SOFC Development at PNNL: Overview

J.W. Stevenson, B.J. Koeppel, Y.S. Chou, J.S. Hardy, J.P. Choi, C.A. Coyle, K. Lai, Z. Xu, and N.K. Karri

Pacific Northwest National Laboratory
Richland, WA 99354

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Scope of Work

- Materials Development
  - Cathode materials and interactions
    - Effects of volatile Cr compounds
      - **Poster: SOFC Testing in Cathode Air with Quantified Cr Concentration (John Hardy)**
    - Improved density of ceria barrier layers
      - Sintering aids, PVD
  - Mitigation of Cr poisoning
    - Evaluation of Cr capture materials
      - **Poster: Evaluation of Cr-Gettering Material in a Generic Stack Test Fixture (Matt Chou)**
  - Cathode-to-interconnect contacts
    - Strengthening of cathode/contact materials interfaces (combined experimental/modeling approach)
      - **Poster: Effect on Sintering Aids on Densification and Contact Strength of SOFC (Matt Chou)**
  - Interconnects/BOP
    - Reactive air aluminization: Dip-coating and reduced fabrication temperatures
      - **Poster: Lower Temperature RAA Process for Planar SOFC Stacks (Jung Choi)**
- Modeling/Simulation
  - SOFC Stack Modeling Tools
    - SOFC-MP (2D and 3D) enhancements to support the Reduced Order Model (ROM) tool for improved system modeling
      - **Poster: Enhanced SOFC-MP Software Tool Set (Brian Koeppel)**
  - Modeling of Stack Degradation and Reliability
    - Reliability of cell and stack structures
      - **Poster: Structural Reliability Considerations for Planar SOFCs (Naveen Karri)**
    - Integration of lower-scale degradation data

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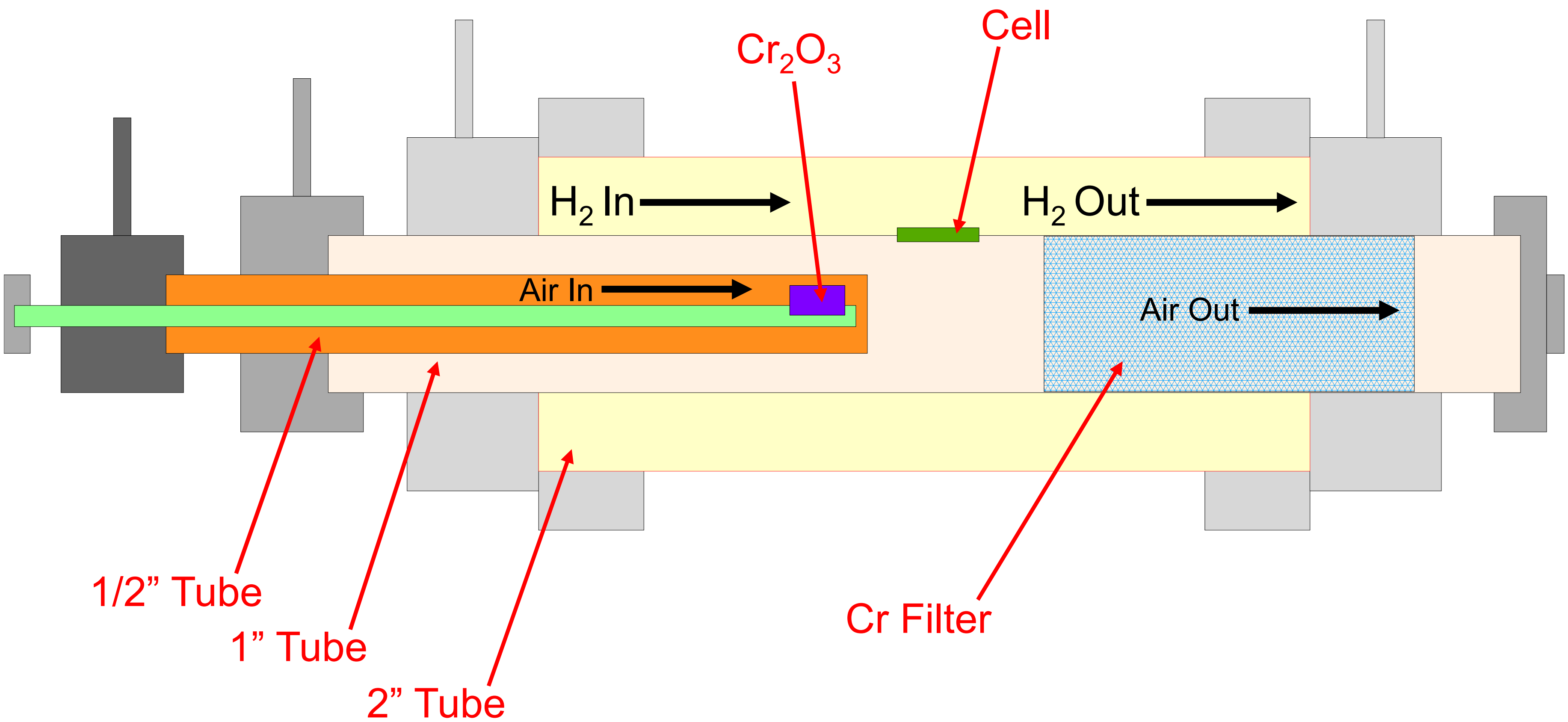
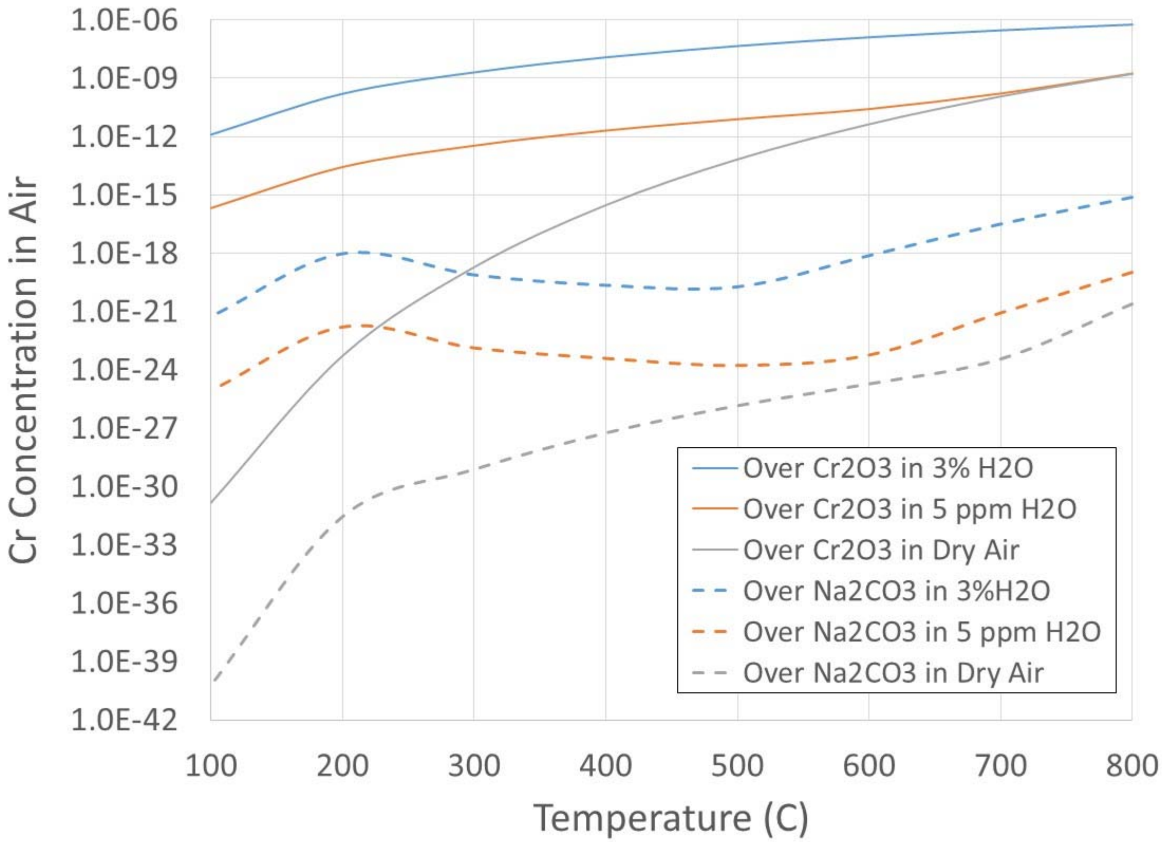
Cathode materials and interactions: Effects of volatile Cr compounds on cathode performance

- Approach
  - Button cell tests to quantitatively assess effects of Cr on cell performance as function of Cr concentration, temperature and time
    - Anode-supported button cells with LSM/YSZ cathodes
    - Correlate Cr dosing with cell performance (power density and stability) and cathode microstructure and chemistry.
    - Constant current testing with I-V and EIS sweeps
    - Post-test characterization: SEM/EDS/EBSD/XRD

PNNL Test Fixture Design (Not to scale)



Equilibrium Cr-content of Air



- Thermodynamic calculations show that sodium carbonate can reduce the concentration of Cr-species in the air by more than 8 orders of magnitude

- The Na_2CO_3 reacts with Cr-species to form water soluble Na_2CrO_4
  $CrO_3(g) + Na_2CO_3(s) \rightarrow Na_2CrO_4(s) + CO_2(g)$
  $CrO_2(OH)_2(g) + Na_2CO_3(s) \rightarrow Na_2CrO_4(s) + CO_2(g) + H_2O($g

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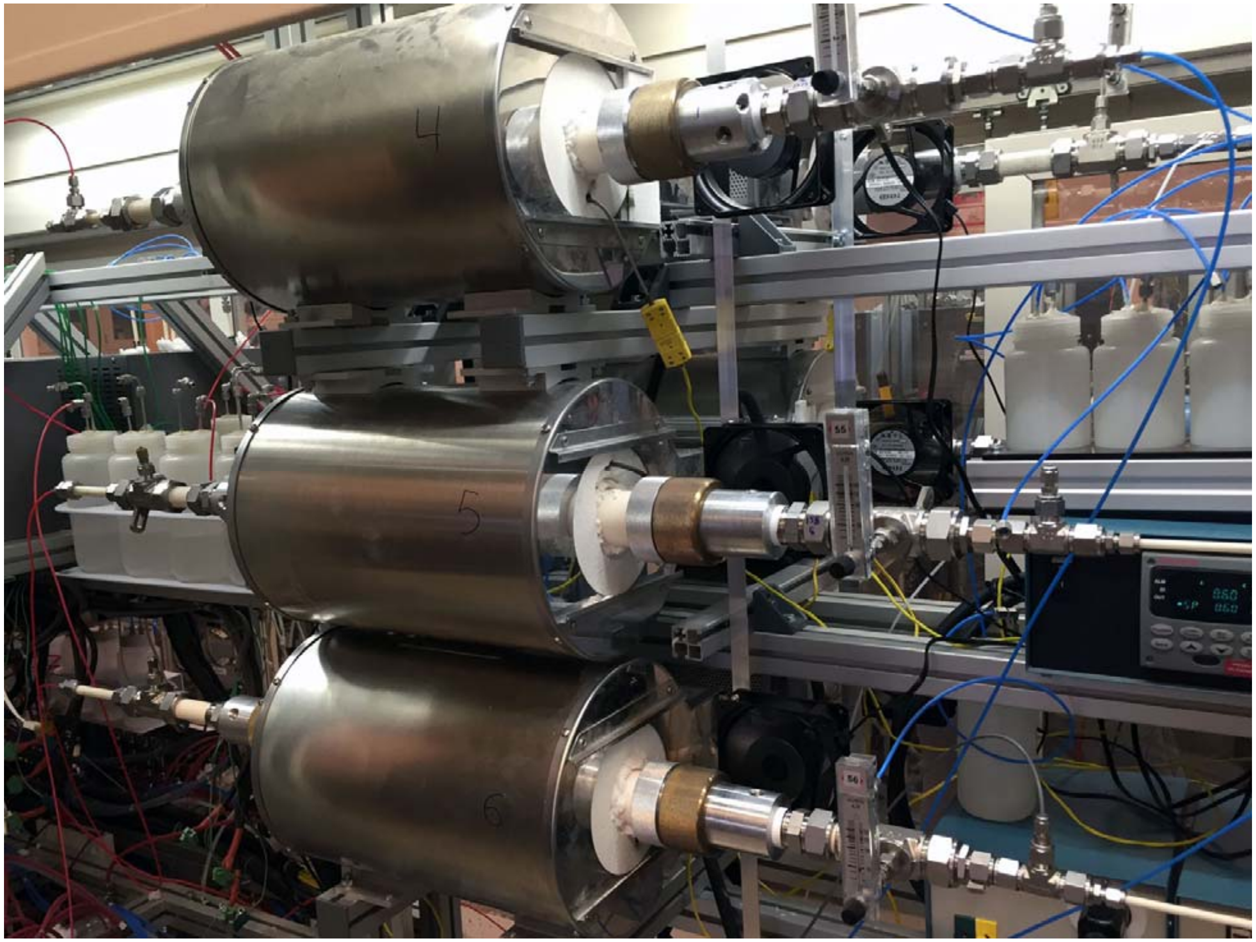
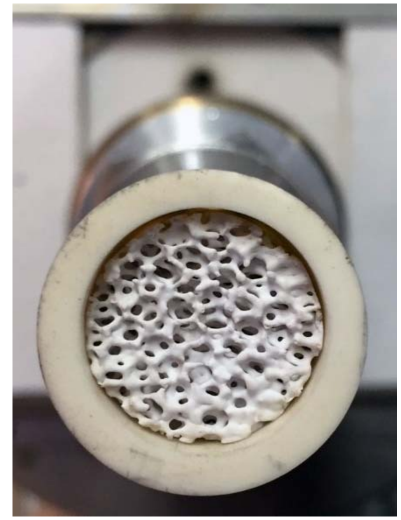
Assembled Cr Test Fixtures



