SOFC Modeling and Simulations at PNNL

SOFC Modeling Team
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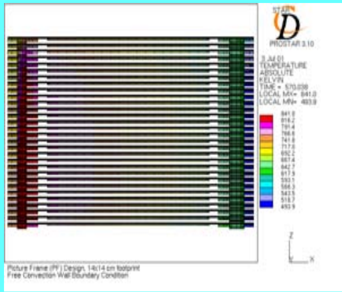
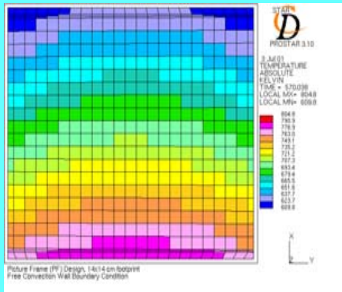
Overview of PNNL’s Modeling and Simulations

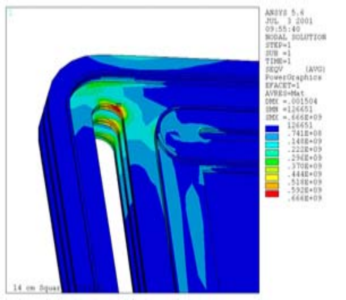
Flow Analysis

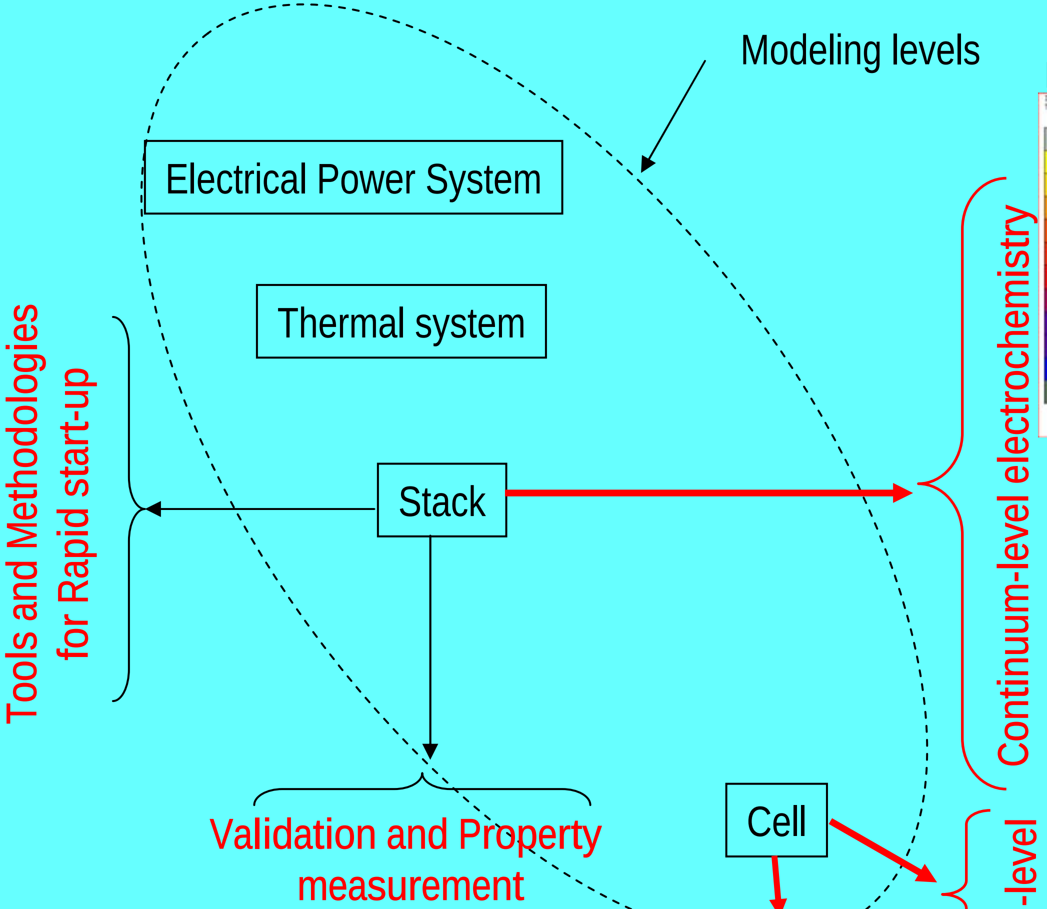


Thermal Analysis



Stress Analysis





Modeling levels

Electrical Power System

Thermal system

Stack

Tools and Methodologies for Rapid start-up

Validation and Property measurement

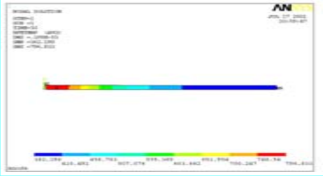
Cell

Continuum-level electrochemistry

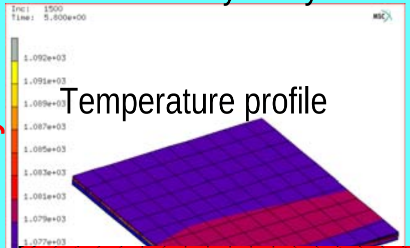
Cell-level

Microstructure-level

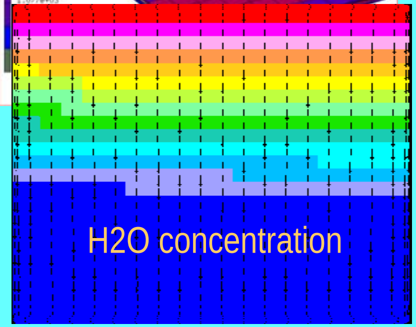
Thermal Shock



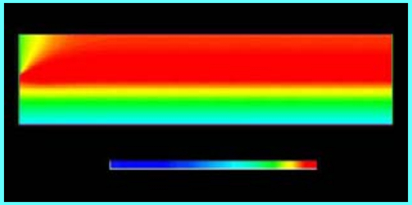
Flow, thermal & Electrochemistry analysis



Temperature profile



H2O concentration

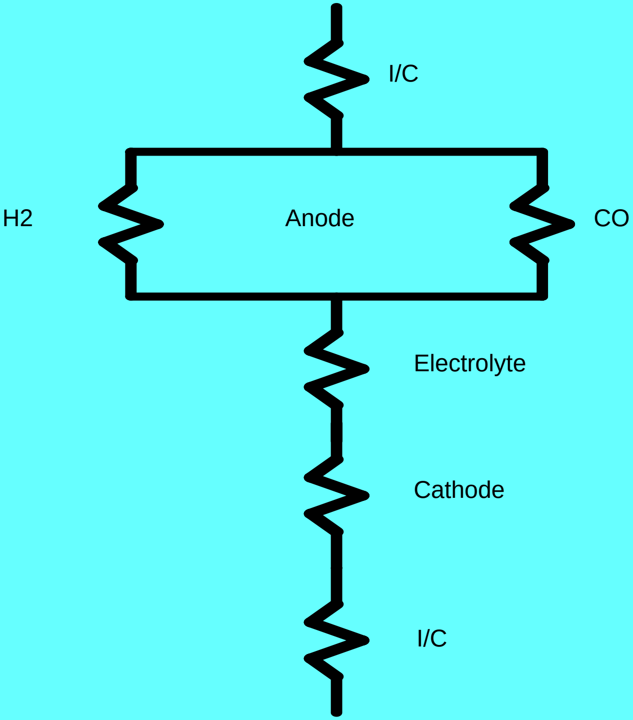


Methane distribution

Electrochemistry at the continuum level: Background

The cell potential, V(I), for a given current density, given also the local values of the temperatures and gas partial pressures, is determined by:

$$V(i) = E_{open} - iR_i - b\sinh^{-1}(i/2i_0) + (RT/4F)\ln(1-i/i_{O2}) + (RT/2F)\ln(1-i/i_{H2}) - (RT/2F)\ln\{1+p^0_{H2}i/(p^0_{H2O}i_{H2})\}$$



Coupling EC and CFD/FEA can address important SOFC problems:

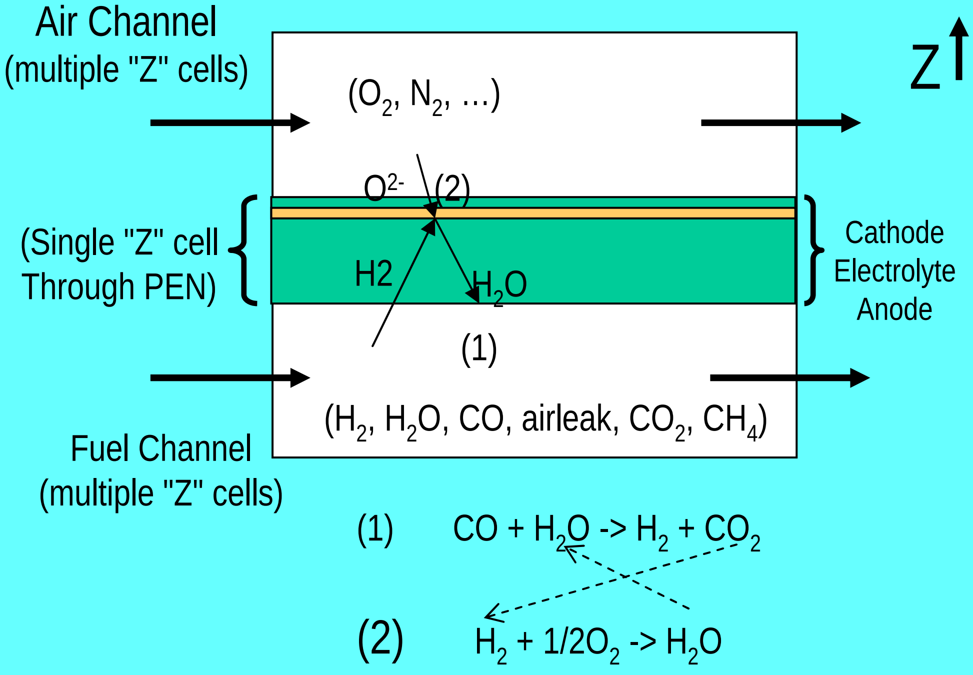
- Transport: heat, momentum, and mass
- Performance: maximize efficiency and fuel utilization
- Reliability: minimize stresses and failures
- Uniform transport enhances performance & reliability

