SECA Core Program – Recent Development of Modeling Activities at PNNL

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February 18-19, 2003

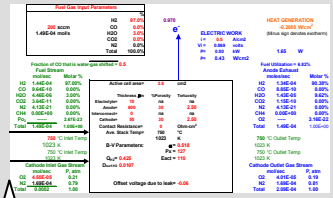
Technical Issues and R& D Objectives

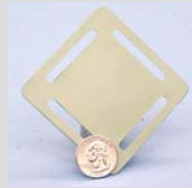
- Technical Issues
  - Concurrent management and control of thermal, physical, chemical and electrochemical processes over various SOFC operational parameters.
- Objectives

  Develop modeling and simulation tools to be used by the SECA vertical teams as an integral part of the design process. Tools to be used for:
  - System design requirements roll-out
  - Sub-system component design
  - Microstructural and material design/optimization
  - Control design
  - Life prediction

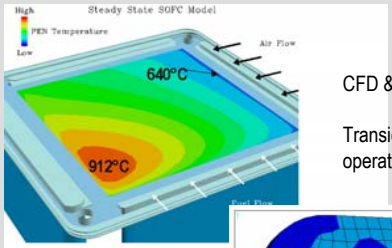
Integrated Modeling of Solid Oxide Fuel Cells

The development of modeling tools for the analysis of fuel cells is essential for the design process. These tools must include the coupling between the fluid, thermal, electrochemical,, and structural behavior. Issues peculiar to SOFC design include elevated operating temperatures, CTE mismatch, flow uniformity and start-up time. The tools being developed will address these issues. They will be used to optimize the design, predict the performance, and assess the reliability and lifetime of the cell. PNNL is taking an integrated approach to incorporate all these effects.



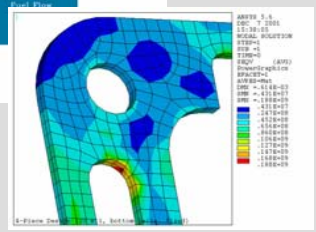


Cell Fabrication & Testing at PNNL



CFD & FEA Models

Transient & Steady state operating conditions



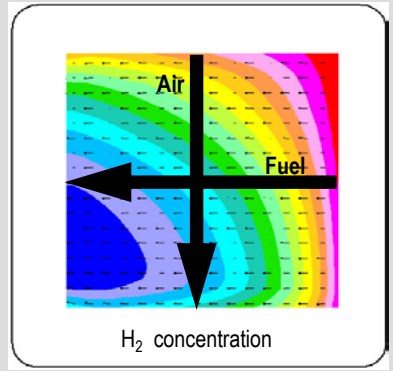
Electrical Power System

Thermal System

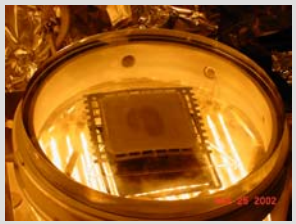
Stack

Cell

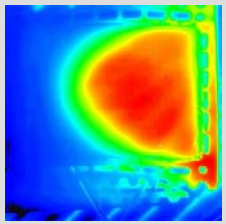
Experimental Validation of Modeling



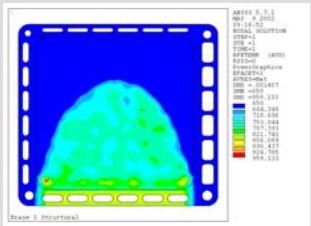
Continuum Electrochemistry Results



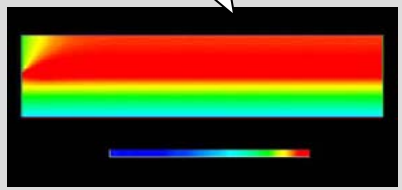
Rapid (<30 sec.) heating of ceramic PEN to 700°C with 20 KW infrared heaters. Temperature profile controlled with parabolic shaped mask

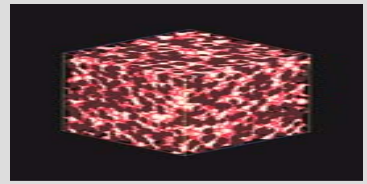


Infrared image of temperature profile



Finite element modeling of test





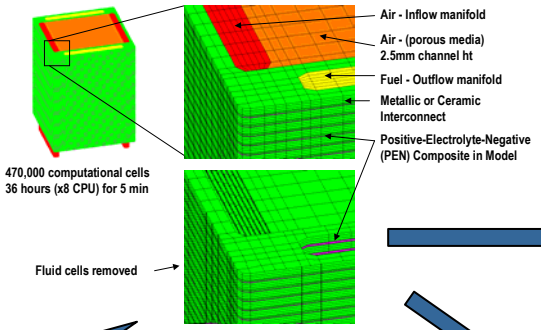
Microstructural electrochemistry modeling shows the hydrogen concentration as the fuel traverses the length of the cell and diffuses through the electrodes.

SOFC Flow – Thermal - Stress Modeling

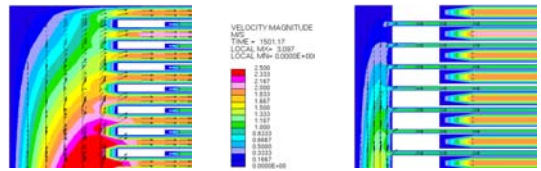
An integrated set of modeling tools is invaluable in the design of fuel cells. The physical phenomena to be modeled include fluid flow, heat transfer, and mechanical response. The methodologies being developed at PNNL provide a unified method for considering these aspects.

A common geometric database provides commonality between CFD and FEA meshes. The CFD analysis provides flow uniformity results and the temperature distribution through the stack. The coupling logic applies the temperatures to the corresponding FEA mesh. Stress levels and component safety factors can be evaluated in FEA results. A custom temperature controller can be designed for the SOFC start-up procedure.

Thermal-Fluids Stack Model



Flow Uniformity Results



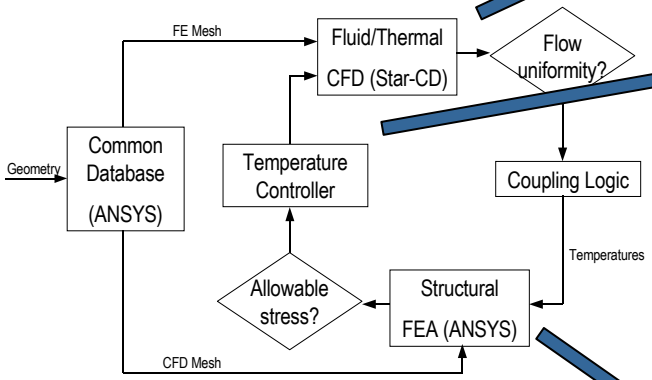
Cathode-Side Velocities
- bulk mean velocity in channels = 1.83 m/s
- max = 2.19 m/s (20% above mean)
- min = 1.37 m/s (25% below mean)

Anode-Side Velocities
- bulk mean velocity in channels = 1.13 m/s
- max = 1.24 m/s (10% above mean)
- min = 1.09 m/s (3.5% below mean)

60-cell Stack Model Contains:
- 15x15x3 fluid cells/chan (typical)
- 400,000+ computational cells total

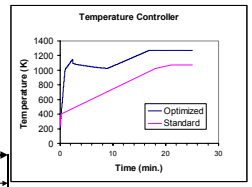
Anode side flow is within 10% of mean => small channel height

SOFC Flow – Thermal – Stress Modeling Flow Chart



Start-up Temperature Controller

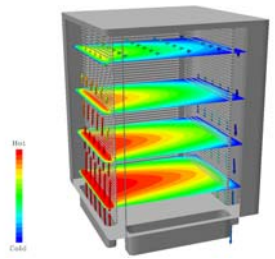
- Time to reach 20C - 0.98 min
- Time to reach 650C - 13.2 min
- Time to reach 700C - 14.8 min
- max DT - 424K



Ave PEN temp	ΔT allow
523	504
640	380
724	245

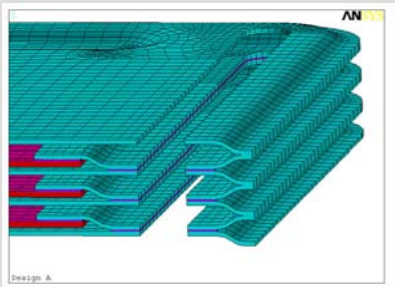
Optimized temperature controller safely provides additional heat early in the start-up resulting in greatly reduced start-up times.

Thermal-Fluids Stack Model: Start – Up Transient



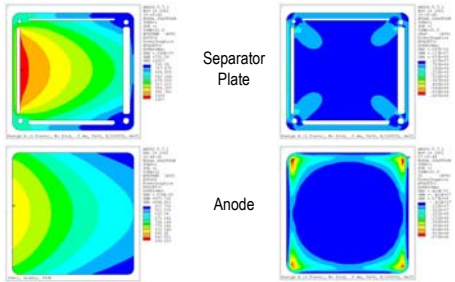
Modeling demonstrates that temperature profiles are non-isothermal during start-up.

