AN INTEGRATED APPROACH TO MODELING AND MITIGATING SOFC FAILURE

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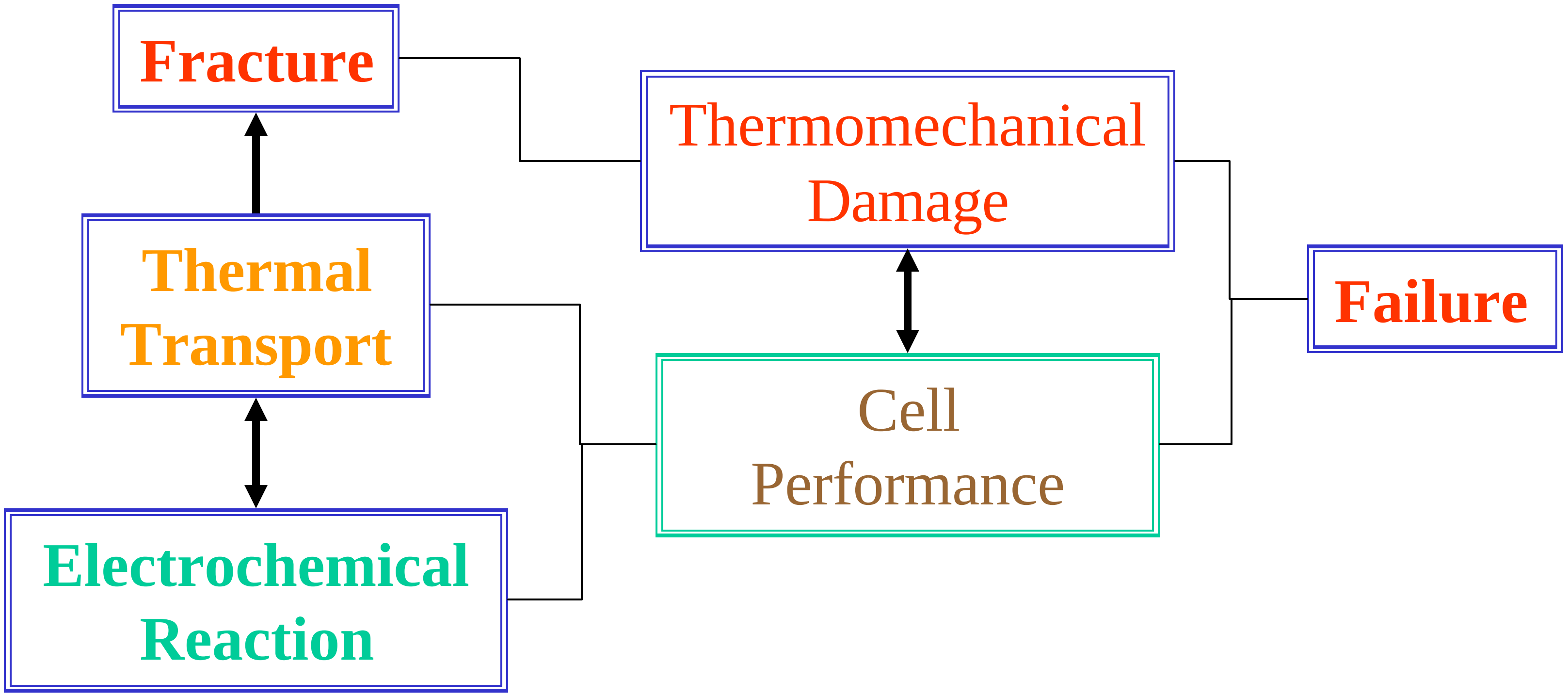
Project Overview



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

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

Technical Issues to be Addressed

Thermomechanical Damage and Failure

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

Thermal Transport

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

Electrochemistry

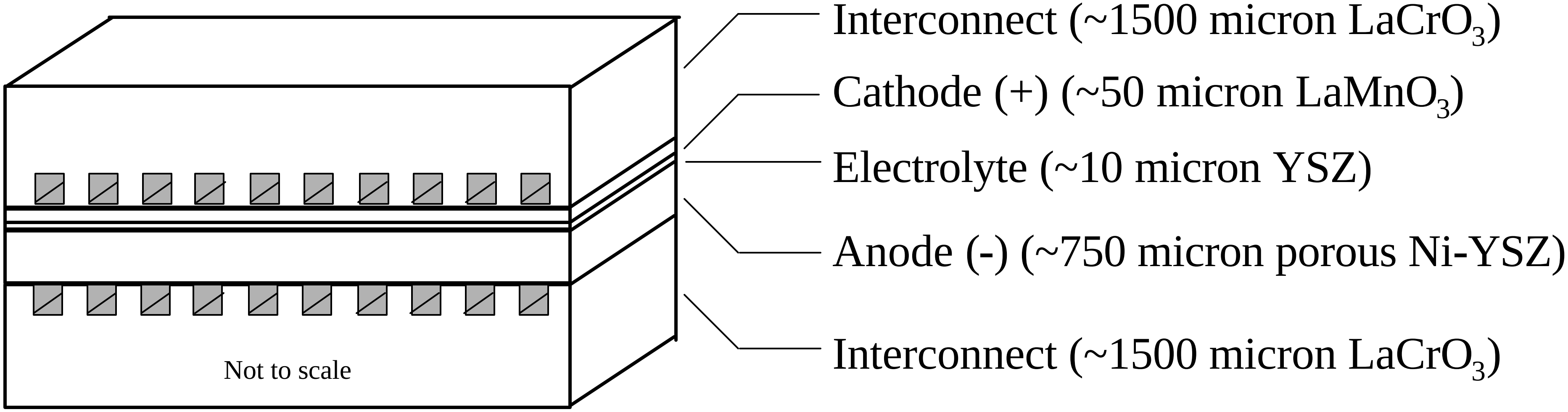
- Cell and stack level engineering models
- Interdependency between electrochemistry and thermal/mass transport
- Transient processes and failure modes

Electrochemistry

Model Objectives Achieved

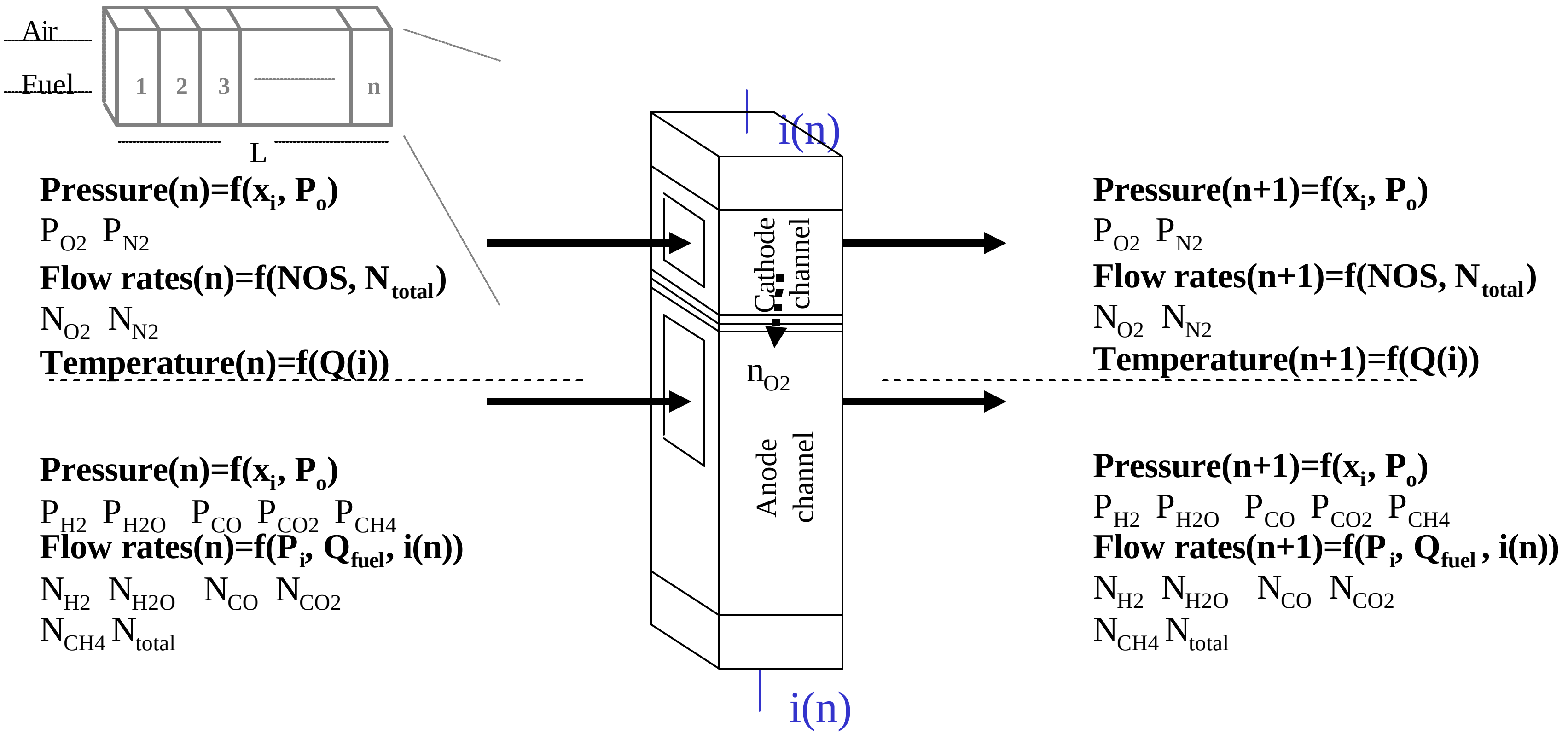
- Engineering Code
  - Accurate and viable
  - Customized structural-language algorithms that are portable to software
  - Enhanced designer insight via graphically *intuitive* trends
- Complement to SECA DOE National Labs' Efforts
  - Resolution of reformate stream analysis (NETL)
  - Automated convergence upon set fuel utilization (PNNL)

