AN INTEGRATED APPROACH TO MODELING AND MITIGATING SOFC FAILURE

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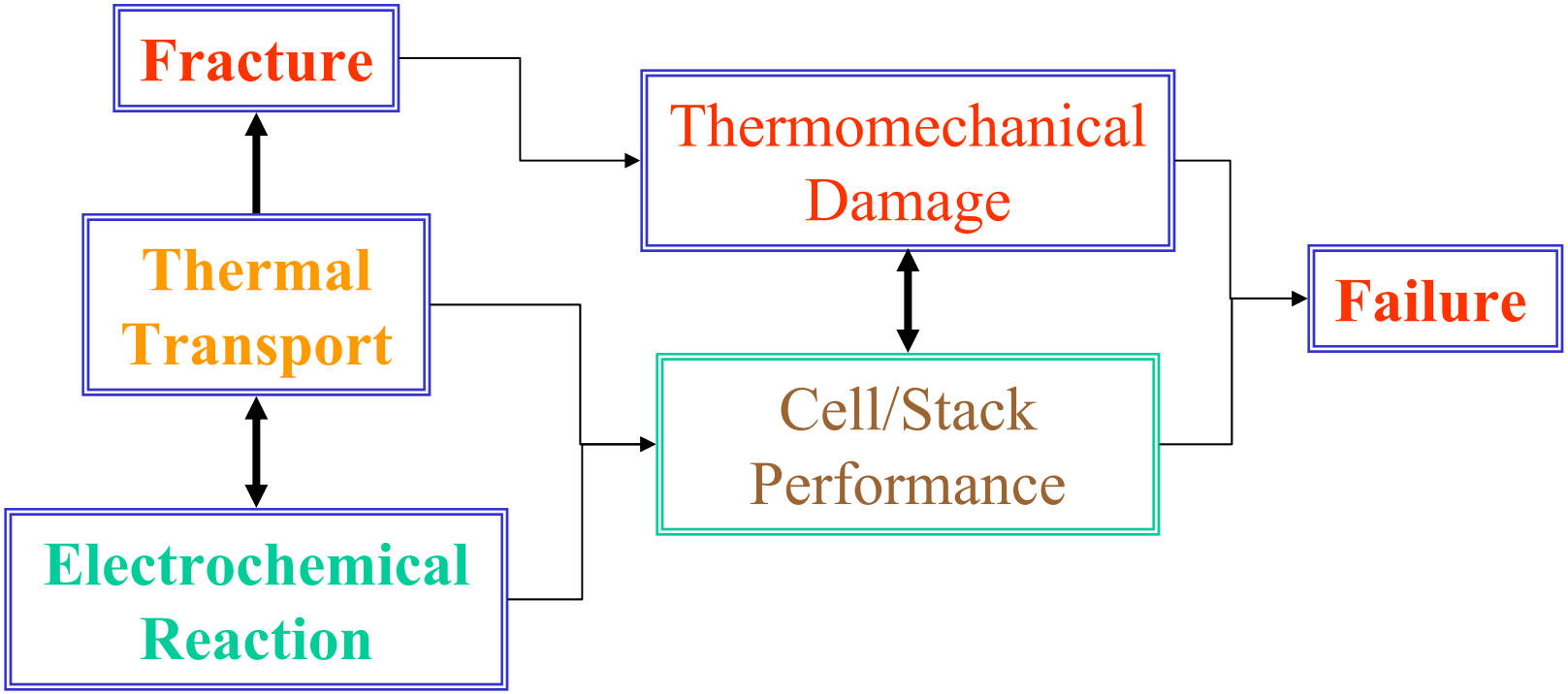
Project Overview and Objective



Through integrating structural, electrochemical and thermal transport analysis, we will develop numerical modeling and simulation tools for design analysis and reliability/durability predictions of SOFCs.

Overview of GA Tech-Developed Tools

- Identify dominant physical mechanisms for structural failure
- Computational algorithms for crack-tip parameters (*K, G, J*)
- Computational algorithms for thermal/fluid transport
- Computational algorithms for evaluating the effects of cracks on electrochemical reactions
- Constitutive laws for SOFC materials under operating environment
- Micromechanics modeling of inhomogeneous SOFC materials (anode, cathode and possibly seals)
- Failure criteria and damage accumulation models and associated MARC subroutines

Utility: User defined subroutines to be integrated into the SECA design tools

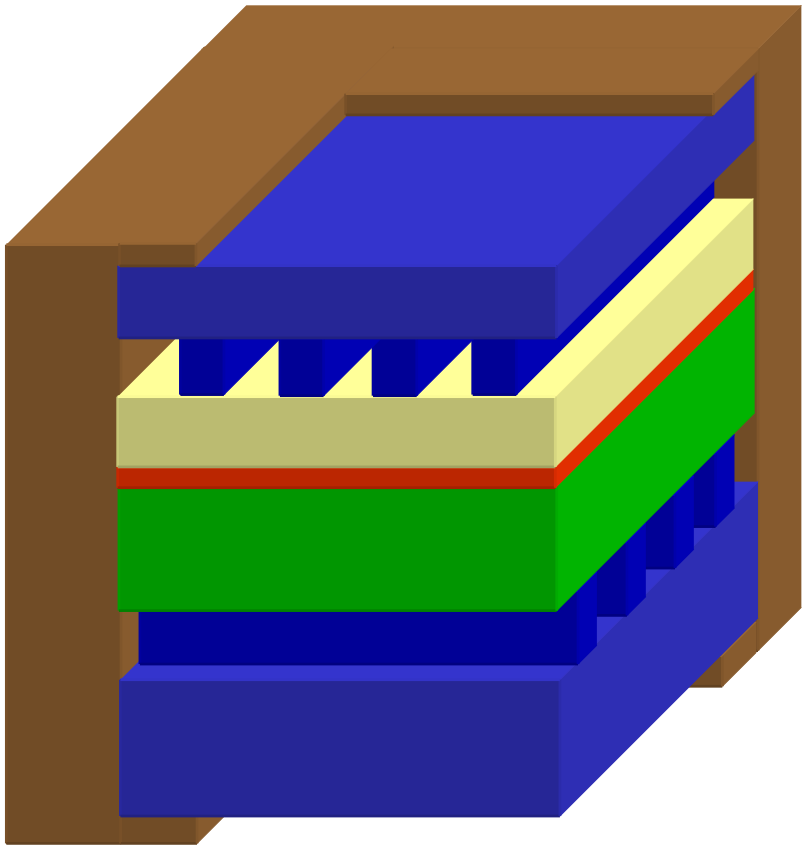
Some Major Technical Accomplishments To Date

- Developed a simplified two-flux approximation for radiative heat transfer calculations in SOFC cells, resulting in a ten-fold reduction in the required computational time as compared to the standard discrete ordinate method (1/03).
- Energy release rates for both the edge delamination and buckling-driven blister delamination of SOFC cells were obtained, which can be used to assess cell fracture. Developed criteria for estimating maximum tolerable fabrication defects based upon fracture analysis (11/02).
- Developed a model for the spalling phenomenon and thermal expansion-induced stress during thermal transients and shock. The model relates the rate of heat generation in the cell to microcrack initiation and may be used predict the maximum allowable heat generation before microcracks are initiated (2/03).
- Developed methods for accurately calculating the stress intensity factors and the energy release rate in SOFC cells. Developed an advanced theoretical methodology for modeling gas flow, mass, and heat transfer in the porous electrodes (3/03).
- A global/local analysis scheme was developed and illustrated on a 3D co-flow cell model that allows the integration of thermal/fluid simulation results directly combined with local stress analysis (6/03).
- Developed a domain integration formulation to evaluate crack tip parameters for fracture analysis (9/03).

Some Major Technical Accomplishments To Date

- It was experimentally determined using FTIR spectrometer that the electrode (anode made of 40 vol% Ni; 60 vol% 8YSZ and cathode made of Sr-doped Lanthanum ferrite) samples appear to be opaque over the entire near and mid infrared spectra (10/03).
- Developed a general formulation (on a spectral basis) of the radiative heat transfer in the optically thin electrolyte of the planer SOFC, and wrote and validated a code for implementation of the formulation (2/04).
- Compiled a database of radiative properties of SOFC materials (3/04).
- Developed a computational algorithm to include creep deformation in the electrodes (4/04).
- It was determined, based on certain subjective assumptions, that in typical SOFCs, the local thermal equilibrium assumption holds.

Major Structural 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

Potential SOFC Cell Mechanical Failure Mechanisms

Common Thermomechanical Failure Mechanisms at the Material Level

Computing Stresses

- ✓ **Thermoelastic Deformation:** coefficient of thermal expansion, elastic modulus, tensile strength.
- ✓ **Elastic-Plastic Deformation:** yield criterion and strength, hardening rules, flow rules.

Design against Initial Failure

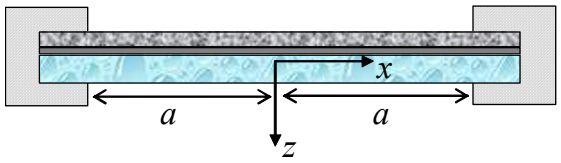
- ✓ **Fracture:** fracture toughness.

Design against Degradation

- ✓ **Fatigue:** *S-N* curve, *da*/*dN* curve.
- ✓ **Creep:** creep exponents.
- ✓ **Migration:** diffusivity.

