AN INTEGRATED APPROACH AT MODELING AND MITIGATING SOFC FAILURE

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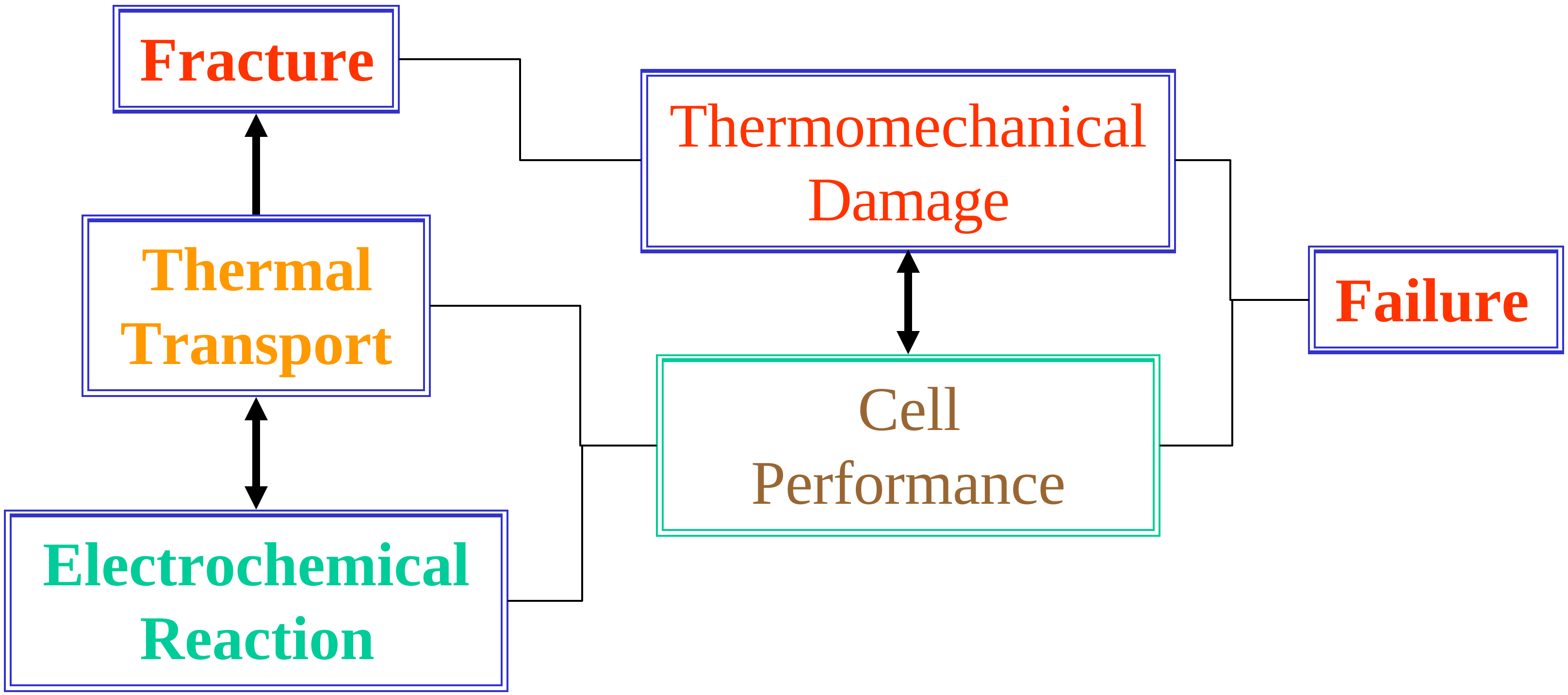
Project Overview



Given: Material properties, cell structure and operating environment

Questions: Is it possible (1) to optimize cell performance? (2) to predict cell failure? and (3) to predict how many fast start-ups it can sustain?

Technical Issues to be Addressed

Thermomechanical Damage and Failure

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

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

Electrochemical Reaction

Three-dimensional electrochemical models
Interdependency between electrochemistry and thermal transport

Challenges
(Uncertainties and Risks)

Knowledge of the State-of-the-Art (PNNL, ORNL, NETL, SECA members)

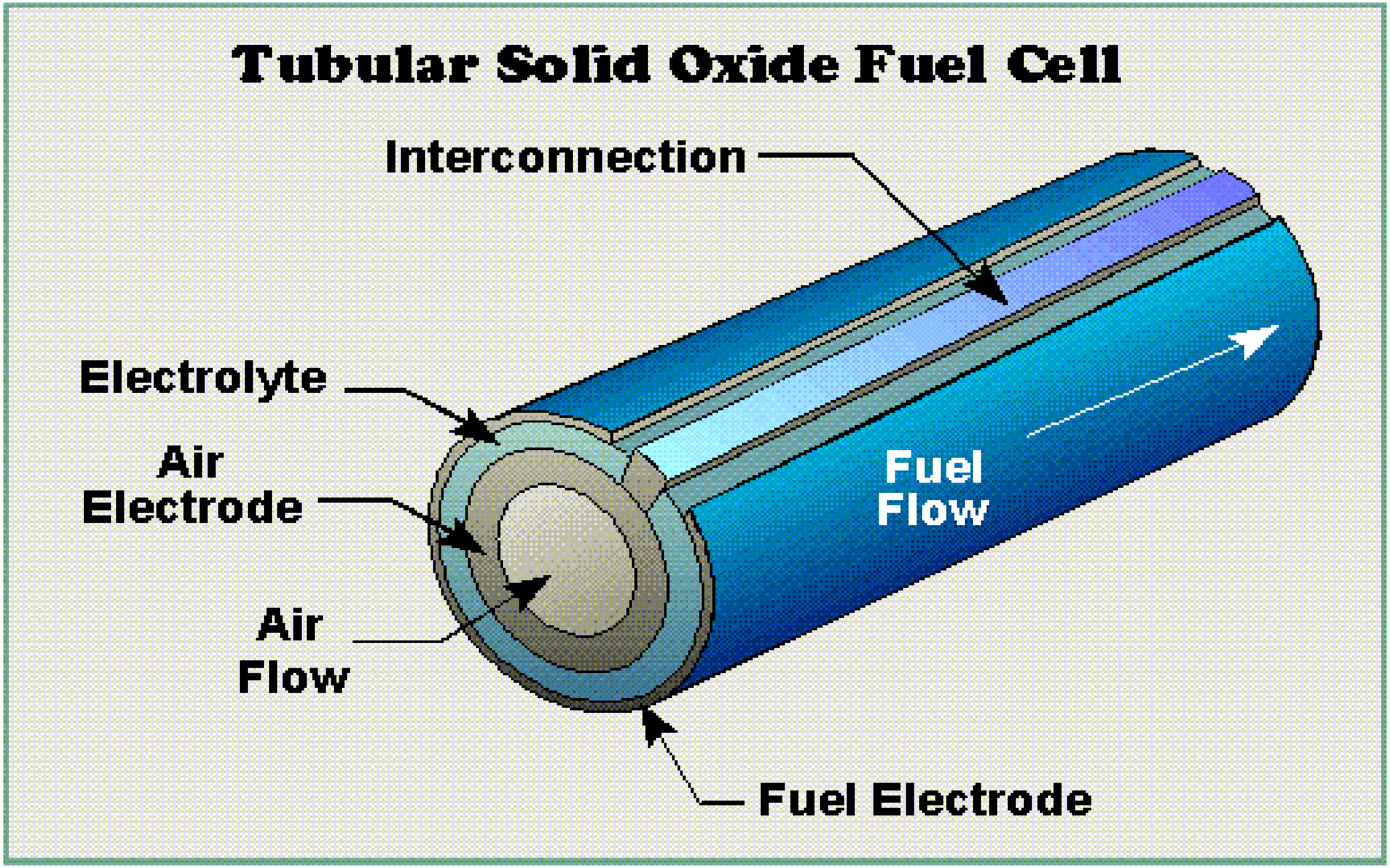
- Learn and communicate
- Provide algorithms for program modules in our areas of expertise for the overall software tool

Availability of Material Properties (thermomechanical and thermophysical)

- Search literature
- Get help from other partners (PNNL, ORNL, NETL, SECA members)

- ➢ Fracture of Interfaces and Porous Media
- ➢ Coupling Between Radiation and Other Modes of Heat Transfer in Porous Media
- ➢ Interdependency between Electrochemistry and Thermal Transport

