# Modeling Tools for Solid Oxide Fuel Cell Design and Analysis

**Moe A Khaleel**
BJ Koeppel, W Liu, K Lai, KP Recknagle, EM Ryan, EV Stephens, X Sun
*Pacific Northwest National Laboratory*
*Richland, WA 99352*

11th Annual SECA Workshop
Pittsburgh, PA
July 27-29, 2009

Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by* Battelle *Since 1965*

# PNNL SOFC Modeling Tools

- SOFC-MP
  - Stack level model for fast analysis of co/counter-flow SOFC stack performance
- Detailed electrochemistry model
  - Cell level model for the investigation of secondary reactions (degradation/contamination) mechanisms within the tri-layer
- Component-based design and performance modeling
  - Contact material
  - Interconnect
  - Glass seal

# SOFC-MP Stack Simulation Code Recent Accomplishments

- Major memory improvements of 3D model to accommodate 50-cell stacks on LINUX platform.
- Previously, developed a 2D (or stacked 1D) model for fast analysis of co/counter-flow SOFC stack performance
  - Benchmarked with literature cases
- New features added for design and evaluation of realistic stack experiments,
  - Allows users to maximize understanding of actual experiments where uniform nominal performance is not always achieved
  - Allows users to implement custom $CH_4$ reforming and I-V relationships
  - Allows users to quickly evaluate different conditions with automated output of stack performance metrics
- Capable of modeling cell-to-cell variations, e.g.:
  - Thick measurement plate in middle of stack
  - Different flow rates into cells, e.g. due to blockage, leak, or by-pass
  - Different I-V performance of cells
  - Short current in cells
  - Partial contact loss in cells
- Capability to analyze large stacks, e.g., a 96-cell 25 kW stack

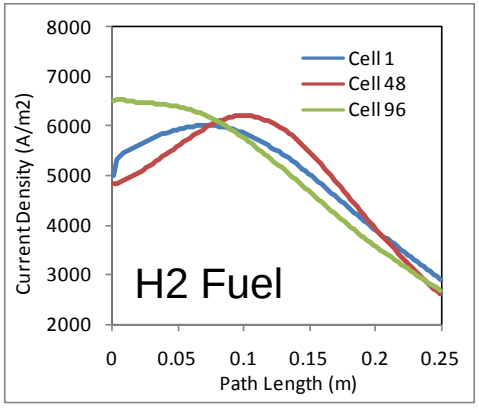
# SOFC-MP Stack Simulation Code
# Nominal Stack Performance – $H_2/CH_4$ Fuels

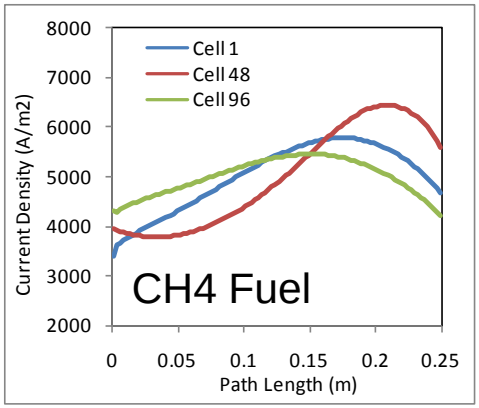
- 96-cell stack, 625 $cm^2$, 65% UF, 15% UA
- Electrical Performance
  - Hotter inflow gases cause current consolidation on leading edge of $H_2$ stack
  - 50% OCR fuel resulted in 7.5% less power
- Thermal Performance
  - Cell $\Delta T$ for top/bottom cells smaller than middle cells due to heat transfer to environment
  - Highest $\Delta T$ nearer bottom due to cooler inlet gas
  - OCR reduced $T_{max}$ by 31°C and $\Delta T$ by 20°C

## Results Comparison

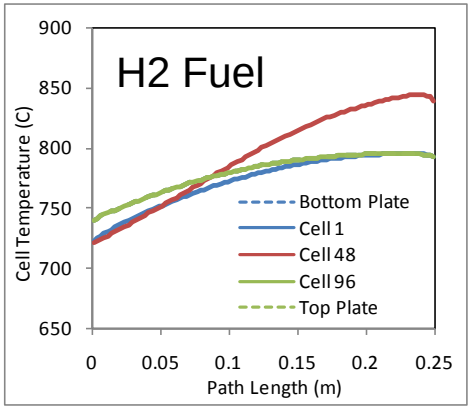
| | H2 Fuel | CH4 Fuel |
|---|---|---|
| Power (kW) | 25.5 | 23.6 |
| $V_{avg}$ (V) | 0.852 | 0.785 |
| $\Delta V$ (V) | 0.015 | 0.023 |
| $J_{avg}$ (A/cm2) | 0.5 | 0.5 |
| $J_{max}$ (A/cm2) | 0.65 | 0.64 |
| $T_{avg}$ (C) | 793 | 743 |
| $T_{max}$ (C) | 848 | 817 |
| $\Delta T$ (C) | 139 | 119 |