Planar SOFC Co-flow Diagram



- Anode-supported cell
- Designs capable of 2 W/cm^2
- P-E-N dimensions from Kim, J., Virkar, A. V., Fung, K., Mehta, K., and Singhal, S., 1999

Planar SOFC Co-flow Model

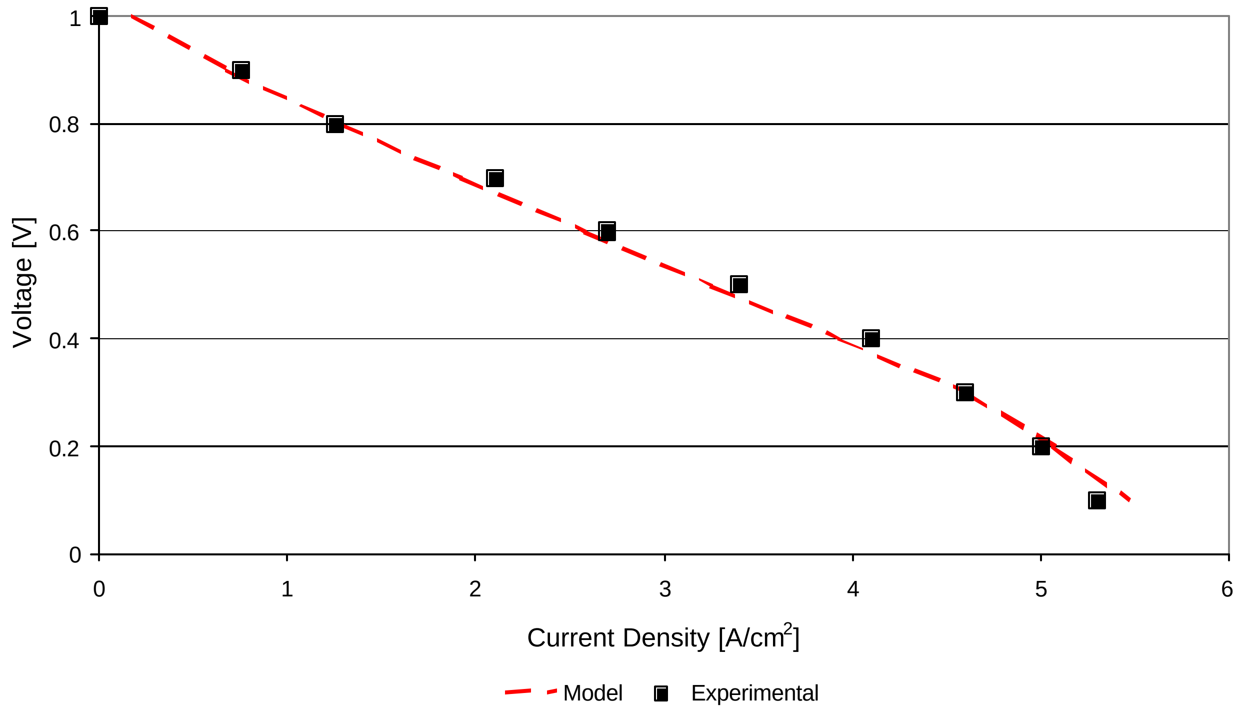


$$V(i) = E_o - i\mathbf{R}_{\mathbf{i}} - \mathbf{a} - \mathbf{b}\ln i + \frac{RT}{2F}\ln\left(1 - \frac{i}{\mathbf{i}_{\mathbf{as}}}\right) - \frac{RT}{2F}\ln\left(1 + \frac{p^{\circ}_{H_2}\, i}{p^{\circ}_{H_2O}\, i_{as}}\right)$$

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

Planar SOFC Co-flow Model Validation

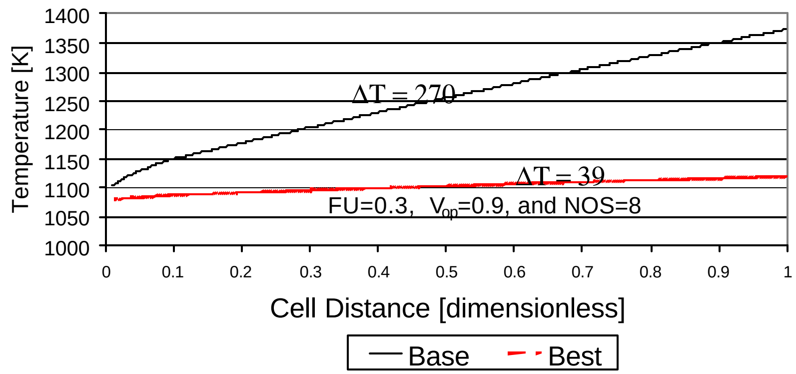
- Model agrees with experimental data
- Discrepancies, primarily differences in fuel utilization, caused by comparing a button cell to a much larger channel model

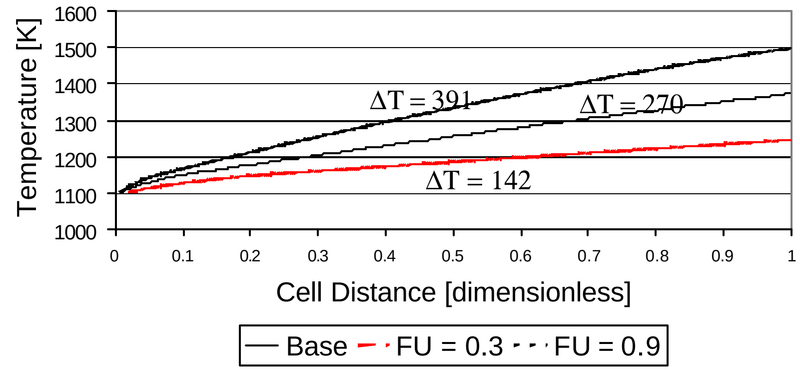


Thermal Model for Cells

- Assumptions
  - Isothermal channels as a design goal
  - Convection to air stream is the ***dominant*** form of cell thermal management
  - Laminar, hydrodynamically fully developed flow at the leading edge due to extensive manifolding
- Methodology
  - Use well-regarded laminar flow Nusselt correlations for airflow within rectangular ducts, to determine appropriate inlet air temperatures and resulting cell temperature profile
  - Vary parameters as required to determine impact
    - Voltage
    - Fuel utilization
    - **Fuel-based** inverse equivalence ratio / “number of stoichs” (NOS)