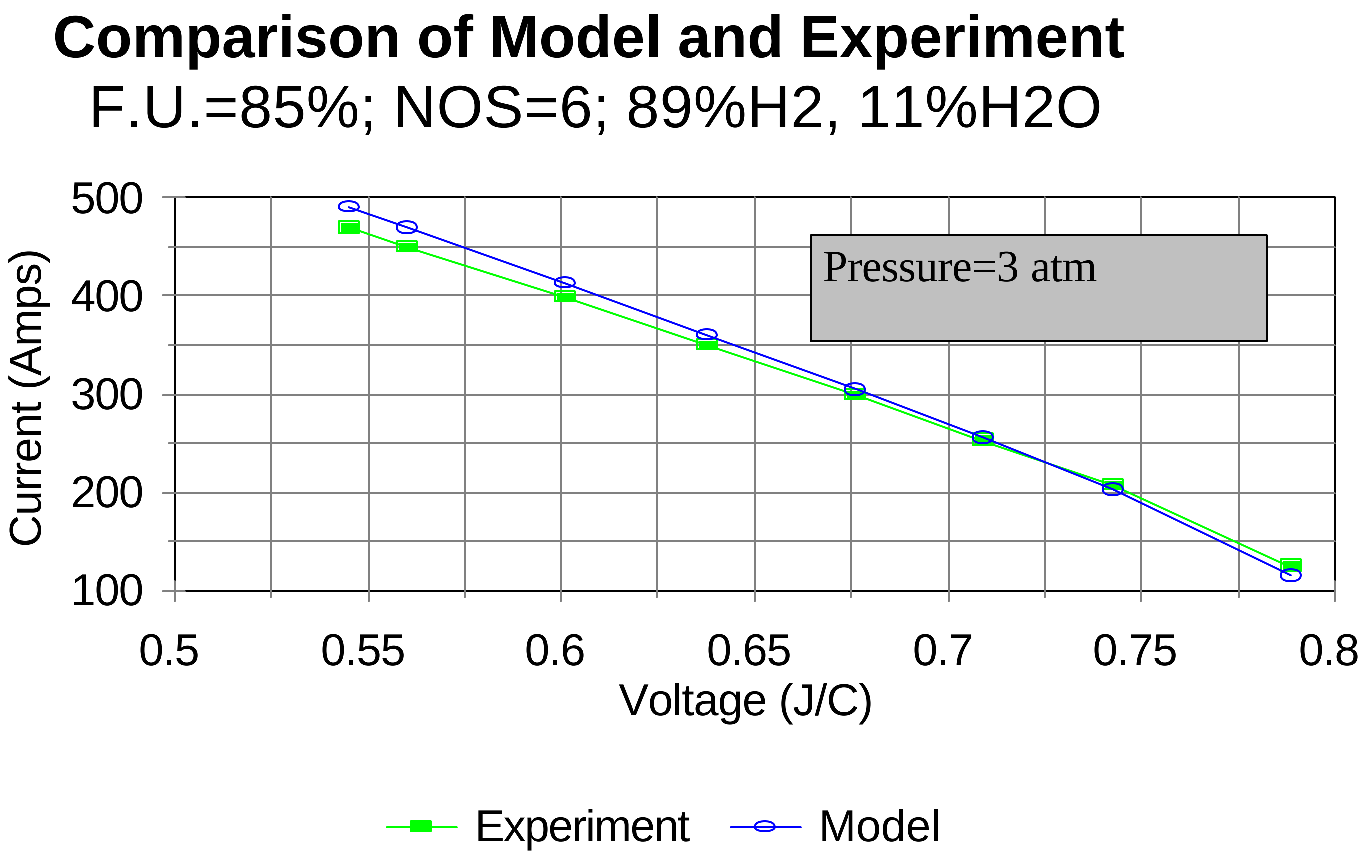
Previous Successes with Electrochemical Modeling of Solid Oxide Fuel Cells: SWPC



Modeling Assumptions

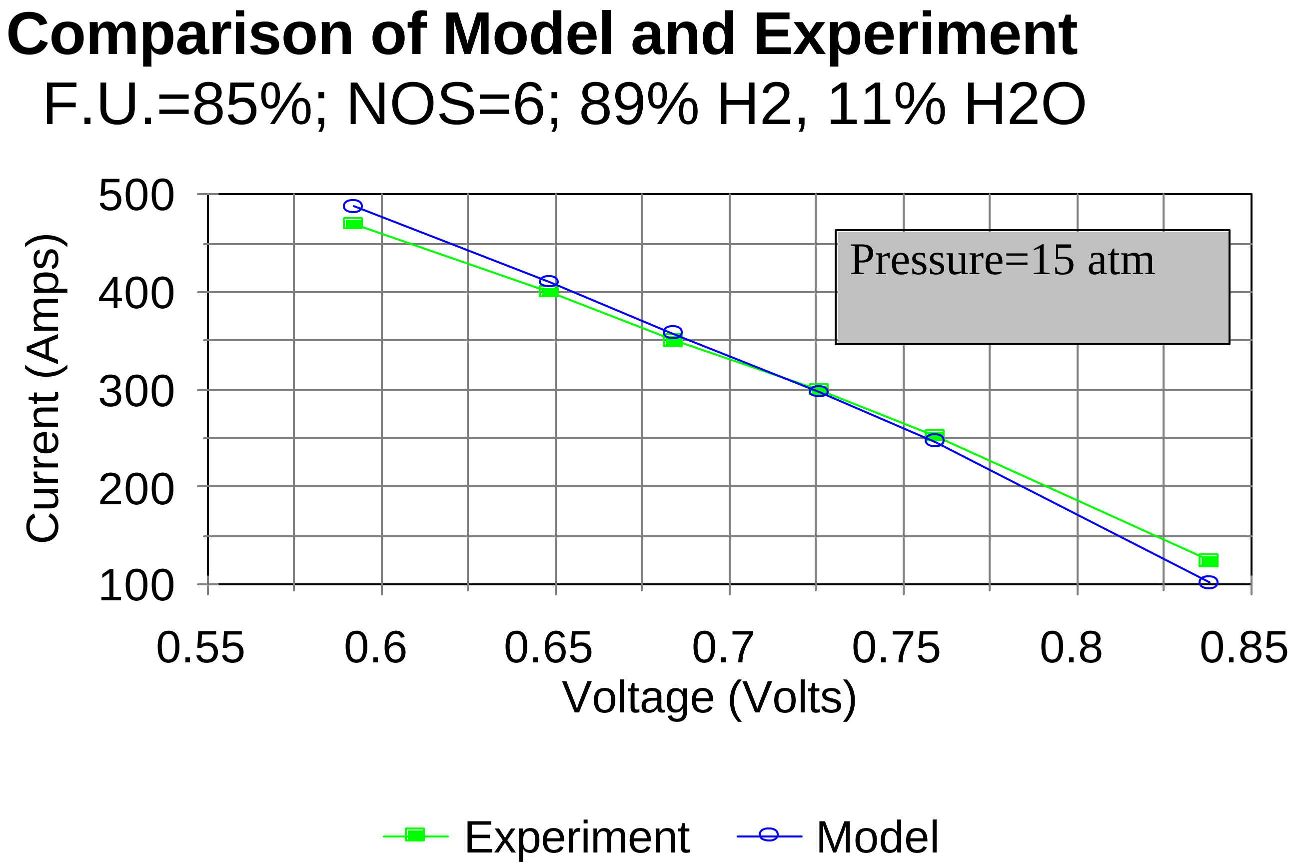
- Tubular solid oxide fuel cells operate at a uniform operating voltage (Kanamura, Zen-ichiro, Shoji, 1989).
- Activation polarization is small in comparison to other polarizations (Maskalick, 1989).
- Carbon monoxide oxidation happens via shift to hydrogen (Minh and Takahashi, 1995).
- The fuel stream has equilibrium chemistry.
- Current is one-dimensional (radial) in the electrolyte (Sverdrup, Warde, Eback, 1973).
- Current is two-dimensional in the electrodes and interconnect as described by the "line-transmission" model (Sverdrup, Warde, Eback, 1973).

