SOFC Development at PNNL: Overview

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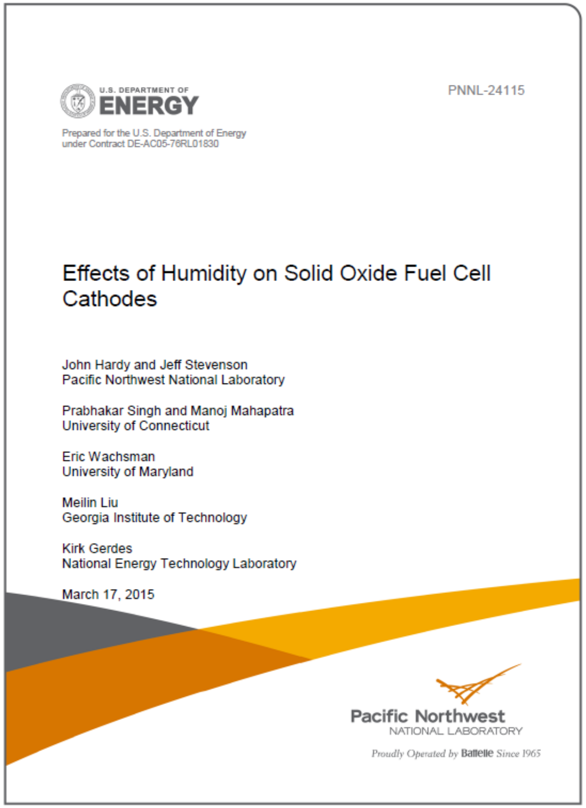
16th Annual Solid Oxide Fuel Cell Workshop

Outline

- Introduction
- Materials Development
  - Cathode materials and interactions
    - Effects of humidity and CO_2
  - Cathode to interconnect contacts
    - Strengthening of cathode/contact materials interfaces (combined experimental/modeling approach)
  - Interconnects/BOP
    - Reactive air aluminization: Dip-coating
- Modeling/Simulation
  - Contact layer and interface reliability
    - Sintering of cathode contact materials
    - Effect of roughness on interfacial strength
  - Reduced order models (ROMs) for improved system modeling

SECA CTP Cathode Team: Effect of Cathode Air Humidity

- LSM/YSZ
  - Immediate, reversible increase in polarization when water was introduced
    - Attributed to adsorption of water
  - Increased rate of performance degradation when water was introduced
    - Microstructural and chemical changes
  - Humidity effects more prominent at higher current density
- LSCF
  - Adverse effects of water increased with decreasing temperature
    - Increased polarization
    - Increased degradation rate



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Effects of Humidity on Solid Oxide Fuel Cell Cathodes