Modeling Methodologies

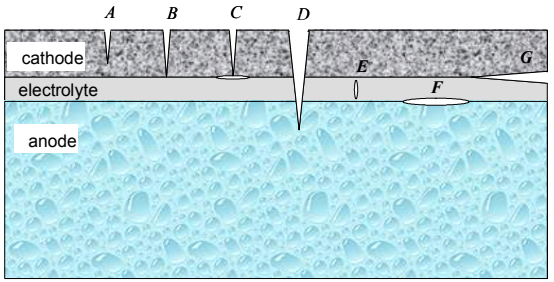
Cell Structure
($L > 10^{-3}$ m)



- Warpage
- Seal failure
- Seal design
- Residual stresses

- *Plate and laminate theories*

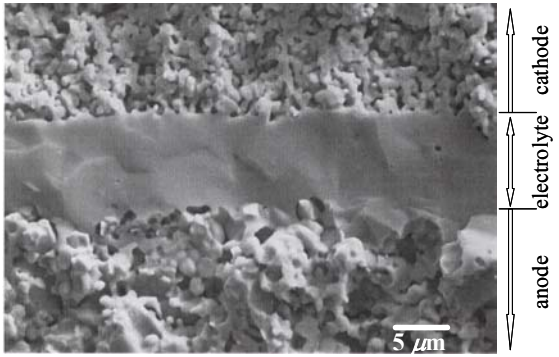
PEN Structure
(10^{-5} m < L < 10^{-3} m)



- Cracks growth
- Delamination
- Spalling

- *Fracture mechanics*
- *Finite element method*

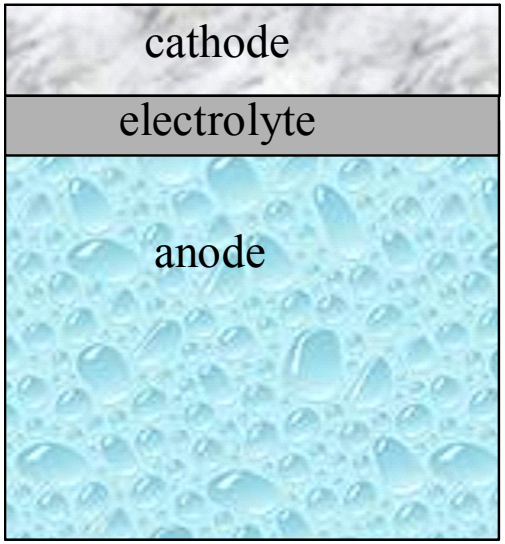
Material Structure
$L < 10^{-5}$ m

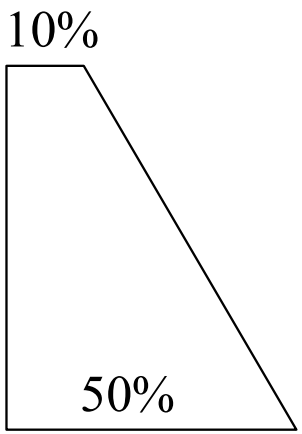


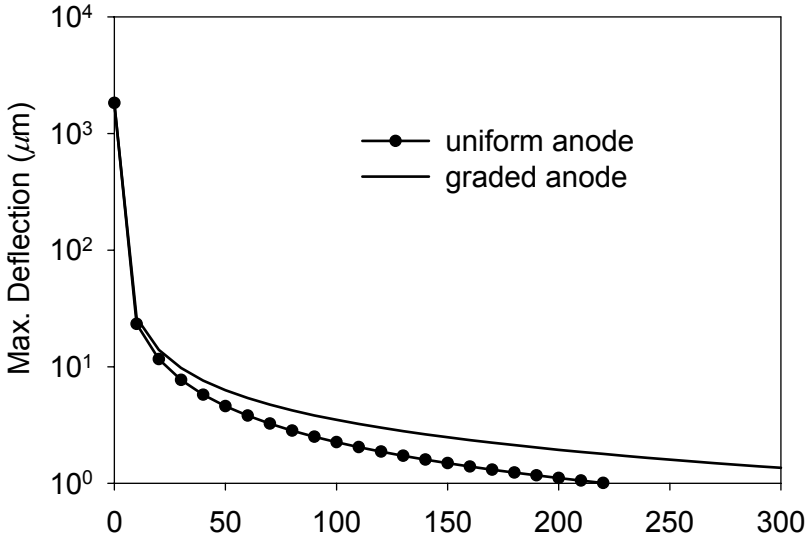
- Crack initiation
- Plasticity
- Creep

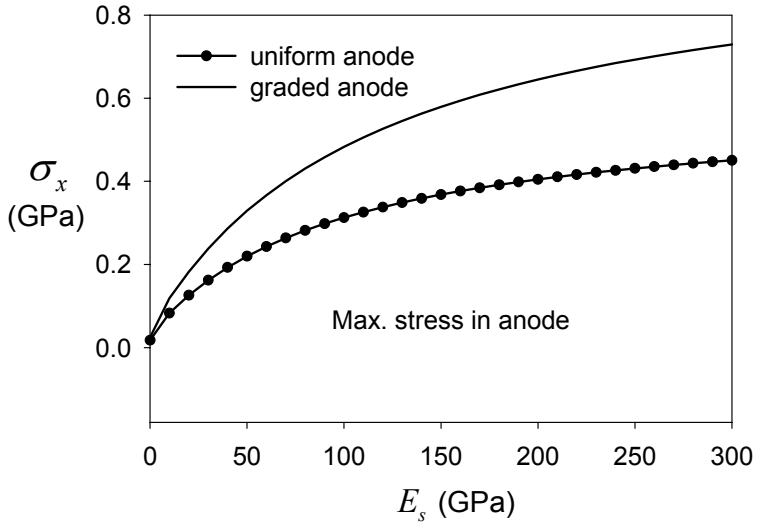
- *Micromechanics*
- *Damage mechanics*

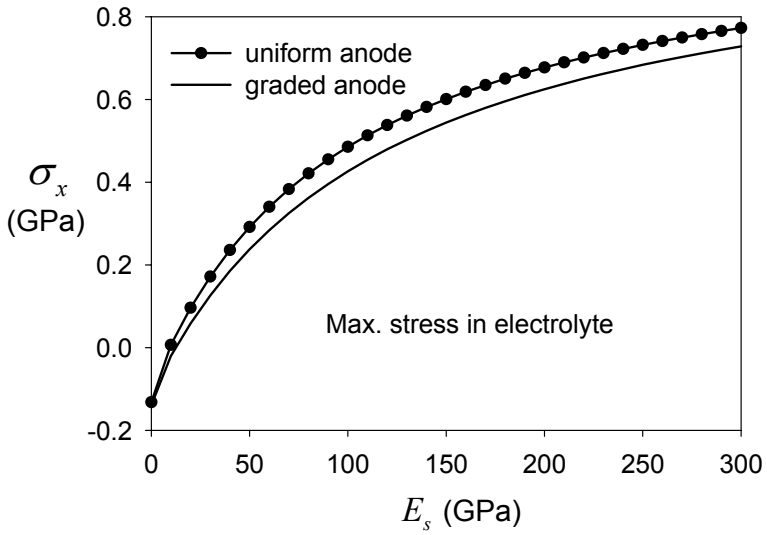
Design Criteria Against Fracture (graded anode)