Proven Model Fidelity



Accuracy to within 3-5%

Proven Model Fidelity



Accuracy to within 3-5%

Challenges of Characterizing Electrode-supported Designs

- Insufficiency of planar electroactive area model
- Dependency of electrochemistry upon electrical, thermal and concentration potential fields *within* and *along* porous electrodes
- Impact of microstructural parameters upon component-level properties

Distinctive electrode considerations

- Anode: Parallel chemical/electrochemical reaction paths for carbonaceous species
- Cathode: Complexity of transport and reactions occurring within MIEC cathodes

R&D Approach

- *Insufficiency of planar electroactive area model*
- Derivation of effective charge transfer resistance based upon "porous composite electrode" analysis

Kenjo et al. (1991,1992); Deng et al. (1994); Tanner et al.(1997)

$$R_{ct}^{\ eff} \approx \sqrt{\frac{BR_{ct}}{s_{\ e}\left(1 - V_{v}\right)}}$$

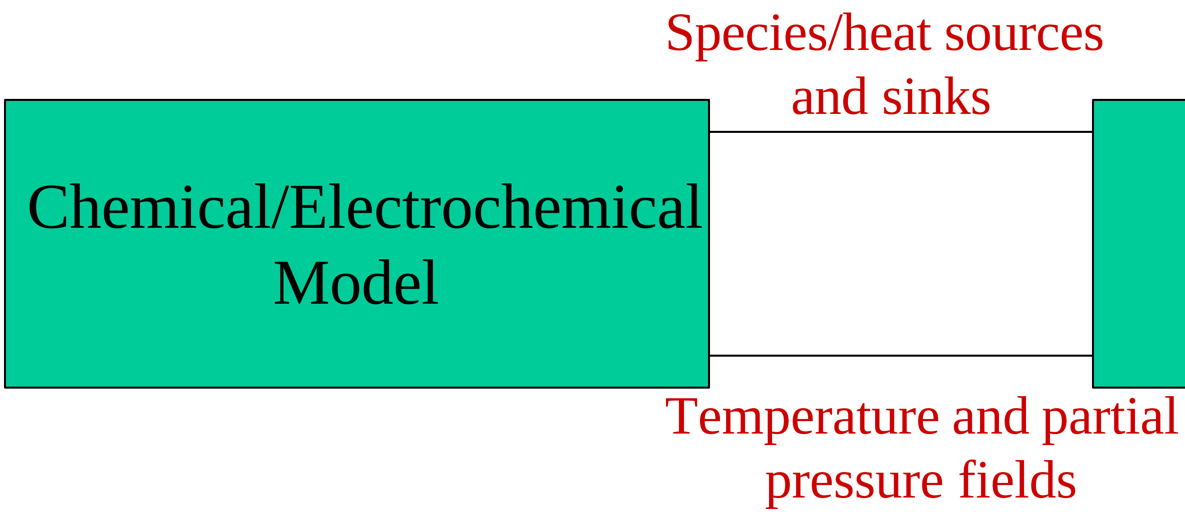
Electrode significantly thicker than reaction zone

Tanner et al., 1997

- **Comparison of porous media transport and reaction rates as resolved by coupled electrochemical-thermal model**

R&D Approach

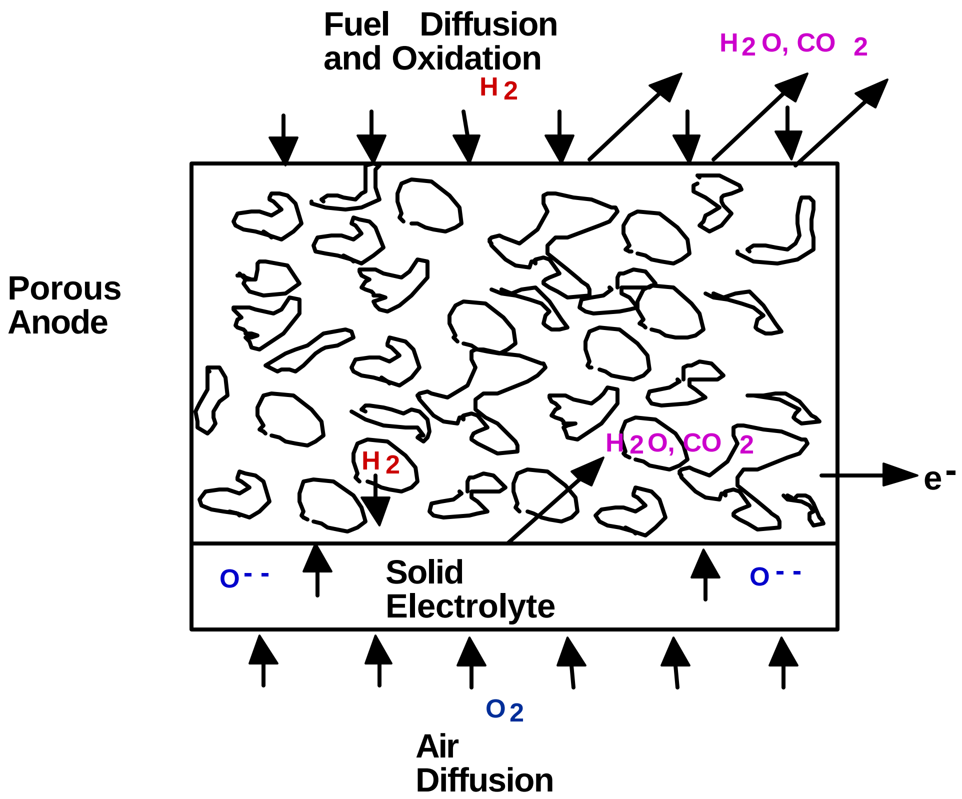
- *Resolution of potential fields throughout electrodes*



- **Sufficient iteration between electrochemical and thermal models will yield temperature, partial pressure, and voltage fields to the needed level of resolution**

R&D Approach

- *Impact of microstructural parameters upon component-level properties*



Detailed SOFC Reaction Zone

(Cathode Similar, exc. Oxidant Reduction)

- Translation of electrode microstructure into pertinent thermophysical properties via extensive interaction with SECA teammates

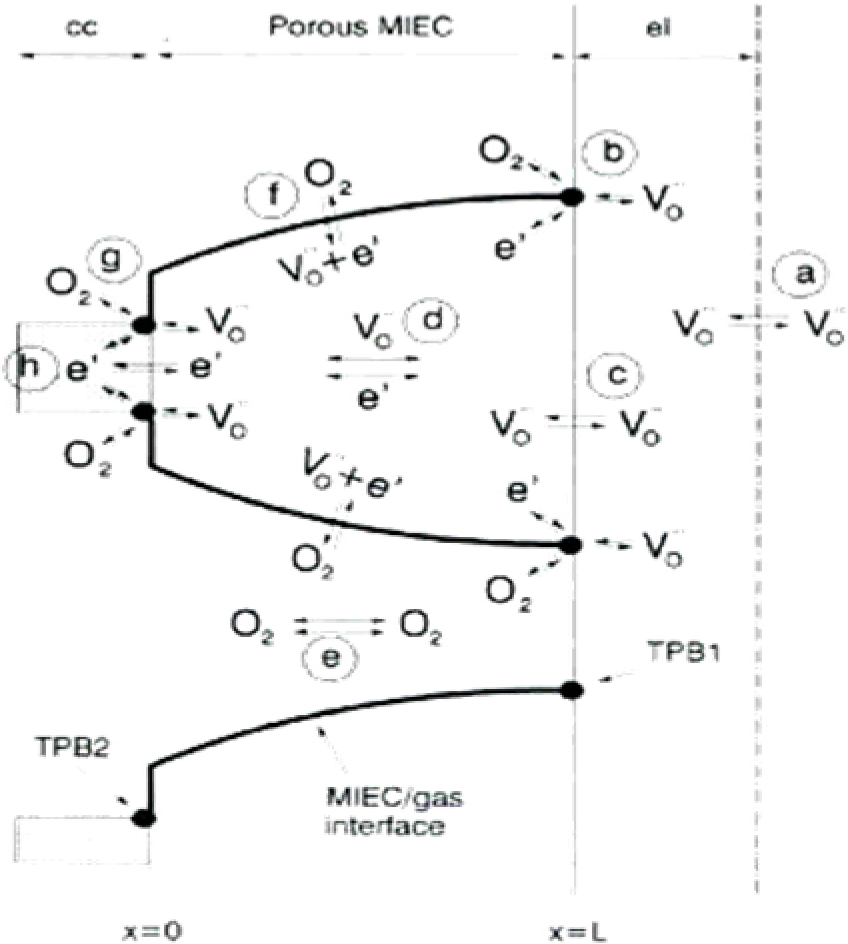
PNNL, Nov. 14 2001 Review

R&D Approach

- *Distinctive electrode considerations*
- Anode: Reaction rates data from industry and labs (e.g., reaction rate constants and V-j data for electrochemical oxidation of carbonaceous fuels)

- **Cathode: Extensive communication/collaboration with Georgia Tech colleague Meilin Liu regarding MIEC cathode modeling**

R&D Approach



Equivalent Circuit Approximation: Illustration of multiple reaction/transport processes within a MIEC cathode

Liu, 1998

R&D Approach

- Integration within (i.e. Georgia Tech)
- Integration without (i.e. SECA teammates)

Collaboration with DOE Labs and SECA partners is critical to an effective Phase I !!!

