SECA Core Program – Recent Development of Modeling Activities at PNNL

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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

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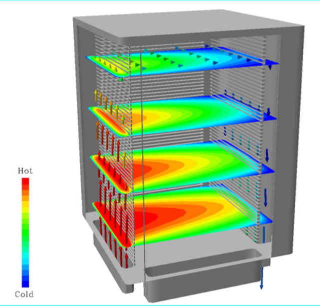
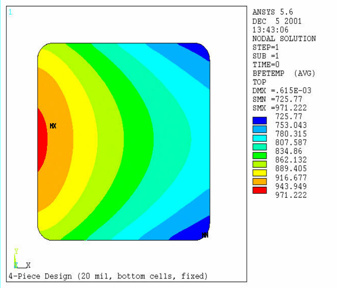
Technical Approach

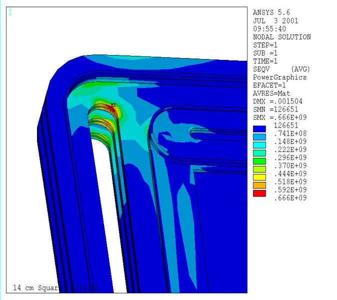
Flow Analysis



Thermal Analysis



Stress Analysis



Modeling levels

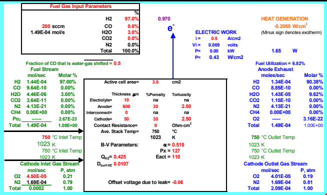
Electrical Power System

Thermal system

Stack

Cell

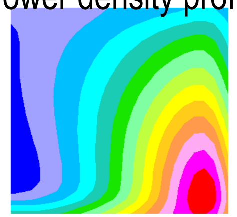
Tools and Methodologies for Rapid start-up



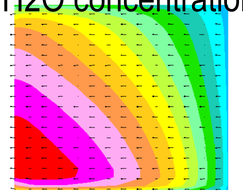
Excel System Model

Flow, thermal & Electrochemistry analysis

Power density profile

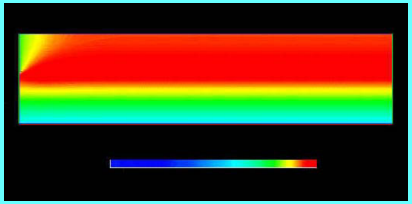


H2O concentration



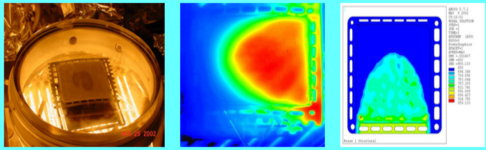
Continuum-level electrochemistry

Cell-level



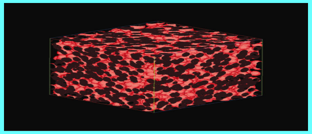
Methane distribution

Validation and Property measurement



Thermal Shock

Microstructure-level



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Cell Electrochemistry Performance Model

Input Parameters:
- Fuel composition and flow rate
- Temperature
- Adjustable cell parameters

Output Data:
- I-V curve and power
- Heat generation
- Fuel utilization and exhaust composition

Fuel Gas Input Parameters

		%
200 sccm	H2	97.0%
1.49E-04 mol/s	CO	0.0%
	H2O	3.0%
	CO2	0.0%
	N2	0.0%
	Total	100.0%

0.970

e^-

Fraction of CO that is water-gas shifted = 0.5

Fuel Stream

	mol/sec	Molar %
H2	1.44E-04	97.00%
CO	9.64E-10	0.00%
H2O	4.46E-06	3.00%
CO2	3.64E-11	0.00%
N2	4.13E-21	0.00%
CH4	0.00E+00	0.00%
Po_2	------	2.67E-23
Total	1.49E-04	1.00E+00

750 °C Inlet Temp
1023 K
750 °C Inlet Temp
1023 K

Cathode Inlet Gas Stream

	mol/sec	P, atm
O2	4.50E-05	0.21
N2	1.69E-04	0.79
Total	0.0002	1.00

Active cell area= 3.8 cm2

	Thickness ,µm	%Porosity	Tortuosity
Electrolyte=	10	na	na
Anode=	600	30	2.50
Interconnect=	0	na	na
Cathode=	50	30	2.50

Contact Resistance= 0 Ohm-cm^2

Ave. Stack Temp= 750 °C
1023 K

B-V Parameters: α = 0.518
Px = 127
Q_{H2}= 0.425 Eact = 110
$D_{surf\text{-}H2}$ 0.0107

Offset voltage due to leak= -0.06

ELECTRIC WORK

i =	0.5	A/cm2
Vi =	0.869	volts
P=	0.00	kW
P=	0.43	W/cm2

1.65 W

HEAT GENERATION
-0.2088 W/cm^2
(Minus sign denotes exotherm)

Fuel Utilization = 6.82%

Anode Exhaust

	moles/sec	Molar %
H2	1.34E-04	90.38%
CO	8.85E-10	0.00%
H2O	1.43E-05	9.62%
CO2	1.15E-10	0.00%
N2	4.13E-21	0.00%
CH4	0.00E+00	0.00%
O2	-----	3.16E-22
Total	1.49E-04	1.00E+00

750 °C Outlet Temp
1023 K
750 °C Outlet Temp
1023 K

Cathode Outlet Gas Stream

	mol/sec	P, atm
O2	4.01E-05	0.19
N2	1.69E-04	0.81
Total	2.09E-04	1.00

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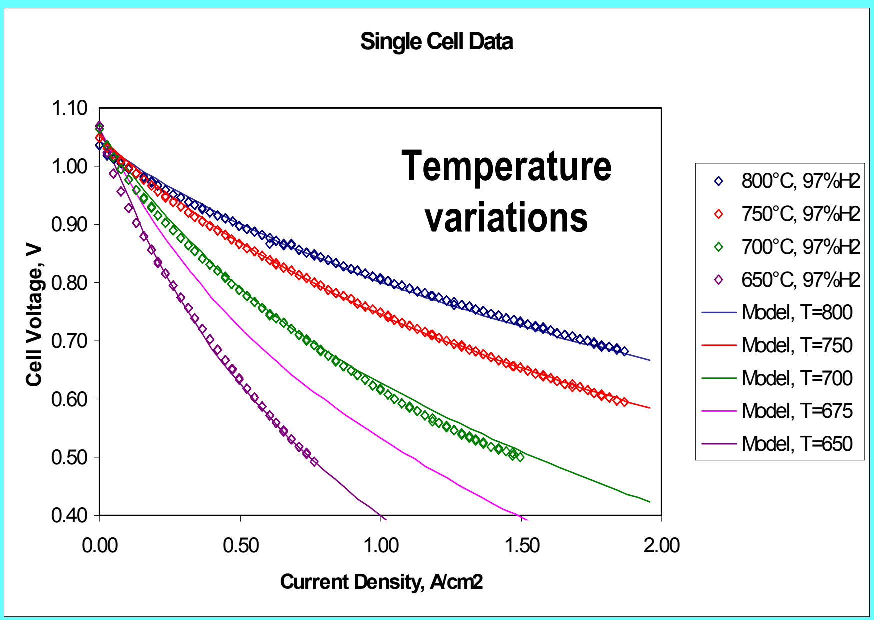
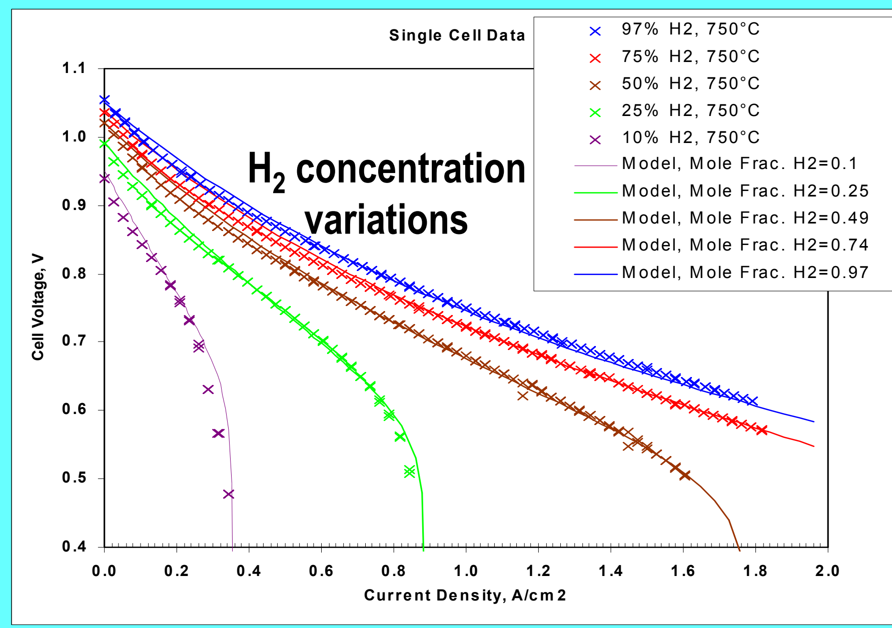
Model Output

•Cell parameters can be adjusted so that one set of cell parameters provide excellent fit of a family of IV curves for a “unit” cell operated over a range of temperatures and a range of hydrogen concentrations.

• The “calibrated” model can then be used to predict large stack performance by applying it within a CFD code to computational unit cells.