Structural Models



Include details as necessary to capture items of interest. e.g. Multi-element seals, subdivide PEN into layers.

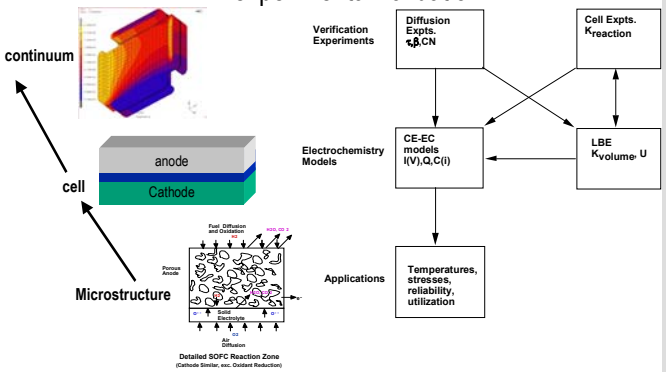
Rapid Start-up – Stress Analysis Results

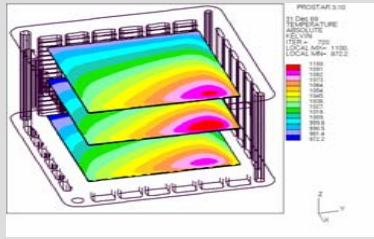


Electrochemistry Modeling of Solid Oxide Fuel Cells

Fuel cells are projected to play an important role in energy production in the future. Solid oxide fuel cells offer attractive benefits in high power density and fuel flexibility. Electrochemical modeling provide a means of assessing the steady state behavior of the cell. Modeling is being conducted at the continuum level for inclusion in the stack engineering analyses. Microstructural modeling is being performed to evaluate the effects of electrode porosity, tortuosity, and grain size. The combination of these two approaches provides a comprehensive method for evaluating electrochemistry.

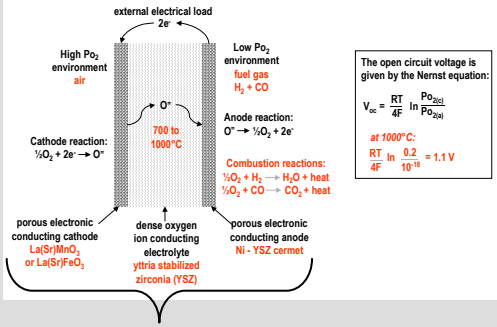
Approach:
Integrated multi-level models with experimental validation





Continuum Modeling

Electrochemistry Basics



The open circuit voltage is given by the Nernst equation:

$$V_{oc} = \frac{RT}{4F} \ln \frac{Po_{2(c)}}{Po_{2(a)}}$$

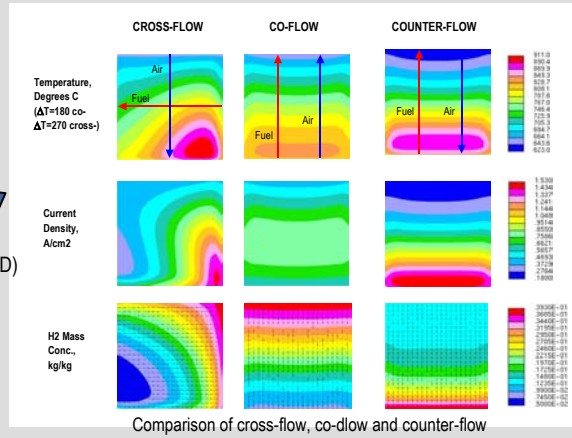
at 1000°C:

$$\frac{RT}{4F} \ln \frac{0.2}{10^{-18}} = 1.1\ V$$

Anode, electrolyte and cathode are collectively referred to as the PEN

Development of electrochemical models.

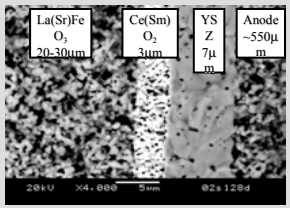
Computational fluid dynamics (CFD)
Finite element analysis (FEA)



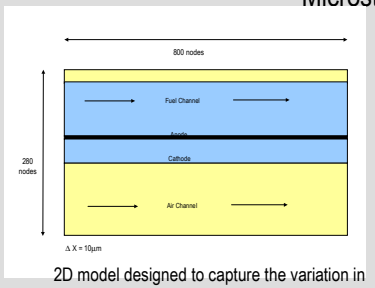
Comparison of cross-flow, co-dlow and counter-flow designs demonstrates the advantages of the co-flow design. The temperature gradient decreases which lowers the stress in the cell. Tthe current density is also more uniform, decreasing the potential for fuel depletion.

Lattice Boltzmann (LBE)

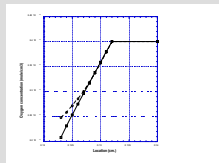
Microstructural Modeling



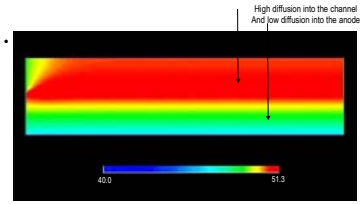
Variations in the PEN microstructure are evident.



2D model designed to capture the variation in gas concentration through the PEN microstructure and in the flow direction.



Gas concentration increases if the reactive surfaces extend into the electrolyte rather than only at the electrode – electrolyte interface.



Hydrogen distribution is a function of the flow rate and diffusion through the PEN

Electrochemistry Analysis

- Activity 1: Temperature control for 1-Cell stack models in CFD framework.
  - Suitable for cases using both serial and parallel processing
  - Dynamic simulation control (DSC) of the inflow boundary temperature to expedite the convergence to a predetermined, average cell temperature.
  - Speeds parametric simulation.
- Activity 2: An efficient modeling tool for SOFC development of coupled thermochemical stress and electrochemistry analysis in MARC.

Activity 1: Temperature Control

- Simulation of stack in insulated box (ie. Not in heated oven)
  - Requires large flow rate of oxidant to ensure best power density.
  - Fuel Utilization controlled by fuel delivery rate.
  - Therefore: cell temperature is controlled by temperature of inflowing fuel and oxidant.
- Previously in simulations a desired cell temperature was achieved by:
  - Running constant boundary temperature cases
  - Iterating on boundary temperature to give desired cell temperature.
- With a temperature control scheme that allows the boundary temperature to adjust during simulation, the desired average cell temperature can be achieved with one simulation run.

Activity 1: (continued) Temperature Control Scheme

Steps to controlling boundary temperature

- Cell Temperature (Tgoal) is chosen prior to STAR-CD simulation run
- Initial boundary temperature set (Tinflow)
- Calculate average cell temperature at each iteration (Tnew)
- Store average cell temperature of previous iteration (Told)
- Determine increment to add or subtract from Tinflow (dTin):
  - Magnitude of deviation from goal temperature: (dTgoal) = Tnew - Tgoal
  - Rate of temperature change per iteration: (Tdelt) =Tnew - Told
  - The change made to Tinflow (dTin) is proportional to both dTgoal and Tdelt
- Tinflow = Tinflow + dTin
- Procede to next STAR-CD iteration

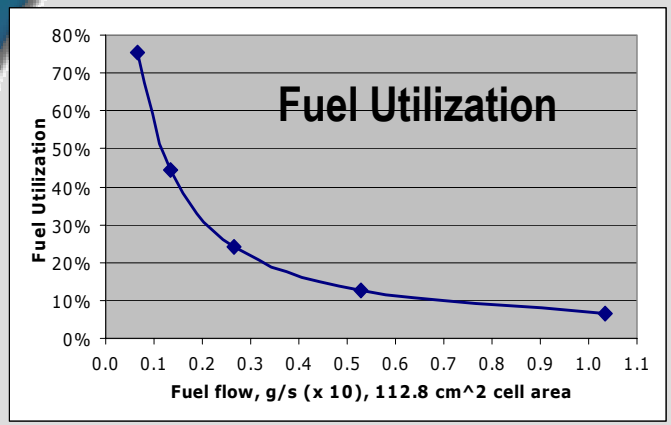
Activity 1: (continued) Using Temperature Control

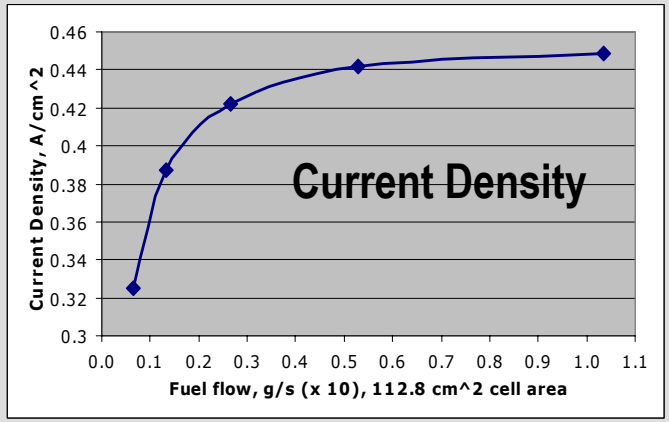
An Example Case Study: The following slides will show:

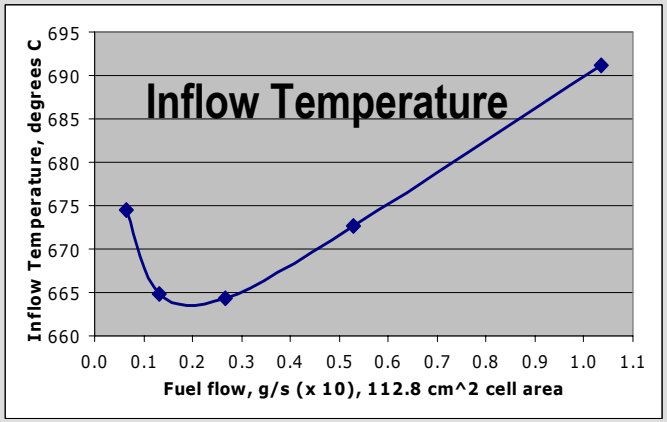
The Effect of Fuel Flow Rate on the Fuel Utilization and Electric Current Density for a Typical Cross-Flow SOFC operating at 750 degrees C and 0.7 Volts.