Constraints for uniformity

- Geometry: transport vs fuel/air separation & circuits
- Heterogeneous chemical reactions at boundaries
- Localized heat generation (Q)
- CE-EC models quantify constraint relationships

Continuum-Level EC: Approach

- STAR-CD solves the Navier-Stokes and transport equations to obtain the flow, species concentrations and temperatures at each time step.
- The electrochemistry module calculates the local current distribution based on the applied voltage and local conditions. The current is used to calculate the local hydrogen combustion rates.
- The shift reaction rates are adjusted such that equilibrium conditions are satisfied at every location in the cell.
- Heat generation rates and species source rates are supplied to STAR-CD based on the local hydrogen combustion and shift reaction rates.
- Species concentration and temperature distributions are calculated for the next time step.



(1) $CO + H_2O \rightarrow H_2 + CO_2$

(2) $H_2 + 1/2O_2 \rightarrow H_2O$

Shift Reaction Procedure

- Assume that chemical equilibrium exists at every location
- Calculate the target equilibrium coefficient using

$$K_{eq} = \exp\left[-\frac{\Delta G(CO) + \Delta G(H_2O) - \Delta G(CO_2)}{RT} \right]$$

- Calculate the actual equilibrium coefficient using

$$K_{eq} = \frac{[CO][H_2O]}{[CO_2][H_2]}$$

- Adjust the shift reaction rate based on the difference between the two

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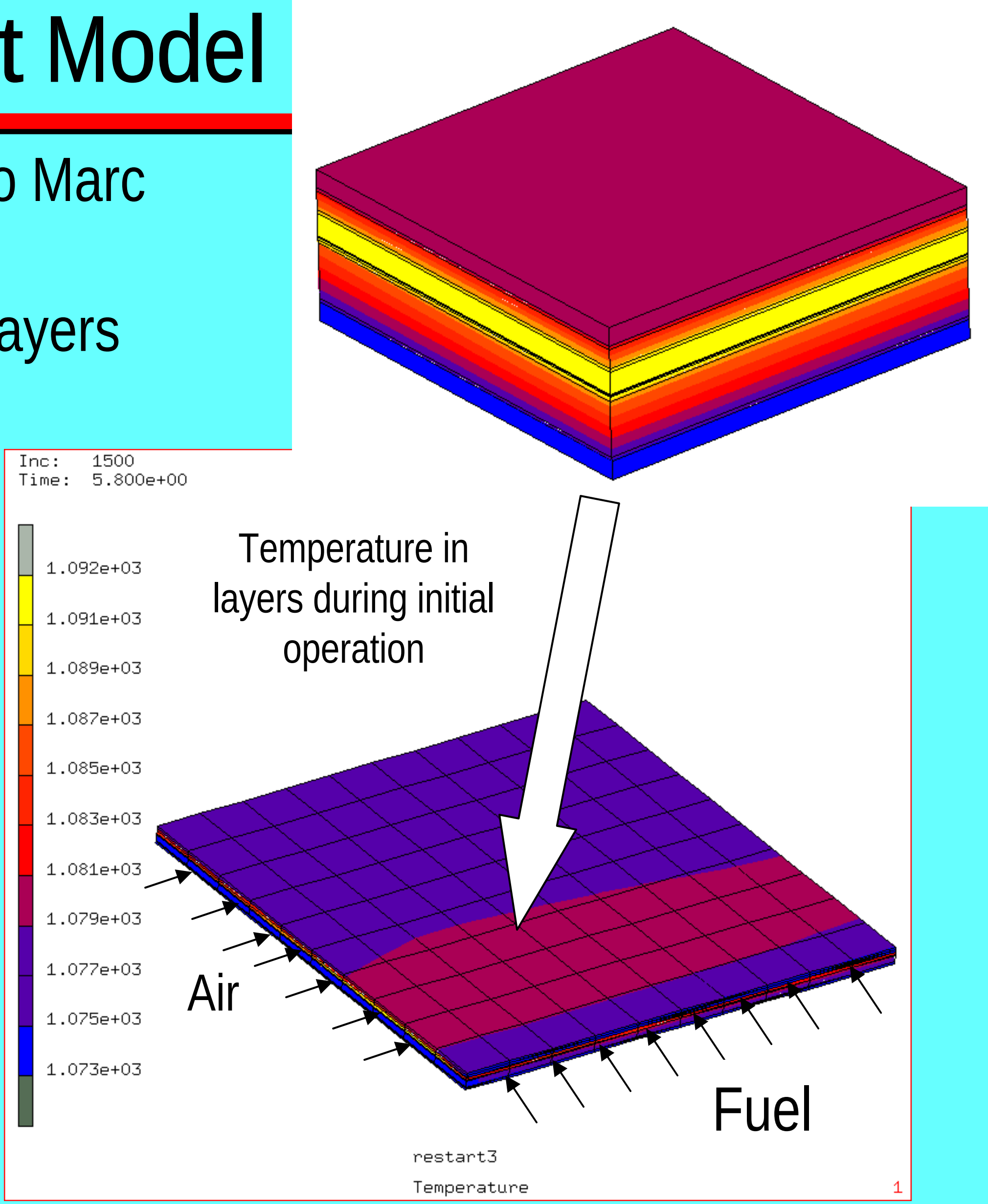
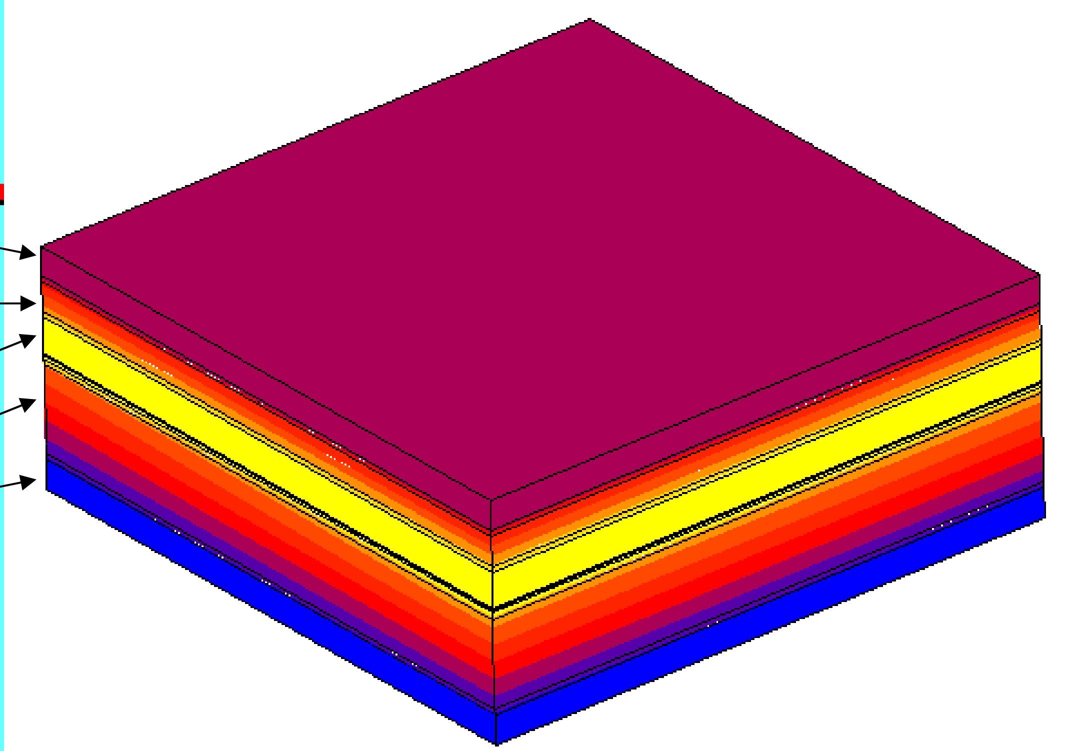
Coupling of Electrochemistry with Fluid-Thermal Finite Element Model

- Electrochemistry module coupled to Marc fluid-thermal simulation.
- Transport of reaction heat to solid layers and moving fluids is considered.
- Model used to study:
  1) Effect of inlet flow conditions on equilibrium cell operation.
  2) Distributions of reaction species and heat generation in cell.
  3) Required time stepping for accurate transient and steady state solutions.



Temperature in layers during initial operation

Model Assumptions



1/2 Interconnect

Fuel Channel

PEN

Air Channel

1/2 Interconnect

Temperatures of top and bottom of interconnect layers equated to represent a cell in the center of the stack.

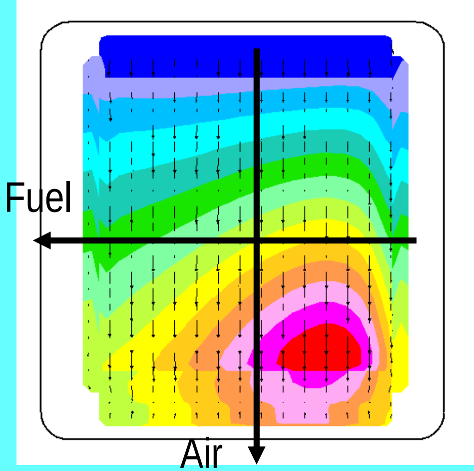
Fuel and Air channels include boundary layer effects as additional layers with convective film resistance and low thermal mass.