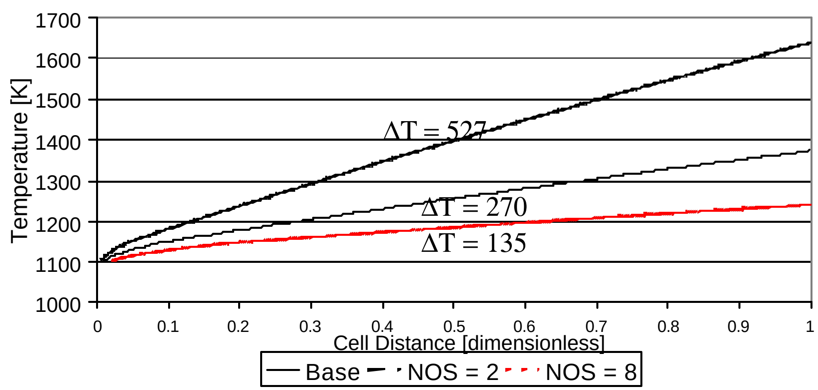
Promoting Isothermal Cells

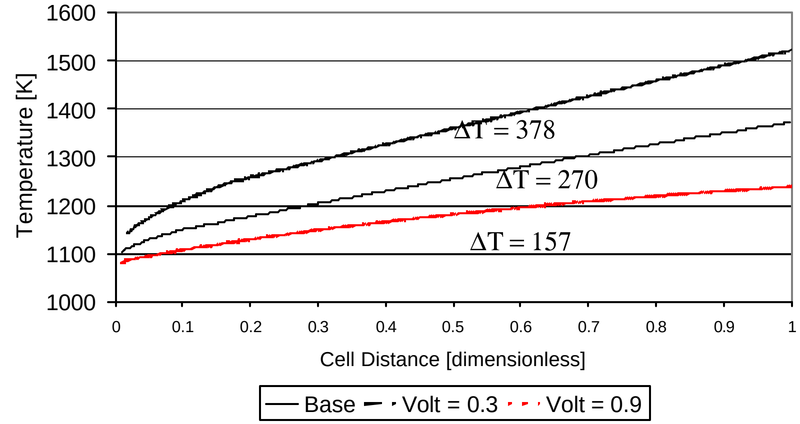




Best Case

¯ Fuel Utilization





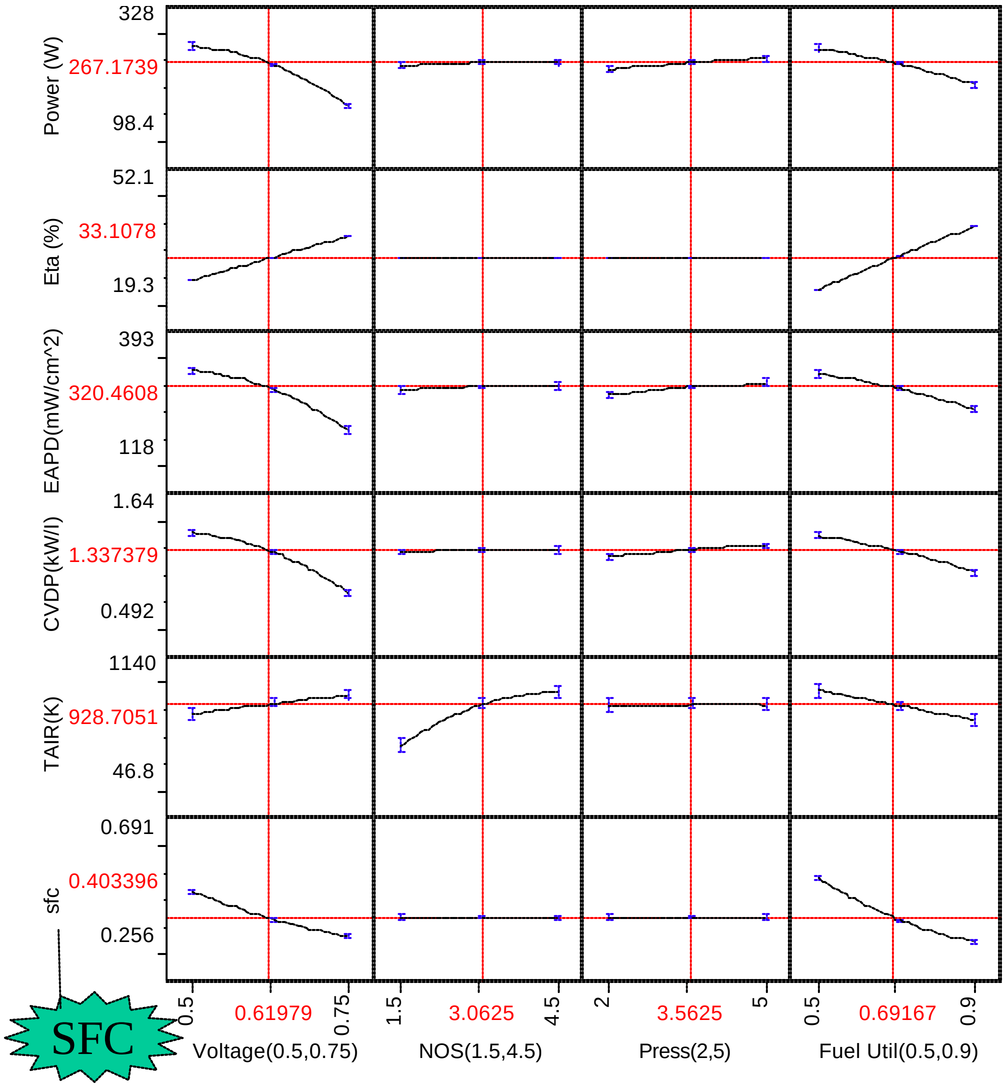
- V_{op}

- NOS

Graphically Intuitive Design Aids Development

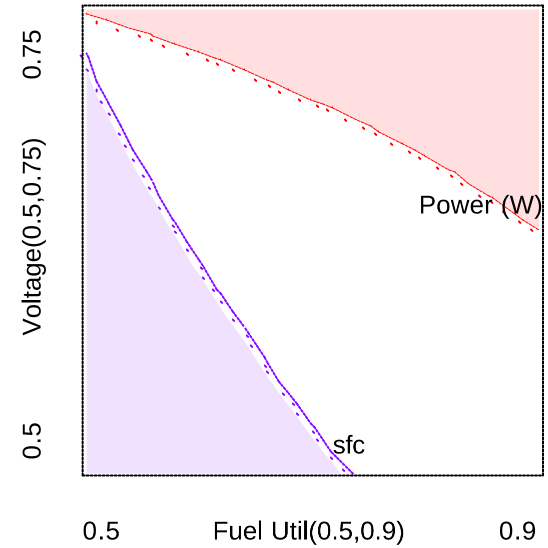
Fuel Cell M&S Updates

Real-Time Visualization of Constraint Space



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^2)	.	320.46083	.	.
CVDP(kW/l)	.	1.3373789	.	.
TAIR(K)	593.4	928.70515	.	.
sfc	0.4736189	0.4033964	.	0.48



Latter Phase I/ Phase II Developments

- Greater collaboration with SECA-affiliated national labs

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

Latter Phase I/ Phase II Developments

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

Examples:

▪Strength requirements for designated operating conditions

▪Gleaming *effective* mass transport diffusivities for better characterizing concentration polarization

➢Viable performance/reliability tools and training for industry

Thermal-Fluid Modeling of SOFC

Thermal-Fluid Modeling of SOFC

Focus of Thermal – Fluid Modeling Efforts

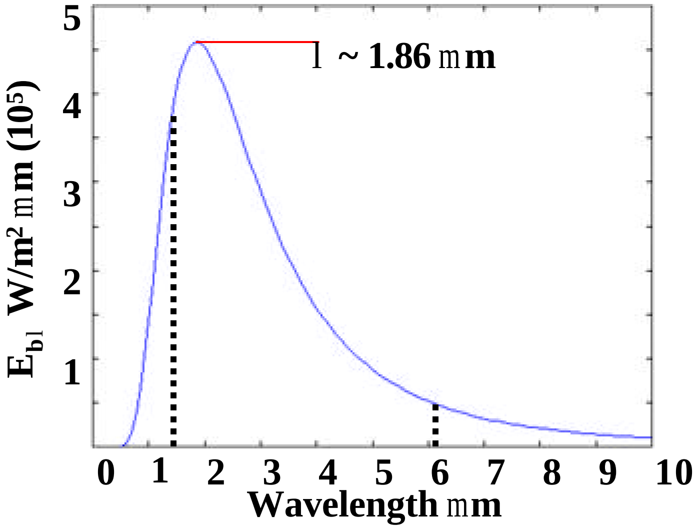
Porous Media Modeling

- Knudsen, dispersion, diffusion-thermo (Soret) and thermo-diffusion (Dufour) mass and heat transfer effects
- Non-equilibrium heat transfer in porous electrodes to account for unequal gas and solid matrix temperatures
- Effective thermal conductivity of solid matrix of porous electrodes

Radiation Modeling

- SOFC's are high temperature systems – radiation modeling important
- Coupling between radiation and other modes of heat transfer affects reaction rates and cell output voltage
- Discrete Ordinate Method is computationally intensive – need for alternate modeling schemes

Radiation Modeling – Optical Properties

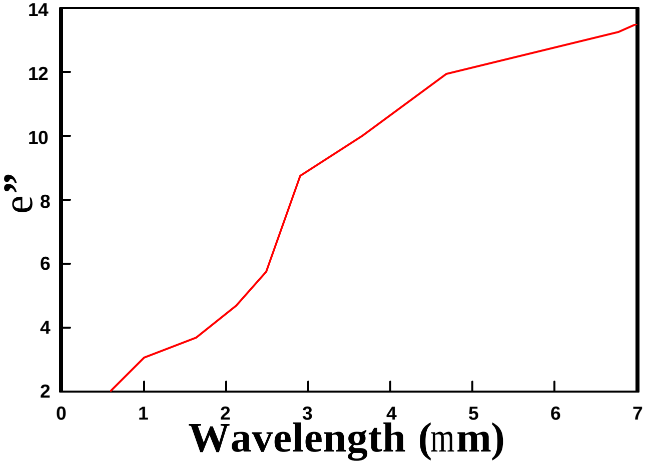


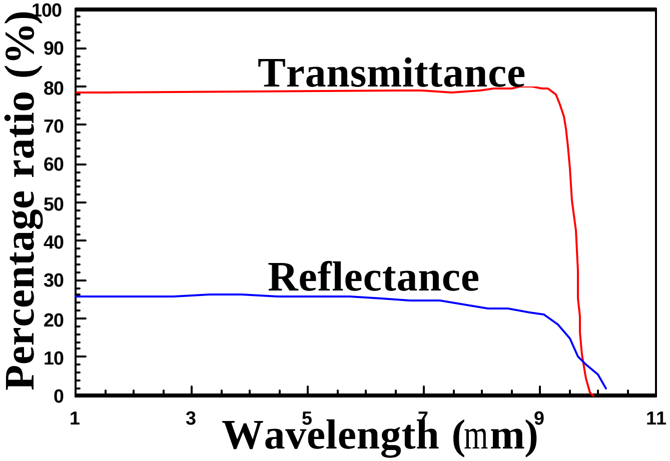
Wien's law: $(n\,\lambda\,T)_{max}$ = 2898 μm.
n ~ 1.6; T = 700 °C = 973 K; λ_{max} = 1.86 μm