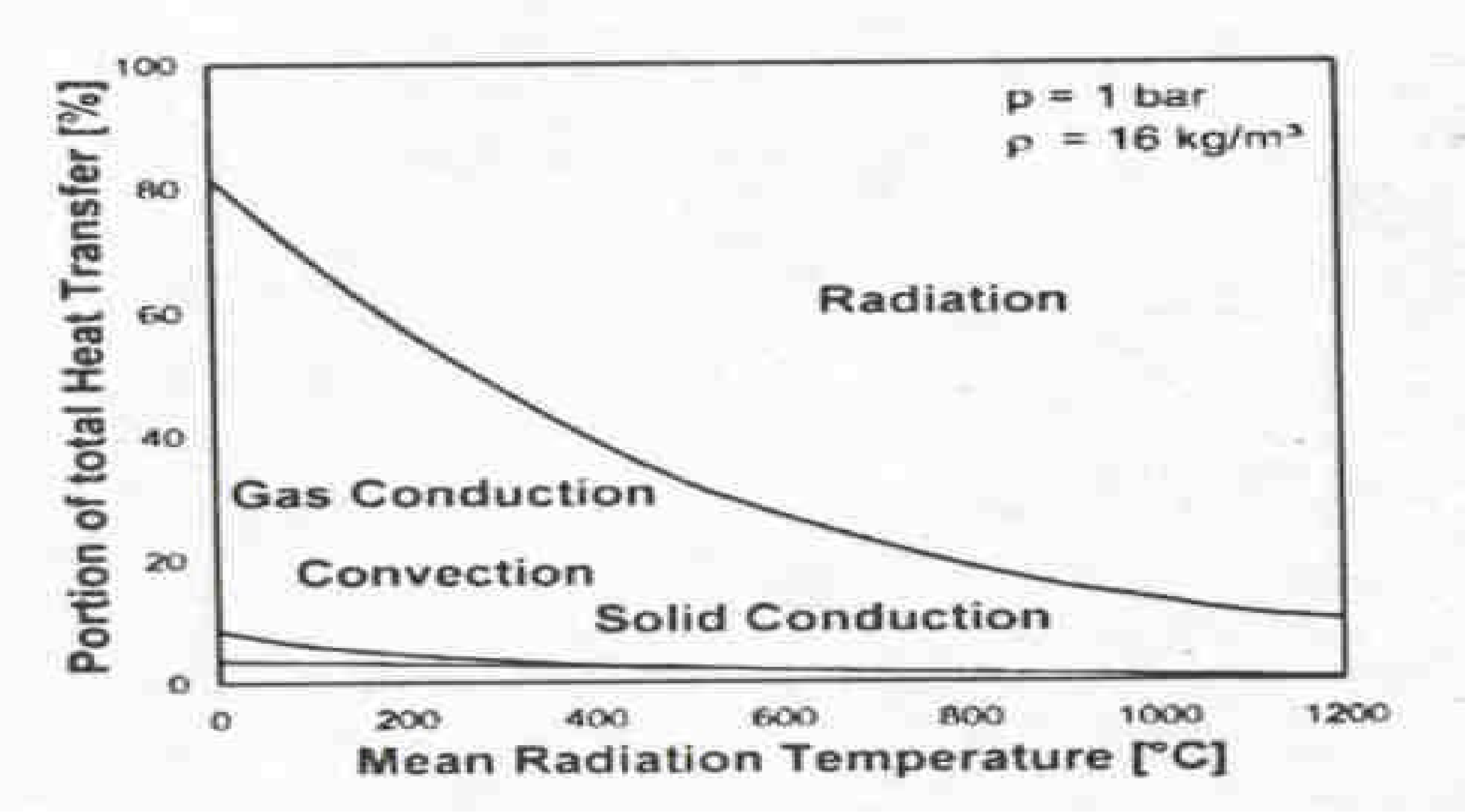
Challenges/Research Issues

<u>What needs to be modeled</u>:

- 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

Challenges/Research Issues

Importance of Radiative Heat Transfer:



Spinnler et al., *Proceedings of 26th International Thermal Conductivity Conference*

Modeling Approach

Continuity (mass conservation) -- quasi steady-state:

$$\nabla \cdot \left(r\vec{V} \right) = 0$$

Momentum Conservation (Forchheimer & Brinkman Model) -- quasi steady-state

$$\nabla \cdot \left(r\vec{V}\vec{V} \right) = -\frac{1}{f}\nabla p + \nabla \cdot \left(m\nabla\vec{V} \right) - \frac{m\vec{V}}{K} - r\, f f\, \frac{\left|\vec{V}\right|\vec{V}}{\sqrt{K}}$$

Here: $\underbrace{f - \text{porosity [-]};\ K - \text{permeability [m}^2\text{]};\ f - \text{inertia coefficient [-]}}_{\text{Need to be modeled (usually semi-emprically) for given type/topology of porous media (literature search)}}$

Species Conservation (Reagent & Intermediate Mole Fraction) -- transient

$$\frac{\partial Y_i}{\partial t} + \nabla \cdot \left(r\vec{V}Y_i \right) = \nabla \cdot \left(D_i \nabla Y_i \right) \pm S_i$$

Here: $\underbrace{D_i - \text{diffusion coefficient [m}^2\text{/s]};\ S_i - \text{ species production/depletion rate [s}^{-1}\text{]}}_{D_i \text{ - diffusion/dispersion coefficient (needs to be modeled); } S_i \text{ has to come from electrochemistry modeling (single or multiple step chemistry)}}$

Potential Conservation Equation??? Is it needed to model reaction rates???

Modeling Approach

Energy Conservation (Solid and Gas Phase)-- transient

$$\frac{\partial r c_{p\Sigma} T_g}{\partial t} + \nabla \cdot \left(r \vec{V} c_{p\Sigma} T_g \right) = \nabla \cdot \left(k_{g,eff} \nabla T_g \right) - h_v \left(T_g - T_s \right) \pm \sum_i S_i \times \Box H_i \quad \text{(Gas Phase)}$$

$$\frac{\partial r c T_s}{\partial t} = \nabla \cdot \left(k_{s,eff} \nabla T_s \right) + h_v \left(T_g - T_s \right) \quad \text{(Solid Phase)}$$

Here: $\underbrace{k_{g,eff} - \text{gas phase thermal conductivity [W/mK]; } \Box H_i - \text{ enthalpy of reaction [J/kgmol]}}$

D_i - diffusion/dispersion coefficient (needs to be modeled); $\Box H_i$ has to come from electrochemistry modeling (single or multiple step chemistry)

We assume here all reactions can be modeled as gas phase reactions despite their catalytic nature

Modeling Radiative Transfer

Use diffusion (optically thick) approximation

$k_{s,eff} = k_{s,cond} + k_{rad}$ (+ Simple; - Often Inaccurate)

Solve RTE (Radiative Transfer Equation) to compute radiative heat fluxes

(+ Rigorous; - Difficult to Solve Even for Simple Geometries)

Simulation Approach

TRANSPORT EQUATIONS:

- Single Domain Approach with Boundary Conditions on the Outer Boundaries only
- SIMPLER Algorithm to Solve Pressure Coupled Equations Expressed in Unified Form:

$$\partial\Phi/\partial t + \nabla\cdot(r\vec{V}\Phi) = \nabla\cdot\left(\Gamma\nabla\Phi\right) + S$$

RADIATIVE TRANSFER EQUATION:

- Develop an Analytical Expression for Radiative Thermal Conductivity Using Discrete Ordinates Method (available in FLUENT)

COUPLING OF EQUATIONS:

- Temperature – Heat Flux Iterative Exchange Until Full Convergence

Model Input Parameters: Needs

What is needed for reliability of modeling:

Anode & Cathode:

- Detailed pore structure and pore size distribution
- Porosity, Permeability, Tortuosity, and Specific surface area
- Structure (spatial catalyst distribution) of the transitional electrode/electrolyte layers
- Thermophysical properties (density, specific heat, and thermal conductivity) as function of temperature
- Optical properties (complex index of refraction or complex dielectric function) as function on temperature and wavelength of radiation
- Volumetric heat transfer coefficient between the flowing gases and porous matrix as function of flow conditions

Model Input Parameters: Needs

What is needed for reliability of modeling:

Electrolyte:

- Thermophysical properties (density, specific heat, and thermal conductivity) as function of temperature
- Optical properties (complex index of refraction or complex dielectric function) as function on temperature and wavelength of radiation

Reagents:

- Feed composition (mass/mole fractions) and thermophysical properties (density, specific heat, thermal conductivity, and species diffusivity) as function of temperature
- Rate constants and enthalpy of reactions for selected set of reactions to be modeled.

