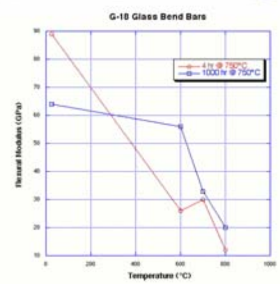


Test Temperature (°C) (aging time)	Flexural Modulus (GPa)	Mean Strength (MPa)	Std Dev Strength (MPa)	Maximum Strain
25 (4 hr)	89	80	10	0.13%
600 (4 hr)	26	83	15	0.25-0.45%
700 (4 hr)	30	64	10	0.17-0.30%
800 (4 hr)	12	39	4	0.50-0.80%
25 (1000 hr)	64	43	3	0.09-0.13%
600 1000 hr)	56	42	6	0.07-0.10%
700 (1000 hr)	33	35	2	0.10-0.14%
800 (1000 hr)	20	31	2	0.30-0.60%

Data File

Materials preparation: G18 glass bend bars were cut and machined from fired thick plates from lamination of multiple G18 glass green tapes. The G18 green tapes were made by conventional tape casting of G18 glass powders in an organic solvent system and dried in ambient air before lamination with a hot press at ~70-80oC. The laminated multiple G18 tapes were fired very slowly to burn away all the organics at 500-600oC for a couple of hours followed by firing to 850oC for 1 hour, and then heat treated at 750oC for 4 or 1000 hours. After heat treatment the G18 plates were ground to flat and cut into standard 4-pt bend bars (3.0 mm x 4.0 mm x 50 mm, standard dimensions for 4-pt bend test of ceramics). The edges (on the tensile side) of the bend bars were rounded with SiC grit paper (#800) to remove stress concentration from machined defects.

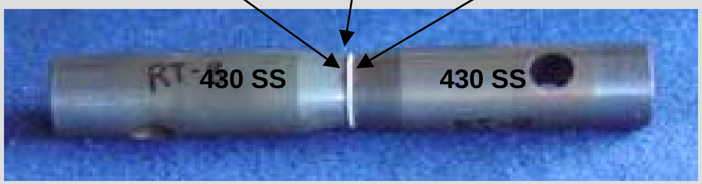
4-pt bend tests: The above-mentioned G18 bend bars were tested in an Instron (Model 5581) mechanical tester using a fully articulated SiC test fixture with an inner span of 20 mm and outer span of 40 mm (typical for 4-pt bend test for ceramics). The tests were run under ASTM, C1161-02c (Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature) and ASTM, C1211-02 (Standard Test Method for Flexural Strength of Advanced Ceramics at Elevated Temperatures). The cross-head speed was set at 0.5 mm/min. For testing at elevated temperatures, the sample was heated in a clam shell high-temperature furnace with a heating rate of 10oC/min to the test temperature and held for 30-45 minutes before the bend test. All the bend tests were conducted in air without environment control. For each temperature, about 8 bend bars were tested. The material response was elastic at all temperatures except 800°C, at which temperature there was some non-linear behavior. The modulus was estimated from load train displacement and subtraction of load train compliance, which may introduce some errors at small strains.

Data Collected on Bulk G18 Glass

Test Temperature (□C) (aging time)	Flexural Modulus (GPa)	Mean Strength (MPa)	Std Dev Strength (MPa)	Maximum Strain
25 (4 hr)	89	80	10	0.30-0.60%
600 (4 hr)	26	83	15	0.30-0.60%
700 (4 hr)	30	64	10	0.30-0.60%
800 (4 hr)	12	39	4	0.30-0.60%
				0.30-0.60%
25 (1000 hr)	64	43	3	0.30-0.60%
600 1000 hr)	56	42	6	0.30-0.60%
700 (1000 hr)	33	35	2	0.30-0.60%
800 (1000 hr)	20	31	2	0.30-0.60%

