Modeling Tools for Solid Oxide Fuel Cell Analysis

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Modeling Project Overview

- Motivation
- Objectives & Approach
- Project Accomplishments
- Collaborations
- Overview of Modeling Tools
- Conclusions & Ongoing Work

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
- Disseminate/transfer modeling tools to SECA industry teams and CTP members

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
    - Durable interfaces
    - Cathode contact paste durability
    - Pressurized operation for large stacks
    - Secondary reactions
- Collaboration with NETL, ORNL, and ASME to establish a stack design approach

Project Accomplishments

- Continued to promote and support the use of SOFC-MP and Mentat-FC software packages with industry teams and CTP university teams
- Enhanced calculation speed and efficiency of SOFC-MP and porting to multiple platforms
- Developed a stack calculator (2D SOFC-MP) that quickly solves the temperature distribution and is suitable for incorporation into a system level model.
- Completed first-of-a-kind design guide for SOFCs
- Implemented time dependent constitutive model for glass seal materials in stack simulations.
- Developed a modeling capability to evaluate densification and strength of cathode contact materials, load path, and residual stresses due to stack assembly processes.
- Investigated the effect of oxide growth and metallic IC surface quality on interfacial strength of oxide scale and substrate.
- Developed a model to include creep of SOFC materials and to examine the effect on stress distribution with the stack components.
- Added elevated pressure capability to the EC and reforming models and examined effects on performance of large stacks.

Collaborations

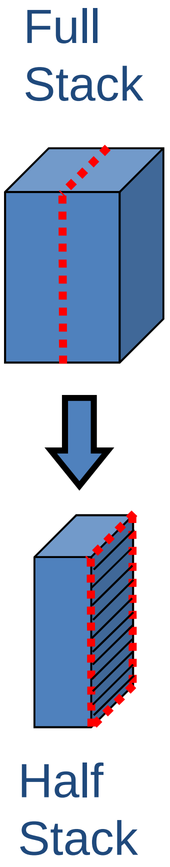
PNNL modeling staff are currently collaborating with SOFC researchers on several technical issues

- ASME design document
  - ORNL: E Lara-Curzio, Y Wang, A Shyam
  - ASME: J Powers, R Swayne
- Contact paste characterization
  - ORNL: E Lara-Curzio, Y Wang
  - NDSU: L Pederson
- Interconnect coatings
  - PNNL: J Stevenson
- SECA test cell
  - PNNL: J Stevenson, M Chou
- Modeling tool support
  - Delphi
  - Siemens
  - FCE
  - UCI: J Brower
- Seal characterization & modeling
  - PNNL: M Chou, J Stevenson
  - ORNL: E Lara-Curzio
  - GaTech: H Garmestani
- Secondary reactions
  - Carnegie Mellon: E Ryan
  - PNNL: O Marina
  - NDSU: L Pederson

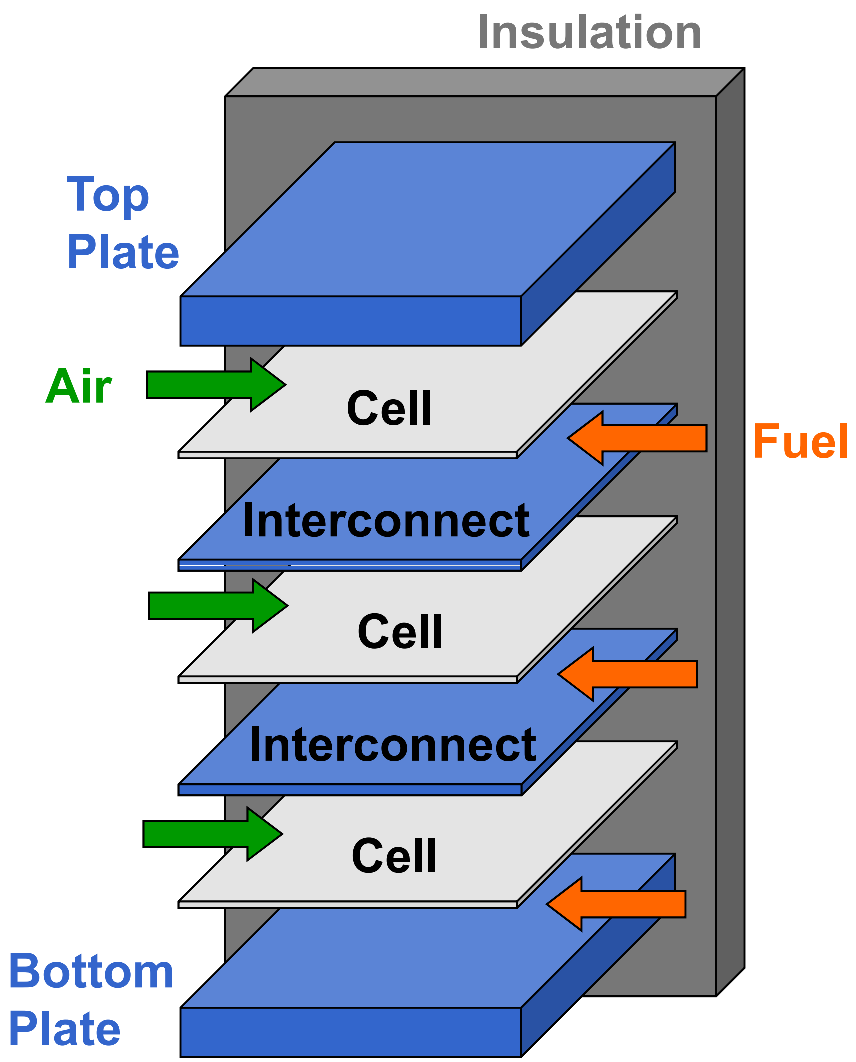
SOFC-MP: Capabilities and Features

- SOFC-MP Capabilities
  - 3D 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
  - 2D version for symmetric stacks adapted from 3D SOFC-MP
  - Slice model computes results along stack centerline
    - Co/counter-flow only
    - Can handle many cells
    - Faster for parametric studies of large stacks
  - Computations
    - Current distribution
    - Voltage distribution
    - Thermal distribution
    - Species distribution
    - Heat losses