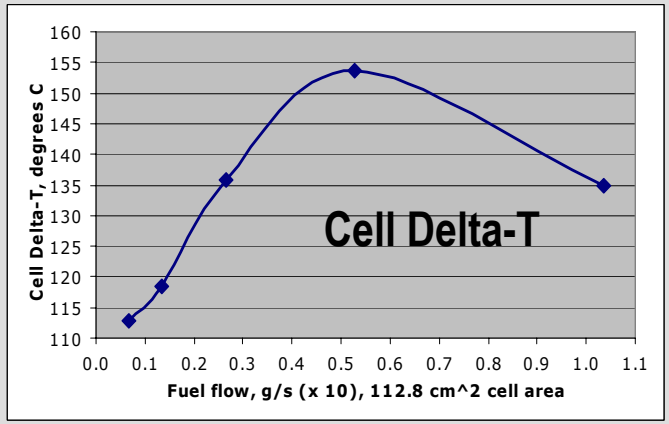
- Fuel Composition: 37%H2, 3%H2O, 34%CO, 7%CO, and 18%N2.
- Oxidant Composition (air): 21%O2, 79%N2
- 112 cm2 active cell area
- Cell Performance model used was that of cell I-6 (ie. 0.442 A/cm^2 @ 0.7 Volts)

Activity 1: (continued) Using Temperature Control - Plotted Results



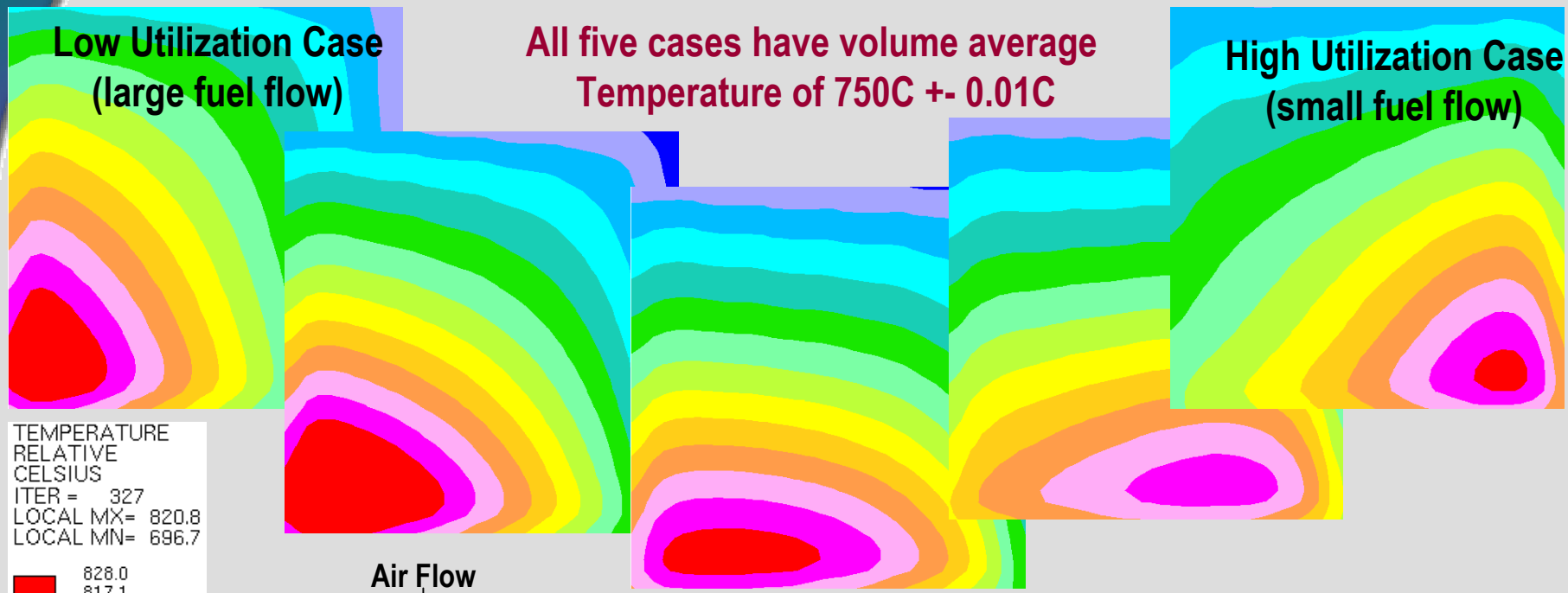


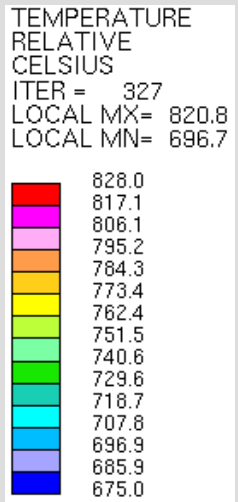


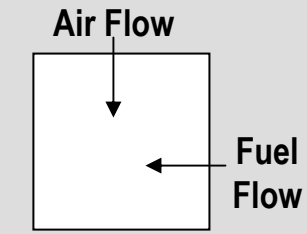


A quick inspection of the plots at left show the relationship of fuel utilization and fuel flow rate as well as how to best attain large current density and manageable delta-T on the cell depending on the inflow temperature - all at cell temperature 750C.

Activity 1: (continued)
Cell Temperature Distributions







Cell Flow Configuration

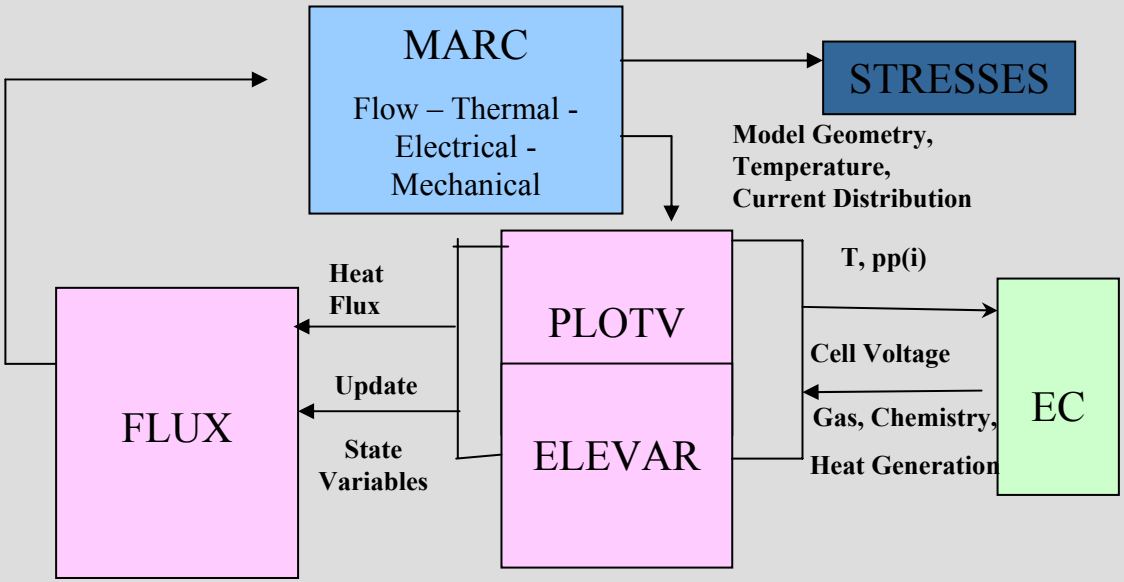
ABOVE: Results include the distribution of temperature on the cell area (and the surrounding stack structure) for prediction of thermally induced stress.

Distributions of other variables are also available for plotting and analysis.

