# Modeling Tools for Solid Oxide Fuel Cell Analysis

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# Motivation

- The SOFC is a complex system:
  - Multiple physical phenomena including fluid flow, electrochemistry, electric fields, thermal field, mechanical deformations, materials compatibility
  - Physical phenomena are tightly coupled (i.e. not independent)
  - High operating temperature range
- SOFC testing is very expensive:
  - Characterization of material properties, stability, and performance required
  - Stack fabrication, assembly, monitoring, and testing are time intensive
  - Only a minimal number of experimental tests can be done to validate long term technical performance targets (e.g. 10,000 hr)
- Modeling can be used for numerical design experiments:
  - Can simulate the multiple physical phenomena
  - Can be used repetitively to quickly evaluate the effects of design changes or explore the viable design space
  - Can be used in conjunction with testing to optimize performance
  - Can investigate long term behaviors

# Objectives & Approach

## Objectives

- Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid SOFC manufacturers with materials development
  - Allow SOFC manufacturers to numerically test changes in stack design to meet DOE technical targets
- Support industry teams use of modeling for SOFC development
- Provide technical basis for SOFC stack design

## Approach

- Multiphysics-based analysis tools coupled with experimental validation:
  - SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
- Targeted modeling tools for specific cell design challenges:
  - Reliable sealing
  - Interface and coating durability
  - Thermal management of large stacks
  - Cathode contact paste durability
- Collaboration with ORNL and ASME to establish a stack design approach based on modeling and experiments

# SOFC-MP: Capabilities and Features

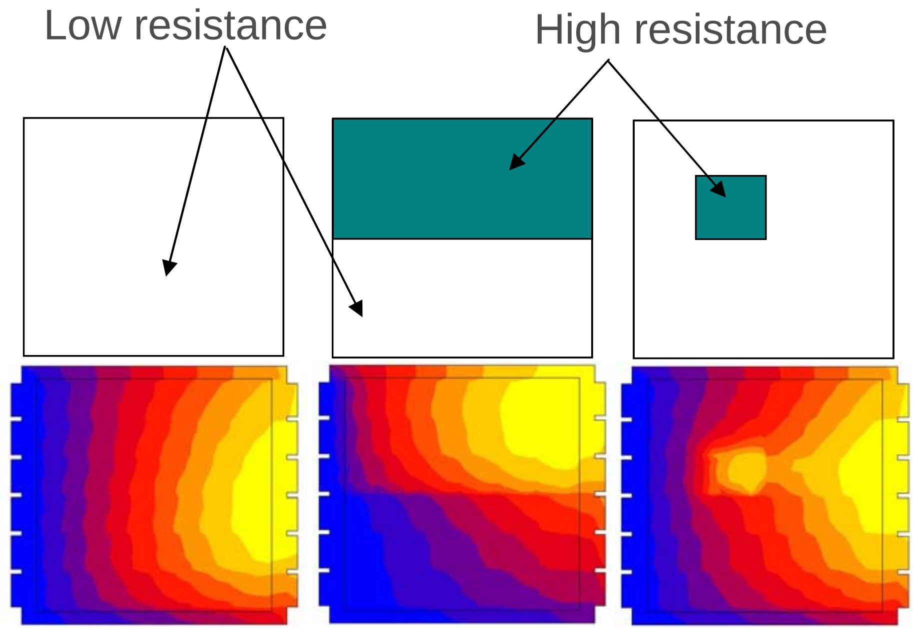
- SOFC-MP Capabilities
  - Coupled flow, EC, and thermal solutions
  - Reduced order models for computational efficiency
  - Contact of incompatible meshes
  - Single or multi-cell models
  - Generic fuel and oxidants
  - Operation at assigned voltage, current, or fuel utilization
  - Thermal and electrochemical results output for visualization

- Recent Improvements
  - Improved solution speed with use of AMG solver on PC
    - ~5hr for 8-cell stack model w/ 100k nodes and 200 solution iterations
  - Elimination of memory restrictions to solver larger problem sizes
    - Models w/ 100k nodes and 55k elements on PC w/ 4Gb memory
    - Port to Linux to take advantage of large shared memory
  - Improved energy balances with non-conformal meshes
  - Internal code restructuring to facilitate requested enhancements

# SOFC-MP: Capabilities and Features (cont'd)

- SOFC-MP has the ability to compile and utilize subroutines to customize the solution
- User subroutines can be defined to include proprietary EC models
  - Generic I-V relationship can be coded to compute voltage as a function of partial pressures, temperature, current, etc.
- User subroutines can be use to control the flow resistance
  - Different interconnect media can be simulated
  - $$\frac{dP}{dL} = RV$$