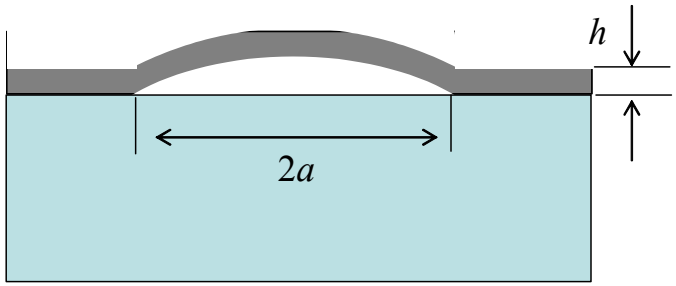


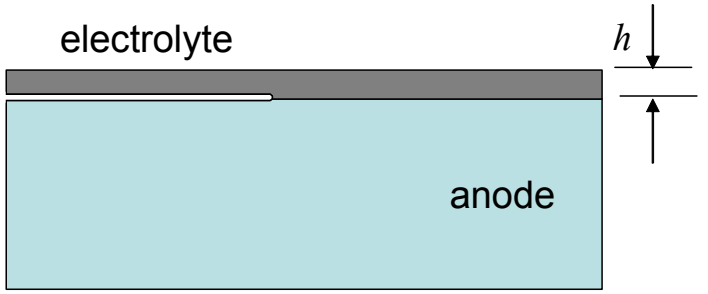


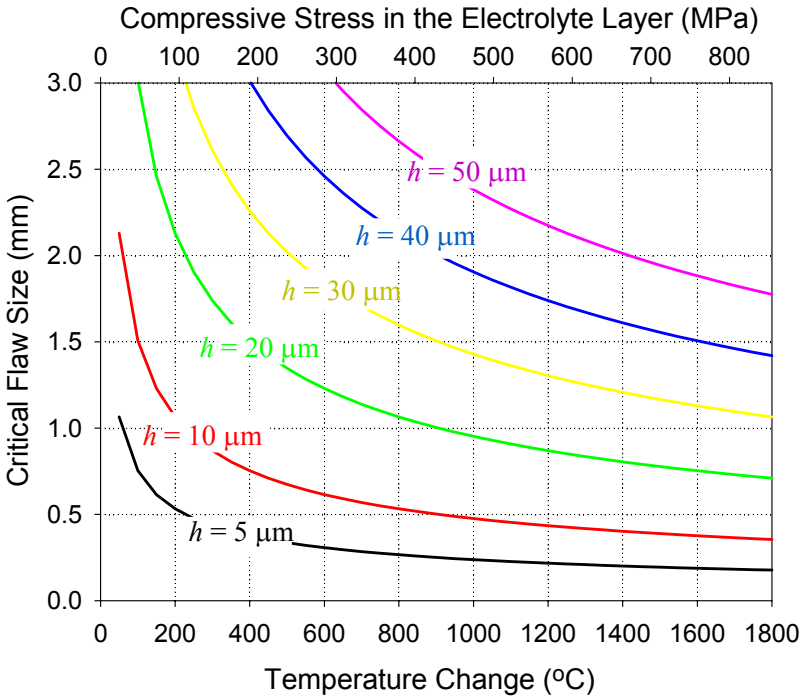


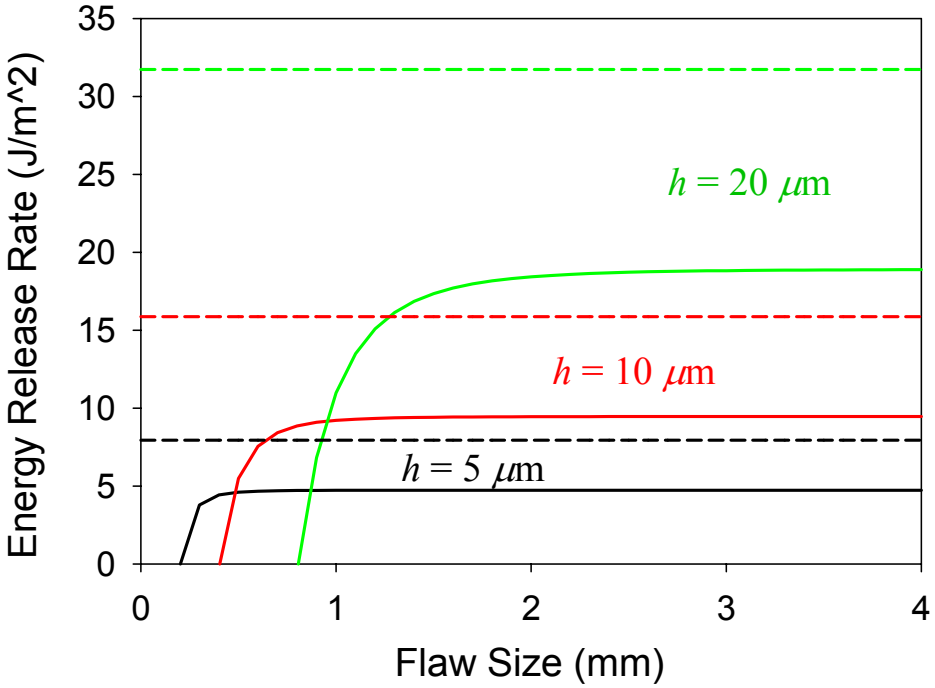


Design Criteria Against Fracture (Flaw Tolerance)









Thermal Shock Induced Microcrack Initiation

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

Temp Distribution

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

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

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

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

q = rate of heat generation (J/sec)