Downstream Filter



Chromia Pellet

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Validation Testing of Fixture for Cell Tests w/ Cr

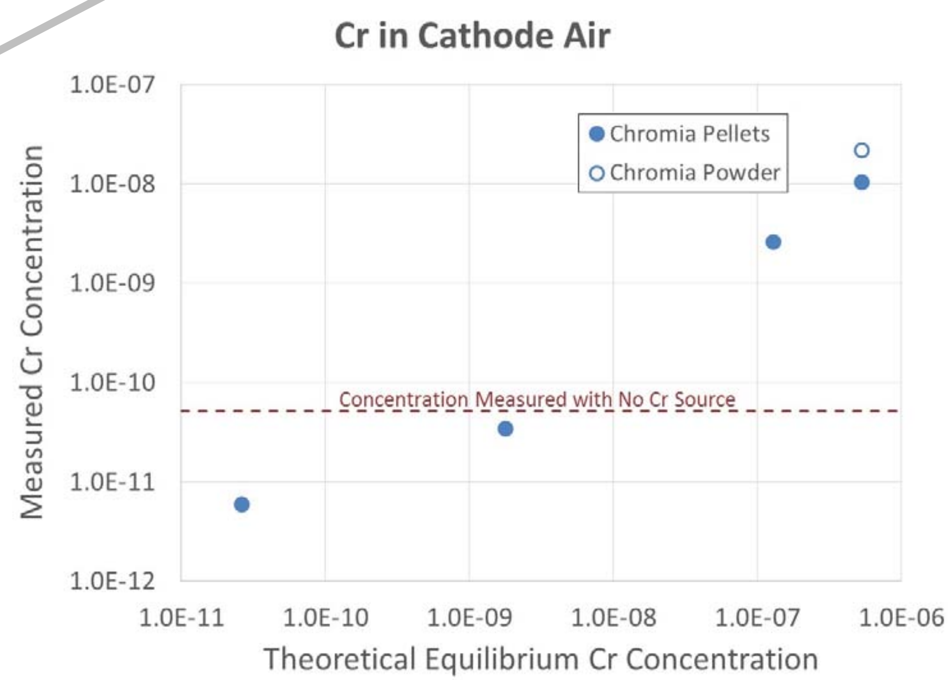
- 1) Preliminary tests at 850ºC with no cell in air stream ***(complete)***

# of Tests	Cr2O3 Source	Cr2O3 Temperature (C)	Humidity Level	Time (h)
1	None	N/A	<5 ppm	200
1	Pellet	800	<5 ppm	200
1	Pellet	600	<5 ppm	200
1	Pellet	800	~3%	200
1	Pellet	600	~3%	200
1	Powder	800	~3%	200

Parameters	Cr Mass (µg)	Cr Conc in Air	Theo. Eqm. Conc	Meas/Theo
Cr2O3 Powder at 800C 3% Water	306.17	2.20E-08	5.33E-07	4.13E-02
Cr2O3 pellet at 800C 3% Water	143.21	1.05E-08	5.33E-07	1.97E-02
Cr2O3 pellet at 600C 3% Water	35.83	2.59E-09	1.28E-07	2.03E-02
Cr2O3 pellet at 800C Dry Air	0.46	3.41E-11	1.78E-09	1.92E-02
Cr2O3 pellet at 600C Dry Air	0.08	5.95E-12	2.62E-11	2.27E-01
No Cr Dry Air	0.70	5.13E-11	0	N/A

Some Chromia blew out of the container

Very similar ratios



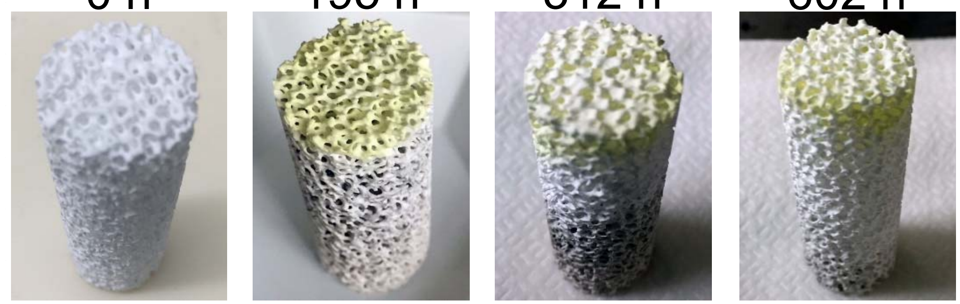
Preliminary Testing of Cr Cell Test Apparatus

- 2) Determine time-to-saturation of Cr filters at high Cr concentration (*in progress)*

# of Tests	Cr2O3 Source	Cr2O3 Temperature (C)	Humidity Level	Time (h)
1	Pellet	800	~3%	200
1	Pellet	800	~3%	400
1	Pellet	800	~3%	600
1	Pellet	800	~3%	800
1	Pellet	800	~3%	1000

Time (h)	Cr Conc in Air	Meas/Theo Cr Conc
195	7.08E-09	1.33E-02
312	7.17E-09	1.34E-02
602	1.15E-08	2.16E-02
~800	Test in Progess	
~1000	Test in Progess	

0 h 195 h 312 h 602 h



- 3) Determine time-to-detection for low Cr concentration exposures ***(in progress)***

# of Tests	Cr2O3 Source	Cr2O3 Temperature (C)	Humidity Level	Time (h)
1	None	N/A	<5 ppm	1000
1	Pellet	600	<5 ppm	1000
1	Pellet	800	<5 ppm	1000
1	None	N/A	<5 ppm	2000
1	Pellet	600	<5 ppm	2000
1	Pellet	800	<5 ppm	2000

Cr-contamination Button Cell Test Plan

- 1) Baseline Cr-contamination tests of LSM/YSZ cells ***(Upcoming)***

# of Tests	Cr2O3 Source	Cr2O3 Temperature (C)	Humidity Level
3	No	N/A	<5 ppm
3	Yes	800	<5 ppm

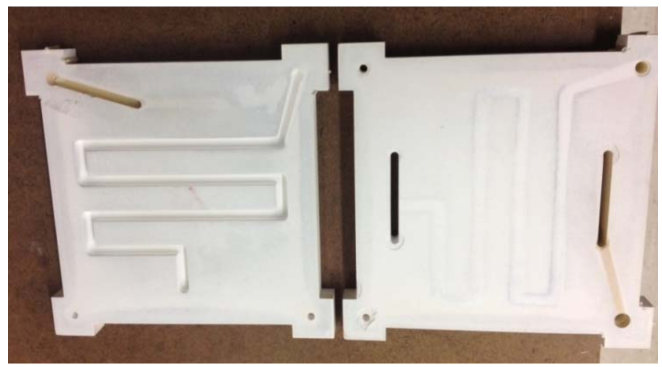
- 2) LSM/YSZ cell tests with variable Cr dosing ***(Upcoming)***

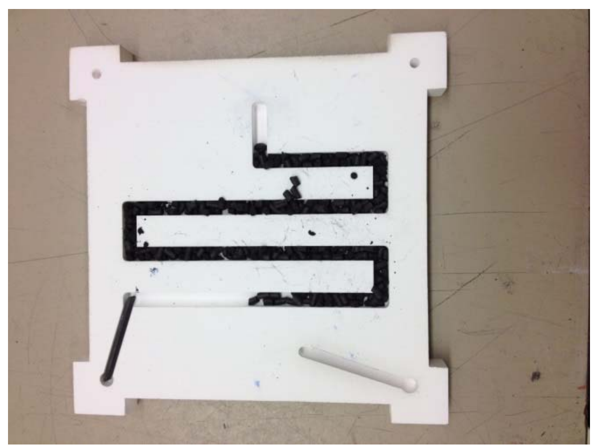
# of Tests	Cr2O3 Source	Cr2O3 Temperature (C)	Humidity Level
3	Yes	800	~3%
3	Yes	600	<5 ppm

- 3) Seek Cr concentration threshold below which cell performance and stability is not significantly affected ***(Upcoming)***
  - 3 conditions with progressively lower Cr source temperatures in <5 ppm water

Mitigation of Cr Poisoning

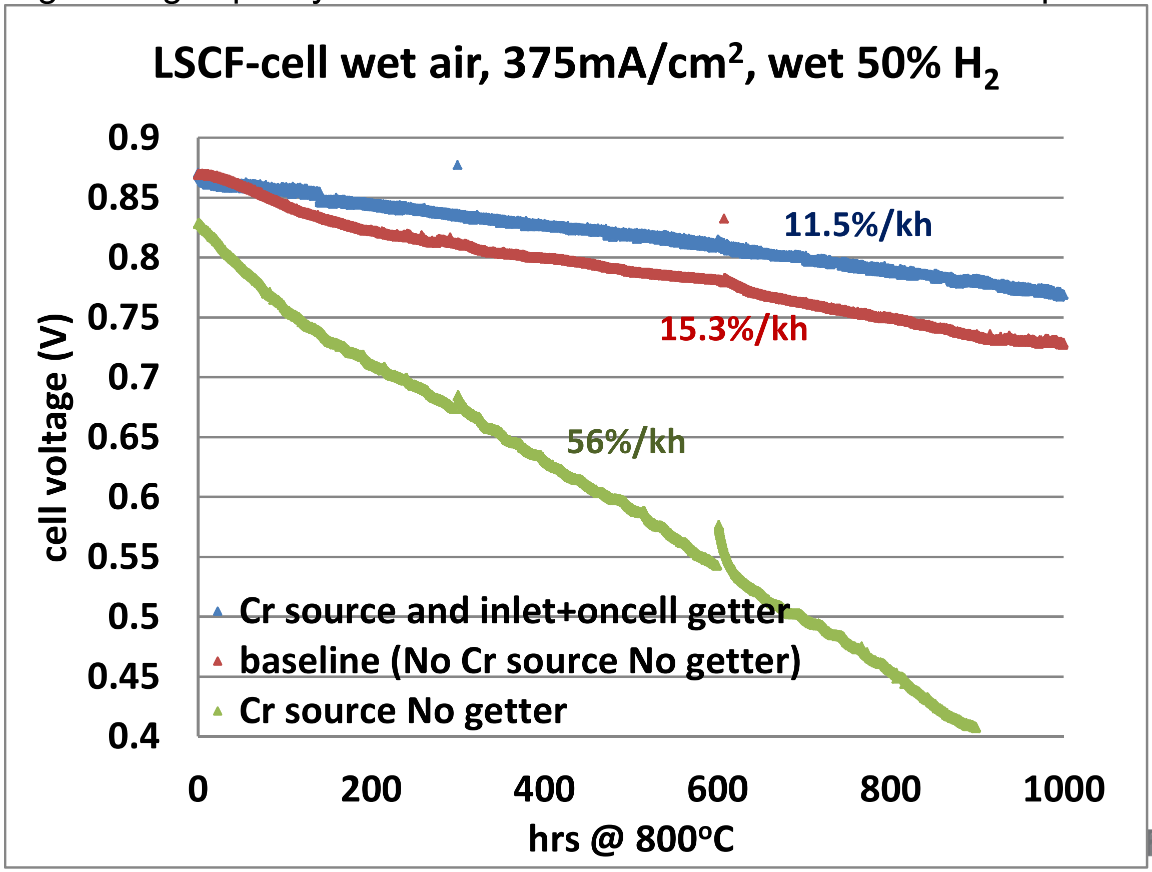
- Objective: Evaluate/optimize novel Cr getter materials
  - Collaboration with P. Singh’s group at U. Conn.
  - Cell tests in Core Technology Program stack test fixture
    - Baseline 1: Cr-free; Baseline 2: Cr source, no getter
    - Evaluation of getter in upstream and/or on-cell configurations