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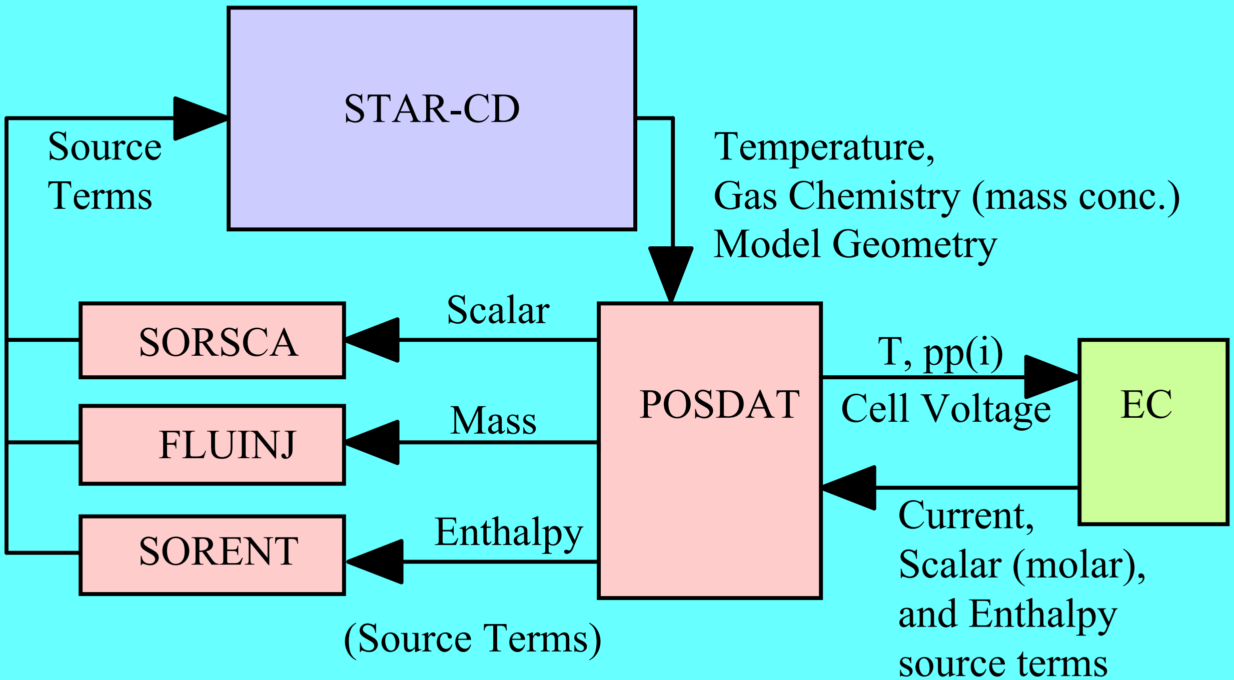
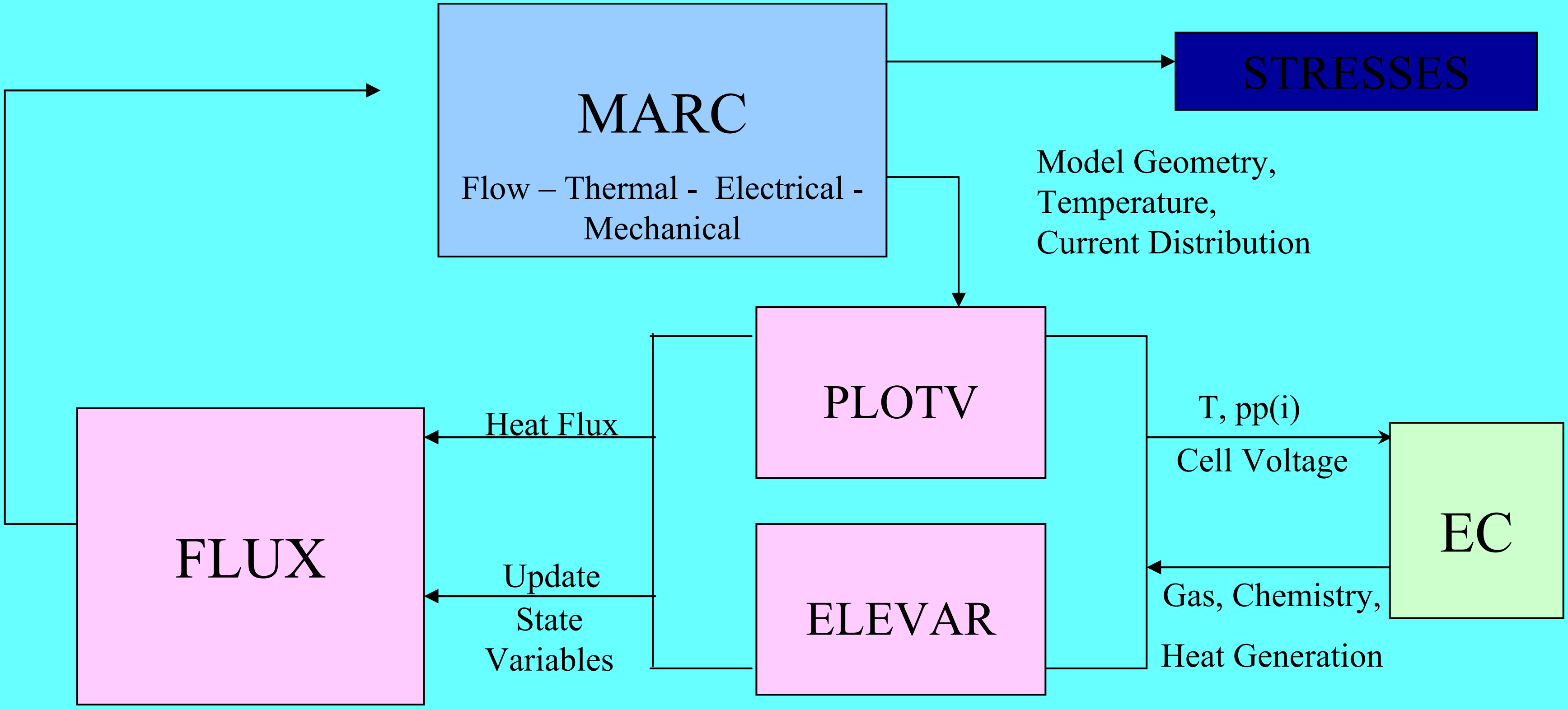
Topics for Continuum Electrochemistry Modeling

- Calculation Flow Diagram For 1-Cell Stack
- Generic Cross-Flow Case
- Alternate Flow Configurations
- Transition from Transient Heating to Steady State
- Calculation Flow Diagram For Multiple-Cell Stacks
- Multiple Cell Stack Modeling Results

STAR-CD/EC (1-Cell Stack) Flow Diagram



MARC/EC (1-Cell Stack) Flow Diagram



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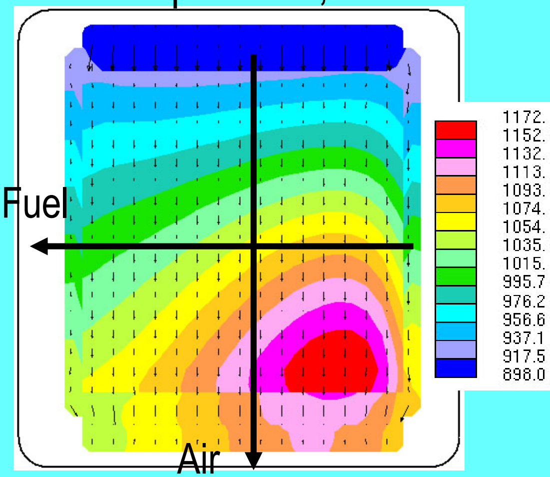
Cross-Flow Case: Conditions

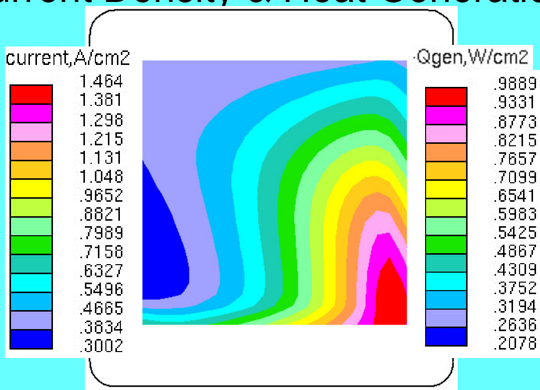
- Inflow Air & Fuel Temperature = 625°C
- Air delivery rate = 15 gm/sec/60cells
- Fuel delivery rate = 1.08 gm/sec/60cells (9.5×10^{-4} moles/sec)
  - Composition: shifted to equilibrium at 625 °C
    - [H2] = 0.37443
    - [H2O] = 0.03449
    - [CO] = 0.33662
    - [CO2] = 0.06759
    - [N2] = 0.18687
- Cell Voltage = 0.7 (as in all other cases)
- Cyclic boundary conditions at top and bottom of unit cell.

Cross-Flow Case: Results

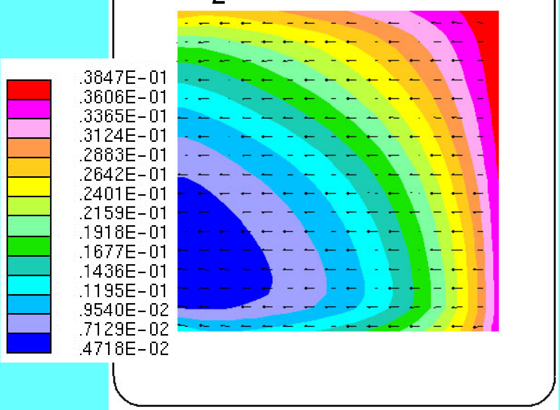
Air Temperature, Kelvin

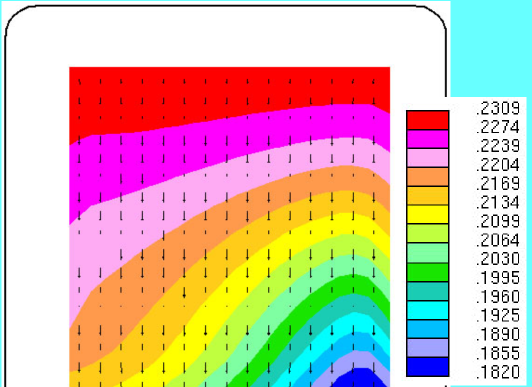


Current Density & Heat Generation



H_2, Mass Fraction





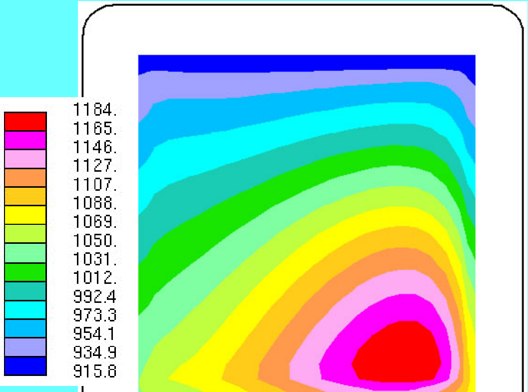
O_2, Mass Fraction

62% Fuel Utilization Case:

Current Density = 0.300-1.46 (0.687 A/cm2)
Heat Generation = 0.21 - 0.99 (0.477 W/cm2)
PEN Temperature = 643 - 912 (769 °C)