G_c = Fracture toughness of the material

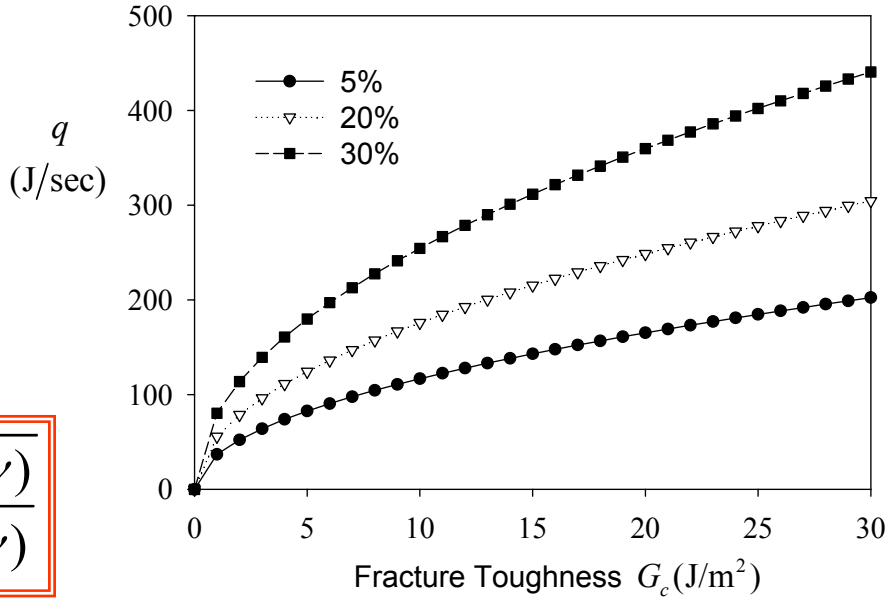
b = crack size

N = number of cracks per unit volume

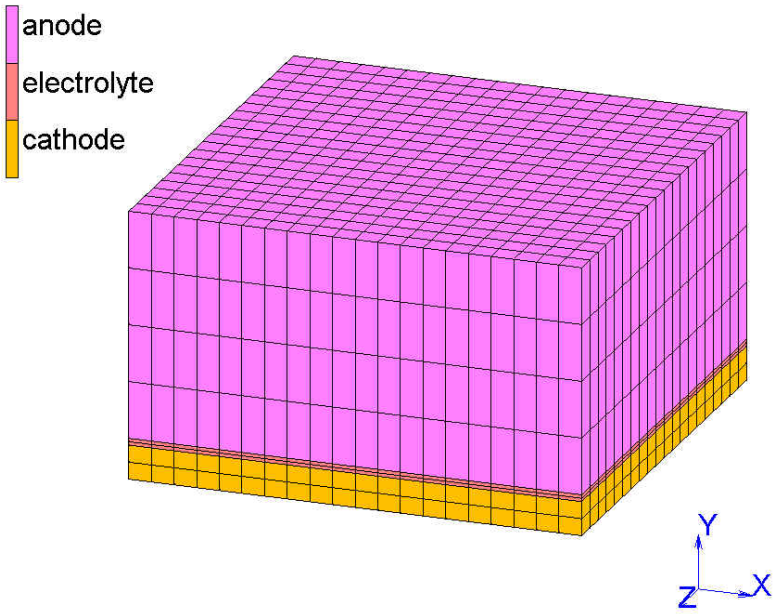
k = Thermal conductivity

α = Coefficient of linear thermal expansion

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



Effect of Creep on Stress Evolution During Operation



	A	n_c	Q
Ni/YSZ	2.0e-6	1.2	550kJ/mol

YSZ (T_m ~ 2400^{0}C): no creep

Ni (T_m ~ 1450^{0}C): power law creep

LSM (T_m ~ ??): no creep

Steady-State Creep

$$\dot{\varepsilon}_c = A\sigma^{n_c} \exp(-\frac{Q}{RT})$$

$\dot{\varepsilon}_c$ = strain rate

σ = effective stress

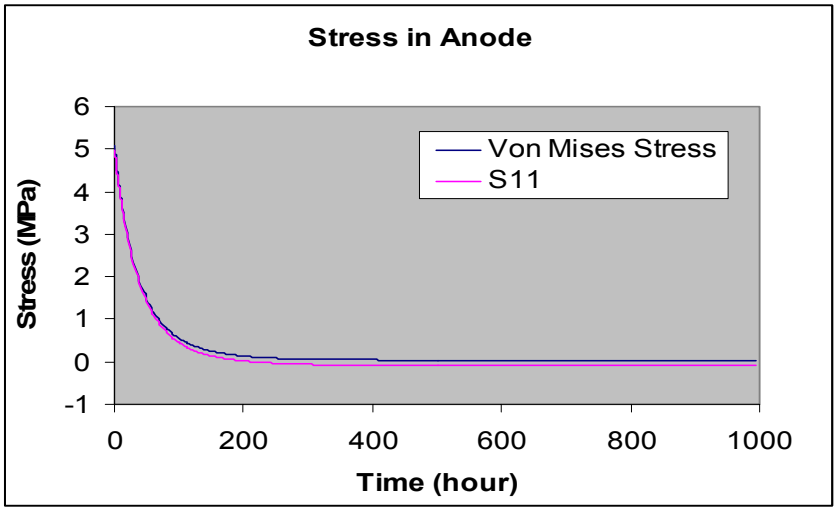
n_c = stress exponent for creep

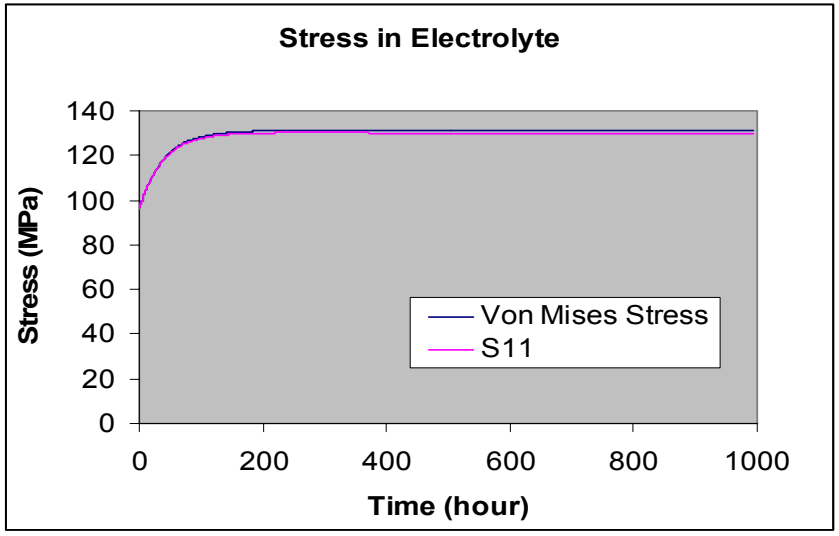
Q = is activation energy,

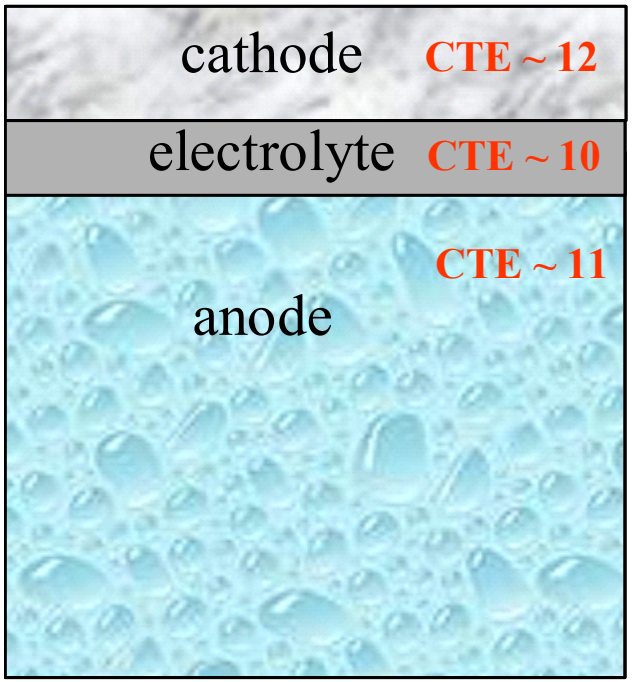
R = the universal gas constant

A = a parameter that depends on the material and test conditions (e.g. oxygen partial pressure in the case of oxides).

Anode Supported Cells

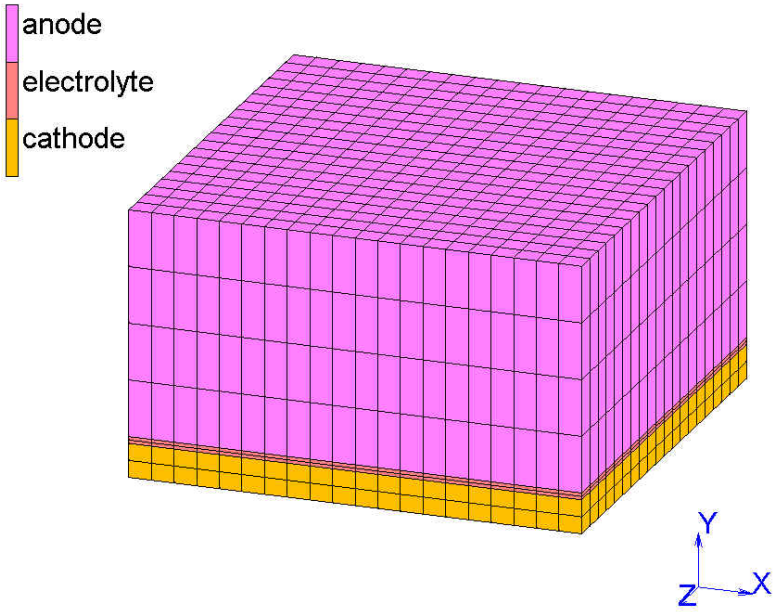


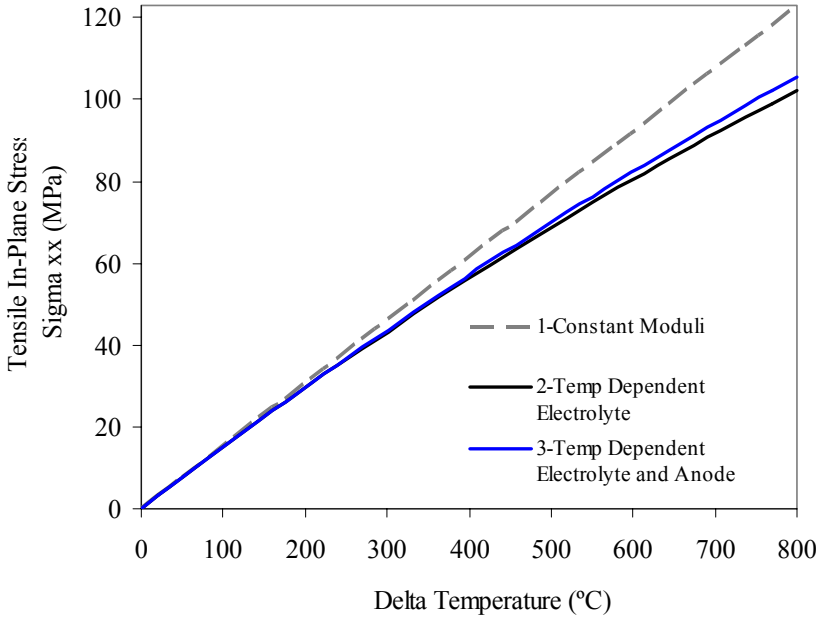




The anode sheltered the electrolyte. As creep progresses, such sheltering decreases!

Temperature Dependant Material Properties





25mol%Ni/75mol%YSZ

$$E_a(T) = (-.058T + 196)[1 - 1.96p]$$

$$G_a(T) = (-.021T + 76)[1 - 1.93p]$$

8mol % YSZ

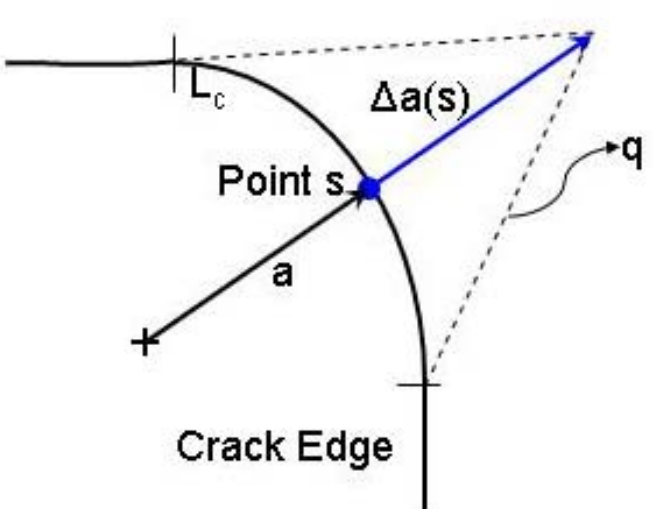
$$E_e(T) = -.051T + 233$$

$$\nu = 0.3$$

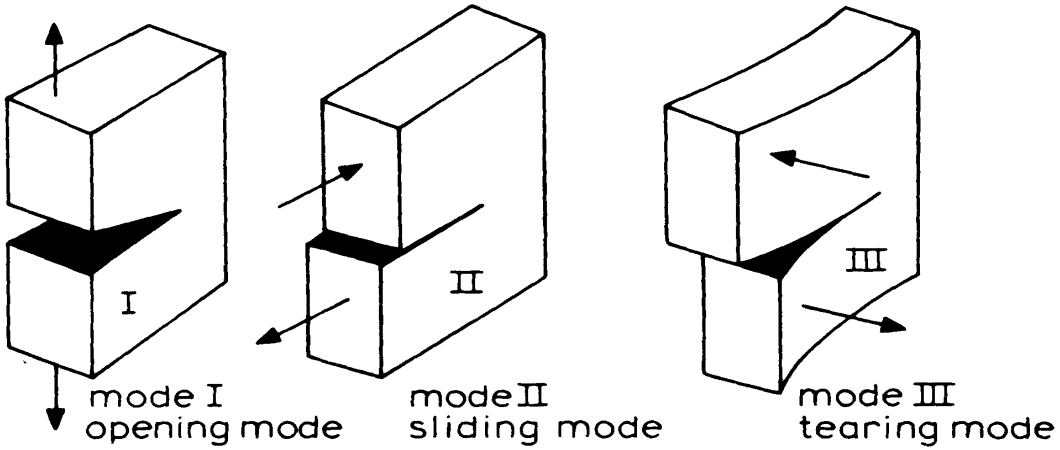
Current Work for Mechanical Failure Prediction

Calculating K_I, K_{II}, and K_{III} using the crack-tip interaction integral

$$\bar{I} = -\int_V tr[(\mathrm{P}\cdot\vec{\nabla}\mathrm{q}) + (\vec{\nabla}\cdot\mathrm{P}^{\mathrm{T}})\cdot\mathrm{q}]dV$$



Crack grows typically in the direction where $K_{II} = 0$

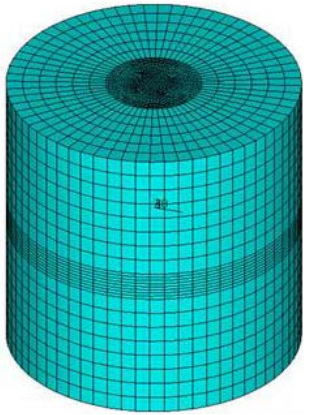


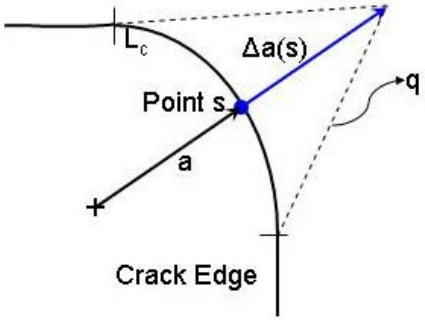
Currently, no commercial code is capable of doing this! We are writing the code in MatLab so it is portable to MARC, ANSYS, ABAQUS, etc.