Validation with Inlet and On-cell Cr-Gettering

- 2 pre-oxidized AISI 441 metal strips (~7 cm^2)
- LSCF-based cell (2"x2"), spinel-coated and aluminized AISI 441 interconnect plates, humidified 50% H_2 vs. air, 800°C
- Inlet with both solid-state reaction pellets and chemically impregnated foam
- On-cell painted with LSCo ink (10% gettering material) on cathode
- Calculated Cr-gettering capacity about 15-20 times of available Cr volatile species



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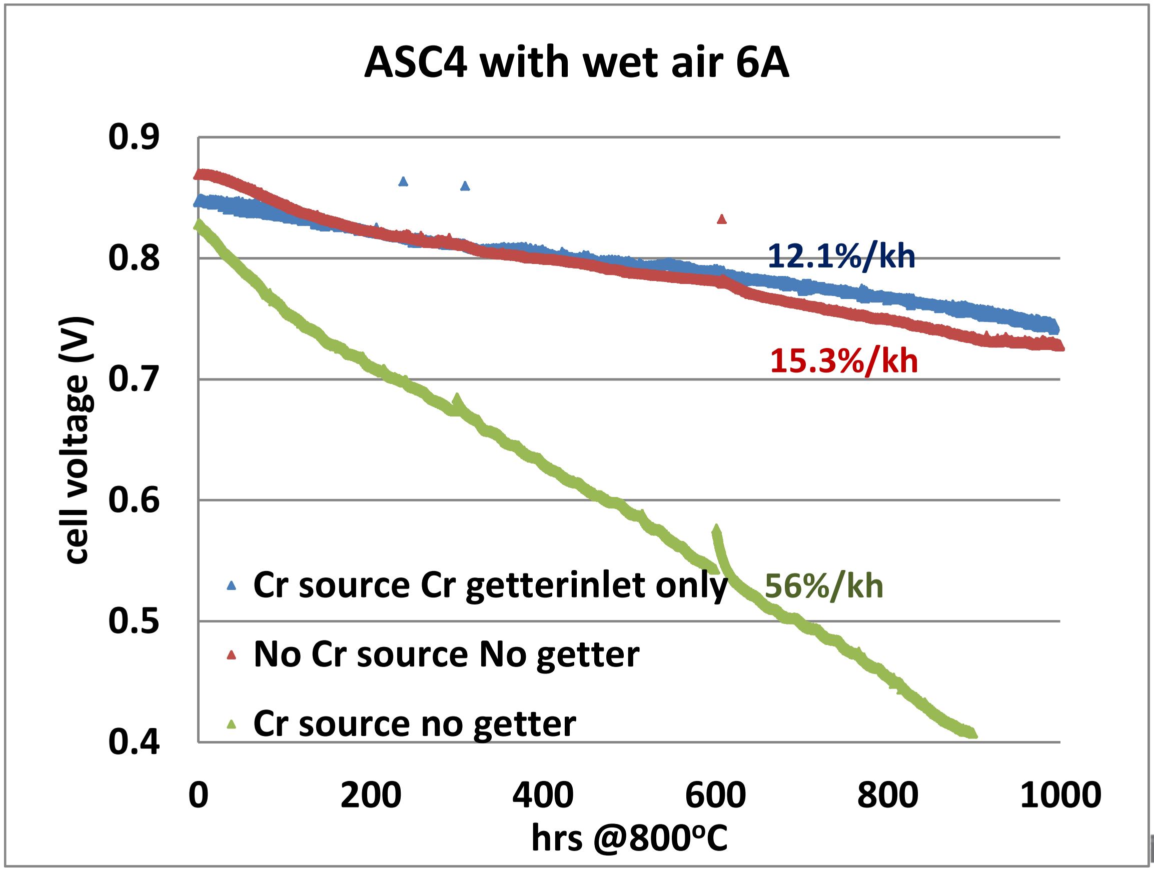
Validation with Inlet Cr-Gettering Only

- 2 pre-oxidized AISI 441 metal strips (~7 cm^2)
- LSCF-based cell (2”x2”), humidified 50%H_2 and air (~4.75% H_2O) @375mA/cm^2, 800^oC
- Inlet with solid-state reaction pellets only
- Calculated Cr-gettering capacity about 15-20 times of available Cr volatile species

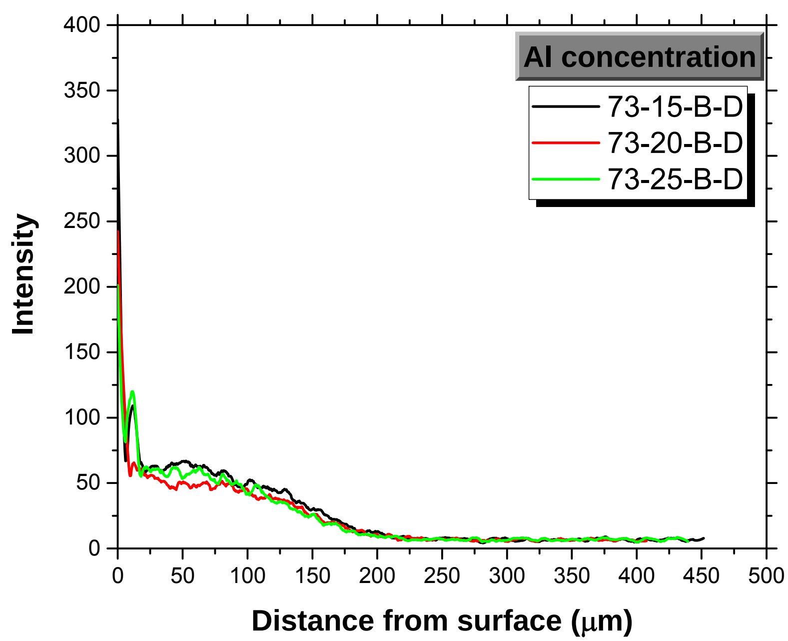


Reactive Air Aluminization (RAA)

•Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., $SrCrO_4$), which degrade interfacial strength

•Cr volatility from alloys can poison cathodes

•Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects (and BOP components)



- Simple process (aluminum powder slurry, single heat treatment in air)
- PNNL has developed screen-printing, aerosol spray, and dip-coating fabrication processes

- <u>Current emphasis:</u>
  Reduction of heat treatment temperature to <1000ºC

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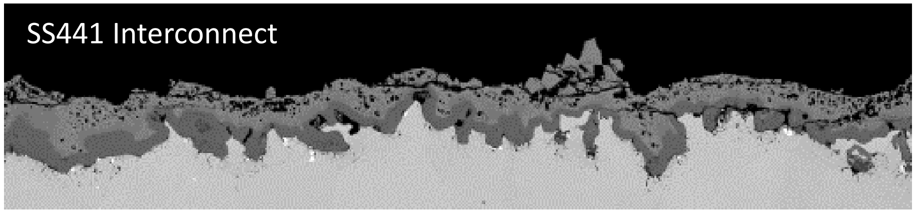
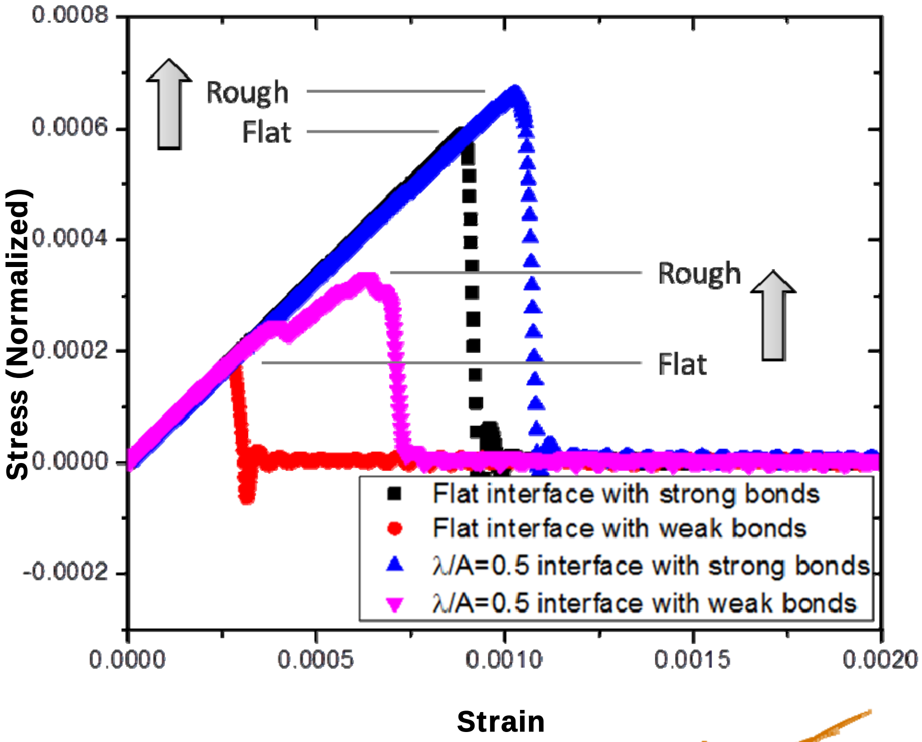
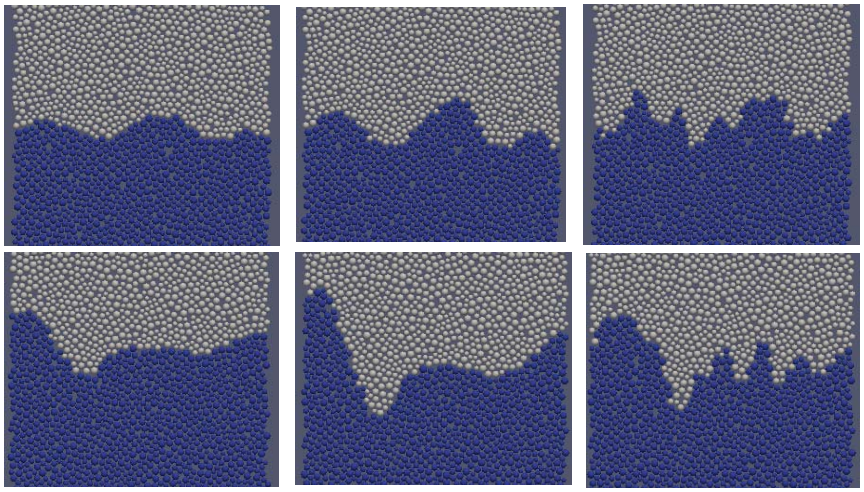
Modeling of Rough Interfaces

Strength of Rough Bi-Material Interfaces

- Last year, demonstrated the DEM particle method could simulate effects of roughness on interfacial delamination of metallic interconnects
- Apply to cathode contact materials under development
  - Evaluate sinusoidal and random interface geometries







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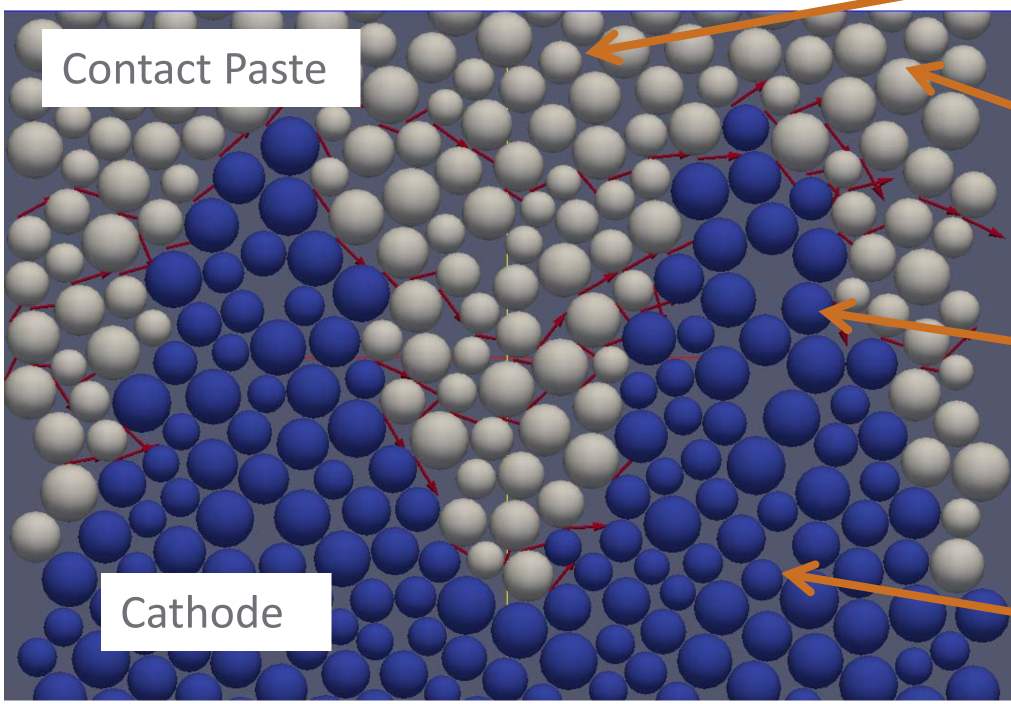
Application to Cathode Materials