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March 17, 2015

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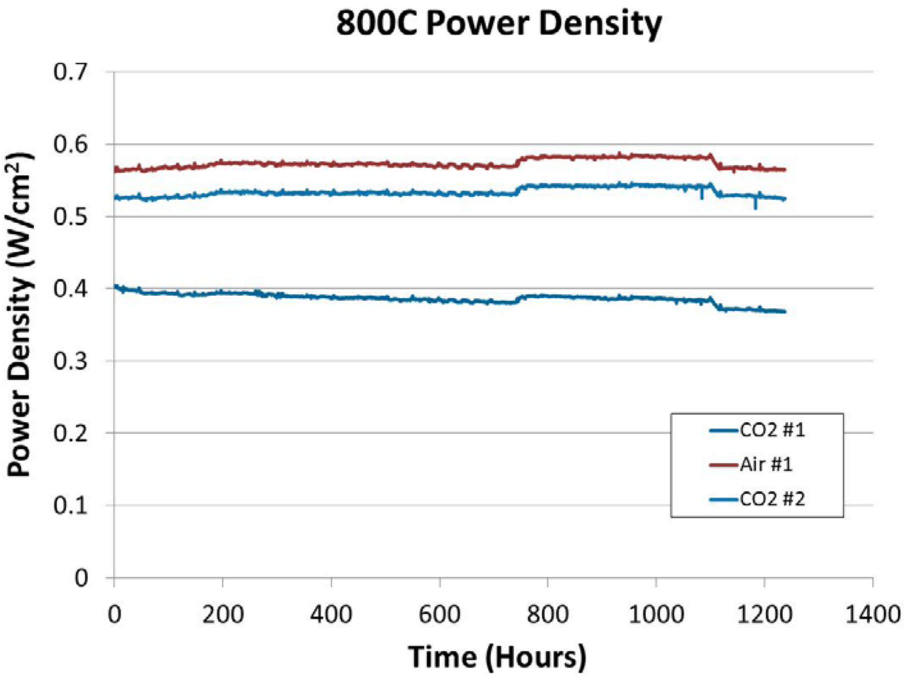
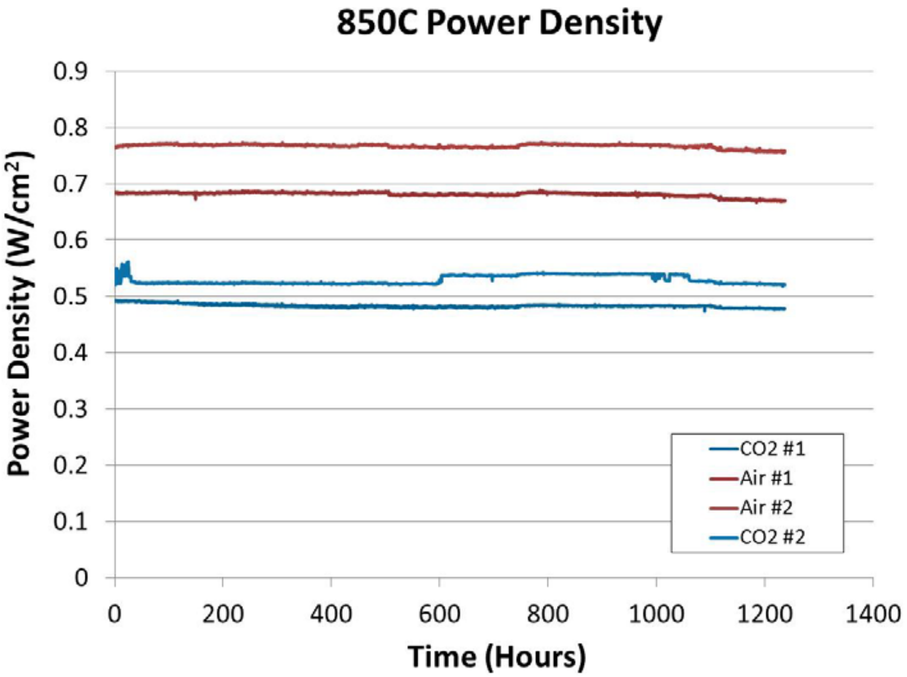
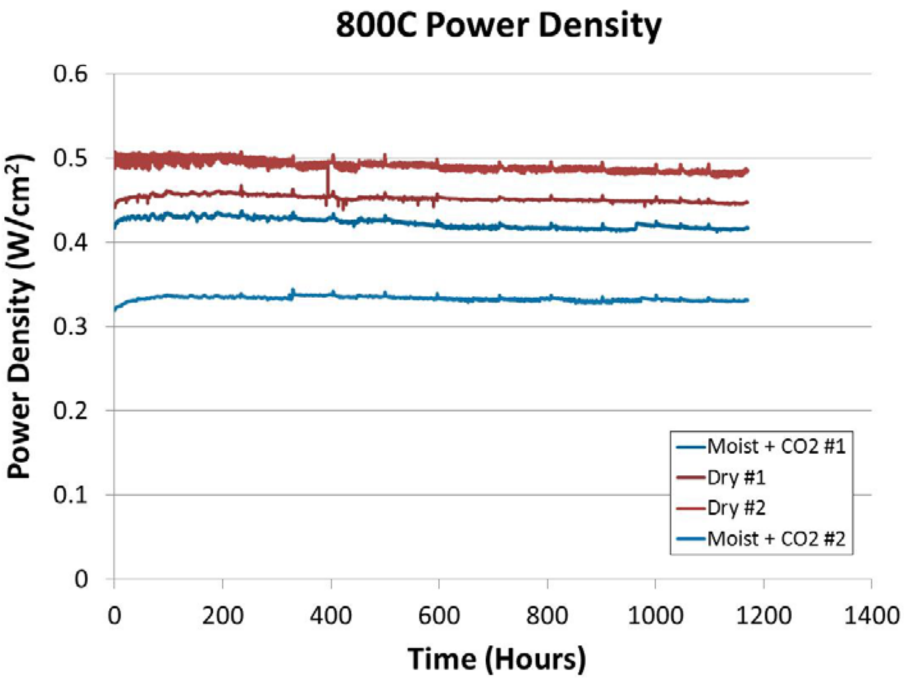
Effect of 12% CO_2 on LSM/YSZ Cathodes