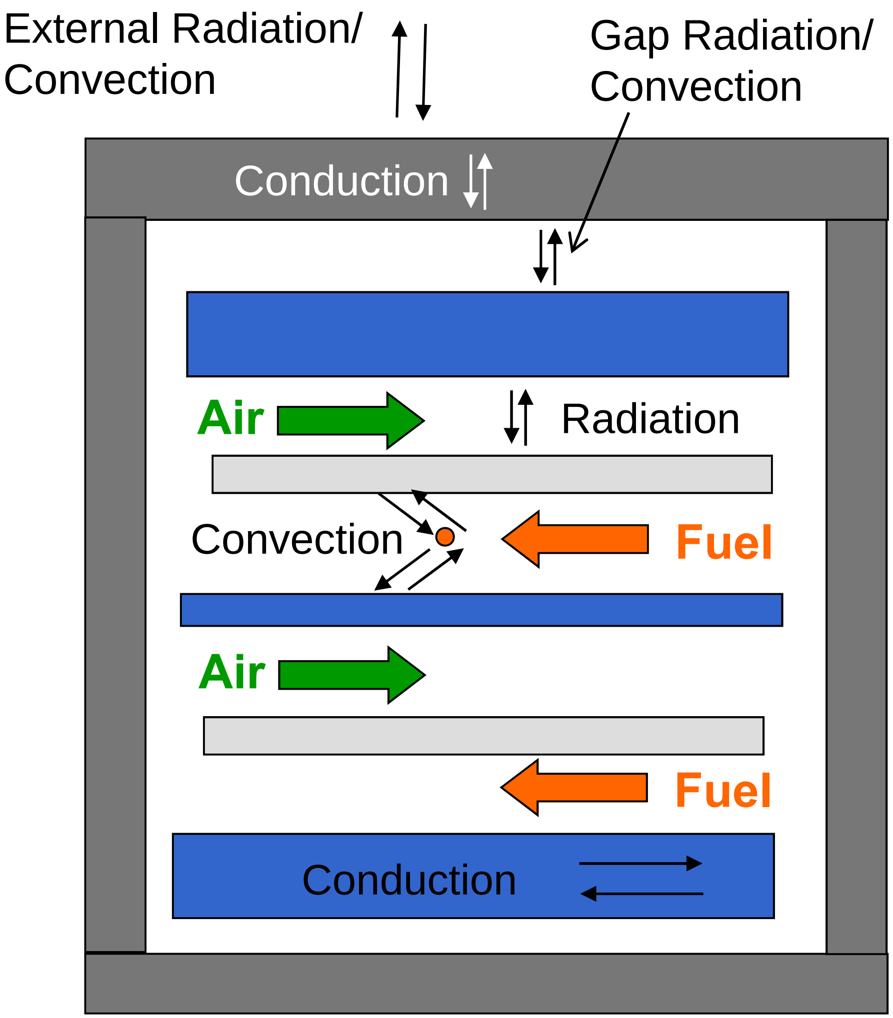


2D SOFC-MP- Stack Model Description



- Geometric features
  - Co/Counter flow
  - Number of cells
  - Cell length/width
  - Thicknesses
  - Top/bottom plates
  - External insulation
- Thermal-EC properties
  - I-V curve parameters
  - Conduction, convection, and radiation parameters
- Assumption
  - Distributions are uniform in the lateral direction

2D SOFC-MP- Stack Model Description

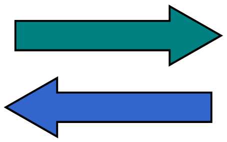


- Thermal model accounts for the coupled heat transfer modes of the fluid domains, solid components, and insulating enclosure
- Assumptions
  - Temperatures are uniform in the lateral direction
  - Currently, no explicit rib conduction link

2D SOFC-MP- Example Results

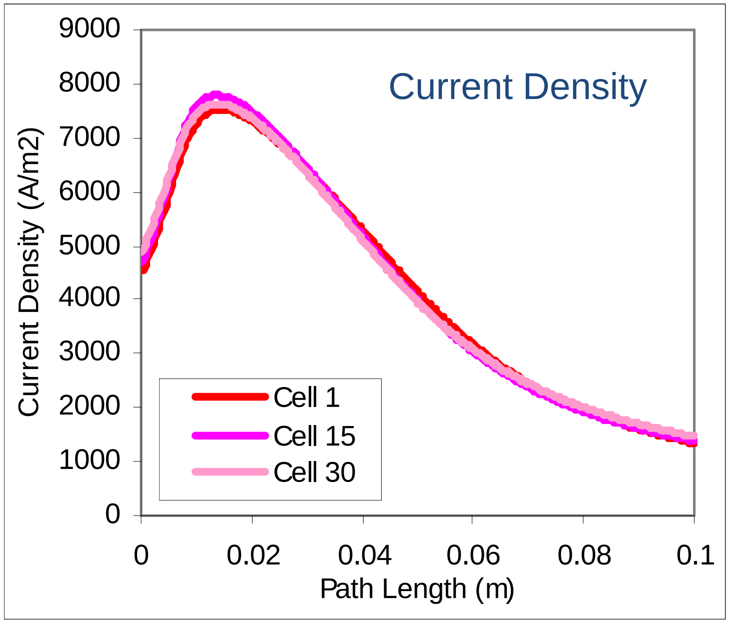
- Example: counter-flow, 10 cm long cell, 30 cells, adiabatic
- Operation: 428 mA/cm^2, 0.8 V, 65% UF, 15% UA

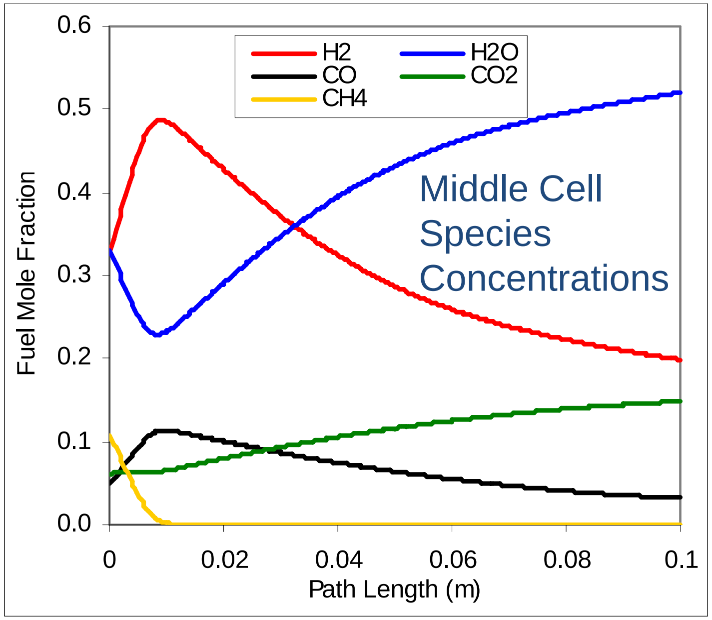
- 50% OCR Fuel: 0.324 H_2, 0.333 H_20, 0.049 CO, 0.061 CO_2, 0.110 CH_4, 0.124 N_2, 1 atm
- Air 0.21 O_2, 0.79 N_2, 1 atm