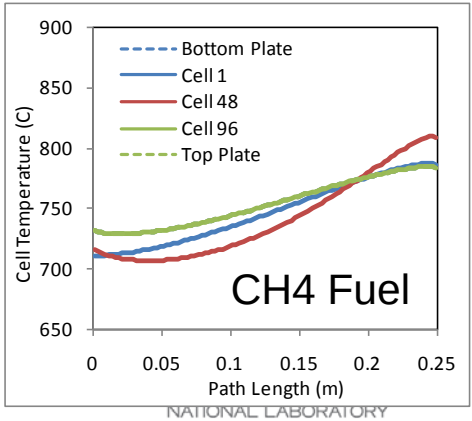
## Current Density




## Cell Temperature

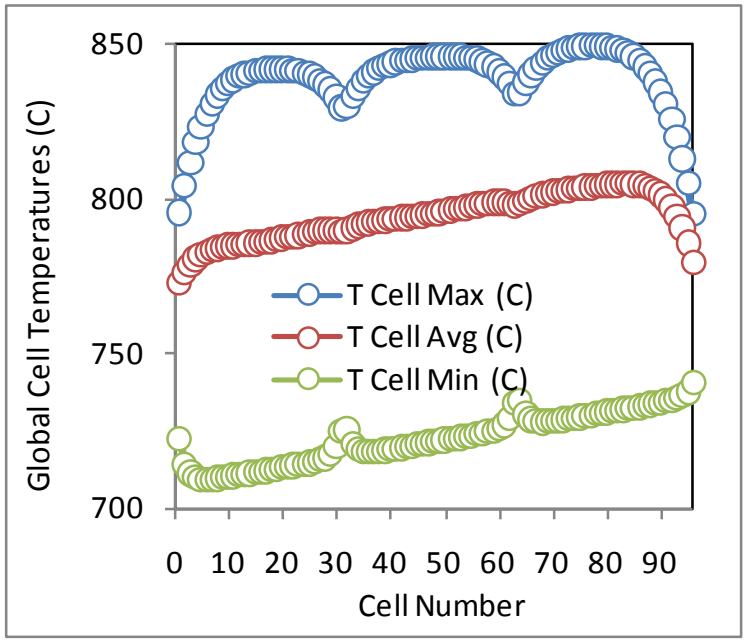


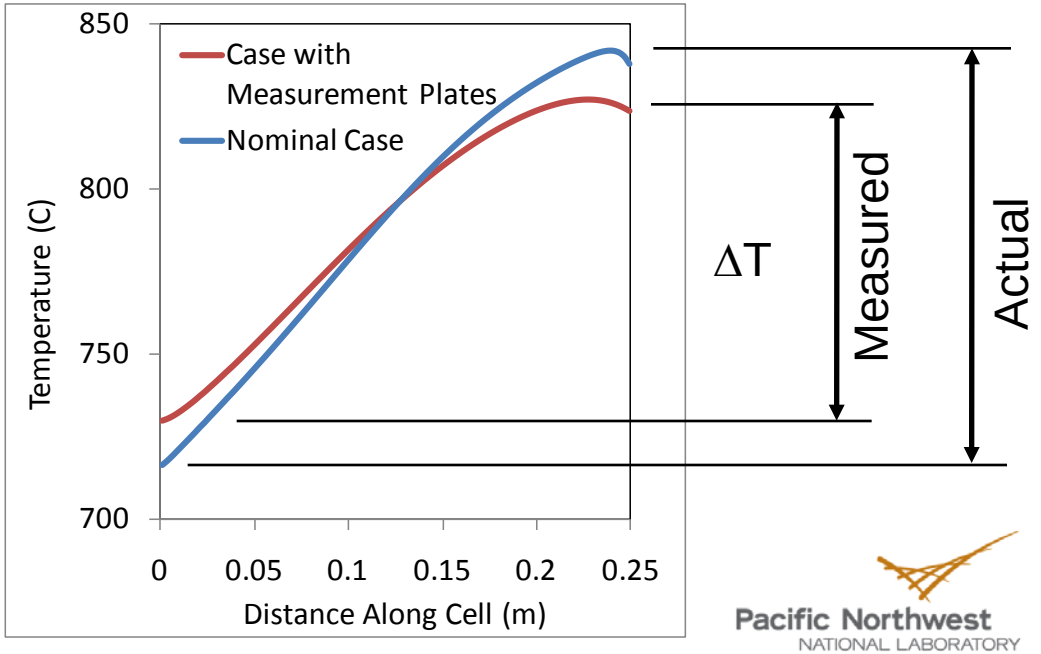
# SOFC-MP Stack Simulation Code
# Effect of Thick Plates – H2 Fuel

- ½" measurement plate (e.g. thermocouples) used for cells #32 and #64
  - Observer effect: the measurement itself affects the data
  - Larger thickness plate makes good thermal conductivity path to spread heat better and provides better thermal communication with ambient
- Mean cell temperature about the same, but ΔT underestimated by 21%
- Power actually increased 0.2% due to hotter leading edge

Cell Temperatures




Cell #32 Temperature Distribution

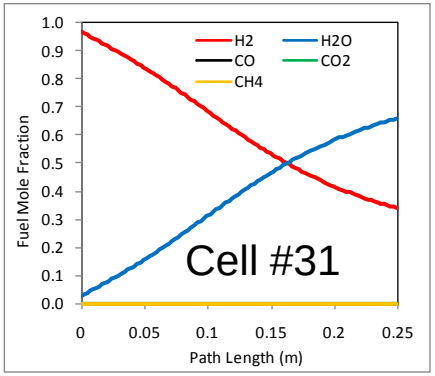


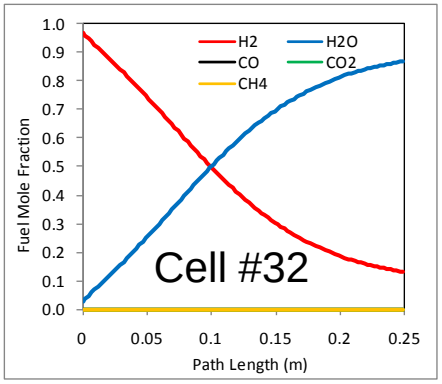

Pacific Northwest NATIONAL LABORATORY
*Proudly Operated by Battelle Since 1965*

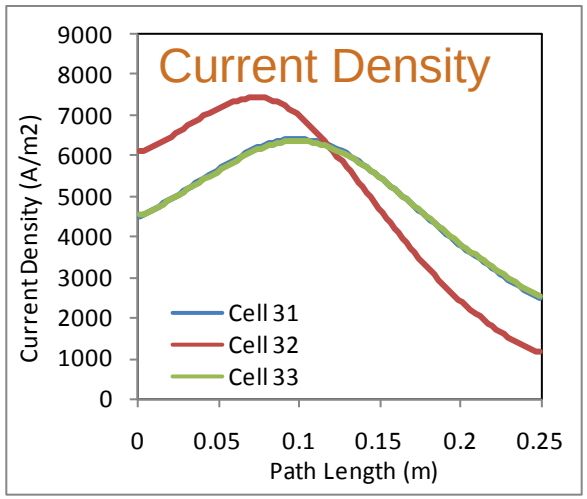
# SOFC-MP Stack Simulation Code
# Effect of Flow Maldistribution – H2 Fuel

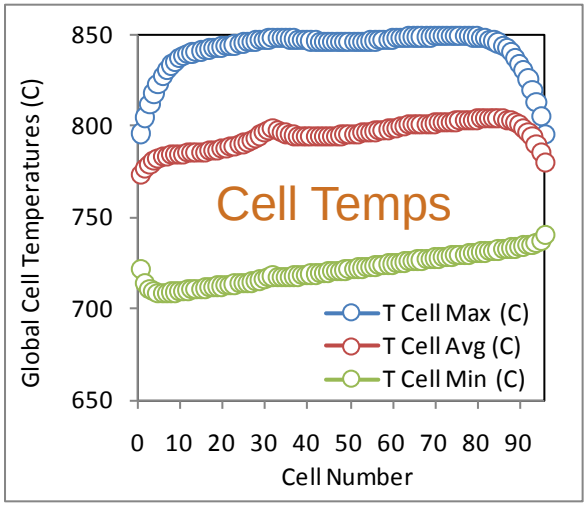
- Cells may have off-nominal flow rates
  - Flow blockage due to excessive spread of seal materials
  - Fuel by-pass around cell
- Example $H_2$ case
  - 75% fuel flow in cell #32, 50% air flow in cell #64
- Results
  - Min voltage on cell #32  0.81V
  - Higher max current density of 0.74 A/cm$^2$
  - Local utilization on cell #32 increased to 87%