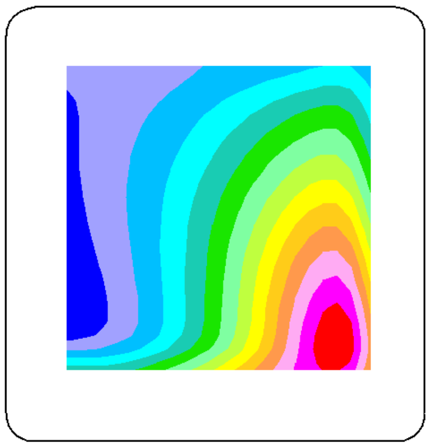
The Electrochemistry module tracks the distribution of chemical species and heat fluxes in the 10x10 grid in X and Y (one grid in X and Y is shown above).

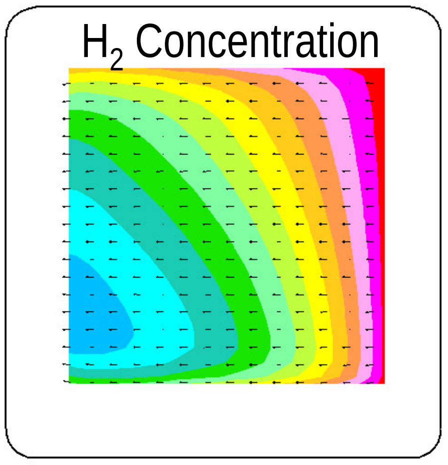
The coupled physics requires a transient solution to reach steady state heat and flow balance.

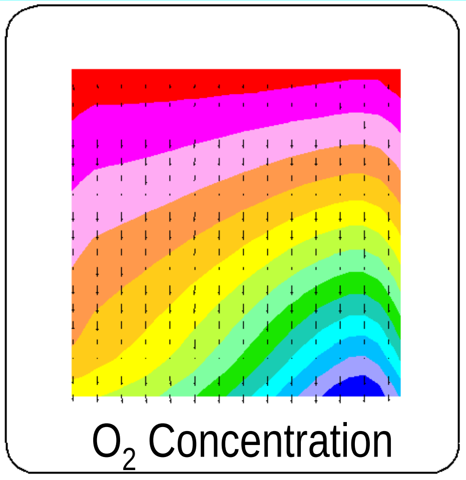
Fuel and Air inlet flow velocity and temperature can be varied to determine resulting steady state temperatures and current output.

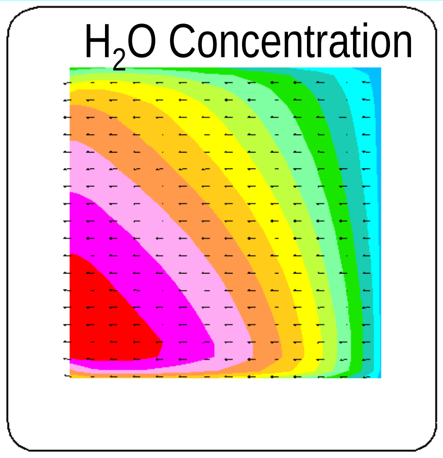
Typical Continuum EC Results


Air Temperature


Current Density & Heat Generation


H_2 Concentration


O_2 Concentration


H_2O Concentration

60% Fuel Utilization Case:

Current Density = 0.337-1.19 (0.643 A/cm2)
PEN Temperature = 660 - 828 (743 °C)

	in, moles/s	out, moles/s
h2	3.5032E-04	1.4673E-04
h2o	2.6674E-05	2.3027E-04
co	3.0522E-04	1.2033E-04
co2	6.7439E-05	2.5234E-04
n2	1.7228E-04	1.7223E-04
moles/s	9.2193E-04	9.2190E-04

Fuel Utilization= 59.3%

Test Cases- Goal 750 °C Stack Temperature

Case	T(in), °C	T(PEN), °C
Adiabatic Single Repeating Cell Unit	575	705 and dropping
	650	857 (775 Stack)
Adiabatic w/ Extra Air Cooling Channel	575	650 and dropping
	650	754
Cyclic Temperature w/ 27 gm/s	575	637 and dropping
	650 (60% util)	739 (713 Stack)
Cyclic Temperature w/ 15 gm/s	625	~785 (~753 Stack)
	(~65-70% util. Est.)	

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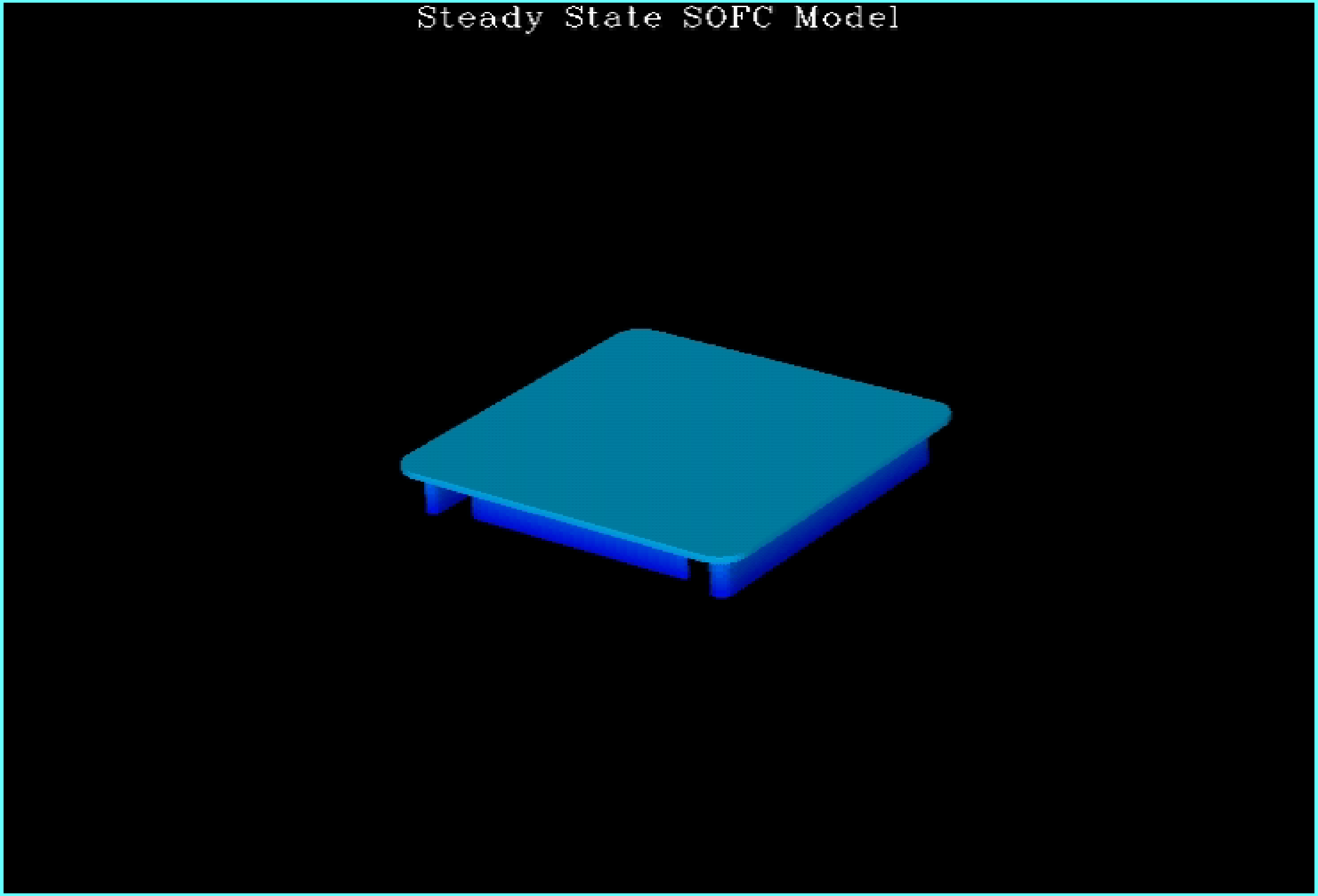
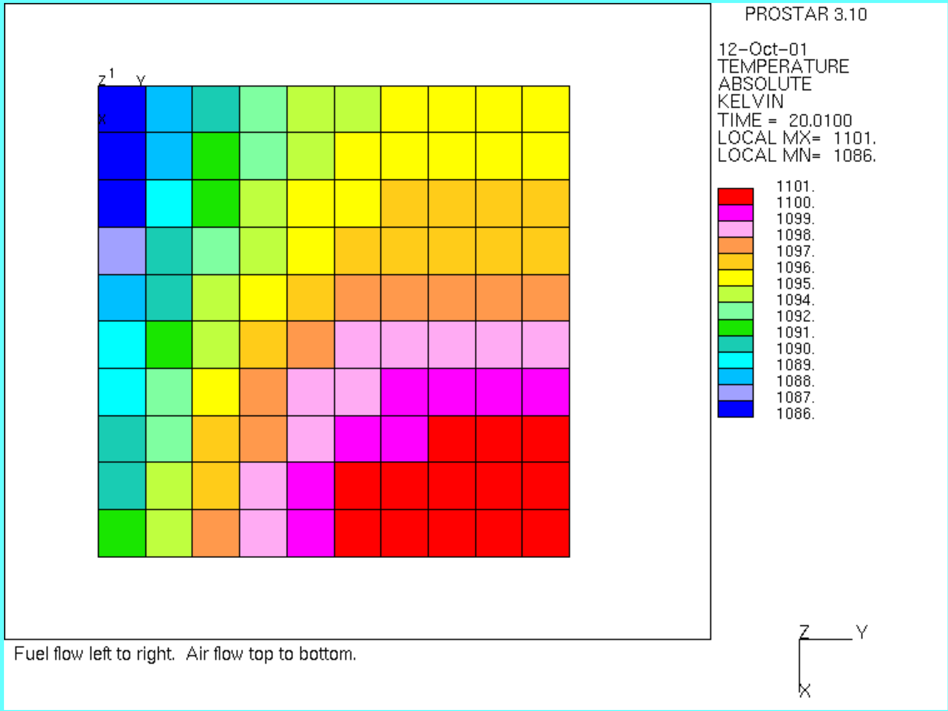
Technical Accomplishments