Test Temperature (□C)	Condition (aging time @ 750□C)	Elastic Modulus (GPa)	Shear Modulus (GPa)	Flexural Modulus (GPa)	Poisson Ratio	Number of tests
25	4 hr.	80.5	31	89	0.3	4
25	1000 hr.	80.2	30.6	64	0.31	5
600	4 hr.			26		6
700	4 hr.			30		6
800	4 hr.			12		6
600	1000 hr.			56		6
700	1000 hr.			33		6
800	1000 hr.			20		6

Data From Seal Assembly Analogs



Tension

Torsion

Testing Method	Test Temperature (□C)	Mean Failure Stress (MPa)	Number of Samples
Tension	25	22.8	2
	700	23.2	2
	750	16.5	6
	800	5.3	3
Torsion	25	46.7	6
	700	50.9	6
	750	22.8	6
	800	11	6

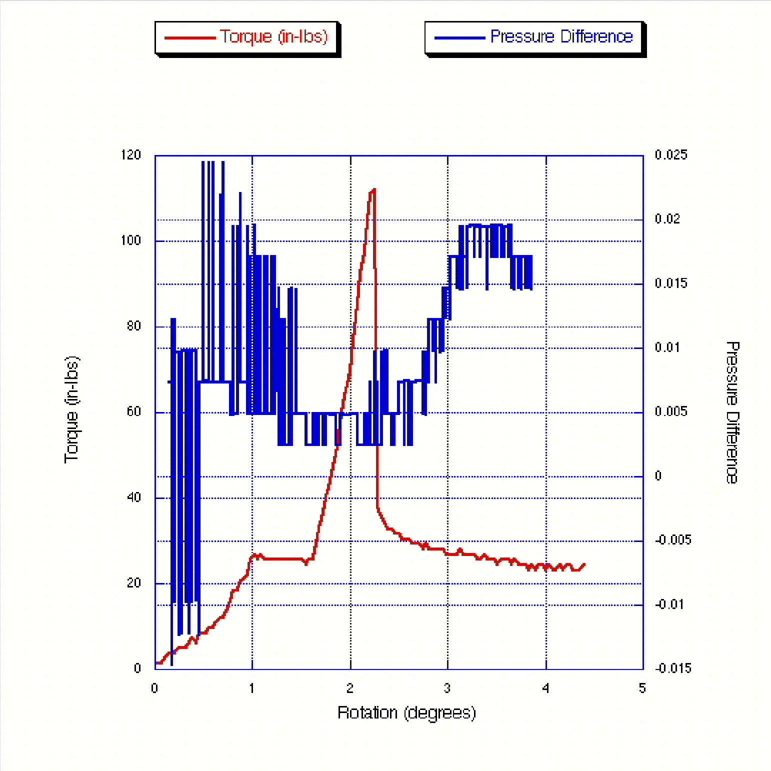
Thin-film analogs to test the entire seal assembly