- Model development performed on interconnect materials (i.e. SS441)
- Apply to cathode contact materials (e.g. LSM20)
- Utilize test data from materials experiments



Bulk strength of sintered paste from diametral compression test

Elastic properties for sintered paste from acoustic test

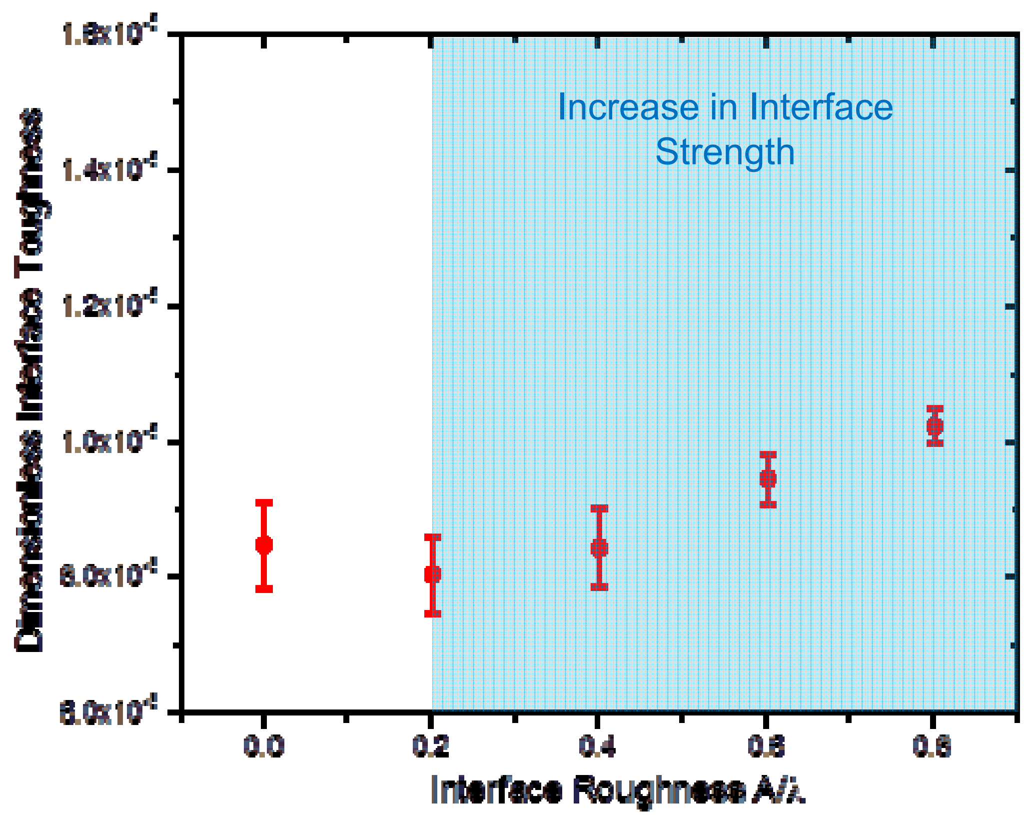
Interfacial strength of sintered paste from couple tensile test

Elastic properties for cathode from acoustic test of fully sintered pellet and adjusted for porosity

Partially Sintered LSM20

- Evaluated mean and standard deviation for different surface roughness values (sinusoidal interface)
  - 2 hour 950°C heat treatment
- Little benefit for A/λ < 0.2
- Benefit begins to reduce for roughness ratios A/λ > 0.8
  - Fracture through the paste layer away from the interface favored for high roughness
  - 20% improvement
  - Consistent with observations using the interconnect data set
  - Use of a textured cathode surface is preferred

Typical Densification



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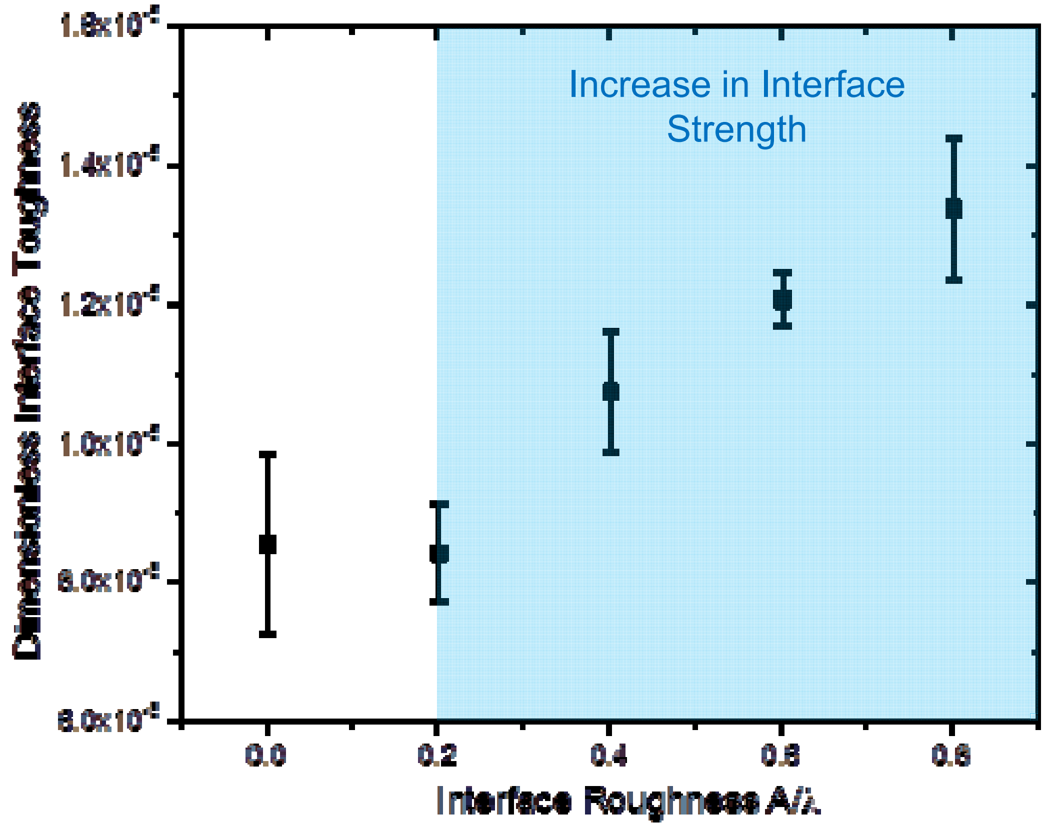
Fully Sintered LSM20

- Evaluated the strength improvement assuming full densification can be ultimately achieved due to further material enhancements
- Little benefit for $A/\lambda < 0.2$
- Greater improvement (relative to a flat interface) compared to the partially dense material
  - 50% improvement
- Use of sintering aids to increase densification in stack applications should exhibit greater benefit from interface roughness

Optimal Densification



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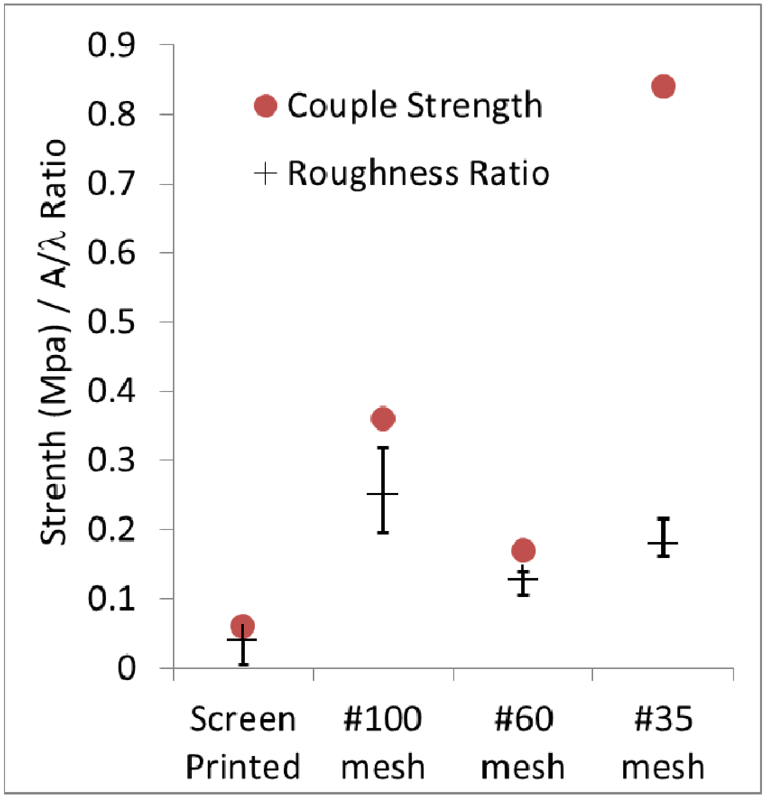
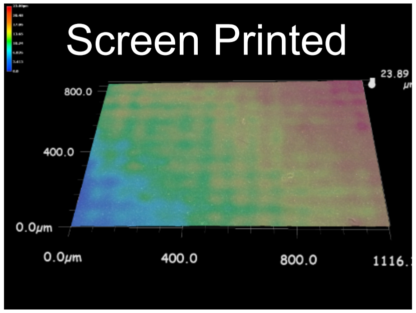
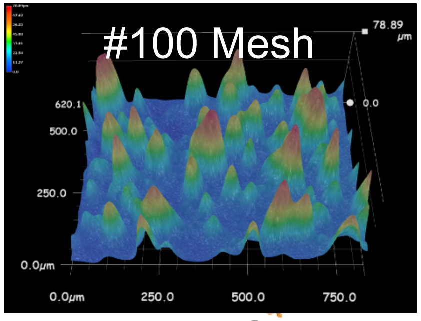
Comparison to Generated Topologies

- Semi-quantitative estimate of the A/λ ratio for the different topologies obtained visually
  - Average number of peaks for a given path length
- All estimated roughness ratios are $A/\lambda < 0.3$
  - Less than the value at which strengthening was incurred
- The finest particle #100 mesh had the highest A/λ ratio but only the second highest strength
- The largest particle #35 mesh had the next highest A/λ ratio but overall highest strength
  - May be due to particle size and propensity for interlocking

