SECA Core Program – Recent Development of Modeling Activities at PNNL

MA Khaleel

Email: moe.khaleel@pnl.gov Phone (509) 375-2438

KP Recknagle, Z Lin, B Koeppel, S Moorehead, KI Johnson, N Nguygen, D Rector, and G Grant

Pacific Northwest National Laboratory

Richland, WA 99352

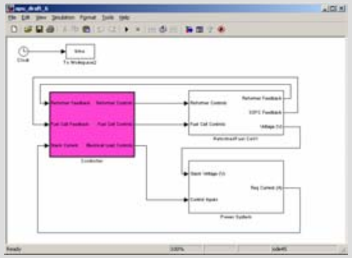
Travis Shultz

National Energy Technology Laboratory

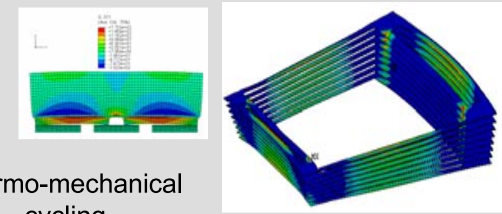
Integrated Modeling of Solid Oxide Fuel Cells

Consolidated Computational Modeling for SECA

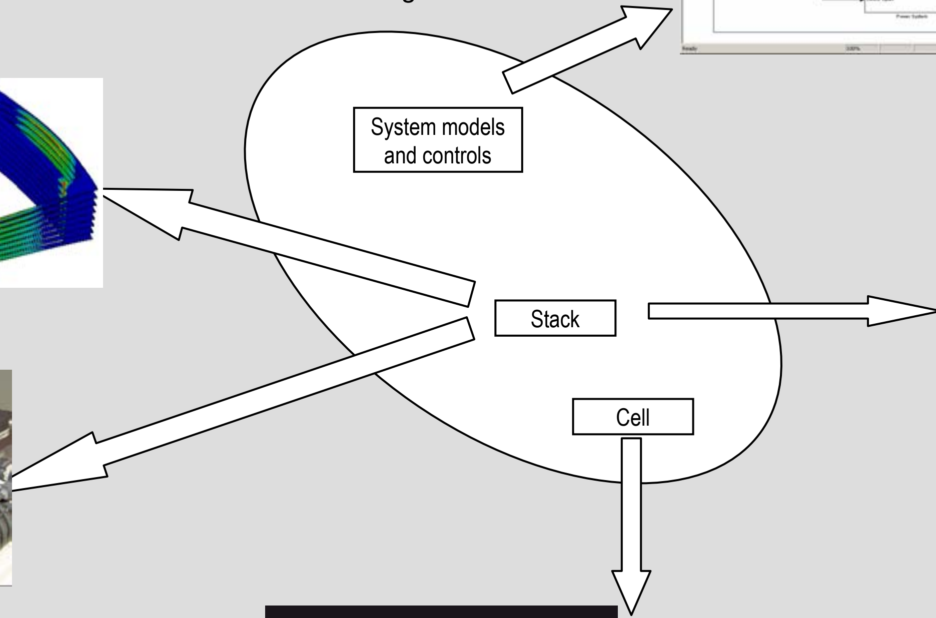
Training

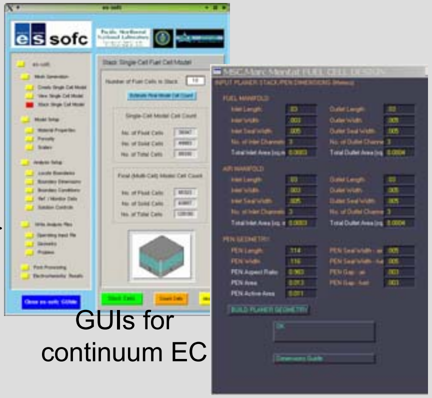


Controls and system dynamics



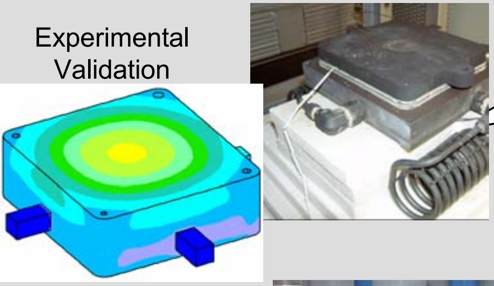
Thermo-mechanical cycling



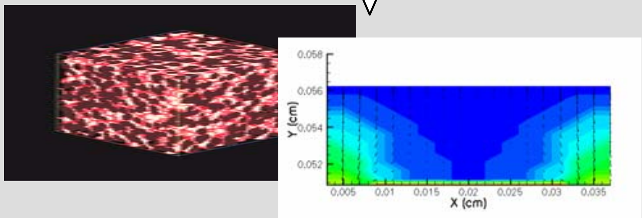


GUIs for continuum EC

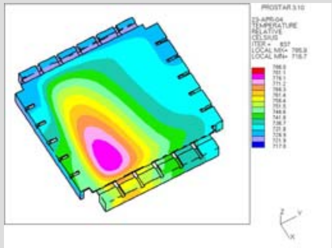
Experimental Validation



Experimental data for models (seals)



Microstructural electrochemistry
Fracture and Electrochemistry



On Cell Reforming

SECA Computational Resource

- **Provides SECA partners access to a high-performance computer for numerical analysis of fuel cell designs**
- **Commercial software packages and PNNL developed fuel cell sub-models are installed**
- **Platform for continued sub-model development and testing**
- **Silicon Graphics Inc**
  - 3700 Altix Server
  - Linux based
  - 24 Intel "Madison" CPUs
  - Expandable to 32 CPUs in current chassis
  - 64 GBytes RAM - Shared Memory - also greatly expandable
  - Binary compatibility with PNNL 128 CPU SGI computer

Offsite Access for SECA Industrial Team Members

- All offsite non-PNNL users will need to be hosted by a PNNL staff member
- Host will complete a Computer Access Request Form and Smartcart Request
- Offsite computers must have a Hardware Firewall (PNNL staff use Linksys), or a software Firewall (Hardware Firewall is preferred)
- Access is via:
  - VPN software for PC or Macintosh Platforms (provided by PNNL)
  - ssh (secure shell) for Unix/Linux
  - Users connect into PNNL using Smartcard (transient passwords in sync with PNNL base station)

Solid-State Energy Conversion Alliance (SECA) Modeling and Simulation Training Session Week of July 12, 2004

AGENDA

Day 1: Fluent
Morning : Introduction to Fluent Basics
CFD Modeling of SOFCs
Afternoon :Fluent on Newton Computer
Hands-on modeling activity

Day 2:MARC
Morning :Introduction to Marc basics MARC SOFC GU
Afternoon :MARC on Newton Computer
Hands-on modeling activities with MARC

Day 3: Star CD
Morning : Introduction to Star CD basics
ES-SOFC
Afternoon : Star CD on Newton
Hands-on CFD Modeling

Day 4: Miscellaneous SOFC Modeling
Controls, system modeling.
Structural modeling, stress, strain, thermal cycling
Materials database
Lattice Boltzman models

August 28th and 29th, 2003

Power Generation

FuelCell Energy

General Electric Company

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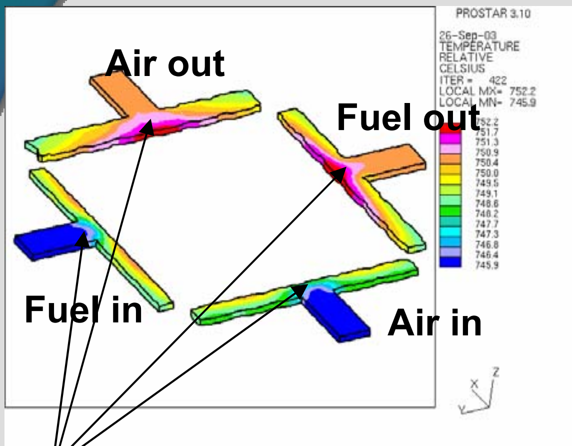
Georgia Institute of Technology