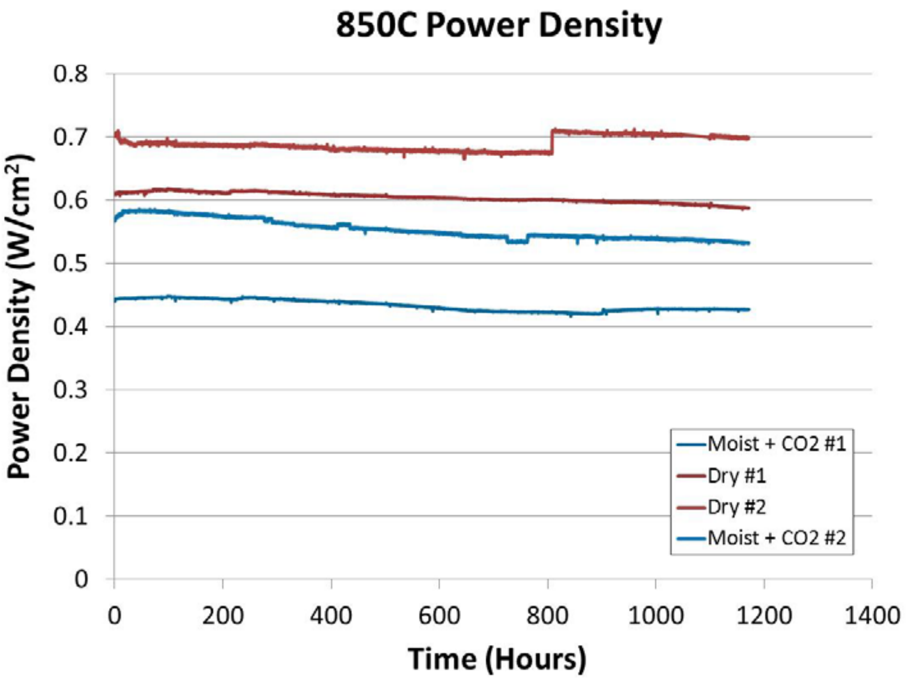




- Anode-supported button cells tested in dry air with and without CO_2
  - Lower initial performance in presence of CO_2 (dilution, adsorption?)
  - No impact on degradation rate
- Similar behavior in alternating atmospheres (no clear impact from presence of CO_2)

Effect of 12% CO_2 + 3% H_2O on LSM/YSZ Cathodes


800C Power Density


850C Power Density

- Anode-supported button cells tested in dry air with and without CO_2
    - Lower initial performance in presence of CO_2 and H_2O (dilution, adsorption?)
    - No clear impact of CO_2 on degradation rate