Fuel Flow

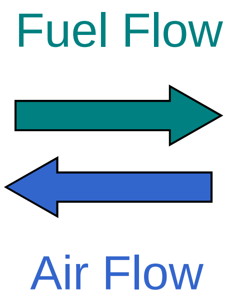
Air Flow

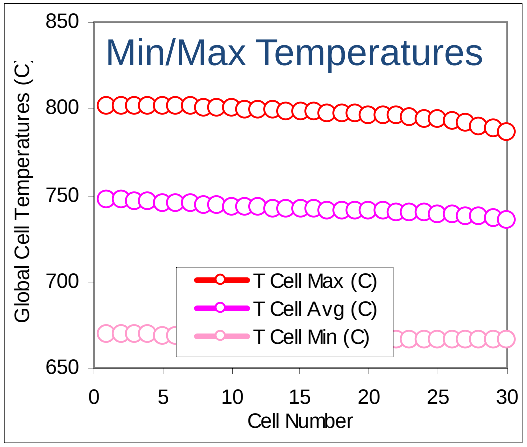


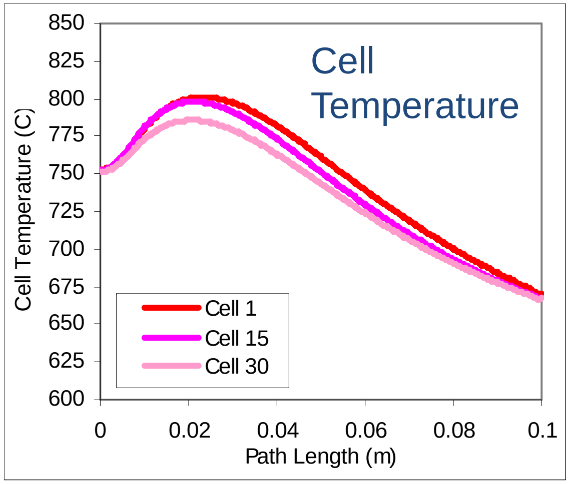


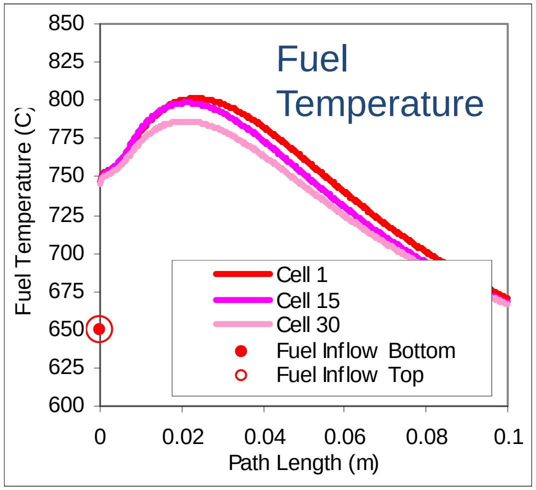
2D SOFC-MP- Example Results

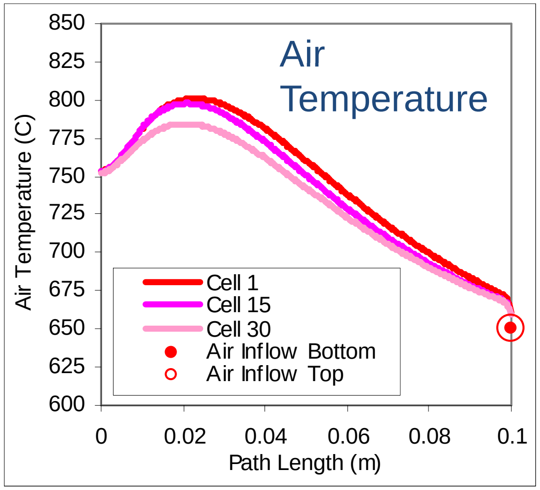
- Results
  - Cell min/average/max 667/742/802°C
  - Fuel in/out: 650/668°C
  - Air in/out: 650/753°C
- In summary, model is useful for more quickly characterizing large stacks











Modeling the Effect of Pressurization on Electrochemistry and Methane Reforming

Background

- Pressurized operation increases electrochemical efficiency and thus decreases the net heat load
- On-cell steam-methane reforming is used effectively to decrease the heat load and is also affected by pressure

Objectives

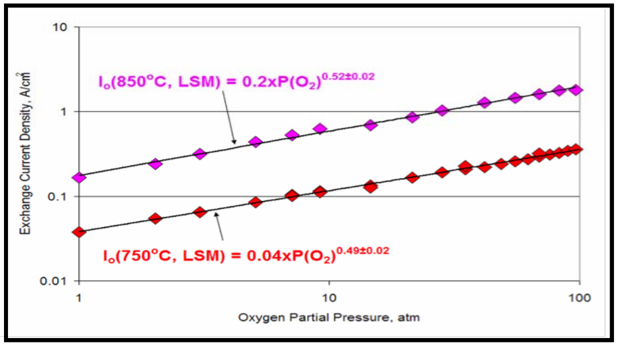
- Extend the SECA modeling capabilities to include the pressurization effects on the SOFC electrochemistry and on-cell steam-methane reforming performance
- Incorporate the updated models into stack level tools to enable prediction of thermal and electrical performance of stacks operating at elevated pressure