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

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

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





Input
- Element connectivity
- Nodal coordinates
- Nodal displacements
- Nodes on crack tip

Select Node S
- Select volume of elements
- Calculate Unit Outward Normal
- Transform coordinates
- Transform displacements

Loop through elements

Begin Gaussian Quadrature by looping through integration points.

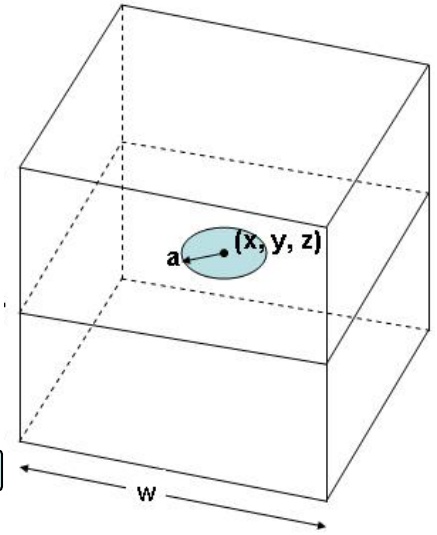
Calculate components of integrand
- Strain energy density
- Stress tensor
- Derivatives displacement
- Derivatives test function

Calculate integrand and add to previous component.

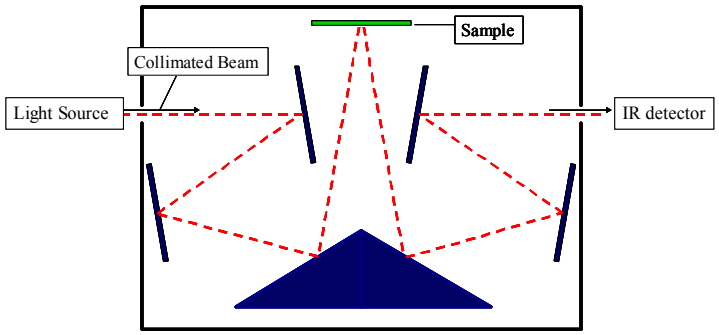
Go to next integration point

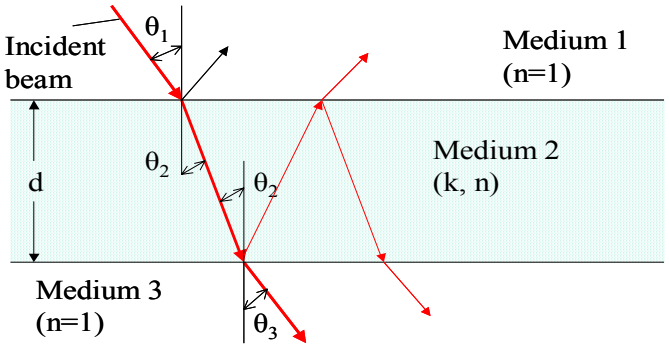
Go to next element

Calculate pointwise value of domain integral

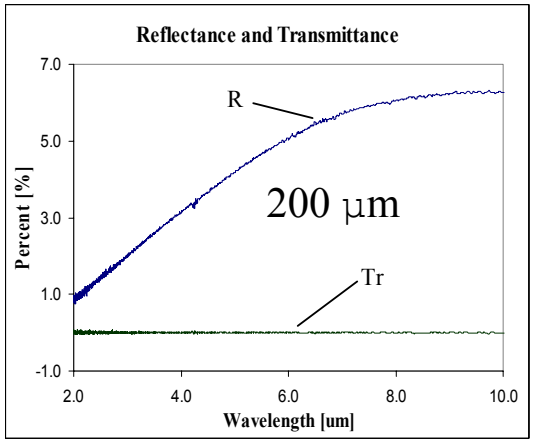


Experimental Determination of Optical Properties of YSZ, Ni/YSZ and LSF using FTIR Spectroscopy

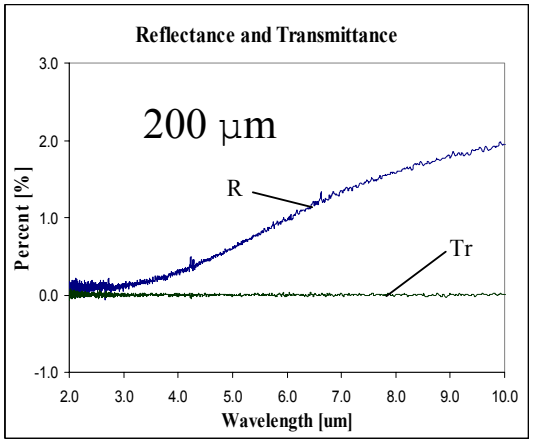




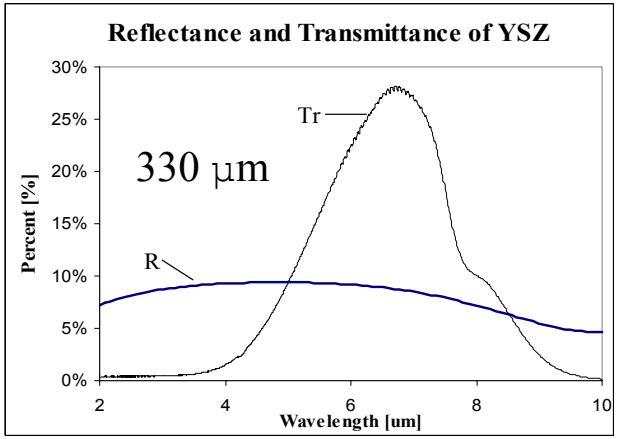
A 10-degree specular reflectance accessory fitted to an FTIR spectrometer



$(La_{1-x}Sr_x)FeO_{3-\delta}$



$Ni\text{-}(Zr_{1-x}YxO_{2-\delta})$

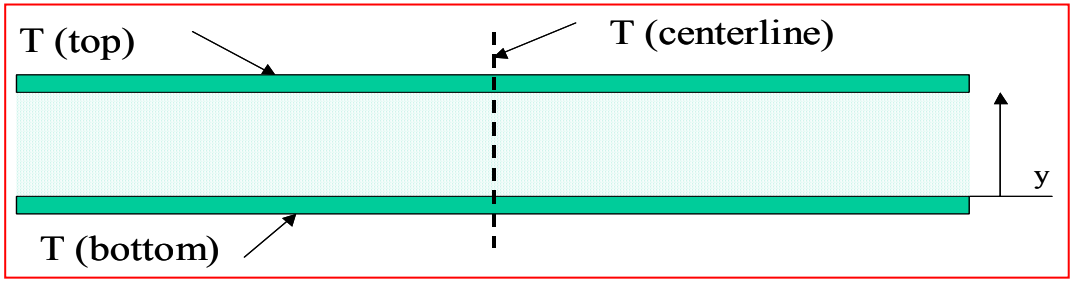


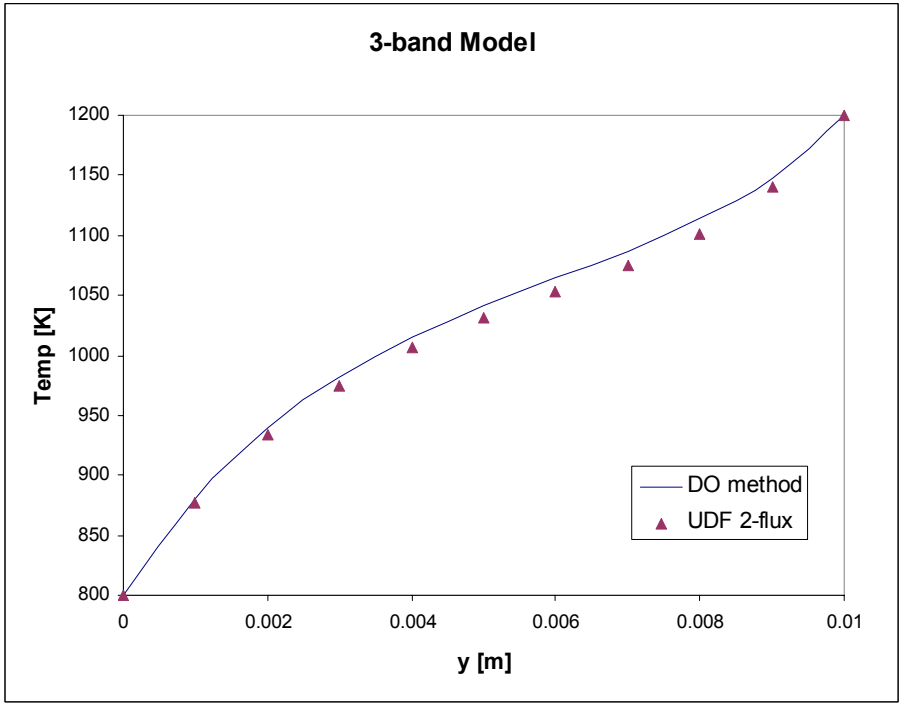
$Zr_{1-x}Y_xO_{2-\delta}$

Radiation Modeling – Spectral 2-flux Formulation

Validation of spectral 2-flux User Defined Function (UDF) for FLUENT

1-D, plane-parallel medium; isothermal boundaries





3-band model approximates measured spectral variation of YSZ extinction coefficient

$$\beta = \begin{Bmatrix} 160\ cm^{-1}; & 0.0 < \lambda < 3.5 \\ 110\ cm^{-1}; & 3.5 \le \lambda < 5.0 \\ 50\ cm^{-1}; & 5.0 \le \lambda < \infty \end{Bmatrix}$$

Validation vs. Discrete Ordinates method built-in FLUENT

Porous Electrodes – Non-Equilibrium Analysis

Assumption of local thermal equilibrium (LTE) is questionable when:

a) Difference in solid and fluid thermal properties is significant (√ in SOFC)

b) Significant heat generation in porous media – existence of hot spots (√ in SOFC)

c) Low Reynolds number or flow velocities through porous media (√ in SOFC)

$$\nabla \cdot \left(\rho \, \vec{V} \, c_p \, T_g \right) = \nabla \cdot \left(k_{g,eff} \, \nabla \, T_g \right) - h_v \left(T_g - T_s \right) \qquad \text{(Gas phase)}$$

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

Performed Scaling Analysis of Solid Phase energy equation

1. Volumetric solid-to-gas phase heat transfer coefficient order of magnitude:

$$h_v = h_{g-s} a_s \sim 10^{11} \left[W/m^3 \right]$$

2. Volumetric heat generation due to exothermic reaction and Ohmic heating:

$$\dot{Q}'''_{gen} \sim 10^{9} \left[W/m^3 \cdot K \right]$$ ← Global (cell-level) estimate!