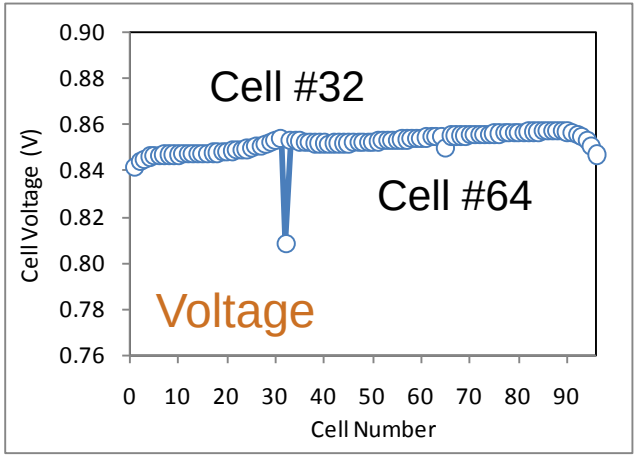
Species Distributions



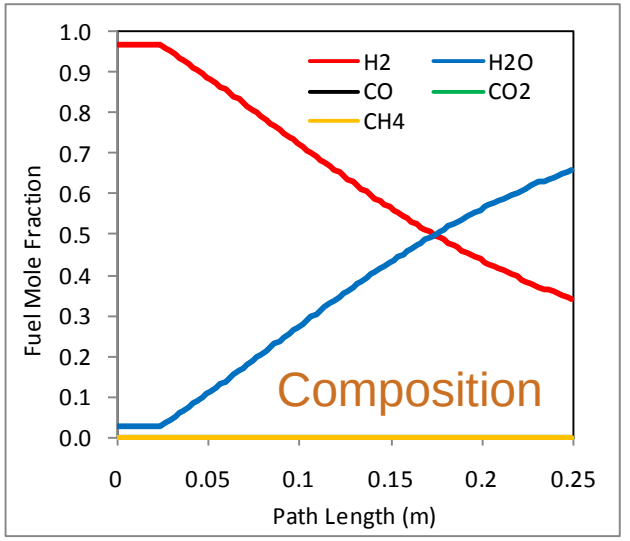



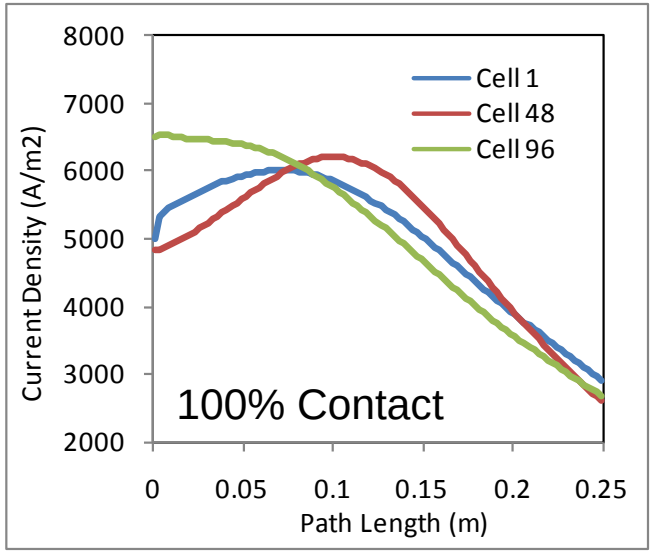



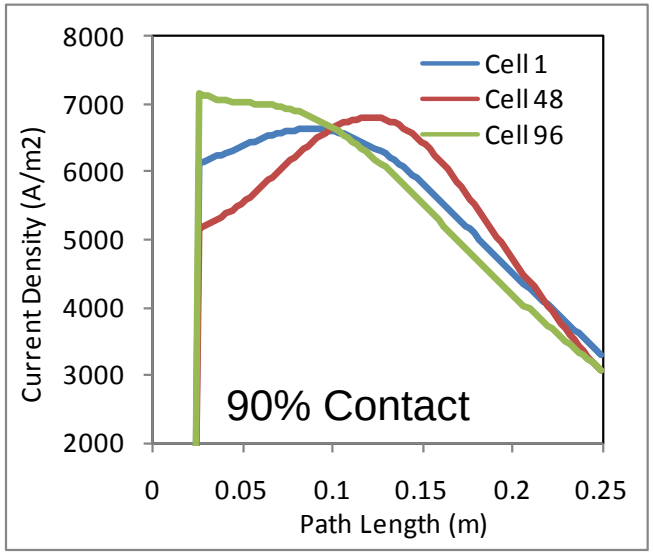
# SOFC-MP Stack Simulation Code
# Effect of Contact Loss – H2 Fuel

- Case with contact loss at cooler inlet entrance for 10% of active area
- Power loss -0.7%
- Peak current density increased 10% on the top cell with hottest inflow temperature
- Peak cell temperature increased 5°C
- Stack ΔT increased 7°C




Current Density



# Detailed Electrochemistry Modeling

## Objective

- Resolve the local fields (potential, species, thermal) through the thickness of the tri-layer
- Understand the local conditions that contribute to the onset of secondary reactions in the tri-layer to enable prevention
  - Secondary Reactions: Any reactions not directly related to the electrochemistry which can cause degradation and damage to the fuel cell
- Investigate the effects of secondary reactions on the operation and performance of the SOFC

## Accomplishments

- Developed 2D electrochemistry model which resolves the potential, current density and species through the anode-electrolyte-cathode assembly.
- Implemented chemistry model for the gas reforming reactions within the anode
- Validated the model with previous modeling data from literature.

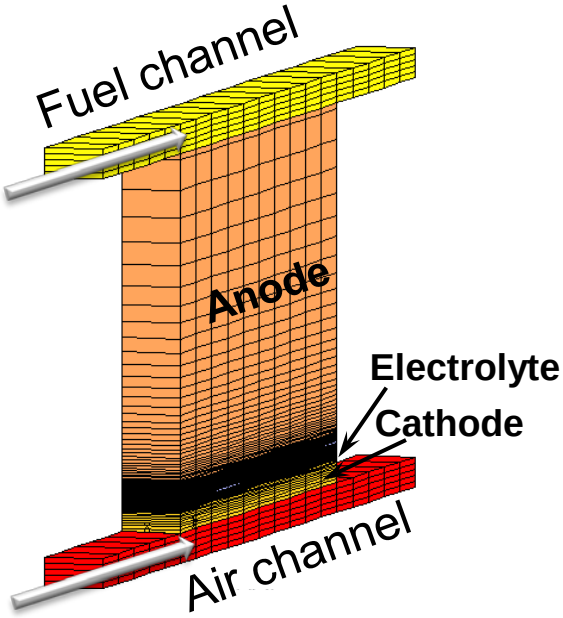
Pacific Northwest
NATIONAL LABORATORY

# Detailed Electrochemistry Modeling: Approach

- Effective properties (transport, surface reaction, electrochemistry) model to calculate the species, thermal and electric potential distributions in the tri-layer
- Solves for the electrochemistry through the tri-layer which removes the assumption of a zero thickness reaction zone and allows calculation of the physical potential distribution within the electrodes
- Resolves the 2-D distributions through the thickness of the tri-layer, with implementation extendable to 3-D
- Begins by modeling the physics of the active cell and then overlaying the secondary reaction mechanisms and threshold energies

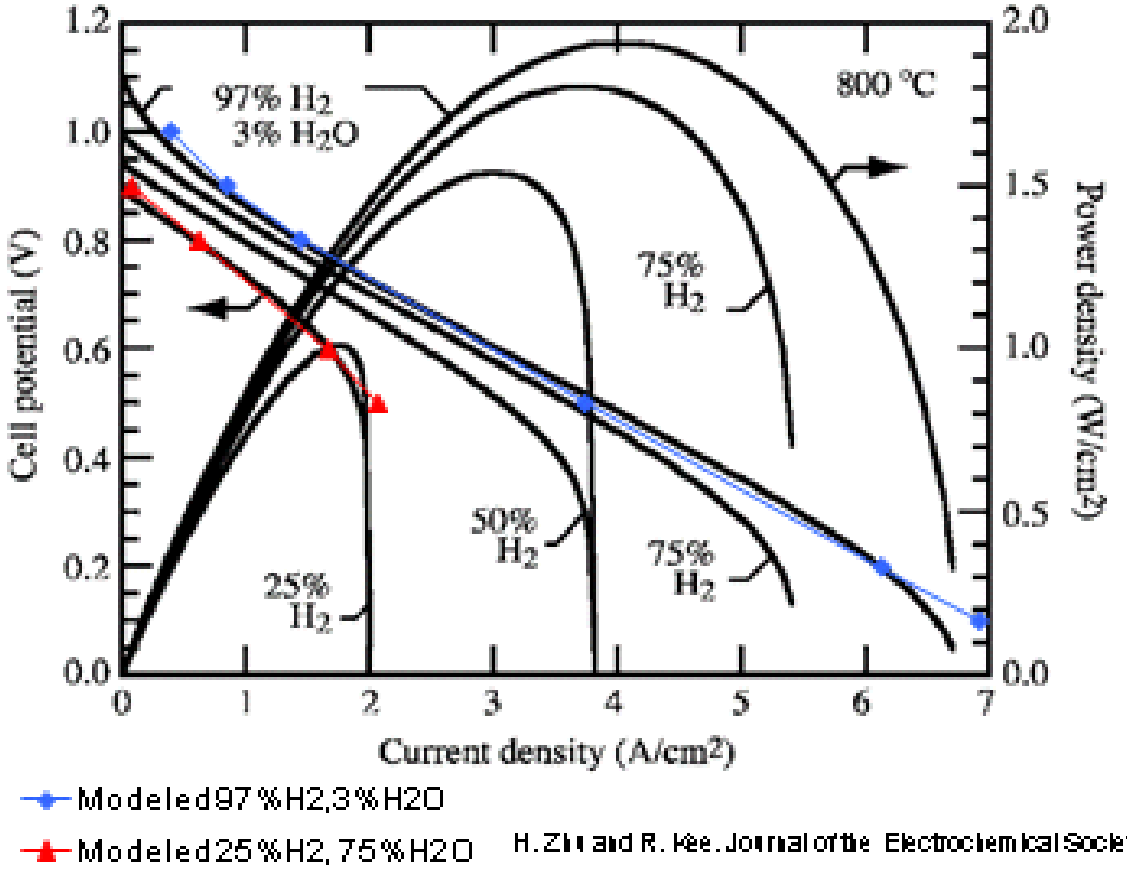
# Detailed Electrochemistry Model: Physics