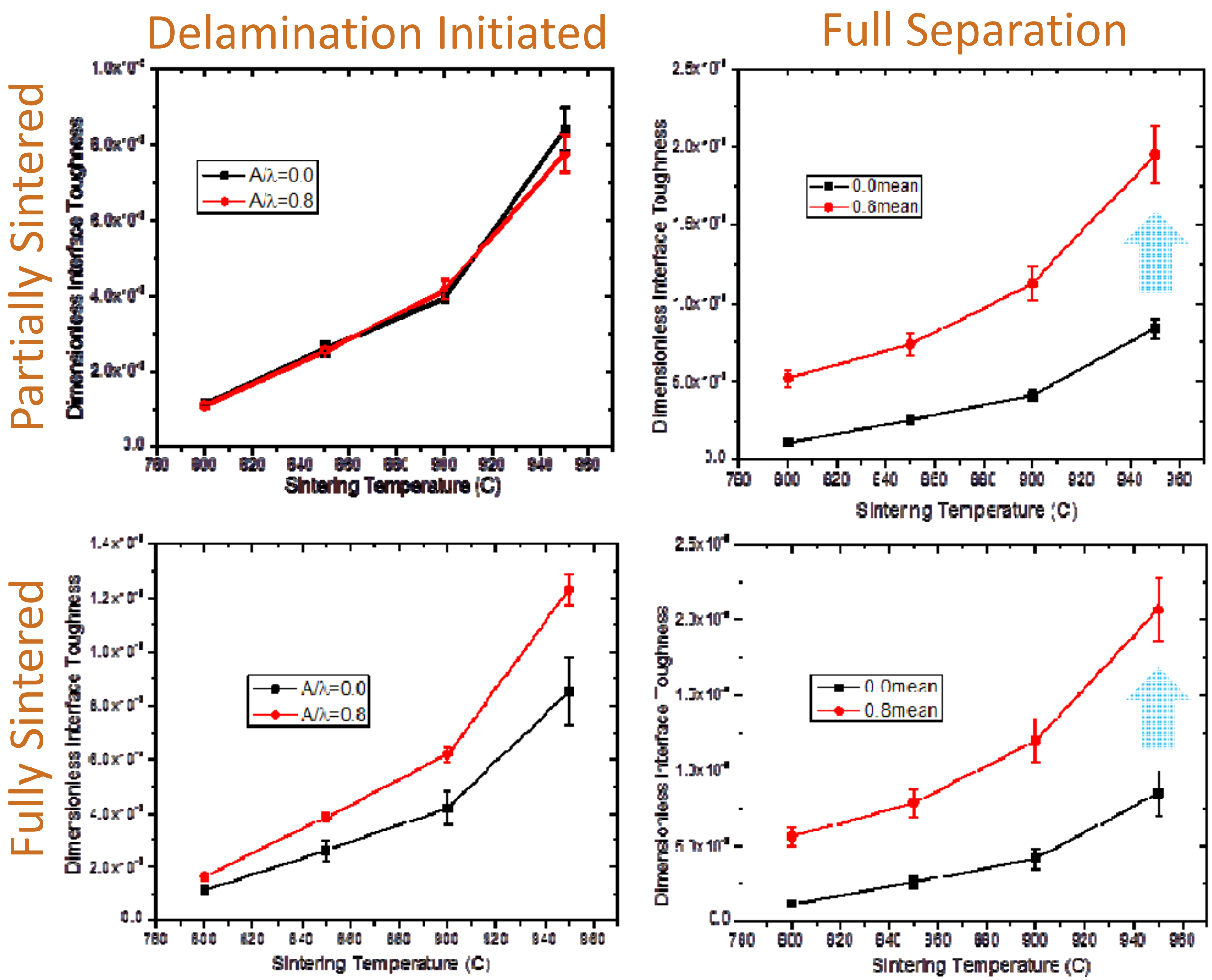






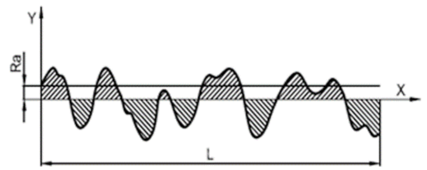
Contact Material Delamination Loads

- The roughened interface exhibited two failure loads:
  - Initiation of delamination
  - Ultimate load for full separation
  - Strengthening due to local stress state and particle orientation
- Enhanced sintering will help delay the initial delamination, but the ultimate load capacity was almost unchanged
  - Interface was the weak link for this material set

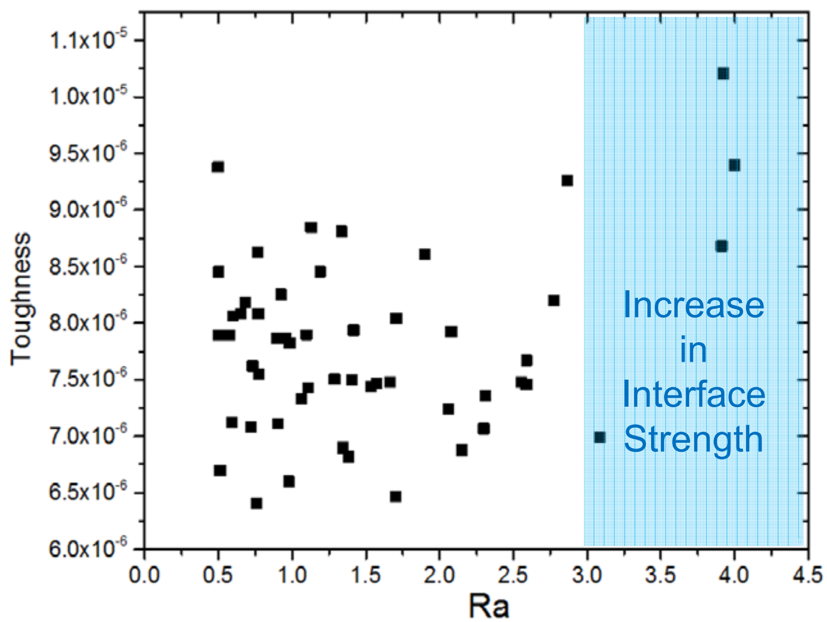


Variation of Interface Toughness with Roughness Value Ra

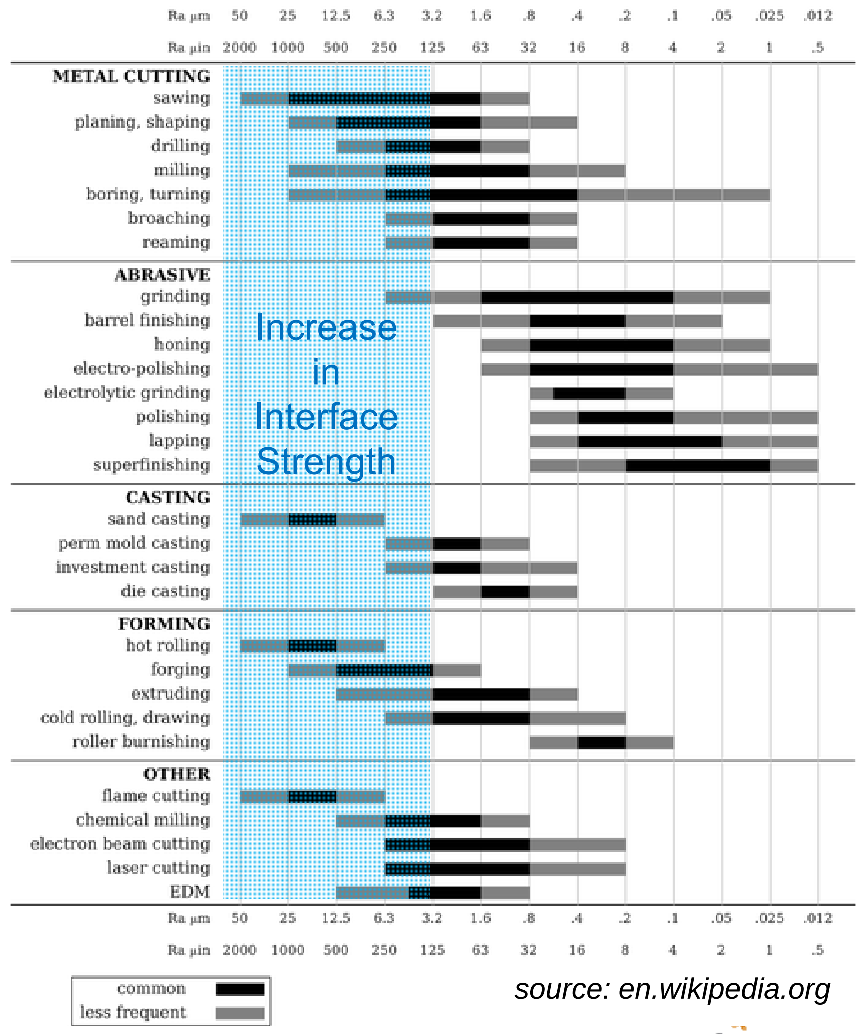
- Computed roughness for random interface geometries
- Strength enhancement of LSM20 interface for Ra > 3μm



$$R_a = \frac{1}{L}\int_0^L \left|\phi(x)\right| dx$$



Surface Roughness Produced by Common Production Methods



source: en.wikipedia.org

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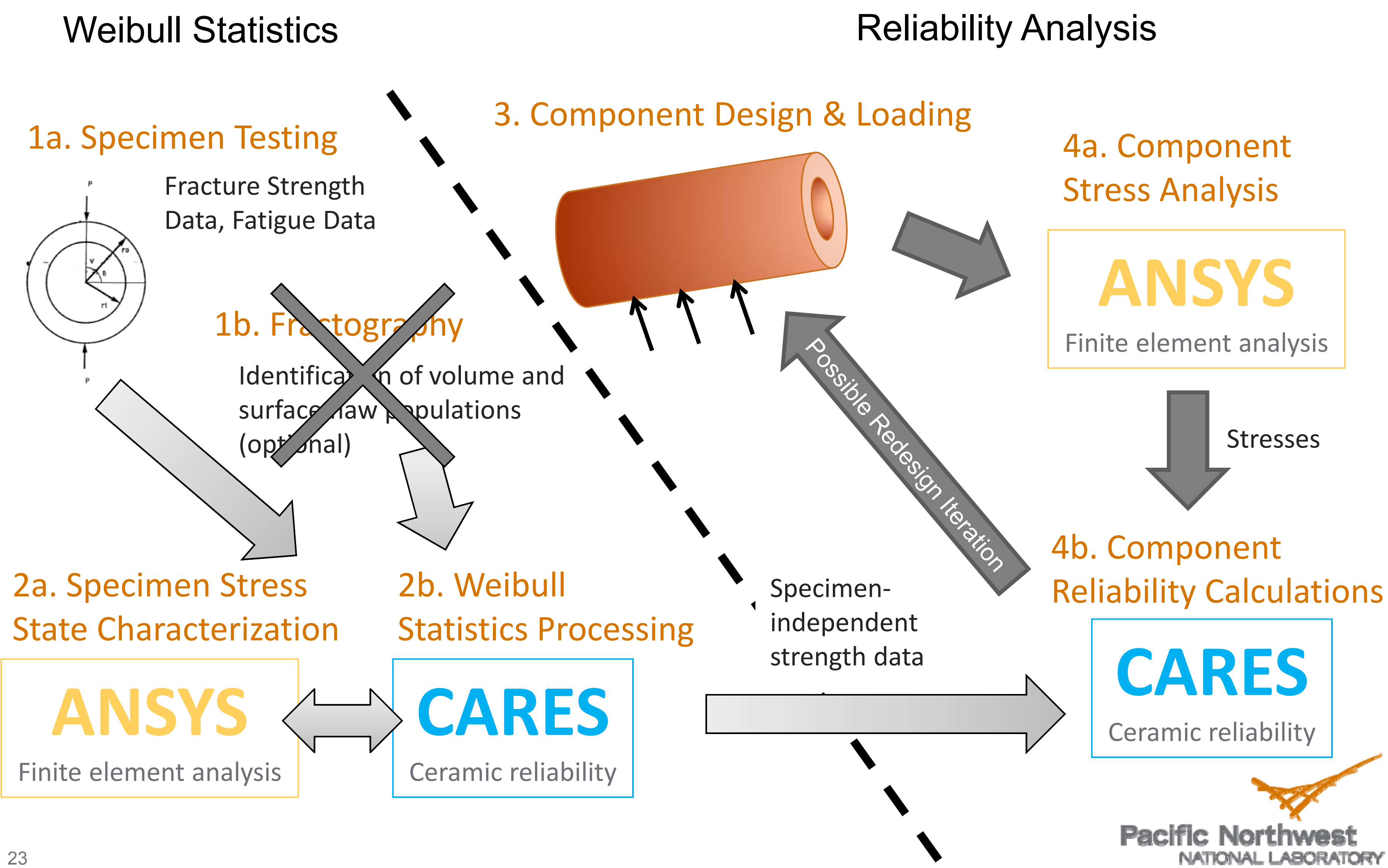
Reliability