Oxidant Channel Flow Resistance

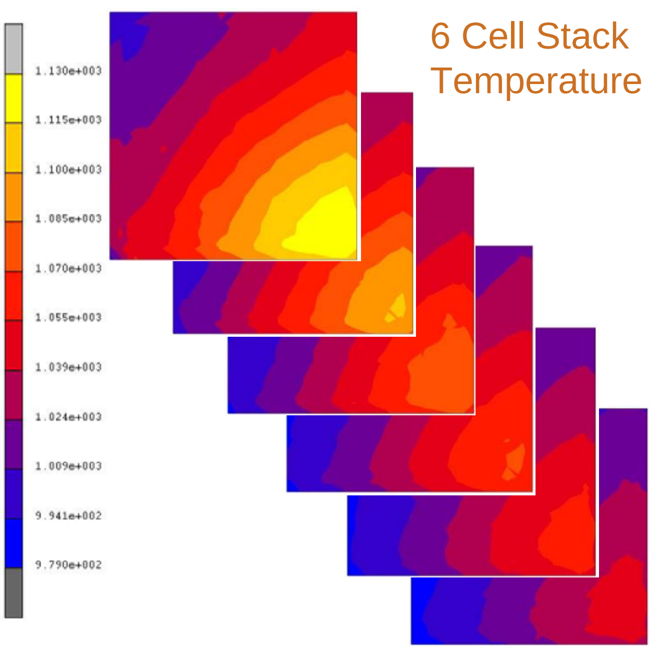


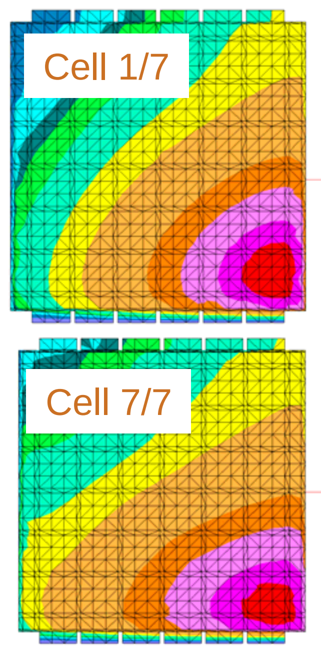

Resulting Oxidant Flow Field Temperature

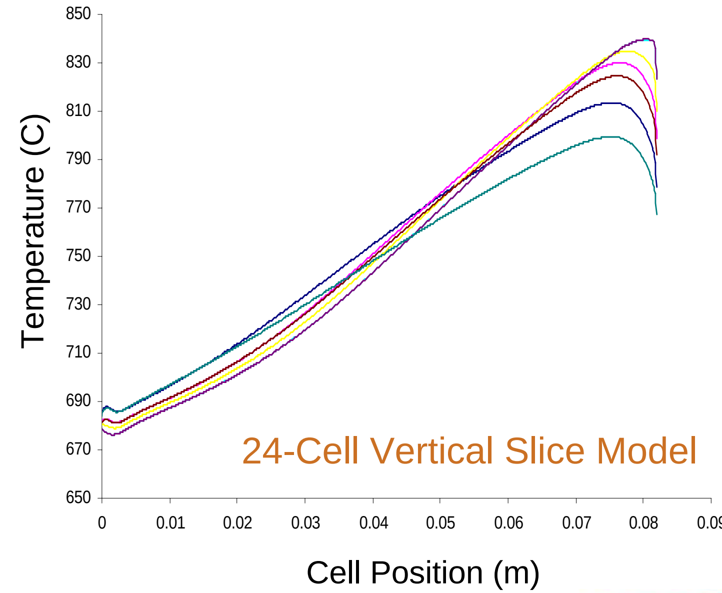
# SOFC-MP: Stack Modeling Examples

- Multi-cell 3D stacks using SOFC-MP
  - 6-cell: 360min for 76k nodes and 200 iterations
    - Stack ΔT: 160°C, Cell ΔT: 73-127°C
  - 7-cell: 18min for 88k nodes and 60 iterations
    - Faster due to low UF & different EC model
  - AMG solver: time/memory scales with # of cells

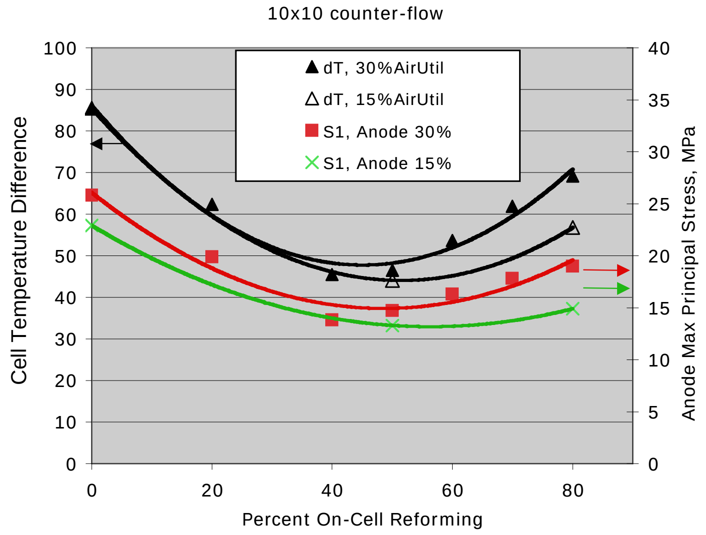
- 2D vertical stack slice model
  - Useful for co/counter-flow
  - Can be adjusted for cross-flow
  - Can handle internal reforming
  - Example: temperature profiles for various cells in 24-cell stack

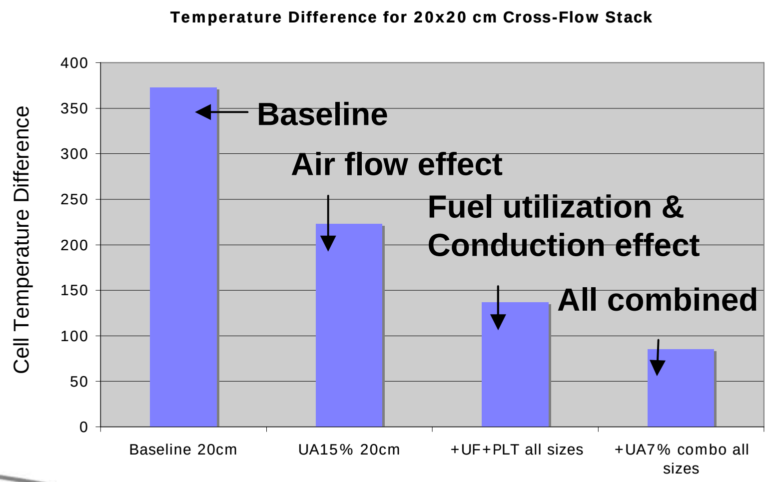


# Thermal Management: Internal Reforming



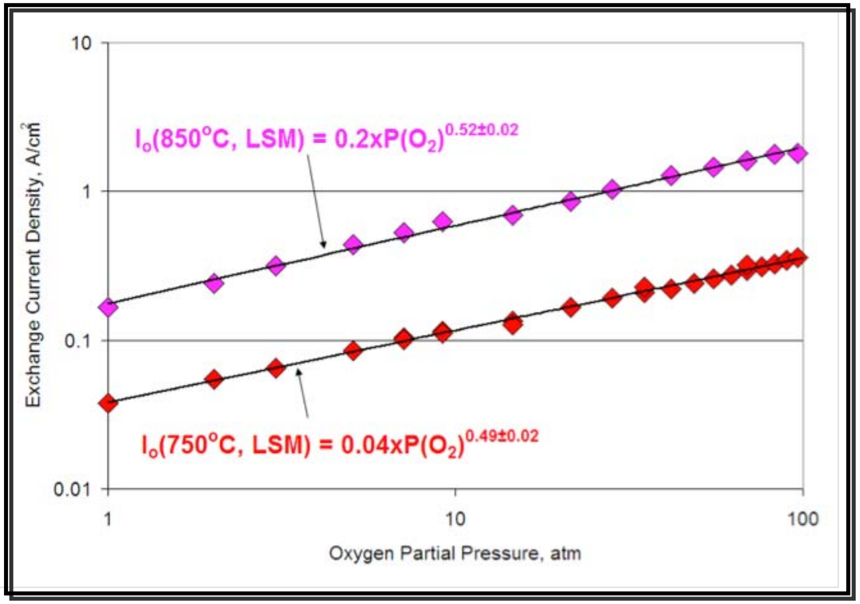




- Previous work demonstrated possible performance improvement by manipulation of the percent of reformation on-cell
  - Stack ΔT and component stress could be decreased depending upon methane content in fuel
- Separate work manipulated heat transfer and heat distribution within stack to optimize the operating condition and performance
  - Both the improved conduction, and decreased air (and fuel) utilizations decreased the stack ΔT
- Present study is a continuation of the manipulated heat transfer work to further optimize stack performance including:
  - Internal reforming
  - Pressurization