Porous Electrodes – Non-Equilibrium Analysis

Consider Volumetric Heat Generation Within the Solid Phase

$$\dot{Q}''' = \nabla \cdot \left(k_{s,eff} \nabla T_s \right) + h_{g-s} a_c \left(T_g - T_s \right)$$

Assume negligible

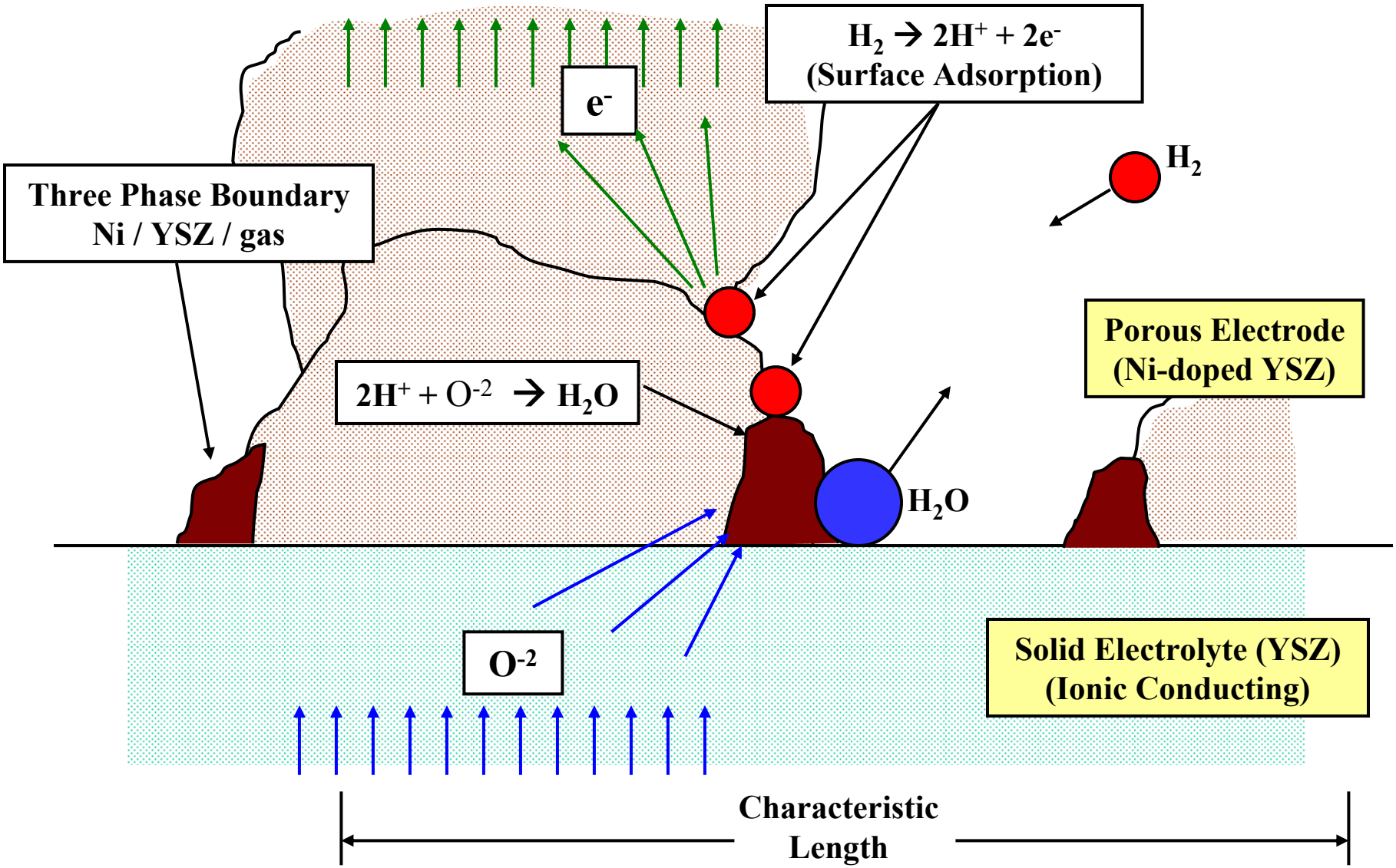
Negligible – LTE is Valid!!!

$$\rightarrow \dot{Q}''' = h_{g-s} a_c \left(T_g - T_s \right) \rightarrow \boxed{\Delta T = \left(T_g - T_s \right) \; \square \; 10^{-2} K}$$

Key Assumptions

- Depend on nature of porous microstructure: approximately spherical particles (0.5–1.5 μm average diameter) & 30-40% electrode porosity.
- Average (global) current density used in analysis: local current density on microscale level might be several orders of magnitude greater leading to much higher heat generation and expected solid-gas temperature difference!
- Validity of LTE depends on validity of these assumptions!

Porous Electrodes –Microscale Analysis, Local Current Density



Future Work

- Material failure modeling and MARC integration
- Transient heating effects during start-up/shut-down
- FLUENT and MARC Integration of two-flux approximation for radiative transfer
- Effects of mechanical damage on cell stack's electrical performance

Electrolyte (8 mol% YSZ)

Tensile strength: The probability of a sample of volume V can survive a given stress σ is given by

$$P_s(V) = \exp\left[-\frac{V}{V_0}\left(\frac{\sigma}{\sigma_0}\right)^m\right]$$

Elastic-Plastic Deformation: plasticity can be neglected below 900^0C

Fracture: Sub-critical crack growth (transgranular)

$$G_c \sim 3.5\,\mathrm{J/m^2} \qquad \frac{t_f}{t_0} = \left(\frac{\sigma_0}{\sigma}\right)^n \qquad n \sim 10$$

Fatigue: Sub-critical crack growth (transgranular)

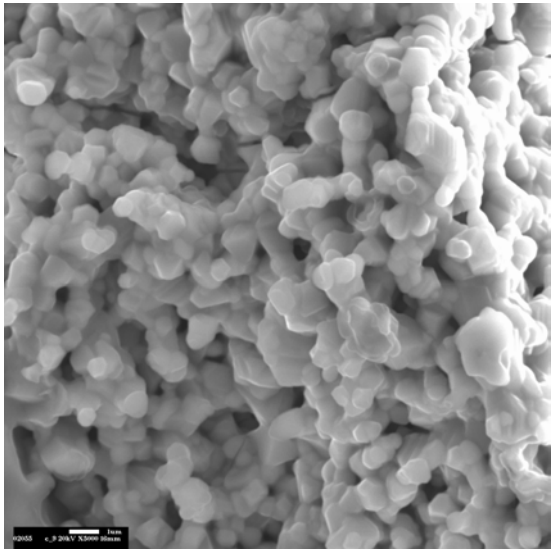
$$da/dN = AG^n \qquad n = 8 \sim 12$$

Steady-State Creep: diffusion creep (cation transport along grain boundaries)

$$\dot{\varepsilon}_c = \frac{A\sigma^{n_c}}{d^q T}\exp\left(-\frac{Q}{RT}\right) \qquad n_c \sim 0.7 \qquad Q \sim 320\,k\mathrm{J/mol}$$

Migration: ??