Reliability of Ceramic Components



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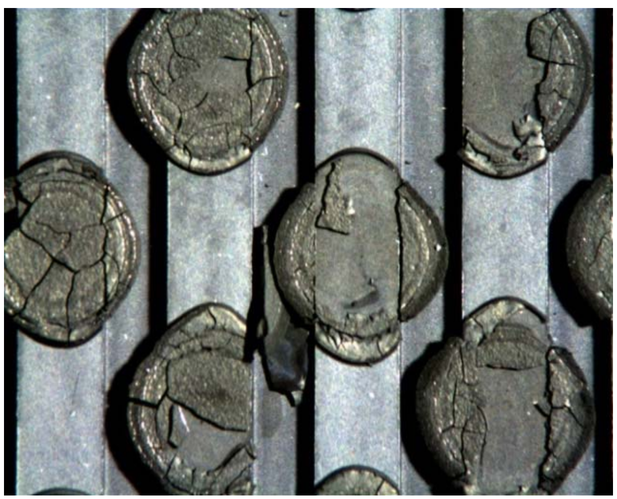
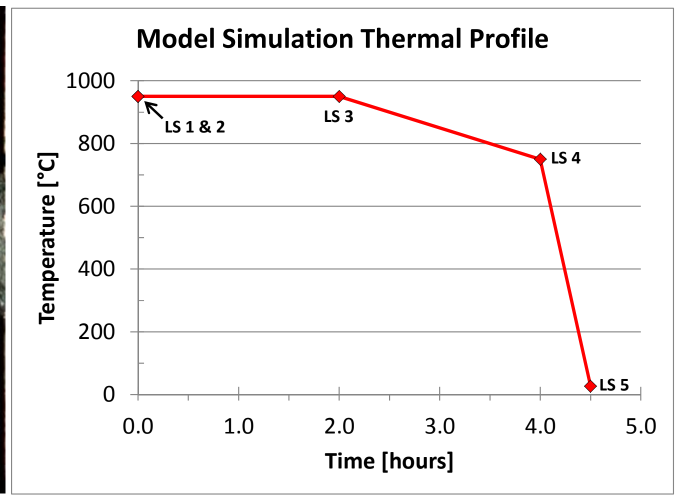
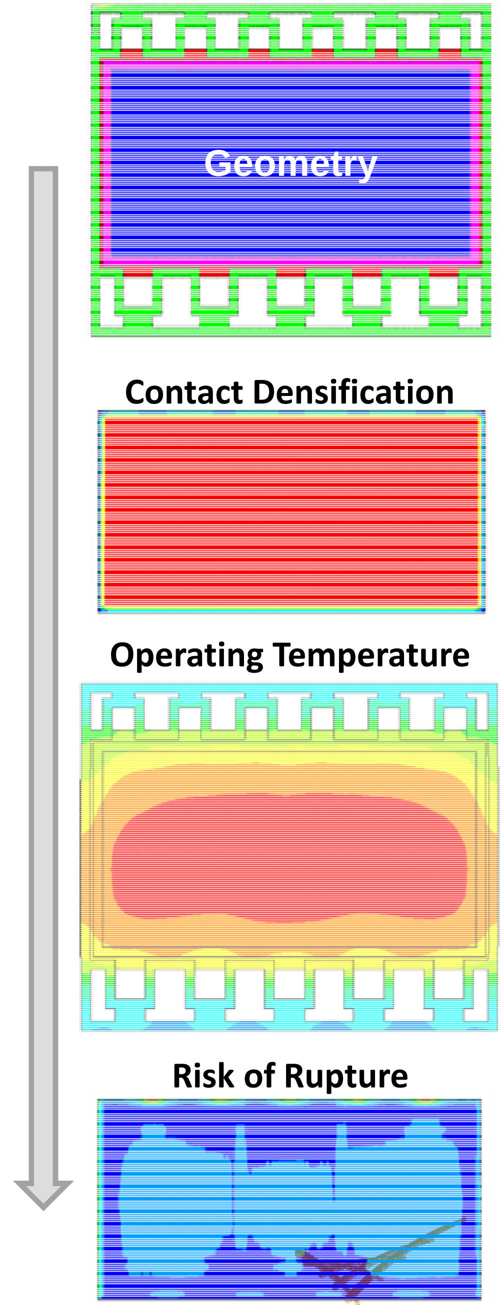
Stack Contact Material Sintering

- Reliability of cathode contact materials formed in-stack by constrained sintering needed to optimize the density and strength of this structural ‘weak link’
- Used continuum sintering model to predict the temperature/stress-dependent densification and residual fabrication stresses in a planar 400 cm^2 SOFC stack with uniform cathode contact layer
- Characterized effect of material, geometry and heat treatment parameters on the maximum densification and subsequent risk of layer failure under stack operating/shutdown conditions







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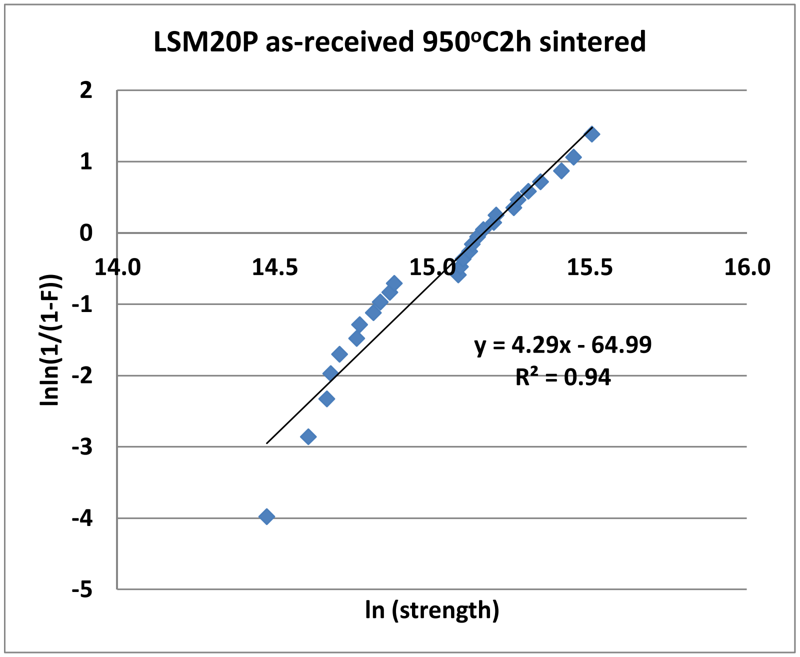
Cathode Contact Materials

- Evaluated experimental data for 3 candidate contact materials
  - Diametral compression tests
- Calculated Weibull statistics
  - Assume single flaw population
  - Highest reported strength from LSC
  - LSC also had most scatter though
  - LSCF more uniform properties, so has highest scale parameter



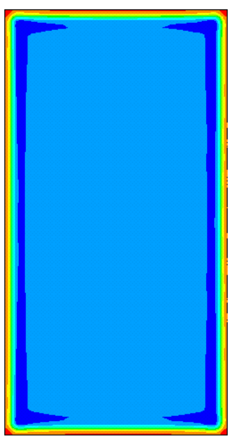
Material	Characteristic Strength (Pa)	Weibull Modulus	Scale Parameter (Pa-$m^{3/\alpha}$)
LSM20	3,817,690	4.57	113,052
LSC20	**6,551,610**	4.27	151,928
LSCF6428	6,388,830	**4.93**	**240,953**

Contact Material Stresses

- Stresses due to constrained sintering are small but non-zero
- Thermal stress increases during stack operation
  - Stresses increase as the cell thermal gradient increases
  - Magnitude comparable to strength of partially sintered contact materials
- Shutdown has highest stresses

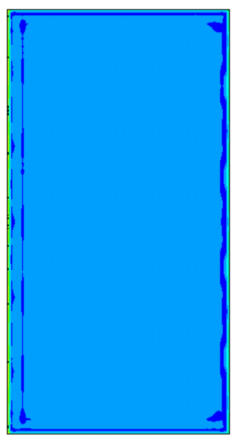
End of Sintering

0.4 MPa



Isothermal operating condition - 750°C

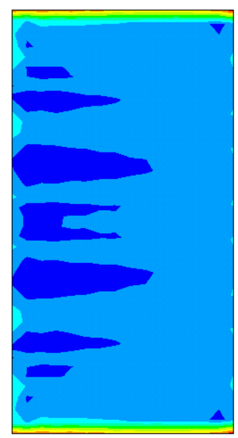
1.7 MPa



$\Delta T = 0$

Realistic operating condition - 750°C avg

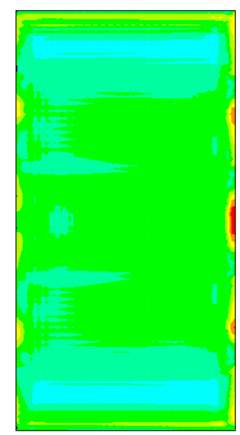
2.5 MPa



$\Delta T \neq 0$

Shutdown Condition

16 MPa



Contact Material Reliability

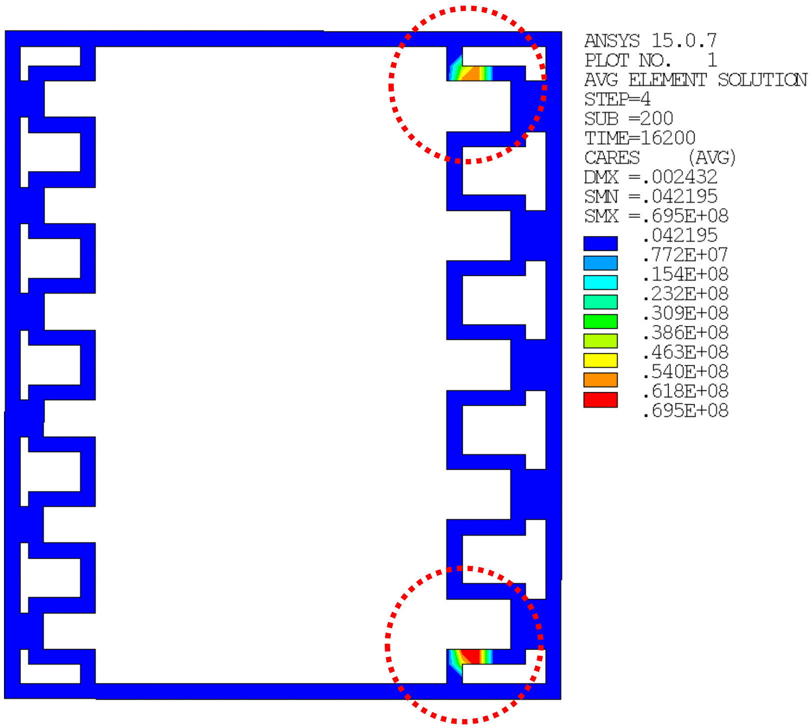
- Calculated reliability based on the experimentally measured material properties for the 3 candidate materials
  - The LSM showed the lowest reliability at shutdown (29%) while the LSCF showed the highest reliability (90%)
  - Enhanced densification using sintering aids and strength improvement would still be highly advantageous
- Reliability of the electrolyte and cathode layers were also low in the generated stack design

Loading Condition	Anode	Electrolyte	Cathode	Paste
Stress Free	100 / 100 / 100	100 / 100 / 100	100 / 100 / 100	100 / 100 / 100
Compression	100 / 100 / 100	100 / 100 / 100	100 / 100 / 100	99.9 / 99.9 / 99.9
After Sintering 2hr	99.9 / 99.9 / 99.9	99.9 / 99.9 / 99.9	98.8 / 98.8 / 98.8	99.9 / 99.9 / 99.9
Isothermal Operation	100 / 100 / 100	96.0 / 96.0 / 96.1	99.0 / 99.9 / 99.9	99.9 / 99.8 / 99.9
Actual Operating State	100 / 100 / 100	11.2 / 11.2 / 11.2	29.8 / 29.8 / 29.8	93.1 / 99.1 / 99.6
Shutdown state	100 / 100 / 100	86.3 / 86.3 / 86.3	99.9 / 99.9 / 99.9	28.9 / 88.7 / 90.5

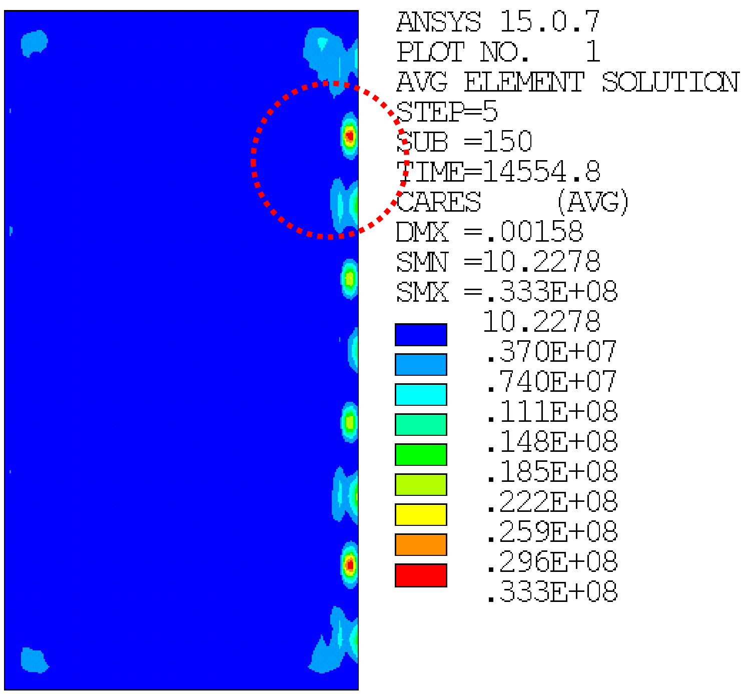
NOTE: xxx / xxx / xxx indicate the %Reliability when evaluated with LSM20/LSC20/LSCF6428 Weibull data respectively