- 2D domain made up of the anode, cathode, electrolyte and fuel and air channels
- Gas transport in the porous electrodes including the species: $H_2$, $H_2O$, CO, $CO_2$, $O_2$, $CH_4$
- Surface chemistry with adsorption, desorption, reformation, and water-gas-shift, including the surface species: H, O, OH, $H_2O$, $CH_4$, $CH_3$, $CH_2$, CH, CO, $CO_2$, HCO, $O^{2-}$, $OH^-$, and free Ni sites
- Modified Butler-Volmer relationship for the electrochemistry in the electrodes
  - Based on the electrochemical reactions
  - Assumes one of the charge transfer reactions is rate limiting
- Within electrolyte and electrode phases
  - Solid state conduction of $O^{2-}$ and $e^-$
  - Electric potential distribution



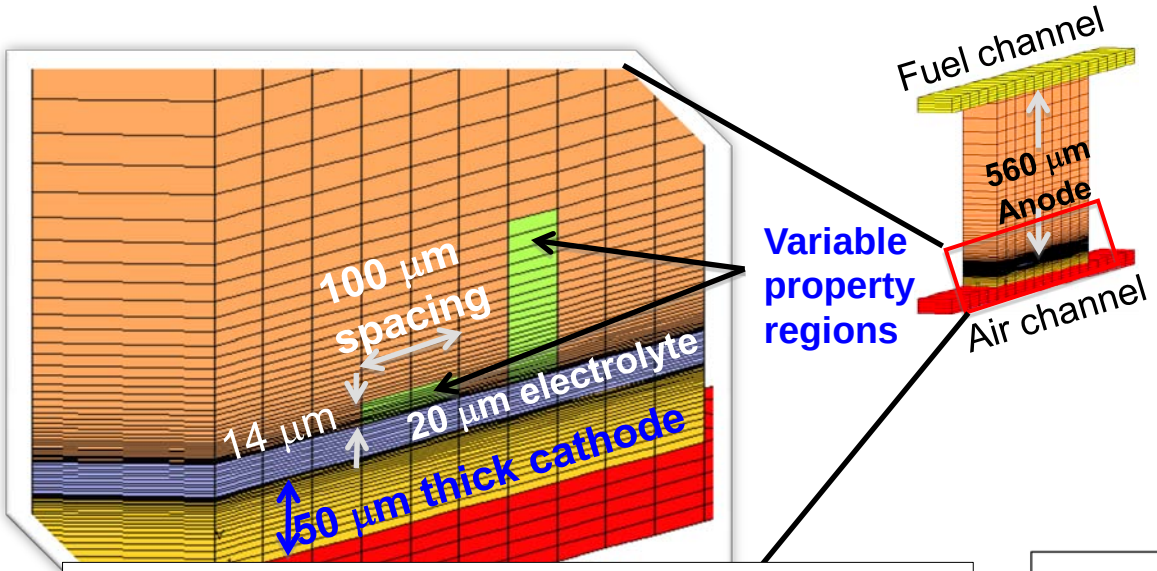
# Detailed Electrochemistry Model: Verification

- Verifying the model for the $H_2$ – $H_2O$ binary fueling system
- Further verification and validation ongoing

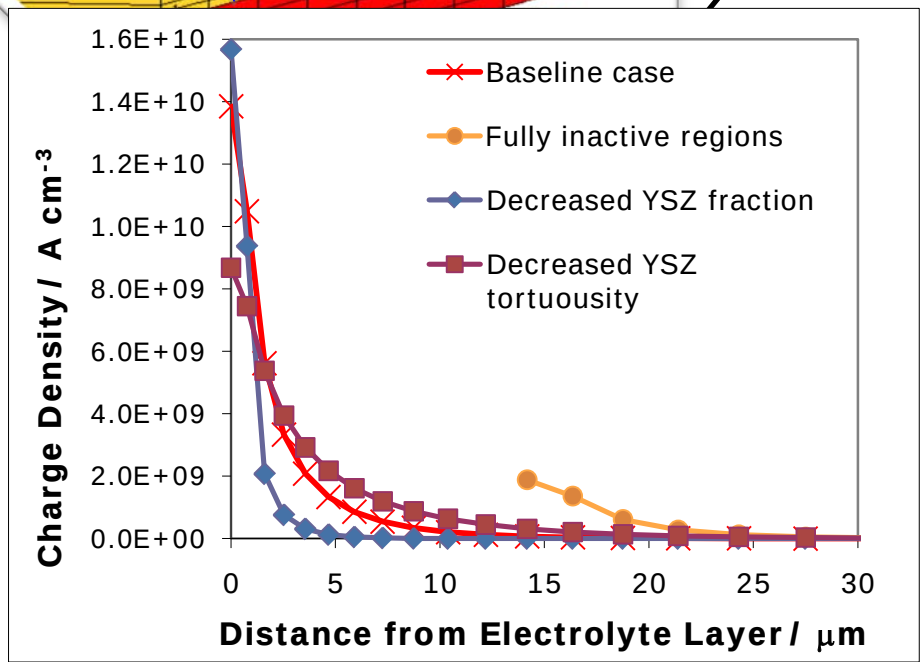


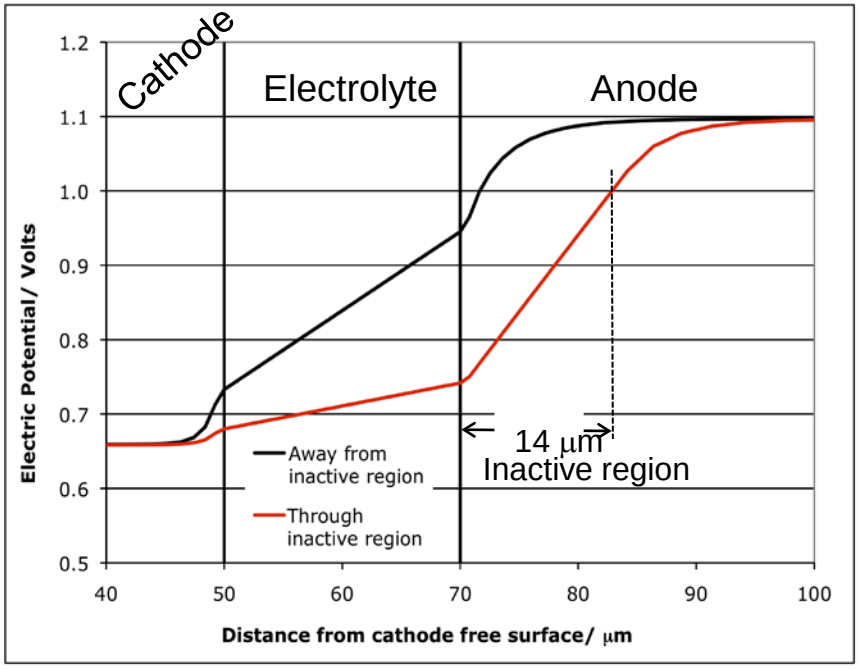

H. Zhu and R. Kee, Journal of the Electrochemical Society, 155 (7) B715-B729 (2008)

# Detailed Electrochemistry Model: Two-Dimensional Variable Property Model




- Variable properties in anode (green sections)
- Four cases:
  - Baseline
  - Electrochemically inactive zones
  - Decreased ionic conductivity (decreased YSZ fraction)
  - Increased ionic conductivity (decreased YSZ tortuosity)