Failure Criterion

"Stress" > "Strength" → Failure

Stress: (calculated)

temperature, geometry, constraint conditions

Strength: (measured)

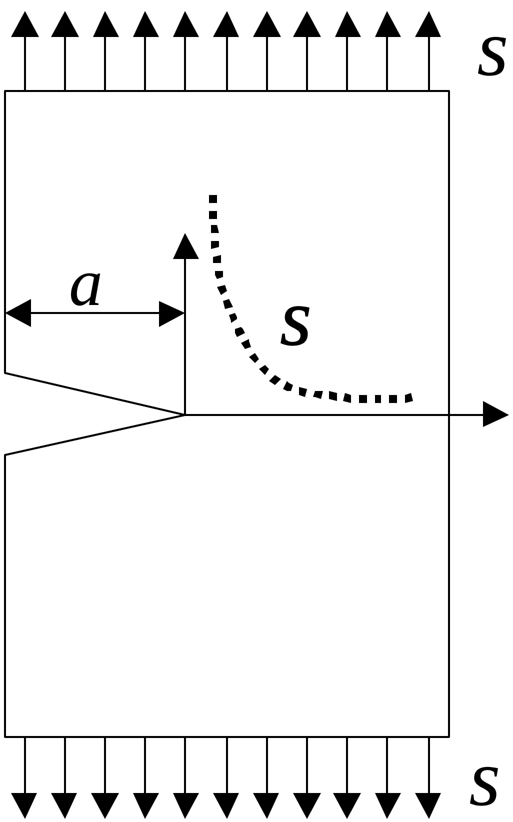
Material properties, defects, processing conditions

Failure Criterion: (modeled)

Life prediction based on mechanics of materials.

FRACTURE MECHANICS

The theory of fracture mechanics rests on the observation that near the crack tip in a brittle material, the magnitude of the singular stress fields is usually controlled by a single parameter.



In linear elastic fracture mechanics (LEFM), the singular stress near a crack tip can be written as

$$s = \frac{K}{\sqrt{2px}}$$

where x is the distance to the crack tip as illustrated on the left. The parameter K is called the stress intensity factor (SIF), which is an indication of the stress magnitude near the crack tip.

Failure Criterion: There is a critical value so that failure occurs when

$$s \geq s_c$$

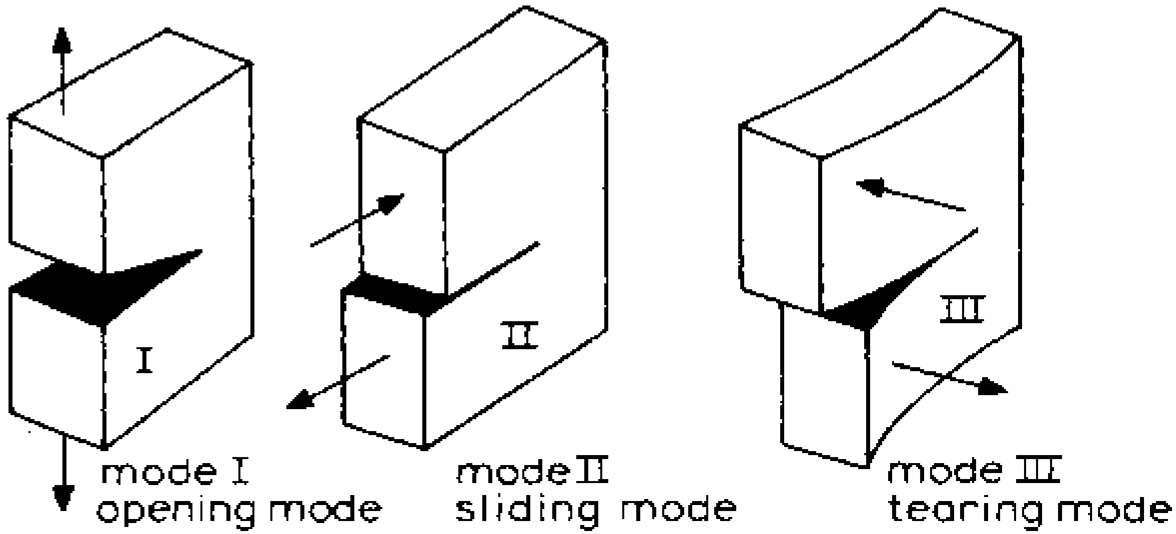
Fracture Criterion: There is a critical value so that fracture occurs when

$$K \geq K_c$$

The material's ability to resist fracture is then defined as the critical value of the stress intensity factor, K_c, at which fracture is about to occur. This value is called the fracture toughness. It is an intrinsic material property that can be measured using a number of techniques. Fracture toughness for commonly used engineering materials can be found in many handbooks. Once the fracture toughness is known, the onset of fracture can be predicted by the theory of fracture mechanics.

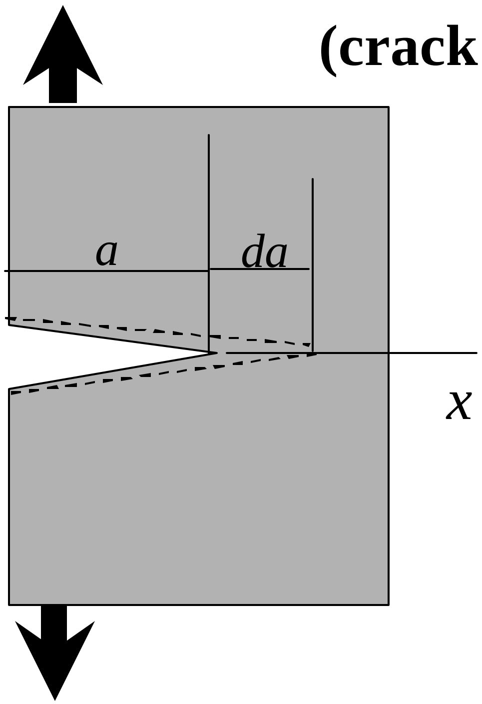
Stress Intensity Factors

$$s = \frac{K_I}{\sqrt{2px}} \qquad s = \frac{K_{II}}{\sqrt{2px}} \qquad s = \frac{K_{III}}{\sqrt{2px}}$$



The SIFs, in general, are a function of the load, specimen geometry, and crack size. For a given sample with cracks under given loading conditions, the SIFs can be calculated either analytically, or numerically.

Energy Release Rate
(crack extension driving force)



G = energy release rate
= energy released/crack extension

$$G = \frac{1-\nu^2}{E}\left(K_I^2 + K_{II}^2 + \frac{K_{III}^2}{1-\nu}\right)$$

<u>Griffith Energy Criterion:</u>

Crack growth can occur if the energy required to form an additional crack size *da* can just be delivered by the load.

↓

$G > G_c$ ⟶ Fracture may occur

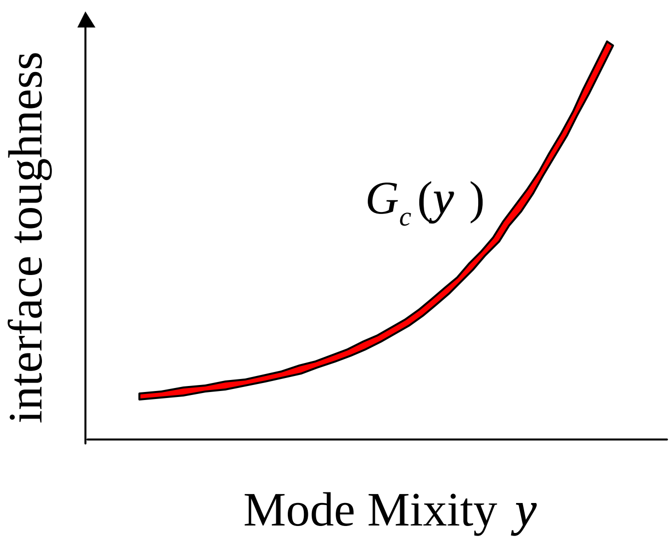
- G: energy delivered to the crack-tip by the load
- G_c: energy required to form new crack surfaces