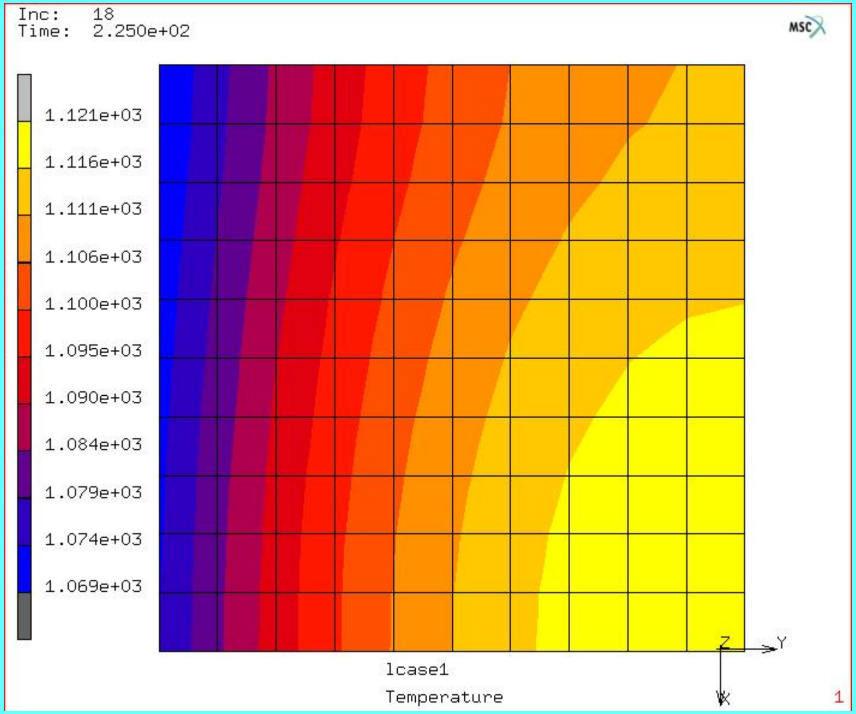


FEA – Electrochemistry Modeling: PEN Temperatures



Fuel flow left to right. Air flow top to bottom.

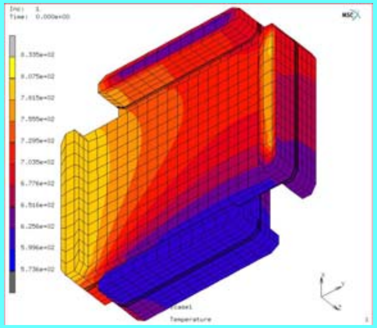
STAR - EC



MARC - EC

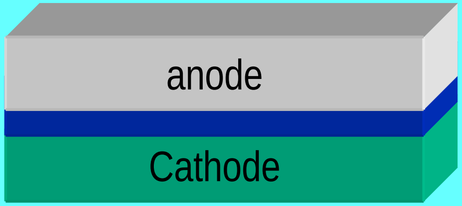
Technical Approach
Integrated multi-level models with experiments

continuum



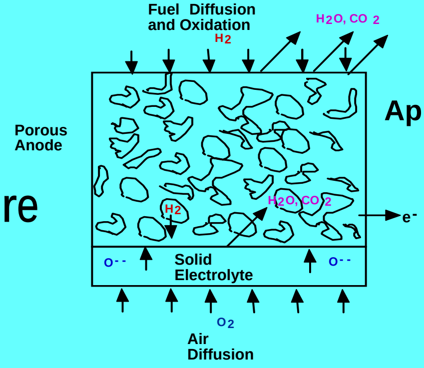
Verification Experiments

cell



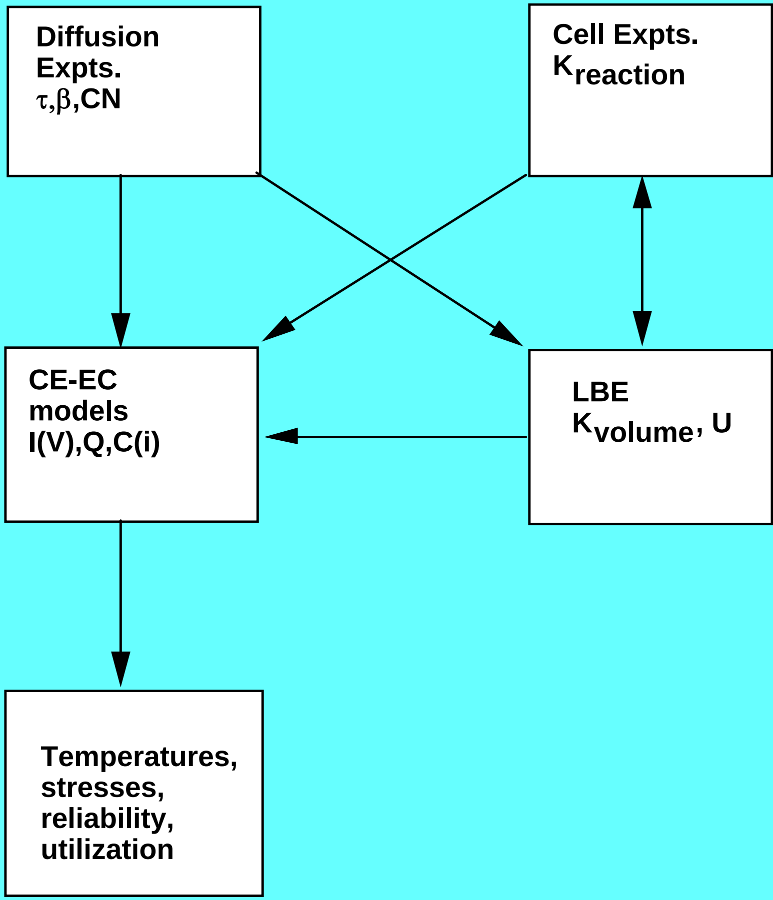
Electrochemistry Models

Microstructure



Detailed SOFC Reaction Zone
(Cathode Similar, exc. Oxidant Reduction)

Applications



Diffusion Expts.
τ,β,CN

Cell Expts.
$K_{reaction}$

CE-EC models
I(V),Q,C(i)

LBE
K_{volume}, U

Temperatures, stresses, reliability, utilization

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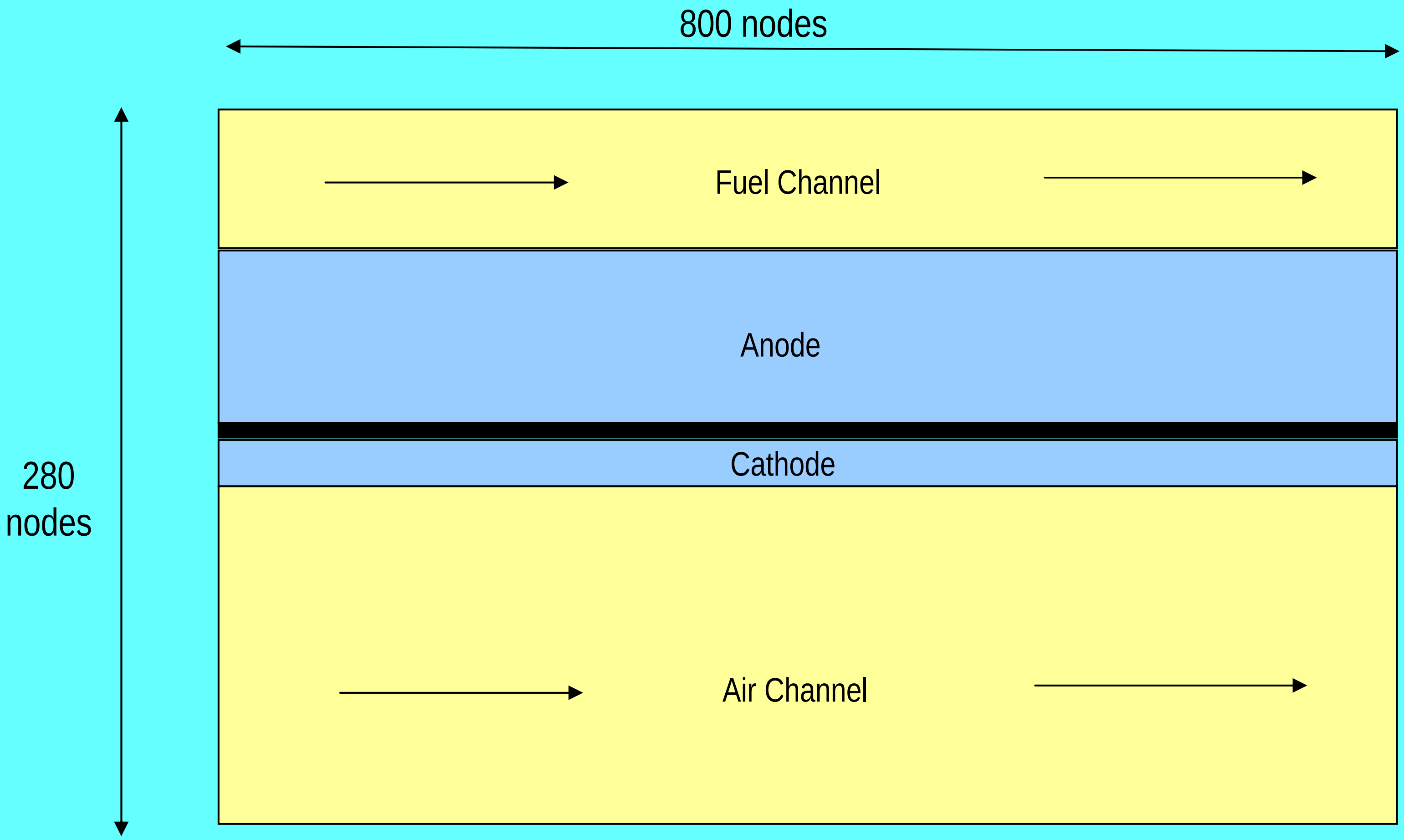
Two-Dimensional Model