MSRI

Experimental Validation of Electrochemistry Models

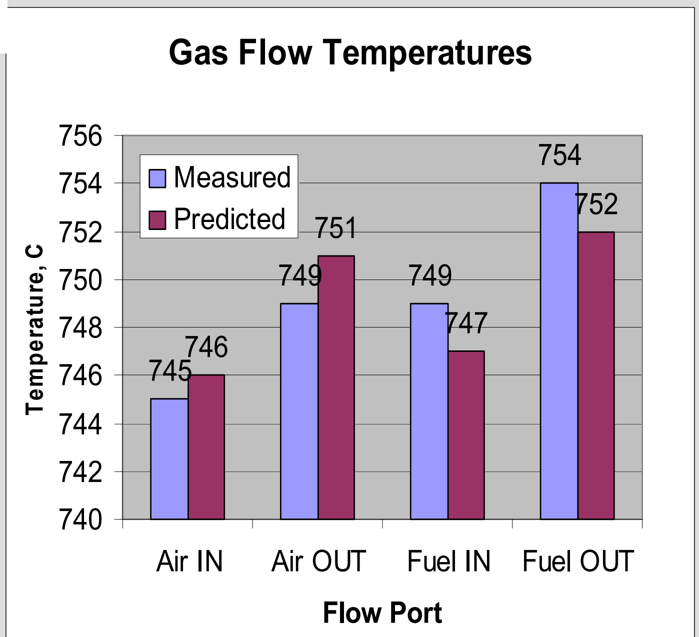


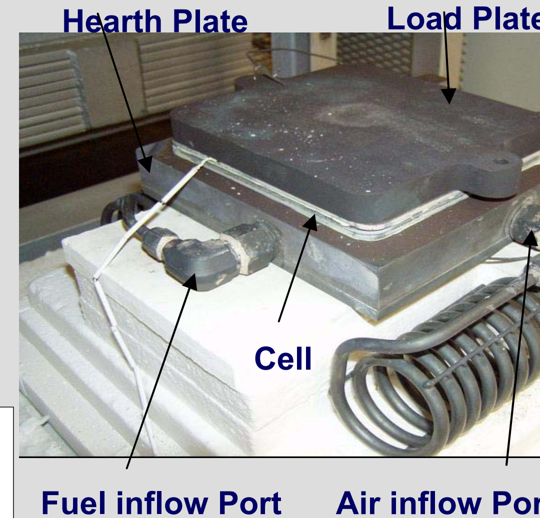
Temperature Plot: Subset of model containing air & fuel elements at level of ports

Fuel Utilization:
- Experiment: 20%   - Model: 22%
(current x 6.96 = cm3/min H2 burned)

Predicted Temperature - Inflow range: 744-749 C

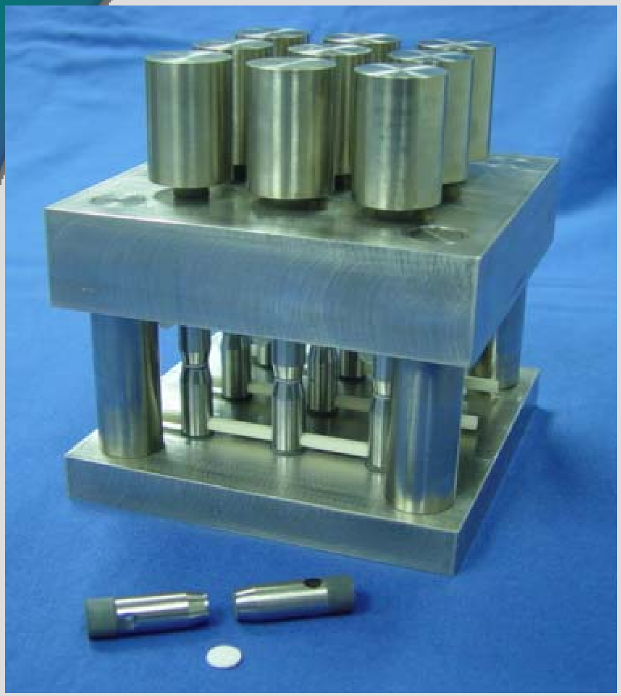
Outflow range: 747-752 C





Power & Fuel Utilization
Experimental: Power = 40 W (57 Amps @ 0.7 Volts), [20% fuel utilization]
***Predicted:* Power = 44 W (63 Amps @ 0.7 Volts), [22% fuel utilization]**

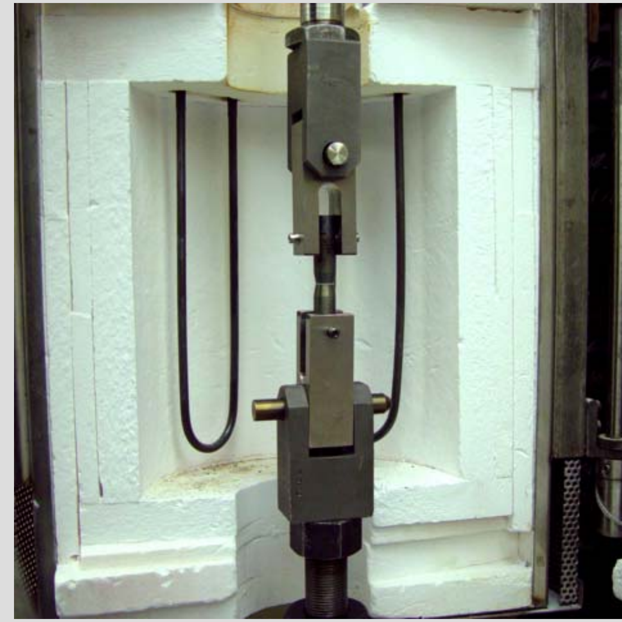
Tests on Joined Assemblies for Fundamental Properties



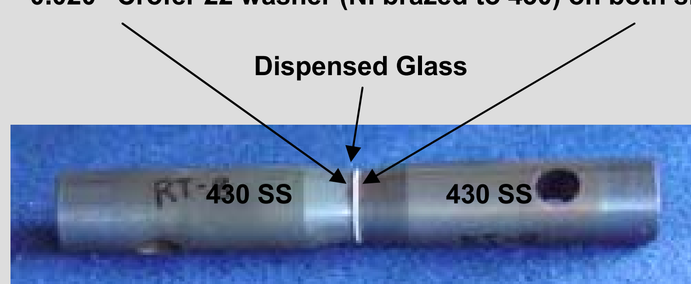
<u>Specimen fabrication fixture</u>

- **Inconel fixture allows for 9 specimen to be fabricated in one furnace run.**
- **Sealing surface pressures can be achieved from 1 to 20 psi through the use of different size weights.**
- **Fixture can be used to fabricate glass seals, bonded compliant seals, or braze joints to 1100 C**

Test modified from adhesives industry (ASTM D2095) to carefully handle seal alignment