80% of fractional emissive power is contained within 1.4μm < λ < 6.1μm

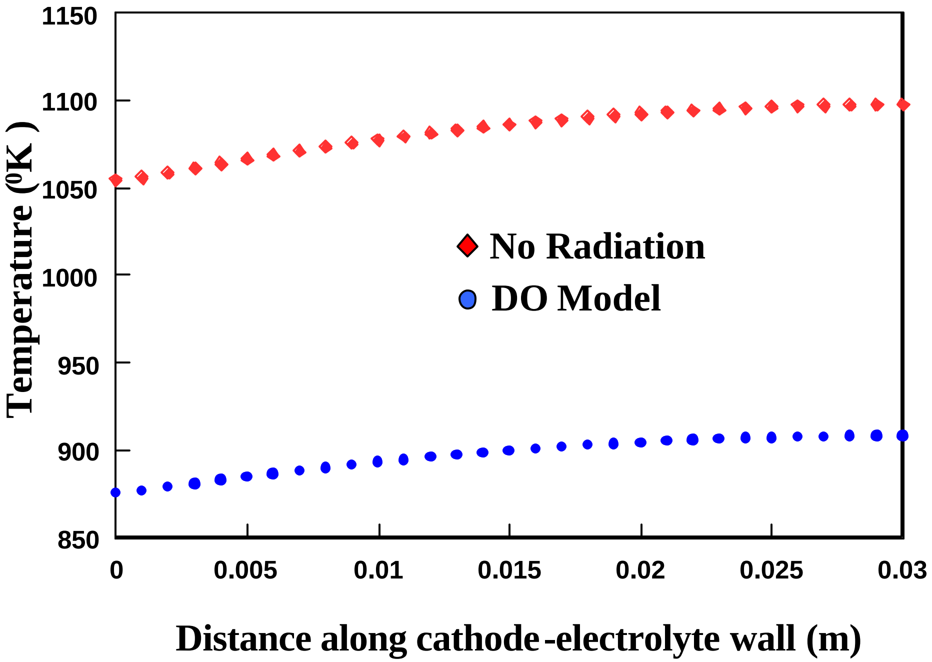
Electrolyte: Weakly absorbing (κ=496.2 m^{-1}) and optically thin (κL<0.003)

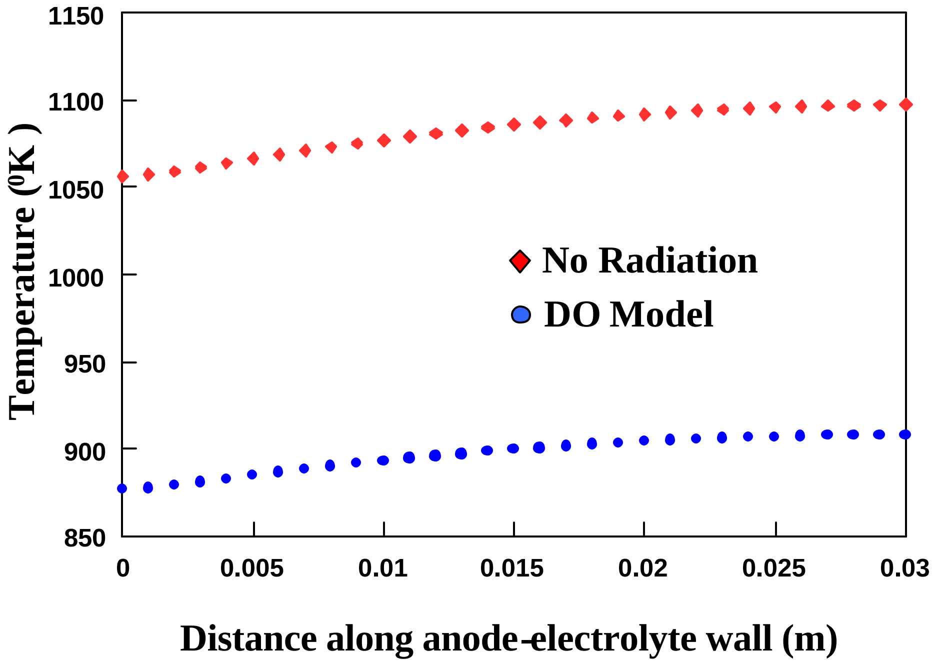
Electrodes: Optically thick/opaque





Radiation Modeling – Discrete Ordinate Method

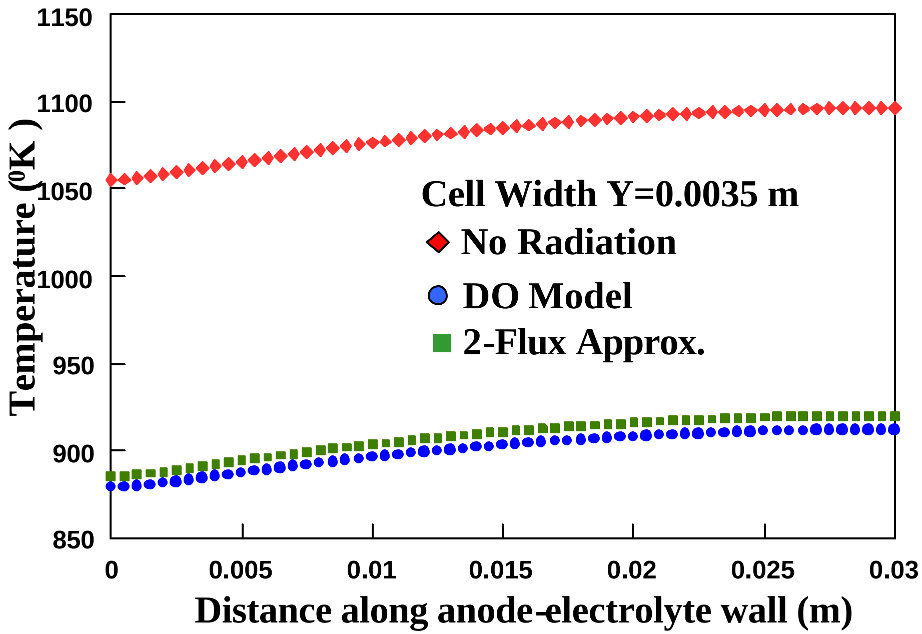


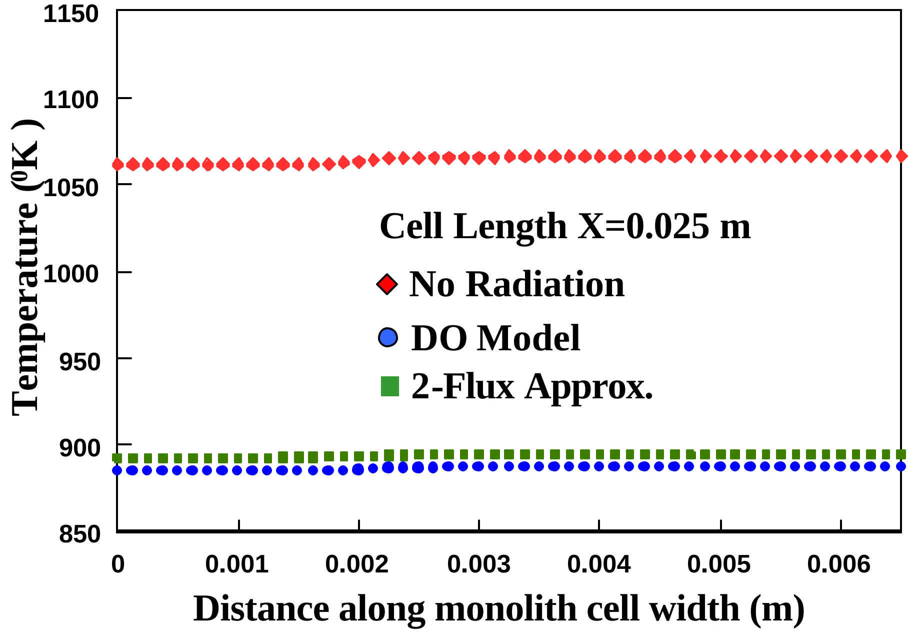


- Inclusion of radiation results in ~150 ^{o}K drop in the overall temperature level of the monolith type SOFC