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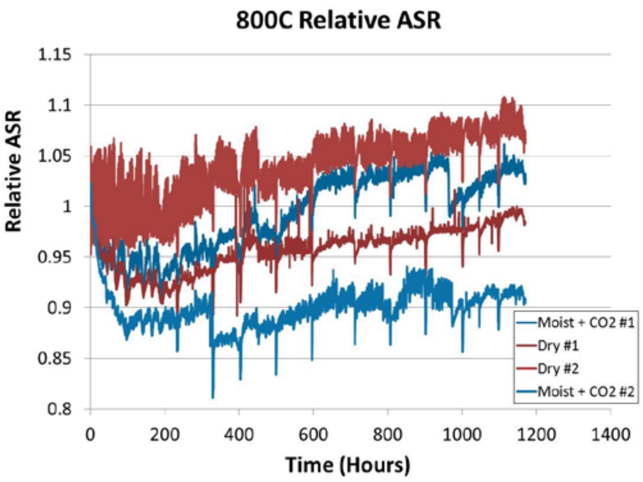
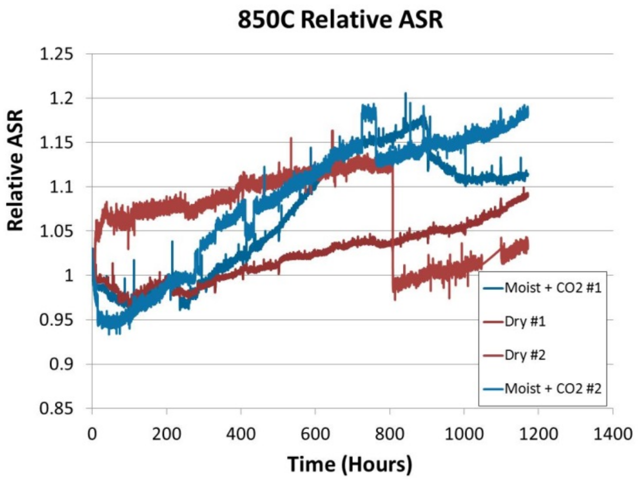
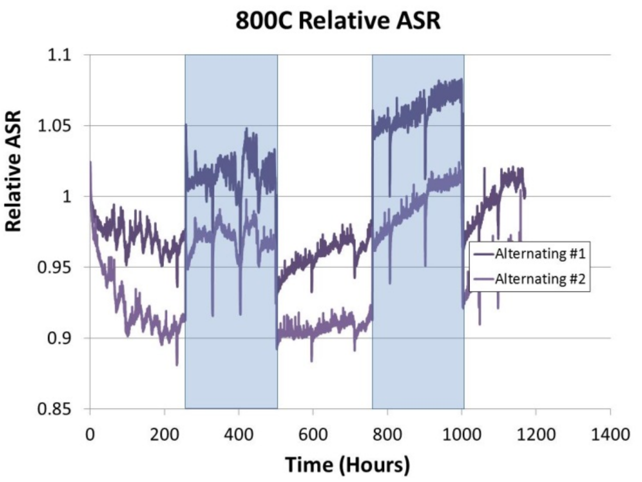
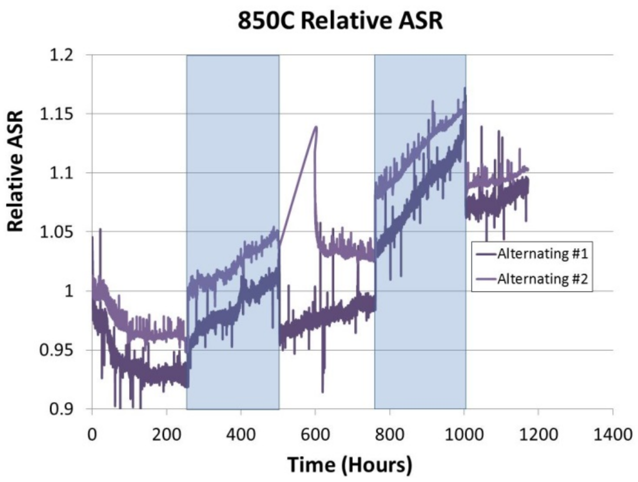
Effect of 12% CO_2 + 3% H_2O on degradation









- Blue background denotes contaminant exposure
- Behavior with 12% CO_2 + 3% H_2O is similar to that observed for 3% H_2O only

Poster: “In-Operando XRD of LSM/YSZ Cathodes in Combined H_2O + CO_2 during 1000+ h SOFC Tests” (John Hardy)

Strengthening of cathode/contact materials interfaces

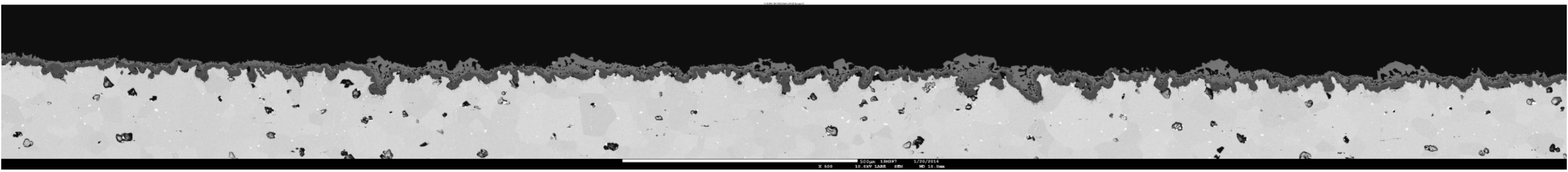
Cathode/Interconnect Contact Materials

- **Requirements:**
  - High electrical conductivity to reduce interfacial electrical resistance between cathode and interconnect
  - Chemical and structural stability in air at SOFC operating temperature
  - Chemical compatibility with adjacent materials (perovskite cathode, interconnect coating)
  - Adequate mechanical strength and bonding to adjacent components
  - Low cost materials and fabrication
- **Challenges:**
  - Low processing temperature during stack fabrication (800-1000ºC)
    - Low density results in low intrinsic strength and low bond strength
  - Brittle nature of ceramics; Cost/volatility of noble metals
- **Goal:**
  - **Develop cathode/interconnect contacts with low electrical resistivity and increased mechanical strength**

Engineered cathode surface texture

Objective: Enhance mechanical interlocking at cathode/contact material interface for improved mechanical strength during thermal cycling.