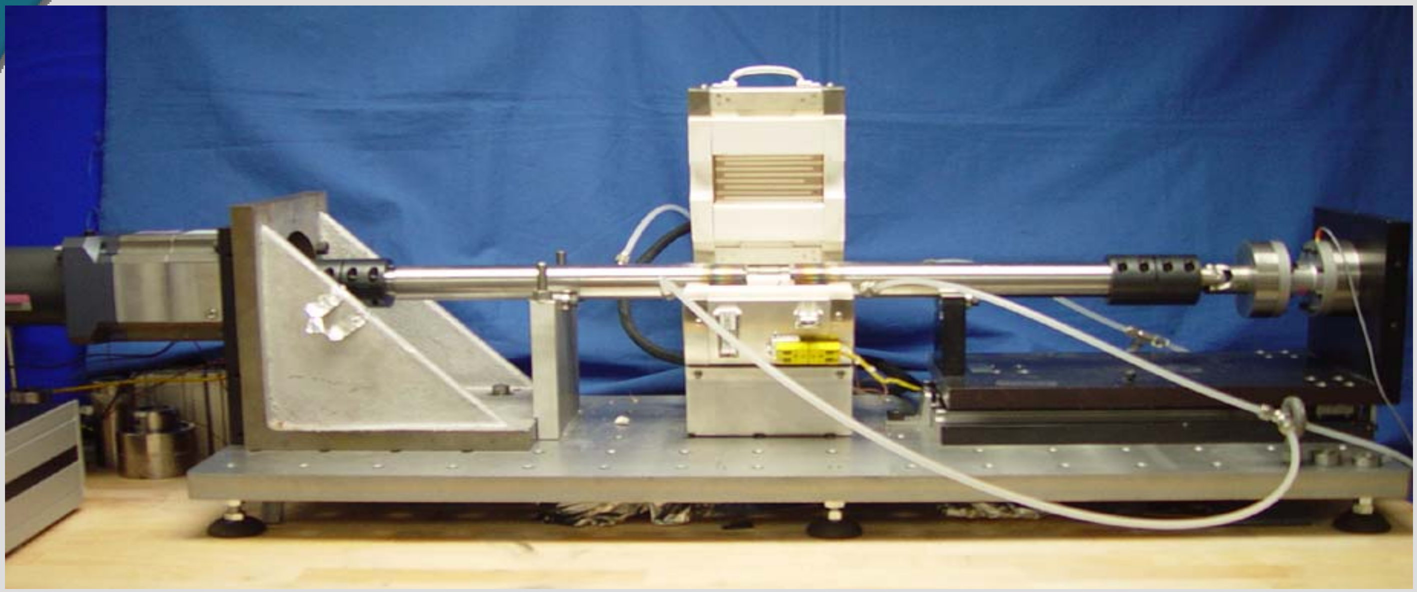


Sample construction



Shear Strength of the Interfaces and Seals

(modified ASTM F734-95 (2001)



Advantages of a torsion test for shear strength

- Torsion tests are among the 'cleanest' tests for pure shear.
- Bending and axial loads easy to control with misalignment couplers
- Test sample easy to machine from bar stock
- Test sample easy to align during seal cure and during testing
- No stress concentration issues normally seen in other types of flexural or shear testing methods
- Apparatus and specimen design easily adaptable to shear fatigue testing (esp. reverse shear)
- Multi-interface tests easy to assemble and align

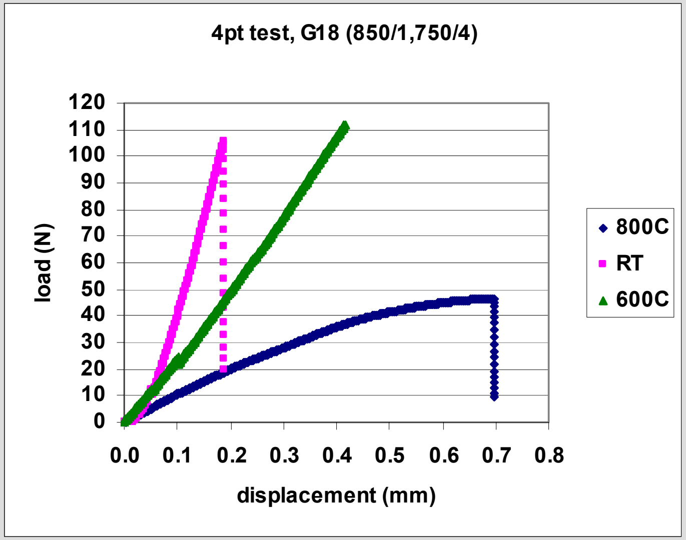
- **Device capable of testing up to 5000 in-lbs at temperatures up to 1200 C.**
- **Data acquisition records torque and angular displacement.**
- **Device can also apply axial load and torque simultaneously (strength, leak etc. of a loaded and cycled seal)**
- **New capability is currently being added for fuel gas or atmosphere introduced to inner cavity during test (inside the sealed annulus)**

Flexure Strength G18 glass

Four point bend testing

- Fully articulated SiC fixture
- Cross-head speed = 0.5 mm/min
- Sample size 3 mm x 4mm x 50 mm

- **Linear elastic up to 600C, Brittle failure**
- **Nonlinear (plastic deformation) at 800C**



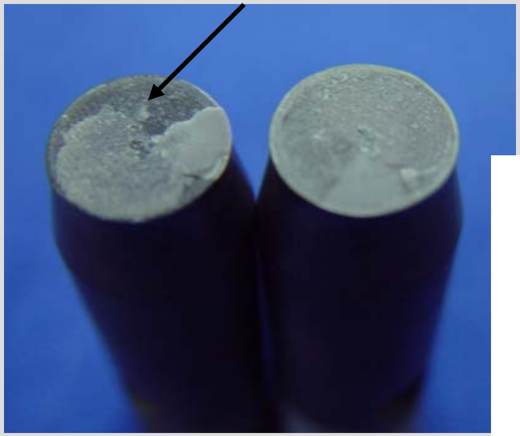
Flexure strength of G18 glass

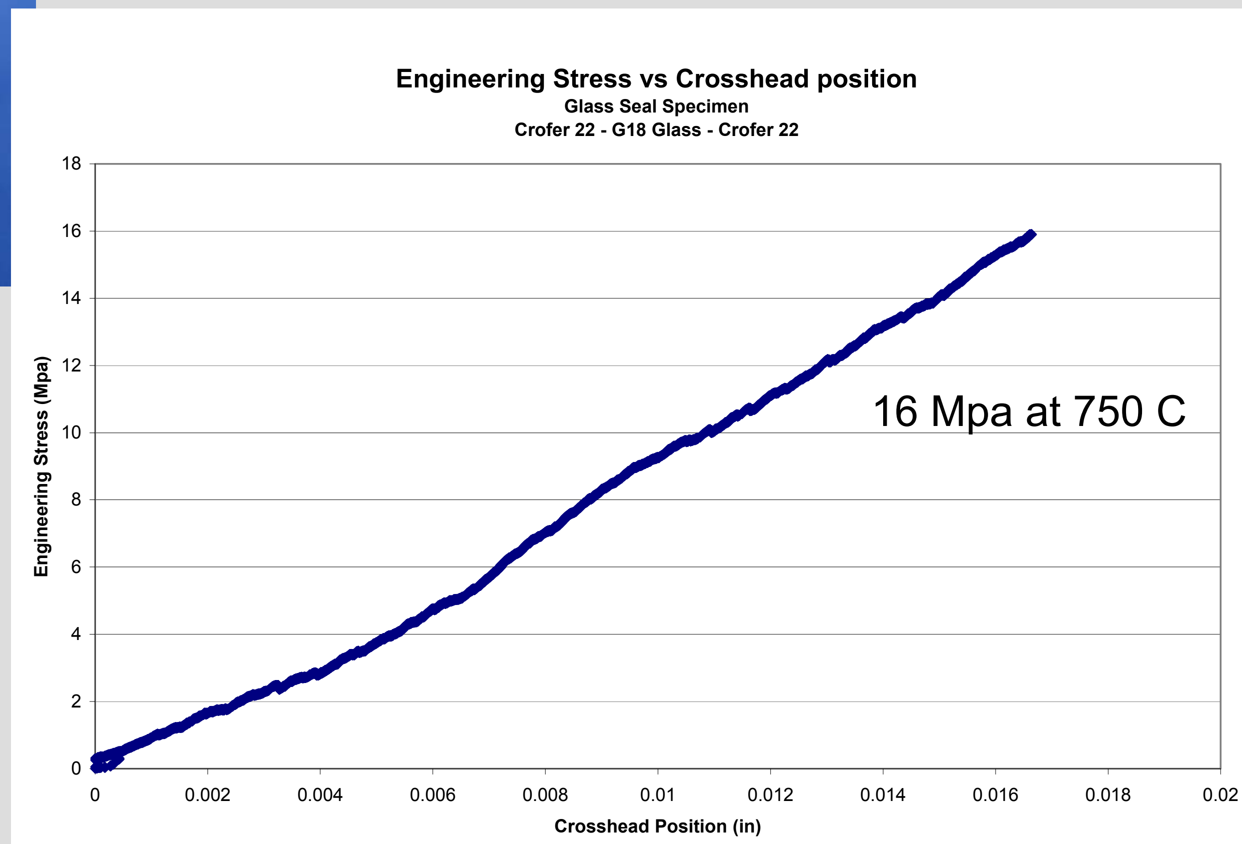
Average of 8 to 10 bend bars

	batch #1	stdev	batch #1	stdev
RT	84	14	80	10
600C			85	15
800C				

Seal Failure Data and Analysis

Higher strength samples show fracture that crosses the thickness of the glass seal indicating an interface strength higher than the seal material.