Risk of Rupture

- The risk of rupture plots indicate the potential locations of failure initiation (cracking) within the ceramic contact material layers
- The low reliability estimates for the contact layer and cell components arise from very localized regions due to mechanical interaction with the frame
  - Emphasizes the extremely high importance of integrated mechanical design to avoid initiation of damage in the ceramic components



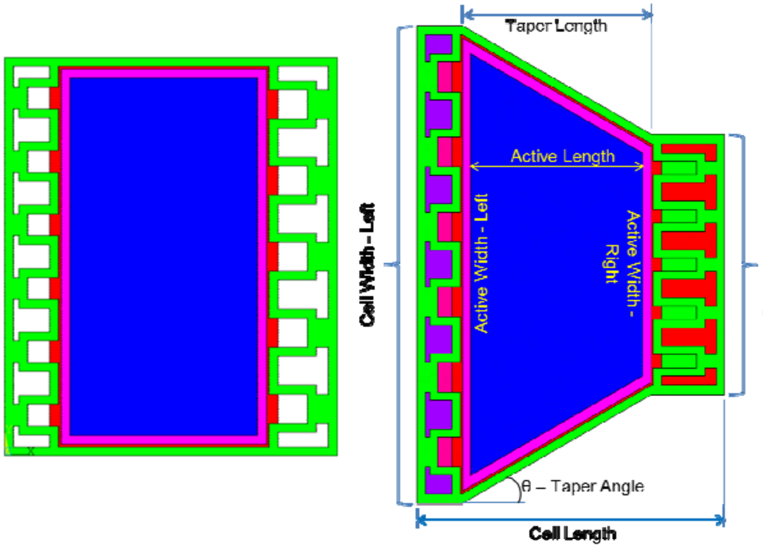
Rigid Seal - Shutdown Condition

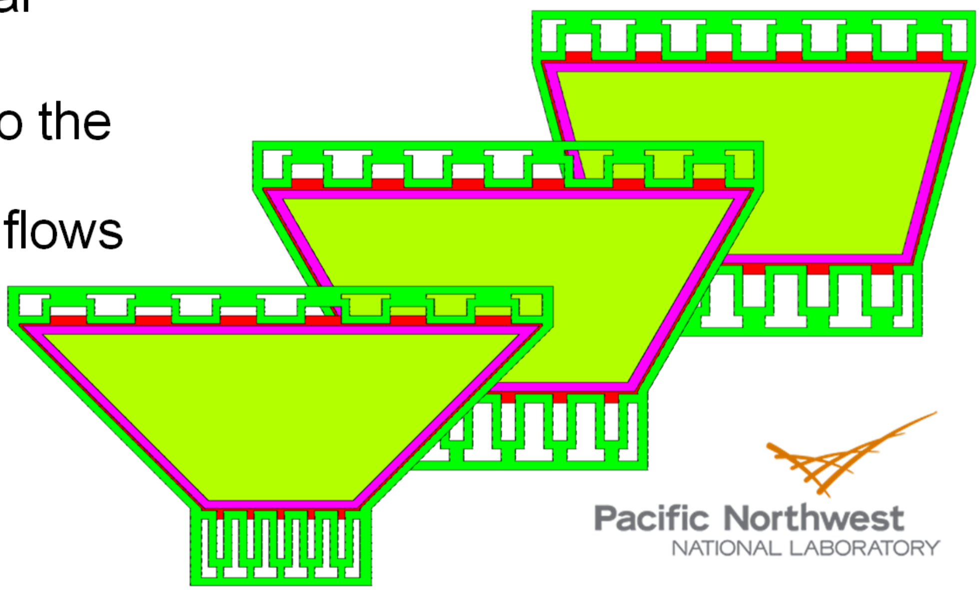


Contact Material - Shutdown Condition

Alternate Stack Designs

- Working with E. Lara-Curzio at Oak Ridge National Laboratory (ORNL) on alternative stack design topologies that may be able to improve the mechanical reliability of SOFC stacks
- Investigated different stack tapers in an effort to increase the velocity and convection heat transfer of planar co-flow stacks to reduce the thermal gradient at the stack outlet
- Only minor improvements due to the low flow rates and total thermal capacity of the fuel and oxidant flows





See Poster: Structural Reliability Considerations for Planar SOFCs: Cathode Contact, Cell Thermal Gradients & Alternate Geometries

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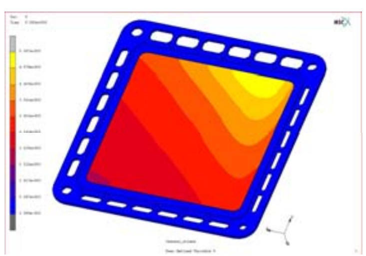
SOFC Stack Modeling Tools

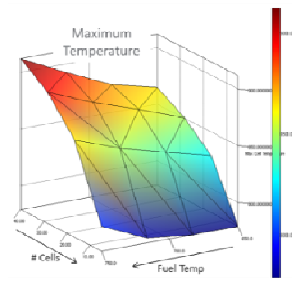
SOFC Stack Modeling Tools

- Last year, successfully demonstrated ROM approach to simulate stack performance in system modeling tools
  - Accuracy for key parameters and metrics of interest greater than ~98%

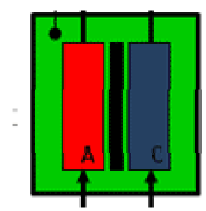
SOFC Stack Model



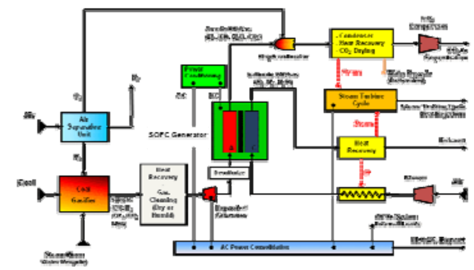
Response Surface Analysis



Reduced Order Model (ROM)



NGFC Power System



- Based on the demonstration, several improvements were identified to the improve the ROM/SOFC-MP tools and implementation
  - Application to other NG compositions
  - Recirculation capability for the fuel and oxidant recycling loops
  - Pressurized electrochemistry
  - Use of 3D SOFC-MP models
  - Calculation of the pressure drop in 2D SOFC-MP
  - Variable pre-reformer fraction in the NGFC material flow balance
  - Simplified Aspen Plus integration
  - Application to IGFC

See Poster: Enhanced SOFC-MP Software Tool Set

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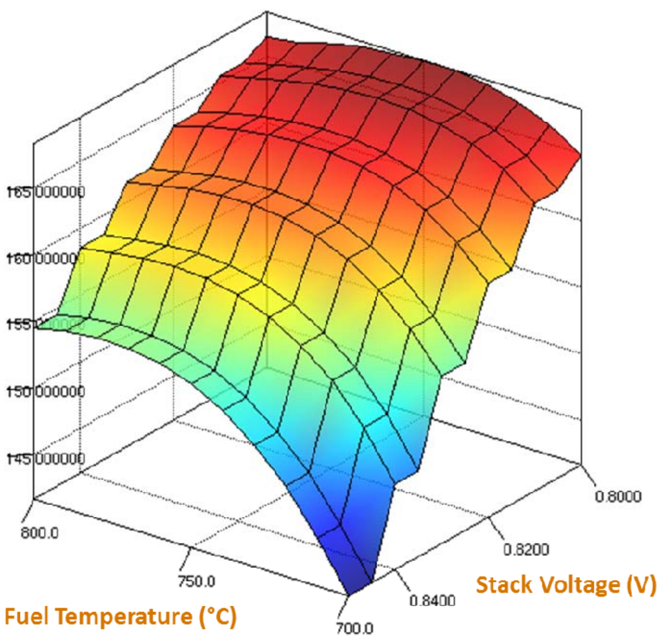
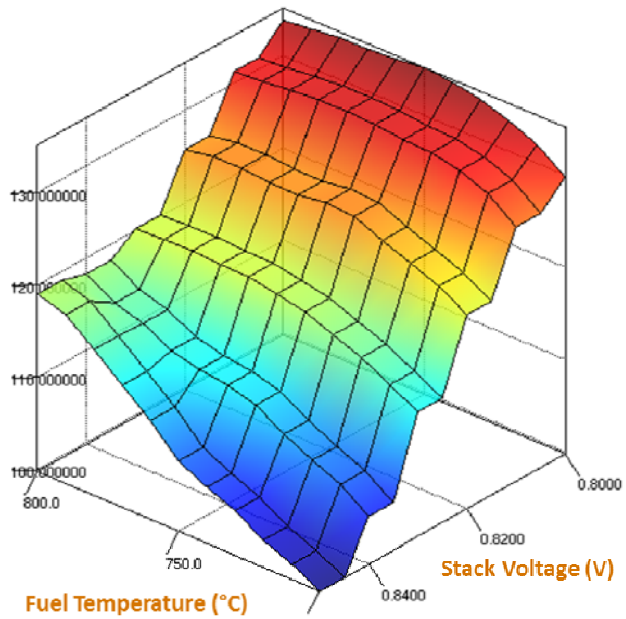
ROM Creation From 3D Model

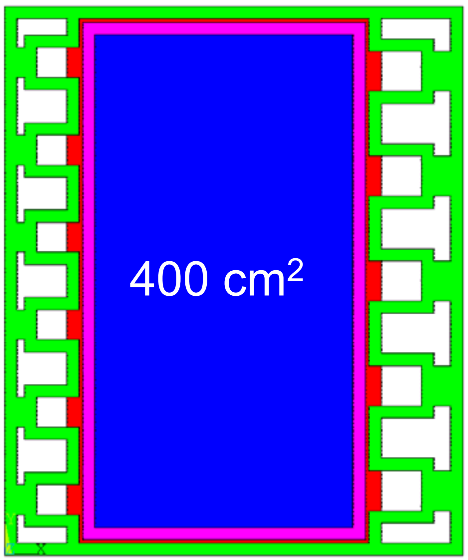
- ROM demonstration originally used SOFC-MP 2D tool
- Added ability to use detailed SOFC-MP 3D solver in the ROM tool
- Demonstrated with a large area co-flow single cell stack
- Two parameter ROM creation
  - Inlet fuel/oxidant temperature: 700-800°C
  - Cell voltage: 0.8-0.85V

Stack Power (W)



Stack Temperature Difference (°C)