Interfacial Toughness Curve

Energy Release Rate

$$G = \frac{|K|^2}{E^* \cosh^2 pe}$$

$$\frac{2}{E^*} = \frac{1}{E_1} + \frac{1}{E_2}$$



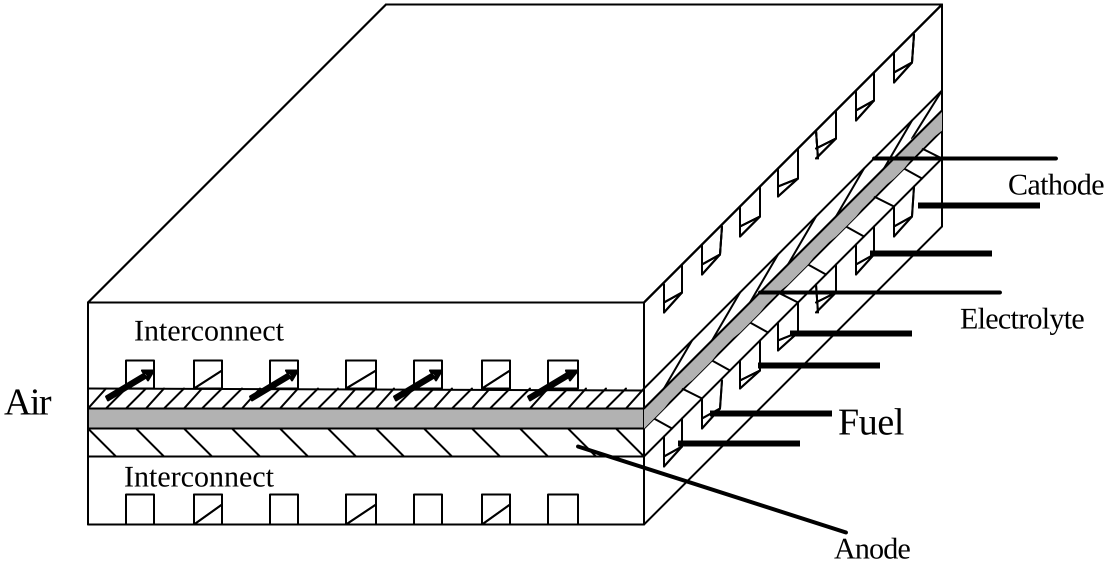
Crack Driving force

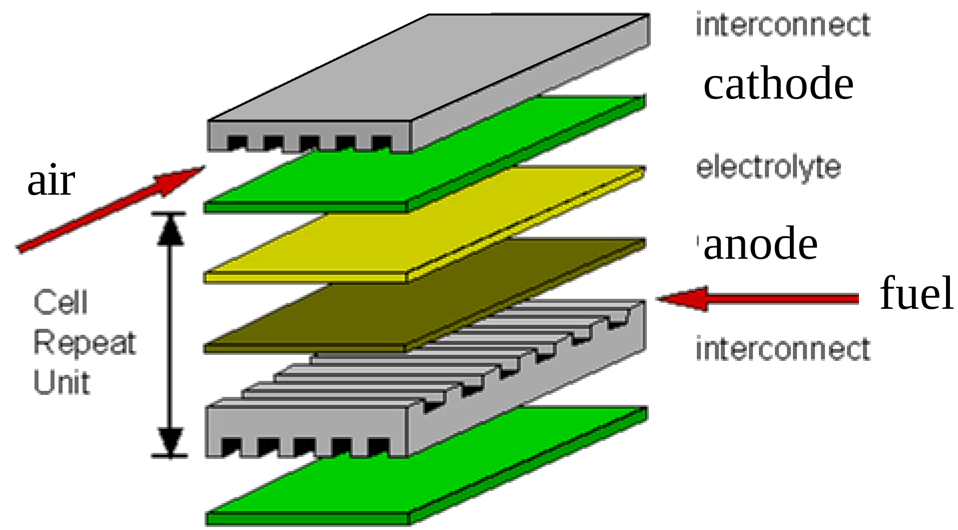
$$G = f(\text{load, geometry, mat'l})$$

Fracture Criterion

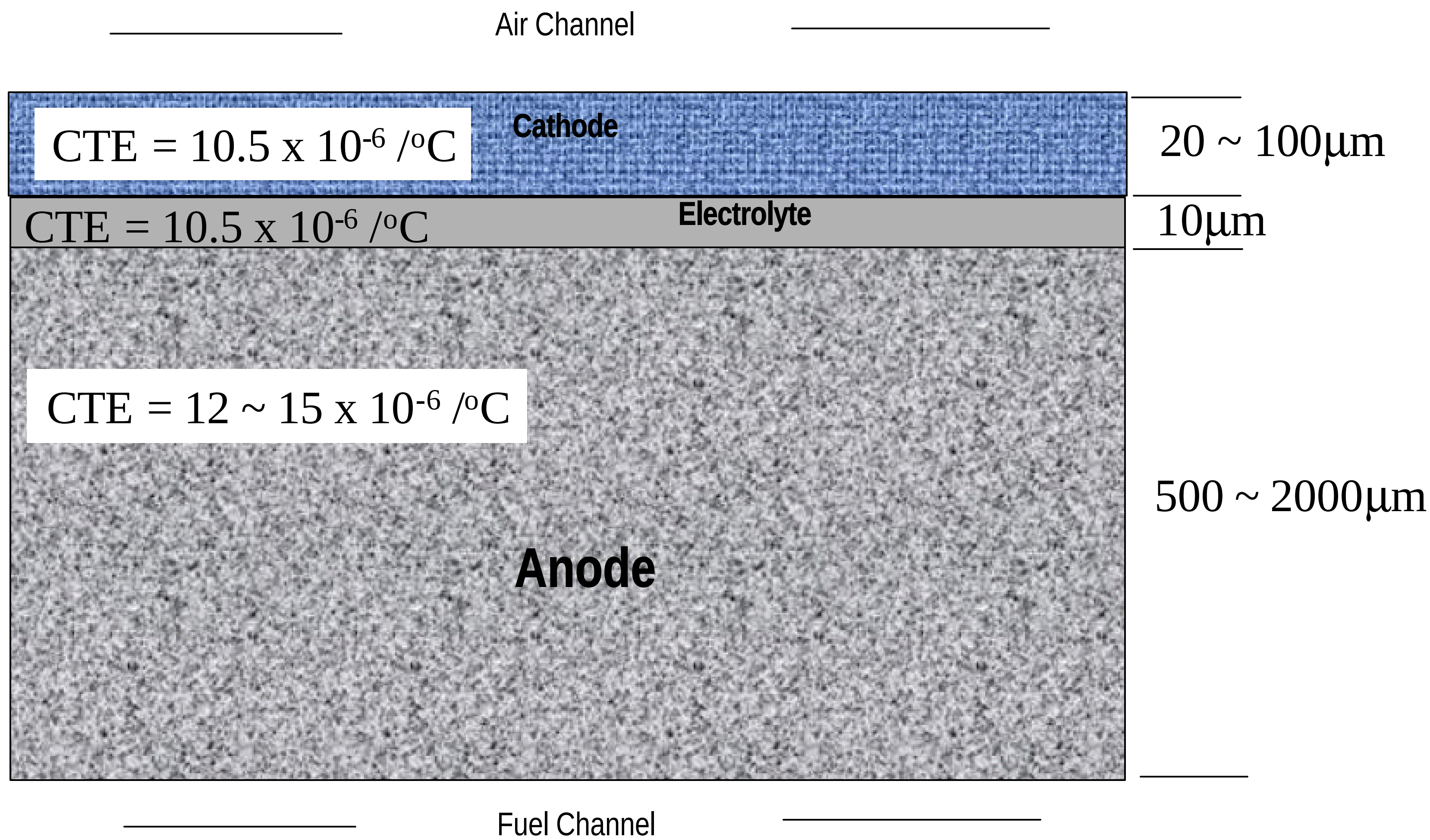
$G > G_c$	→	Fracture may occur

For an interface, its ability to resist debonding depends on how the interface is loaded. At a given phase angle y, the max. loading amplitude $G(y)$ that an interface can sustain without decohesion is called the toughness of the interface at this phase angle.