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

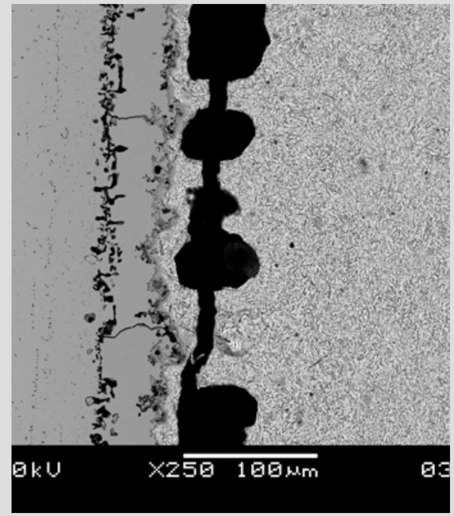
Initial Results on Mica Seals

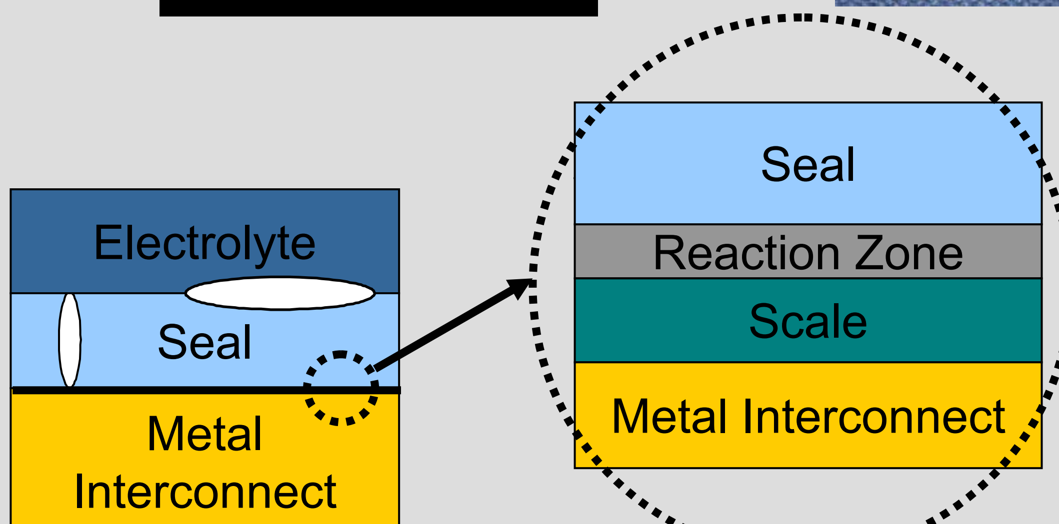


Torsion-Leak test of Mica seals revealed that as the mica slides it may show slip-stick behavior and during the “stick” phase there might be some leakage. Preliminary tests show only small leaks.

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





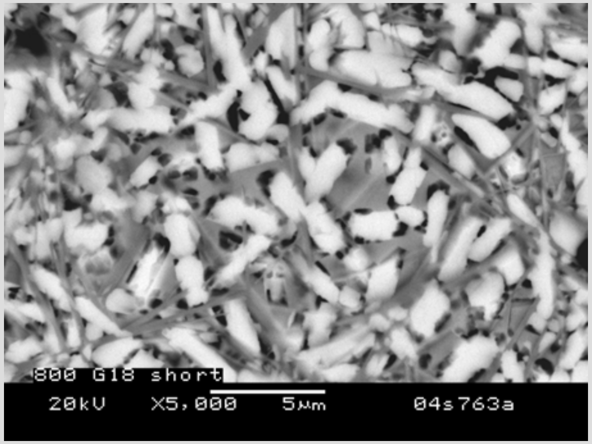
Thermal-Mechanical Seal Damage
G18 Continuum Damage Model

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

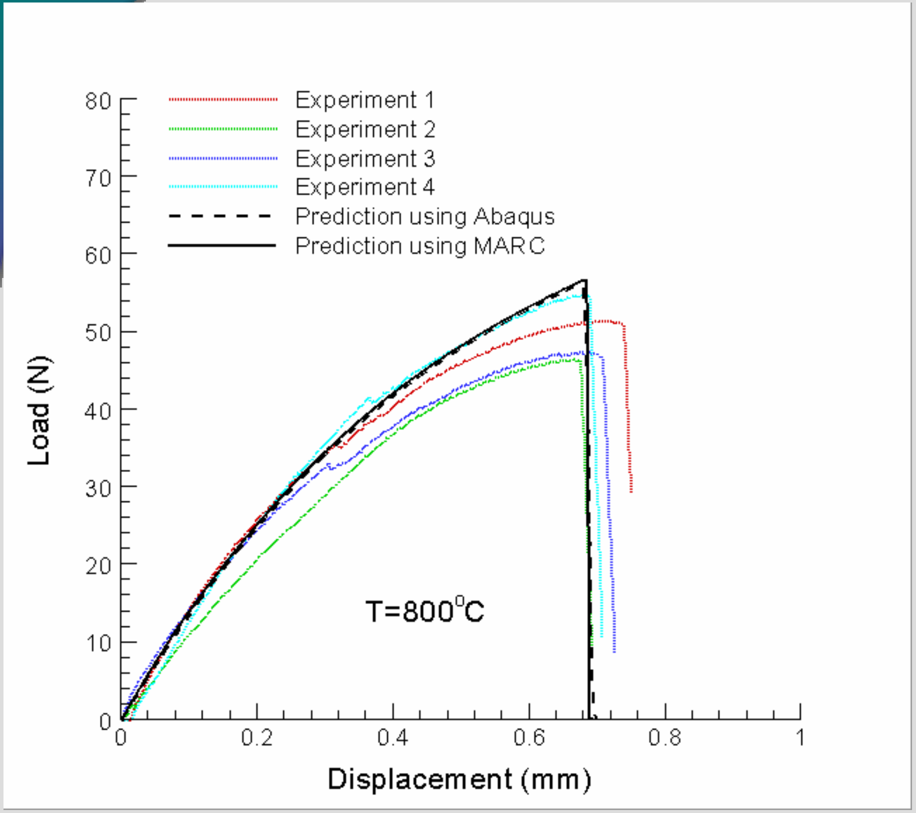
➔ Nonlinear stress/strain responses until failure