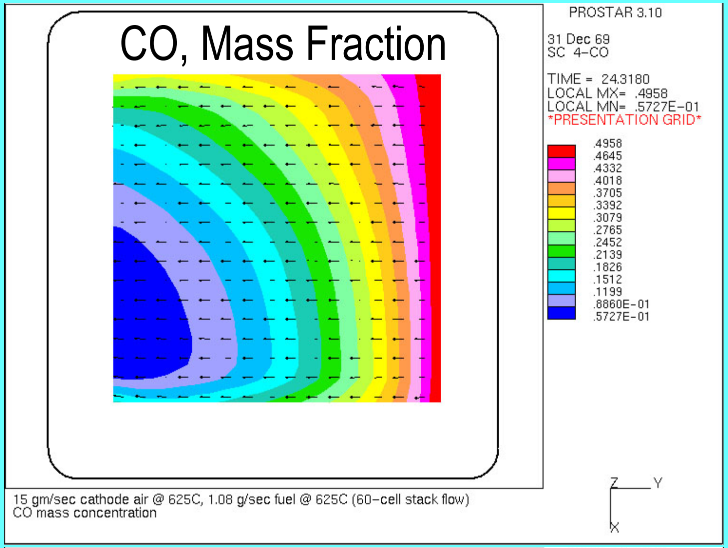
	in, moles/s	out, moles/s
h2	3.5480E-04	1.3963E-04
h2o	3.2680E-05	2.4776E-04
co	3.1898E-04	1.1871E-04
co2	6.4050E-05	2.6423E-04
n2	1.7706E-04	1.7704E-04
moles/s	9.4756E-04	9.4737E-04

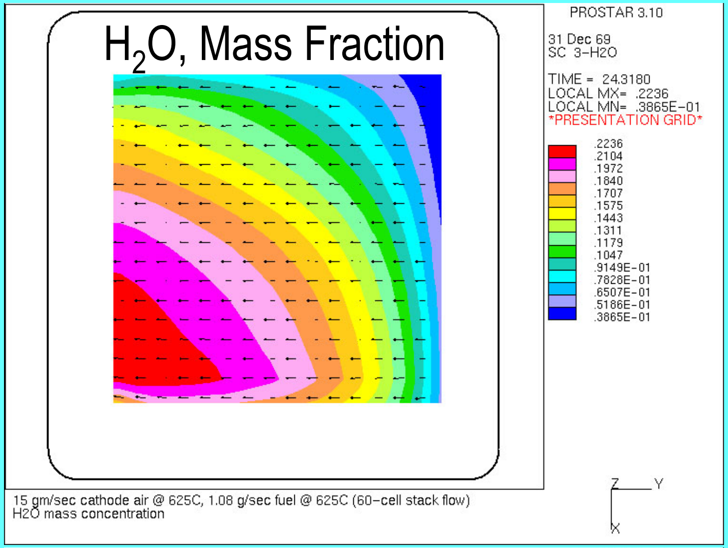
Fuel Utilization= 61.7%

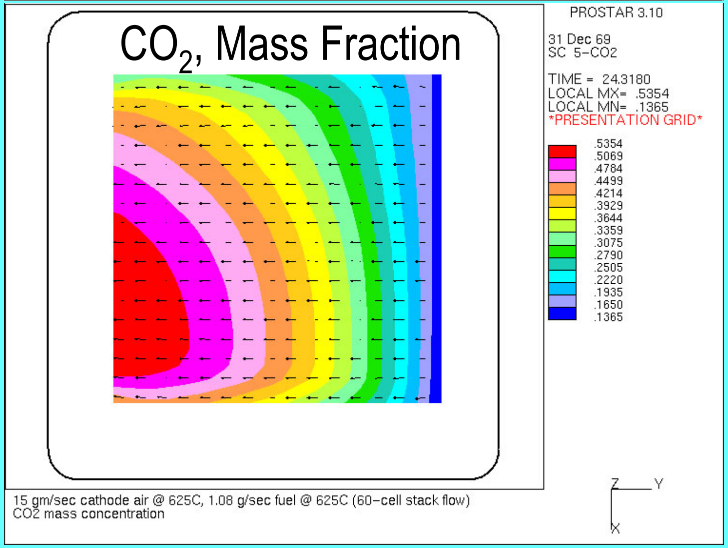


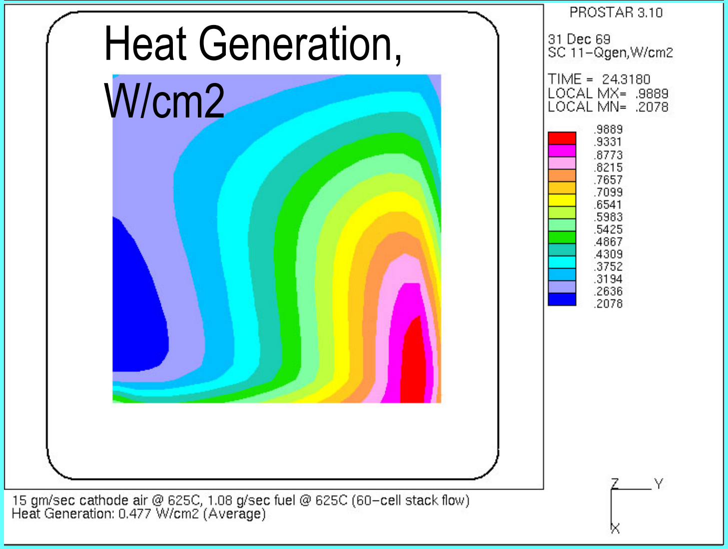
PEN Temperature, K

Cross-Flow Case: Results (Continued)









Alternate Flow Configurations – Steady State

Flow configuration	Conditions		Results			
	Air delivery, gm/s @ °C	Fuel delivery, gm/s @ °C	ΔT_{PEN}, °C	T_{PEN}, °C	I_{ave}, A/cm^2	Fuel Utilization
Cross-flow	0.25 @ 625	0.018 @ 625	269	769	0.69	62%
Co-flow	0.25 @ 625	0.018 @ 625	184	763	0.71	64%
Counter-flow	0.25 @ 595	0.018 @ 595	267	758	0.73	63%

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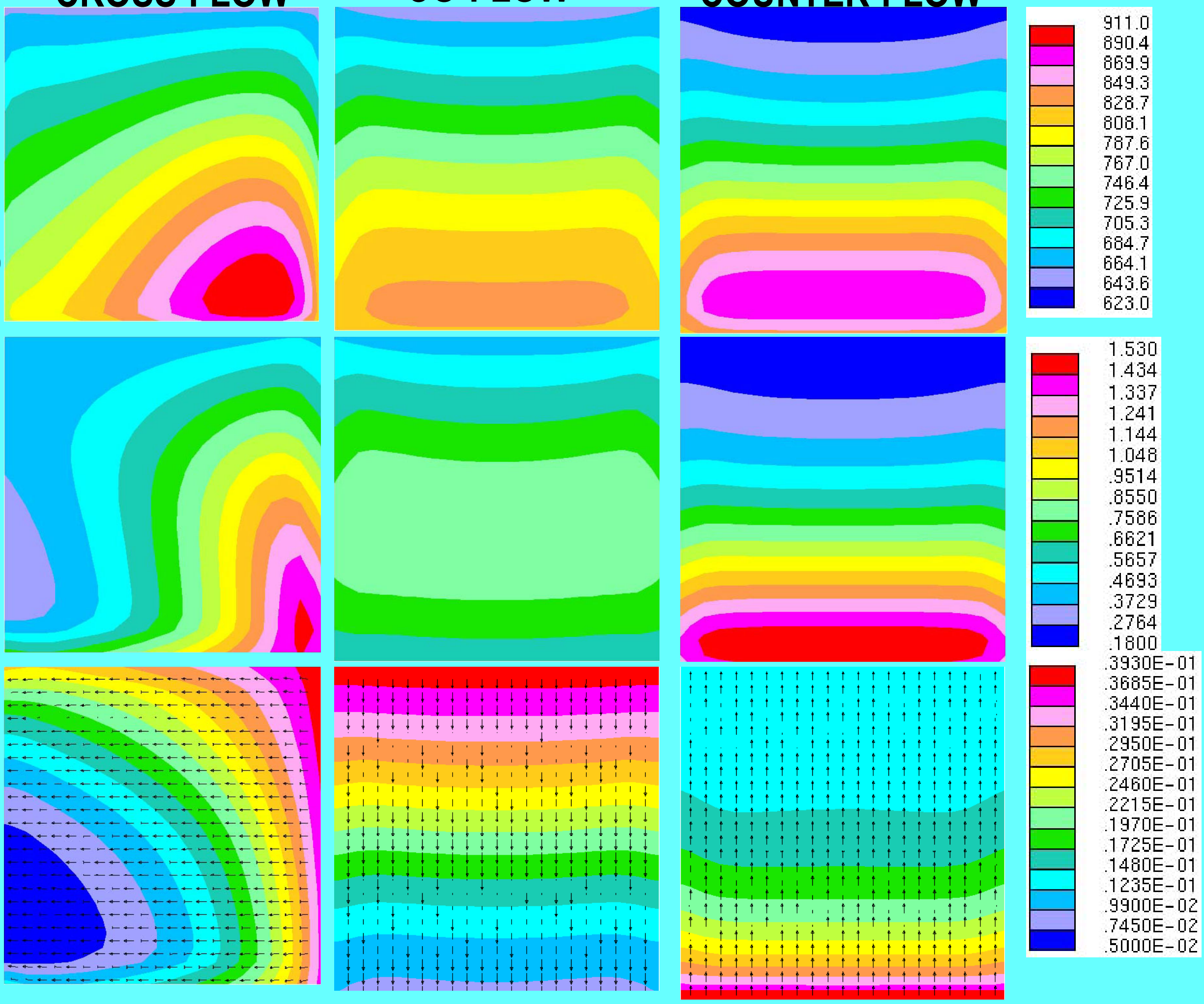
Alternate Flow Configurations – Steady State

CROSS-FLOW | CO-FLOW | COUNTER-FLOW | 04/09/02

Temperature, Degrees C (ΔT=180 co- ΔT=270 cross-)

Current Density, A/cm2

H2 Mass Conc., kg/kg



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Modeling of Transition from Transient to Steady State – Cross Flow Case

Start with Transient Temperatures (temperature range ~900-1075K)