Approach

- Examine and model the coupled effects of pressurization on the SOFC electrochemistry, fuel gas composition, and reforming rates
- Validate model by parts (no public data for pressurized reforming operation of SOFC)
- Exercise the extended models on an example stack model to examine expected effects on thermal and electrical performance

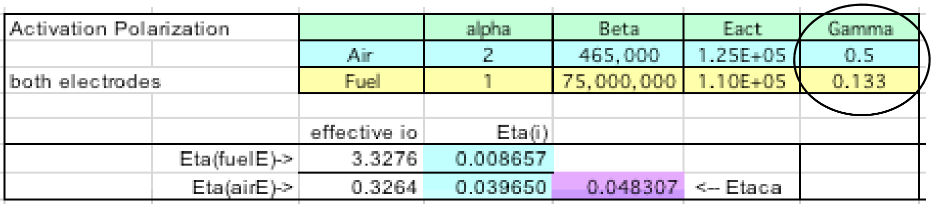
Effect of Pressure on Electrochemistry and Steam-Methane Reforming Rate

- Advanced SECA Electrochemical model considers activation polarization of both electrodes as described by the Butler-Volmer equation, which depends on the exchange current density (j_o)
    - PNNL tests showed : $j_o = j_o(PO_2^{0.5})$ for cathode
    - Others agree and find $j_o = j_o(PO_2^{0.133})$ for the anode



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

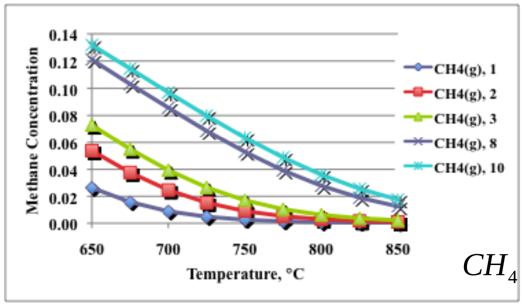
$$\eta_{act,e} = \frac{RT}{\alpha F}\sinh^{-1}\left(\frac{j}{2j_0}\right)$$



Activation Polarization			alpha	Beta	Eact	Gamma
		Air	2	465,000	1.25E+05	0.5
both electrodes		Fuel	1	75,000,000	1.10E+05	0.133
		effective io	Eta(i)			
	Eta(fuelE)->	3.3276	0.008657			
	Eta(airE)->	0.3264	0.039650	0.048307	<-- Etaca	

Typical activation polarization model settings

- The recently developed reforming <u>rate expression</u> considers effects of pressure on forward and reverse reaction, and maintains consistency with the literature, being 1st order in methane pressure, and with previous validated PNNL model



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

Equilibrium CH_4 concentrations

$$R_r = C_K\left((2.09e+9)\exp\left(\frac{-E_{act}}{RT}\right)P_{CH_4}P_{H_2O} - (1.54e-4)P_{CO}P_{H_2}^3\right)$$

$$C_K = (4.8e-7)\exp\left(\frac{-1.45e4}{RT}\right)$$

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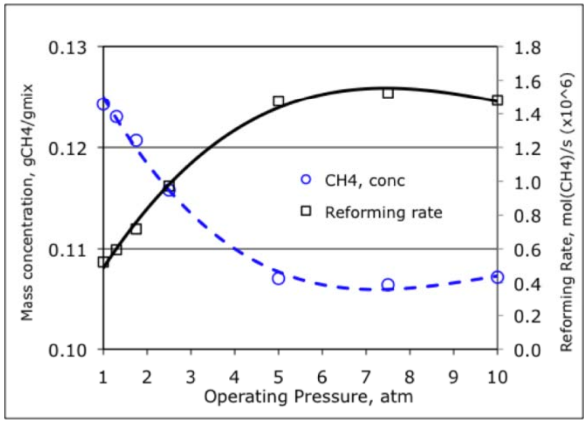
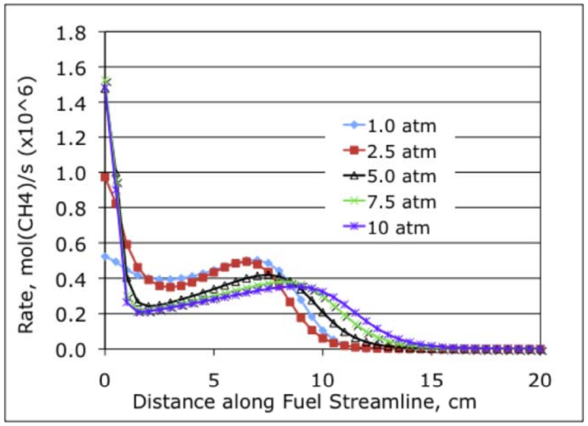
Effect of Pressurization on Performance: Simulations of 20x20 cm Cross-Flow Stack

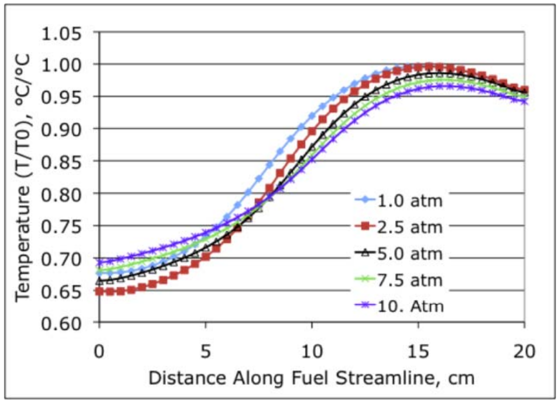
- Reforming rate near fuel inflow increased with pressure to a maximum at 7.5 atmospheres limited by available CH_4
  - Low fuel utilization would support further rate increase
  - CH_4 concentration mirrored the reforming rate being decreased when the local rate was high
- Reforming rates varied downstream, as effected by the electrochemistry, depending on concentration and temperature
- Maximum temperature and ΔT decreased for operating pressures above 2.5 atmospheres
- Electrical performance increased steadily with increased operating pressure



Reforming rate and CH4 concentration near fuel inflow as a function of operating pressure