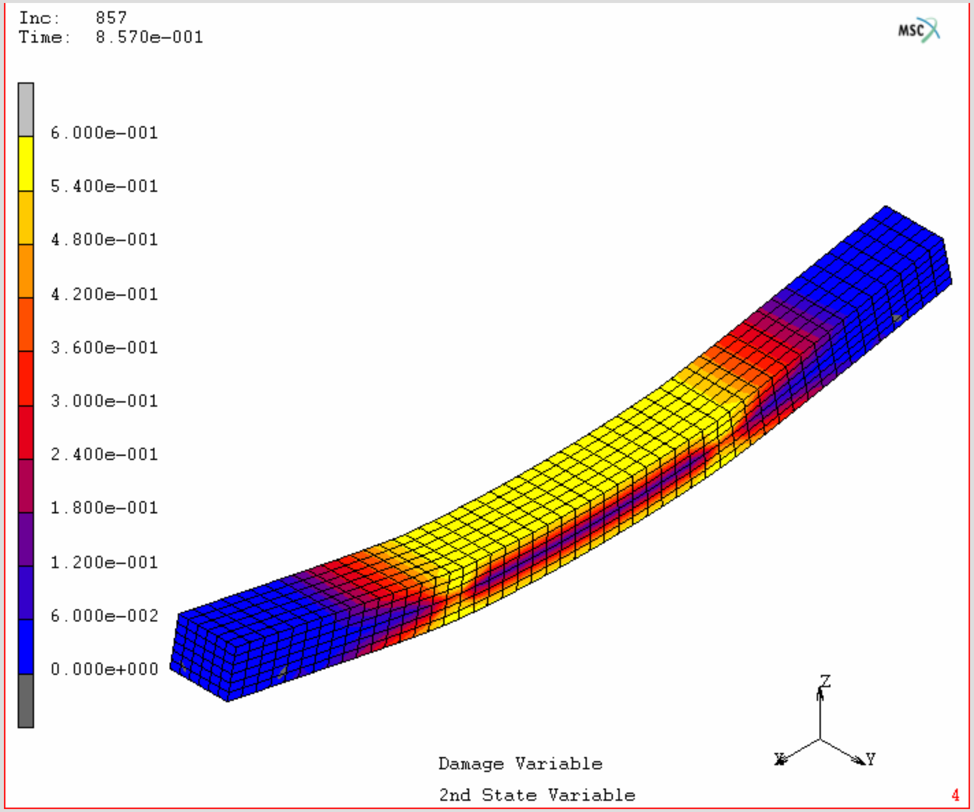
Microstructure of G18 glass in a stress free region