- Coupled radiation effects result in increase of cell voltage from 0.65 V — 0.74V

Radiation Modeling – Two-flux Approximation





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

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

Porous Media – Reagent Transport Modeling

Momentum Conservation - Forchheimer and Brinkman Model:

$$\frac{1}{e^{2}}\nabla\cdot\left(r\,\vec{V}\,\vec{V}\right) = -\nabla p + \nabla\cdot\left(m_e \nabla \vec{V}\right) - \frac{m\,\vec{V}}{K} - r\,f\,\frac{\left|\vec{V}\right|\,\vec{V}}{\sqrt{K}} + r\,\vec{g}\,b\left(T - T_\infty\right)$$

m_e - effective viscosity   e - **porosity**

K - permeability

f - inertia coefficient

Species Conservation – Reagent and Intermediate Mole Fraction:

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

D_i - effective diffusion coefficient

$D_{i,T}$ - thermal diffusion coefficient

S_i - species production / depletion rate

$$D_i = \frac{e}{t}\left(\frac{1 - a_i\,x_i}{D_{i,m}} + \frac{1}{D_{i,k}} + \frac{1}{D_{i,d}}\right)^{-1}$$

$D_{i,m}$ - molecular diffusion   e - **porosity**

$D_{i,k}$ - Knudsen diffusion   t - **tortuosity**

$D_{i,d}$ - dispersion

Porous Media – Diffusion Modeling

Diffusion Coefficient for Species Conservation :

$$D_i = \frac{e}{t}\left(\frac{1-a_i\, x_i}{D_{i,m}} + \frac{1}{D_{i,k}} + \frac{1}{D_{i,d}}\right)^{-1}$$

where

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

M_i - molecular weight of component i

M_m – average molecular weight

Molecular Diffusion Coefficient:

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

x_i - molar fraction

D_{ik} - binary diffusion coefficient

Knudsen Diffusion Coefficient:

$$D_{i,k} = \frac{2}{3}\left(\frac{8RT}{pM_i}\right)^{1/2} r$$

R - gas constant

T - fluid temperature

r - pore radius

Thermal Diffusion Coefficient:

$$D_{i,T} = -2.59\times 10^{-7}\, T^{0.659}\left[\frac{M_i^{0.511} x_i}{\sum_{i=1}^{N} M_i^{0.511} x_i} - Y_i\right] \bullet \left[\frac{\sum_{i=1}^{N} M_i^{0.511} x_i}{\sum_{i=1}^{N} M_i^{0.489} x_i}\right]$$

Dispersion Coefficient:

$$D_{i,d} = f\left(Pe, e\right)$$

Pe = $uR/D_{i,m}$ (Peclet #)

Y_i - mass fraction of i

Porous Media – Energy Conservation Modeling

Energy Conservation: Non-Equilibrium Thermal Model:

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

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

$k_{g,eff}$ - gas phase thermal conductivity
$k_{s,eff}$ - solid phase thermal conductivity
h_v - volumetric heat transfer coefficient
$\mathrm{D}H_i$ - enthalpy of reaction species

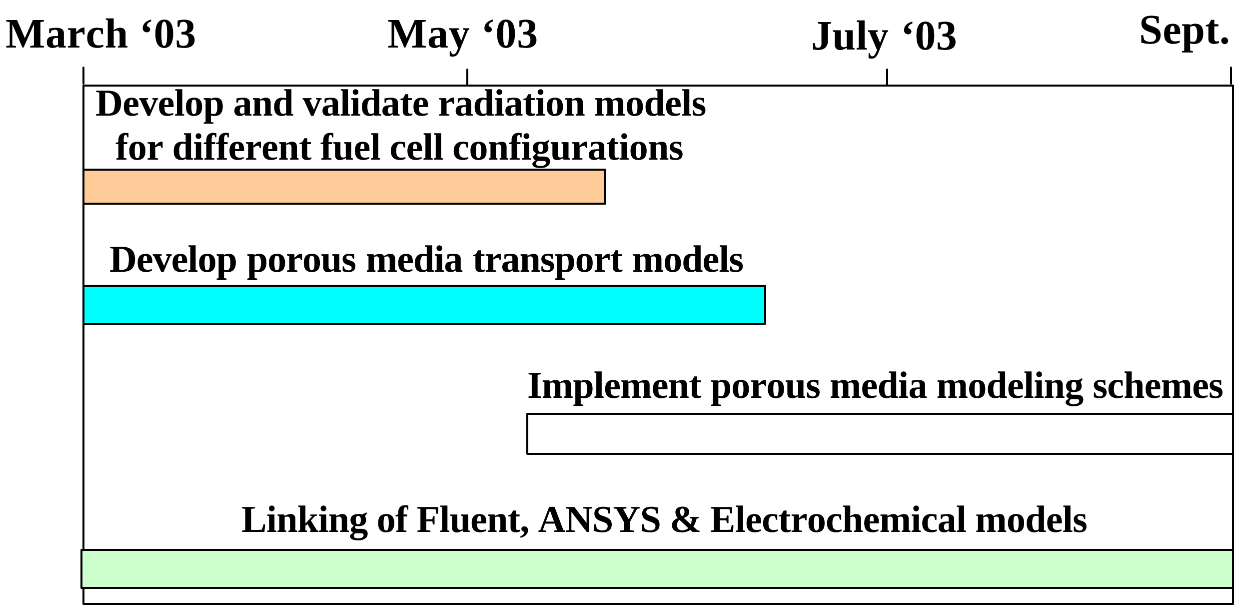
Non-equilibrium thermal model necessary when:

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

Research Tasks – Accomplishments & Future Work

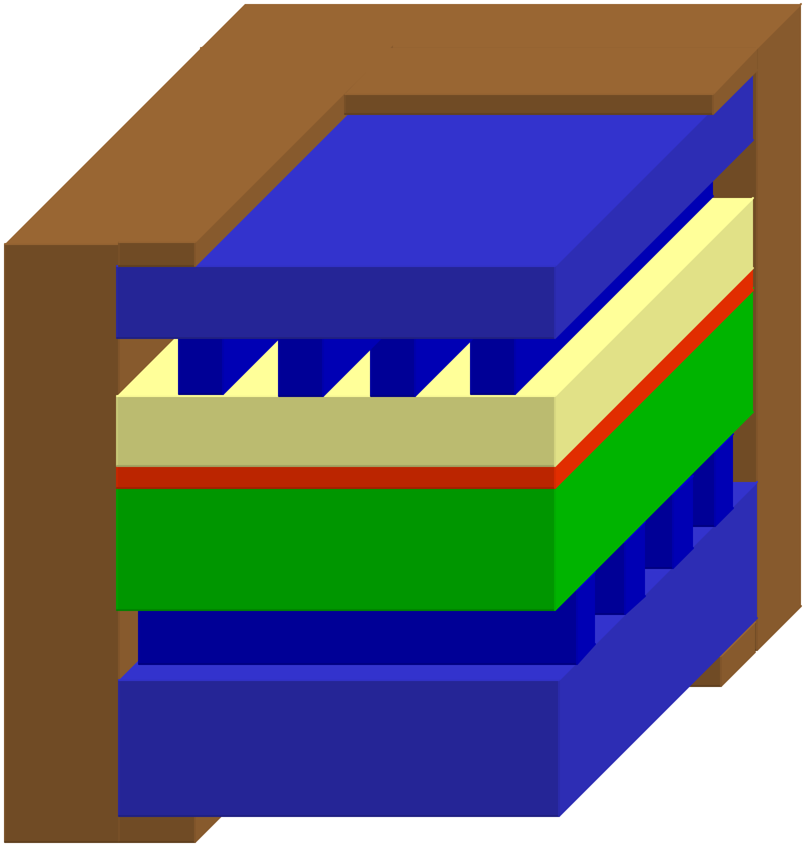
- Thermal radiation effects were investigated by coupling of radiative heat transfer and other modes of heat transfer → significant effects on the temperature and cell voltage were found warranting more detailed analysis, including experiments.