Reforming rate along the anode as a function of operating pressure



Temperature along the anode as a function of operating pressure

Pressure, atm	Cell Voltage
1.0	0.653
2.5	0.678
5.0	0.690
7.5	0.717
10.0	0.721

Cell voltage as a function of operating pressure

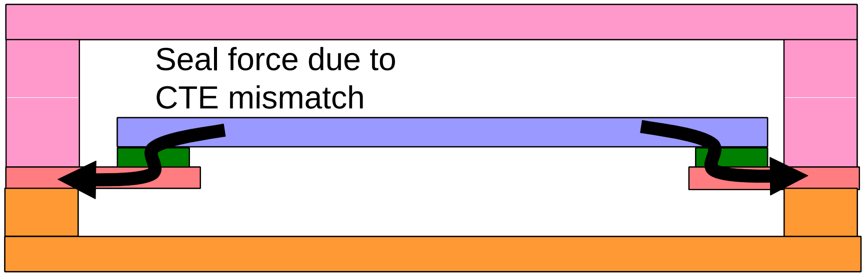
Modeling of Contact Paste and Load Path

Technical Drivers	Technical Approach
▶ How does the interconnect geometry and contact paste layer affect load path and stresses in the stack?	▶ Stack simulations to evaluate seal loads and stresses due to contact layer and interconnect features
▶ How does in-stack densification affect the load path and stresses in the stack?	▶ Stack simulations with densification strains for the contact paste layer
▶ What are the mechanical properties of the contact paste?	▶ Experimental testing at PNNL/ORNL and literature
▶ How much in-stack densification of the contact paste can be achieved to increase its strength?	▶ Combined materials model development and modeling effort

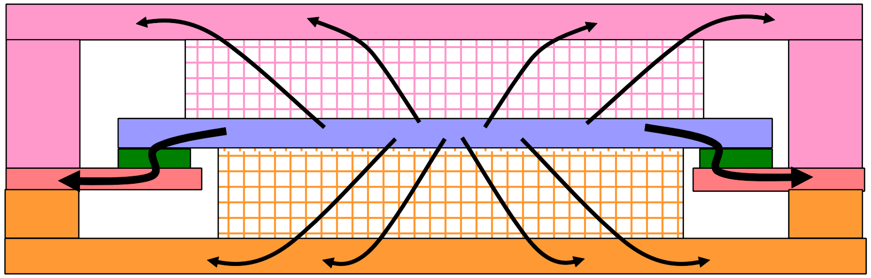
1. Stack Load Path
Concept of Seal Load Reduction

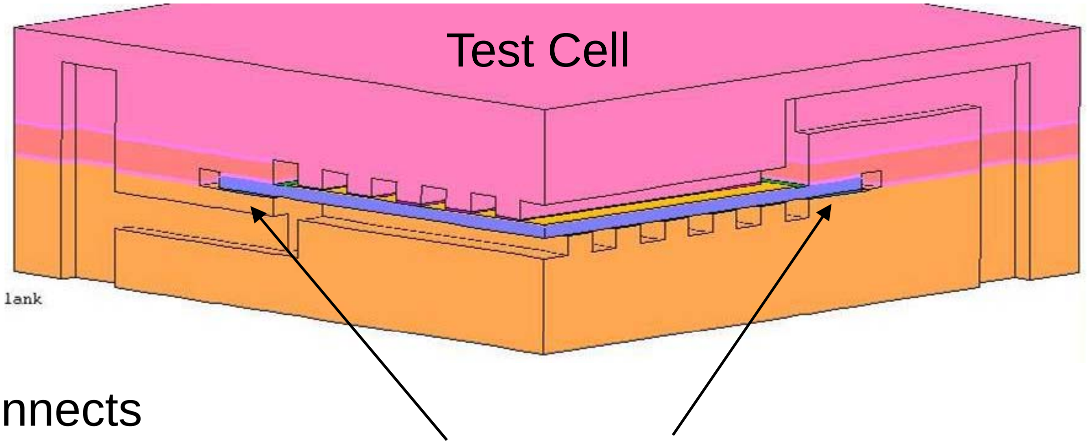
- Previously, the potential for the cathode contact bond to beneficially reduce edge seal forces by I.C. load transfer was shown