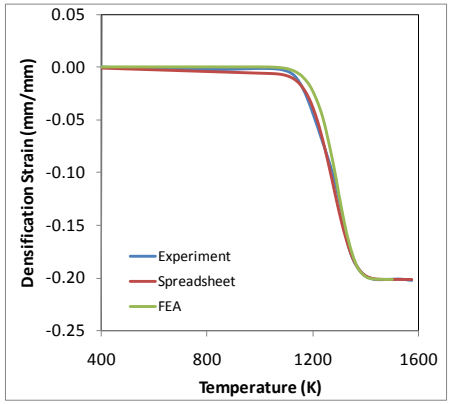
# Contact Materials and Stack Load Path Recent Accomplishments

- Previously, developed models to study influence of contact layers on load path through the stack
- Recently, evaluated densification behaviors of actual contact materials under development and sensitivity to initial material state, applied loads, and kinematic constraints
  - LSM + 3mol% CuO + $BaCuO_2$
  - LNF + 3mol% $Bi_2O_3$
  - LSCF + 3mol% CuO
  - Ni-Co oxides
- Results:
  - Method established to obtain model parameters for low temperature sintering from dilatometric screening test
  - Good densification (>80%) of candidate material systems predicted as possible based on dilatometer testing (e.g. 4 hour treatment at 950°C)
  - If possible, initial grain sizes <1 μm very beneficial for low temperature sintering
  - Constrained contact layers <1 mm have nearly uniform density but normal and shear stresses vary through the section
  - Expected maximum stress levels in stack structures up to 10-15 MPa

# Contact Materials and Stack Load Path Material Data from Experiments

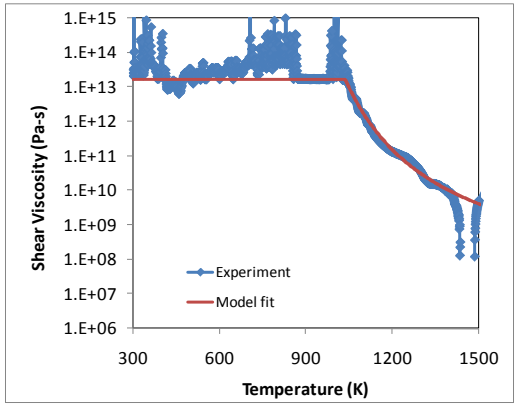
LSM + 3mol% CuO+$BaCuO_2$

Dilatometer Data




Densification Rate

Material Parameter $\eta_0$

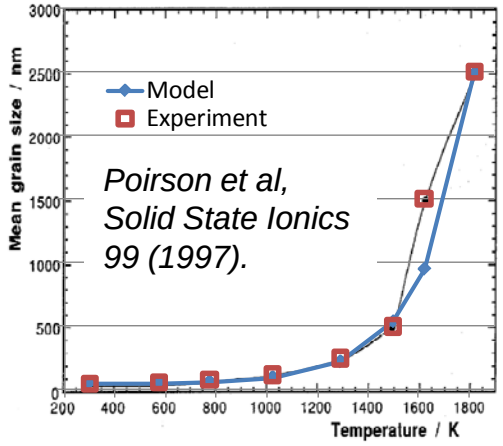



$$\eta_0 = -\frac{P_L}{6\dot{\varepsilon}\psi}$$

$$P_L = \frac{3\alpha}{r_0}(1-\theta)^2$$

- Use densification strain data for candidate contact materials from dilatometry under ramped heating
  - LSM + 3mol% CuO + $BaCuO_2$
  - LNF + 3mol% $Bi_2O_3$
  - LSCF + 3mol% CuO
- Fit parameters from the material constitutive model
- Include grain growth rate model from literature
- Verify performance of the constitutive model in FEA

Grain Growth



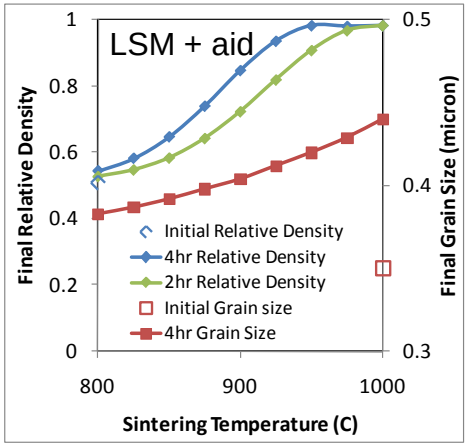


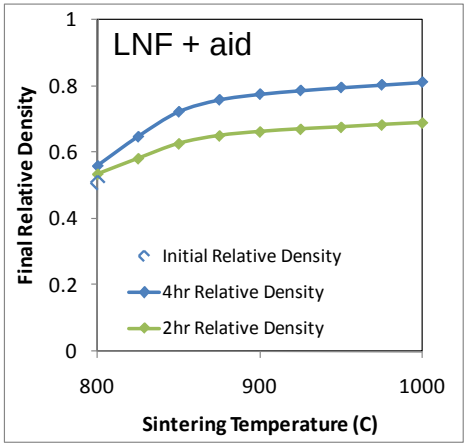

Pacific Northwest NATIONAL LABORATORY

# Contact Materials and Stack Load Path Free/Pressurized Sintering

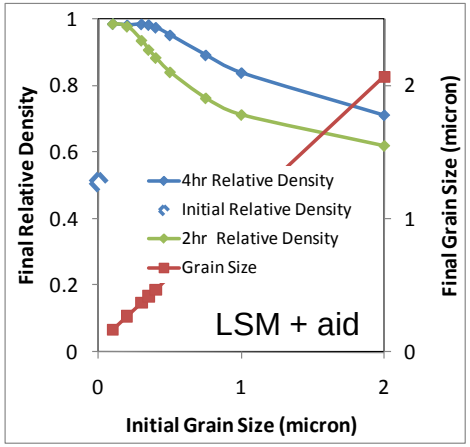
- For LSM+aid, much higher densification in 900-1000°C processing range
  - Less benefit for LNF+aid due to flat densification curve
- Great benefit to initial densification with grain sizes less than 1.0 micron
  - 0.1 micron gives 99% relative density; 1.0 micron give 72% relative density
  - Small grain growth rate for this temperature range so sintering is sustained
- Uniaxial pressure will increase the densification rate
  - Preload less than the sintering stress (~5 MPa) shows only small benefit