Activity 2:Motivations for EC in FEA Framework

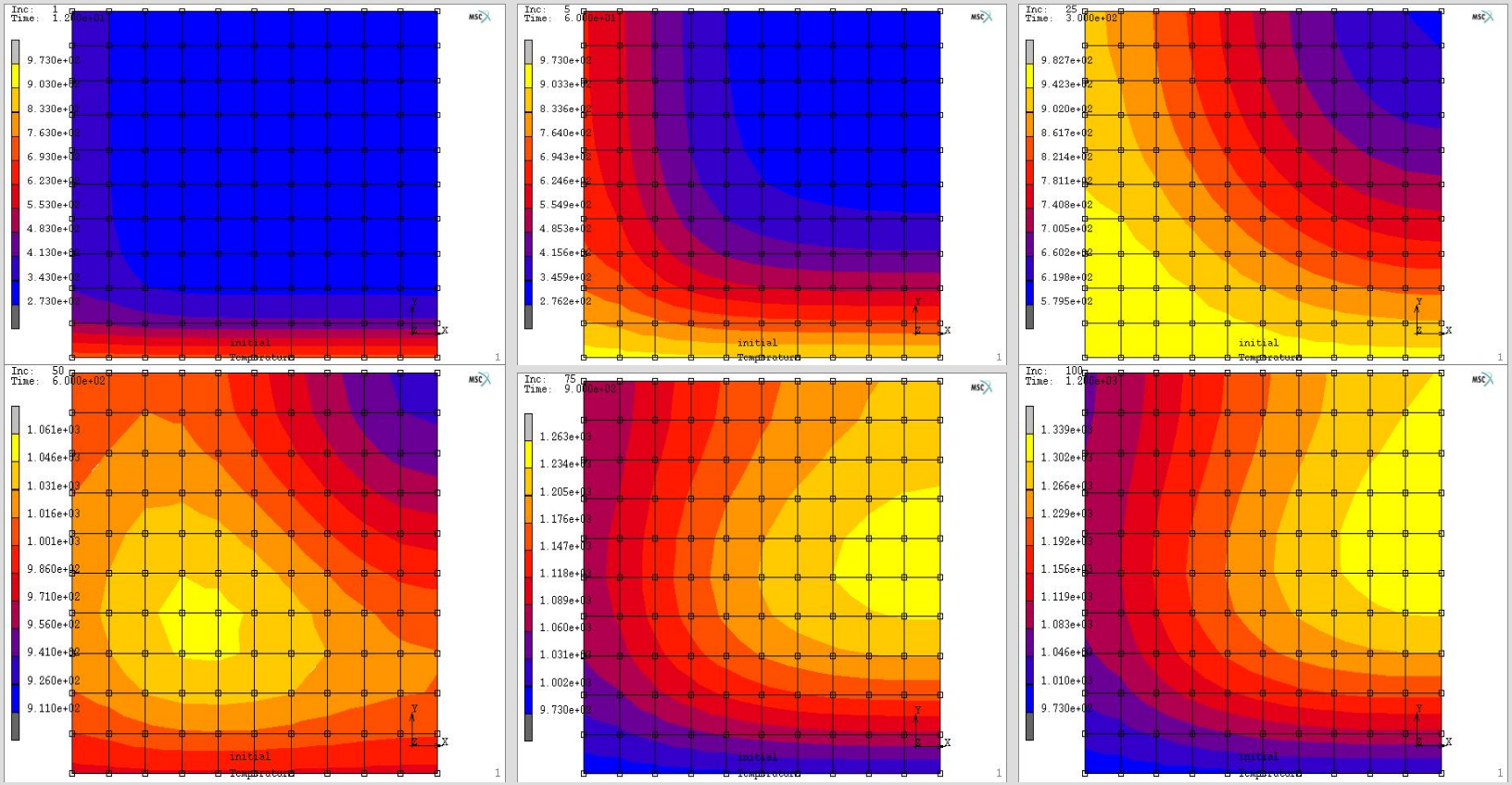
- Fuel cell operations involve multi-physics processes; the constitutive thermal, chemical, electrochemical and transport processes are strongly coupled => requiring versatile multi-physics tool for realistic description
- Technology development involves design optimization of various geometric, material and operation parameters; the cost of such parametric studies increases exponentially with the number of the working parameters and there are many such parameters involved

=> Computational efficiency is critically important



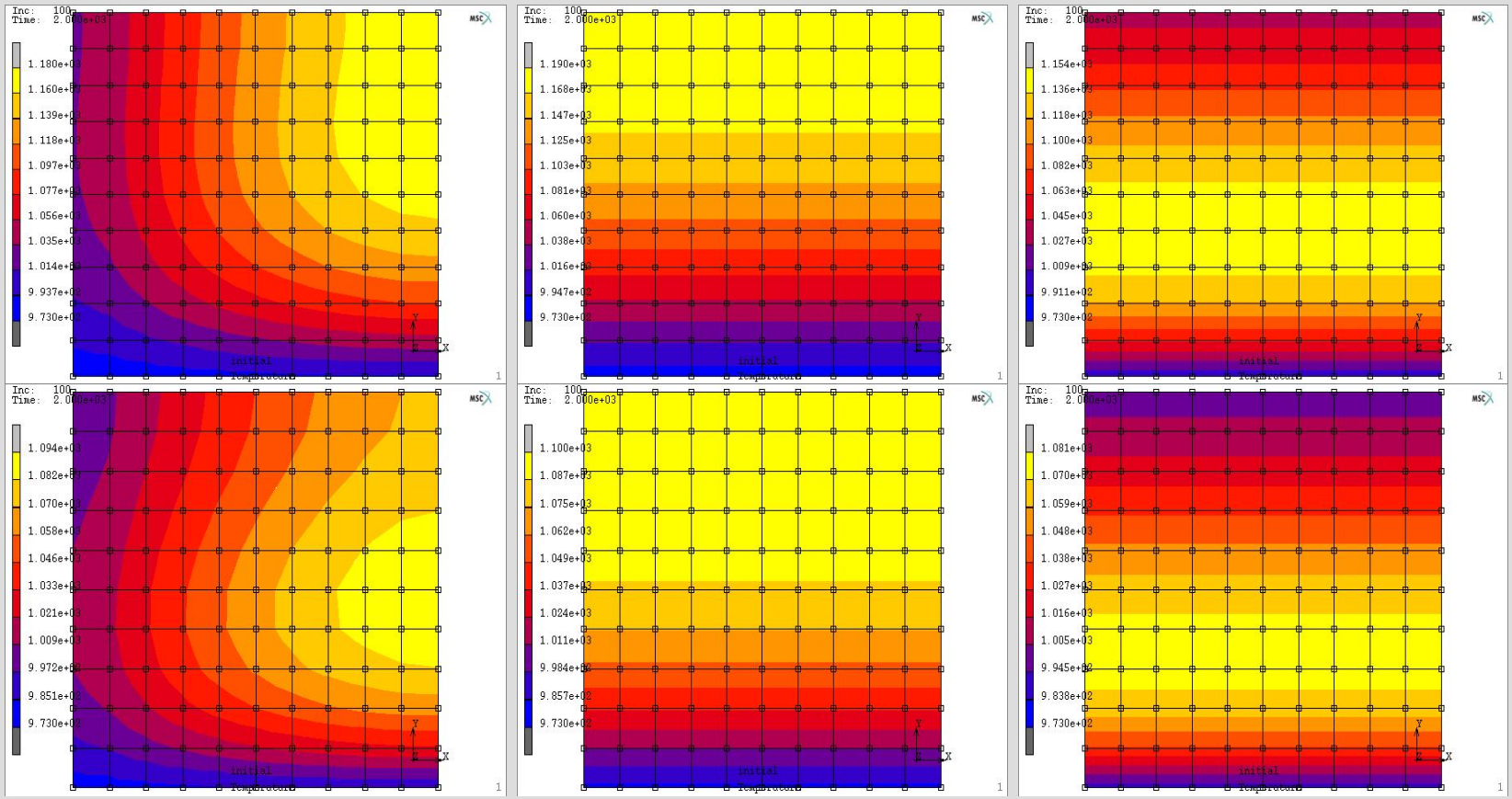
Sample results: Snapshot for startup to steady state transition

- T_0=0C, $T_{air/fuel}$=700C, V_{air}=0.33l/s, V_{fuel}=0.0825l/s, V=0.7Volt
- t: a)12s; b)60s; c)300s; d)600s; e)900s; f)1200s
- Transient results almost identical for time steps from 0.2s to 12s