No mechanical support from interconnects

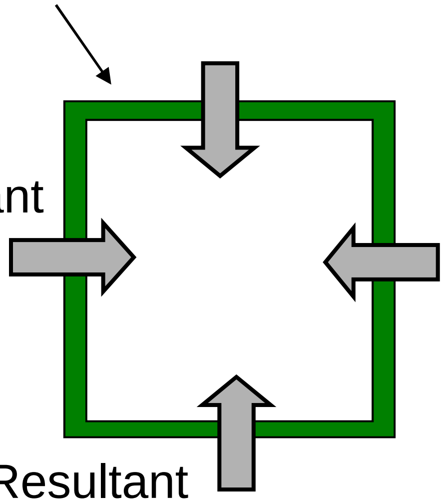


With mechanical support from interconnects





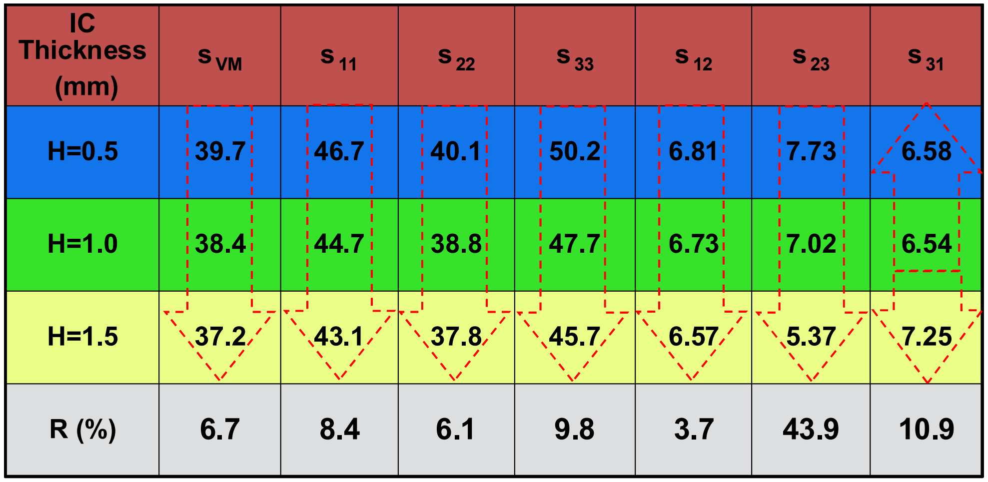
PEN Perimeter Seal



1. Stack Load Path
Results: Effect of IC Thickness/Creep

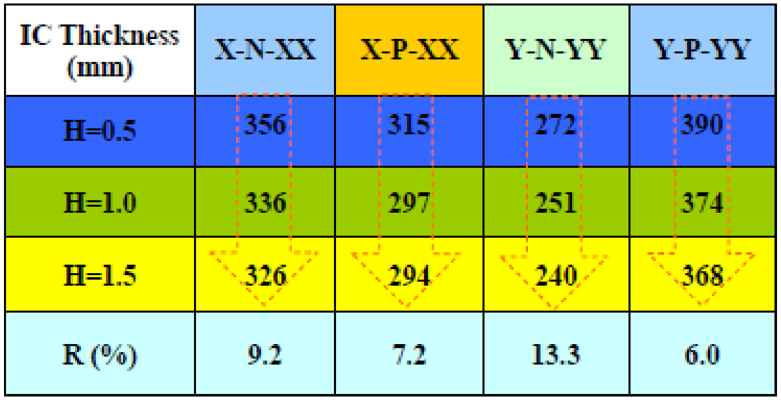
- Thicker interconnects with good cathode contact bonding were demonstrated to beneficially decrease the stresses in the perimeter glass-ceramic seal
  - Seal interface shear stresses less than experimental strengths, but localized seal and interface normal stresses predicted to be too large
  - Creep deformations of IC's also caused seal stress increase

PEN seal stresses decrease with IC thickness



IC Thickness (mm)	s_{VM}	s_{11}	s_{22}	s_{33}	s_{12}	s_{23}	s_{31}
H=0.5	39.7	46.7	40.1	50.2	6.81	7.73	6.58
H=1.0	38.4	44.7	38.8	47.7	6.73	7.02	6.54
H=1.5	37.2	43.1	37.8	45.7	6.57	5.37	7.25
R (%)	6.7	8.4	6.1	9.8	3.7	43.9	10.9

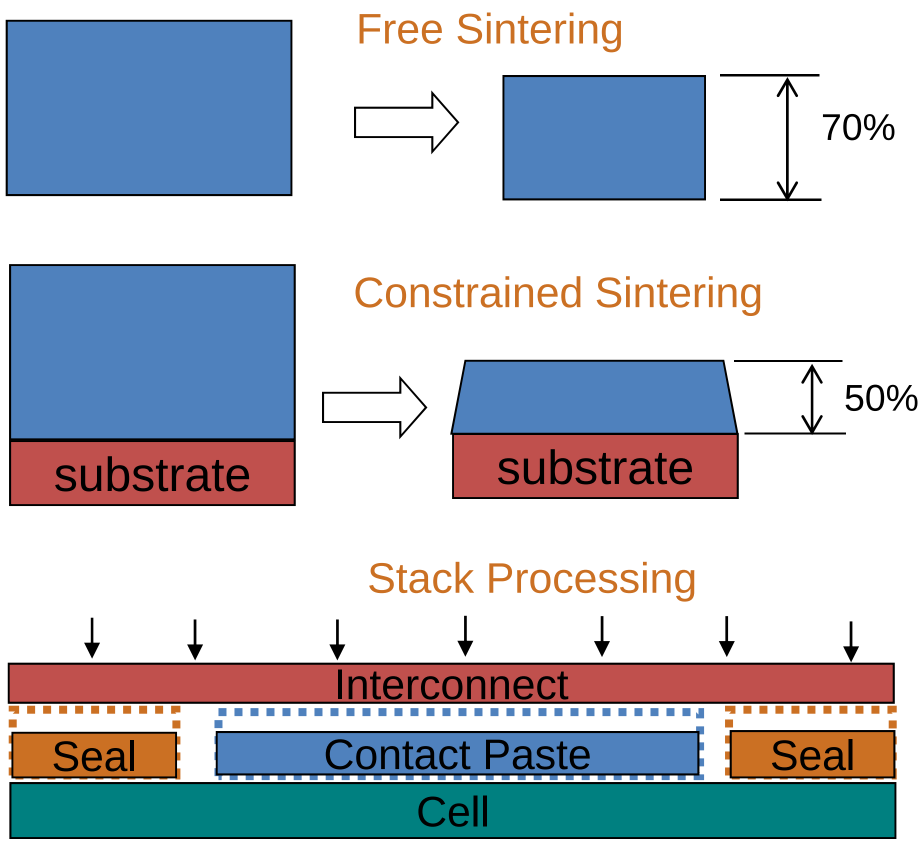
PEN seal interface stresses decrease with IC thickness



IC Thickness (mm)	X-N-XX	X-P-XX	Y-N-YY	Y-P-YY
H=0.5	356	315	272	390
H=1.0	336	297	251	374
H=1.5	326	294	240	368
R (%)	9.2	7.2	13.3	6.0

2. Cathode Contact Paste Modeling Impacts of Densification on SOFC

- Densification is necessary to improve the mechanical properties of contact pastes
  - Higher density provides a higher elastic modulus
  - Higher density provides a higher strength and fracture toughness
- Densification in the cell causes volumetric changes that may be important for good contact
  - In-plane constraint causes higher out-of-plane strains
  - Glass-ceramic seals also experience volumetric changes due to devitrification
  - Will the contact paste/seals form correctly for strong bonds?
- Continuum constitutive model implemented for FEA evaluations

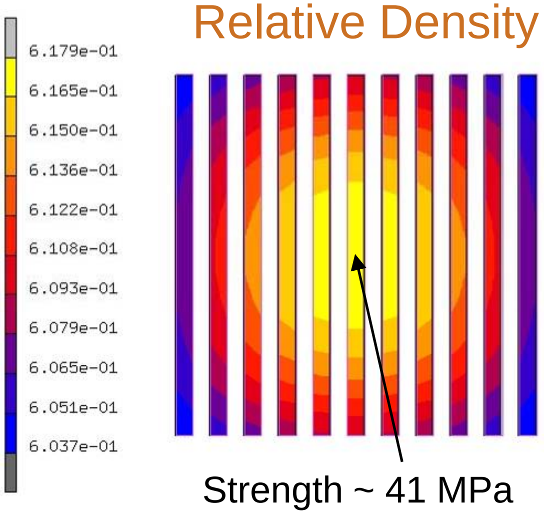


$$\sigma_{ij} = \frac{\sigma(W)}{W}\left[\varphi\dot{\varepsilon}_{ij} + \left(\Psi - \frac{1}{3}\varphi\right)\dot{e}\delta_{ij}\right] + P_L\delta_{ij}$$