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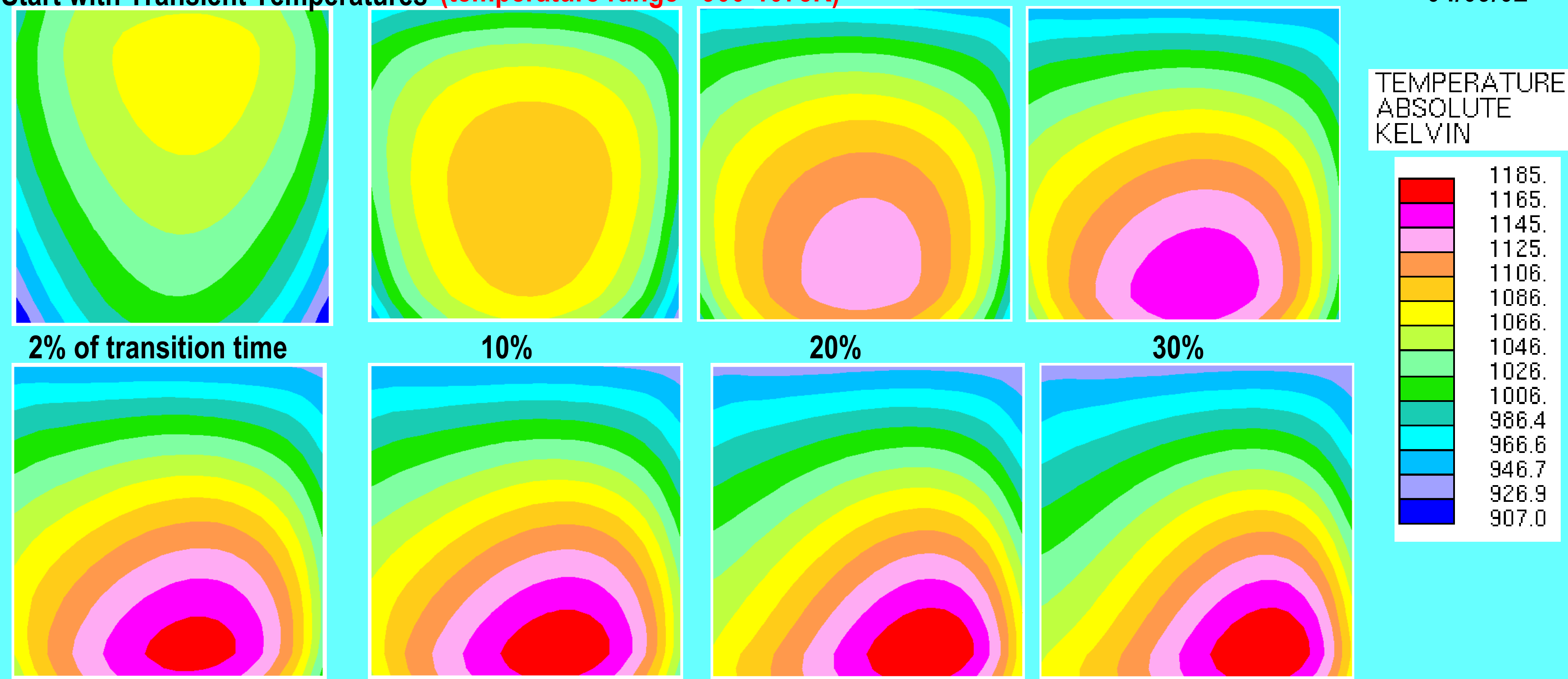

40% 50% 80% 100% Steady State Solution

(temperature range = 931-1185K)

- Is the heating method sound?
- Will start of reaction cause instabilities?
- Can we actually shorten the “startup” time?

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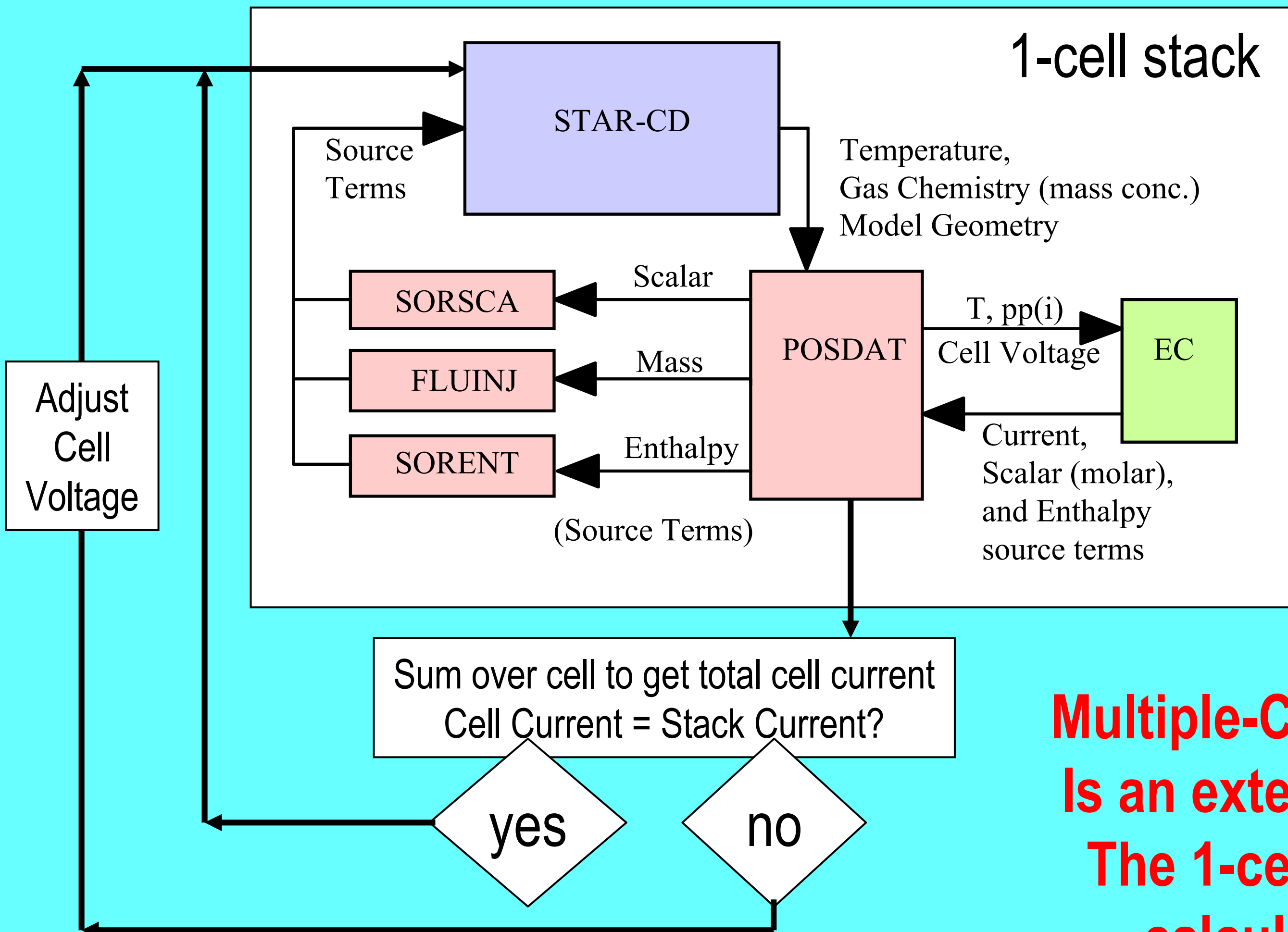
STAR-CD/EC (Multiple-Cell) Flow Diagram



Multiple-Cell Stack Is an extension of The 1-cell stack calculation

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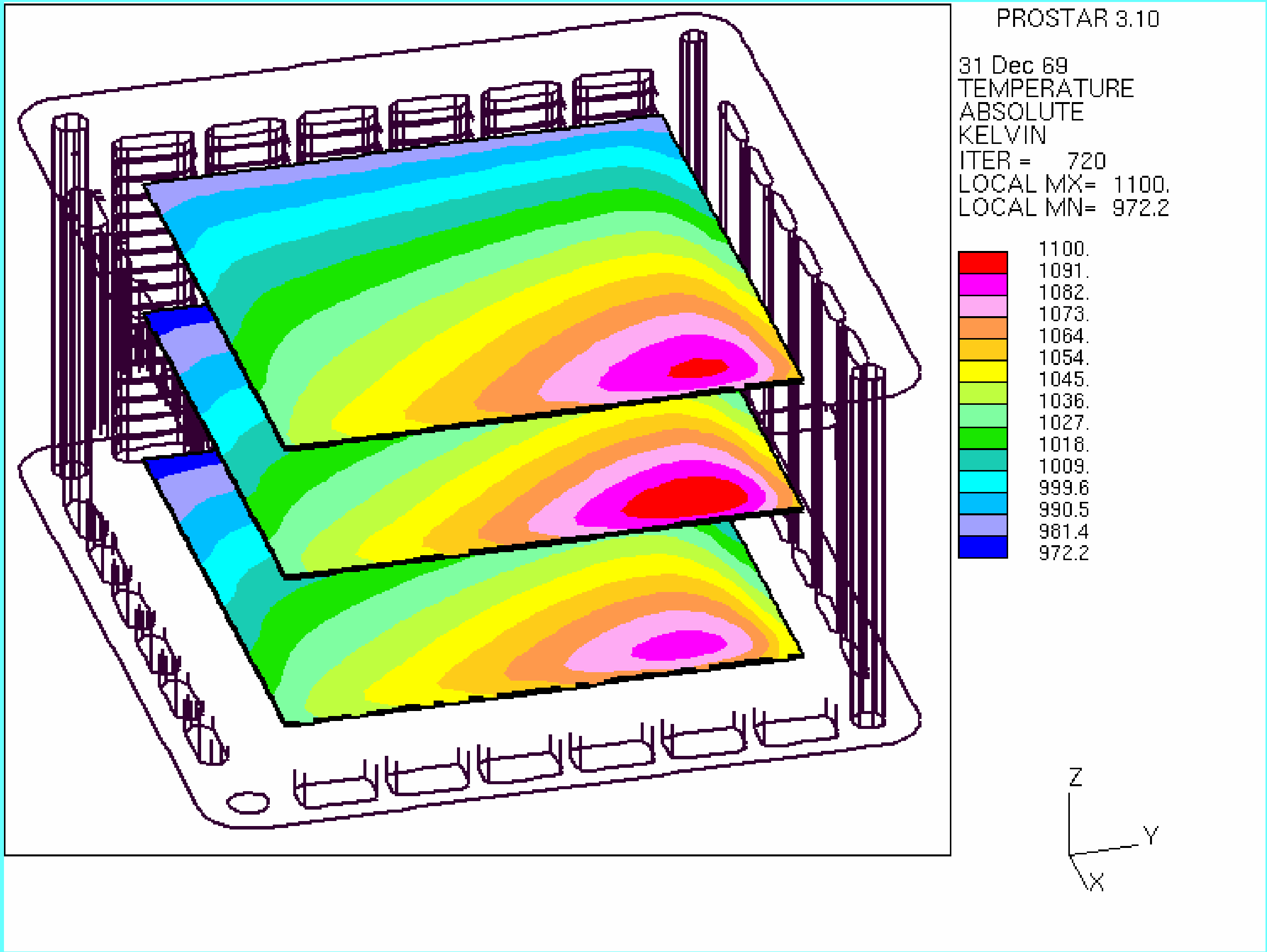
Steady State: 16-Cell Stack Model