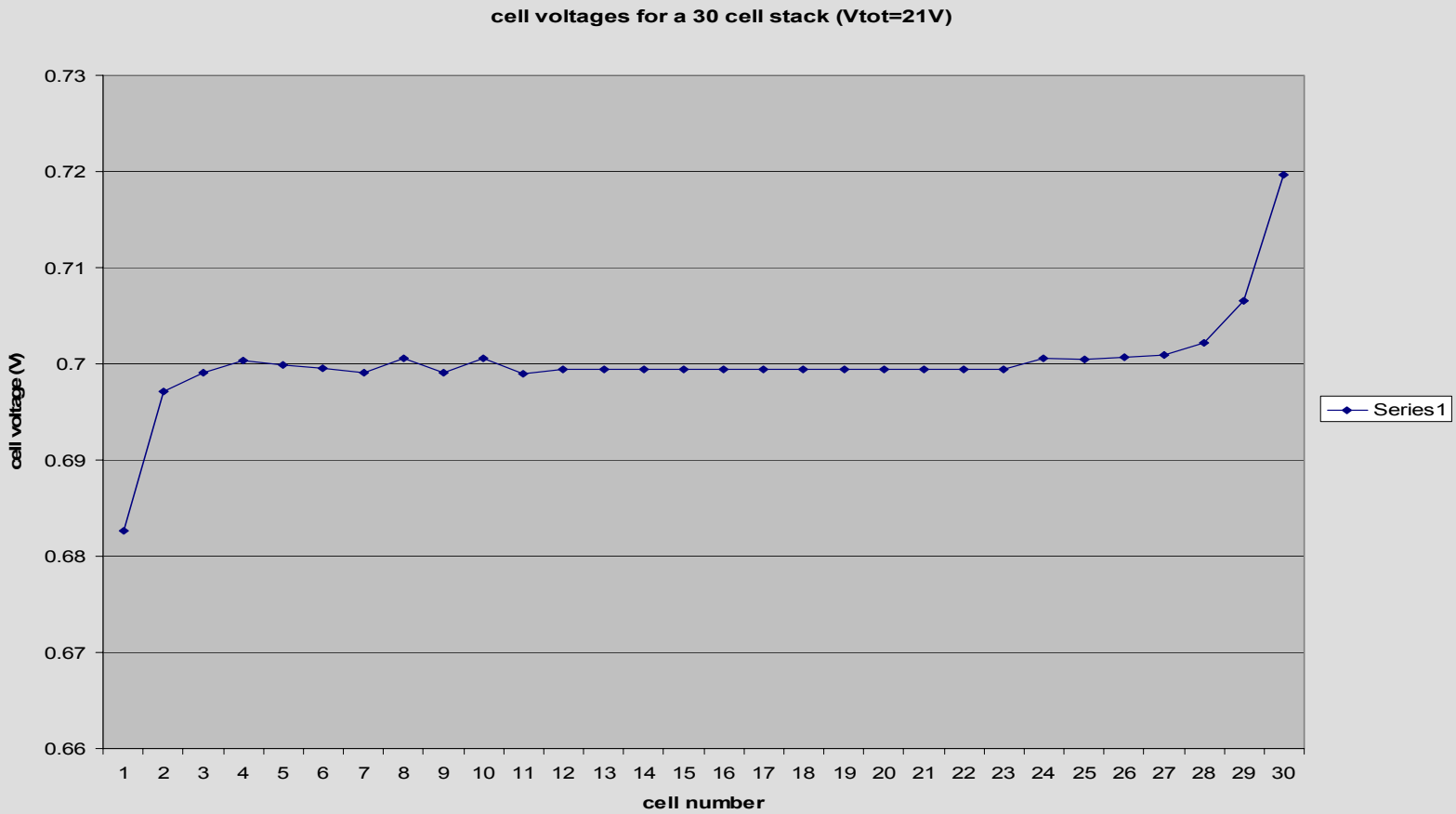
Comparison of different flow design

- Temperature profile for cross-, co-, counter-flow
- H_2+CO fuel; V_{fuel}=0.055 & 0.0275l/s, respectively.



Sample Results for Multi-cell Stacks

- Cell voltage variation for a 30-cell stack (V_{tot}=21V)
- Only the outmost top and bottom 2-3 cells deviate substantially from the average; similar results for 8- & 15- cell stacks



CPU time requirement

- Table 1, CPU time when specifying total current

# of cells	2	3	4	5	8	15	30
Time/inc(s)	0.45	0.68	0.91	1.15	1.83	3.48	6.93

- Table 2, CPU time when specifying total voltage

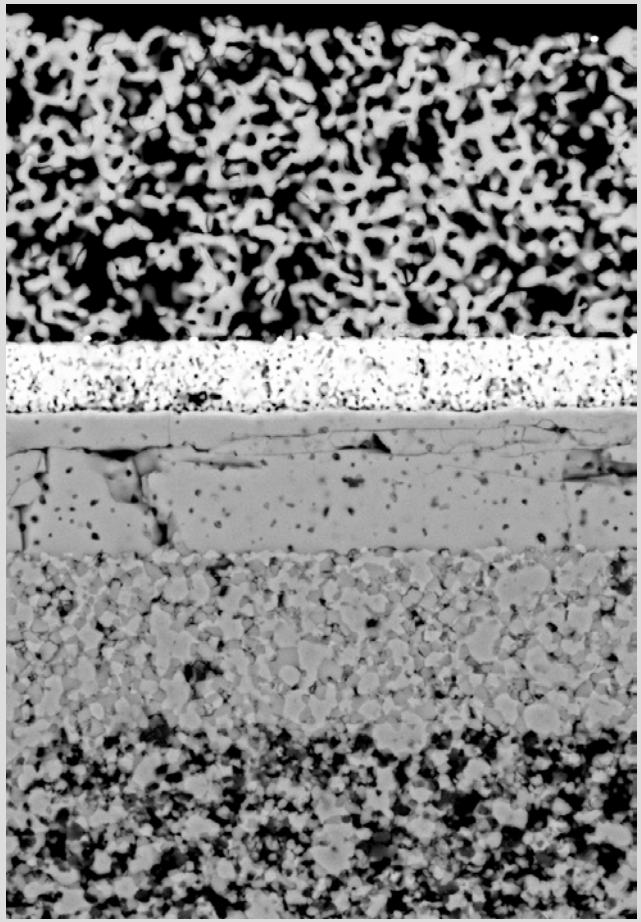
# of cells	2	3	4	5	8	15	30
Time/inc(s)	14.0	26.8	36.3	51.8	53.0	149	326

- CPU time increases roughly linearly with the number of cells in the stacks
- Typically 20-40 increments are needed for a steady state run

Micro Structural Analysis Activities

- **Activity 1**: Develop a one-dimensional single cell model with the following features:
  - Oxygen vacancy and electron transport through MIECs
  - Charge transfer kinetics
  - Surface adsorption, diffusion and reactions
- **Activity 2**: Predict cell performance under different operating conditions
- **Activity 3**: Create a three-dimensional microscopic model of cathode using digitized information from SEM images.

Single Cell Model (cont.)



LSF Cathode

30 µm (5x25µm; 25x0.2µm)

Sm-Doped Ceria

5µm (25x0.2µm)

YSZ (dense)

8µm (40x0.2µm)

Active anode
(50% Ni/50% YSZ)

10µm (25x0.2µm; 5x1µm)

Bulk anode
(40% Ni/60% YSZ)

500µm (50x10µm)

Single Cell Model (cont.)

- Predicted fields:
  - Gas concentrations (O_2, H_2, H_2O, CO, CO_2, CH_4)
  - Surface concentrations (O_2, H_2, H_2O)
  - Oxygen chemical potential (μ_O)
  - Electron electrochemical potential (η_e)
- Connection to Continuum Models
  - Results may be used to define parameters for continuum electrochemistry model.
  - This model may be extended to include flow in the air and fuel channels and arranged in a 2D matrix (e.g., 20x20) to form a three-dimensional cell model.

Single Cell Model (cont.)

- The purpose of this model is to predict cell performance based on material specific properties. Once the basic parameter set (surface specific kinetic rates, transport coefficients) have been established, the model will predict performance changes for
  - Change in electrolyte layer thicknesses
  - Change in cathode or anode microstructure
  - Change in electrode materials

Charge Transfer (Cathode)

- The oxygen exchange across the surface occurs through the reaction

$$\frac{1}{2}O_2 + V_{\ddot{O}} \xleftrightarrow{k_f, k_r} O_O^X + 2\dot{h}$$

- The forward and reverse reaction rates are given by ($E=E_{eq}+\eta$)

$$i_f = Fk_f \exp\left[\frac{\alpha F E_{eq}}{RT}\right] \exp\left[\frac{\alpha F \eta}{RT}\right] P_{O_2}^{\frac{1}{2}} c_v$$

$$i_r = Fk_r \exp\left[\frac{-(1-\alpha) F E_{eq}}{RT}\right] \exp\left[\frac{-(1-\alpha) F \eta}{RT}\right]$$

- Redefine in terms of a exchange current density, i_0 ($\eta=0$)

$$i_0 = Fk_f \exp\left[\frac{\alpha F E_{eq}}{RT}\right] P_{O_2}^{\frac{1}{2}} c_v = Fk_r \exp\left[\frac{-(1-\alpha) F E_{eq}}{RT}\right]$$

Charge Transfer (Cathode)

- The net reaction rate then becomes

$$i_{net} = i_f + i_r = i_0 \left[\exp\left(\frac{\alpha F \eta}{RT}\right) - \exp\left(\frac{-(1-\alpha) F \eta}{RT}\right) \right]$$

which is the same form as the global Butler-Volmer expression, but there are separate expressions for the cathode and anode which are defined in terms of local kinetic coefficients and concentrations.

Gas Diffusion

- Diffusion of gas species through porous media is given by

$$q = -D_{eff} \nabla c = -\frac{\varepsilon}{\tau} D \nabla c$$

where ε is the porosity and τ is the tortuosity.

