

# **AN INTEGRATED APPROACH TO MODELING AND MITIGATING SOFC FAILURE**

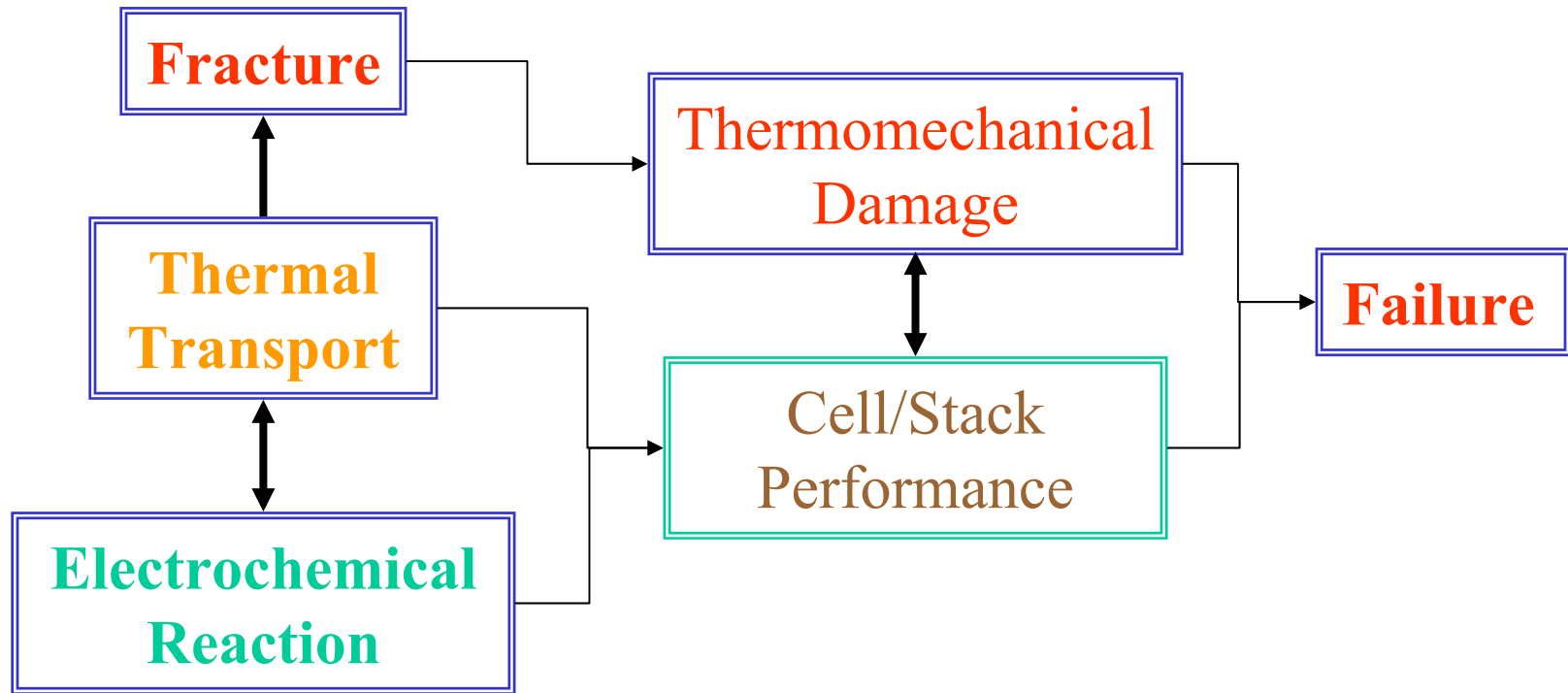
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**DE-AC26-02NT41571**

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National Energy Technology Laboratory

# Project Overview

Develop a multi-physics modeling approach to collectively characterize the interdependency between structural issues and electrochemical/thermal transport phenomena in order to create greater fidelity within thermomechanical failure analysis models.

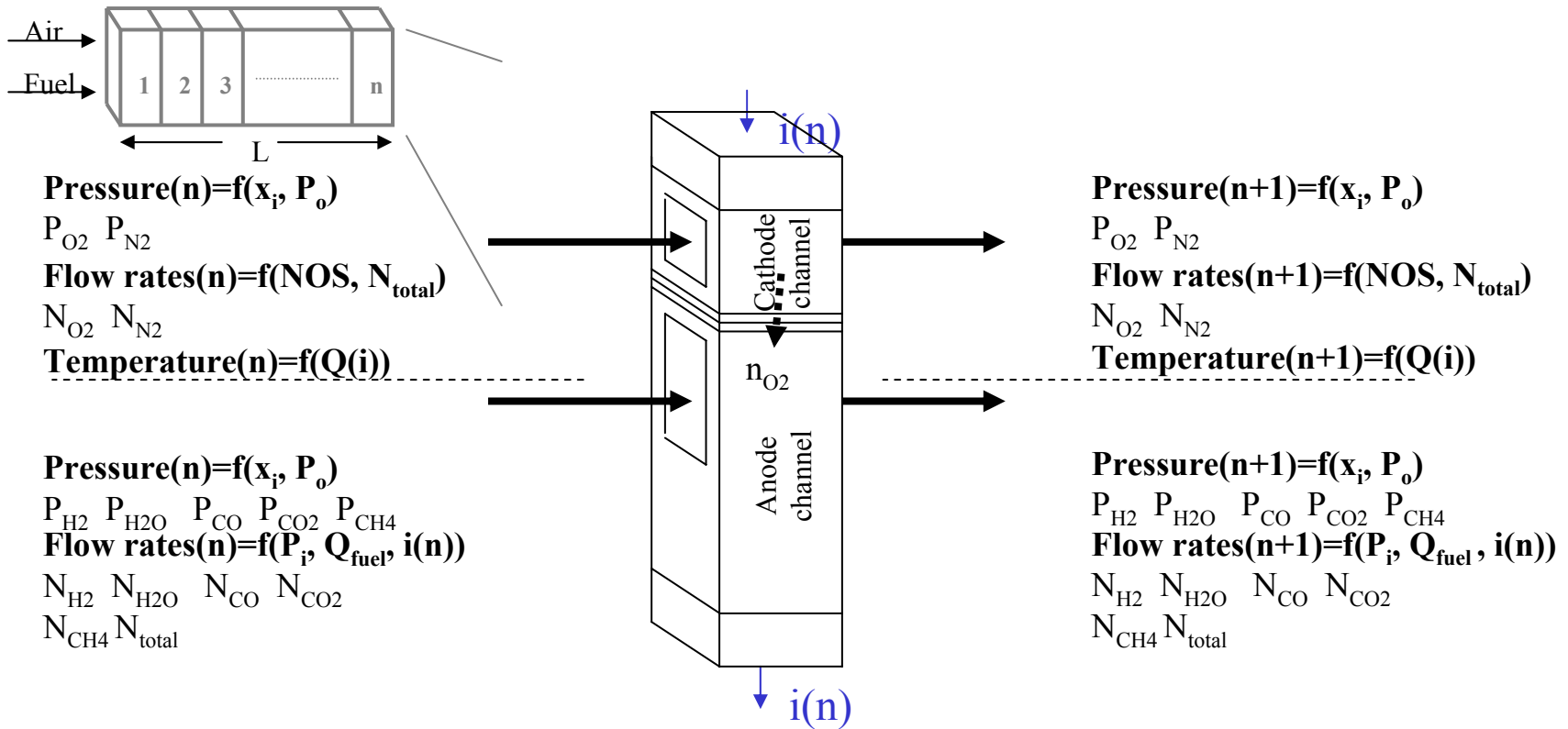


Phase I is a one-year effort to investigate and evaluate the feasibility of the solution proposed and/or the merits of the scientific path of inquiry.

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.

# Electrochemistry

# Planar SOFC Co-flow Model

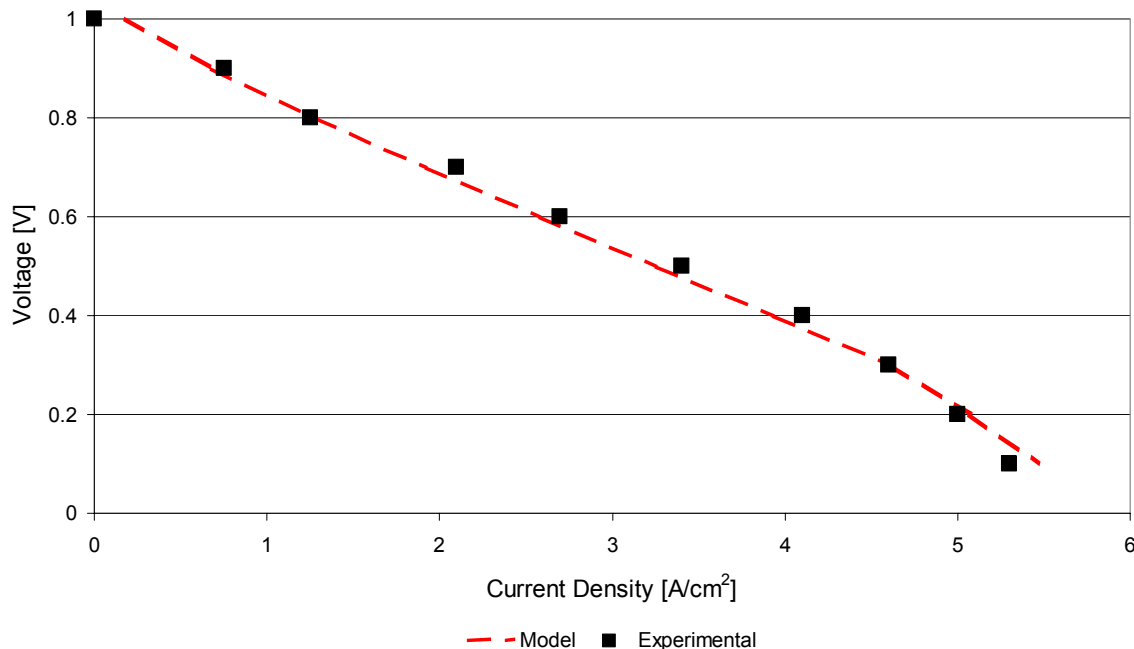


$$V(i) = E_o - i - \ln i + \frac{RT}{2F} \ln \left( 1 - \frac{i}{i_{as}} \right) - \frac{RT}{2F} \ln \left( 1 + \frac{p_{H_2}^\circ i}{p_{H_2O}^\circ i_{as}} \right)$$