2. Cathode Contact Paste Modeling Results: Paste Densification

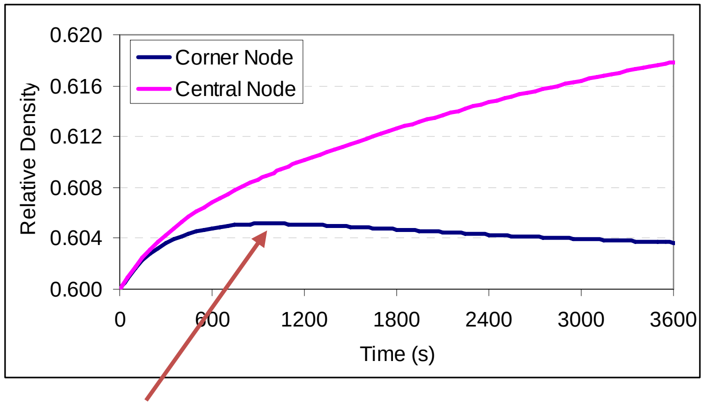
- Greatest volumetric shrinkage in the out-of-plane direction
  - Strains ~50X greater than in-plane directions due to lateral constraint of the cathode/IC rib
    - Same behavior as during electrolyte formation during co-firing
- Higher preload through the center cause enhanced sintering leading to relative density increase to 0.618
- The reduced sintering on the corners causes less densification to 0.604
- The corner region actually experiences tensile stresses during heat treatment that reverses the densification
- *<u>Preload distribution during paste formation determines final properties</u>*

Relative Density



Strength ~ 41 MPa

Strength ~ 40 MPa

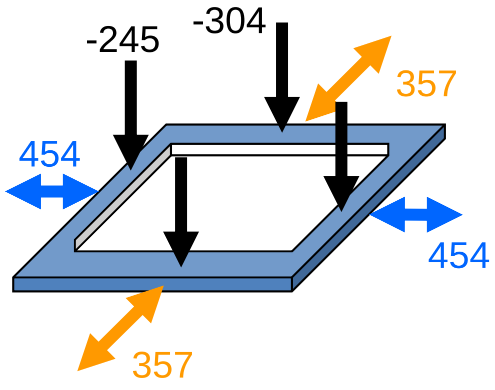


Local loss of compression

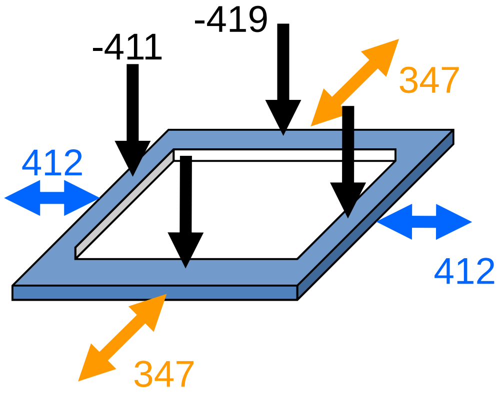
2. Cathode Contact Paste Modeling Results: Loads and Stresses

- Models were evaluated with and without consideration of the densification strains in the contact paste layer
- With inclusion of densification strains:
  - Contact paste stresses increased slightly, but the maximum value was still less than the experimental strength (~1-14 MPa)
  - For the seal, in-plane shear loads decreased and out-of-plane normal loads were more compressive (to beneficially hinder delamination)
  - For the seal, in-plane peak stresses were not affected significantly while out-of-plane stresses were beneficially lower at operating temperature but unchanged at shutdown
  - Principal stresses in the anode/cathode/electrolyte layers were not significantly impacted by the contact paste densification at operating temperature or shutdown

Without Densification



With Densification



3. Contact Paste Property Characterization

- Strength testing (PNNL, ORNL)
  - 1-14 MPa for spinel coated Crofer substrate/LSM-10
  - 2-8 MPa for Ce-spinel coated 441SS substrate/LSM-10
  - Average energy release rate of 1.47 Jm^{-2} for spinel coated Crofer substrate/LSM-10
- Material challenges for inks and processing
  - Must ensure ink is calcined and attrition milled for good sintering
  - Must be cognizant of binder burn out rates to prevent void formation
- Currently, fabrication of 441SS specimens with the updated Ce-spinel coating is in progress
  - PNNL: Evaluate high versus low temp interfacial tensile specimens and compare to literature observations
  - ORNL: Evaluate the effect of porosity and thickness on interfacial fracture toughness. Evaluate thermal cycling and thermal aging.

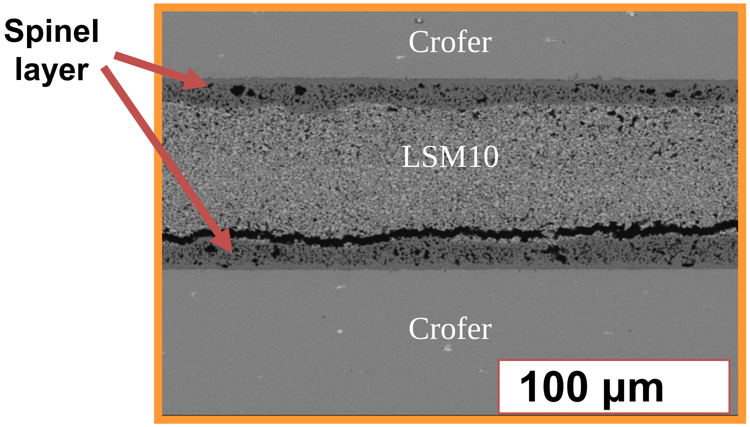


Illustration of the crack propagation path observed at the spinel-paste interface for a fracture toughness specimen