# Thermal Management: Pressurization

- Optimization of stack performance will also include the effect of pressurization:
  - The Nernst Potential correctly captures the pressure effect and requires no further examination
  - The Butler-Volmer equation describes the activation polarization $\eta_{act}$ related to the current ($j$) and the exchange current density ($j_o$). For the SOFC it can be written as:

$$\eta_{act,e} = \frac{RT}{\alpha F}\sinh^{-1}\left(\frac{j}{2j_0}\right)$$




  - Pederson's tests showed : $j_o = j_o(PO_2^{1/2})$
  - The exchange current density model was improved by adding the pressure dependence, and applied to both electrodes as:

$$j_0 = \beta \exp\left(\frac{-E_{act,e}}{RT}\right) PO_{2,e}^{\ \gamma}$$

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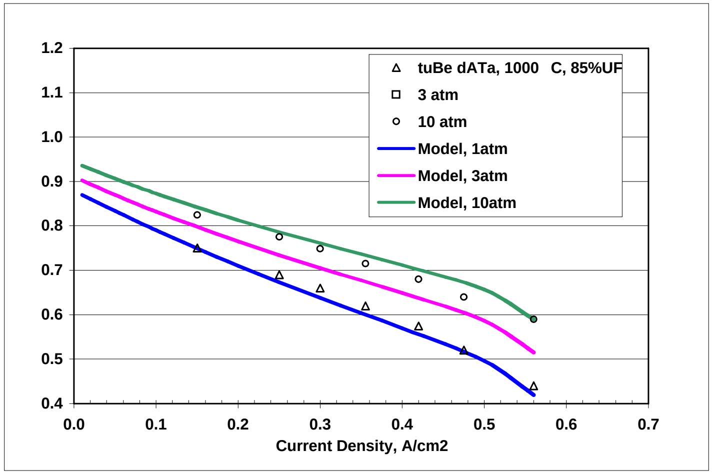
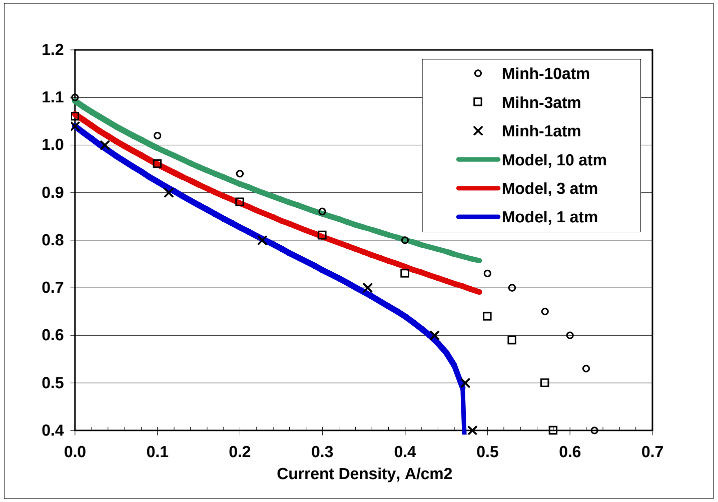
# Thermal Management: Pressurization (cont'd)

- Performance improvements:
  - Increased Nernst potential
  - Decreased activation polarization
  - Increased cell voltage and electrical power -> decreased heat load
  - Decreased Heat load leads to improved thermal performance




**Tubular SOFC data (Siemens), 89% $H_2$, 3% $H_2O$, running at 1, 3, and 10 atm at constant 85% UF**

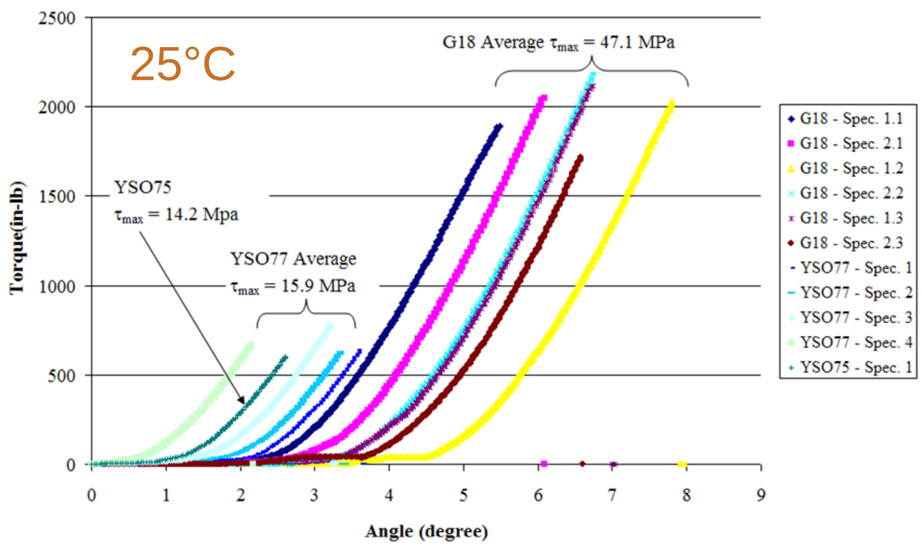
- Electrochemistry model with improved activation polarization properly characterizes the performance improvements for planar and tubular cells operating at elevated pressures