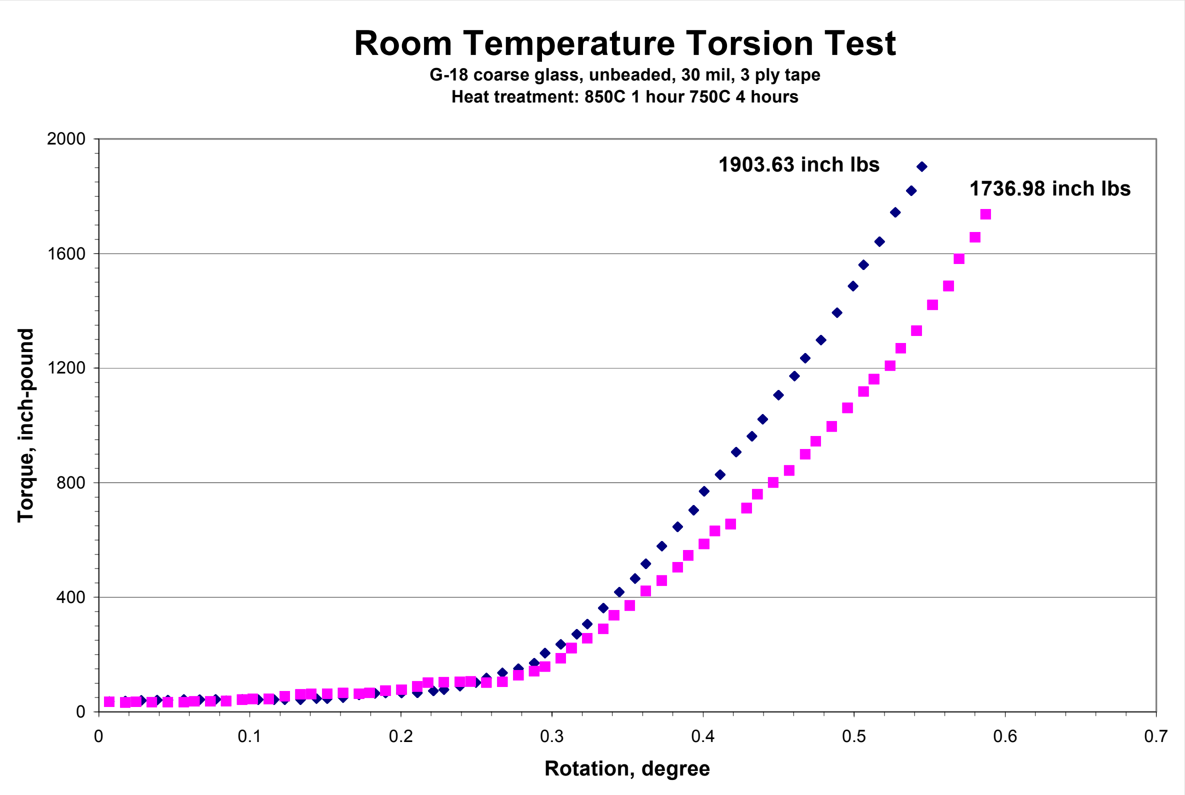


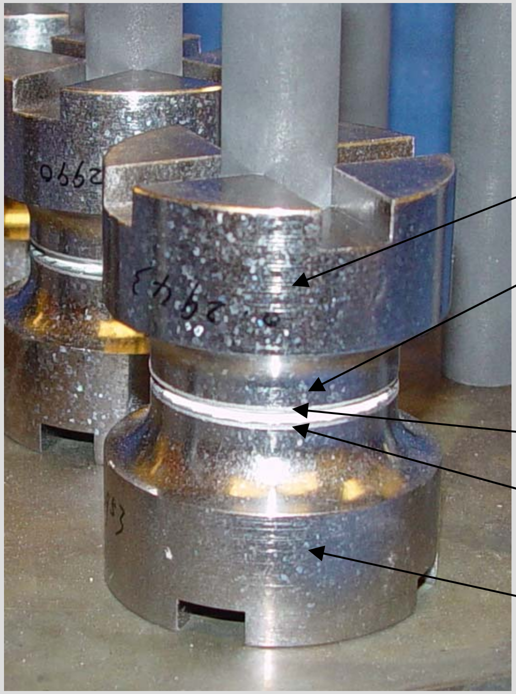


At low sealing pressures, seals show evidence of interface debonding during high temp testing. Most of the glass is left on one side of the test specimen

Torsion Testing

Room temperature shear strength of glass sealed assembly varies from 10 to 25 Mpa depending on fabrication process





Data currently being generated for Modeling

SOFC Materials

Fundamental Properties of G18 and other glasses

Fundamental Properties of braze metals, Cu-Ag and Ni based

Seal Failure Subtask

Glass seal (ferritic stainless to ferritic stainless)

- Pure Tension and Shear stress at failure (Room temp and 720 C)
- Biaxial Tension Torsion (Room temp and 720 C)
- Thermal cycling (720 C tension and shear after cycling)

Braze seal (ferritic stainless to ferritic stainless, and SS to YSZ)

- Pure Tension and Shear stress at failure (Room temp and 720 C)
- Biaxial Tension Torsion (Room temp and 720 C)
- Thermal cycling (Room temp and 720 C tension and shear after cycling)

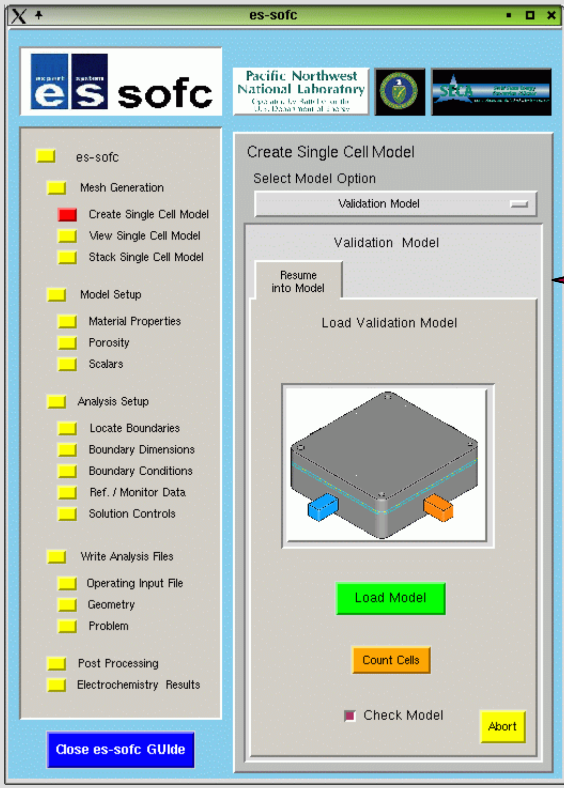
Bonded Compliant seal (ferritic stainless to YSZ)

- Pure Tension and Shear elastic response (Room temp and 720 C)
- Failure (tension) in annular configuration (Room temp and 720C)
- Elastic and failure response in square (frame) configuration
- Thermal cycling (Room temp and 720 C tension and shear after cycling)

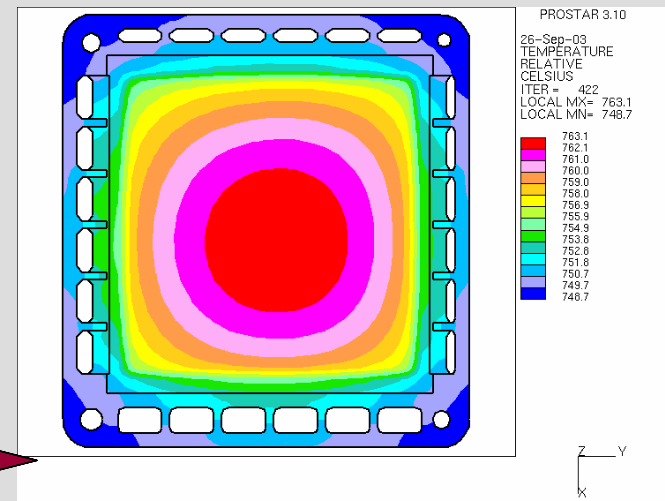
Compressive Mica seal

- Axial load to shear strength response (hot biaxial tension torsion)
- Leak rate with axial load in air and in fuel gas

ES-SOFC: Modeling Tool from Adapco in Collaboration with PNNL



Adapco has created an Expert System Modeling Tool named ES-SOFC based upon the PNNL CFD-Electrochemistry Calculation Methodology.