Anode (NiO/YSZ, Ni/YSZ)



Elastic-Plastic Deformation: After reduction (Ni/YSZ) deforms plastically

Yield condition for Ni

$$(\sigma_{ij} - \sigma_0 \delta_{ij})(\sigma_{ij} - \sigma_0 \delta_{ij}) = \frac{2}{3}\sigma_y$$

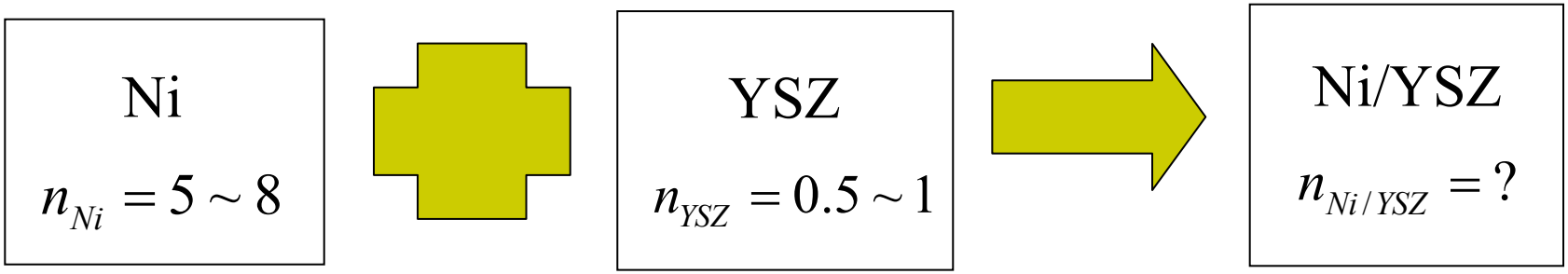
$$\sigma_y = 10 \sim 100\text{MPa}$$

Steady-State Creep: cavitation coalescence $\dot{\varepsilon}_c = \frac{A\sigma^{n_c}}{d^q T}\exp\left(-\frac{Q}{RT}\right)$

$$Q \sim 44\,k\text{J/mol} \qquad n_c = 1 \sim 6$$

Mechanical Failure Prediction

Creep Laws for Ni/YSZ Cermet $\dot{\varepsilon} = \frac{A\sigma^n}{d^q T}\exp\left(-\frac{Q}{RT}\right)$

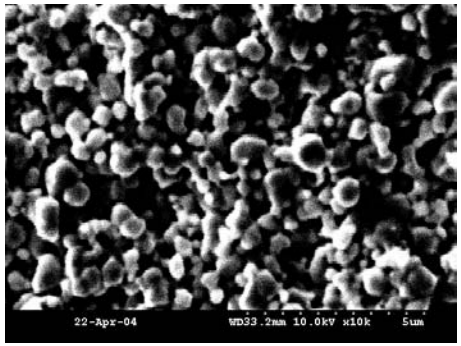


Micromechanics: A self-consistent approach to obtain

$$n_{Ni/YSZ} = F(n_{Ni}, n_{YSZ}, V_{Ni}, V_{YSZ}, V_{Voids})$$

This will be coded into a user defined subroutine in MARC

Mechanical Failure Prediction



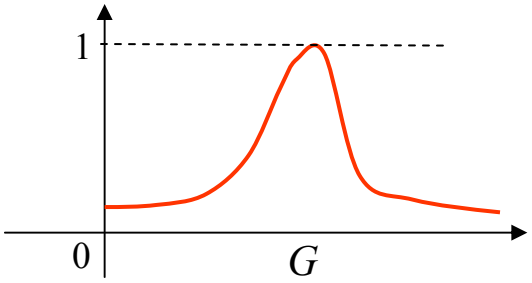
Digital Microscopy

Extract the statistical features of distribution

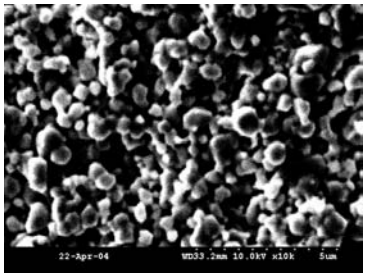
Radial distribution

$$g(r) = \frac{A}{2\pi r N}\frac{d\phi(r)}{dr}$$

$$\phi(r) = \frac{1}{N(r)}\sum_{k=1}^{N(r)} I_k(r)$$

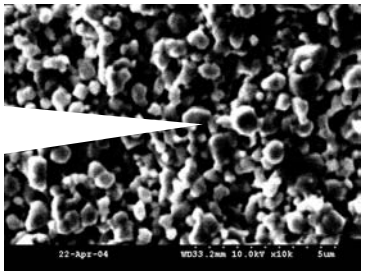


realizations



FEM

MARC



Monte Carlo simulation

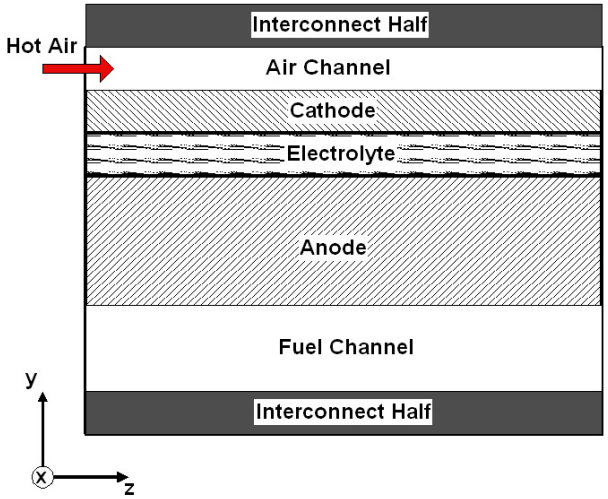
Mean crack-tip parameters

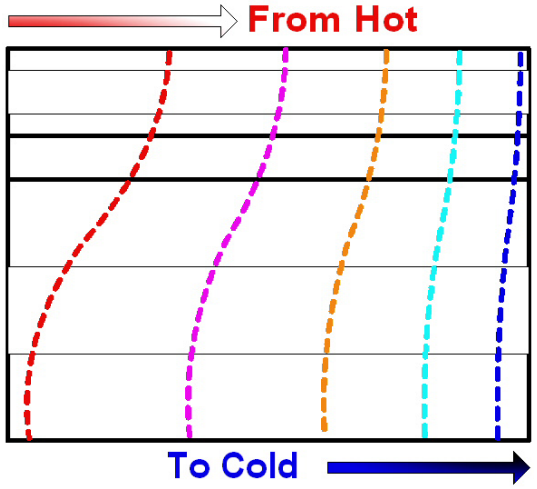
$$\bar{G} = \int_0^\infty g(r)G(r)dr$$

$$\bar{K} = \int_0^\infty g(r)K(r)dr$$

Monte Carlo

Transient Heating During Start-Up/Shut-Down





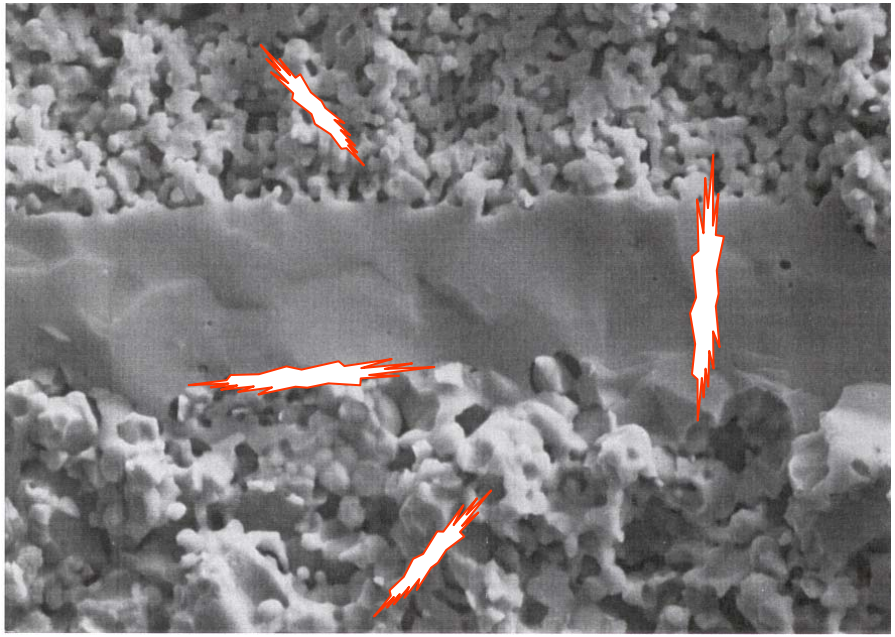
QUESTION: how fast can SOFC be heated without thermomechanical failure?

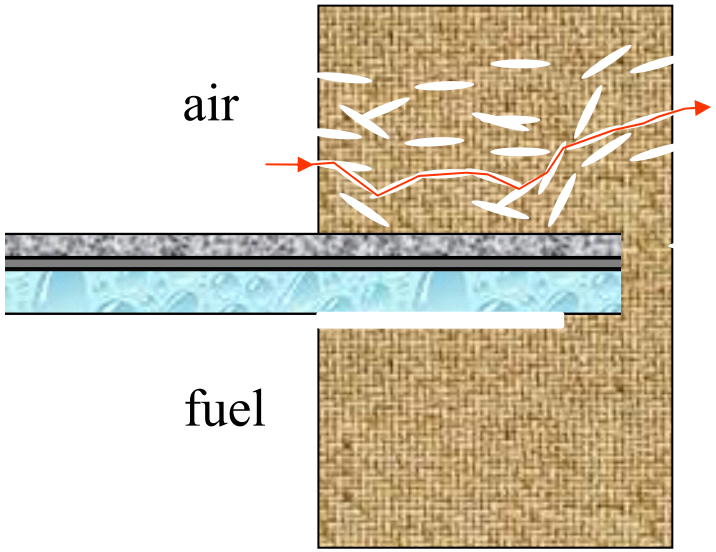
- Analytical solutions for transient temperature distribution with the SOFC are possible for the simplified quasi 1-D case in the limit of the thermally thin cell
- Numerical simulations will be used to analyze more complex and realistic scenarios involving combined convective-conductive-radiative heating

⇓

Develop a simple, yet technically sound transient thermal model which, when combined with failure analysis, could be used by the SECA industrial teams for preliminary design calculations and selection of envelope of "safe" operating conditions

Effects of Mechanical Damage on Cell Stack's Electrical Performance





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
Bulk electrode layer	**Charge/mass transport redirection**	**Smaller impact**
Interlayers	**Changes in TPBs/Electroactive Area**	**Changes in TPBs/Electroactive Area**
Electrolyte	**Substantial increase in resistance**	**Reactants Crossover/ "Leak Current"**

Which cracks/ crack modes does industry deem to be the more prevalent/influential upon cell performance??