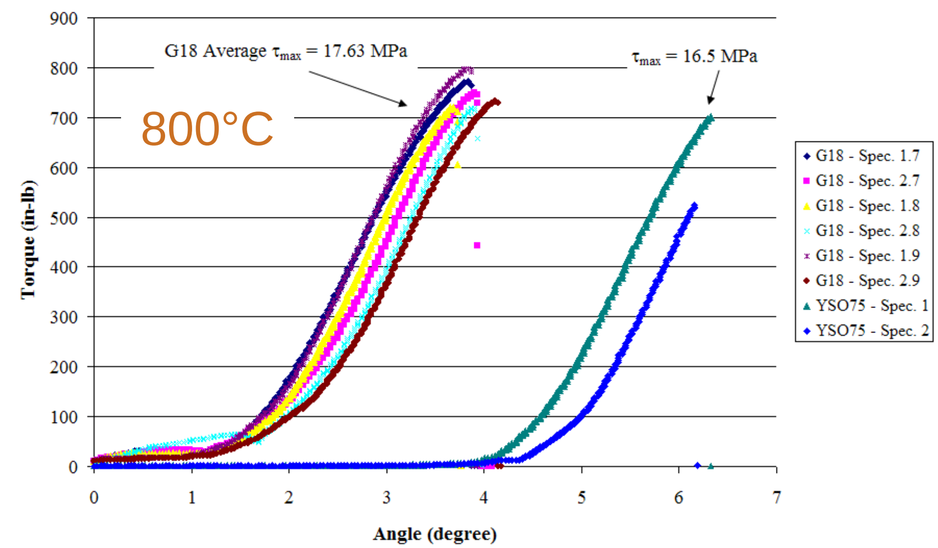



**Planar SOFC data (GE), 25% $H_2$, 3% $H_2O$, 72% $N_2$ running at 1, 3, and 10 atm**

# Seal Property Characterization

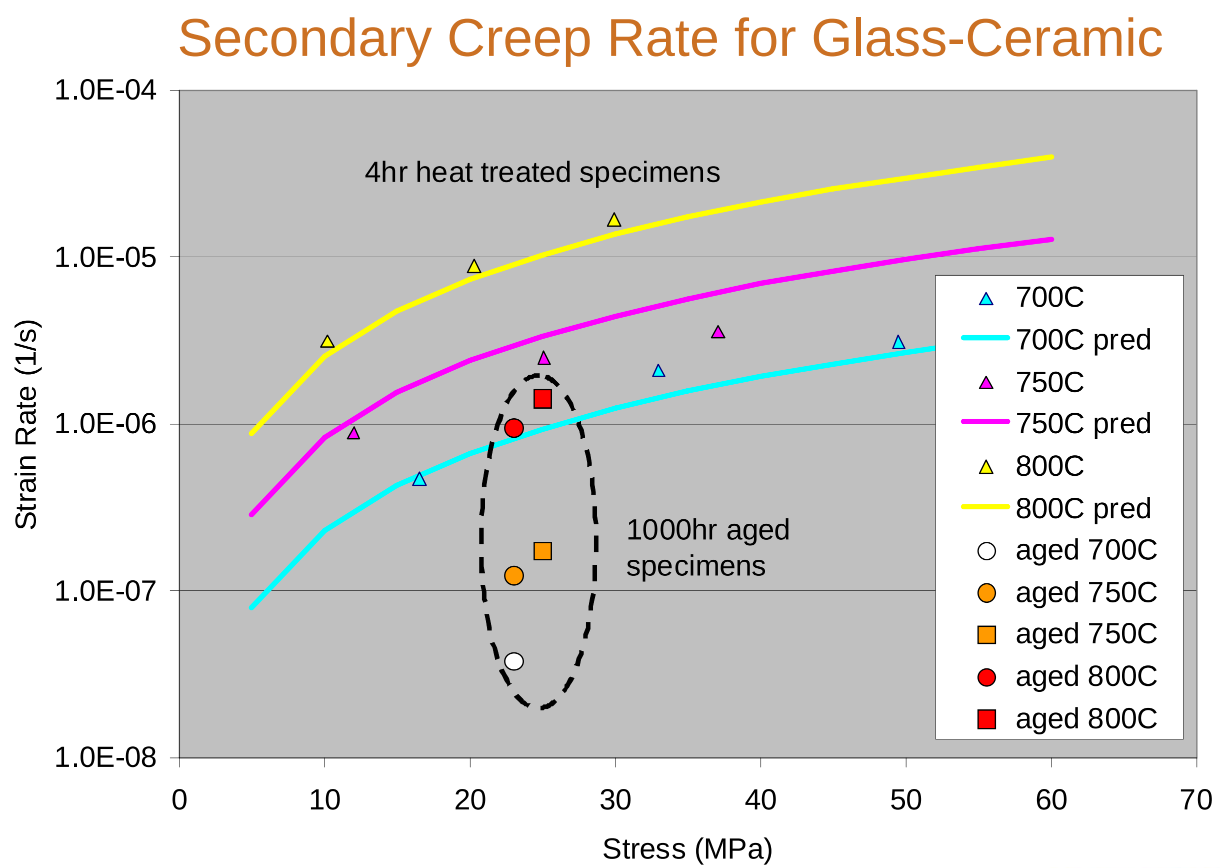
- Performed shear tests of refractory glass sealants at room and elevated temperatures
  - Compared to G18 glass-ceramic
- Results
  - Room temperature strength of refractory glass about 2/3 less
  - Elevated temperature strength comparable (~7% less)



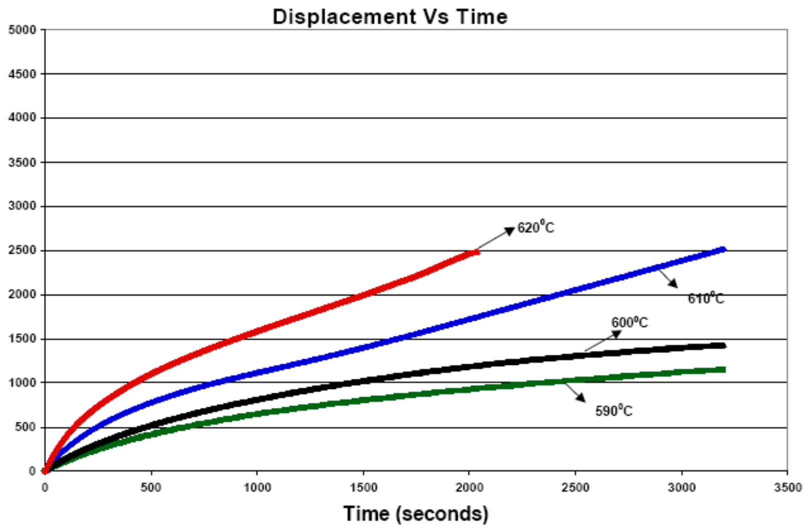
# Seal Property Characterization (cont'd)

- Performed creep experiments to quantify effect of aging on time-dependent response
- Creep rate an order of magnitude less after 1000hr devitrification
- Short-term seal creep expected to accommodate high stresses initially, but much slower creep after aging