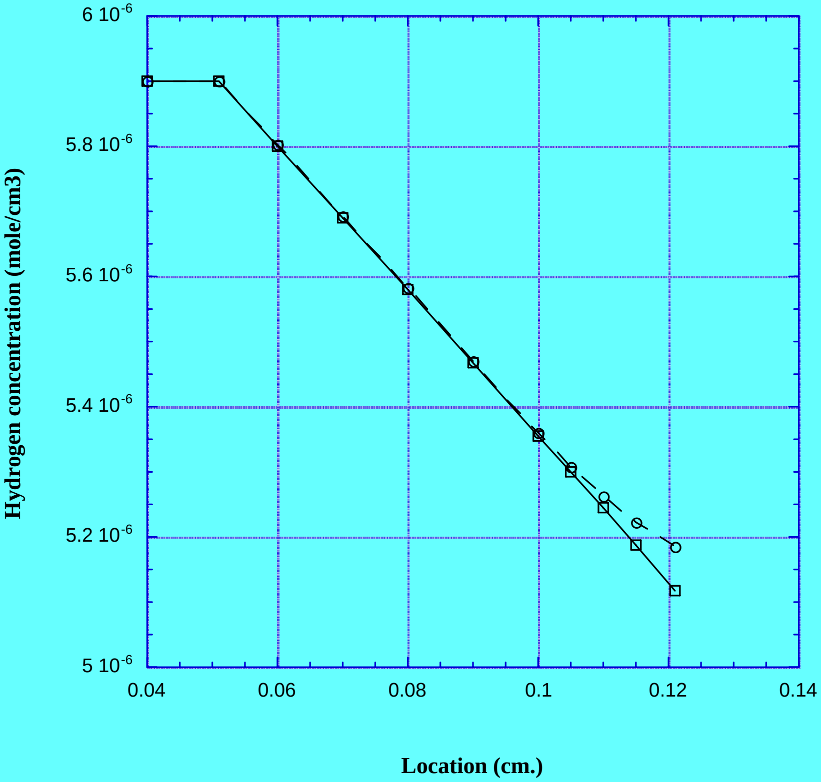


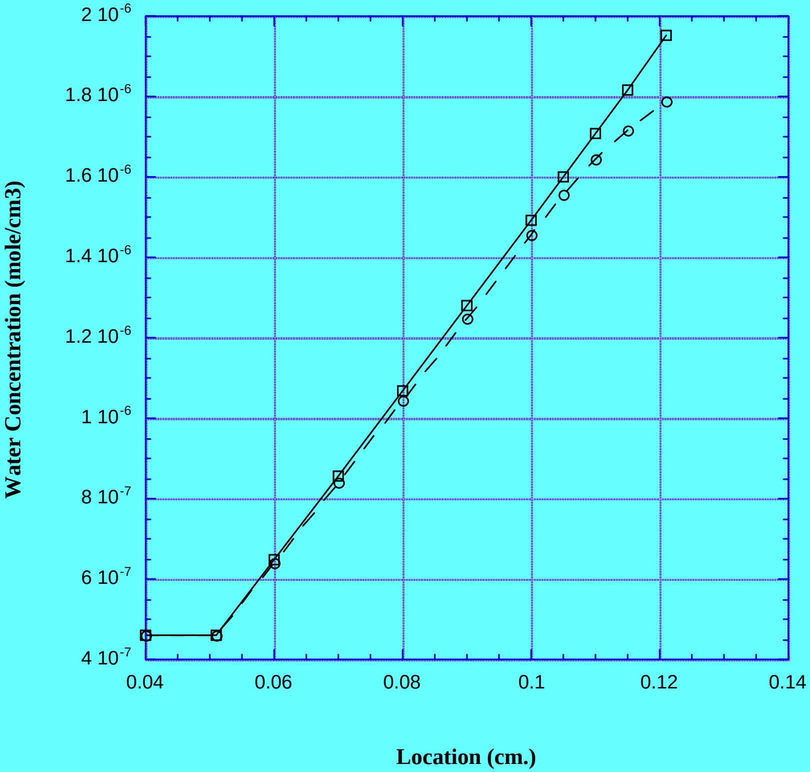
$\Delta X = 10\mu m$

Effect of Distributed Reaction Zone

- The Stack EC module assumes that the electrochemical reactions occur at the electrode-electrolyte interface. However, a portion of the reactive surfaces may extend into the electrode, reducing the diffusion path for some of the gas species.
- Lattice Boltzmann simulations were performed for a portion of a fuel cell where
  - The reactions all occur at the electrode-electrolyte interface
  - Half the reaction surface resides at the interface and the rest is distributed through a quarter of the electrode.
  - The gas composition profiles and voltage are calculated for a given current density.
- Reaction rates were calculated based on local reaction surface area and gas concentrations

Gas Concentration Profiles





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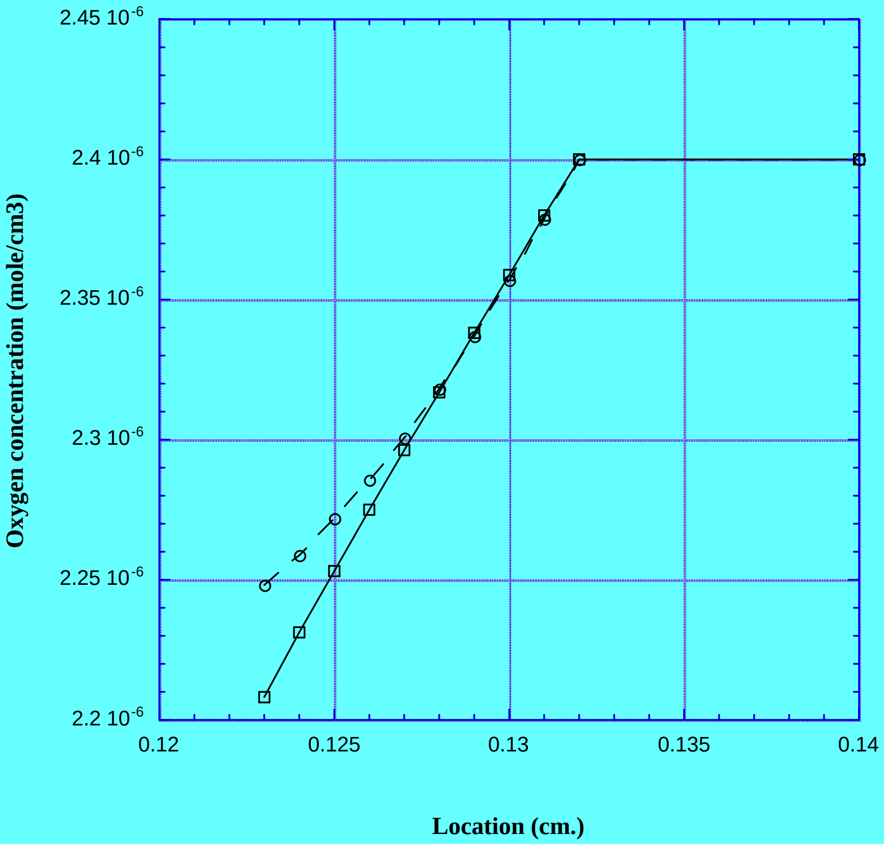
Gas Concentration Profiles