Crack-Electrochemistry Interaction
{Conventional Current Sign Convention}

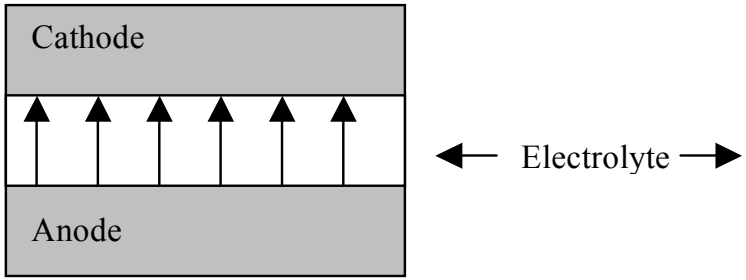


Figure 4(a): Normal, undamaged operation

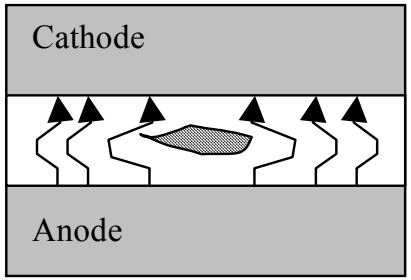
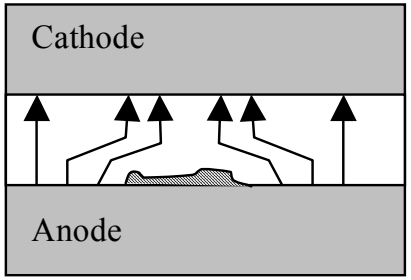


Figure 4(b): Induced sheet resistance within the electrolyte due to cohesive crack



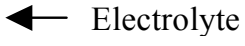
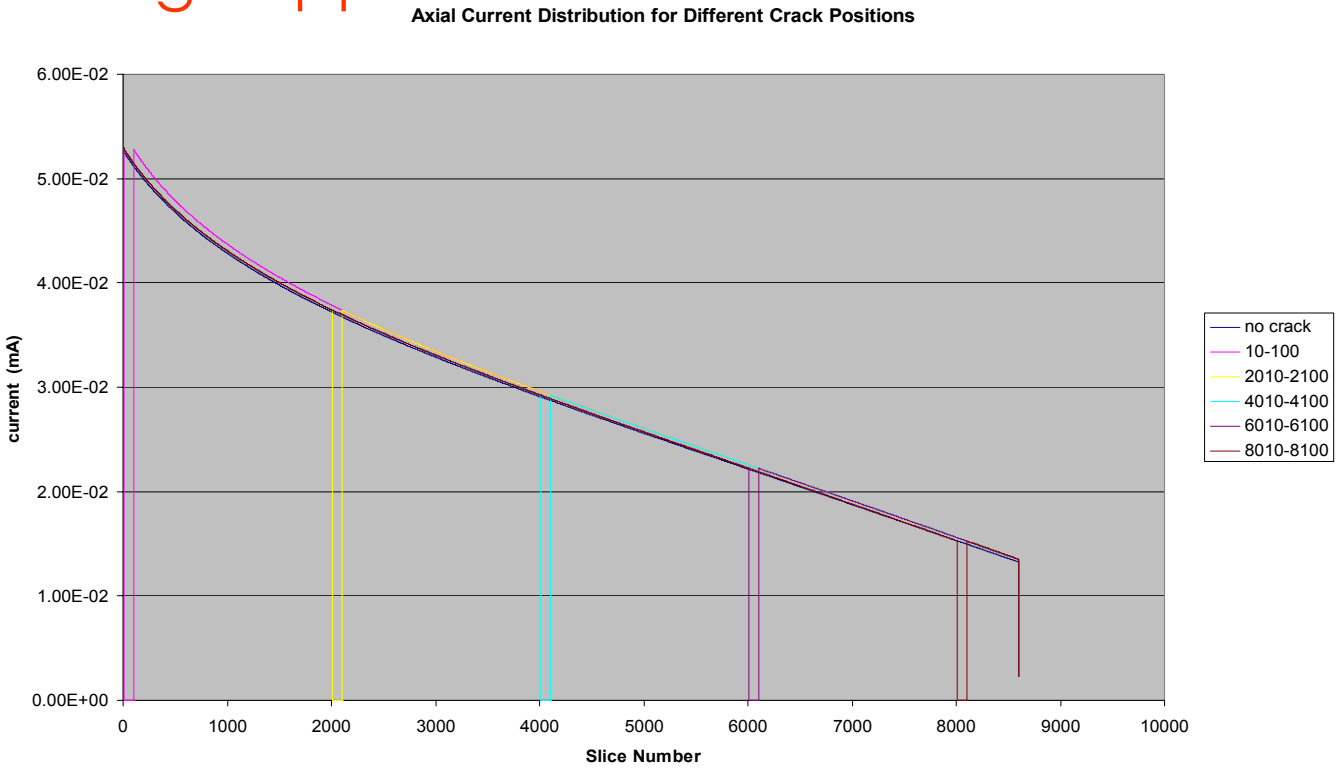


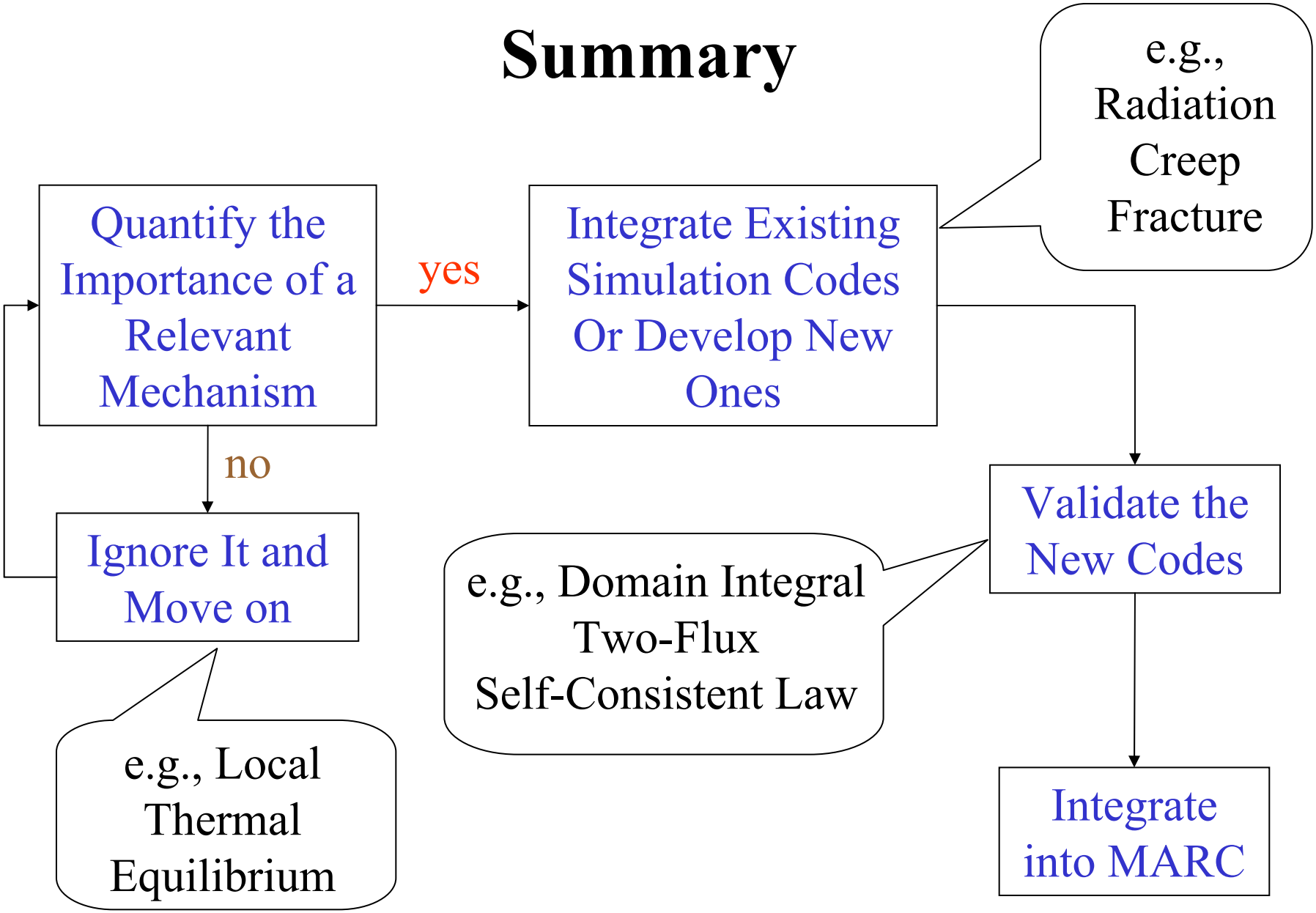
Figure 4(c): Induced contact and sheet resistance about and within the electrolyte via delamin./blistering

"Masking" Approximation: Deactivated Zones



- Pros:
  - Most conservative "safety factor" approach
  - Readily implemented within engineering code such as PNNL MARC development
- Primary Consideration: Resolving the threshold ratio of electrolyte thickness-to-crack characteristic length (e.g., delamination radius) below which masking approximation is plausible --- *potential flow analyses*

Summary


Quantify the Importance of a Relevant Mechanism
yes
Integrate Existing Simulation Codes Or Develop New Ones
e.g., Radiation Creep Fracture
no
Ignore It and Move on
e.g., Local Thermal Equilibrium
e.g., Domain Integral Two-Flux Self-Consistent Law
Validate the New Codes
Integrate into MARC