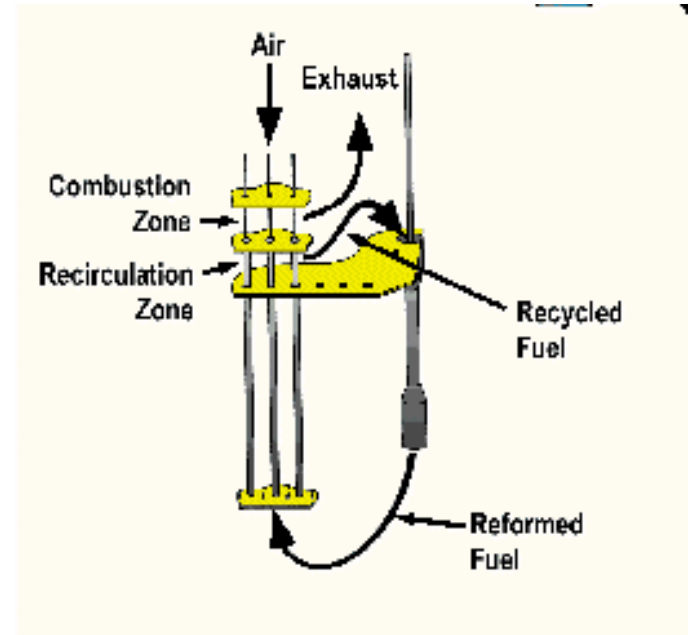
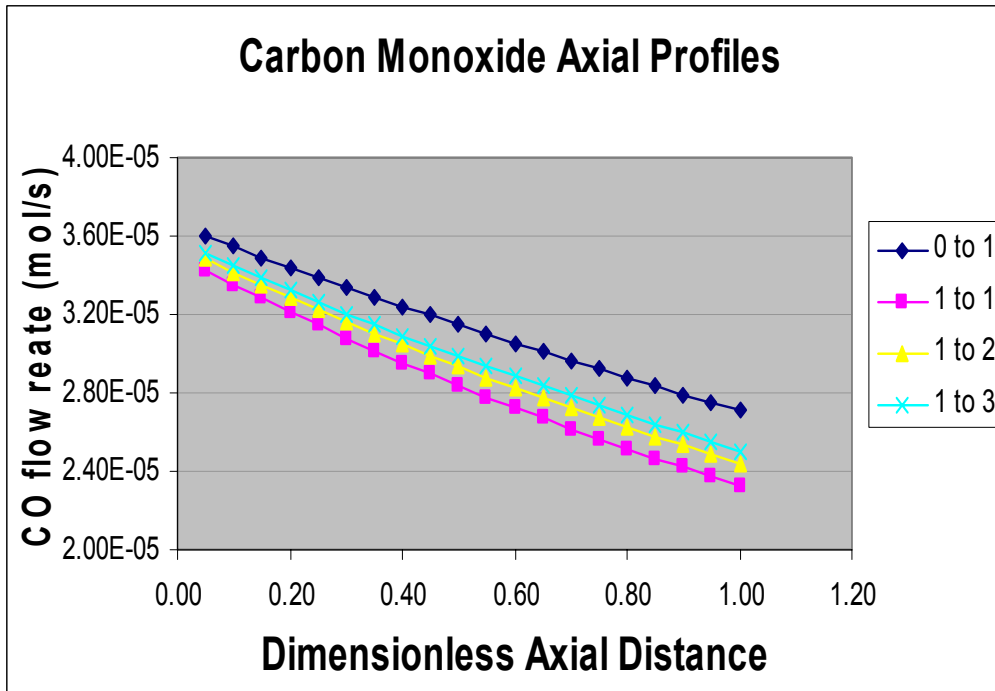
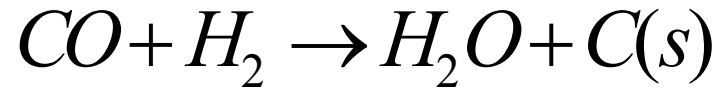
Electrochemical model is currently a combination of the polarization model of Kim et al. (1999) and Haynes' slice technique (Haynes and Wepfer, 1999)

# Preliminary Button Cell Data Verification

- Model agrees with experimental data {Kim et al., '99}
- Analogous to initial NETL validation exercise {Rogers et al., '03}
- Near-term desire to realize short-stack validations wherein scale-up and interconnect “masking” effects (e.g., *planar diffusion within porous electrodes*; “*sheet resistance*”) are considered



# Chemical Failure Mode: Significant CO Presence may Foster Coking



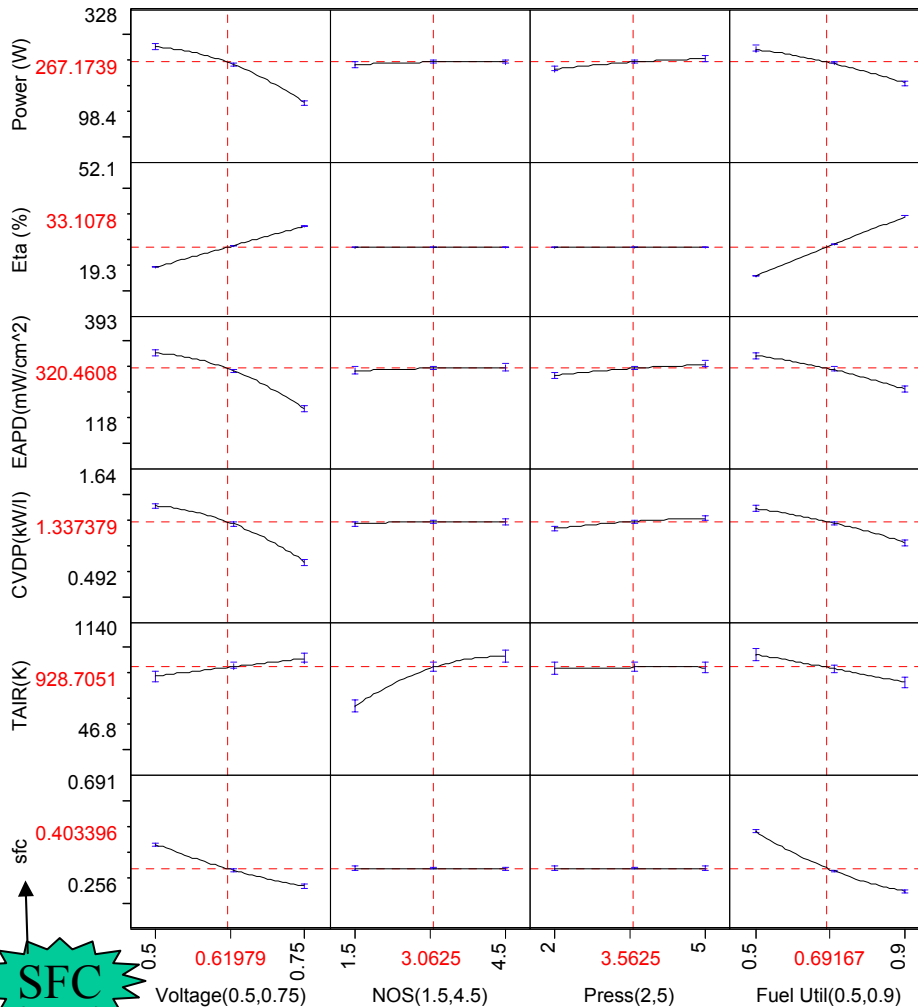
*Frozen CO electrochemistry is the most threatening case.*

$$SFR = \frac{sfr}{1 - \gamma_{CO}sfr - \gamma_{CH_4}sfr}$$

# CO Electro-Oxidation versus Fuel Processing

- Previous SECA simulations predicated upon a stoichiometric ratio of CO electro-oxidation: H<sub>2</sub> electro-oxidation
- Collaborative literature search promotes shift as the dominant reaction with respect to CO
  - Minh and Takahashi, Science and Technology of Ceramic Fuel Cells , 1995.
  - Ahmed and Foger, *JPS (2001)*: Large current densities promotes shift of CO
  - Holtappels, *Journal of Applied Electrochemistry*, 1999: CO electro-oxidation generally an “*order of magnitude*” slower than that of H<sub>2</sub> {Anodic resistances of 10Ω versus 0.5Ω for CO/CO<sub>2</sub> and H<sub>2</sub>/ H<sub>2</sub>O reducing atmospheres, respectively}
- CO electrochemical *inactivity* and high temperature shift may further diminish achievable fuel utilizations at practical voltages
- Recommend empirical verification and chemical-electrochemical kinetics characterization using GT DoE infrastructural developments and Holtappels et al. methodology *in conjunction with engaged SECA teammates*

# Facilitating R&D Insight via Tailored GUI/DoE Development

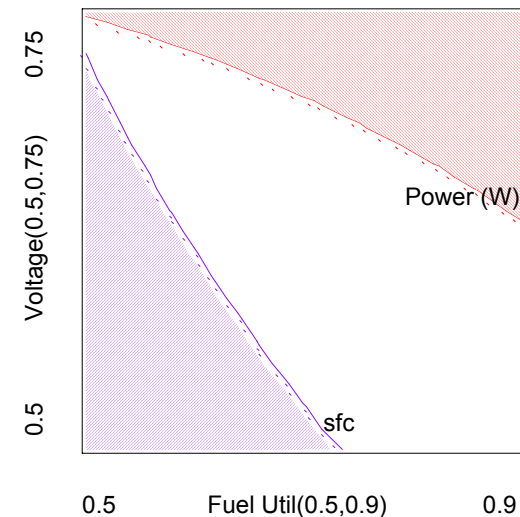


## Real-Time Visualization of Constraint Space

Horiz	Vert	Factor	Current X
⌋	⊙	Voltage(0.5,0.75)	0.6197917
⌋	⌋	NOS(1.5,4.5)	3.0625
⌋	⌋	Press(2,5)	3.5625
⊙	⌋	Fuel Util(0.5,0.9)	0.6916667