Effect of Sintering Temperature

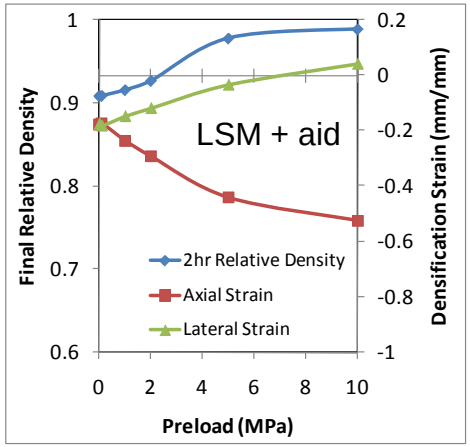



Effect of Initial Grain Size



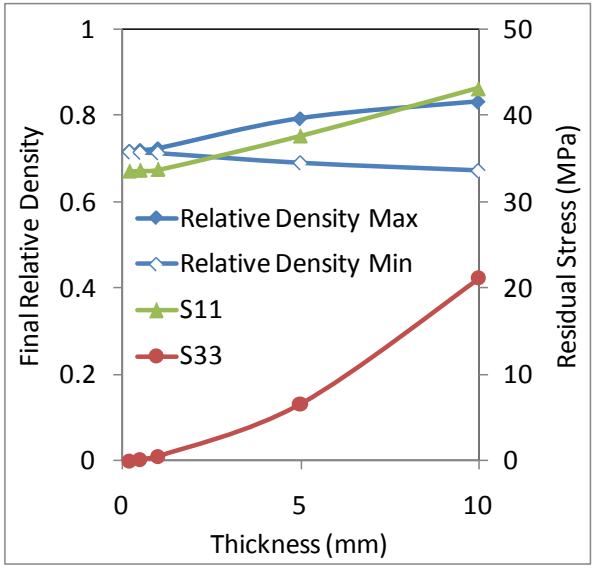

Effect of Compressive Preload

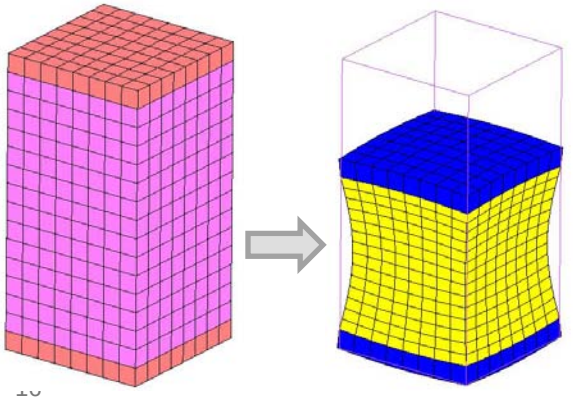


# Contact Materials and Stack Load Path Constrained Sintering (LSM + sinter aid)

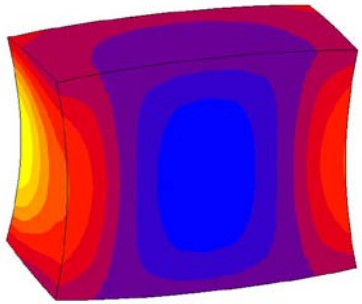
- For bonded structures, the relative density varies through the part due to the constraint and stress field
- Thin contact layers <1.0 mm have more uniform relative density
  - Dominated by constraint of the two bonded surfaces so less variation
- Thin contact layers also showed smaller residual normal stress development
  - In-plane stress remains significant
  - Out-of-plane stress near zero
  - Edge shear stress becoming larger

Effect of Contact Layer Thickness

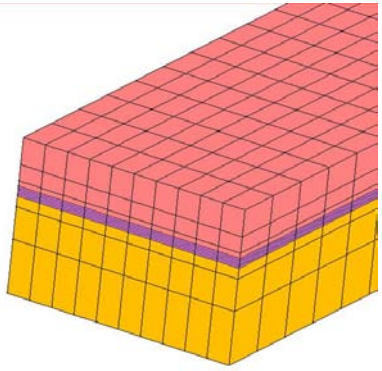


Density Variation

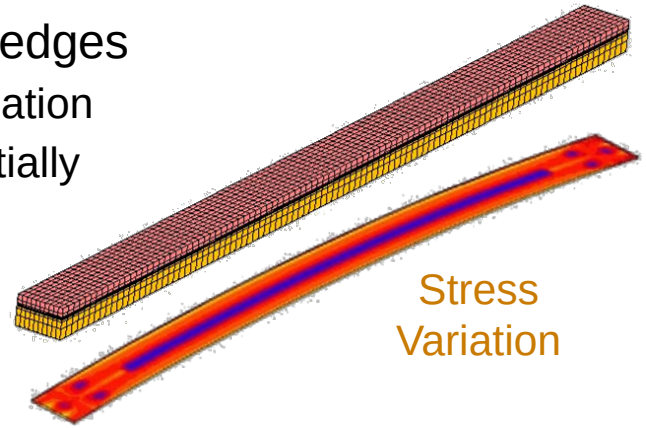


- Extend to stack rib/contact structures
  - 100x5 mm strip
  - 2mm ceramic
  - 0.2mm paste
  - 1mm steel
  - Hypothetical 4 hour treatment at 950°C



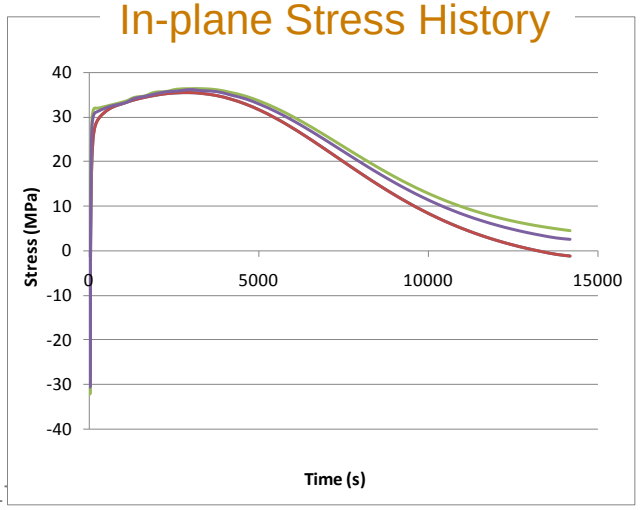
# Contact Materials and Stack Load Path
# Stack Contact Structures (LSM + sinter aid)

- Densification varies across layer with faster rates at edges
  - In-plane stresses initially high but reduce after densification
  - Out-of-plane stresses increase with time and vary spatially
  - In-plane strains 200-400X greater than out-of-plane
- Final stresses at temperature:
  - Highest shear stresses at the edges (~14 MPa)
  - Highest normal stresses at the center (~7 MPa)
- Bulk layer and interfaces will both need adequate strength
  - Construction of lap shear strength testing system in progress

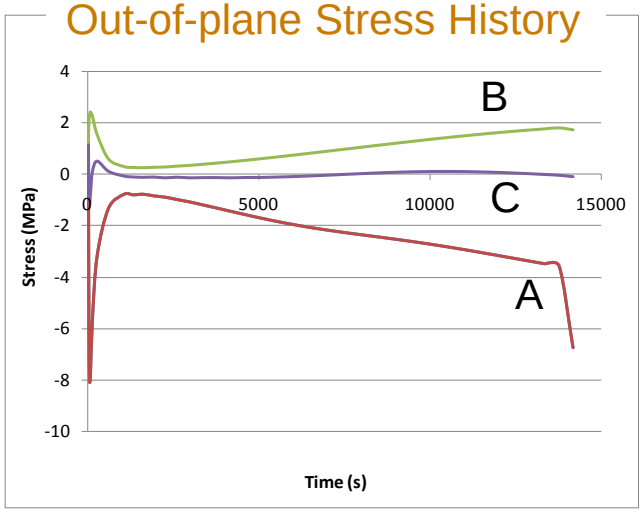



- Peak contact layer stresses from rib in 3D stack models of similar magnitude
  - ~2 MPa shear
  - ~10 MPa normal

In-plane Stress History




Out-of-plane Stress History






Pacific Northwest
NATIONAL LABORATORY

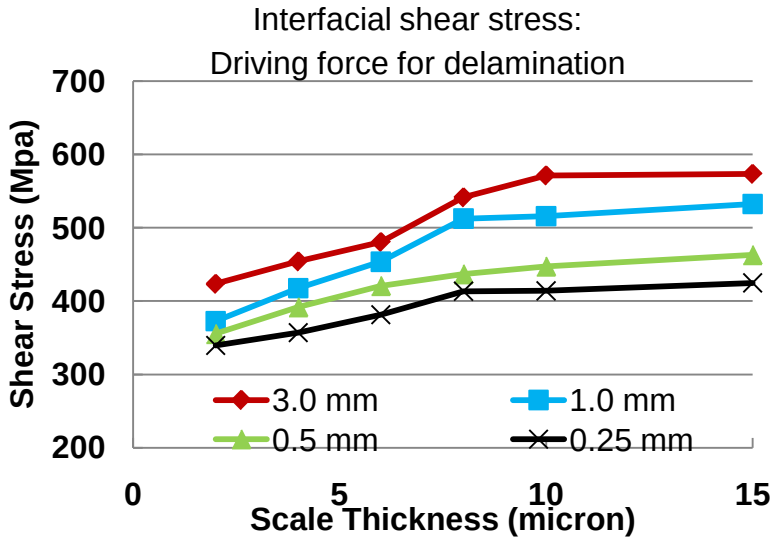
# Lifetime Quantification and Improvement of Coated Metallic Interconnects