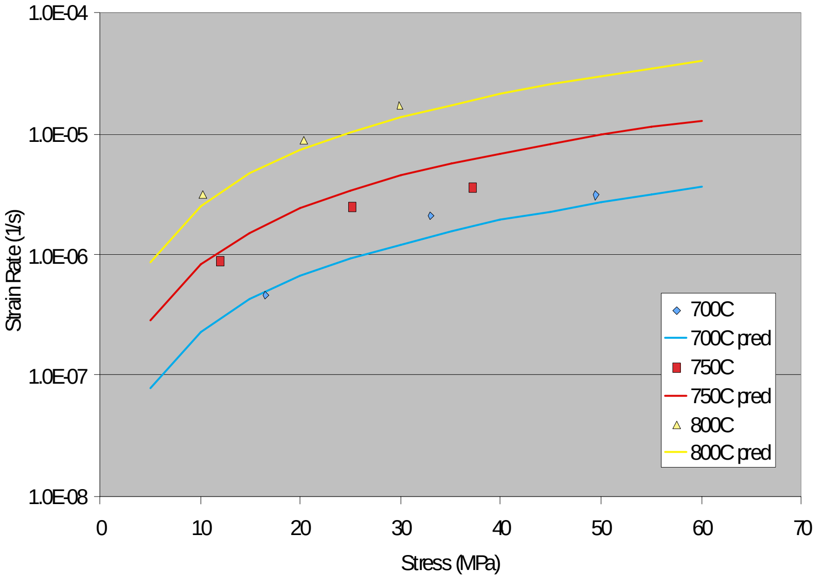


# Modeling of Different Seal Glasses

UC seal-healing glass




G18 glass-ceramic

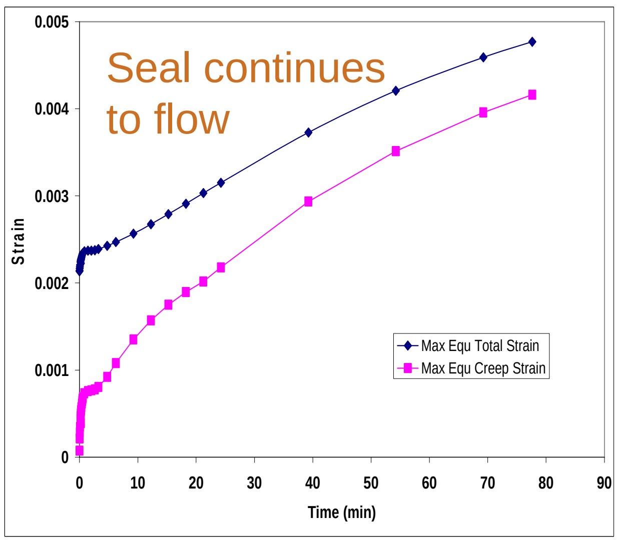


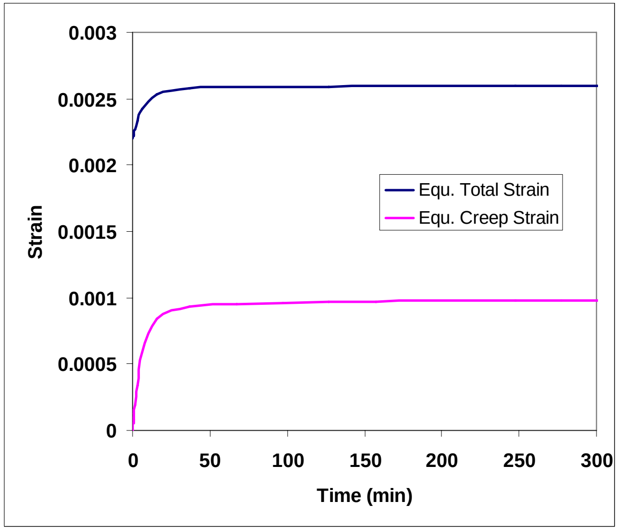

- Greatly different creep rates at 30 MPa applied stress
  - UC glass: 1.0e-3/s at 1000°K
  - G18 glass-ceramic: 1.0e-6/s at 973°K (700°C)

# Modeling of Different Seal Glasses (cont'd)

- For G18 glass-ceramic sealant, maximum equivalent total strain and creep strain keep constant after the initial creep stage:
  - no overflow of the glass ceramic seal materials will occur during the operation of SOFC stacks
- For UC self-healing glass seal, maximum equivalent total strain and creep strain keeps increasing after one hour operation:
  - Overflow of seal glass will occur, control block of total creep deformation is necessary during the desired SOFC operating duration

UC seal-healing glass



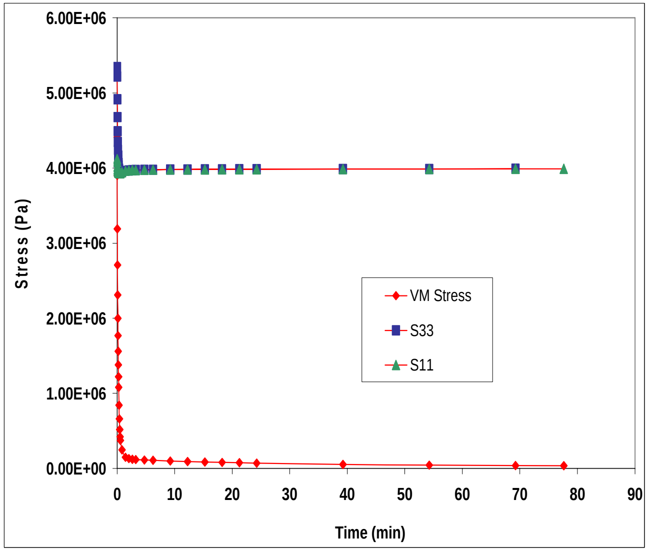



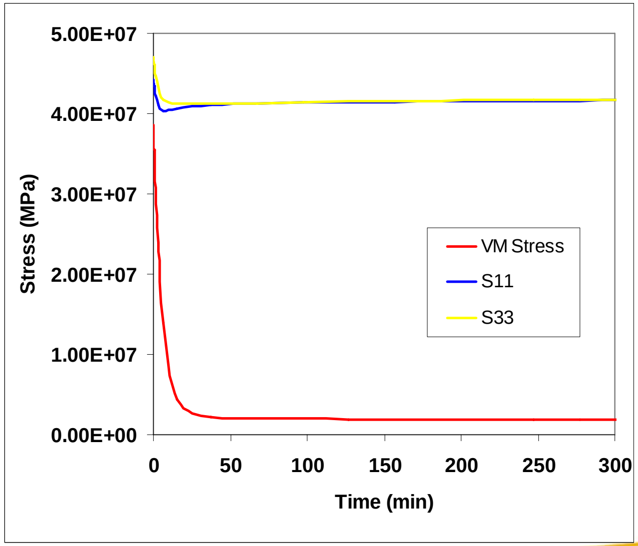

G18 glass-ceramic

# Modeling of Different Seal Glasses (cont'd)

- Maximum equivalent von Mises stress, maximum $\sigma_{11}$, and $\sigma_{33}$, for the PEN seal with the different glass sealants, respectively
- Stress results for both sealants possess similar trends
  - von Mises stress is released rapidly, and
  - normal stress $\sigma_{11}$, and $\sigma_{33}$ are constant after a small drop
- Time to release the shear/deviatoric stress for G18 is much longer than UC seal healing glass

UC seal-healing glass

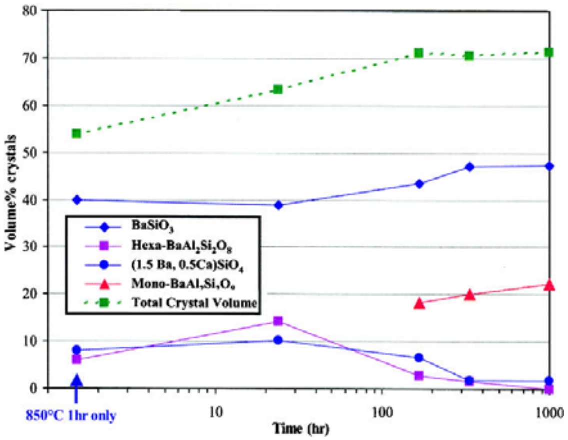


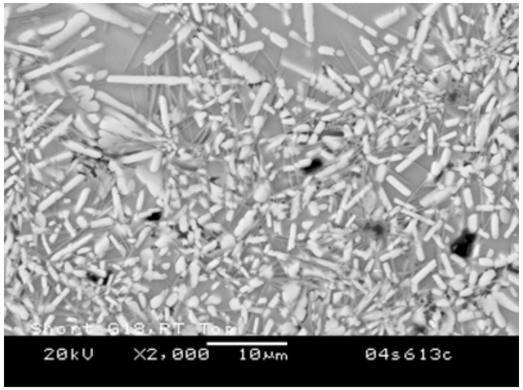

G18 glass-ceramic

# Aging/Self-Healing Behavior of G18

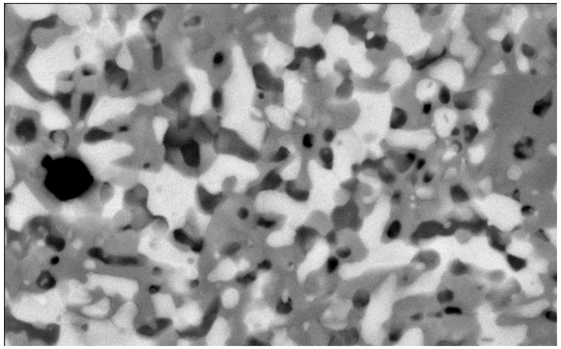
- Evolution of crystalline phase is time dependent