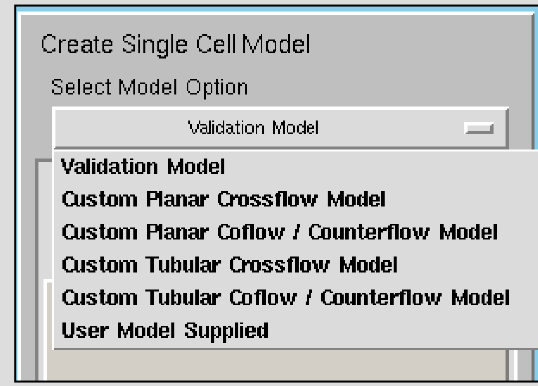


The GUI takes an SOFC model from Concept, to Mesh Creation, to Post-processing

PNNL Validation Case

ES-SOFC: Modeling Tool

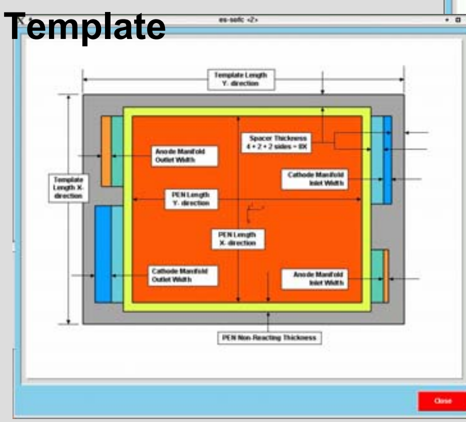
ES-SOFC is capable of creating and performing simulations of a number of flow configurations (soon to include tubular designs)

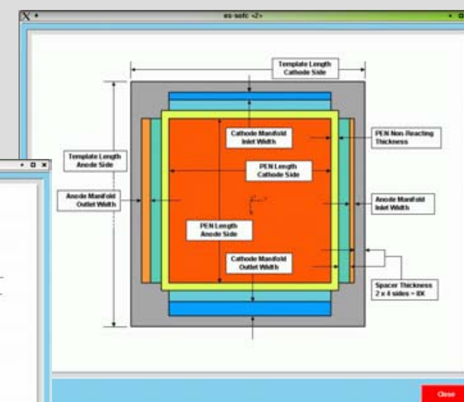


Users can easily create cells of their own dimensioning and flow configurations for parametric simulations.

Built-In Templates for custom cross-, co-, and counter-flow configurations make parametric studies easy for the user.

Co- and Counter-Flow Template



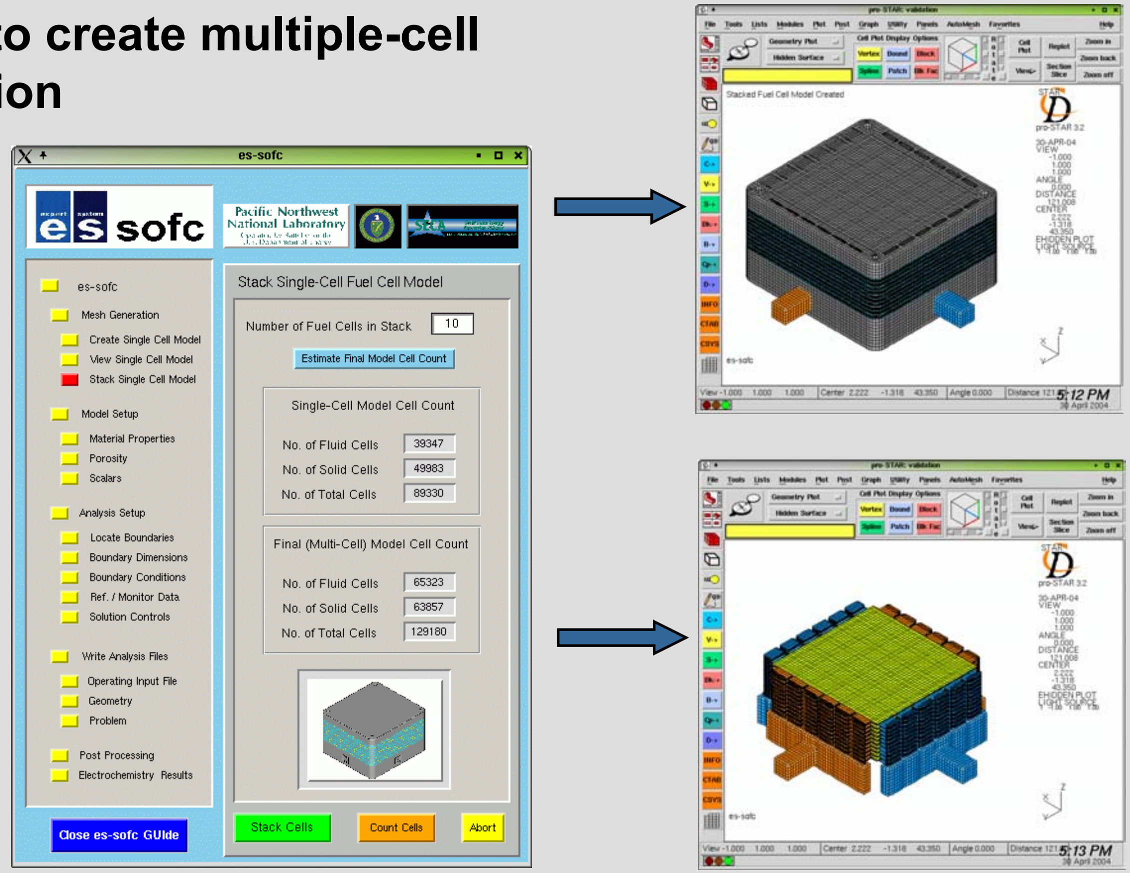


Cross-Flow Template

ES-SOFC: Modeling Tool

ES-SOFC has capability to create multiple-cell stack models for simulation

Adapco will be demonstrating the tool during this SECA workshop.