Fuel Delivery: 8E-6 kg/s/cell @ 944K

Air Delivery: 0.25 kg/s/cell @ 944K

Output:

245 mW/cm^2

Tcell(ave) = 751C

Full 3-D Temperature dataset available for computing thermal stress

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Topics for Microstructural Electrochemistry

- Method.
- Advantages.
- Sample simulation results.
  - Reaction zones in the anode
  - Internal reformation

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Effective Property Method

- Discretize gas channels, electrodes and electrolyte into nodes with 5-25 μm thickness
- Each node has effective transport and reaction properties (gas diffusion, surface diffusion, surface area density, TPB density, etc.)
- Solve flow and transport equations using lattice Boltzmann to obtain three-dimensional distributions for
  - Gas velocity, density
  - Gas species concentrations
  - Adsorbed species, solid diffusing species (oxygen)
  - Energy, temperature

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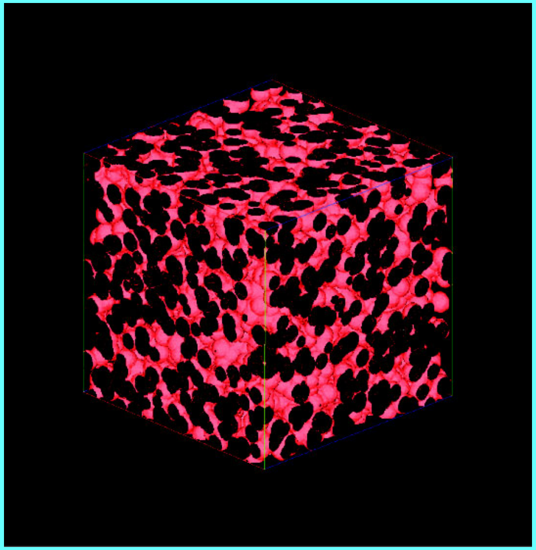
Microstructural Electrochemistry Method

- Geometry may be generated using statistical data taken from digitized pictures of the porous material
- Properties include effective gas diffusion, surface diffusion, solid diffusion, triple phase boundary density, etc.
- Effective properties may be determined using lattice Boltzmann simulations of the discrete microstructure



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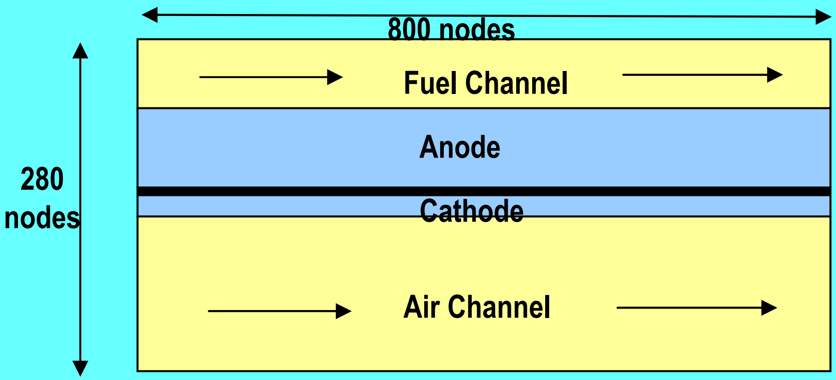
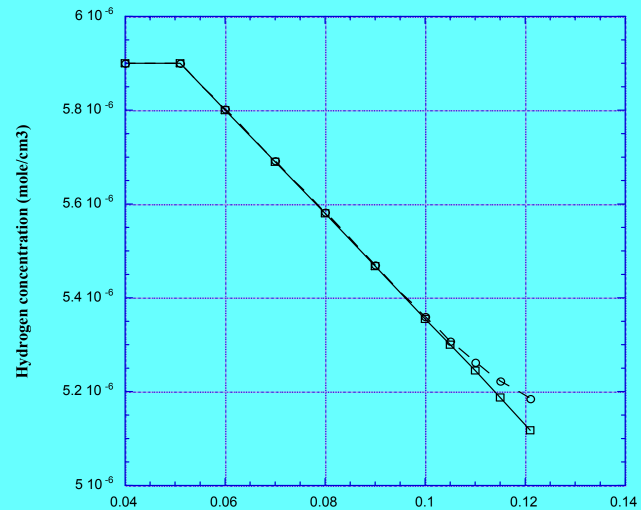
Advantages

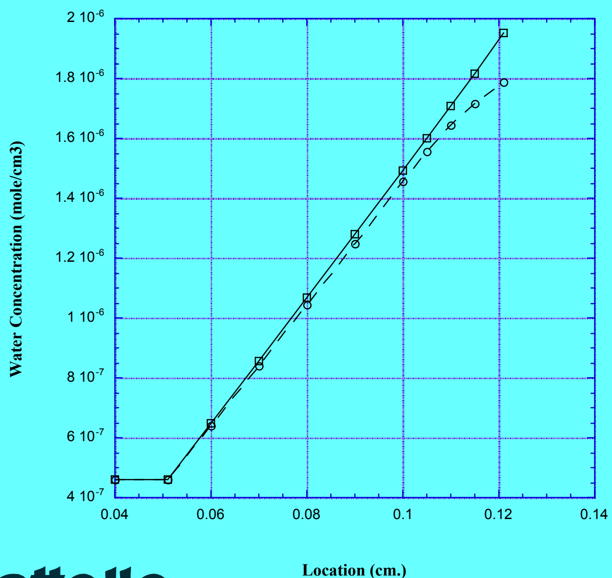
- Spatially varying electrode properties
- Parallel transport paths for oxygen (gas, surface, solid)
- Distributed reaction zones (TPB, internal reformation)
- Link cell performance to electrode microstructure

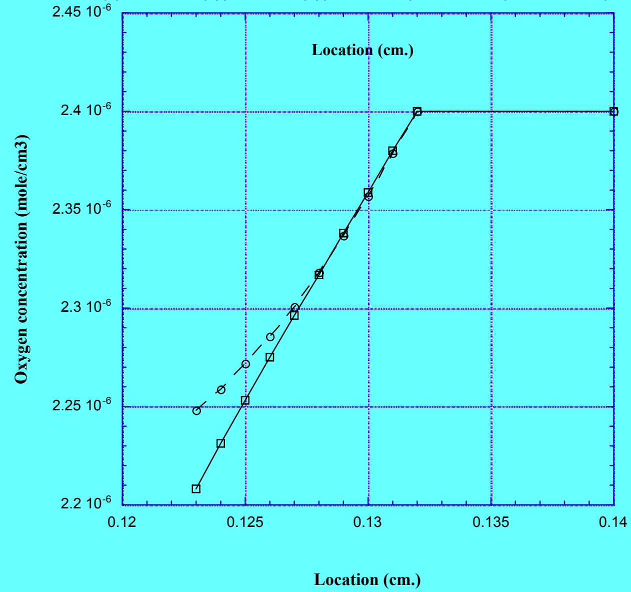
Simulation Results from Effective Property Model



$\Delta X = 10\mu m$







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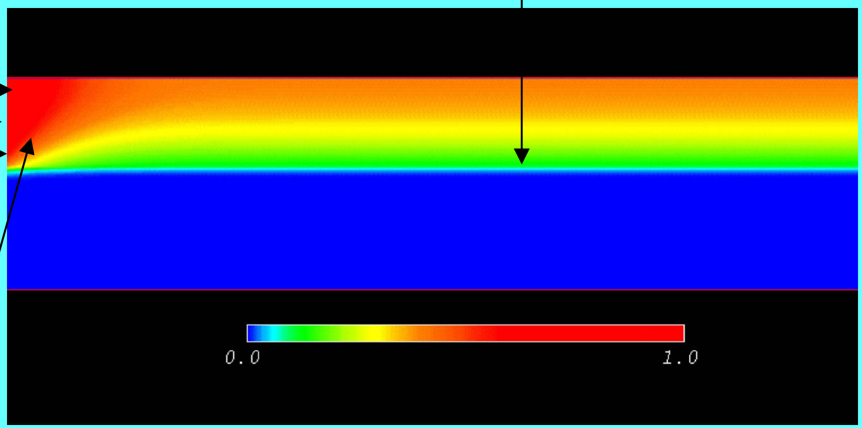
Internal Reformation

- Methane distribution

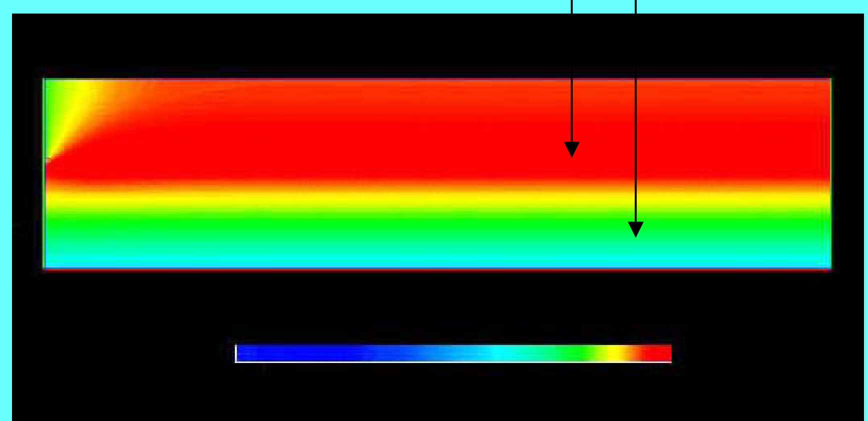
Methane is continually depleted
Gradient is driving it to surface