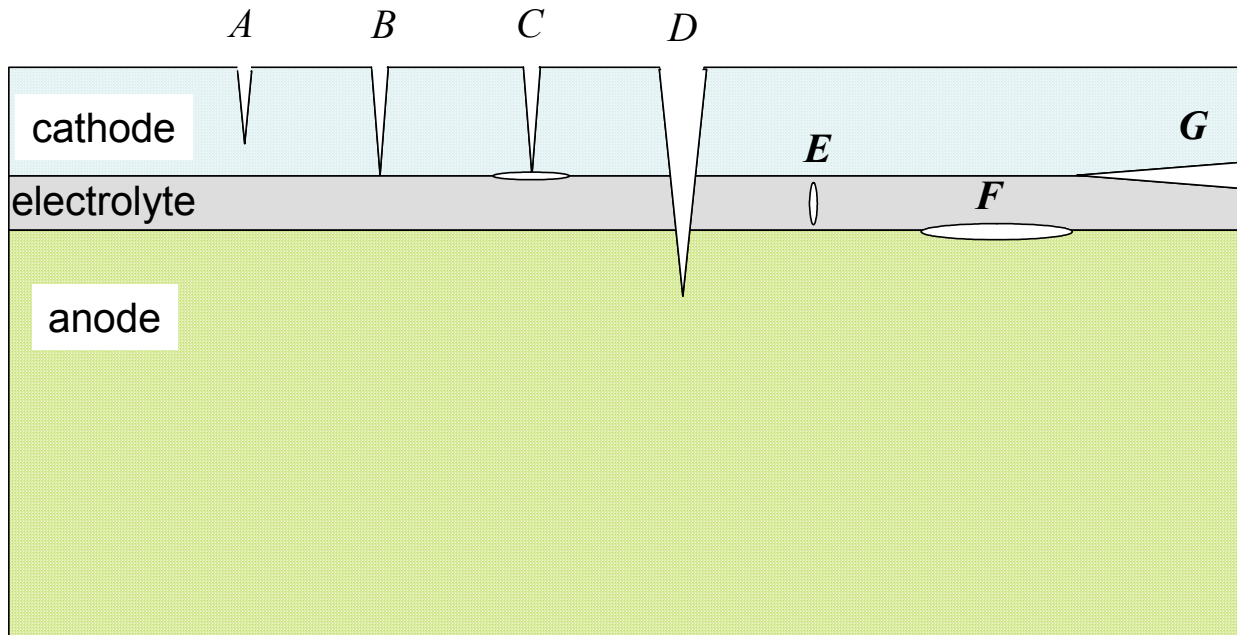
Response	Contour	Current Y	Lo Limit	Hi Limit
Power (W)	213	267.17391	213	.
Eta (%)	.	33.107801	.	.
EAPD(mW/cm <sup>2</sup> )	.	320.46083	.	.
CVDP(kW/l)	.	1.3373789	.	.
TAIR(K)	593.4	928.70515	.	.
sfc	0.4736189	0.4033964	.	0.48





# Future Direction: Electrochemistry-Fracture Interaction

**Possible “Design for Reliability” Trade-offs: All cracks are not created equal!!**



Electrochemical degradation sensitive to effective losses in electroactive area and current paths, impact upon surface phenomena, possible reactants crossover, etc.

# Electrochemical Impact of Fracture

Component Layer	Parallel Crack Impact	Vertical Crack Impact
<b>Bulk electrode layer</b>	<b>Charge/mass transport redirection</b>	<b>Smaller impact</b>
<b>Interlayers</b>	<b>Changes in TPBs/Electroactive Area</b>	<b>Changes in TPBs/Electroactive Area</b>
<b>Electrolyte</b>	<b>Substantial increase in resistance</b>	<b>Reactants Crossover</b>

# Enhanced Integration of GT/SECA Labs for Characterizing Degradation

- Semi-empirical assessment of changes in electrochemical activity/electrical performance  
*{In conjunction with PNNL/ORNL microstructural simulation and experimental fracture efforts}*
- Coordinated effort to identify the critical fracture developments that lead to significant degradation

# Thermal-Fluid Modeling of SOFC

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## Focus of Thermal – Fluid Modeling Efforts

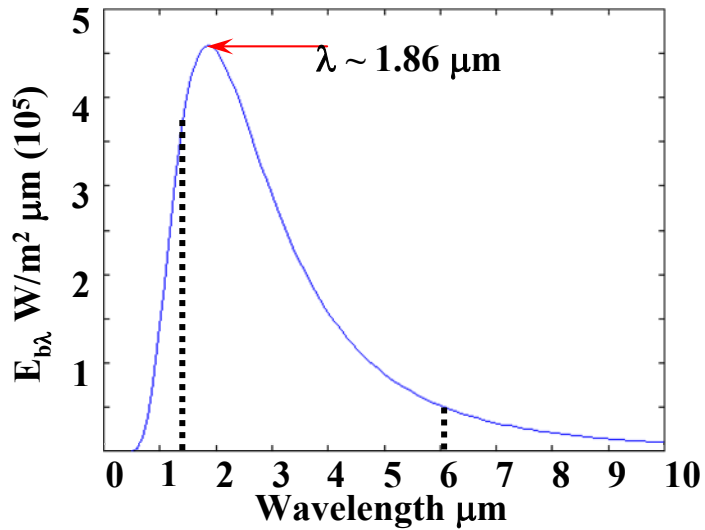
### Porous Media Modeling

- Studied 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 (Phase II)
- Transient heating effects during start-up/shut-down (Phase II)

### Radiation Modeling

- Discrete Ordinate Method is computationally intensive – Alternative model based on two-flux approximation has been developed
- Preliminary FTIR experiments were carried out to determine optical properties of electrodes and electrolyte – Need more detailed data for thinner samples (Phase II)
- Resolve convergence issues with thin electrolyte/electrodes (Phase II)

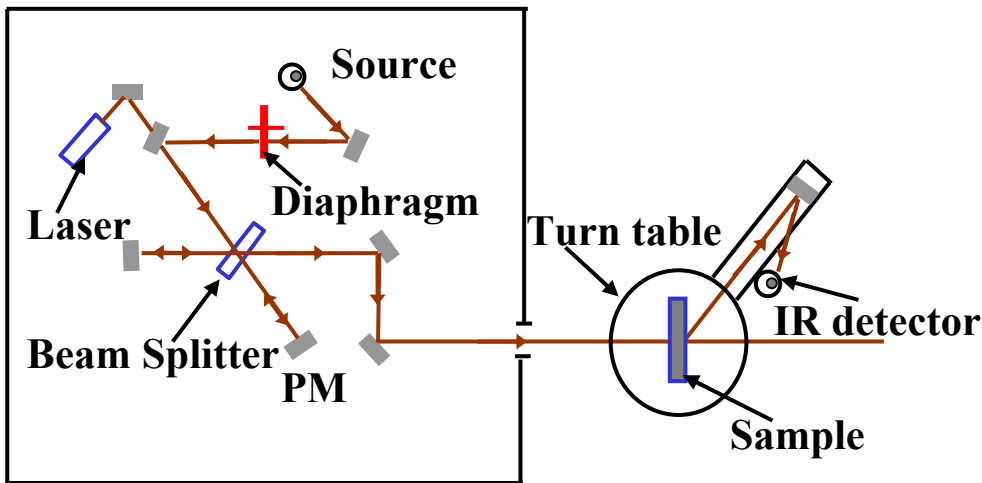
# Radiation Modeling – Measurement of Optical Properties



Wien's law:  $(n \lambda T)_{\text{max}} = 2898 \mu\text{m}$ .  
 $n \sim 1.6$ ;  $T = 700 \text{ }^\circ\text{C} = 973 \text{ K}$ ;  $\lambda_{\text{max}} = 1.86 \mu\text{m}$

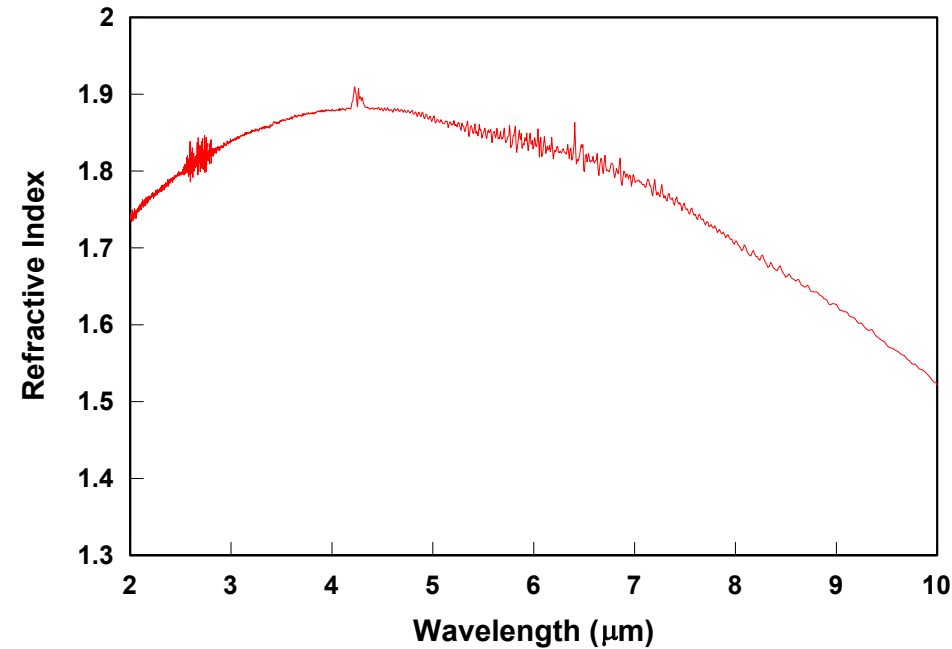
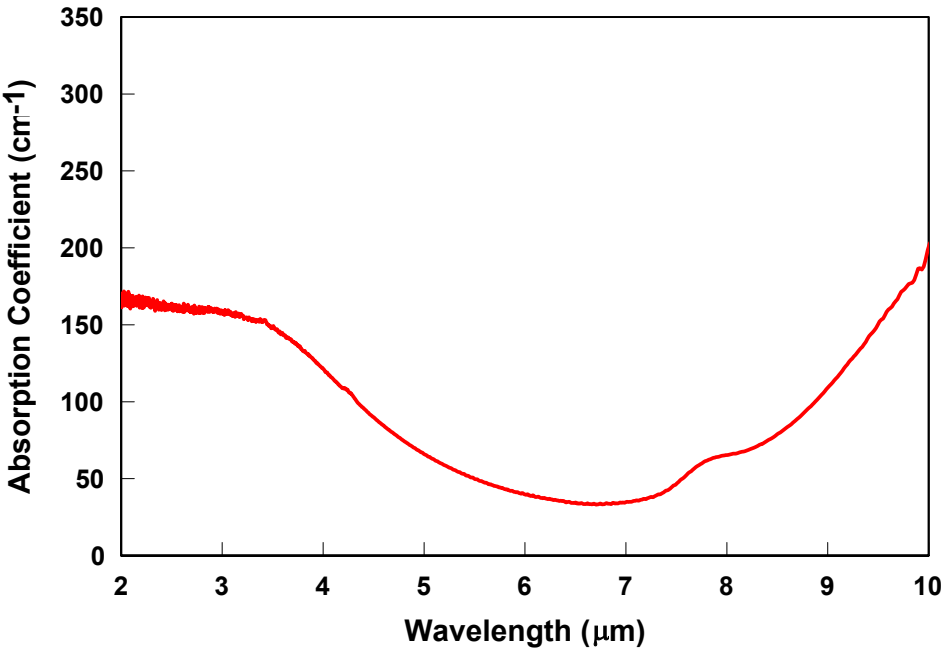
80% of fractional emissive power is contained within  $1.4 \mu\text{m} < \lambda < 6.1 \mu\text{m}$