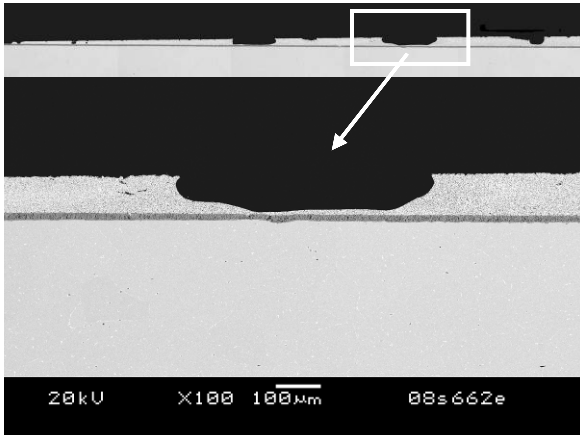


Illustration of voids formed during fabrication of interfacial tensile specimens

Lifetime Quantification of Coated Metallic Interconnects

Current activities:

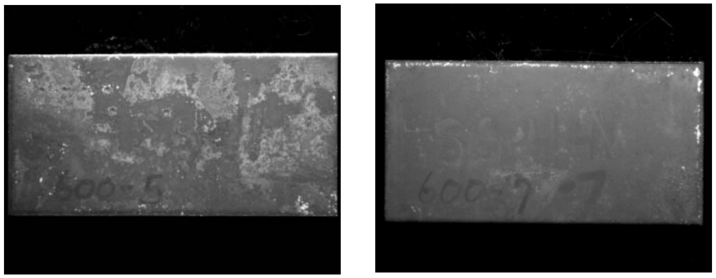
- Quantifying adhesion strength between oxide and substrate for shot peened specimens
  - Bare shot peened 441 SS specimens are being oxidized in air at 850C for 600, 900, and 1200 hours
- Quantifying effects of shot peening on substrate surface:
  - Texture
  - Chemistry on grain boundary
- Quantifying delamination driving force with a shot peened surface
- Preparing Ce-doped spinel coated shot peened specimens

Future activities:

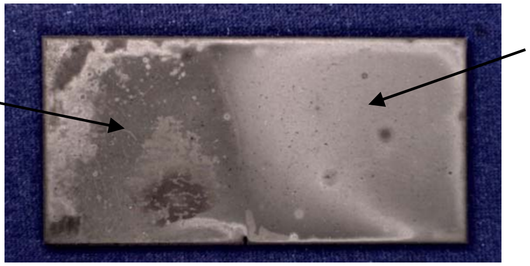
- Quantify interfacial strength of SS441/oxide for shot peened samples:
  - Surface finish
  - Residual stress
  - Surface chemistry/Grain boundary modification
- Quantify interfacial strength of Ce doped MC spinel/oxide for coated SS441 samples
- Life prediction for coated SS441
- Integrate ORNL measured growth stress in IC life prediction
- Optimization of coating thickness for SS441

Accomplishment: Quantified Effects of Batch and Surface Quality on Oxide Adhesion upon Cooling

2007: First batch (left: as received, right: polished)



2008: Second batch (left: as received, right: polished)



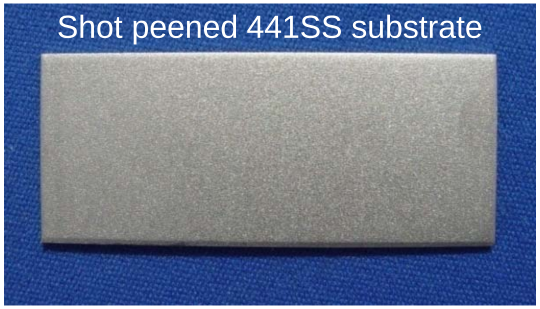
Non-polished surface. Spallation observed

Polished surface

	First Batch		Second Batch	
Surface Condition	*As-received*	*Polished*	*As-received*	*Polished*
Roughness	0.7	0.25	0.4	0.02
Total Number of Specimens	3	4	3	3
Number that Spalled	**3**	**0**	**1**	**0**

- Different batches of as-received materials have different level of spallation tendency upon removal from furnace
  - Different batches of as-received materials have different oxide adhesion strength
- Polished surfaces have less spallation for both batches:
  - Surface quality influences adhesion strength
- Further work in quantifying IC life should consider:
  - Substrate thickness
  - Substrate chemistry composition/thermal mechanical processing parameters
  - Substrate surface quality

Accomplishment: Examined Effects of Shot Peening on Oxide Adhesion upon Cooling for SS441

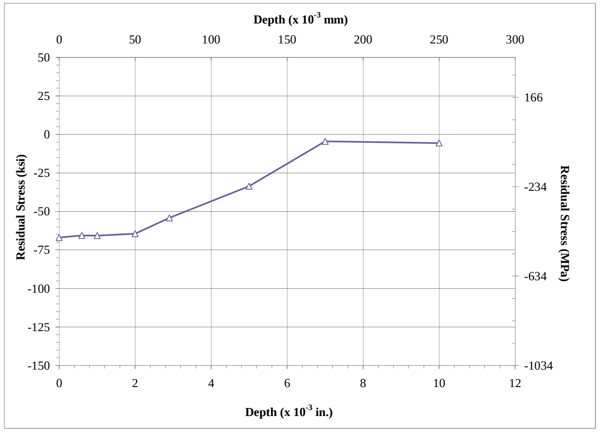

Shot peened 441SS substrate


Oxidized shot peened 441 specimen

Surface roughness measurements of shot-peened samples

Profile	Ra (μm)	Rq (μm)	Rz (μm)
1	2.79	3.49	24.23
2	2.95	3.67	21.03
3	3.00	3.80	24.88
Mean	**2.91**	**3.65**	**23.38**
Std Dev	0.11	0.16	2.06

Residual stress measurements



- Surface modification through mechanical shot peening *dramatically* reduces the tendency for oxide scale spallation during cooling:
  - Surface modification through cold work/mechanical work
  - Higher surface roughness
    - 10 times rougher than a polished surface
  - Surface residual stress
  - Removal of edge spallation:
    - Reduced free-standing length of oxide layer
    - Increased critical buckling load
    - Decreased cooling induced interfacial shear stress

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
- SOFC design document is completed

Ongoing Work

- Release of the SOFC design document
- Release of 2D SOFC-MP
- Develop a modeling framework to examine cell electrochemistry and secondary reactions
- Characterization of contact paste mechanical strengths
- Simulation of contact paste development and cell load paths in SECA test cell geometry
- Develop modeling capabilities and supporting experiments to evaluate feasibility of advanced sealing concepts