Rationale for Approach: Surface blasted steel coupons exhibited excellent scale adhesion after 30,000 hours of testing at 800°C (image below), whereas unmodified coupons exhibited spallation after <10,000 hours

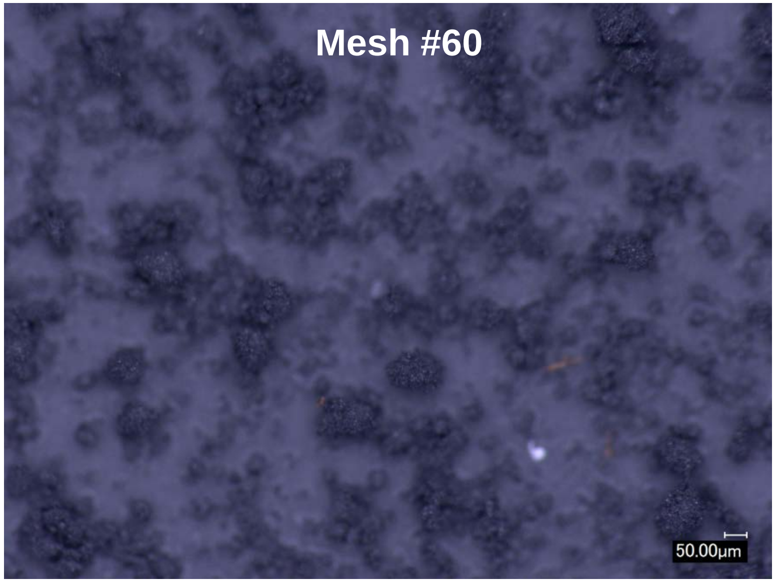


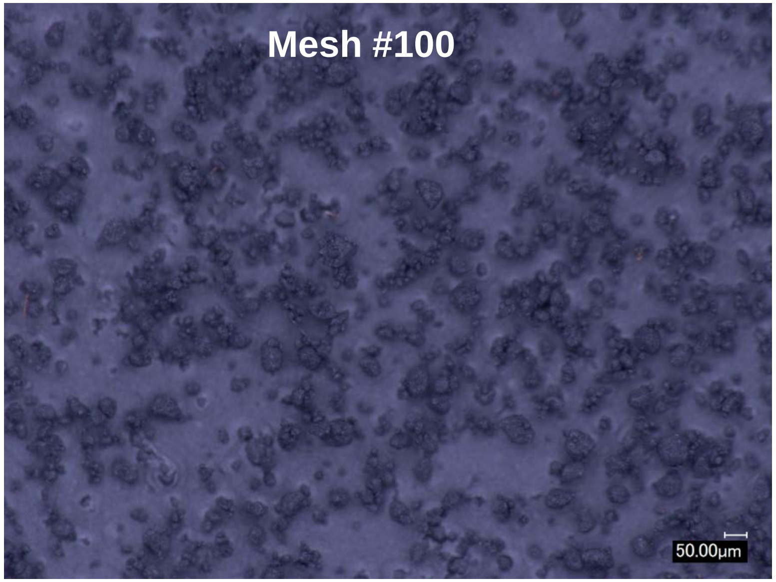
Approaches for surface texturing of screen printed cathodes:

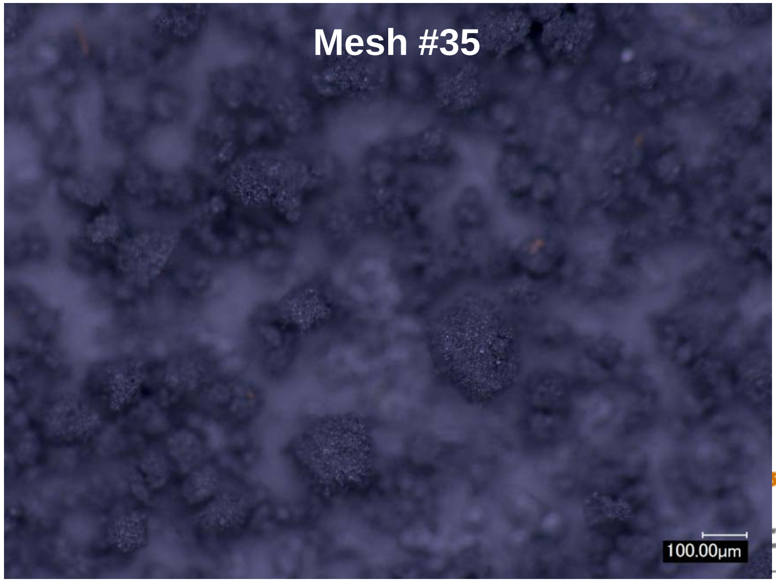
- Impression with SiC grit paper
- Impression with Ni mesh
- Addition of graphite particles
- Print with patterned screens
- **Granule deposition on wet print**