Cathode
Electrolyte
Interconnect
Air
Fuel
Interconnect
Anode


interconnect
cathode
air
electrolyte
anode
fuel
interconnect
Cell
Repeat
Unit

2D Model



Air Channel
Cathode
CTE = 10.5 x 10-6 /oC
20 ~ 100µm
Electrolyte
CTE = 10.5 x 10-6 /oC
10µm
CTE = 12 ~ 15 x 10-6 /oC
Anode
500 ~ 2000µm
Fuel Channel

Input:

Temperature distribution (from electrochem/thermal/fluid)

Material properties (from PNNL/ORNL/NETL, or SECA members)

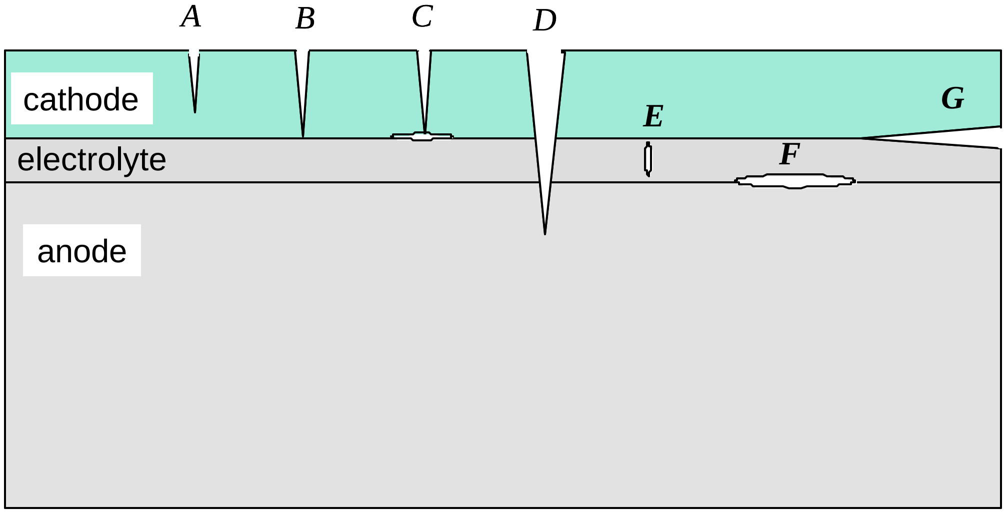
Boundary conditions (symmetry, periodicity)

Tool: ABAQUS or ANSYS

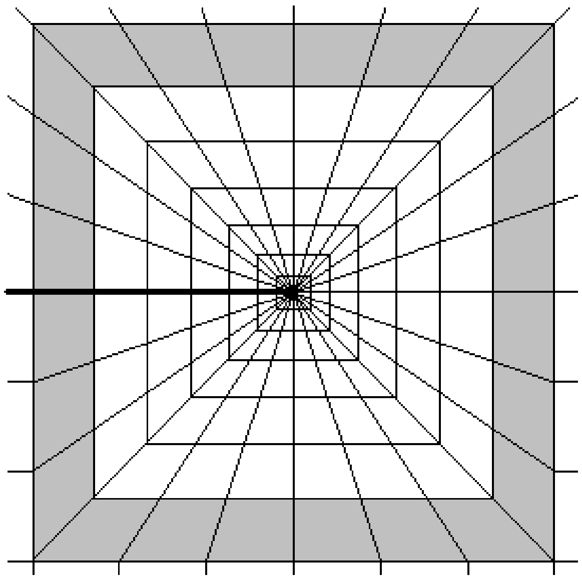
Output:

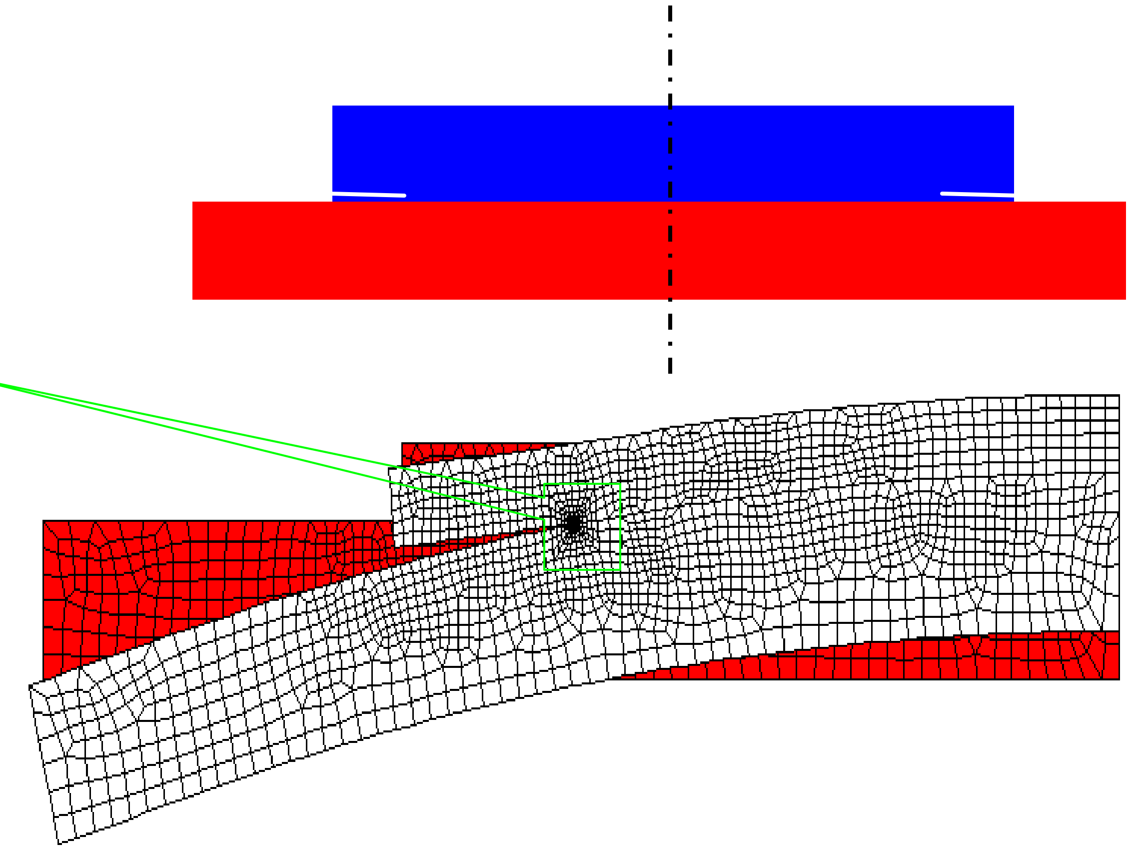
Stress distribution

Stress intensity factors for cohesive, interfacial and impinging cracks



An Example of Calculating *G* Using FEM

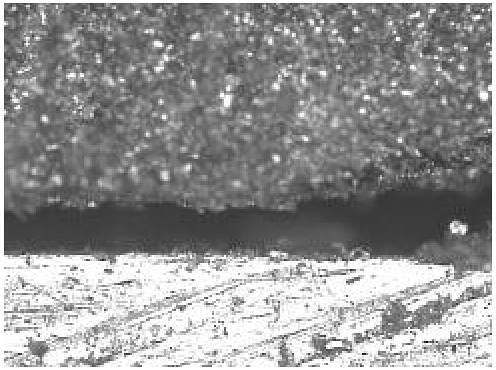




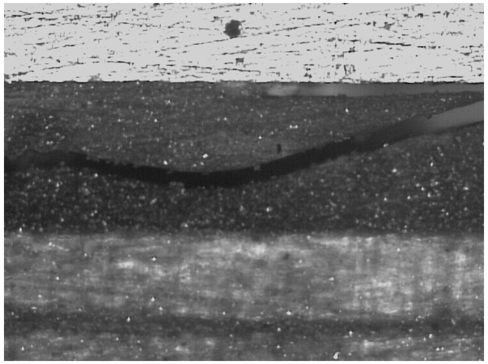
$$G = \oint_{\Gamma} [s_{ij} u_{i,j} n_1 - s_{ij} n_j u_{i,1}] ds$$