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



Thermomechanical Failure Analysis

Major Thermomechanical Failure Modes and Mechanism

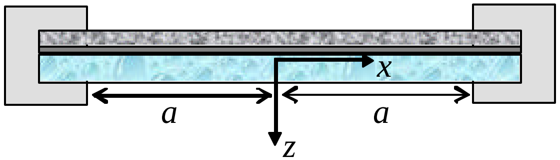


- Warpage
- Cracks in seal
- Cracks in electrodes
- Cracks in electrolyte
- Delamination of interfaces
- Creep/fatigue of interconnects
- ?? (industry inputs)

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

Modeling Methodologies

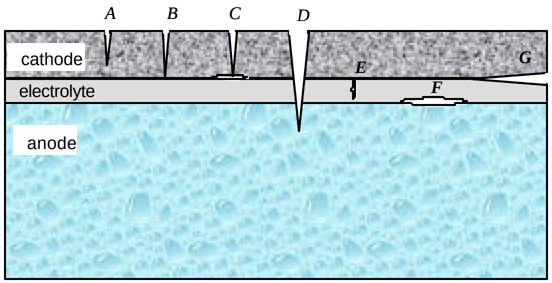
Cell Structure
($L > 10^{-3}$ m)



- Warpage
- Seal failure
- Seal design
- Residual stresses

- *Plate and laminate theories*

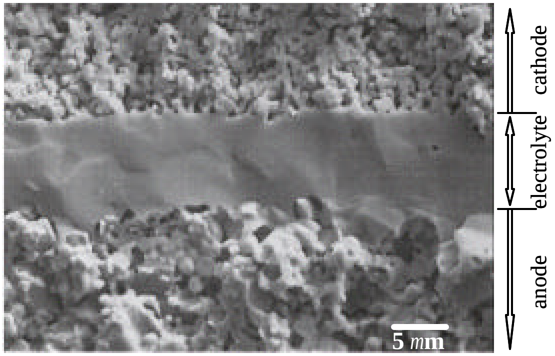
PEN Structure
(10^{-5} m < L < 10^{-3} m)