- **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

Thermal-Mechanical Seal Damage
G18 Continuum Damage Model

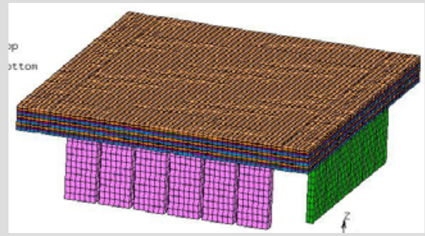


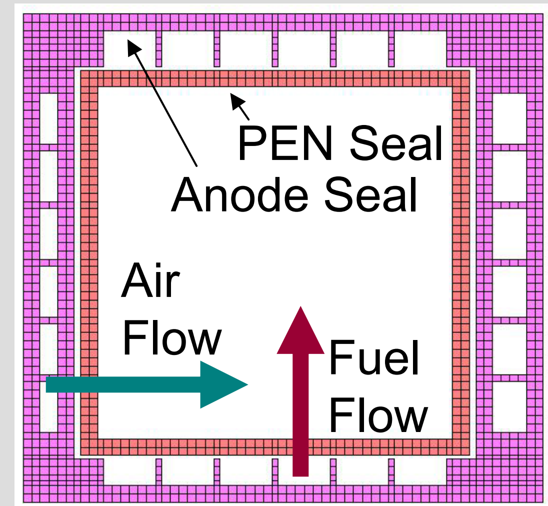


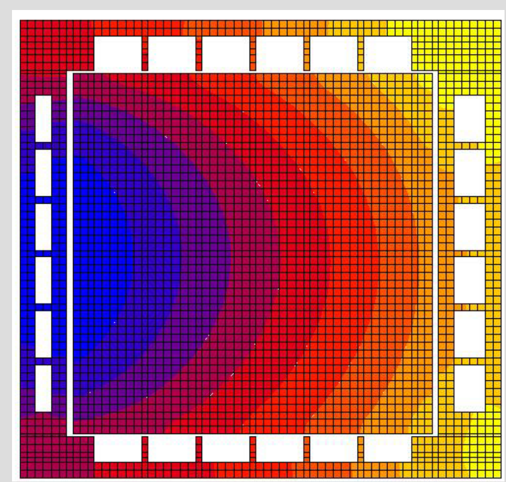
Damage and failure progressions at the maximum applied displacement for a G18 glass sample subjected to 4-point bending at 800°C. Damage is more important on the top and bottom surfaces of the beam as expected. Macro cracks initiate within the loading span and near the locations where the displacement 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