After sintering

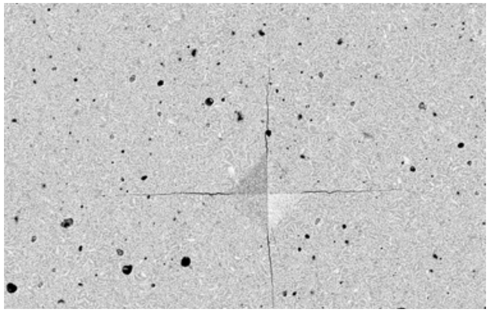



After 1000 h aging

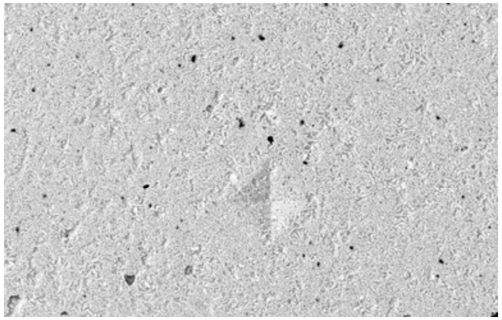


- Aging induced micro-voids in glass-ceramic

- Glass/ceramic displays possible self-healing behavior at high temperature



Typical Vickers impression



at 750$^o$C for half an hour

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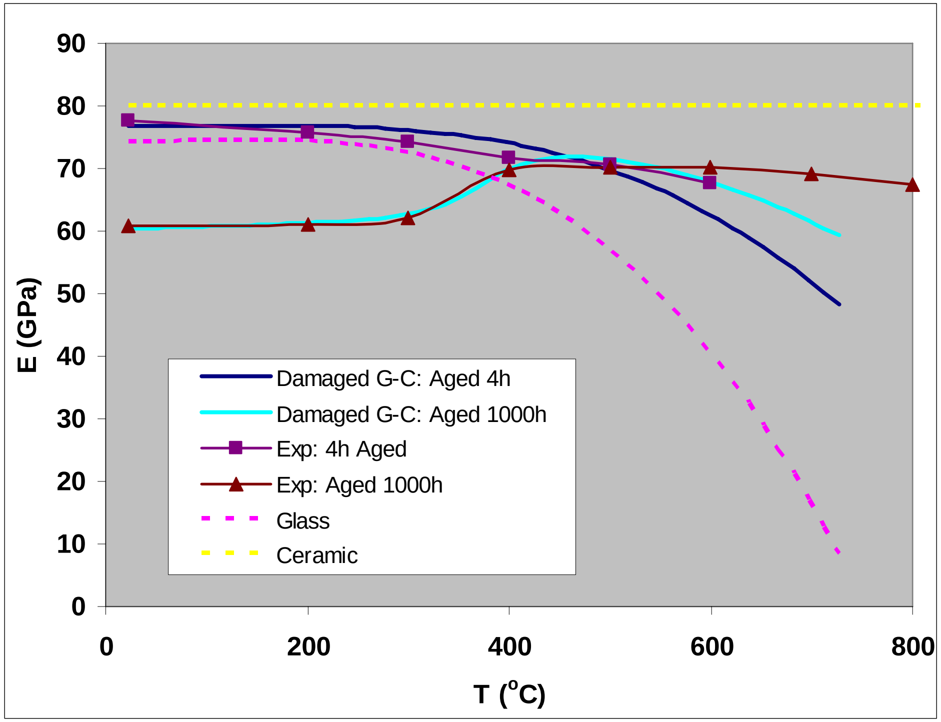
# Aging/Self-Healing Behavior of G18 (cont'd)

$$E^D(t,T,D) = \left[\left(f_C^{\infty} - f_C^0 e^{(-t/A_t)}\right)\left(E_C - E_G(T)\right) + E_G(T)\right]* \left\{1 - \frac{D_0}{\pi}\left(1 - e^{-t/t_c}\right)\left[\pi/2.0 - \arctan\left(\frac{T - T_{th}}{R}\right)\right]\right\}$$

- This model includes:
  - Aging-time-dependent crystalline content model for volume evolution of crystalline phases
  - Temperature dependency
  - Degradation of modulus of glass/ceramic due to aging induced micro-damage
  - Mechanical property restore due to self-healing performance at high temperature
- This model was applicable to general glass/ceramic materials



# Contact Paste: Introduction

- The cathode contact layer is a highly challenging interface
  - Must make bond between ceramic cathode and metallic interconnect (likely with oxide scale and coatings)
  - Must survive oxidizing environment
  - Must likely be formed at temperatures lower than that of the conventional range for sintering of ceramics
- Modeling can aid understanding of load requirements and guide design improvements

- Areas of interest for modeling and experiments:
  - Quantification of expected interface stress levels
  - Characterization of paste mechanical/strength properties
  - Evaluation of the contact layer as a load carrying interface to reduce seal loads
  - Evaluation of contact layer stresses and reliability due to low temperature processing methods

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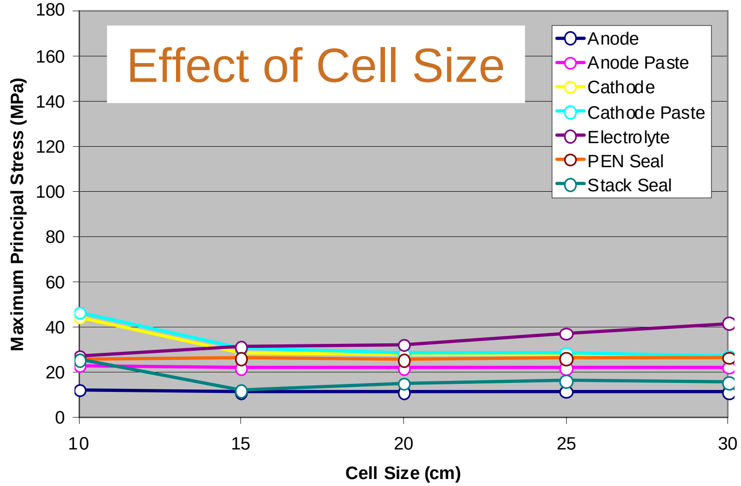
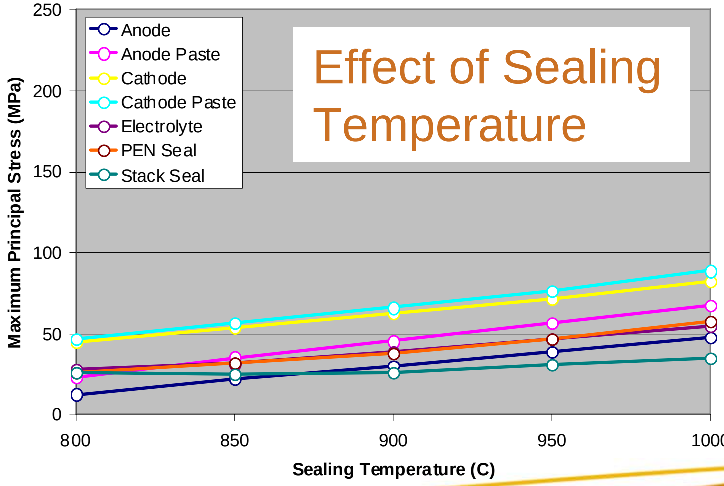
# Contact Paste: Stress Levels

- Evaluated continuous paste support
  - High peeling stresses (35 MPa) and shear stresses (17 MPa) concentrated near the sealed edge of the cell at operating temperature
  - Even higher local peeling and shear stresses at shutdown
  - Cell scale-up from 10-30cm showed only moderate changes in peak stresses- dominated by edge effects
  - Sliding seals were more beneficial than rigid seals
  - Consideration of stack creep effects was beneficial for relaxing stresses
  - Higher stack sealing temperatures with rigid seals increased stresses in all the cell components