- For small pores (diameter d) or low pressure, the Knudsen diffusion is given by

$$D_K = \frac{d}{3}\left[\frac{8RT}{\pi M}\right]^{\frac{1}{2}}$$

- The transition between molecular and Knudsen diffusion is given by

$$D = \frac{1}{(1/D_M + 1/D_K)}$$

Electrolyte and MIEC Transport

- The electrochemical potential for a given species is

$$\mu = \mu_0 + RT \ln c + nF\phi$$

where μ_0 is the reference potential, and ϕ is the electrical potential

- The oxygen ion and electron fluxes are given by the expressions

$$J_{O_2} = -\frac{\sigma_{o_2}}{F^2} \nabla \mu_{O_2}; \quad J_e = -\frac{\sigma_e}{F^2} \nabla \mu_e$$

where σ_{O2} and σ_e are the ion and electron conductivities.

Electrolyte Transport (cont.)

- The electron (or hole) conductivity has the form

$$\sigma_e = \sigma_{e0} P_{O_2}^{-\frac{1}{4}}; \quad \sigma_h = \sigma_{h0} P_{O_2}^{\frac{1}{4}};$$

where P_{O2} is the equivalent partial pressure corresponding to the local oxygen electrochemical potential.

- At lower temperatures, the oxygen ion conductivity is expressed in the form

$$\sigma_O T = A \exp\left(-\frac{E_a}{kT}\right)$$

Anode Model

- The active triple phase boundary concentration (length/volume) is expressed as a function of location. Active means that the nickel, YSZ and gas regions are contiguous.
- The active YSZ volume available for oxygen ion conduction is expressed as a function of location.
- Macroscopic surface diffusion is calculated based on the surface area per unit volume and the surface tortuosity.
- The surface reaction site concentration (sites/unit area) is required for surface reactions.

Anode Reactions

- The reaction set on the anode side is

$$O_{YSZ} + V_{ad} \leftrightarrow O_{ad} \quad (1)$$

$$H_2(g) + 2V_{ad} \leftrightarrow 2H_{ad} \quad (2)$$

$$H_2O_{ad} \leftrightarrow H_2O(g) + V_{ad} \quad (3)$$

$$2H_{ad} + O_{ad} \xleftrightarrow{k_f, k_r} H_2O_{ad} + 2V_{ad} \quad (4)$$

- We assume that water formation (Eq. 4) is the rate limiting step. This reaction is used to create a Bulter-Volmer expression similar to that used for the cathode.

- The other three reactions are treated as Langmuir adsorption

Langmuir Adsorption

- The rates of adsorption and desorption are given by the expressions

$$R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi mkT}} \exp\left(-\frac{E_a^{ads}}{RT}\right) = C_{ads} P f(\theta) \exp\left(-\frac{E_a^{ads}}{RT}\right)$$

$$R_{des} = C_{des} g(\theta) \exp\left(-\frac{E_a^{des}}{RT}\right)$$

- The function dependence on surface coverage depends on the type of reaction. For simple adsorption/desorption, as in the case of water, the functions f and g have the form

$$f(\theta) = 1 - \theta; \quad g(\theta) = \theta$$

and for dissociative adsorption of a homonuclear diatomic molecule, such as oxygen or hydrogen

$$f(\theta) = (1-\theta)^2; \quad g(\theta) = \theta^2$$

Langmuir Adsorption (cont.)

- The net rate of adsorption is given by the expression

$$\frac{ds}{dt} = R_{ads} - R_{des} = C_{ads} P f(\theta) \exp\left(-\frac{E_a^{ads}}{RT}\right) - C_{des} g(\theta) \exp\left(-\frac{E_a^{des}}{RT}\right)$$

- The surface coverage at equilibrium for simple adsorption and dissociative adsorption

$$\theta = \frac{bP}{1+bP}; \qquad \theta = \frac{\sqrt{bP}}{1+\sqrt{bP}}$$

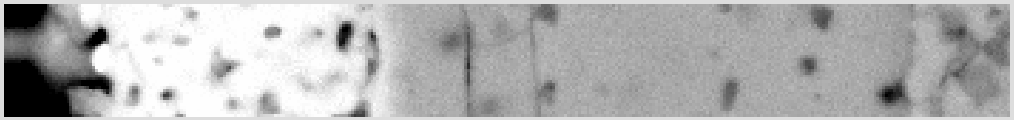
where

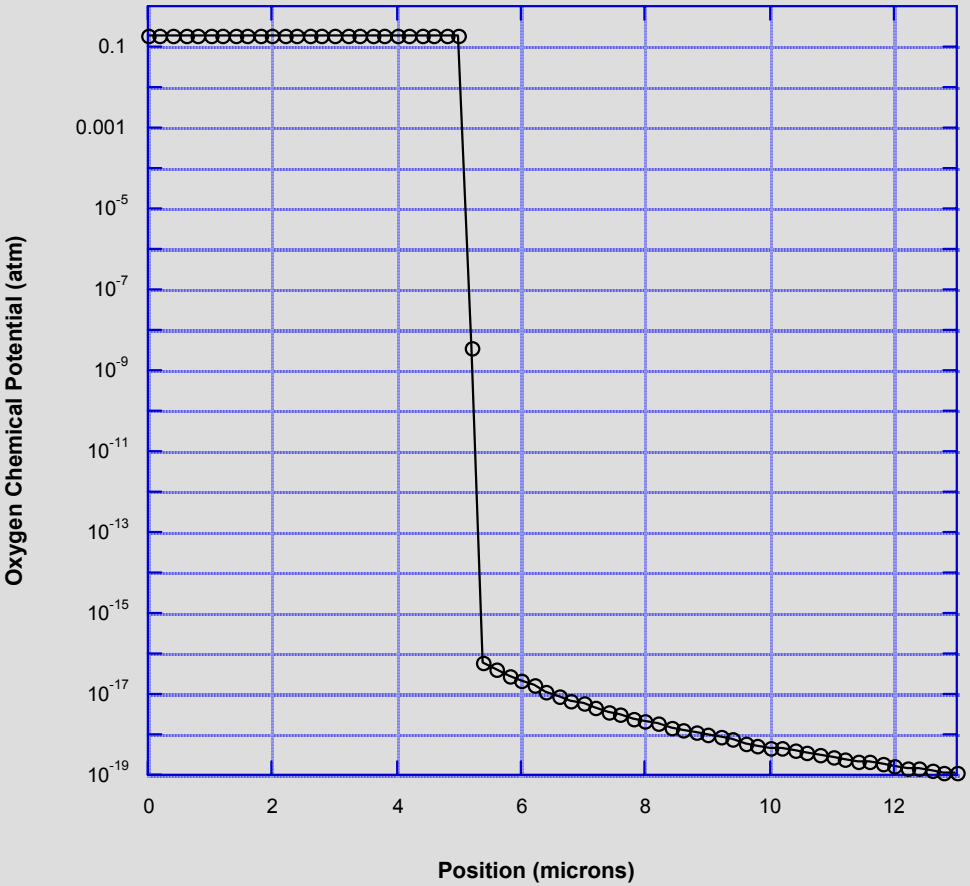
$$b = \frac{c_{ads}}{c_{des}} \exp\left(-\frac{\Delta E}{RT}\right)$$

Model Status

- Using test data to define parameters for charge transfer and adsorption reactions
- Testing regions of the model, such as oxygen transport through composite electrolyte
- Operating Conditions
  - Temperature - 800 C
  - Current - 0.5 A/cm^2
  - Fuel Composition - 97% H_2, 3% H_2O