## FTIR Measurements



1. Obtain Transmittance ( $T_r$ ) and Reflectance ( $R$ ) of the thin sample
2. Compute absorption coefficient ( $\kappa$ ) and refractive index ( $n$ ) from measured values of Transmittance ( $T_r$ ) and Reflectance ( $R$ )

# Experimental Measurements – Optical Properties of YSZ

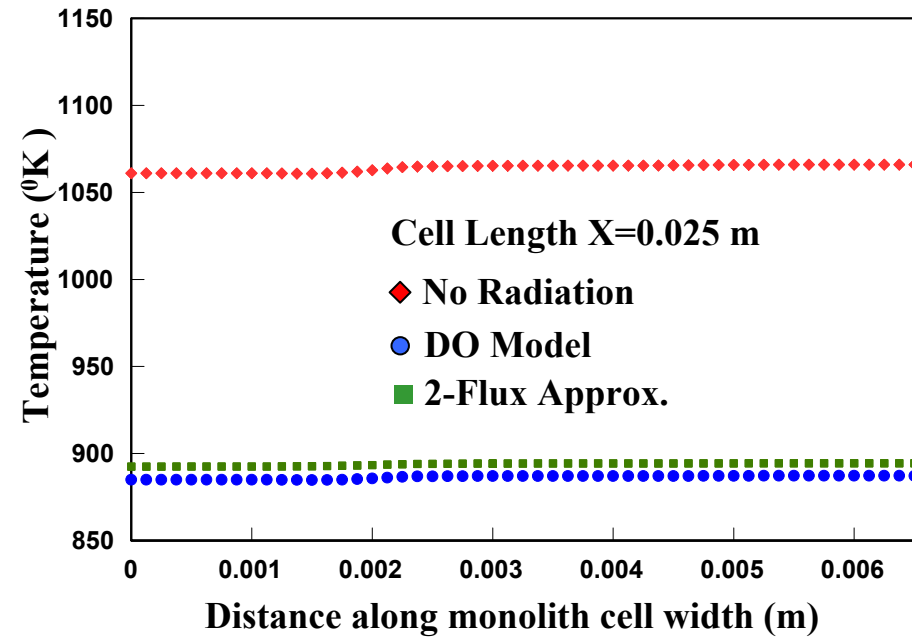
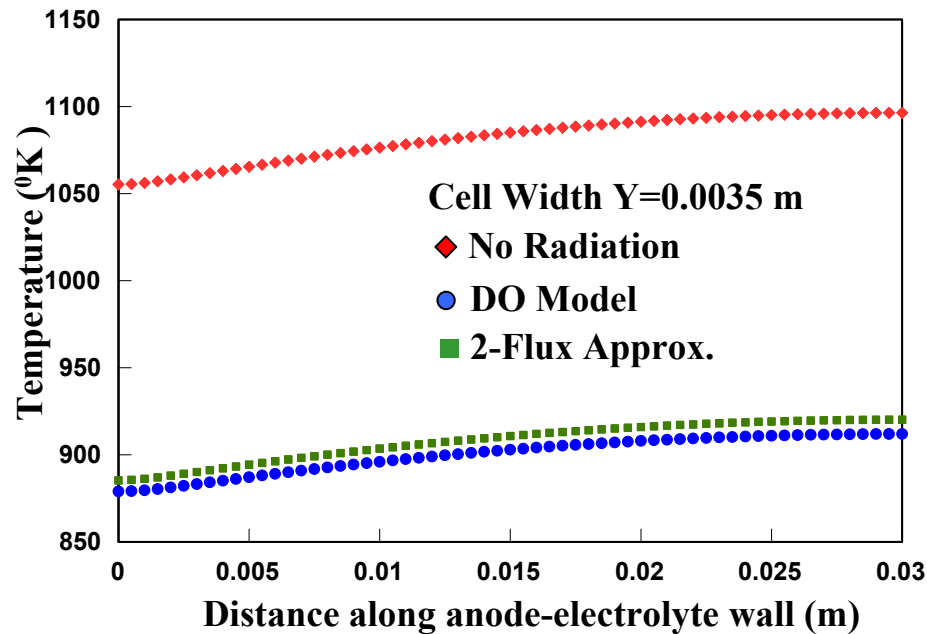


1. Electrolyte is a **semitransparent medium**, whereas electrodes are probably opaque.
2. Large spectral variation in optical properties - **gray body model no longer applicable**

$$\kappa_{\text{electrolyte}} L_{\text{electrolyte}} \sim 0.05 \rightarrow \kappa_{\text{electrolyte}} L_{\text{electrolyte}} \sim 0.15 \text{ for } L_{\text{electrolyte}} = 10\mu\text{m}$$

**Electrolyte is optically thin provided L is sufficiently small (<20-30 μm)!!!**

# Radiation Modeling – Two-flux Approximation

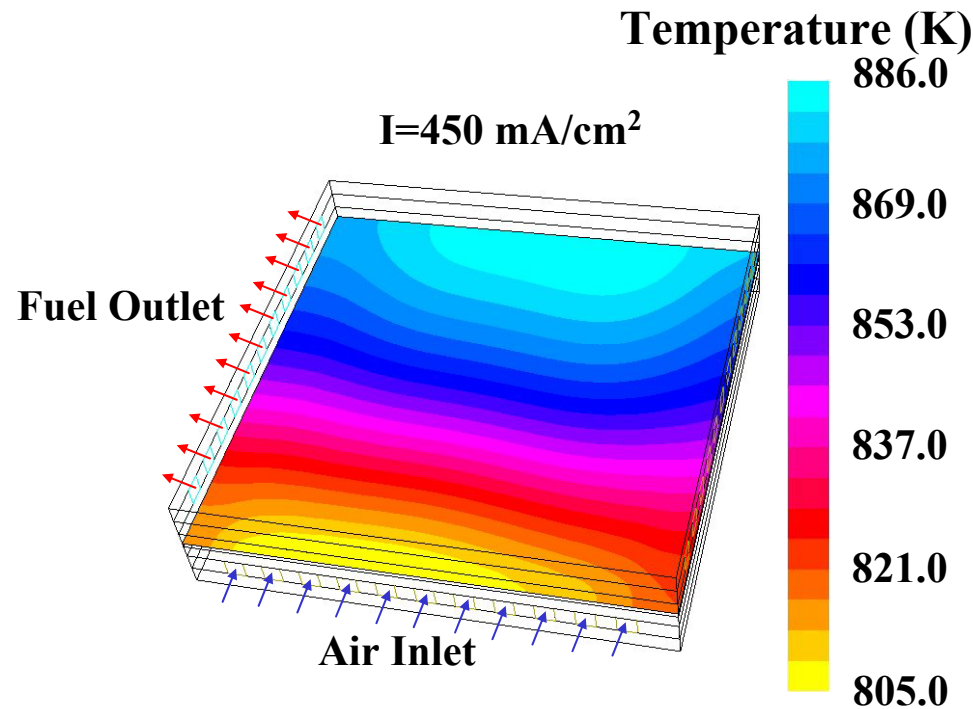


Methodology	Cell Voltage (V)	CPU time* (min)
Discrete Ordinate Method	0.734	658
Two-Flux Approximation	0.731	<b>76</b>

\* Based on time to convergence of Fluent simulations carried out on a 2.8 GHz Pentium 4 personal computer



# Unit Cell Model – Flow Configuration Design



Current Density	Counter-flow	Cross-flow
$\frac{150 \text{ mA/cm}^2}{\text{Voltage (V)}}$	<b>0.971</b>	<b>0.963</b>
$T_{\text{avg.}}(\text{K})$	<b>768.2</b>	<b>786.0</b>
$\frac{450 \text{ mA/cm}^2}{\text{Voltage (V)}}$	<b>0.745</b>	<b>0.733</b>
$T_{\text{avg.}}(\text{K})$	<b>826.0</b>	<b>845.5</b>

- Large temperature gradients observed within electrodes for cross-flow configuration
- **Soret effect** (thermal diffusion) is not significant in co- & counter-flow configurations where there is negligible temperature gradient across the electrodes, but it may become **important in cross-flow configuration**
- Convergence problem for thin electrolytes ( $\sim 15 \mu\text{m}$ ) and electrodes ( $\sim 50 \mu\text{m}$ ) because of the high aspect ratio mesh – requires further work (Phase II)