<u>ES-SOFC Status</u>

- **Development is complete**
- **Validation is nearly complete**
- **Reviewing and testing.**
- **Public release at end of May, 2004**

SOFC Modeling Tools from MSC Software in Collaboration with PNNL

Technical approach

- Commercial software: provide the shortest path to well developed, multi-function tools that are widely accessible. MARC is used for its multi-physics capability, numerical stability and efficiency due to its implicit algorithm
- EC module: in-house developed. a) Electrochemistry based on continuum level I-V relations: two models; b) Chemical reaction (water-gas shift, CH_4 internal reforming) based on equilibrium theory; c) Flow solution based upon assumption of laminar flow, taking conservation law into consideration; d) Distributed heat flux calculated according to respective mechanisms.
- GUI: a) effective way of generating stack model; b) flexibility in adjusting (geometry & operational) model parameters; c) user friendliness.
- PNNL worked with MSC on the development of GUI. GUI details will be presented by MSC

On-Cell Steam-Methane Reforming (SMR)

Motivation:

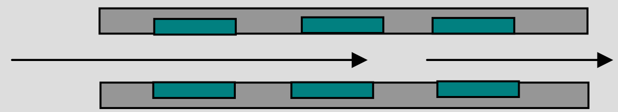
- Create an SOFC system that is:
  - More compact,
  - More efficient, and
  - More energetic

  than an SOFC operating without steam-methane reformation
- The possibility for this exists because:
  - SMR is an endothermic reaction
  - Electrochemical reactions are <u>exothermic</u>
  - When these reactions take place simultaneously, the possibility exists for <u>auto-thermal</u> cell operation
- Results of this would include:
  - Decreased size of External Reformer
  - & decreased cooling air demand (more compact)
  - Improved fuel delivery system (more efficient)
  - Fuel (H_2, and CO) enriched in process boosts power (more energetic & efficient)

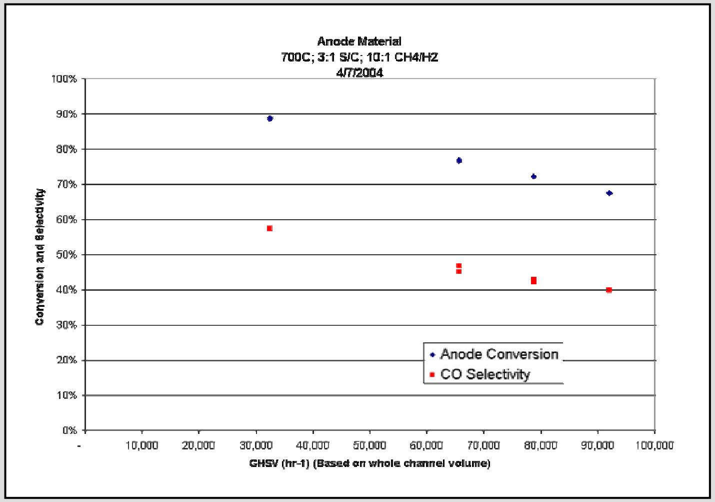
On-Cell Steam-Methane Reforming (SMR)

Experimental Testing to Determine:

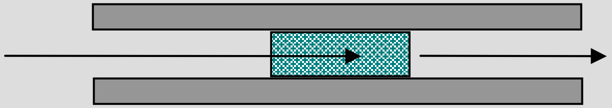
- Catalytic activity of the anode material (relative to other catalysts)
- Dependence of methane conversion rate on CH_4, H_2O, and CO_2.
- Tests with “flow-by” and “plug flow” differential reactors to determine:
  - The intrinsic kinetics of the methane conversion and
  - The final form of the model used in the codes
- The ongoing tests will also provide knowledge of fuel recycling effects on the SMR kinetics.



“flow-by”- like actual cell w/ flow gap



methane conversion and CO selectivity data from “flow-by” reactor tests at PNNL



“plug flow” – pore scale diffusion length

On-Cell Steam-Methane Reforming (SMR)

Kinetics model Presently Implemented:
(Subject to Modification by Experiment)

- Described by Langmuir-Hinshelwood surface reaction mechanism
- The constants (Ki) are equilibrium constants for the gas species adsorbed on the catalyst surface (anode):

$$r_{CH_4}(mol/s-m^2) = \frac{K_1 K_2 K_3 P_{CH_4} P_{H_2O}}{(1+K_2 P_{CH_4} + K_3 P_{H_2O})^2}$$

$$K_i = A_i \exp\left(\frac{-E_i}{RT}\right)$$

Equilibrium constants have Arrhenius temperature dependence

K1 is the overall rate constant for methane conversion
K2 is the equilibrium constant for CH4
K3 is the equilibrium constant for H2O

i	Ai	Ei
1	400-612, mol/s-m2,	49
2	3e-4 to 5e-4, 1/kPa,	-45
3	0.18 to 0.28, 1/kPa,	7

SMR involves two Reactions:

Steam Reformation-

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

Gas-Water Shift-

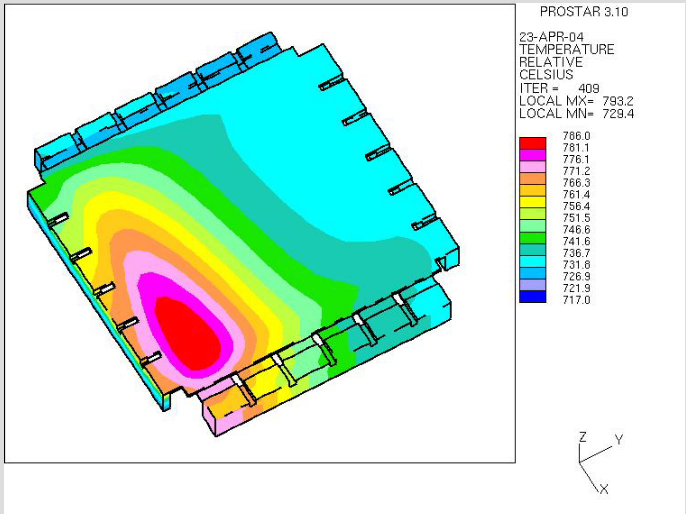
$$CO + H_2O \rightarrow H_2 + CO_2$$

Steam-Methane Reforming (SMR) EXAMPLE Cross-Flow Case

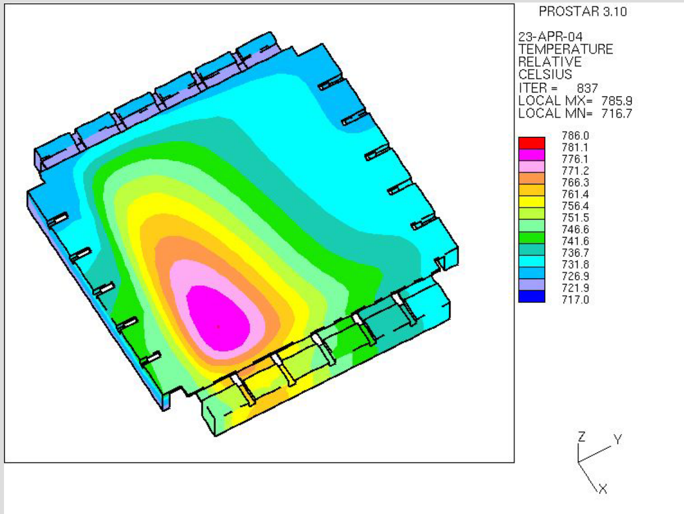
Effect of Steam-Methane Reformation:

- Maximum Cell Temperature Decreased
- Location of Tmax moved toward mid-cell
- Fuel Enriched by H2 and CO released
- Current/Power Density Increased by 50%

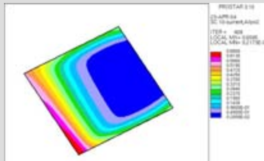
Problem Setup:
Mole fractions of inflow fuel:
H_2=0.3,
H_2O=0.1,
CH_4=0.05 (ie. S:C=2.0), CO,
CO_2=0.01, 0.01
Cell Voltage: 0.7 Volts
Average cell temperature: 750C



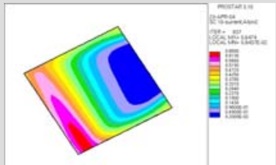
Temperature **without** SMR
(Range: 729-795C)



Temperature **with** SMR
(Range: 714-788C)



I = 0.18 A/cm2



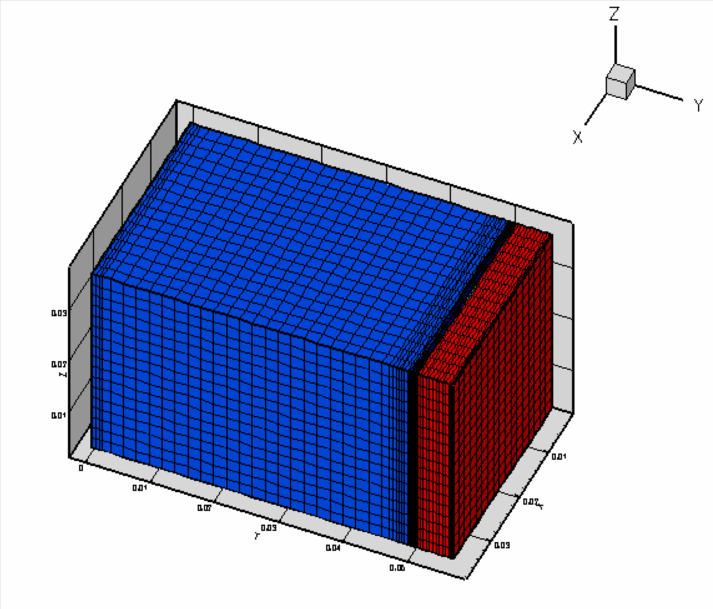
I = 0.27 A/cm2

Degradation Modeling

- Degradation report was completed.
- Fracture & leaks of PEN & seals is 1st priority.
- Flow diversion caused by I/C deformation is 2nd priority.
- Chemical degradation of electrical circuits & electrochemical interfaces is 3rd priority.