Composite Electrolyte Behavior



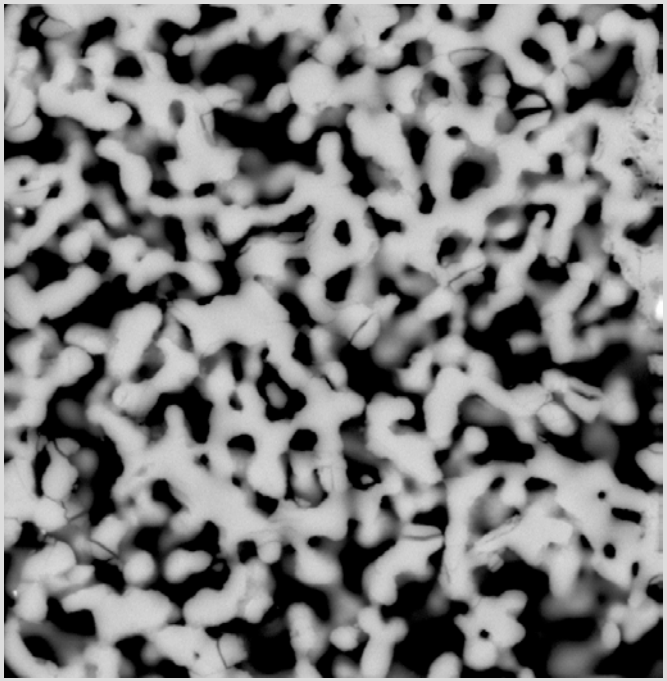


Microstructure Geometry Reconstruction

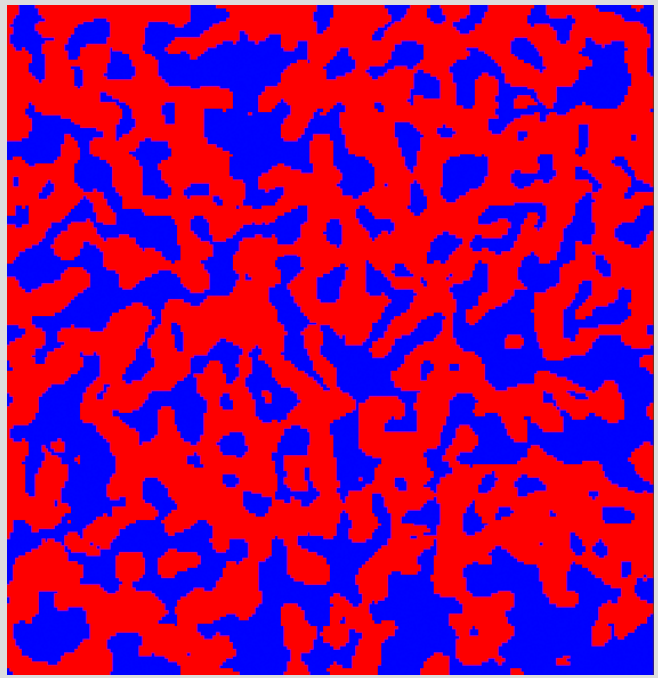
- Digitize a representative portion of a photographic image of the electrode to obtain an array of grayscale values for each pixel
- Developed computer program to convert to a two-dimensional solid map (filter to remove artifacts)
- Collect statistics such as autocorrelation function (variogram) and solid chord length distribution
- Construct a three-dimensional geometry through a stochastic computational method which matches the statistical information taken from the two-dimensional image

Cathode SEM Image

SEM image



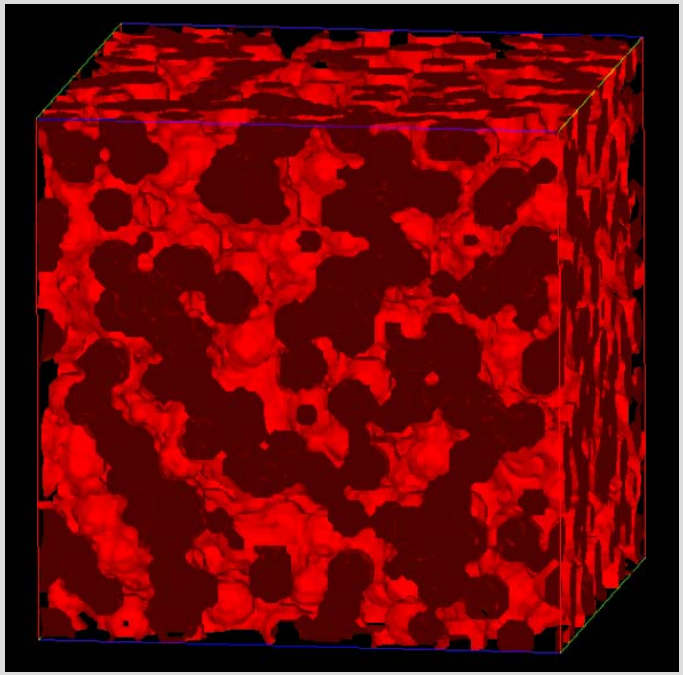
Digitized image



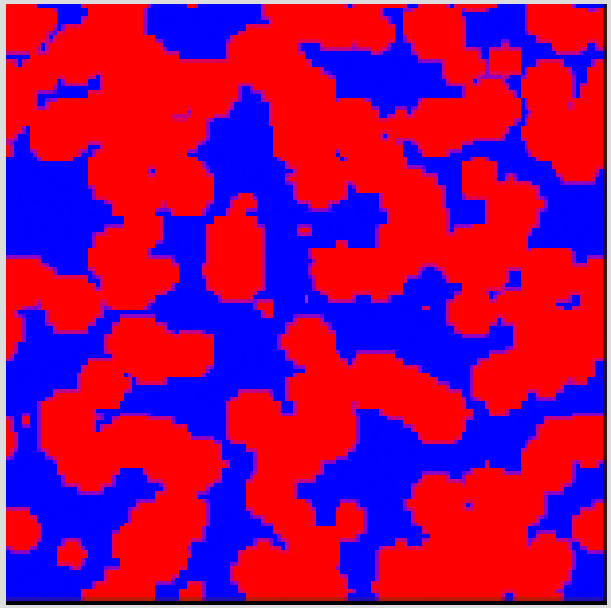
Reconstructed Cathode Material

- A $(100)^3$ node model was constructed to represent a $(15\ \mu m)^3$ section of cathode material based on the variogram and chord length distributions

Model Geometry



2-D Slice



Model Applications

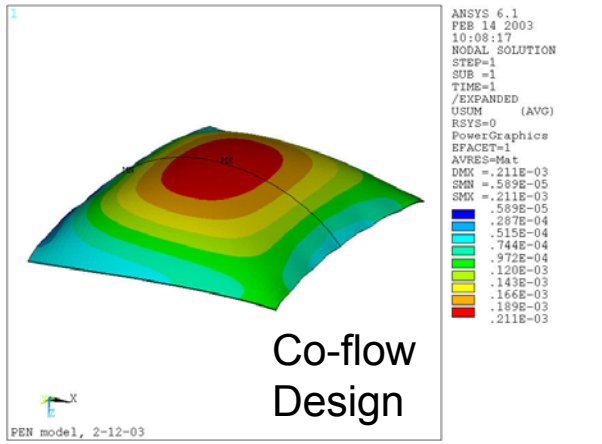
- Detailed three-dimensional transport simulations are performed to determine effective properties
- The single component geometry model will be used to determine
  - Effective gas diffusion parameters (tortuosity)
  - Effective surface diffusion parameters
  - Effective electrical and ionic conductivities
- A multicomponent anode model (with Ni and YSZ solids as well as gas phase) may be used to determine the active TPB distribution as a function of position

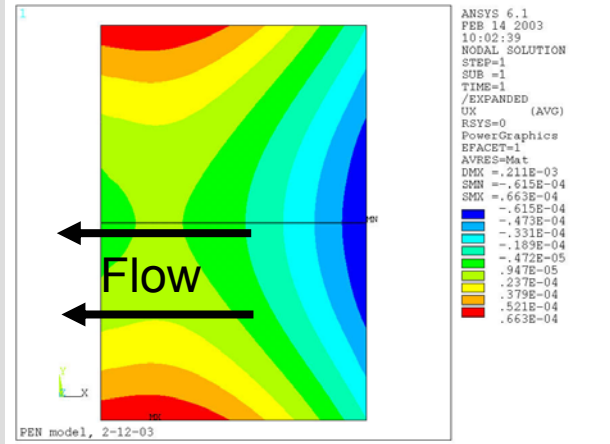
Thermal-Mechanical Modeling Objectives

- Improved constitutive relations for cell/seal materials
  - Include effects of reduction, creep, defects, thermal cycling
- Predict stresses/deformations at seal interfaces
  - Glass and mica seals
  - Leak rate estimate
  - Parametric analysis
- Improved FEA models
  - Thermal cycling
  - Residual fabrication stresses
- Catalog defects in cell materials
  - Predict crack growth
  - Reliability analysis

Thermal-Mechanical Modeling Example Reliability Analysis

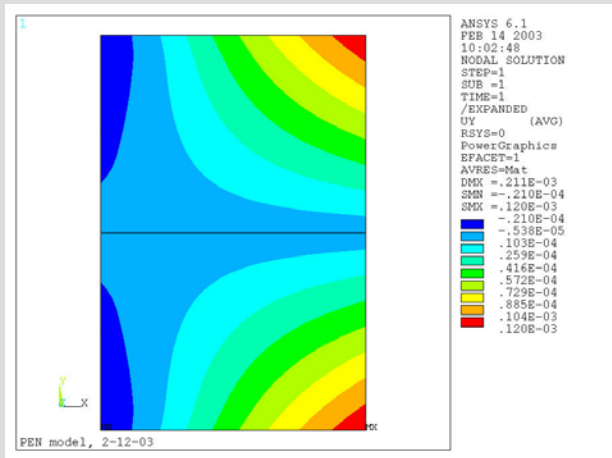
PEN Deformation

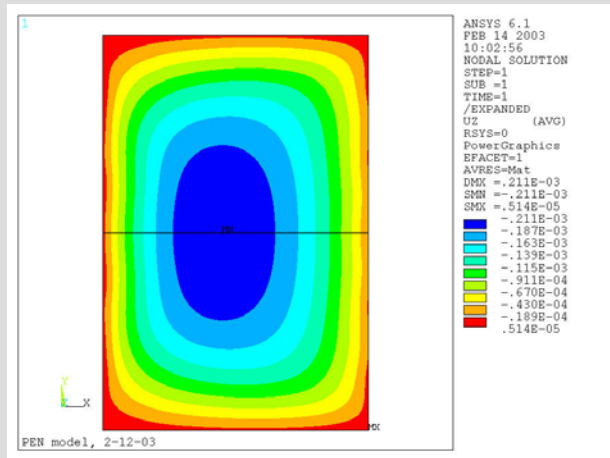




In-plane Displacement Parallel to flow (UX)