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Internal Reformation

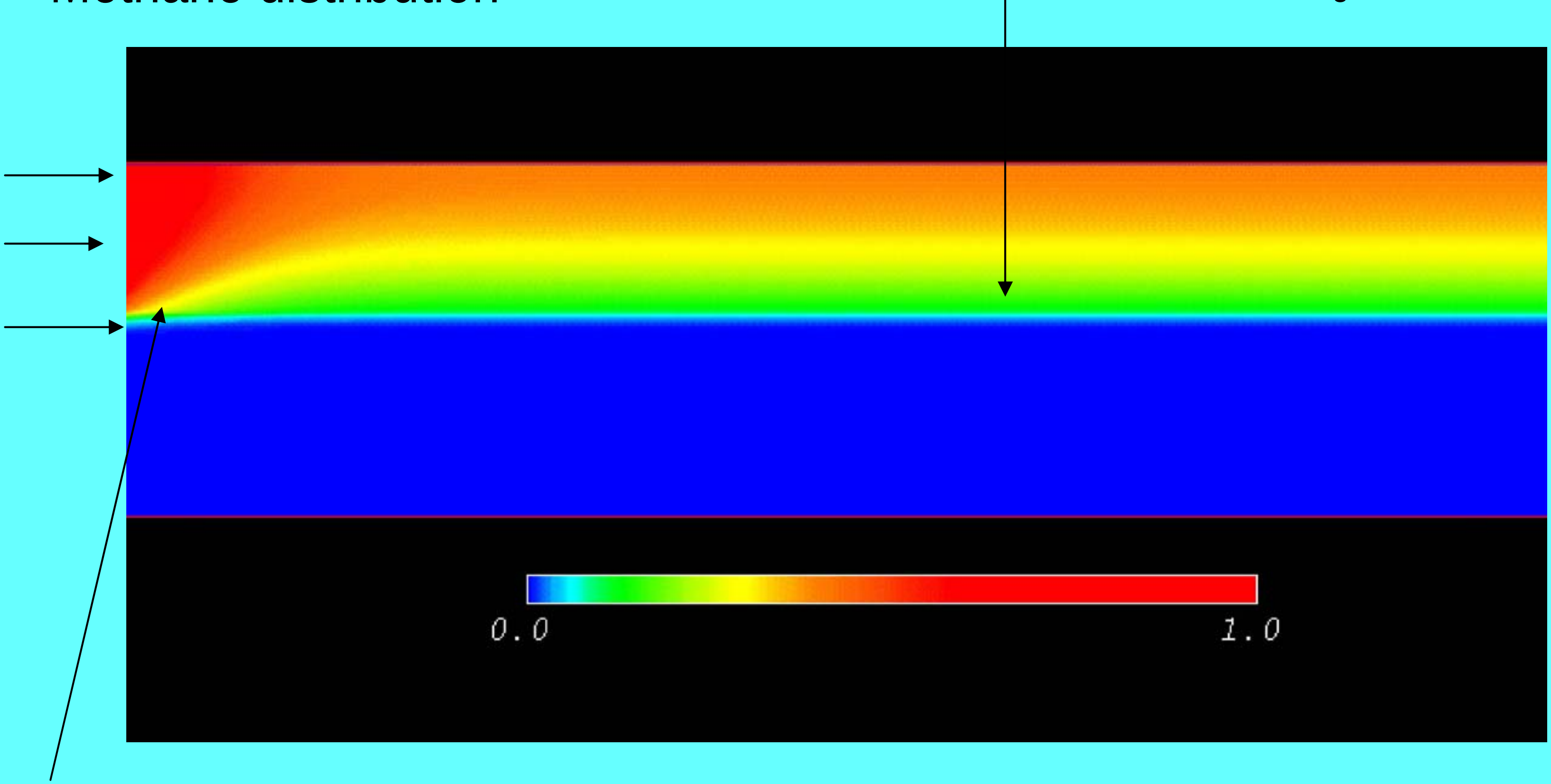
- Additional hydrogen fuel is created when methane reacts with water in the presence of a catalyst. One concept is to distribute a nickel catalyst uniformly through the anode.

- Lattice Boltzmann simulations were performed for a simple two-dimensional geometry to determine the reaction rate and gas composition distributions.
  - Gas inlet contains 49.147 mol% hydrogen and 1.0 mol% methane.
  - Reaction rate is based on local concentration of methane.

Internal Reformation

- Methane distribution

Methane is continually depleted
Gradient is driving it to surface



Methane is reformed upon contact with
Anode surface

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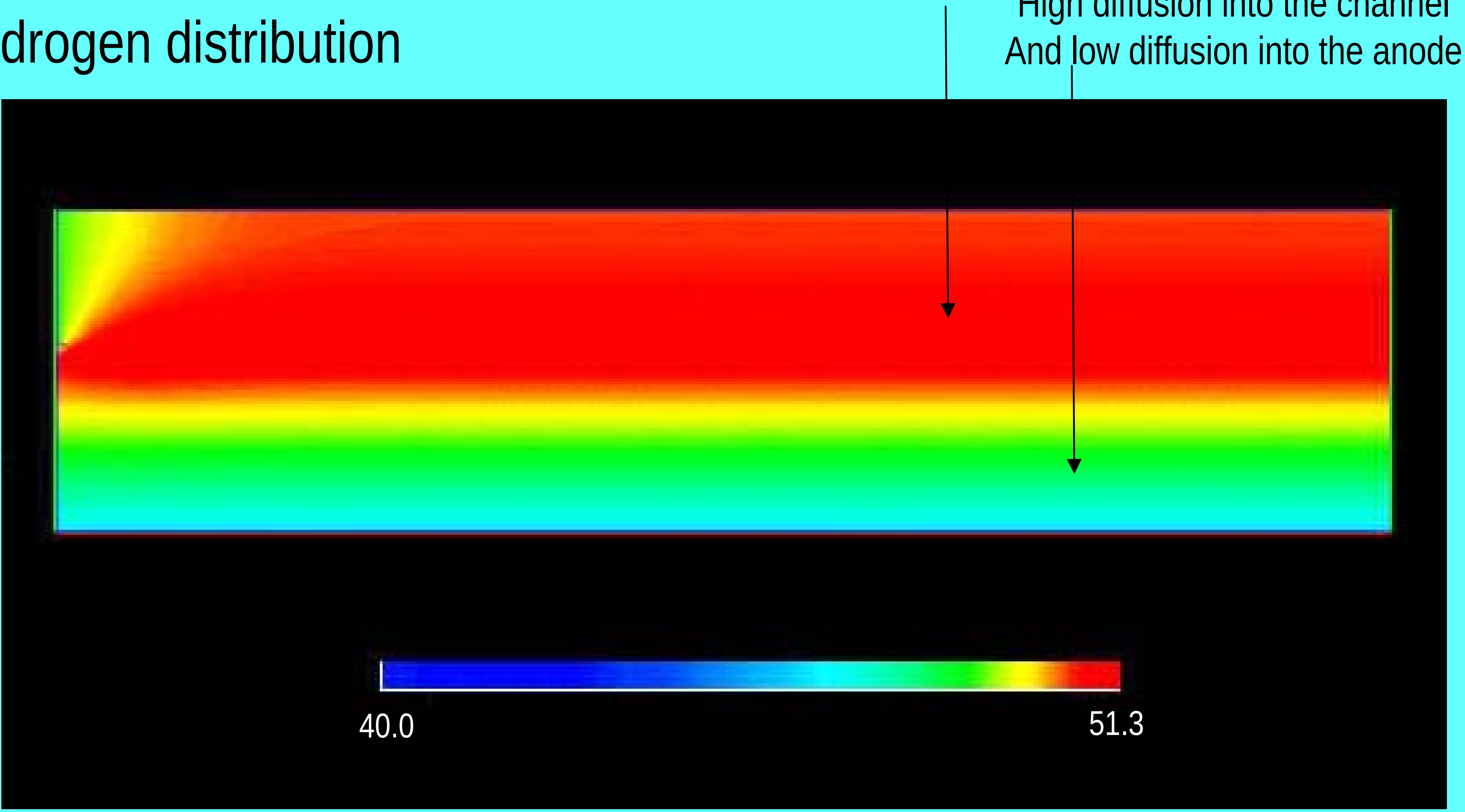
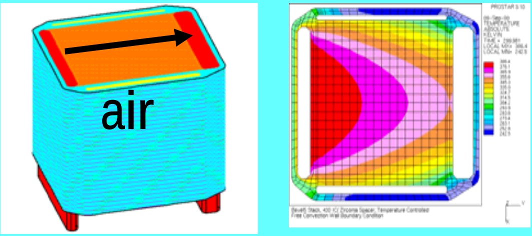
Internal Reformation

- Hydrogen distribution

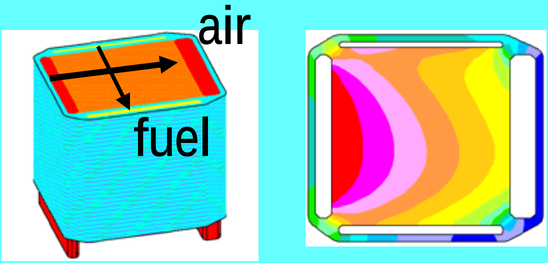


High diffusion into the channel
And low diffusion into the anode

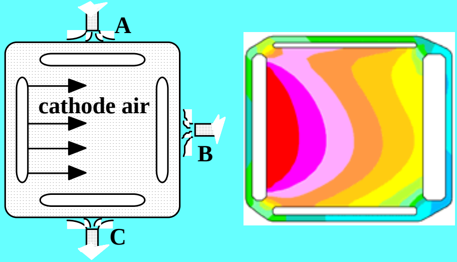
Heating Times and Temperature
Focus is on methodology