I-V Degradation Model

- A section of anode (500μm), electrolyte (8μm) and cathode (50μm) is subdivided into nodes ranging in size from 1-20 μm.
- Averaged transport properties are used to describe gas diffusion, electrical conductivity, vacancy transport, etc.
- A voltage is applied at the electrode surfaces and the integrated current is calculated



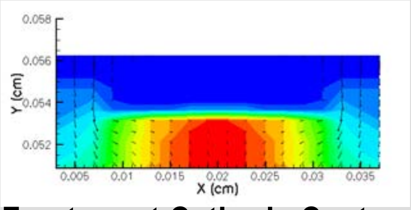
- Defects may be introduced, such as fractures, oxygen leaks and degraded transport properties due to sintering or changes in material composition
- We look at the effect of fracture location on I-V performance

I-V Degradation Model

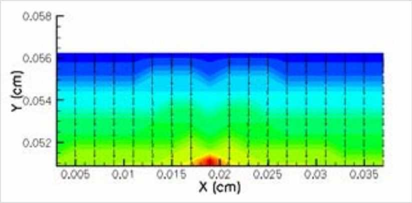
- Provides a detailed distribution of the following fields:
  - Gas concentrations (O_2, H_2, H_2O, CO, CO_2, CH_4)
  - Surface concentrations (O_2, H_2, H_2O)
  - Electron electrochemical potential (η_e)
  - Temperature
- Fracture Simulation Features
  - Boundary conditions at electrode surfaces include specified voltage and gas composition.
  - Kinetics for anode and cathode interfaces modeled using local Butler-Volmer expressions.
  - Circular thumbnail fractures are introduced which disrupt the electric current but have little effect on gas diffusion.

Fractures at Various Cathode Locations

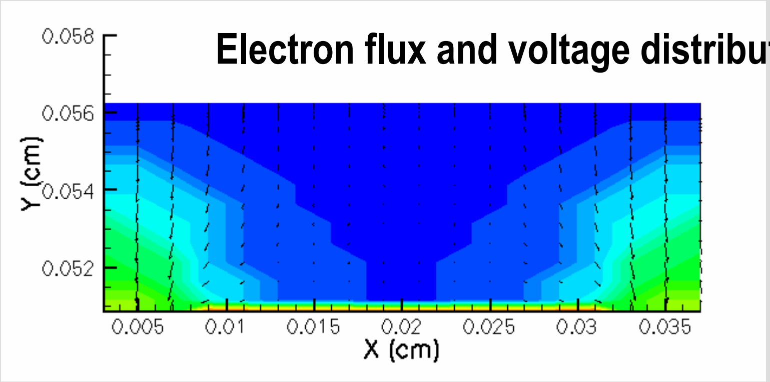
- Fractures that have minimal effect on performance (I-V Curve) are those that do not significantly destroy the current path:
  - At cathode center and parallel to electrolyte plane
  - Vertical fracture through cathode effectively bisecting the cathode
- Example of fracture having substantial effect:
  - The fracture located at electrolyte interface
  - The fracture starves the triple-phase region of current and significantly degrades cell performance



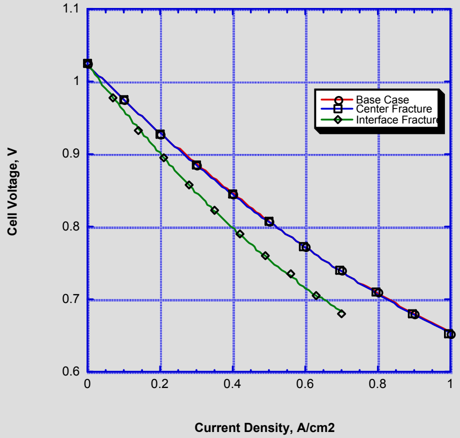
Fracture at Cathode Center



Vertical Fracture



Fracture at Electrolyte Interface



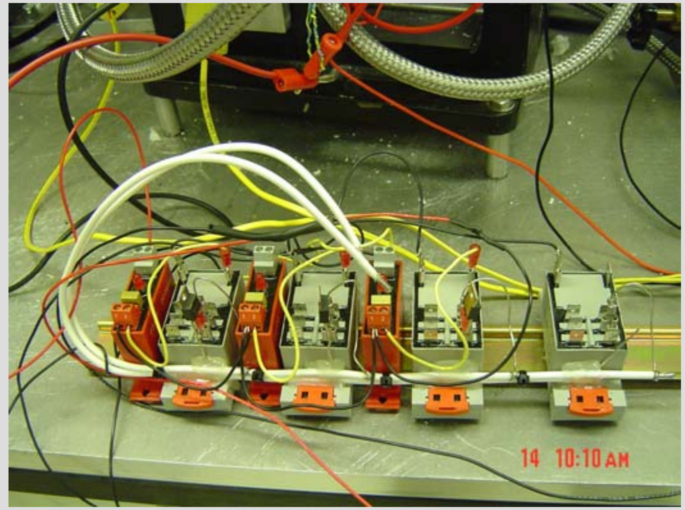
Controlling an SOFC

- To realize the efficiency and reliability goals set out by SECA, SOFCs must be effectively controlled.
- To design good control strategies, the dynamic or transient response of the SOFC must be known.
- For example, the transient voltage response to changing loads affects the control of fuel flow, load management and the control algorithms in the power conversion electronics.

- As a first step, we have investigated the transient voltage-current (V-I) relationship of an SOFC through experimental validation of a theoretical model.

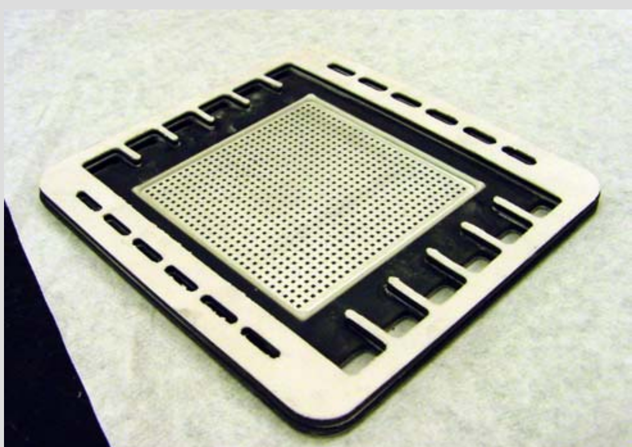
Stack Dynamic V-I Validation Experimental Setup