$G > G_c$ → Fracture may occur

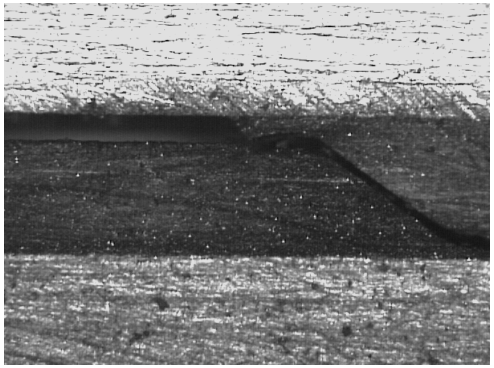
Fracture Patterns



interface crack



in-layer crack

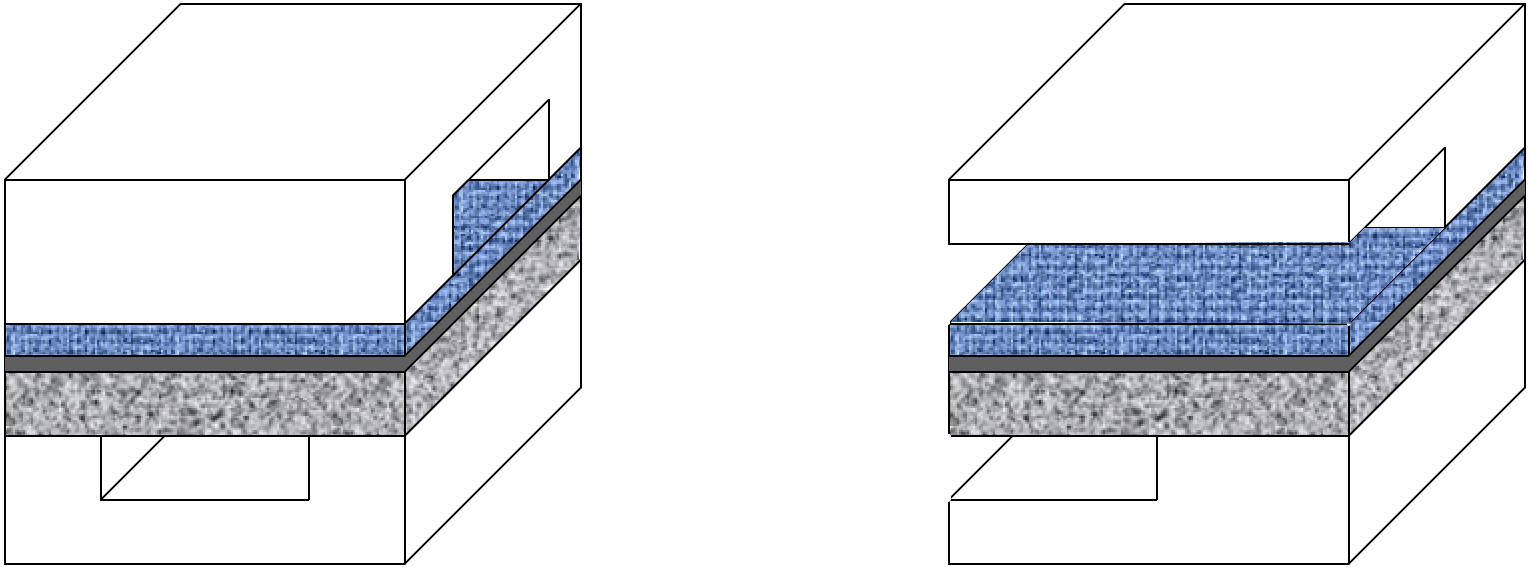


alternating crack

$$G_R = \frac{G_i}{G_p} > \frac{G_{ic}}{G_{pc}} \Rightarrow$$ Along the interface

$$G_R = \frac{G_i}{G_p} < \frac{G_{ic}}{G_{pc}} \Rightarrow$$ Through the interface

3D Model



A unit cell

¼ of a unit cell

Major Challenges

Material Microstructure

- Grain size
- Porosity

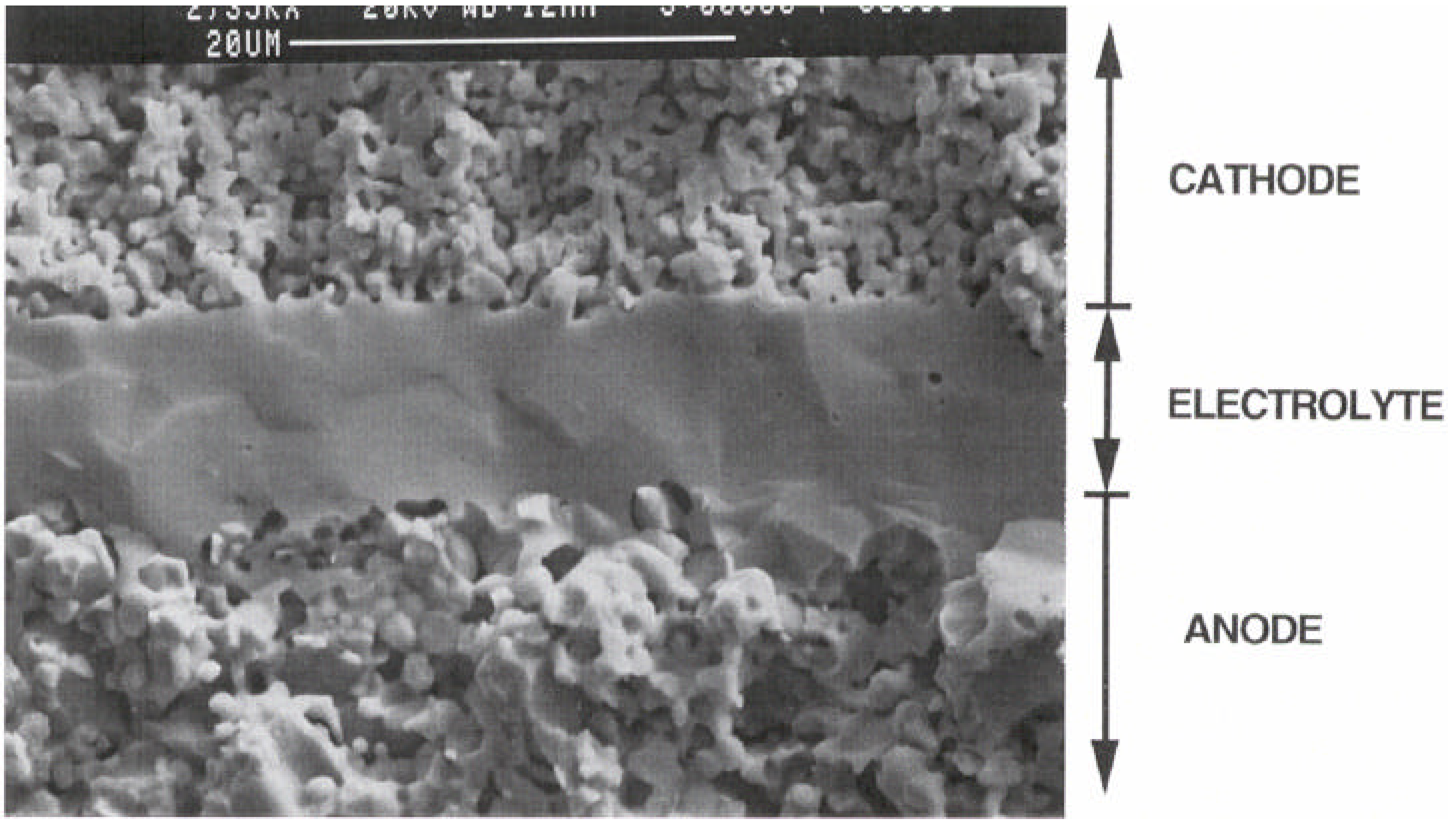
Material Thermomechanical Properties

- Modulus, Poisson's ratio
- CTE
- Tensile and compressive strength
- Fracture toughness
- Interfacial fracture toughness (anode/electrolyte/cathode/interconnect)
- Creep properties of metallic interconnects

Geometrical Parameters

- Cell dimensions
- Layer thickness (anode, electrolyte, cathode and interconnect)
- Channel dimensions
- Seal design and dimensions

Typical Cell Microstructure



Objectives

- Generate new scientific and engineering knowledge to better enable SECA Industry Teams to develop low-cost solid-oxide fuel cell power generation systems.
- Create technology breakthroughs to address technical risks and barriers that currently limit achievement of the SECA performance and cost goals for solid-oxide fuel cell systems.
- Transfer new science and technology developed in the Core Technology Program to the SECA Industry Teams.

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.

Task 1: Fracture Mechanics Modeling

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. The Recipient shall investigate the individual and combined influences of electrochemical and mechanical load stress, as well as temperature gradients on crack initiation and propagation. The Recipient shall 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.

Task 2: Electrochemical Modeling

2.1 Utilize/adapt existing electrochemical models, and develop enhancements necessary to achieve the project objectives and to advance the state-of-the-art.

2.2 Models Extension to include porous electrode phenomena enhancements beyond the current state-of-the-art.

2.3 Evaluate and validate the accuracy of developed electrochemical models and enhancements using either experimental data or modeling results from PNNL/NETL/ORNL or other SECA members

Task 3: Thermal Modeling

3.1 Formulation of 2-D and 3-D models for combined advection, conduction, and radiation heat and mass transfer in the porous electrodes.

3.2 Formulation of an approach for calculation of effective transport, thermophysical and radiative properties for the porous electrodes.

3.3 Formulation of coupled heat/mass transfer and electrochemistry model on the "unit-cell" level. The Recipient shall account for boundary effects, such as oxidant and fuel flow field channels, electrical interconnects and seals.

3.4 Review, select, and develop solution algorithms for numerical solution.

3.5 Evaluate and validate the accuracy of developed thermal models, algorithms and enhancements using either experimental data or modeling results from PNNL/NETL/ORNL or other SECA members.