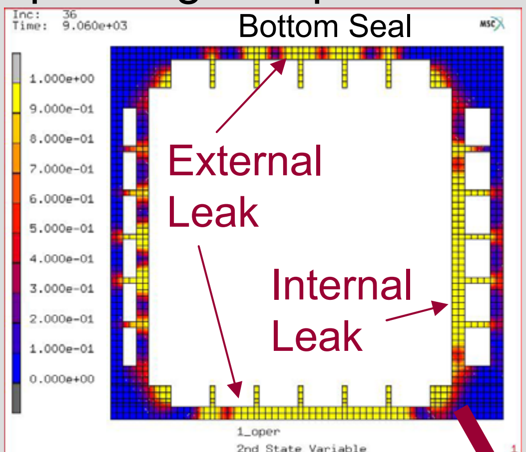


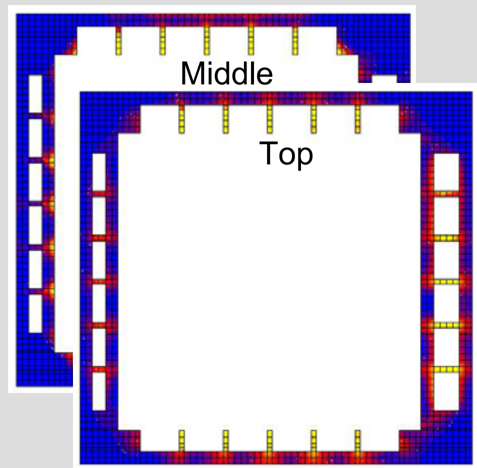
PEN ΔT max: 150°K at steady state

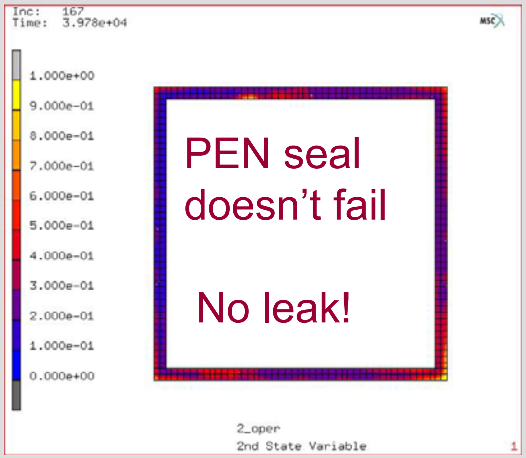
PEN ΔT of 40°K occurs on shutdown

Thermal-Mechanical Seal Damage
Thermal Cycling Results

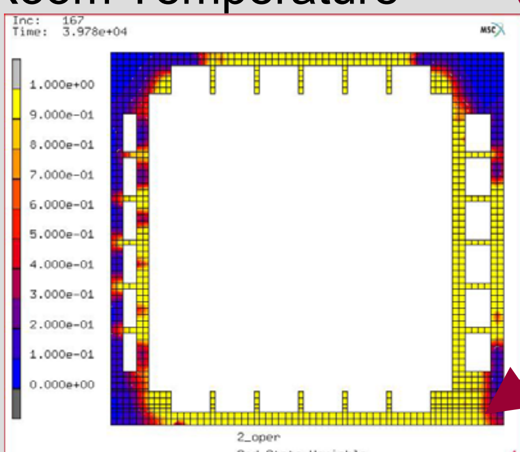
Operating Temperature







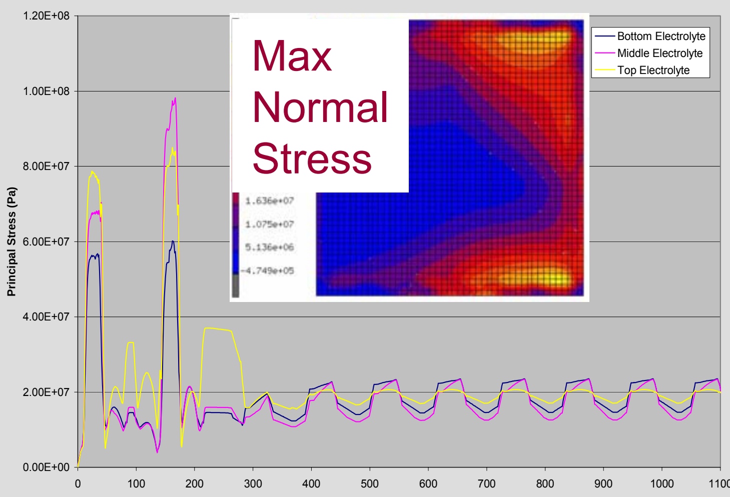
Room Temperature



Damage accumulates

Bottom seal fails due to influence of hearth and leaks expected

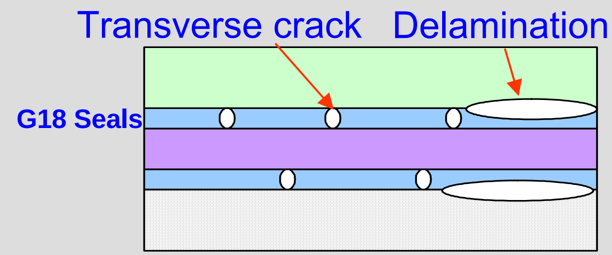
Consistent with experiments



Thermal-Mechanical Seal Damage Leak Rate Estimate Based on Damaged State

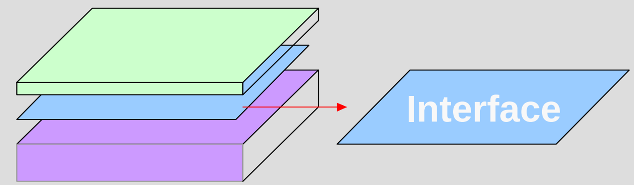
Damage mechanisms causing leak

- Transverse cracking → damage model
- Layer delamination → interface model



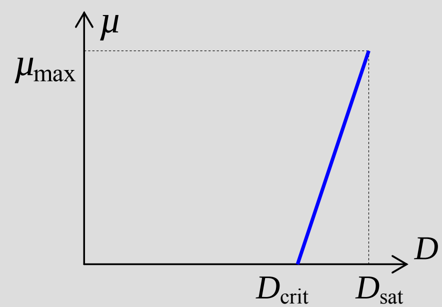
Interface model

- 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_{crit}
- Maximum leak rate, μ_{max} attained at seal failure ($D = D_{sat}$)
- μ_{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