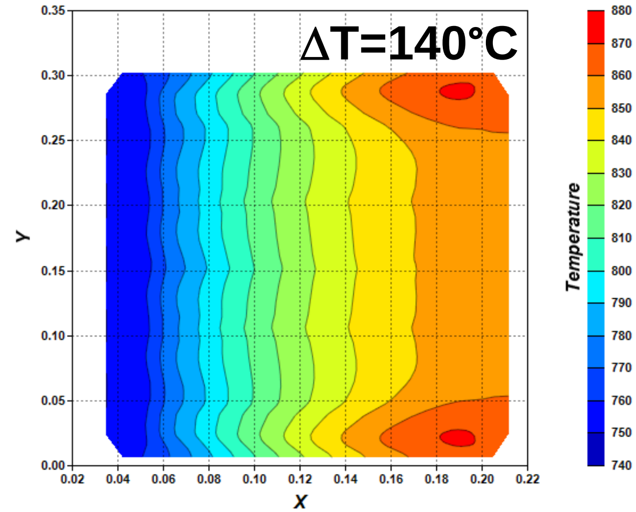




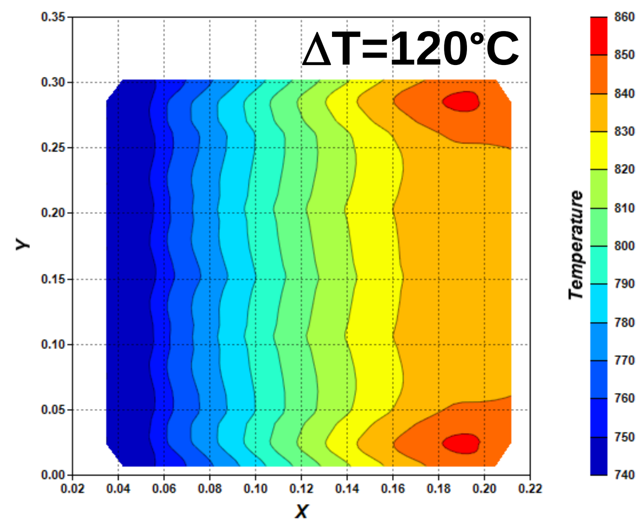
Fuel/Oxidant Recirculation

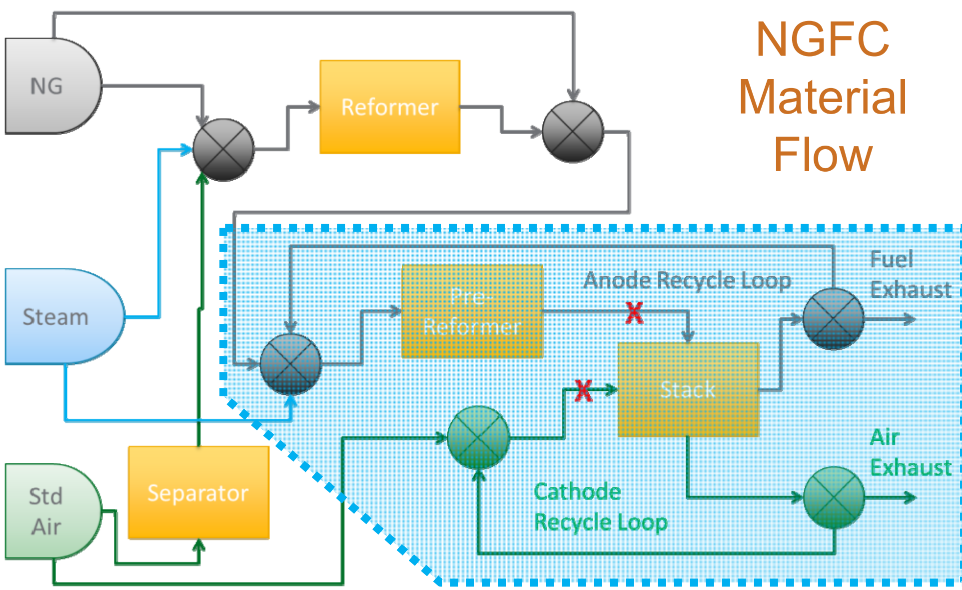
- ROM integration to the NGFC system model can be improved by including the fuel and oxidant recirculation loops directly
  - Includes mixing and heat exchanger functions
  - Implemented in the 3D SOFC-MP model
- Recirculation under fixed fuel utilization and maximum cell temperature constraint provides a more uniform temperature, smaller cell thermal gradient, and more uniform current distribution

No Recirculation



With Recirculation

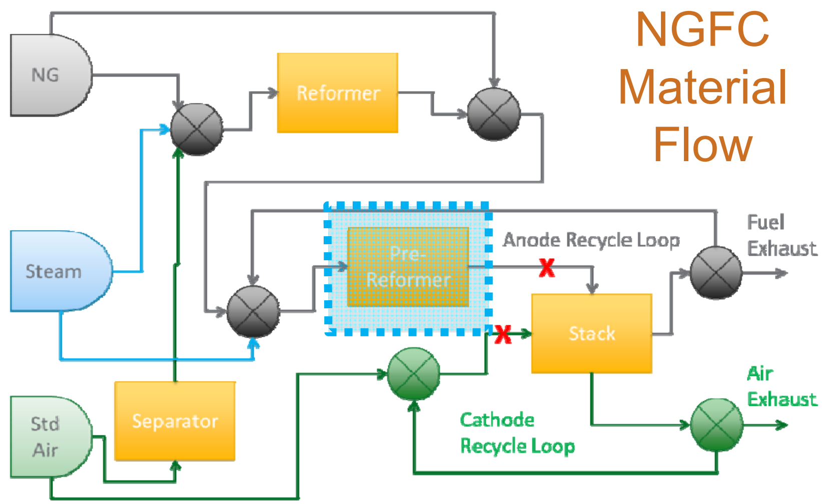




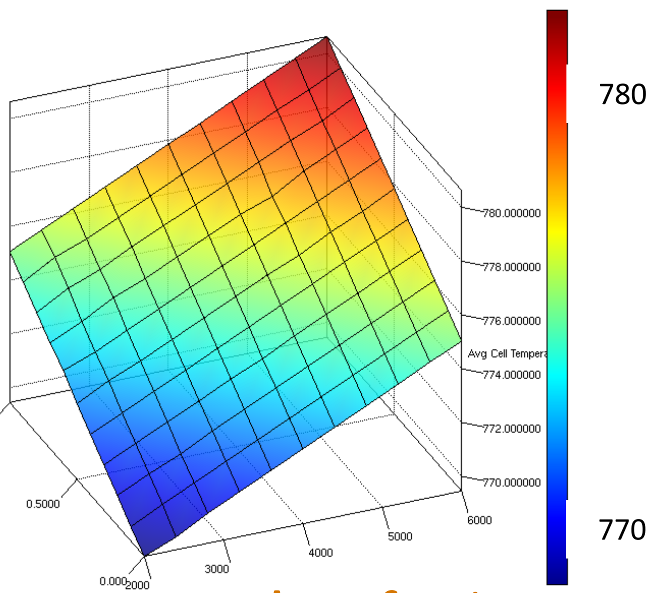
NGFC Material Flow

Pre-Reformer Fraction

- External pre-reformer in the fuel recycle loop controls the amount of CH_4 sent to the stack for on-cell steam reformation to control cell temperature gradient
  - Capability was added to the ROM tool and successfully tested
  - Stack hotter with more external reforming
  - Cell thermal gradient lower with more external reforming

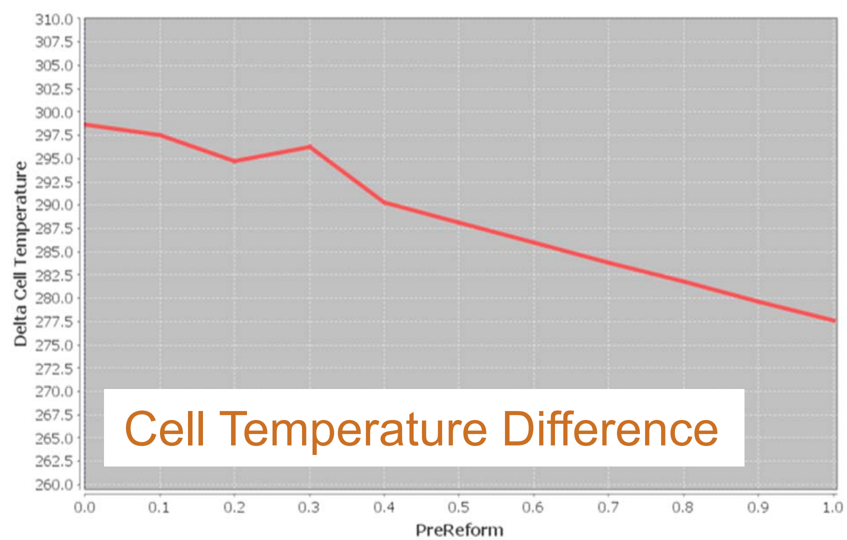


Average Cell Temperature (°C)

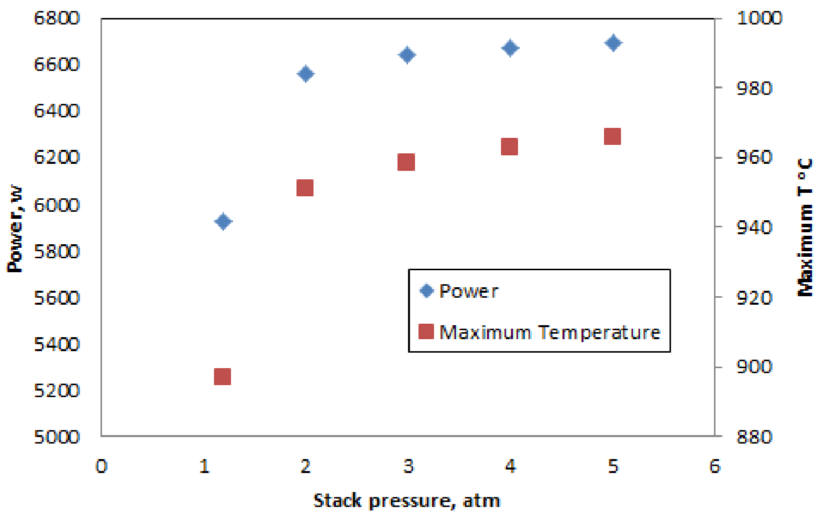


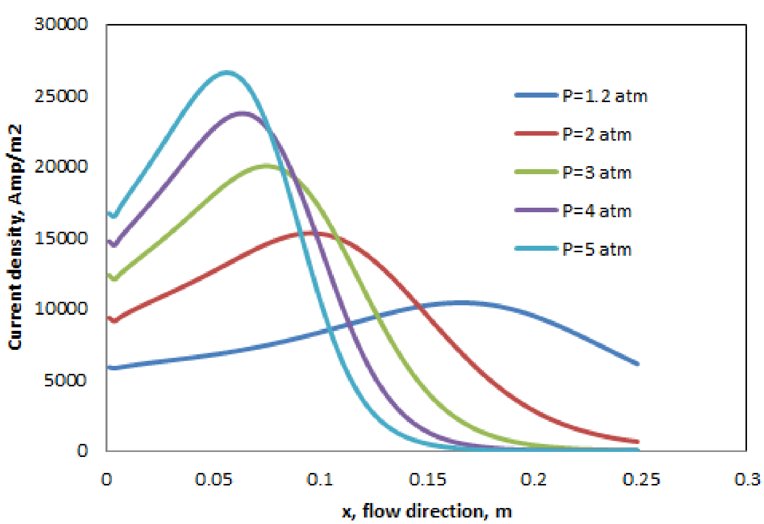
Pre-Reform Fraction

Average Current Density (A/m²)

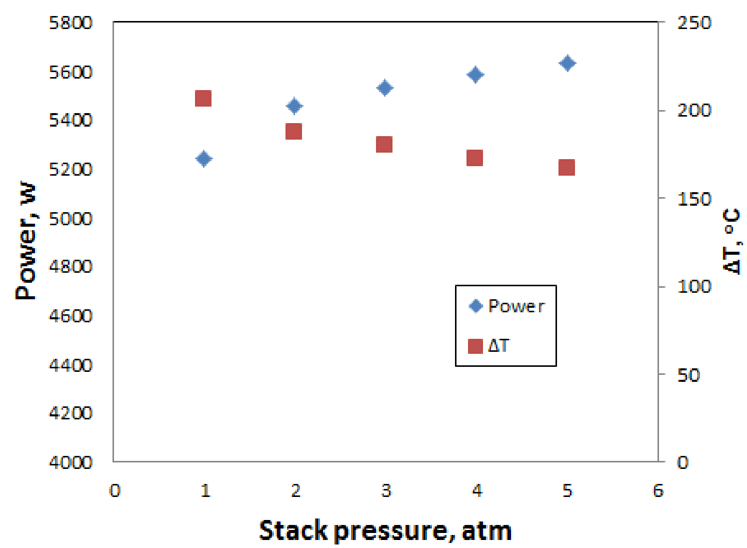


High Pressure Operation





- Pressurized cell operation needed to reduce future SOFC COE
  - Capability added to SOFC-MP/ROM tools
  - Reduction in activation and concentration losses most significant at pressures near atmospheric condition with small additional benefits beyond ~5 atm
  - For fixed fuel utilization and maximum cell temperature, high pressure operation also decreases the cell temperature gradient



Summary

- PNNL is using experimental and computational capabilities to accelerate the commercialization of SOFC power systems.
- For more information at this meeting, contact the poster presenters:
  - **SOFC Testing in Cathode Air with Quantified Cr Concentration (John Hardy)**
  - **Evaluation of Cr-Gettering Material in a Generic Stack Test Fixture (Matt Chou)**
  - **Effect on Sintering Aids on Densification and Contact Strength of SOFC (Matt Chou)**
  - **Lower Temperature RAA Process for Planar SOFC Stacks (Jung-Pyung Choi)**
  - **Enhanced SOFC-MP Software Tool Set (Naveen Karri)**
  - **Structural Reliability Considerations for Planar SOFCs (Brian Koeppel)**

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