Cathode

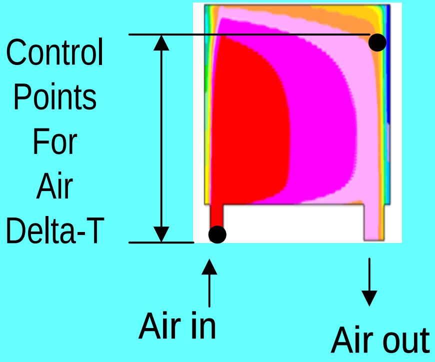


Cathode + Anode



Cathode + Anode+Jet

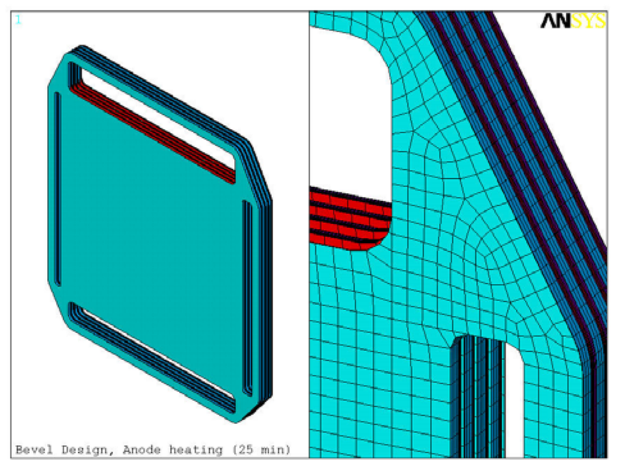
Side View
Cross-Section



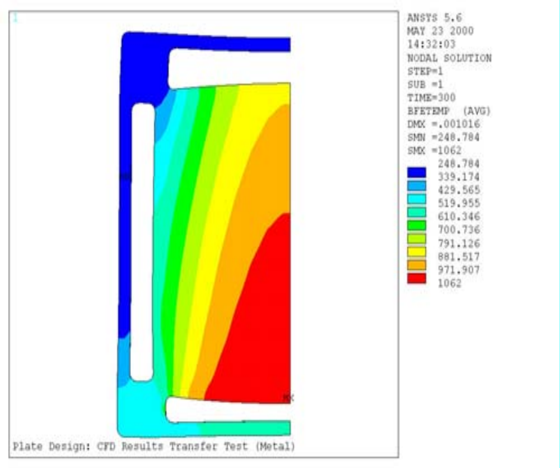
Item Description	Time, minutes to Bulk T=700°C	Maximum delta-T in stack, °C
<u>100 Degree C Delta-T Control Cases</u>		
Cathode only	40	263
Cathode+Anode	38	232
Cathode+A+Jet	40	166
<u>No Temperature Control Cases</u>		
Cathode only	15.7	800
Cathode+Anode	13.0	800
<u>400 Degree C Delta-T Control Cases</u>		
Cathode+Anode	15	688

- Ceramic gas channel spacers
- Thin (0.075mm) 430 SS interconnects
- 4.9 kg (small mass)
- Thin (230 µm) PEN

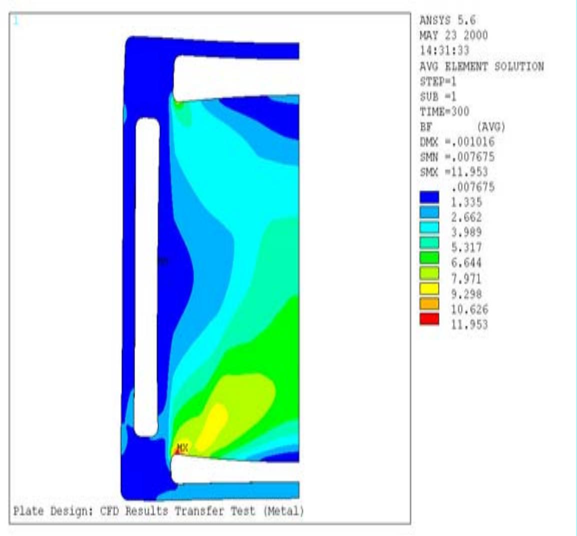
Thermal Stresses
Focus is on methodology



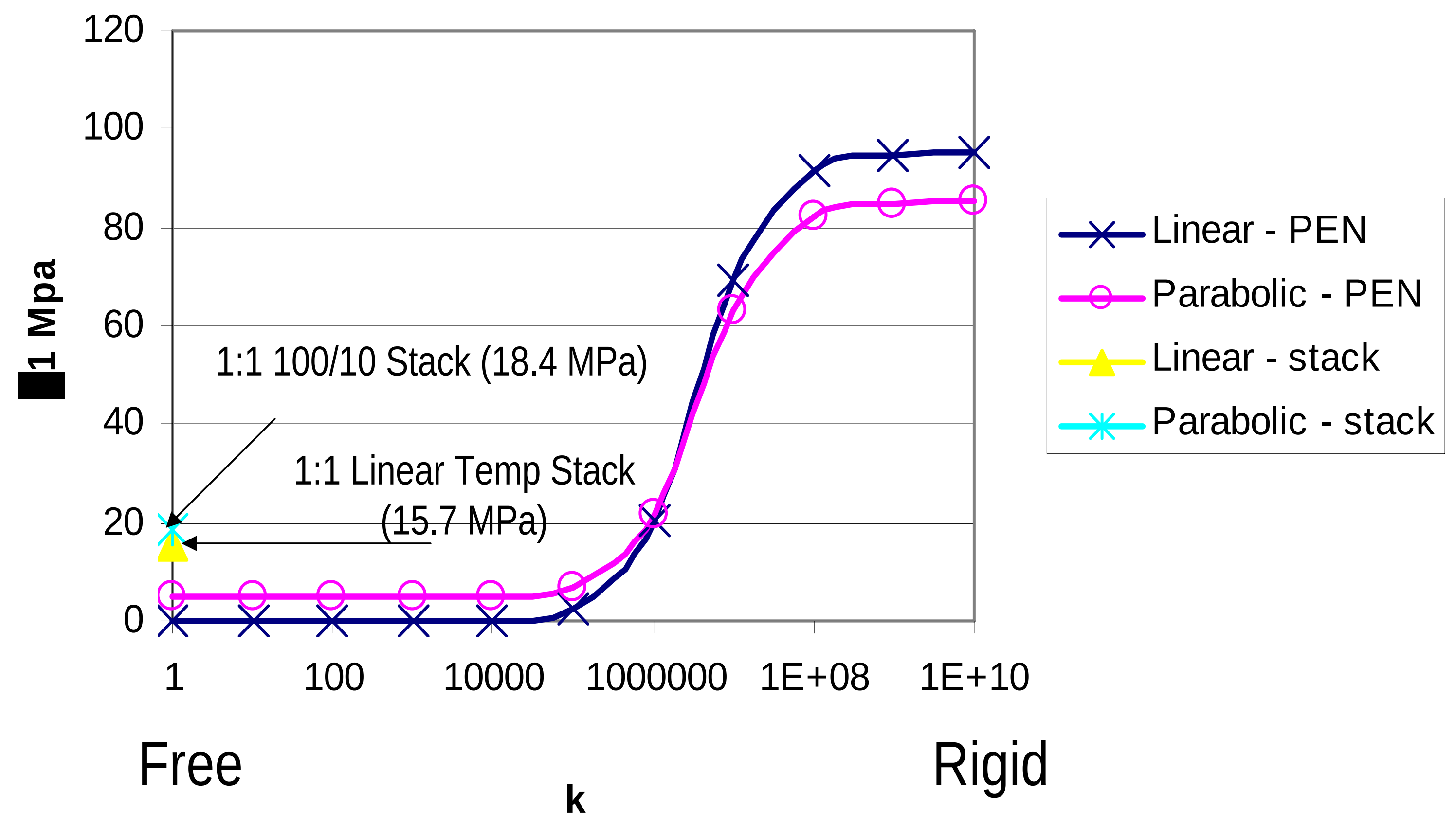
Apply CFD temperature results (5 min)



Case	Heating Description	ΔT Control	Interconnect Equivalent Stress (Mpa)	PEN Principal Stress (Mpa)	Comments
1	Cathode	100	570	192	
4	Cathode + Anode + Jet	100	259	104	Marginal stress levels
7	Cathode	400	1250	462	
10	Cathode + Anode + Jet	400	1070	319	



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



The linear profile does help the stresses in the stack design,

but not nearly as much as the unconstrained PEN model suggests.