# Porous Media – Energy Conservation Modeling

Energy Conservation: Non-Equilibrium Thermal Model

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

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

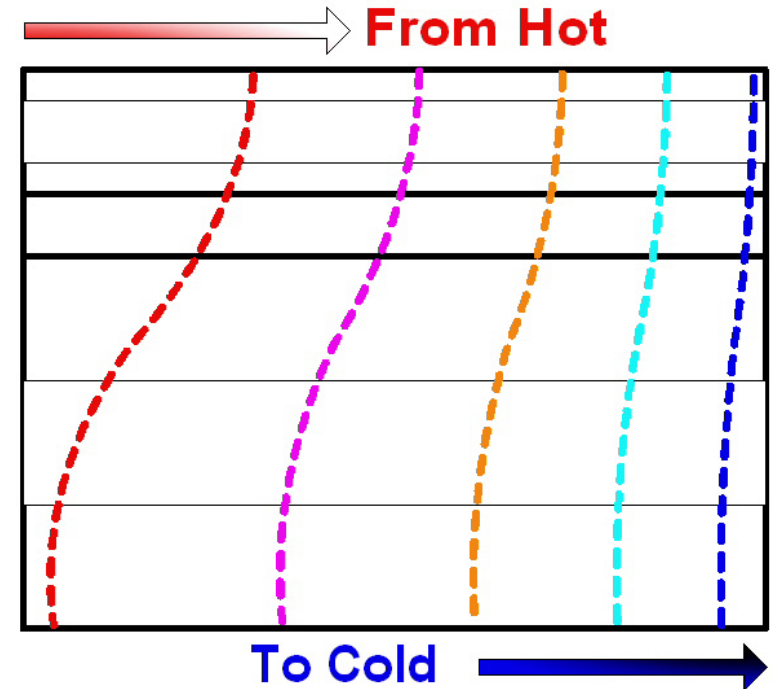
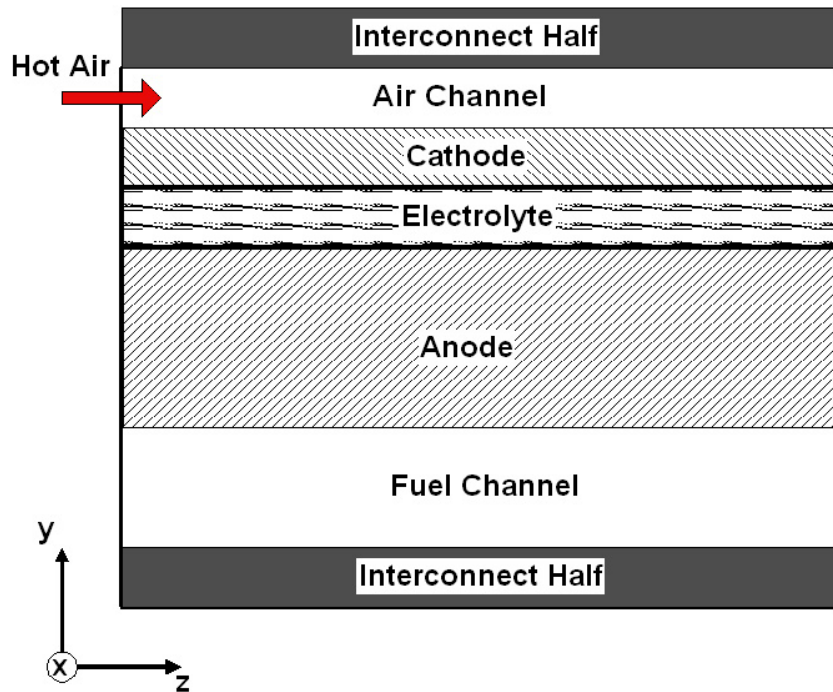
$k_{g,eff}$  - gas phase thermal conductivity  
 $h_v$  - volumetric heat transfer coefficient

$k_{s,eff}$  - solid phase thermal conductivity  
 $\Delta H_i$  - enthalpy of reaction species

Non-equilibrium thermal model necessary when:

- Difference in solid and fluid thermal properties is non-negligible
- Significant heat generation in porous media – existence of hot spots
- Low Reynolds number or flow velocities through porous media

# Transient Heating During Start-Up

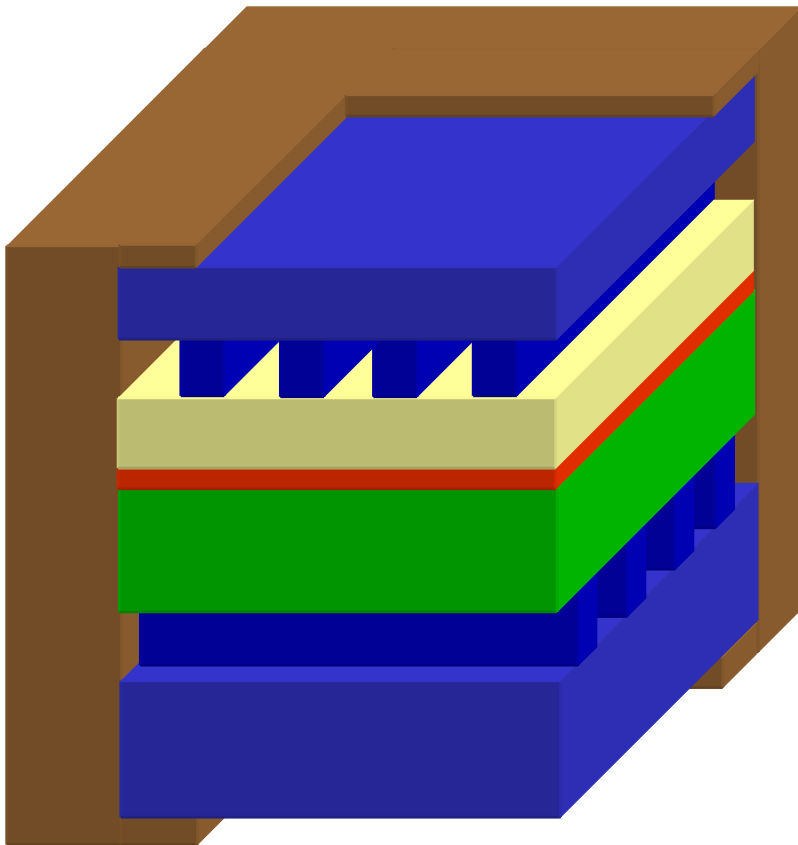


**QUESTION:** how fast can SOFC be heated without thermomechanical failure?

- Analytical solutions for transient temperature distribution with the SOFC are possible for the simplified quasi 1-D case in the limit of the thermally thin cell
- Numerical simulations will be used to analyze more complex and realistic scenarios involving combined convective-conductive-radiative heating

# Thermomechanical Failure Analysis

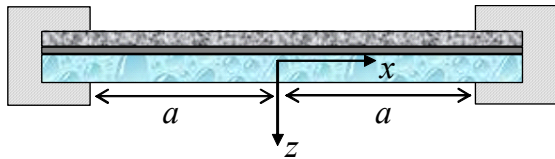
# Major Thermomechanical Failure Modes and Mechanism



- Warpage
  - Cracks/leak in seals
  - 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
  - Cyclic Redox

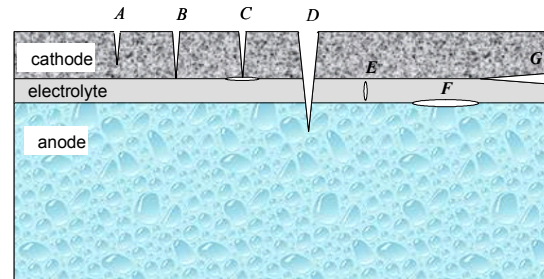
# Modeling Methodologies

## Cell Structure ( $L > 10^{-3}$ m)



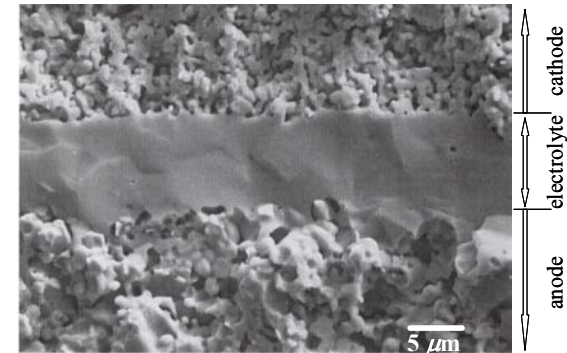
- Warpage
- Seal failure
- Seal design
- Residual stresses
- *Plate and laminate theories*

## PEN Structure ( $10^{-5}$ m $< L < 10^{-3}$ m)



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

## Material Structure $L < 10^{-5}$ m

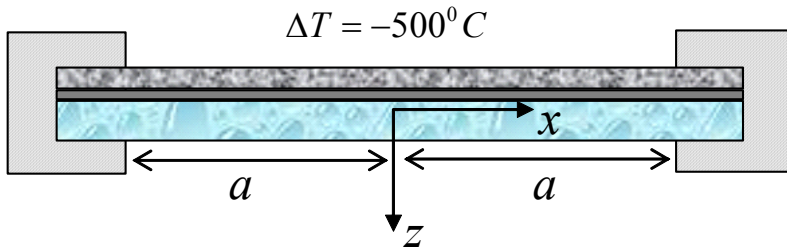


- Crack initiation
- Plasticity
- Creep
- *Micromechanics*
- *Damage mechanics*

# Major Results to Date

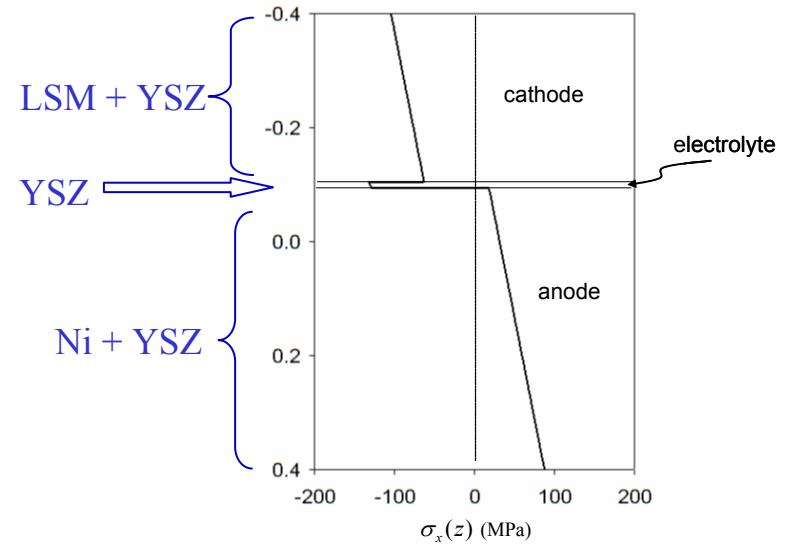
- Model for PEN stress vs. seal stiffness
- Model for thermal residue stress induced deformation in PEN with functionally graded anode
- Model for evaluating max. allowable initial flaw size
- Model for thermal shock induced microcracking
- Model for crack path prediction in PEN
- Model for effective properties of anode/cathode materials
- Algorithm for computing crack-tip fracture parameters
- Algorithm for global and local computational scheme