- Cracks growth
- Delamination
- Spalling

- *Fracture mechanics*
- *Finite element method*

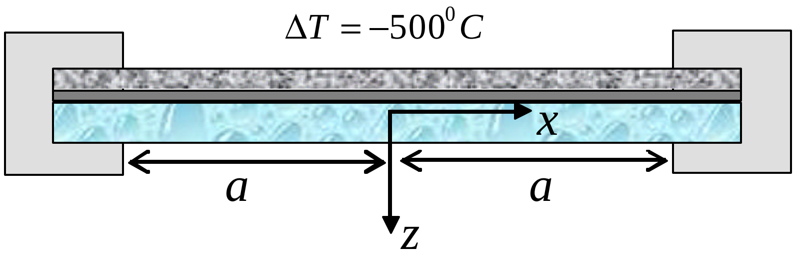
Material Structure
$L < 10^{-5}$ m

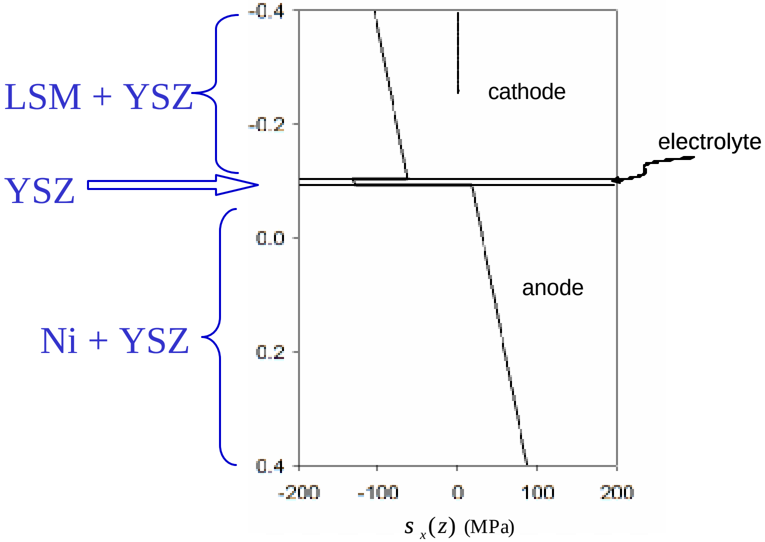


- Crack initiation
- Plasticity
- Creep

- *Micromechanics*
- *Damage mechanics*

Warpage and Stress Analysis

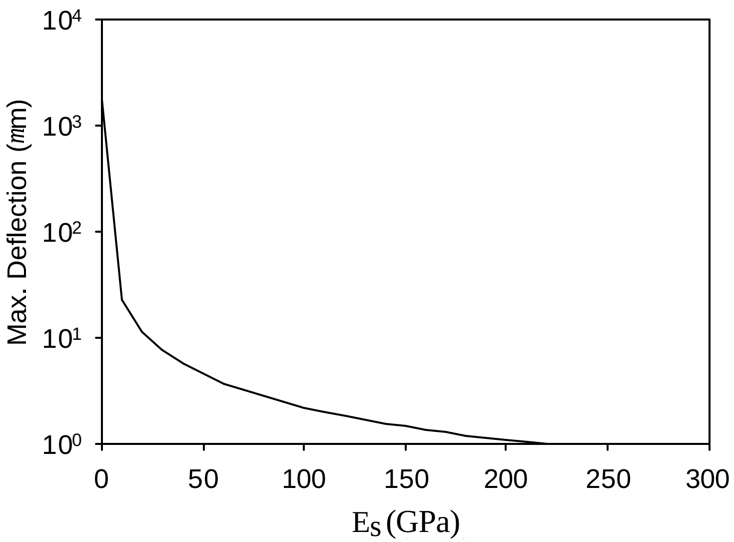




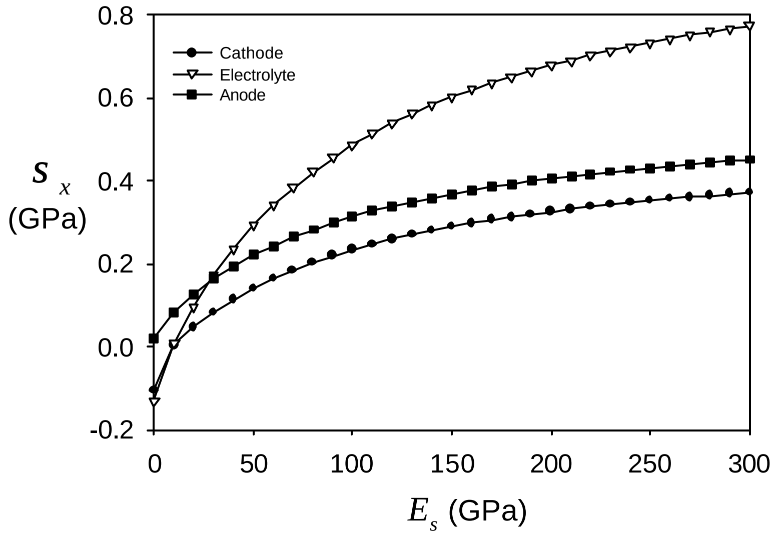
Deflection due to temperature change

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

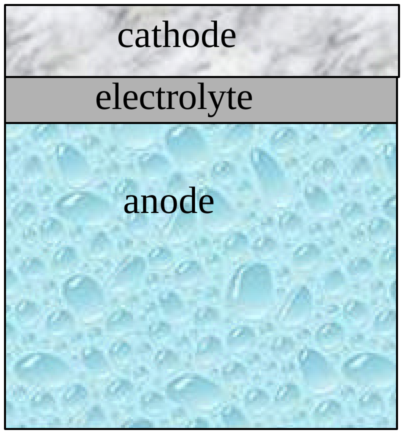
Max. deflection vs. seal stiffness



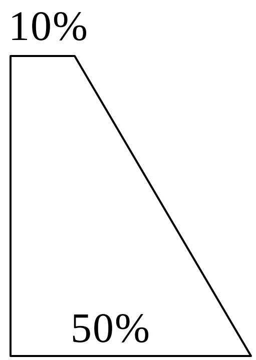
Max. cell stress vs. seal stiffness



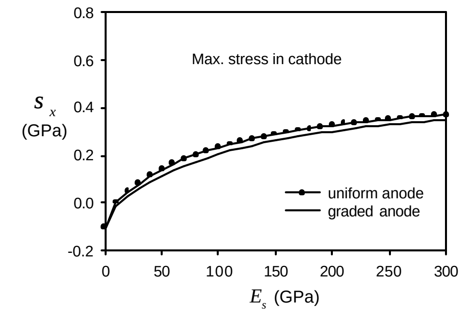
Effect of Graded Anode

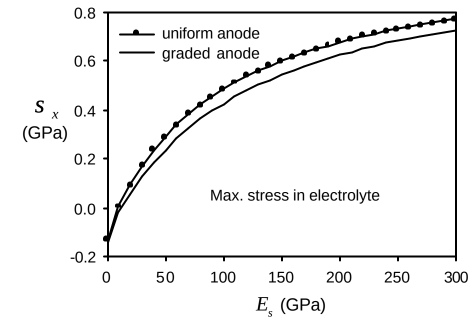


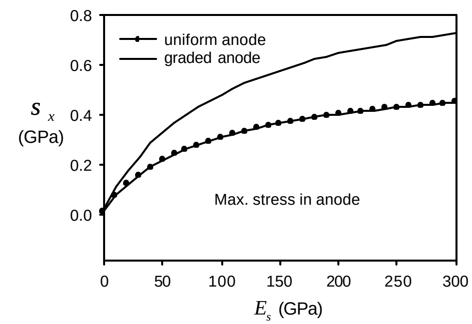
Porosity in anode



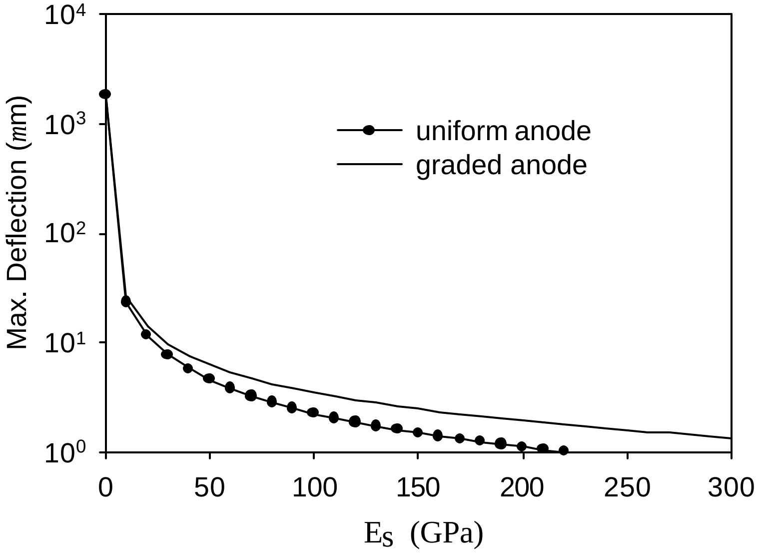
Max. cell stress vs. seal stiffness



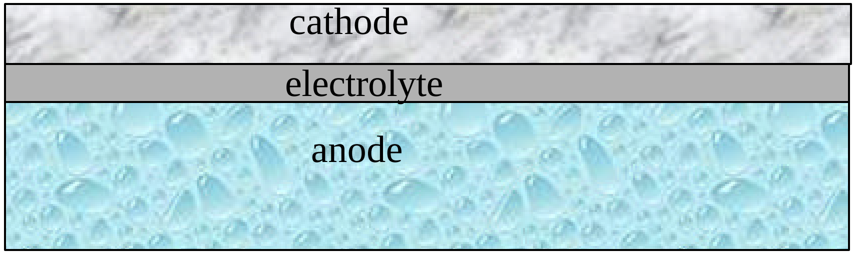




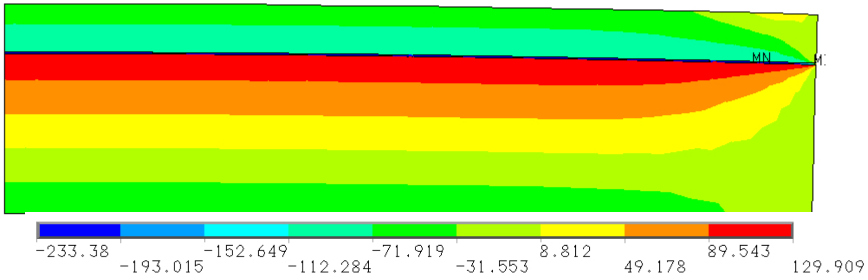
Max. deflection vs. seal stiffness



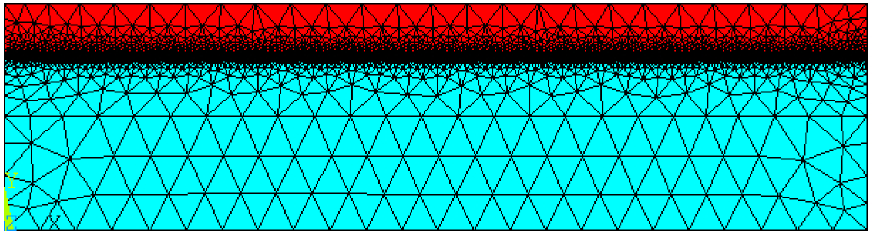
Finite Element Analysis



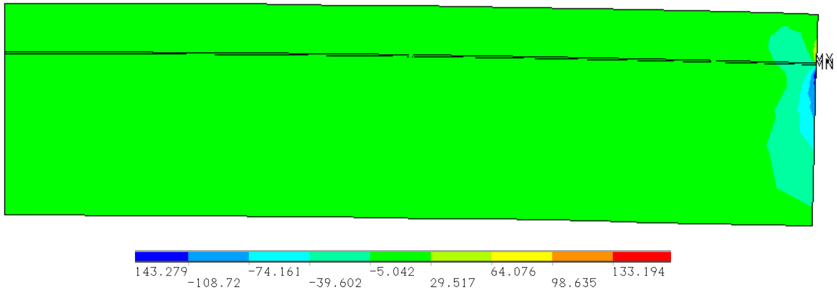
Single cell



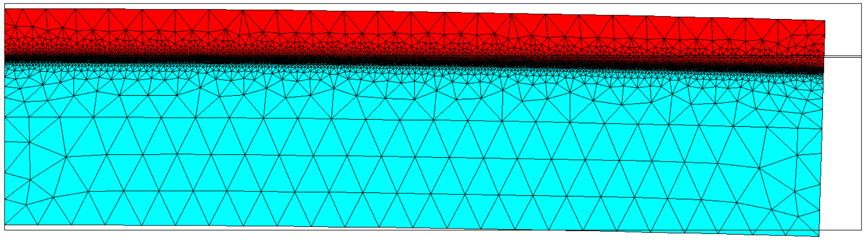
In-plane normal stress (s_x)



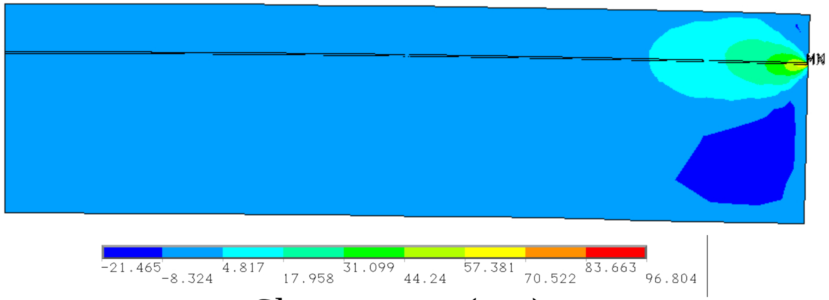
Finite element mesh



Out-of-plane normal stress (s_y)

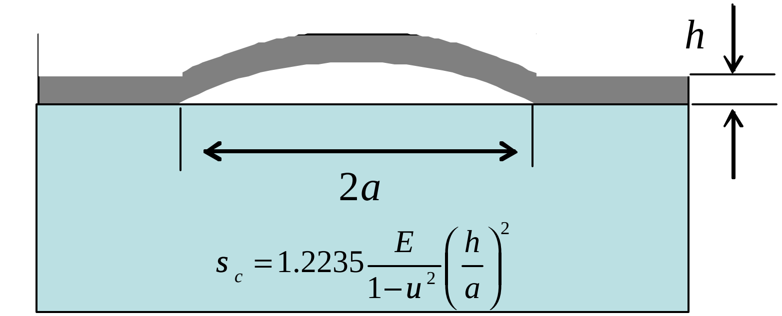


Deformed shape

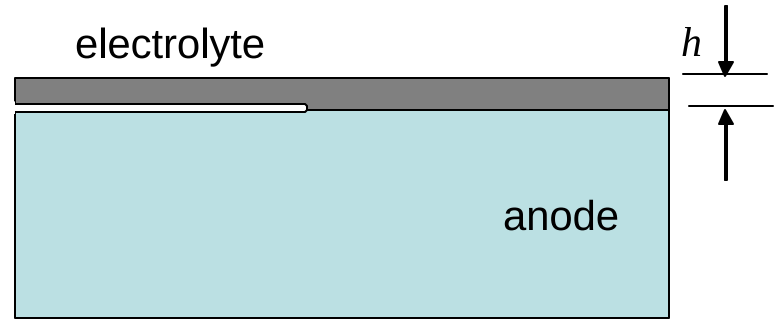


Shear stress (s_{xy})