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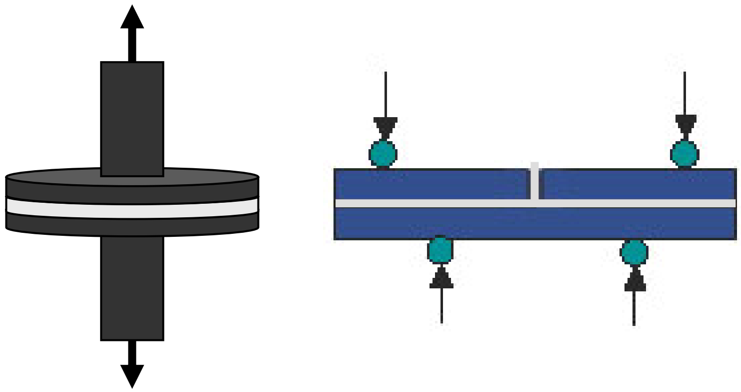
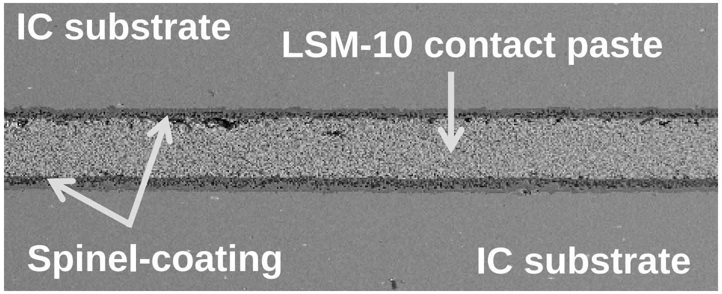
# Contact Paste: Property Characterization

- Joint collaboration between PNNL and ORNL
  - Yanli Wang from ORNL visited PNNL to lwork on specimens fabrication
  - Continued PNNL support to ORNL for fabrication of specimens
- Experimental work in progress
  - ORNL conducting notched specimen bend tests to determine interfacial toughness of fabricated analogs
  - PNNL conducting tensile tests to determine interfacial strength of fabricated analogs
  - Beginning with spinel-coated Crofer interconnect substrate material and LSM-10 contact paste; next step to test Ce-spinel coated 441SS and LSM-10 contact paste
- Preliminary interfacial tensile strengths at test temperatures ranging from RT to 850°C indicate 1-6 MPa



Tension test and bend bar schematic of LSM contact paste/spinel-coated IC interface




Tensile sandwich specimen cross-section of LSM contact paste/spinel-coated IC interface

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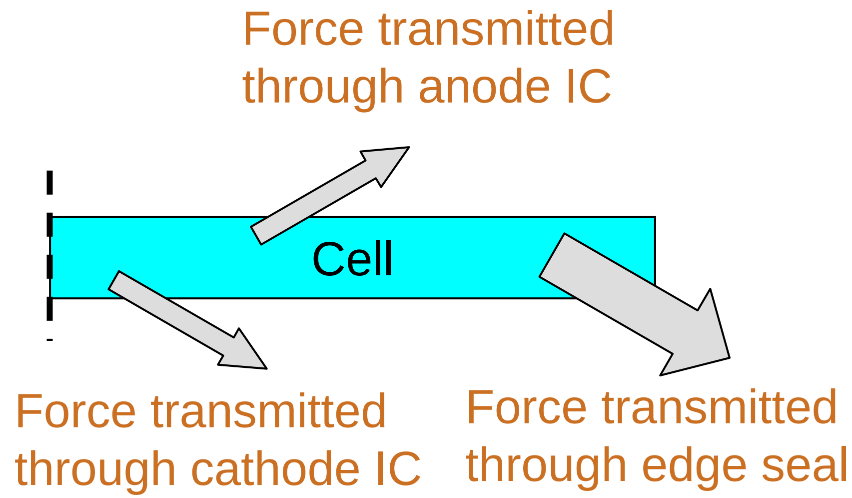
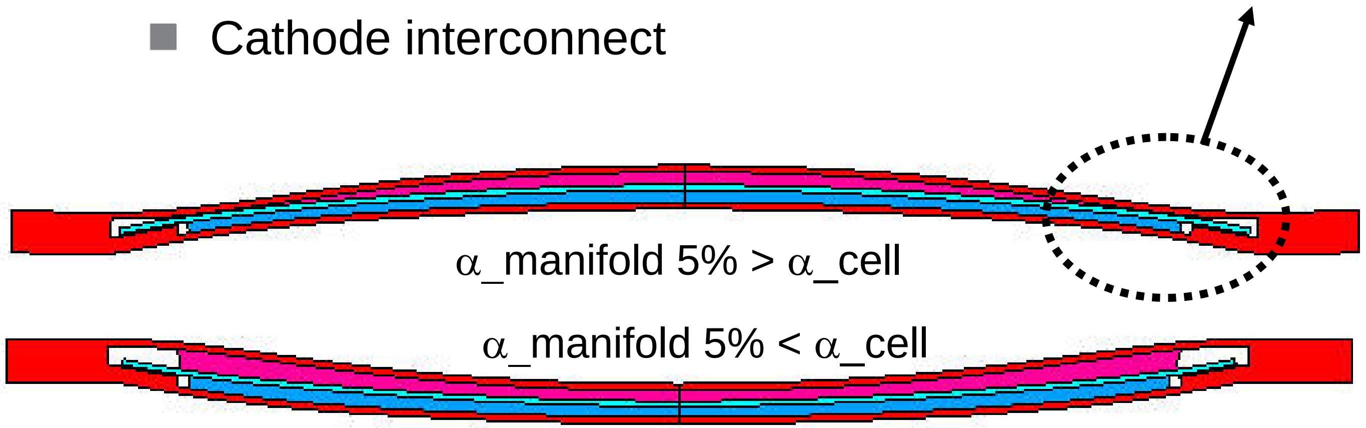
# Contact Paste: Load Transfer

- Q: Can a load-carrying cathode contact layer benefit the seals?
- Load transfer between cell and manifold (due to CTE mismatch) carried potentially by three parallel paths:
  - Edge seals
  - Anode interconnect
  - Cathode interconnect