# Warpage and Stress Analysis

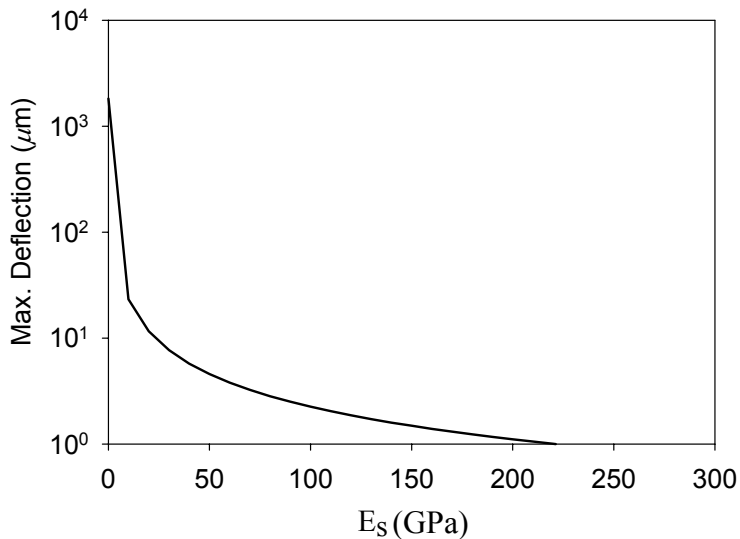


Deflection due to temperature change

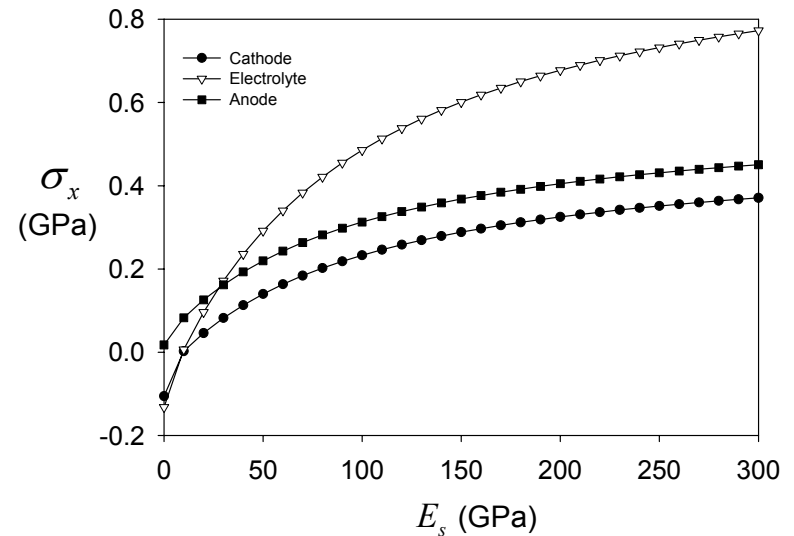
$$w_0(x) = \frac{(A_{11} + E_s h)M_0 - B_{11}N_0}{2[B_{11}^2 - (D_{11} + aE_s h^2)(A_{11} + E_s h)]} (a^2 - x^2)$$



Max. deflection vs. seal stiffness

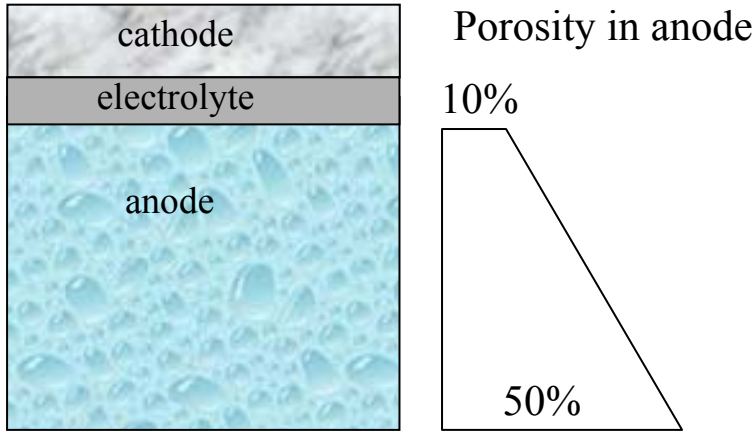


Max. cell stress vs. seal stiffness

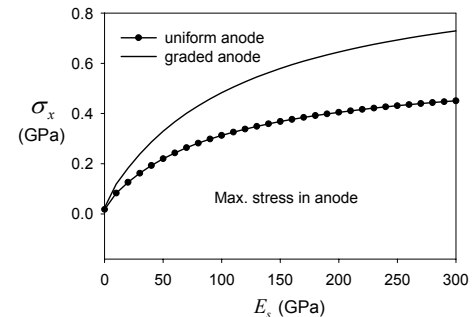
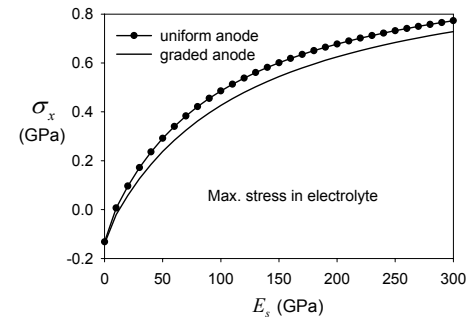
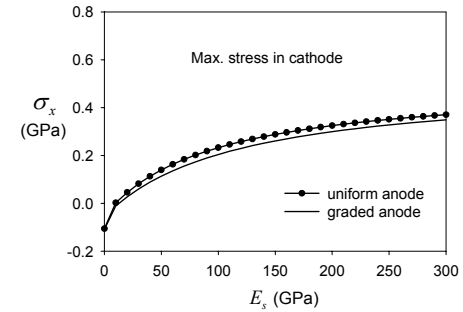




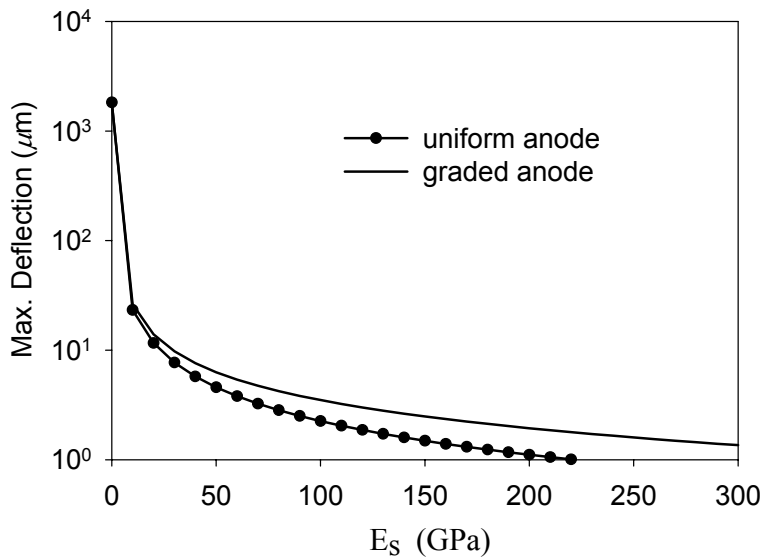
# Effect of Graded Anode



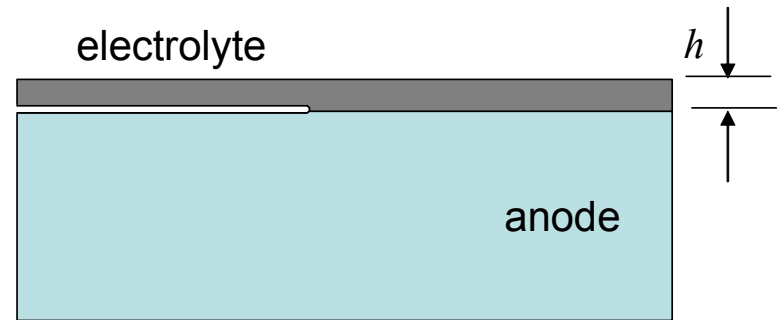
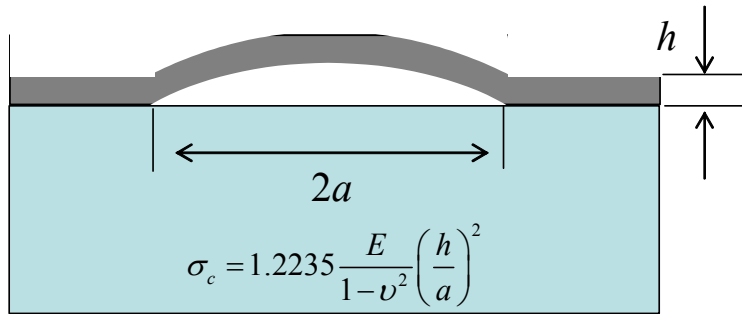
Max. cell stress vs. seal stiffness