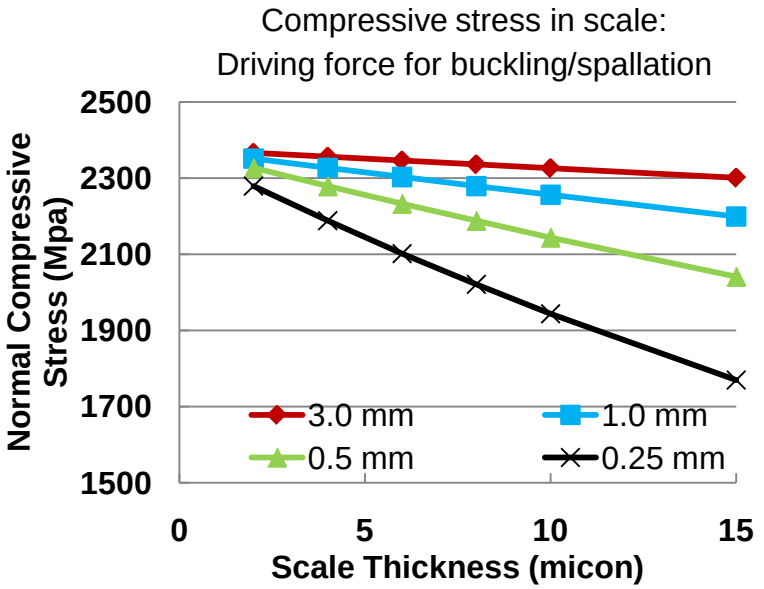
## Accomplishments

- Substrate thickness has significant effect on delamination/spallation of oxide scale
- Shot-peening avoids or delays the spallation of oxide scale
- Optimized cooling profile reduces the compressive stress in oxide scale to some degree → reducing driving force for scale spallation

# Effect of Substrate Thickness on Cooling Induced Oxide Stresses for Uncoated SS441

- Modeled different substrate and oxide scale thicknesses
  - SS441: 0.25mm. 0.5mm, 1.0mm, 3.0mm
  - Oxide scale thickness: 2um, 4um, 6um, 8um, 10um, 15um
- For a given oxide scale thickness, i.e., oxidation time:
  - Shear stress increases with increasing substrate thickness
  - Compressive stress increases with increasing substrate thickness – more likelihood to spall
- For a given substrate thickness:
  - Shear stress increases with increasing oxide thickness, i.e., oxidation time.
  - Compressive stress decreases with increasing oxide thickness, i.e., oxidation time.
    - The magnitude still remains high, ~2GPa
- Thinnest substrate with the lowest oxidation time will have the least chance to spall.



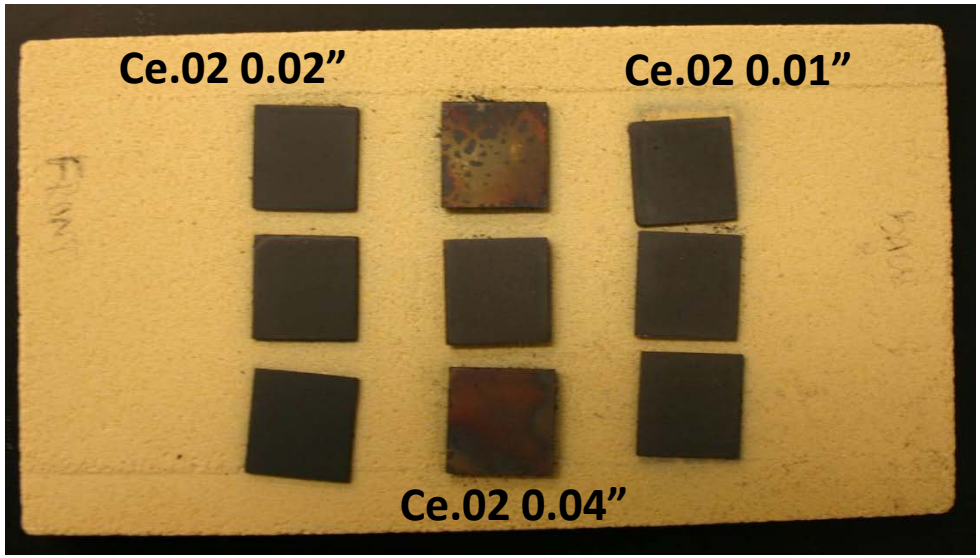
# Verification of Effects of Substrate Thickness on Cooling Induced Spallation

- The thicker the substrate, the higher the driving force for spallation
  - Cooling induced interfacial shear stress calculation – PNNL 17781
  - Interfacial shear strength: 395MPa*
  - Interfacial failure driving force can be reduced by reducing the bulk thickness of SS441.

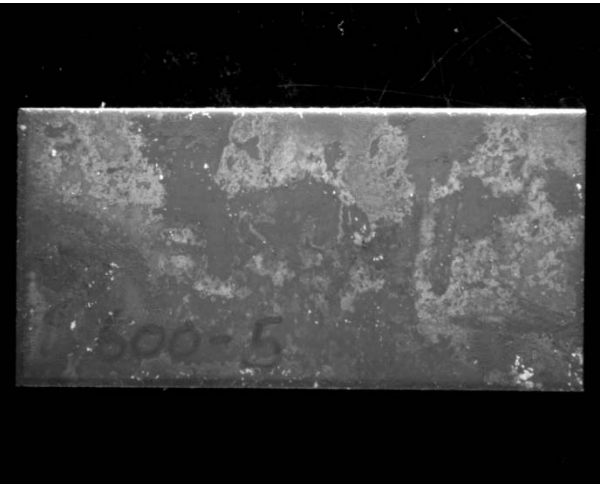
| Substr. Thick. | 1.6mm (0.06”) | | 0.5mm (0.02”) | |
|---|---|---|---|---|
| Coating thick. | 10 um | | 10 um | |
| Scale (um) | Scale/441 | | Scale/441 | |
| 2 | 441 MPa | spall | 361 MPa | No spall |
| 5 | 487 MPa | spall | 410 MPa | critical |
| 10 | 489 MPa | spall | 463 MPa | |
| 15 | 485 MPa | spall | 479 MPa | |

*Liu et al., *Journal of Power Sources* 189 (2009) 1044–1050

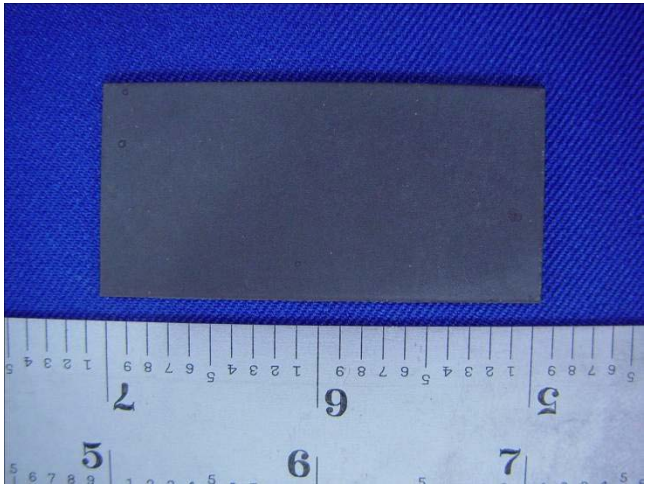
Verified by experimental data from J. Stevenson and PNNL Materials Task



# Effect of Shot-peening: Specimen Oxidized at 850C for 2000h and 2500h




As-received 441 SS oxidized for 600h at 850°C



Shot-peened 441 specimen exposed to two thermal cycles & oxidized for a total of 2500h at 850°C


Shot-peened and Ce-spinel coated 441 SS oxidized for 2000h at 850°C

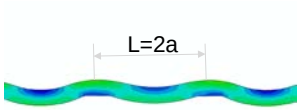
- To date, no spallation has been observed on the shot-peened specimens whether un-coated or coated that have been exposed to at least 2000h or more at 850°C.
- Need to determine whether to expose shot-peened specimens for additional thermal cycles or to cross-section and evaluate.