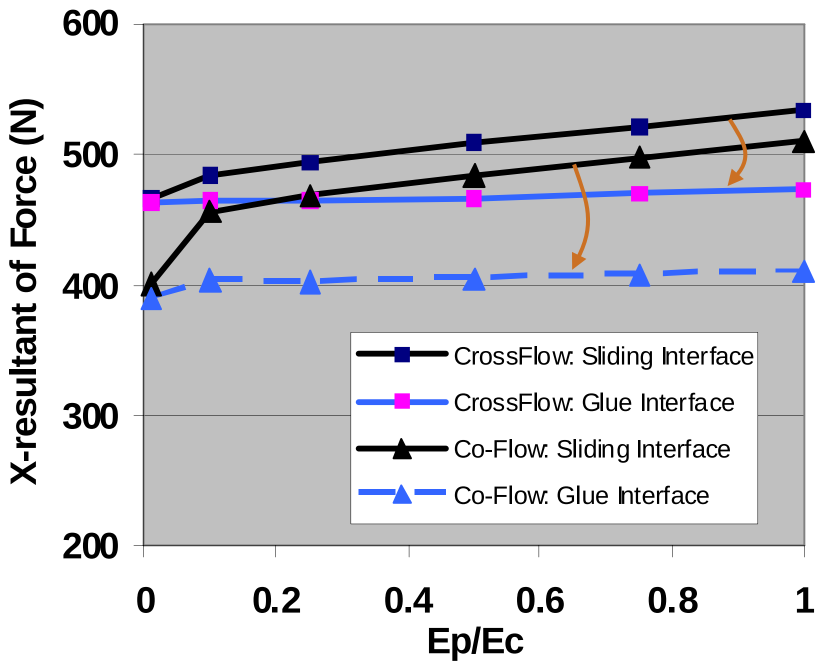



- Can seal load be reduced?
- Depends on relative stiffness of components

# Contact Paste: Load Transfer (cont'd)

- Seal load dependence on contact paste design was simulated
  - Co- versus cross-flow
  - Bonded versus sliding contact
  - Variation of paste modulus as a function of cathode modulus
  - Ribbed and continuous ICs
- Results
  - Bonded paste reduced seal shear load up to 10-20% compared to sliding interface
  - Paste modulus for bonded layer had only small effect (<5%) on seal load
    - Implies low modulus sensitivity good for processing the porosity
  - Seal load varied greatly (~40%) with orientation relative to rib direction
  - Continuous IC evaluations still in progress




- Conclusion: load sharing concept is viable, but not fully characterized yet

# Contact Paste: Sintering

## Modeling Goal

- Material and process for strong, reliable cathode contact
- Develop a model to predict the properties and stress state of the cathode contact layer including effects of:
  - Initial state/stresses due to the sintering/processing step
  - Mechanical stresses induced by any volumetric changes of the anode during reduction
  - Typical thermal stresses due to cell operation and shutdown

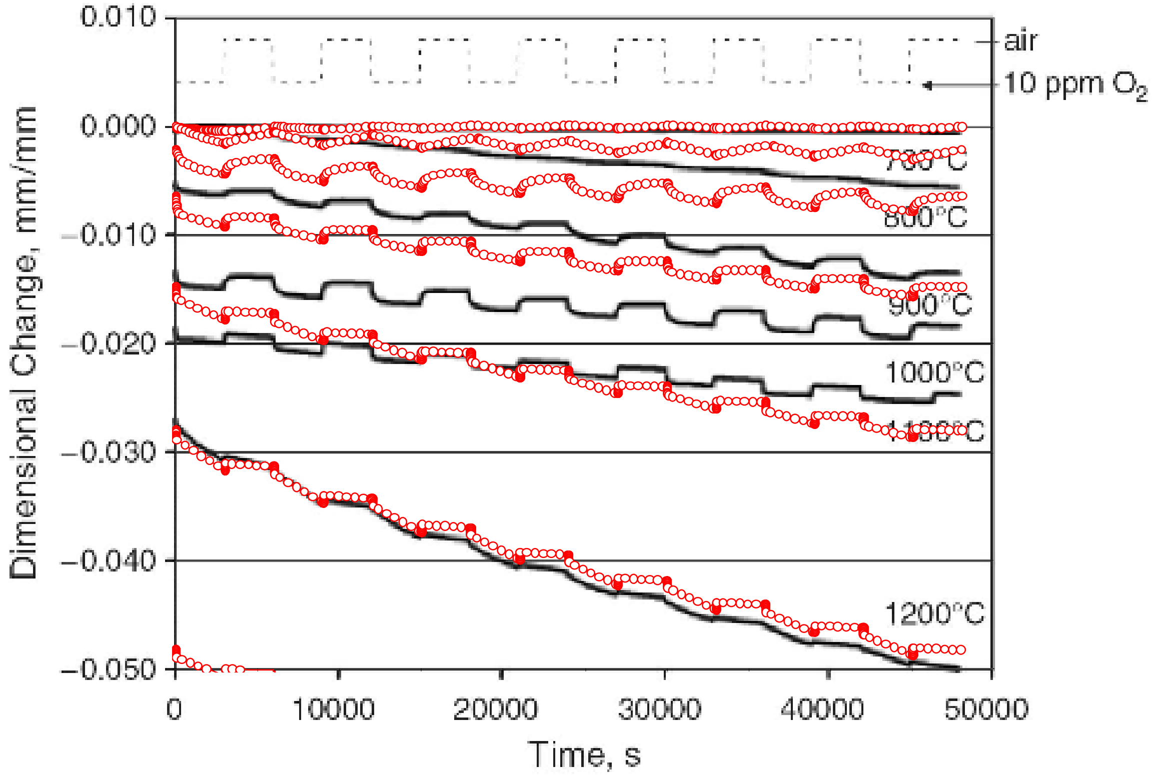
## Technical Approach

- Implement constitutive model to predict the sintering strains and developed stresses
  - Evolution of relative density and grain size
  - Changes in elastic and strength properties as a function of relative density
- Extend the model to include the enhanced densification due to $pO_2$ cycling
- Test in spreadsheet model and then implement in stack models
- Evaluate structural reliability in realistic geometry

# Contact Paste: Sintering (cont'd)

- Model captures densification behavior of LSM10 paste
  - Effect of $pO_2$ cycling and temperature changed observed in experimental tests is simulated
  - Model computes free densification strains, grain growth, and elastic property changes at different stages of sintering
  - Next implement spreadsheet model into 3D FEA tool for actual IC geometries

Densification from atmospheric cycling




McCarthy BP, LR Pederson, HU Anderson, X-D Zhou, P Singh, GW Coffey, and ED Thomsen. 2007. *J Am Ceram Soc* 90(10):3255-3262.

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# Collaborations

- PNNL modeling staff are currently collaborating with SOFC researchers on several technical issues

- ASME design document
  - ORNL: E Lara-Curzio, Y Wang
  - ASME: J Powers, R Swayne
- Contact paste characterization
  - ORNL: E Lara-Curzio, Y Wang
  - PNNL: L Pederson, B McCarthy
- Interconnect coatings
  - PNNL: Z Yang
- SECA test cell
  - PNNL: J Stevenson, M Chou
- Modeling tool support
  - Delphi
- Seal characterization & modeling
  - U of Cincinnati: R Singh
  - GaTech: H Garmestani
  - PNNL: M Chou
- Chrome Migration
  - Carnegie Mellon: E Ryan
- Pressurized EC
  - PNNL: L Pederson

# Conclusions & Ongoing Work

## Conclusions

- Speed and capabilities of SOFC-MP were improved
- Cathode contact paste stresses were evaluated and a sintering model was developed
- An EC model to simulate pressurized SOFC was developed
- Seal mechanical properties continue to be characterized and modeling was used to evaluate novel sealants

## Ongoing Work

- Completion of the SOFC design document
- Release of SOFC-MP v1.1
- Thermal management using coal-based fuels w/ methane and pressurization
- Characterization of contact paste mechanical strengths
- Simulation of contact paste development and cell load paths
- Improved interconnect coating systems