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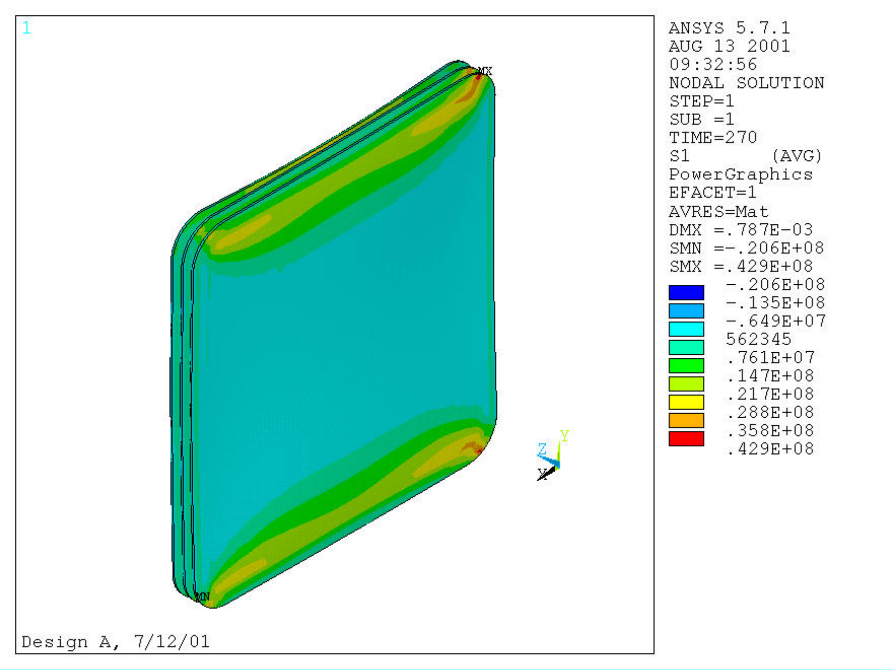
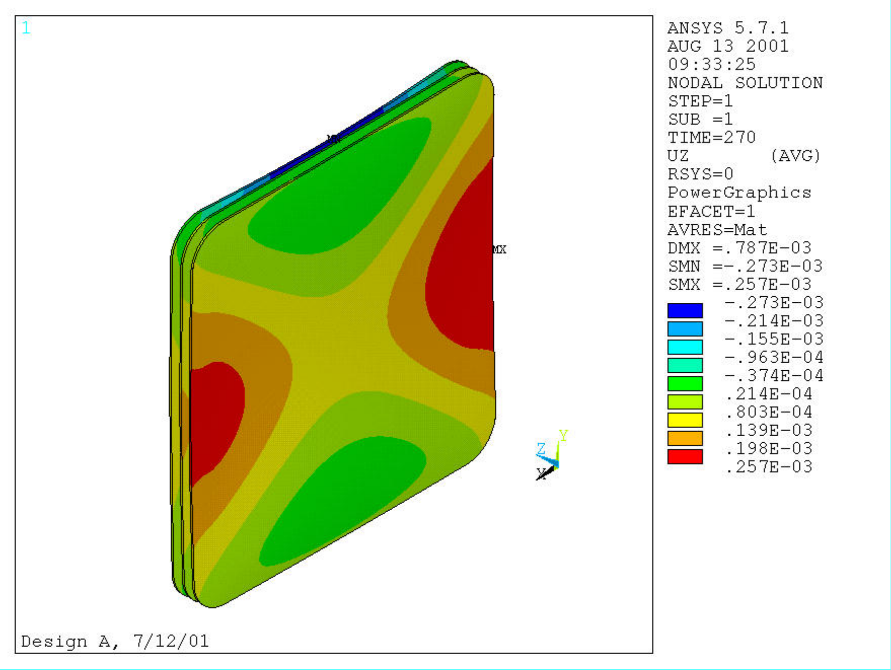
Structural Modeling – Layered PEN



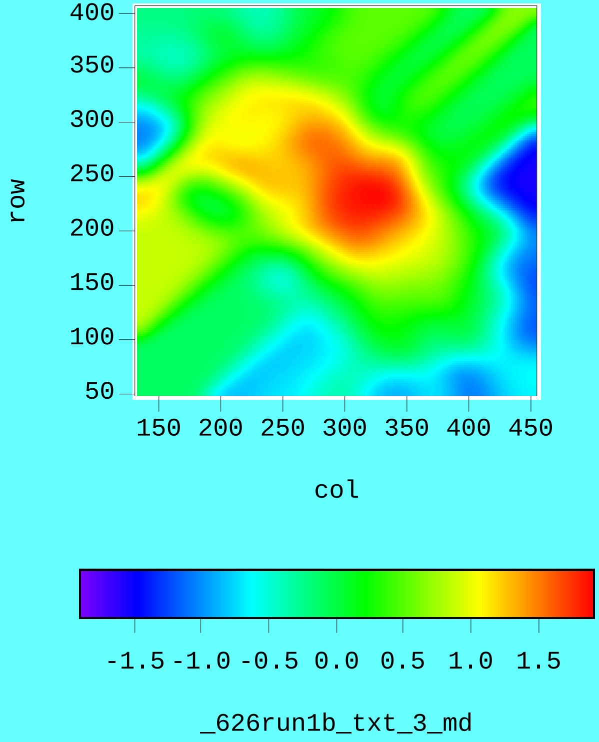
Anode principal stress (Pa)

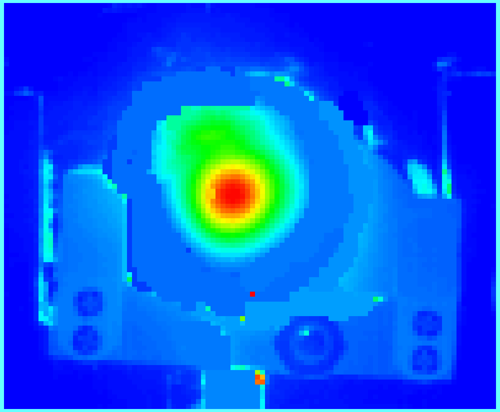


PEN out-of-plane deflection

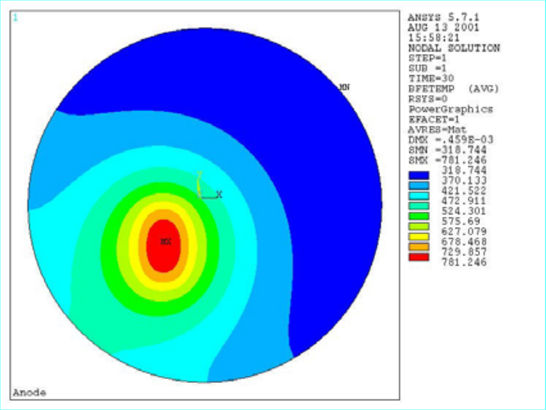
Experimental Validation of Structural Modeling

- Thermal stress failure validation





Infra-red images



Modeling results – good agreement based on 67 MPa tensile strength

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Summary

- Current emphasis is on:
  - Development of validated tools for steady state operation.
  - Establishing mechanical requirement for stack components.
- Future emphasis will be on:
  - Enhancement of continuum level electrochemistry models and steady state parametric studies.
  - Micro-structural level electrochemistry to address internal reformation
  - Predictive models for strength and life
  - Material properties and model correlation/validation.

Additional Slides

Model Setup

Fuel Flow: 1x10^{-5} moles/sec/cm^2, times 10x8.96 cm^2 (8.96x10^{-4} moles/sec)

- Composition: 50% H_2, 3% H_2O, 1% CO, 1% CO_2, and 45% N_2.
- Velocity through active region (average), 2.4 m/s

Air Flow: O_2 flow = 5 Stoicks that of H_2 in fuel … $H_2 + 1/2O_2 \Rightarrow H_2O$

H_2 in fuel = 4.48x10^{-4} moles/sec

O_2 in air => 1.12x10^{-3} moles/sec

- Composition: 21% O_2, 79% N_2
- Flow directed through active region by use of PM model behind manifolds
- Velocity through active region averages ~3 m/s

Temperatures: Initial = 1023 K, Inflow Boundaries maintained at 1023 K

Walls: Adiabatic

Model Setup (continued)

Approach:

- Impose range of cell voltages for identical boundary conditions

  Basic cases:

  1. 0.723 Volts => medium current and fuel utilization
  2. 0.594 Volts => high current and fuel utilization
  3. 0.900 Volts => low current and fuel utilization

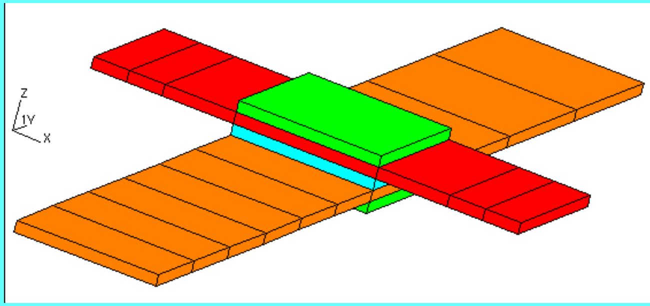
- Run cases in transient mode until steady solution is reached.

- Use STAR-EC calculated Temperature and Current in Spread sheet to compare results.

Model Results - "Mini Stack" - Case 1

Case 1: (0.723 Volts), T=1046K (733C), I=0.4195 A/cm2

	--- STAR-EC -----		SpreadSheet
Specie	masf	molef	molef
H_2	0.03161	0.287	0.283
H_2O	0.2442	0.2467	0.247
CO	0.01839	0.0119	0.0102
CO_2	0.01912	7.90E-3	9.94E-3
N_2		0.446	0.45
Heat Generation		0.2443	0.221 W/cm2
Cell voltage			0.761
Fuel Utilization			42.6%



Model Results - "Mini Stack" - Case 2

Case 2: (0.549 Volts), T=1072K (799C), I=0.647 A/cm2

	-------- STAR-EC -------------		SpreadSheet
Specie	masf	molef	molef
H_2	0.0178	0.178	0.169
H_2O	0.3239	0.3593	0.361
CO	0.0119	8.45E-3	5.93E-3
CO_2	0.0249	0.0113	0.0142
N_2	0.6215	0.443	0.45
Heat Generation		0.4622	0.412 W/cm2
Cell voltage			0.653
Fuel Utilization			65.7%

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Model Results - "Mini Stack" - Case 3

Case 3: (0.900 Volts), T=1026K (753C), I=0.1458 A/cm2

	-------- STAR-EC -------------		SpreadSheet
Specie	masf	molef	molef
H2	0.05251	0.421	0.412
H2O	0.1245	0.111	0.111
CO	0.0275	0.0157	0.0152
CO2	0.0115	4.20E-3	4.86E-3
N2	0.784	0.449	0.45
Heat Generation		0.0583	0.0543 W/cm2
Cell voltage			0.919
Fuel Utilization			14.8%

Model Results - "1-Cell Stack" (14x14cm) - Case 2

Case 2: (0.594 Volts), T=1215K (942C), I=0.844 A/cm2

	--- STAR-EC -----		SpreadShe
Specie	masf	molef	molef
H2	4.67E-3	0.0518	0.0690
H2O	0.3892	0.479	0.461
CO	3.39E-3	2.68E-3	3.75E-3
CO2	0.0344	0.0173	0.0163
N2	0.5683	0.449	0.45
Heat Generation		0.5705	0.565 W/c
Cell voltage			0.621
Fuel Utilization			85.7%