Pacific Northwest
NATIONAL LABORATORY

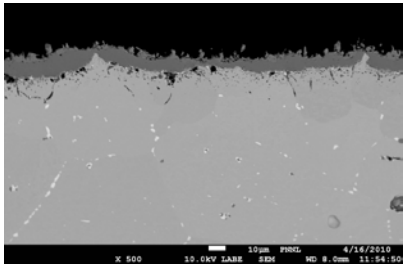
# Effects of Shot Peening on Scale Spallation

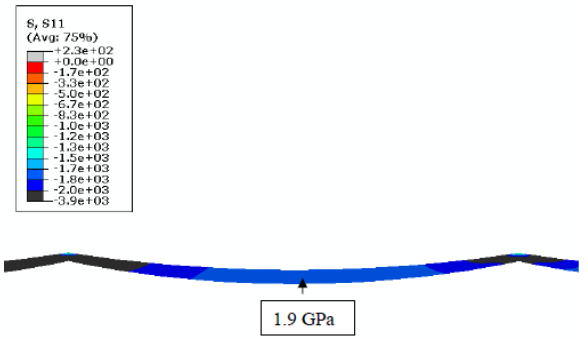
- Increase critical scale buckling strength by reducing critical buckling length (1)

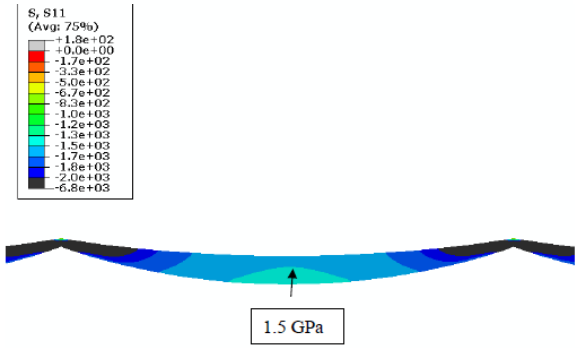
$$\sigma_{cr} = 1.2235 \frac{E}{1-\nu^2}\left(\frac{H}{a}\right)^2$$

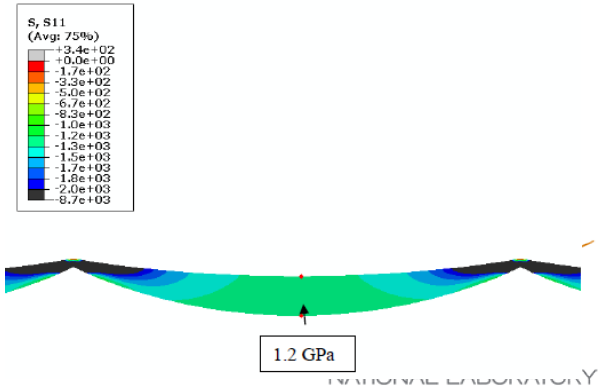



- Decrease buckling driving force, i.e., cooling induced compressive stress, by non-uniform oxidation of the shot peened surface:





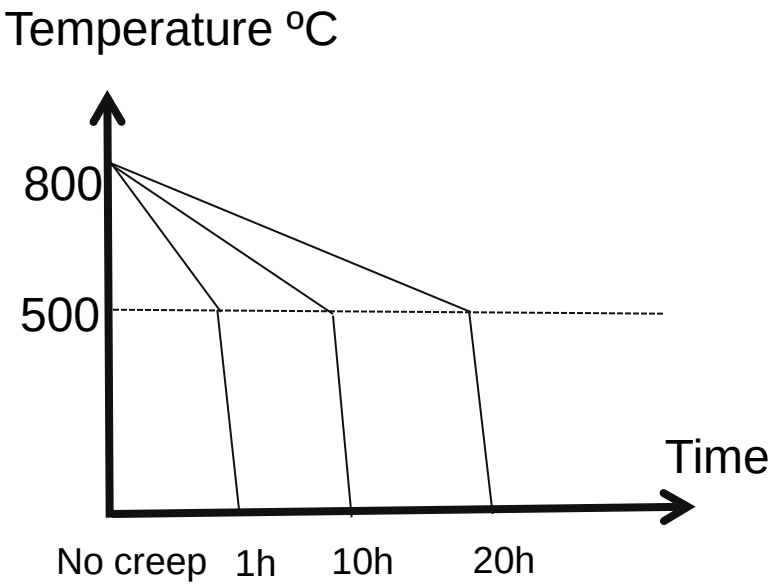

- Reduce scale spallation/buckling tendency from both directions:
  - Increased strength
  - Decreased driving force

(1) Hutchinson, J.W. and Suo, Z., *Advances in Applied Mechanics*, Vol. 29, pp. 64-187, 1992.

# Optimizing Cooling Profile to Minimize Spallation

- Objective: Utilize creep/stress relaxation of SS441 at temperature above 500ºC-600ºC to minimize oxide spallation during cooling

Cooling profile examined:




| Intermediate temperature | | 500ºC | | 600ºC | | No Creep |
|---|---|---|---|---|---|---|
| Max Shear Stress (Mpa) | 10min | 362 | 2.1% | | | 370 |
| | 1 h | 357 | 3.5% | | | |
| | 10 h | 347 | 5.8% | 348 | 6.1% | |
| | 20 h | 345 | 6.7% | 345 | 6.7% | |

- Temperature drops linearly from 800ºC to 500ºC/600ºC within 10min to 20hr in the first step; then drops to room temperature within 10s in the second step
- Slower cooling rate to intermediate temperature can be helpful in reducing spallation
- The shear stress reduction tapers off after 10h, maximum at 6.7% for 20h

# Glass Seal Modeling

- Accomplishments
  - Studied the effects of ceramic stoppers on the geometric stability of the self-healing seals in a simulated stack environment using creep analysis.
  - Studied effects of various interfaces of PEN/Stopper, IC/Stopper, and Stopper/glass on the interfacial stresses upon cooling
  - Modeled the self-healing behavior of glass

- Several topical reports and papers written by PNNL are available on this subject
  - Please see me after the presentation if you are interested in more information.

Pacific Northwest
NATIONAL LABORATORY

# Conclusions and On-Going Work

- Conclusions
  - Array of tools to model SOFCs at various scales (stack, cell, component levels)
  - Models improve understanding of SOFC operation and performance
  - Collaborations with experimentalists can help to design materials, interpret experimental data and understand degradation issues
- On-going work
  - Benchmarking and enhancement of 3D SOFC-MP
  - Validation and verification of detailed electrochemistry model
  - Enhancement of the detailed electrochemistry model to include the energy equation and to investigation of secondary reactions
  - Continued modeling of interconnects and coatings to validate our assumption on reduction of free buckling length
  - Additional modeling of shot peened SS441 for process optimization and lifetime prediction of coatings
  - Strength testing and modeling after contact material is selected