In-plane Displacement Perpendicular to Flow (UY)

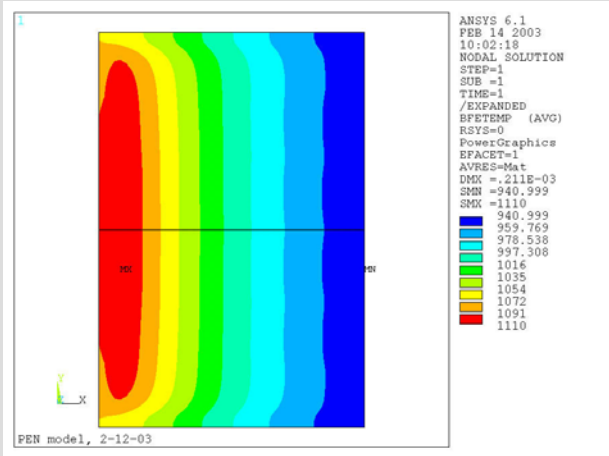


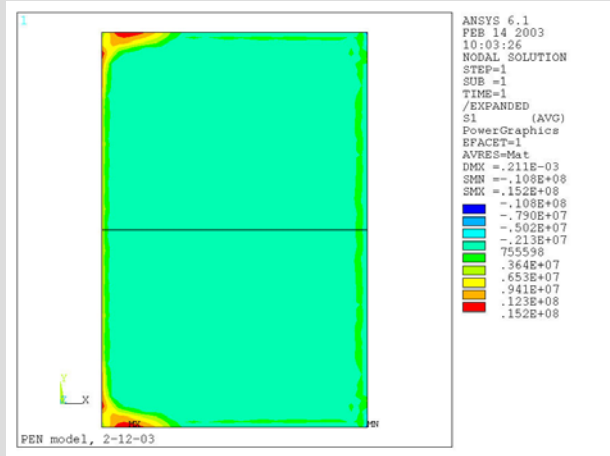


Out-of-plane Displacement (UZ)

Thermal-Mechanical Modeling Example Reliability Analysis

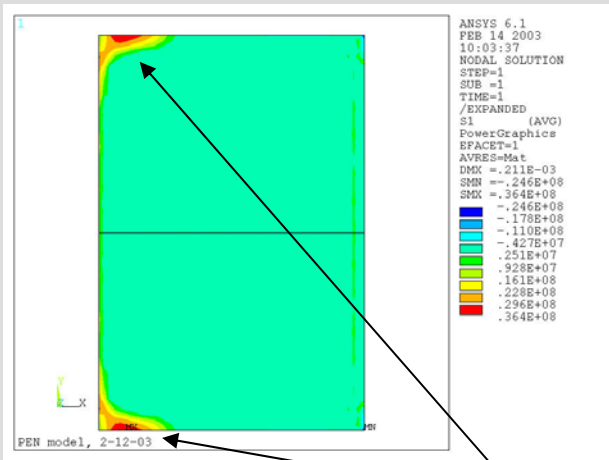
Temperature Distribution

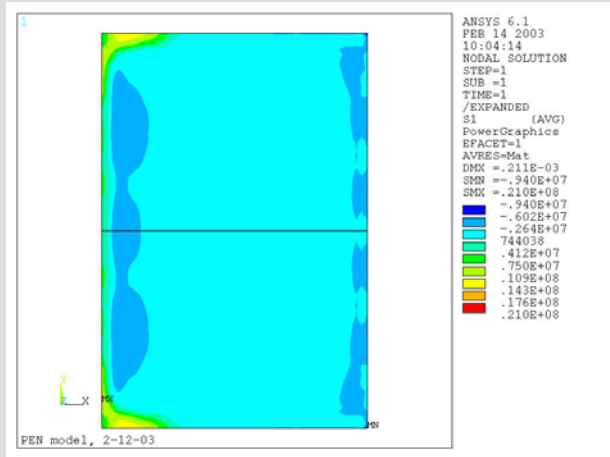




Principal Stress (S1) Cathode

Principal Stress (S1) Electrolyte



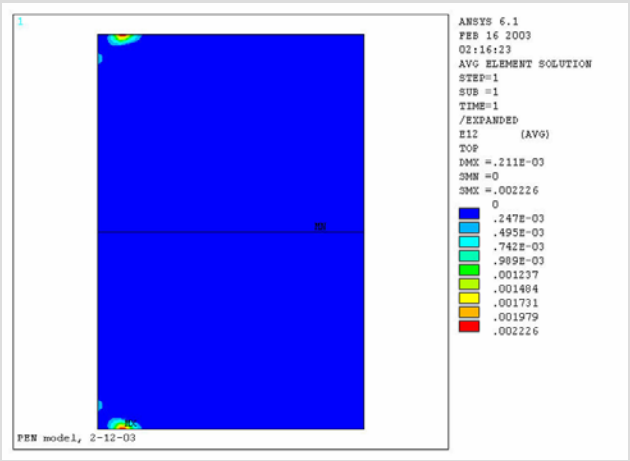


Principal Stress (S1) Anode

High Stresses at Edges (36 MPa)

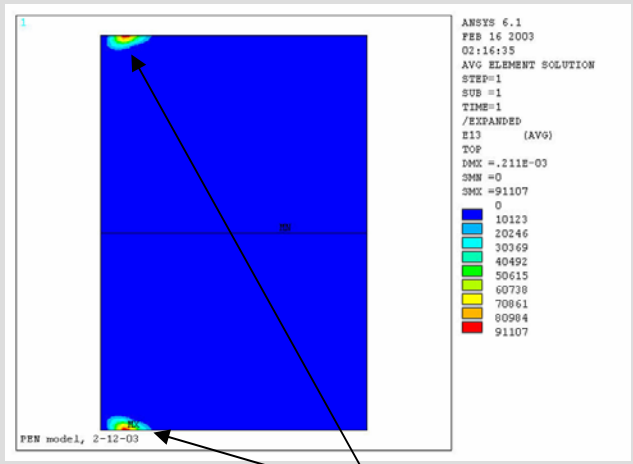
Thermal-Mechanical Modeling Example Reliability Analysis

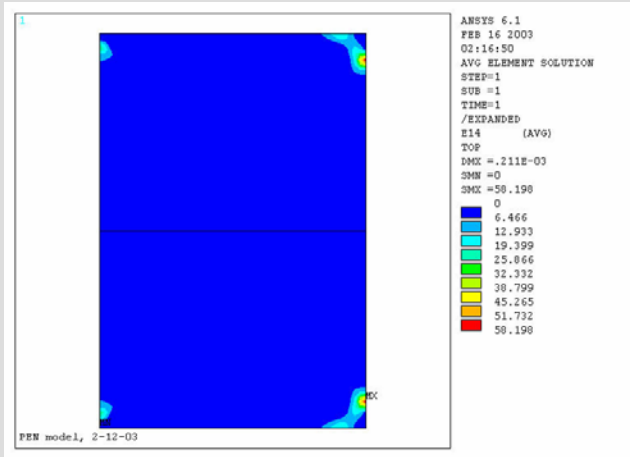
- Risk of rupture intensity for PEN at steady-state operating conditions
- 2.1% failure probability due to fast-fracture



Cathode

Electrolyte





Anode

High on edge as expected

Plans for Remainder of FY03 Continuum Electrochemistry

- Software transfer and SECA vertical team training
- Temperature Control of Multiple Cell Stacks Running on Multiple Processors.
- Expand Simulation Capability of STAR-CD multiple-cell stack model to include current leakage from a selected cell within the stack to enable prediction of effect of one (or more) faulty cells on the overall stack performance.
- Implement additional, local electrical resistance related to life expectancy of the cell/stack (provide hook to MARC for resistance term which is yet to be defined).

Planned Activities for FY03 Micro Structural Electrochemistry

- Software transfer and SECA vertical team training
- Three-dimensional Electrode Models
  - Determine effective properties using reconstructed geometry
  - Continue to improve reconstruction process
- One-dimensional Cell Model
  - Determine charge transfer and adsorption reaction parameters based on comparison of performance data for different cell designs
  - Validate using experimental data
  - Predict cell performance for a variety of cell design changes

Plans for the Reminder of FY03 Thermal-Mechanical Modeling

- Examine ORNL experimental results on PEN materials after reduction
  - Catalog defects
  - Develop constitutive relations (as directed by test data)
- Identify material data required to model high temperature behavior of seals
  - Coordinate with thermal gradient/cyclic testing (PNNL Task 3 and others)
- Construct improved FEA model
  - Higher resolution in the seal interface regions
  - Capability to analyze thermal cycling
- Established methods and models for predicting leak rates in compressive or hybrid seals.
- Update reliability analysis with available test data.

Applicability to SOFC Commercialization

- Modeling tools developed by PNNL for design, optimization and operation of SOFC materials, stacks and systems.
- Engineering insights and guidance regarding SOFC materials, stacks and systems.