Max. deflection vs. seal stiffness

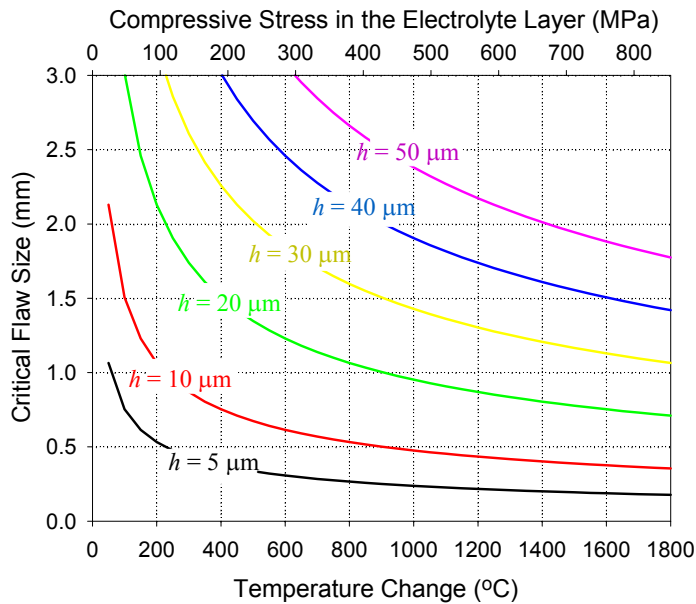


# Blister vs. Edge Delamination

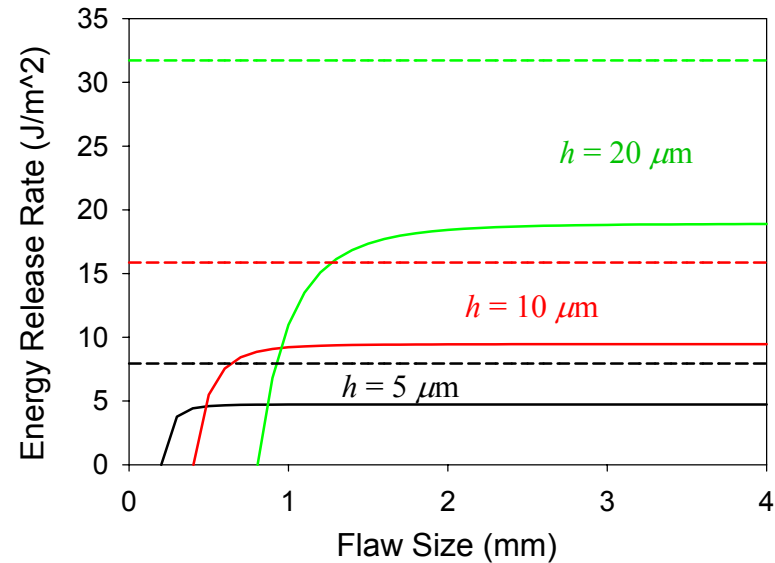


$$G = \frac{(\Delta T \Delta \alpha)^2 E h}{(1-\nu)[1+0.9021(1-\nu)]} \left\{ 1 - \left[ \frac{1.2235}{\Delta T \Delta \alpha (1+\nu)} \left(\frac{h}{a}\right)^2 \right]^2 \right\}$$

$$G = 1.028 \frac{E h}{1-\nu} (\Delta T \Delta \alpha)^2$$

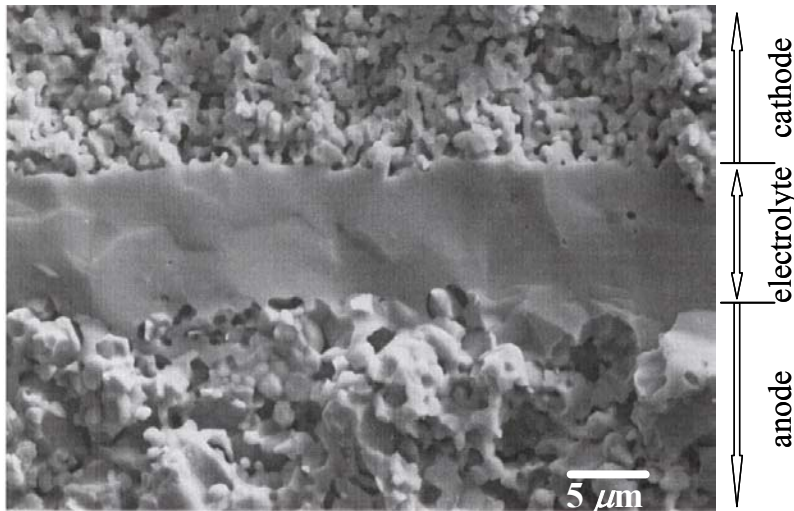


Relationships between processing temperature, electrolyte layer thickness and critical flaw size



Comparison of energy release rate between edge and blister delamination

# Effective Properties of Porous Electrodes



$$E = \frac{2(1-c)(5\nu_0 - 7)E_0}{2(5\nu_0 - 7) + c(13 - 2\nu_0 - 15\nu_0^2)}$$

$$E_0 = \frac{9K_0}{1 + 3K_0/\mu_0}$$

$$\nu = \frac{2(10\nu_0^2 - 9\nu_0 - 7) + c(25\nu_0^2 + 6\nu_0 - 19)}{2(5\nu_0 - 7) + c(15\nu_0^2 + 2\nu_0 - 13)}$$

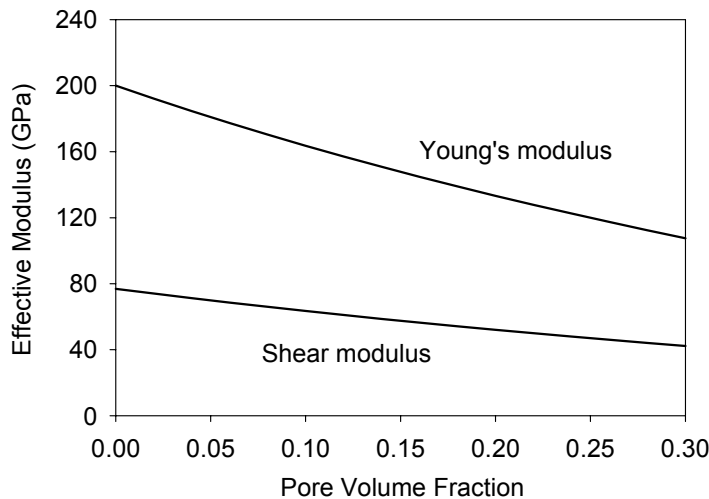
$$\nu_0 = \frac{1 - 2\mu_0/3K_0}{2 + 2\mu_0/3K_0}$$

Input:

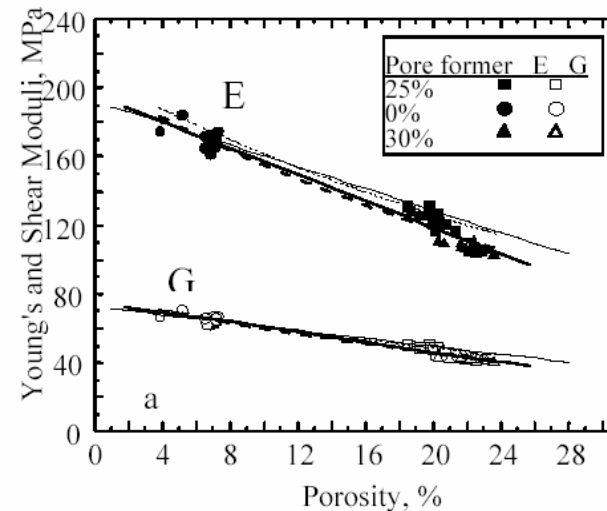
Properties and volume fractions of Ni, LSM and YSZ and porosity

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  $f(\mathbf{r}) = \frac{q}{\rho c (\sqrt{\pi} r_0)^3} \exp\left(-\frac{r^2}{r_0^2}\right)$

Temp Distribution

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

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

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  $U_s = 2\pi N b^2 \gamma$

Griffith Fracture Criterion  $\frac{d(U_s + U_b)}{da} = 0$

$$q = \frac{3\pi^2 k r_0}{2\alpha} \left[ 1 + \frac{16(1 - \nu^2) N b^3}{9(1 - 2\nu)} \right] \sqrt{\frac{G_c \pi (1 - \nu)}{E_0 b (1 + \nu)}}$$

$q$  = rate of heat generation (J/sec)

$G_c$  = Fracture toughness of the material

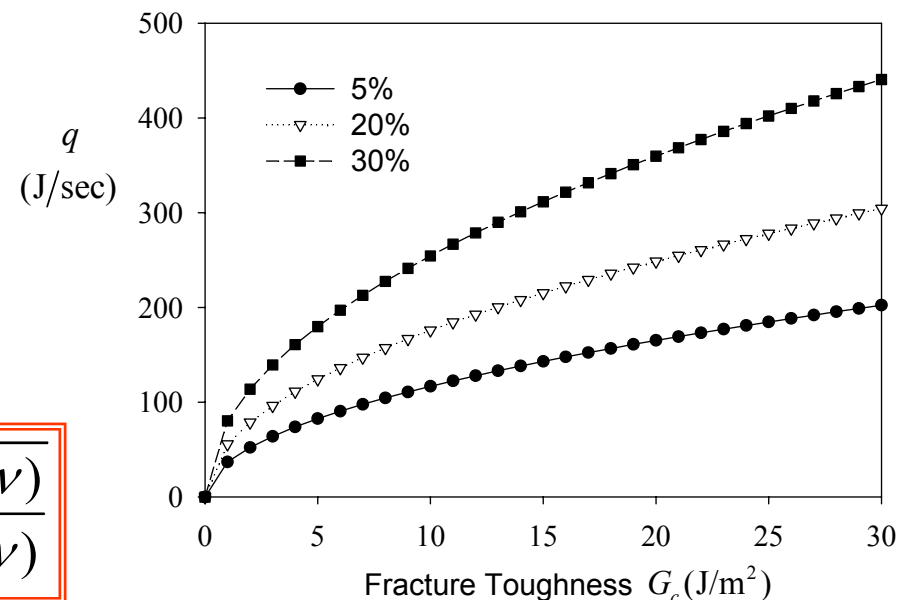
$b$  = crack size

$N$  = number of cracks per unit volume

$k$  = Thermal conductivity

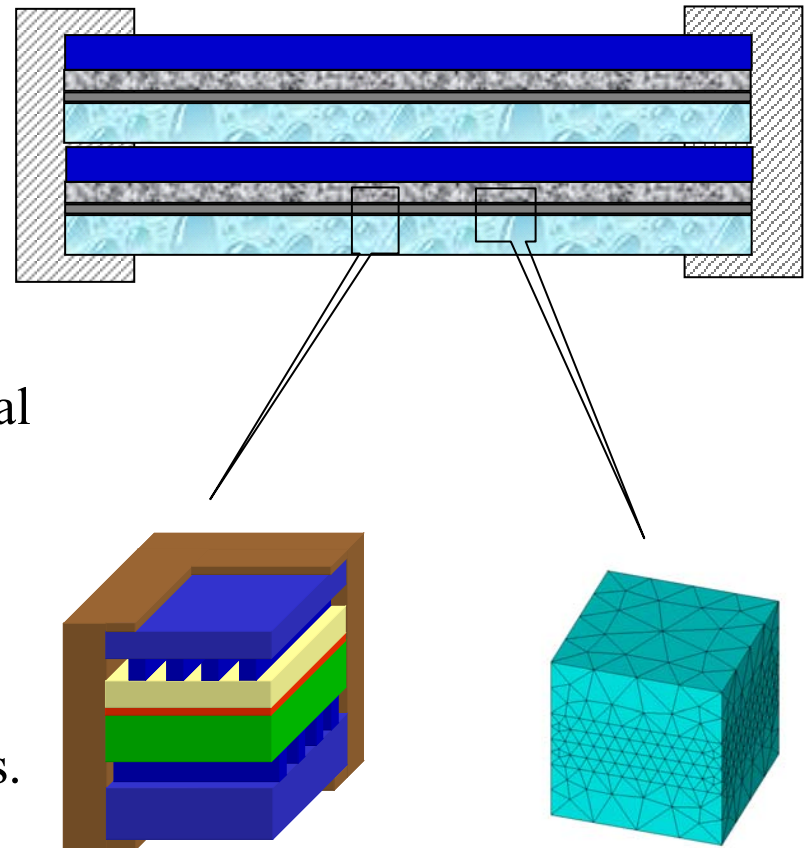
$\alpha$  = Coefficient of linear thermal expansion

$r_0$  = A length parameter characterizes the spatial non-uniformity of the heat source.