Methane is reformed upon contact with
Anode surface

High diffusion into the channel
And low diffusion into the anode

- Hydrogen distribution



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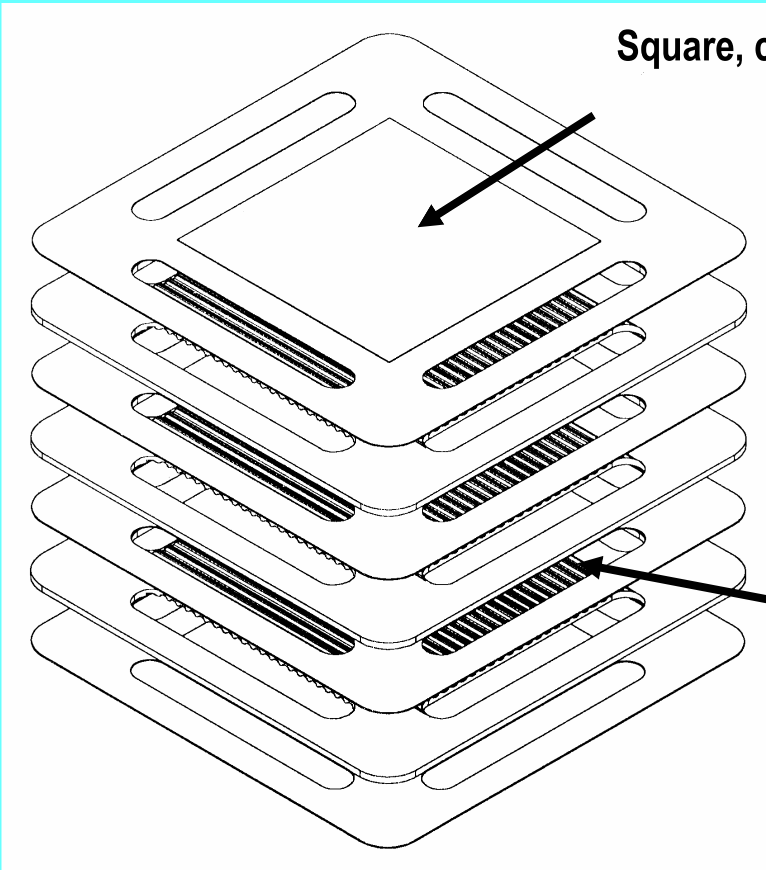
Topics for Start-up

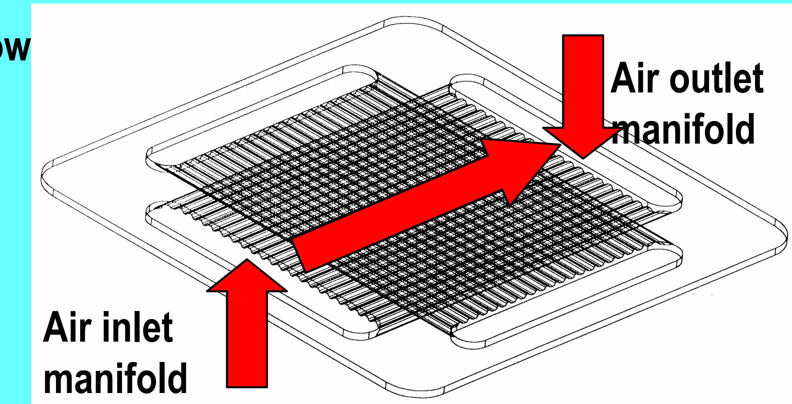
- Start-up issues and challenges.
- Computational tools for start-up simulations and stack design.
- Thermal controller for rapid heating of stacks.
- Structural parametric results.
- Optimization studies
- Experimental validation of structural models.

Rapid Start-up Issues for SOFC

- Flow through stack must be "uniformly" distributed.
- Maintain thermal stresses within material set strength.
- Stack pressure drop to be small.
- Minimize time to heat stack to initiation temperature of 700 ^{o}C (within a few minutes ultimately)
- Issues necessitate survey of designs, with given material set, to discover working options …Stack Geometry, Gas channel and manifold dimensions, flow configurations.

Transient simulations
Target Structure – Basic Planar Stack Design





<u>Design Variables</u>

- Gas flow distribution channel dimensions/types
- Ceramic or metallic interconnect
- Material thickness
- PEN strength
- Rigid or compression seals
- Manifold dimensions
- Flow configuration

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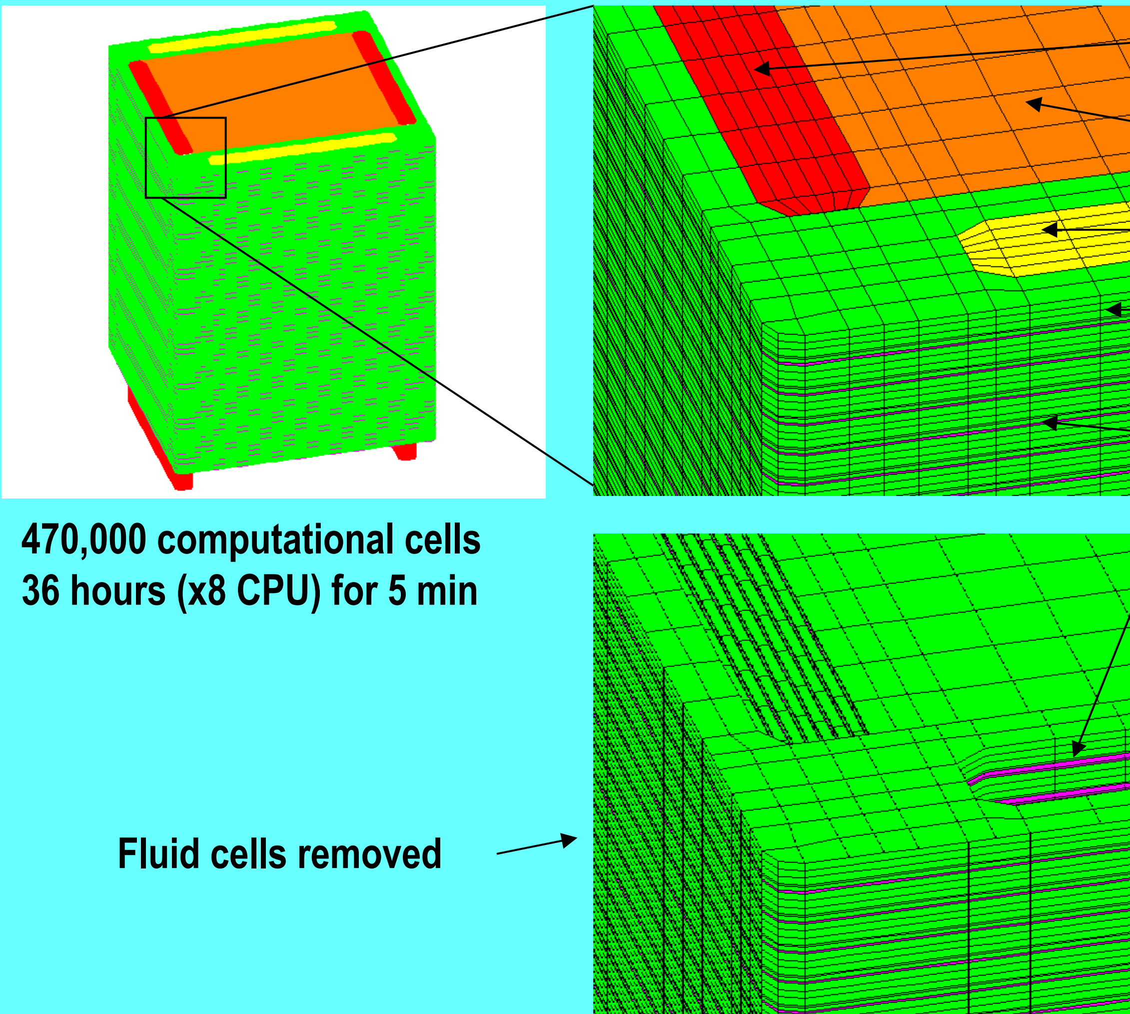
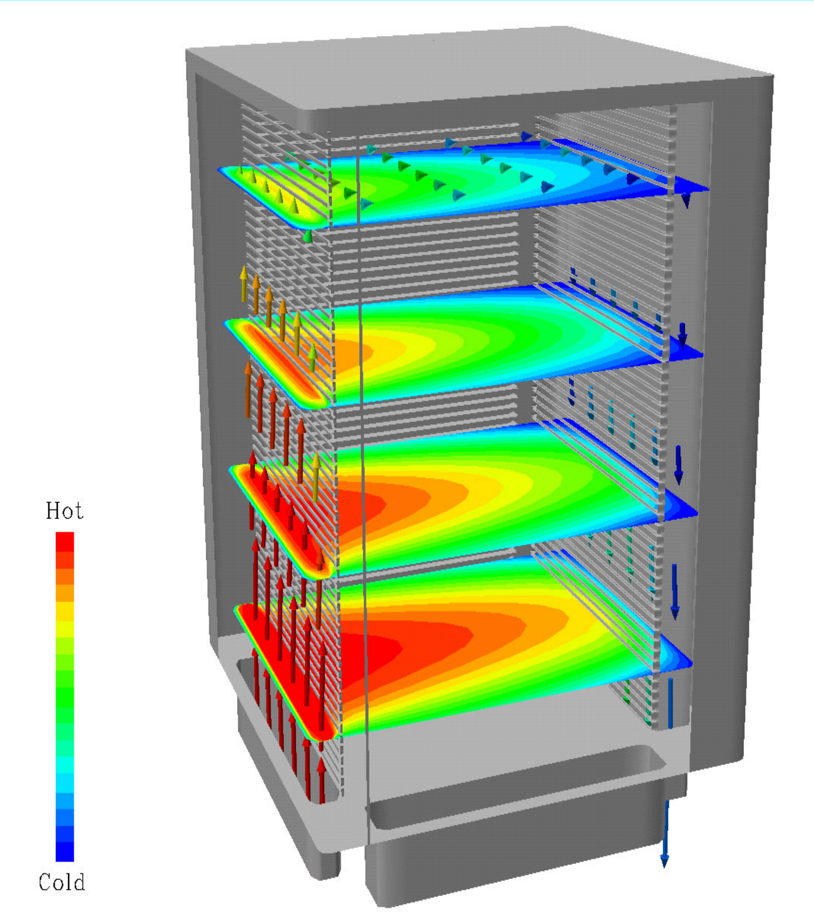
Transient - Rapid Start-up
Thermal-Fluids Stack Model



470,000 computational cells
36 hours (x8 CPU) for 5 min

Stack Model with Temperature Control, Modified Geometry and Boundary Conditions

- Flow channel height shortened to (1.5mm)
- User routine defined free convection BC at walls (T_e)
- User routine defined temperature control



Non-Uniform stack flow and heating…..