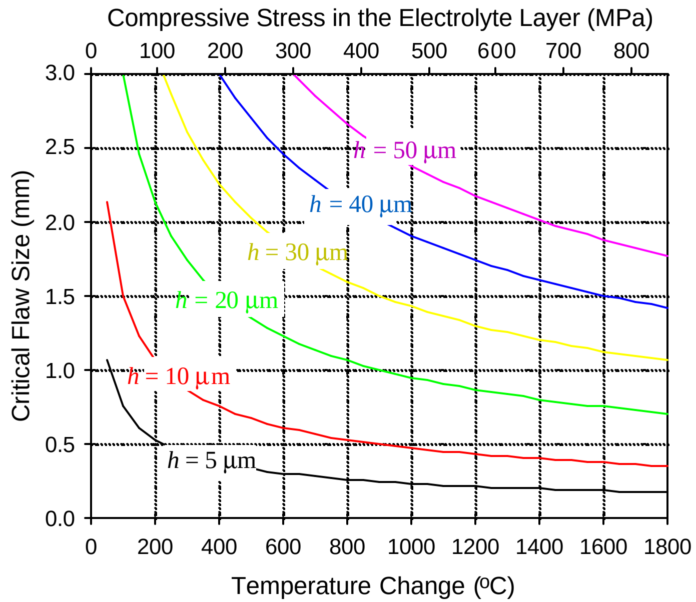
Blister vs. Edge Delamination



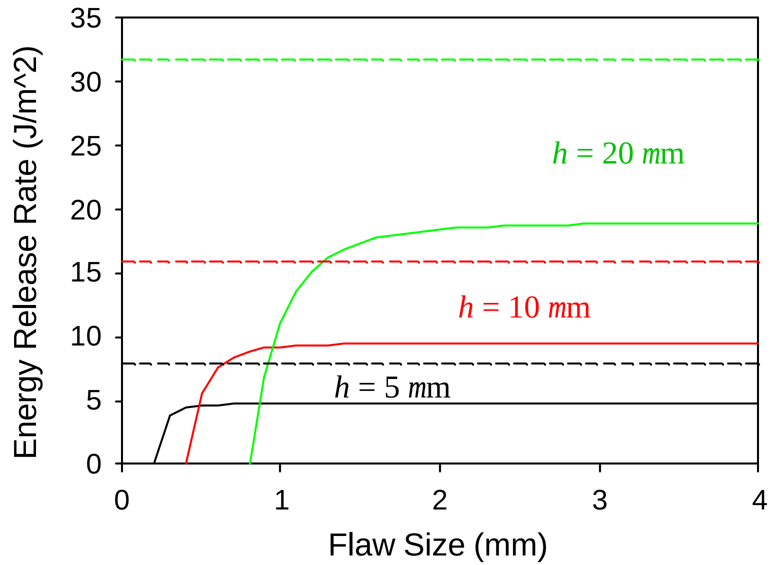
$$G = \frac{(\Delta T \Delta a)^2 Eh}{(1-u)[1+0.9021(1-u)]}\left\{1-\left[\frac{1.2235}{\Delta T \Delta a(1+u)}\left(\frac{h}{a}\right)^2\right]^2\right\}$$



$$G = 1.028\frac{Eh}{1-u}(\Delta T \Delta a)^2$$

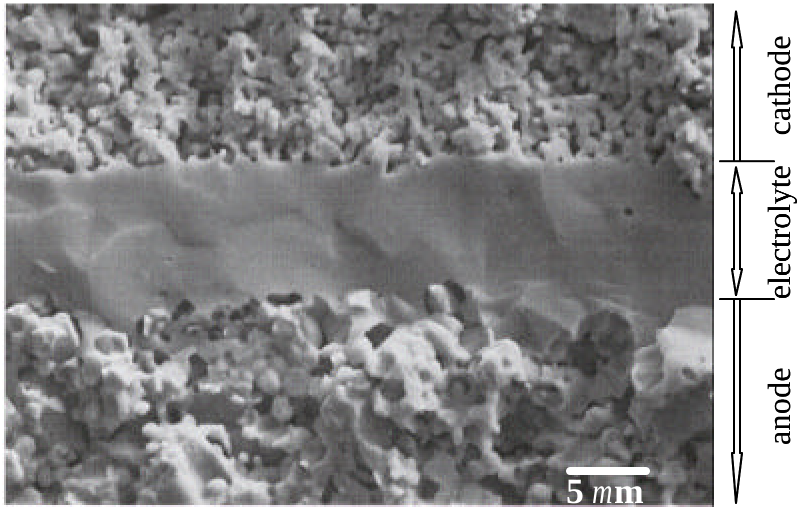


Relationships between processing temperature, electrolyte layer thickness and critical flaw size



Comparison of energy release rate between edge and blister delamination

Effective Properties of Porous Electrodes



$$E = \frac{2(1-c)(5n_0-7)E_0}{2(5n_0-7)+c(13-2n_0-15n_0^2)} \qquad E_0 = \frac{9K_0}{1+3K_0/m_0}$$

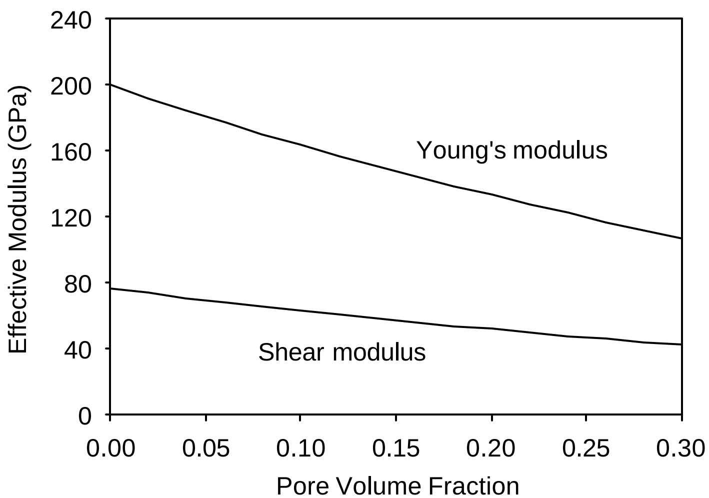
$$n = \frac{2(10n_0^2-9n_0-7)+c(25n_0^2+6n_0-19)}{2(5n_0-7)+c(15n_0^2+2n_0-13)} \qquad n_0 = \frac{1-2m_0/3K_0}{2+2m_0/3K_0}$$

Input:

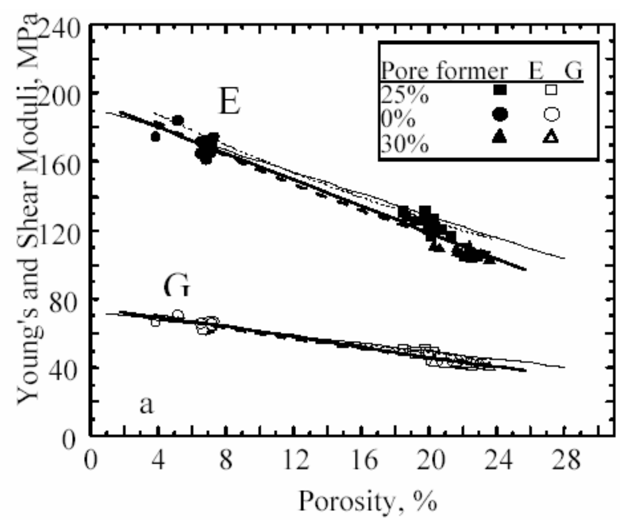
Properties and volume fractions of Ni, LSM and YSZ and porosity

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

Temp Distribution

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

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

Strain Energy $$U_b = \frac{q^2 a^2 E(1-2n)}{6k^2(1-n)^2 p^3 r_0^2}$$

Surface Energy $$U_s = 2p\, Nb^2 g$$

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

$$\boxed{q = \frac{3p^2 k r_0}{2a}\left[1 + \frac{16(1-n^2)Nb^3}{9(1-2n)}\right]\sqrt{\frac{G_c p(1-n)}{E_0 b(1+n)}}}$$

q = rate of heat generation (J/sec)

G_c = Fracture toughness of the material

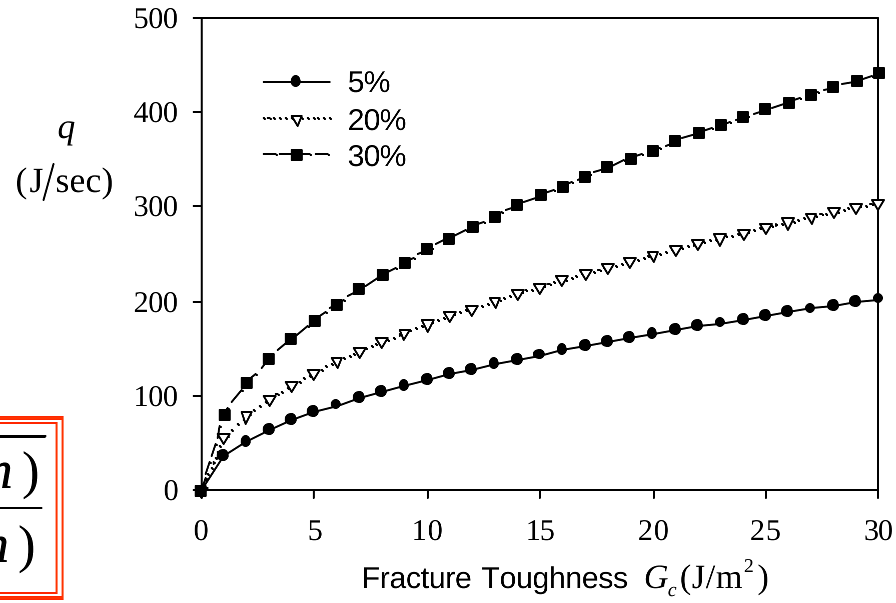
b = crack size

N = number of cracks per unit volume

k = Thermal conductivity

α = Coefficient of linear thermal expansion

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



Failure Analysis Activities for the Next 6 Months

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

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

1.3 Identify and quantify crack path selection and crack propagation.

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

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

GT Project Summary

Major Accomplishments of the First 4 months

- "Slice technique" model/code to simulate the polarization curve, and reformate stream analysis model.
- Radiation models and porous models for thermal/fluid analysis.
- Models for cell deflection, thermal stresses, buckling induced delamination and thermal shock induced microcracking.

Focus for the Next 6 Months

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