# Algorithms and ANSYS Codes for Global-Local Analysis

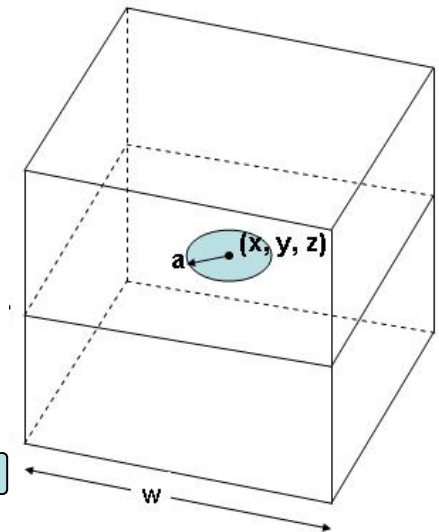
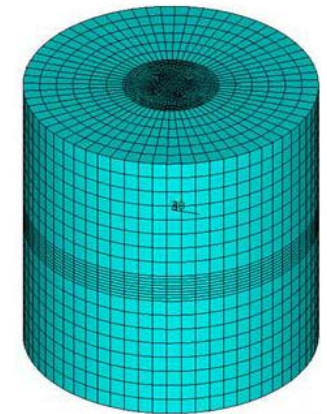
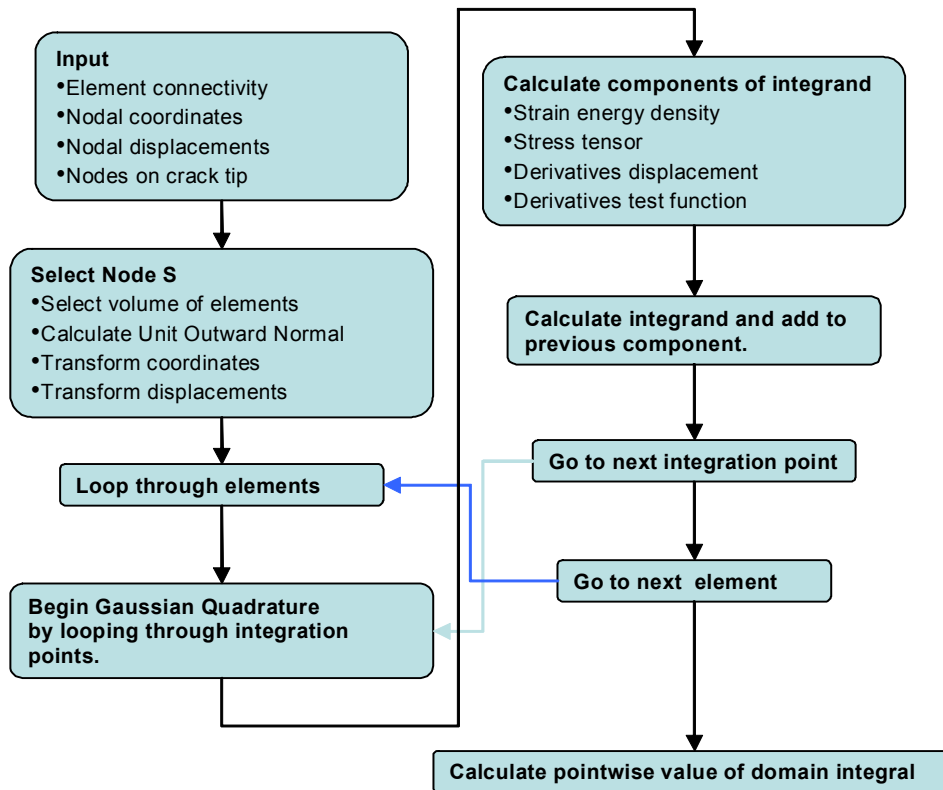
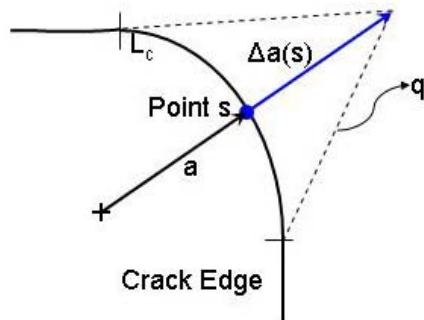
1. Global FEM model with desired boundary conditions and temperature distributions.
2. Solve structural analysis and determine locations of interest.
3. Create local model enclosing cracks/defects.
4. Apply displacements along local model boundaries as extrapolated from the global model.
5. Apply temperature gradient within local model as determined from global model.
6. Solve local structural analysis to obtain detailed stress field around cracks/defects.



# Domain Integral Formulation and ANSYS/MatLab Codes for Calculating Crack-Tip Fracture Parameters

$$\bar{G} = \bar{J} = - \int_V tr \left\{ \left[ W \mathbf{I} - (\bar{\nabla} \mathbf{u} \otimes \boldsymbol{\sigma}) \right] \square \bar{\nabla} \mathbf{q} \right\} dV$$

$$G(s) = \frac{\bar{G}}{\int_{L_c} \Delta a(s) ds}$$



# Activities for the Next 6 – 12 Months

## ***1.1 Develop crack growth models in SOFC materials***

In this task, crack growth rate in the electrode layers will be investigated. High temperature fatigue, creep and fatigue-creep interaction will be considered in the model. Furthermore, microstructural changes due to oxidation and reduction in the anode should be also included in the model. For validation, the model prediction will be compared with the crack growth data obtained by Dr. Lara-Curzio and his team at ORNL.

## ***1.2 Develop fracture mechanics based models for damage accumulation in SOFC stacks***

Based on the models developed in Task 1.1 for crack growth in SOFC materials, a damage accumulation model for the SOFC cell stack will be constructed based on the actual cell stack structure and seal design. This will be carried out through detailed numerical analysis to obtain the stress and strain distributions. Once the stress fields are obtained, they will be used as the driving force in the crack growth model developed in Task 1.1 to establish the relationship between crack size (or microcrack density) and the cell stack service time (see Task 4).

### ***1.3 Seal structure and reliability***

First, stress analysis using the finite element method will be conducted on various seal designs and structures. Then, the fracture mechanics models developed in Task 1.1 will be used here to assess the propensity of leakage and fracture of the various seals under both transient (start-up and shutdown) and steady-state (operation) conditions. Finally, the damage accumulation models developed in Task 1.2 will be used to investigate the long term durability of seals. For validation, the model prediction will be compared with the experimental data from PNNL.

### ***1.5 Develop models for thermal shock induced failure in SOFC***

The transient thermal transfer during startup and shutdown will be analyzed and solved in Task 3.3. We will then compute the transient stress fields resulted from the transient temperature field obtained in Task 3.3. Once the transient stress fields are known, the fracture models developed in Task 1.1 will be used to evaluate the critical parameters, such as heating rate and heating profile, air flow rate, initial fuel supply rate, direct internal reformation (DIR) reaction radii, etc., that may result in microcracking of the electrodes. The objective is to establish guidelines (based on the materials fracture strength) for optimal design and safe operation of SOFC stacks.



# GT Project Summary

## Applicability to SOFC Commercialization

- ❖ In collaboration with SECA industries, the national labs (NETL, PNNL, ORNL) are undertaking a comprehensive study to develop Life Prediction and Structural Modeling Tools for the design, manufacturing, reliability analysis and service life prediction of SOFCs.
- ❖ As part of a coordinated effort, Georgia Tech will assist PNNL/NETL/ORNL in developing the Life Prediction and Structural Modeling Tools for the SECA program. Our role is to provide modeling modules complementary to the existing effort in PNNL/NETL/ORNL. Specifically, Georgia Tech is responsible for developing modules on fracture, damage evolution, radiation and thermal transport.
- ❖ Most of our models (except the studies on seals which are pertinent to flat-planar designs) will be developed at the fundamental material level so that they can be applied to various types of SOFCs including anode-supported, cathode-supported and electrolyte-supported, as well as tubular designs.

# GT Project Summary

## Major Accomplishments of the First 12 months

- ✓ “Slice technique” model/code *rapidly* simulates unit cell performance as a precursor to parametric studies
- ✓ Reformate stream analysis model based upon a more realistic “frozen” CO electrochemistry assumption --- coking/threshold fuel utilizations further realized
- ✓ Studied Knudsen, dispersion, diffusion-thermo (Soret) and thermo-diffusion (Dufour) mass and heat transfer effects
- ✓ Discrete Ordinate Method is computationally intensive – Alternative model based on two-flux approximation has been developed
- ✓ Preliminary FTIR experiments were carried out to determine optical properties of electrodes and electrolyte.
- ✓ Model for PEN stress vs. seal stiffness
- ✓ Model for evaluating max. allowable initial flaw size
- ✓ Model for thermal shock induced microcracking
- ✓ Model for effective properties of anode/cathode materials
- ✓ Algorithm for computing crack-tip fracture parameters
- ✓ Algorithm for Global and local scheme

# GT Project Summary

## GT Activities for the Next 6 – 12 Month

- Develop crack growth models in SOFC materials
- Develop fracture mechanics based models for damage accumulation in SOFC stacks
- Seal structure and reliability
- Develop models for thermal shock induced failure in SOFC
- Transient Heating During Start-Up
- Radiative Property Characterization
- Higher fidelity simulation of fuel stream chemistry effects
- Investigation of fracture-electrochemistry interaction