Would also mean non-uniform reactions and heating during steady operation.

Fix: increased outlet manifold dimension

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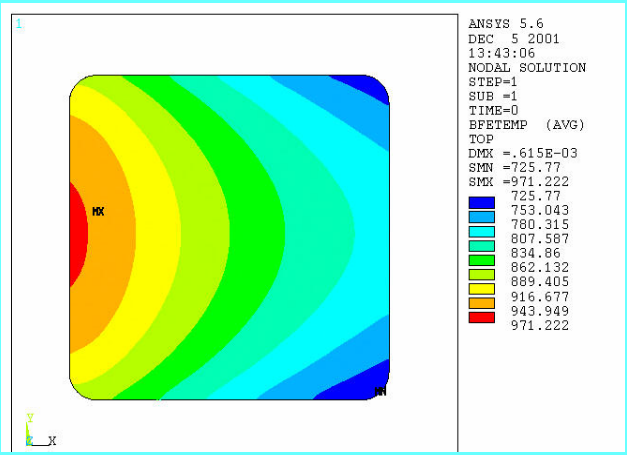
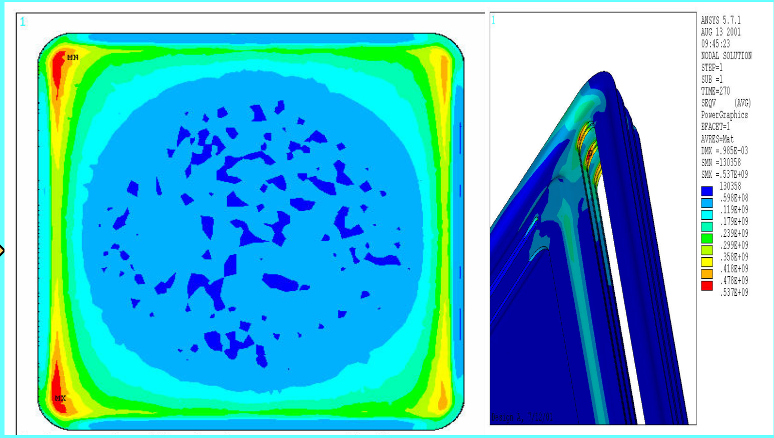
Prediction of Temperature Distribution and Subsequent Thermal Stresses

Temperatures from CFD model



Stresses in various Components From FEA Models



Updated Geometry or Boundary Conditions. New CFD Prediction of Flow and Temperature

Guidance for Modifications:
- **Heating Method**
- **Flow Channels**
- **Manifold Dimensions**

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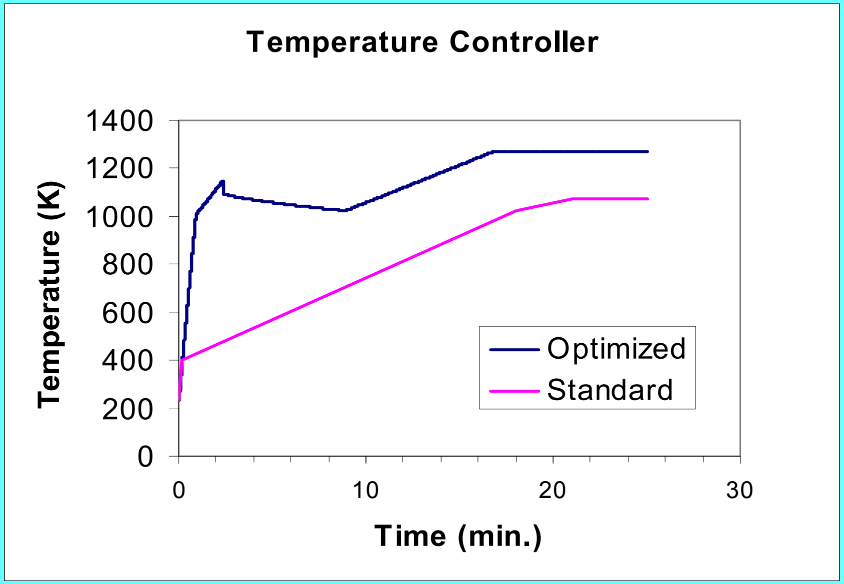
Temperature Controller

- CFD model is run with standard controller to generate temperature distribution
- FEA modeling performed using temperature distribution to determine maximum PEN ΔT allowed based upon strength of material
- CFD model is re-run using optimized temperature controller to meet the maximum ΔT at each average PEN temperature



Ave Pen	Pen ΔT
523	504
640	380
724	245

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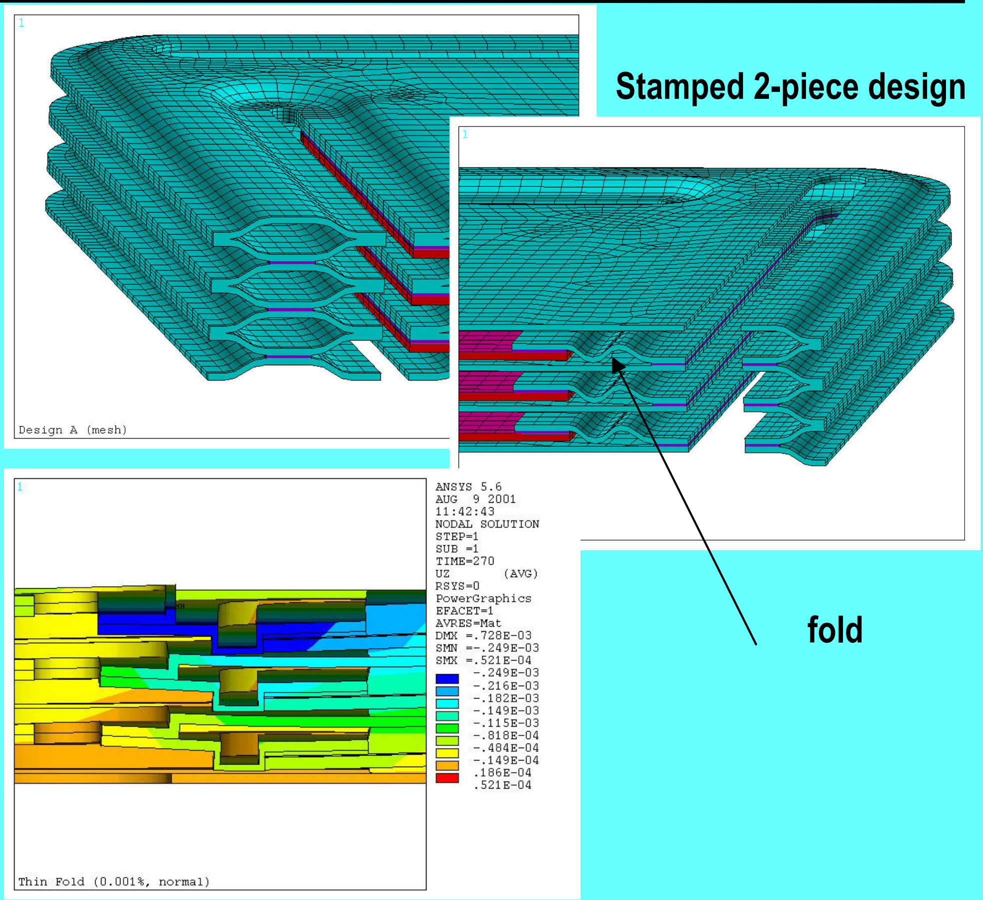
Optimization studies

- Controller for heat-up time optimization
- Geometrical optimization
- Optimization of mesh stiffness



Bounding (minimum) heat-up is the order of 10 minutes
(heat rate of 19.6 KJ/sec and total heat input of 6.81 MJ)

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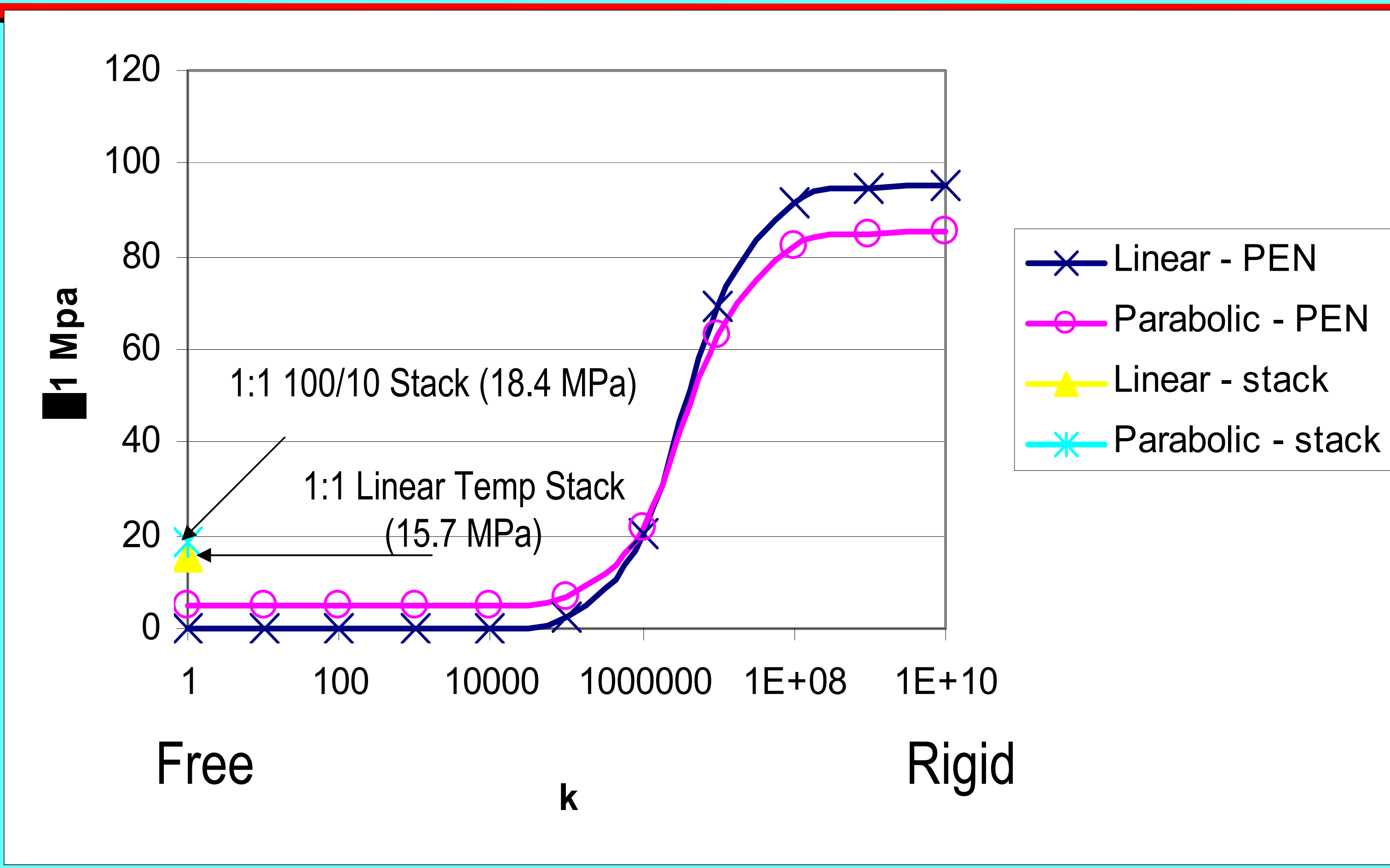
Effect of Temperature Profile and Seal Compliance on Stresses in the PEN