Tensile and torsion tests characterize interface strengths

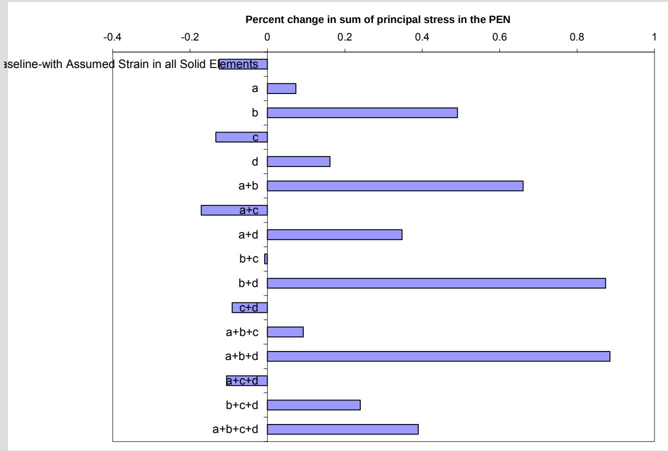
Application to stack in progress

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

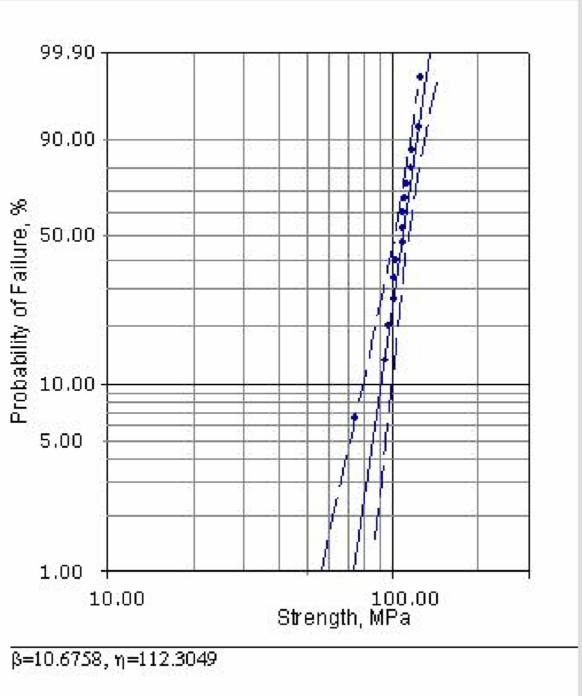
Approach

- 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



$$\beta = \frac{\bar{R}_i - \bar{S}_i}{\sqrt{\sigma_{R_i}^2 + \sigma_{S_i}^2}}$$

Results: Evaluation of Current Design under Steady State Operating Condition

Anode Thickness (microns)	Load: Fuel flow rate(gmol/sec)	Failure Probability (Pf)		
		Anode	Electrolyte	Seal
600	0.00272	<1.0E-5	0.067	0.955
	0.00068	<1.0E-6	0.0001	0.0002

Results: Design Look-up Table – Steady State Operation

Design target: safe index β=3, failure probability Pf=0.0014

$$stress < \alpha \times strength$$

Anode Thickness (microns)	Load: Fuel flow rate(gmol/sec)	Strength Reduction Factor α		
		Anode	Electrolyte	Seal
600	0.00272	0.59	0.312	0.58
	0.000907	0.65	0.318	0.65
	0.00068	0.64	0.319	0.65
720	0.00272	0.58	0.31	0.62
	0.000907	0.60	0.32	0.65
	0.00068	0.65	0.3	0.65

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 ~ 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