Fuel Cell Test Bed with Furnace, Fuel Source and Test Circuit

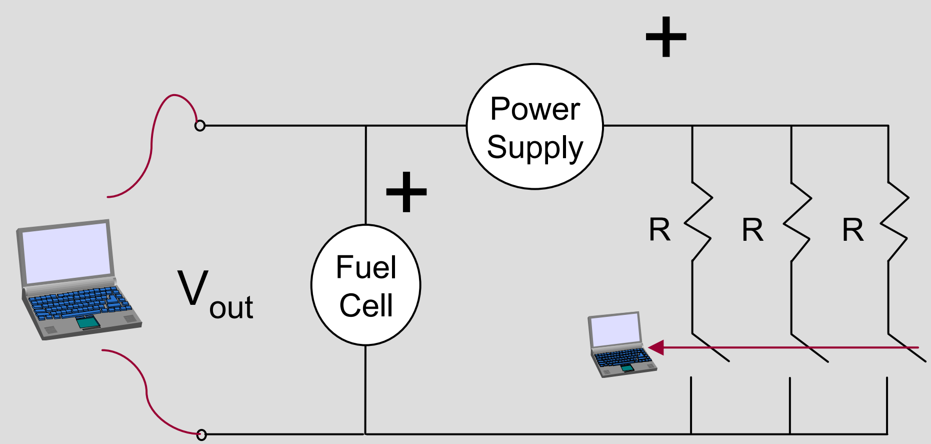


Close-up of test circuit

Cell with hearth plate



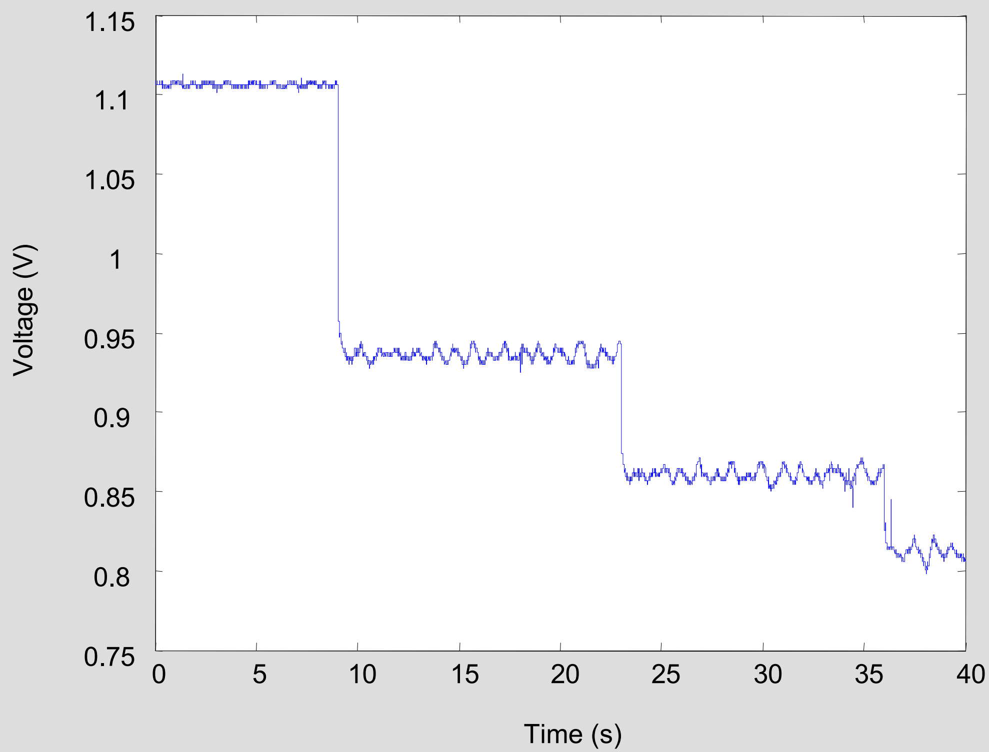
Cell before assembly



Experimental Circuit Schematic

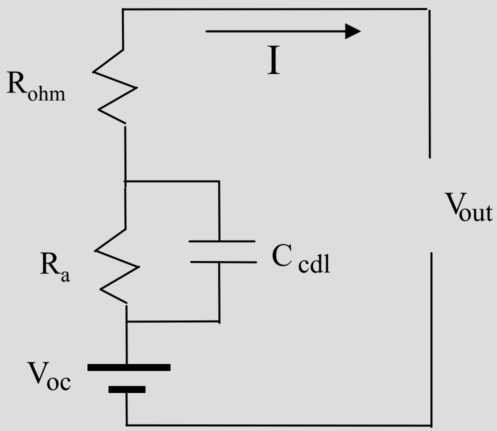
Raw Experimental Data

- Graph shows SOFC voltage versus time. The three load transitions are easily seen.



Dynamic V-I Relationship

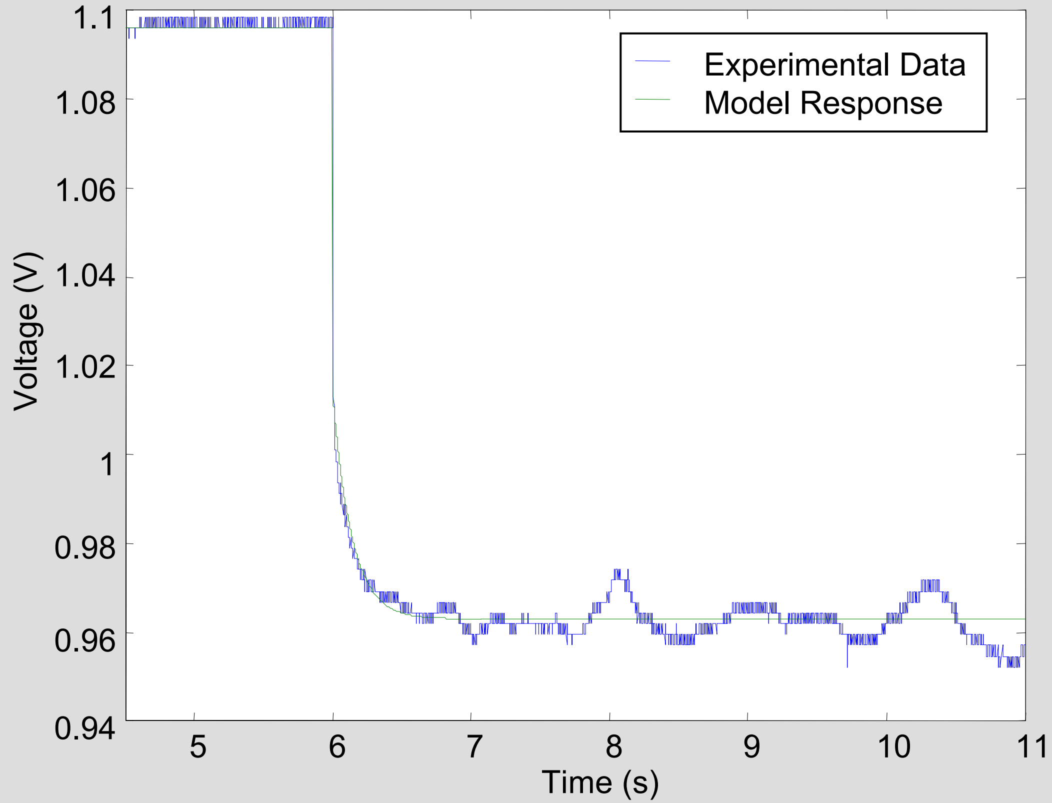
Theoretical Model



Transfer Function

$$\frac{V_{oc} - V_{out}(s)}{I(s)} = \frac{R_a R_{ohm} C_{cdl} \cdot s + R_a + R_{ohm}}{R_a C_{cdl} \cdot s + 1}$$

Voc = open circuit voltage
Rohm = ohmic resistance through cell
Ra = activation loss, caused by slowness of reaction
Ccdl = charge double layer effect capacitance
I = electrical current
s = Laplace variable



Future Modeling

- Validation of SOFC-ES and MSC-SOFC
- Further development of the SMR model including the incorporation of experimentation observations.
- Parametric studies to characterize effect of fracture on I-V relations using microstructural calculations.
- Degradation workshop and development of methodology for modeling degradation (combined with experiments)
- Seal property development
- Material data base development in collaboration with ORNL
- Release of dynamic system control software
- Incorporation of power electronic models in collboration with University of Illinois.
- Thermal cycling of stacks and leak predictions.