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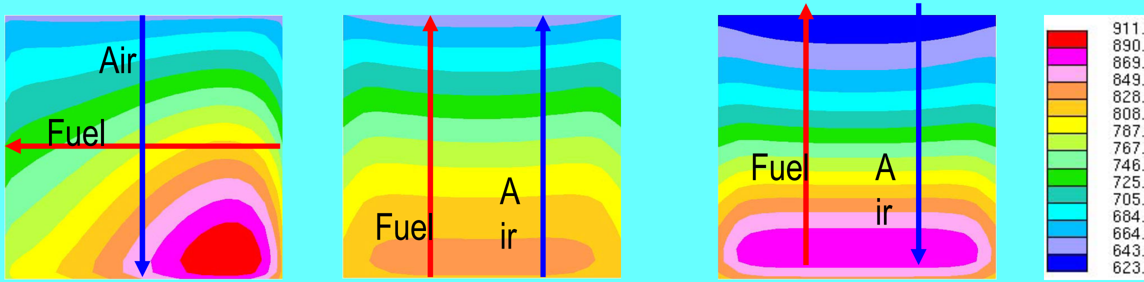
Effect of Temperature Profile and Seal Compliance on Stresses in the PEN

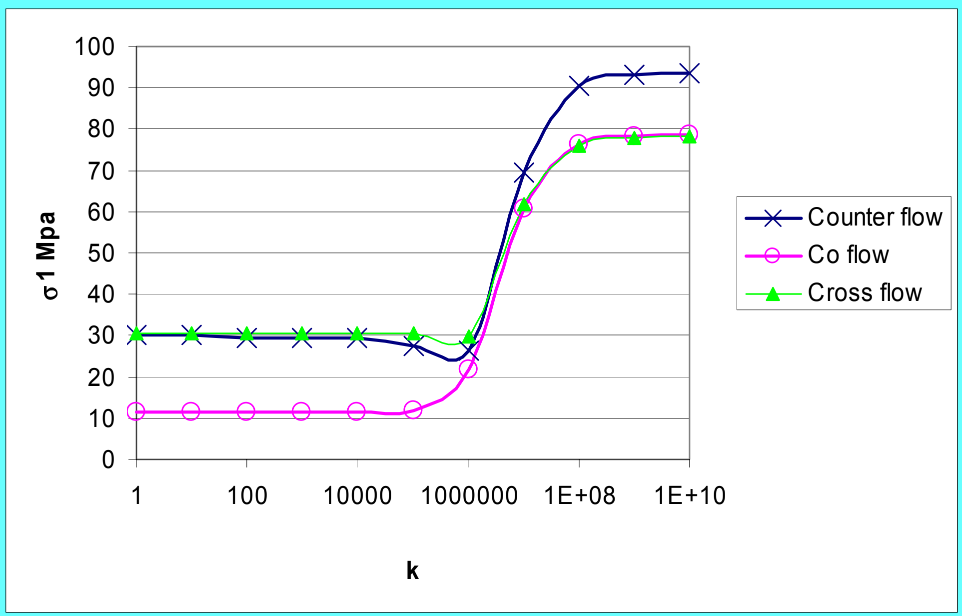
CROSS-FLOW | CO-FLOW | COUNTER-FLOW



Cross-flow: Tave = 771°C, ΔT = 250°C

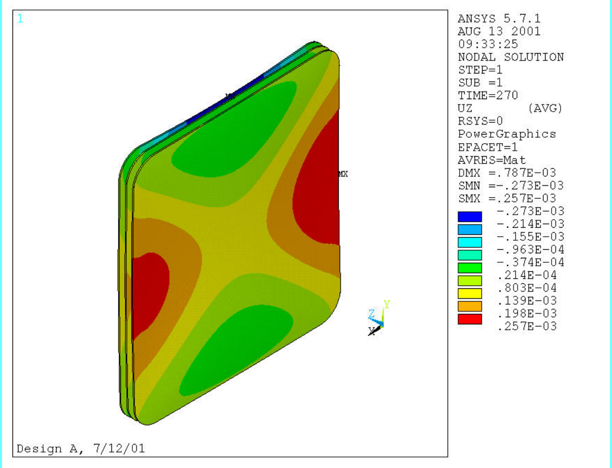
Co-flow: Tave = 761°C, ΔT = 183°C

Counter-flow: Tave = 756°C, ΔT = 265°C

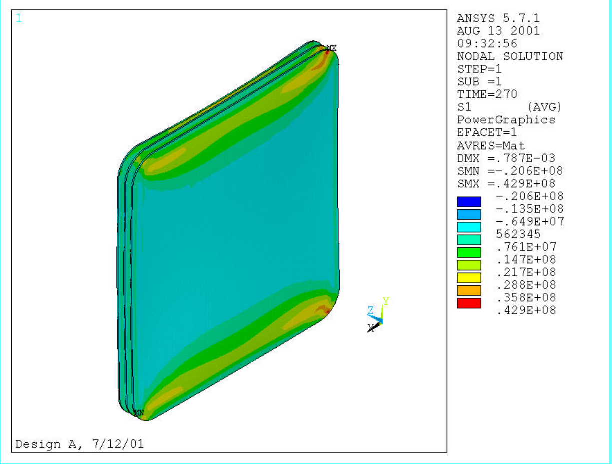


Layered model results

Design	Anode stress (MPa)	Vertical Deflection (mm)
Cross flow	27.3	0.031
Co - flow	10.3	0.035
Counter flow	26.3	0.063



PEN out-of-plane deflection



Anode principal stress (Pa)

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Results 3-Stack Simulations

		Anode $\sigma 1$ MPa	SS σeqv MPa
1% (A)	Bottom	24	370
	Top	22	547
0.001% (D)	Bottom	49.6	313
	Top	32.4	609
0.001% (E)	Bottom	56.4	410
Simple BC	Top	33.8	585
0.001% (F)	Bottom	52.5	326
10% glass	Top	28.9	617

- Will the stack survive thermal stresses? (based on stress/strength failure criteria)
- What is the effect of out of plane stiffness?
- Will softer glass reduce stresses?
- How do the B.C.'s change stress profiles?

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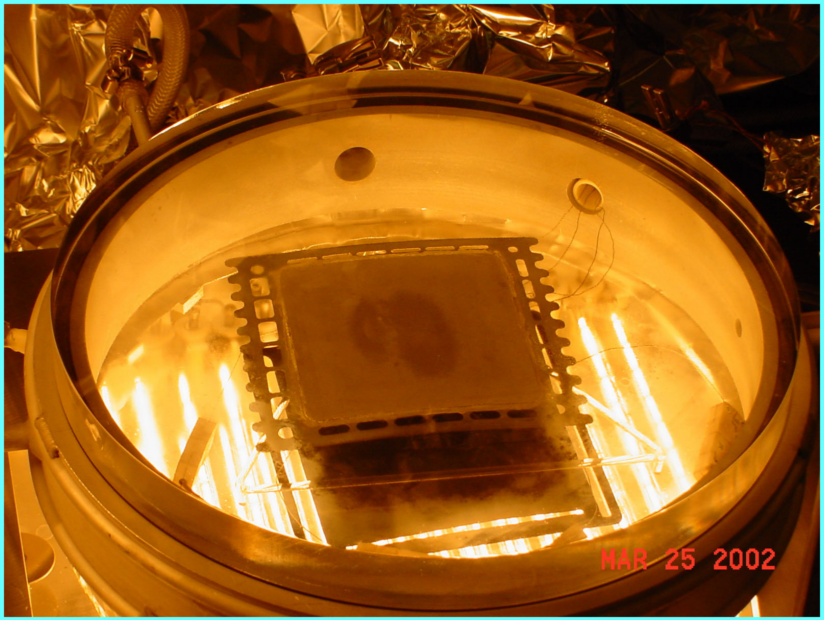
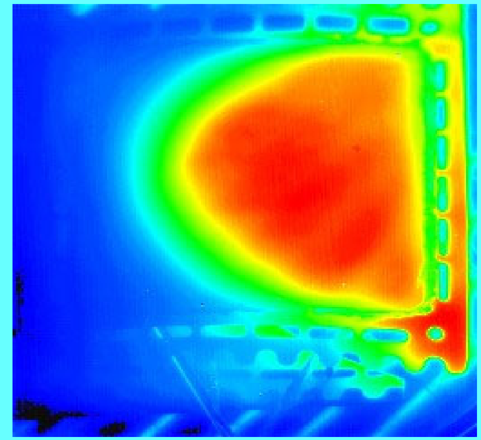
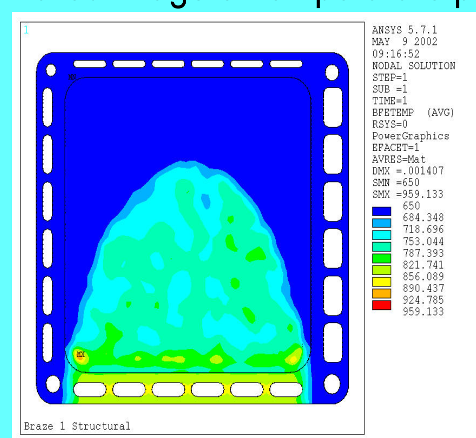
Experimental Validation of Structural Modeling



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

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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.

Future Activities

- Enhancement of continuum level electrochemistry models for full stacks and steady state parametric studies.
- Micro-structural level electrochemistry for microstructural optimization and simulating internal reformation
- Predictive models for strength and life
- Material properties and model correlation/validation.

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