Granule deposition on wet print

- LSM20 powders were mixed with binders, then dried and pressed through sieves #35, #60, and #100 to make large granules for deposition onto surface.
- After deposition and drying, the samples were sintered at 1100^{o}C/2h in air.

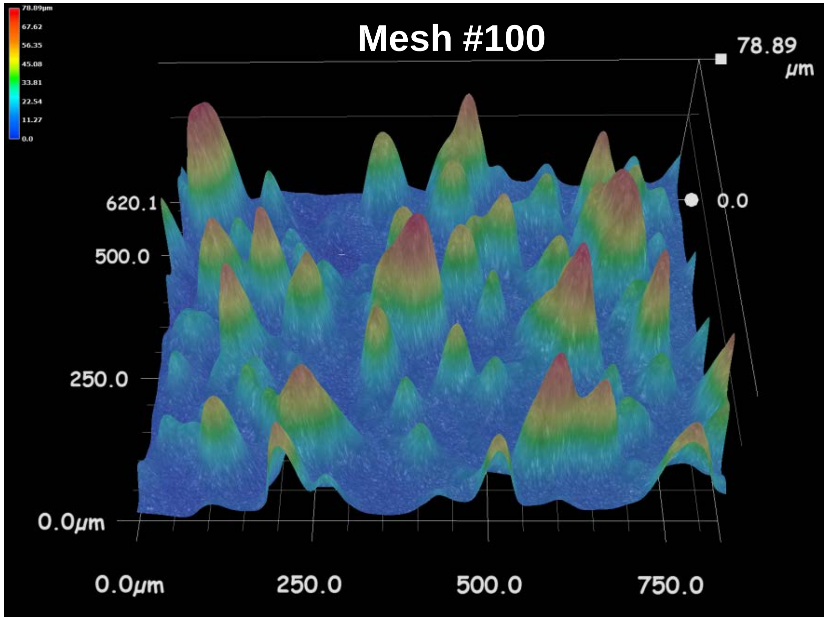

Mesh #60


Mesh #100

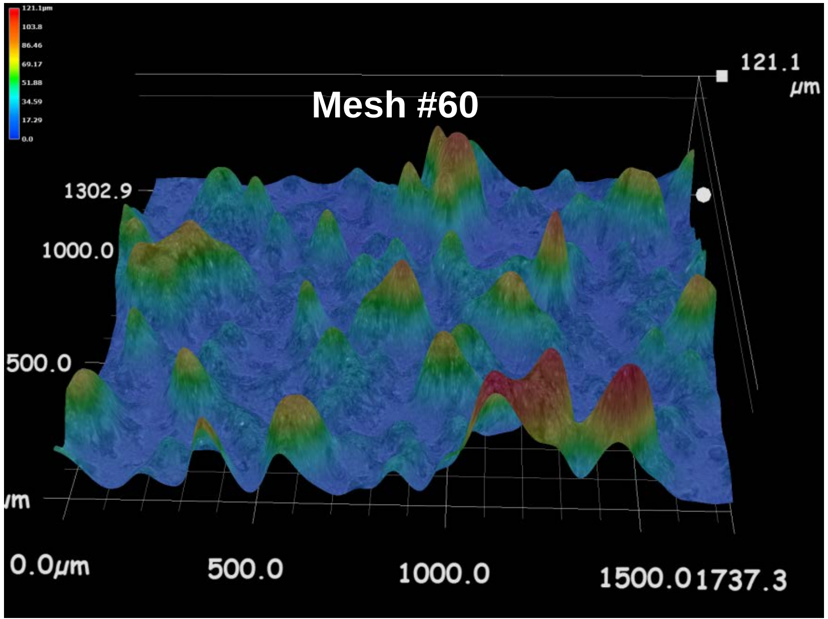

Mesh #35

Powder deposition on wet print

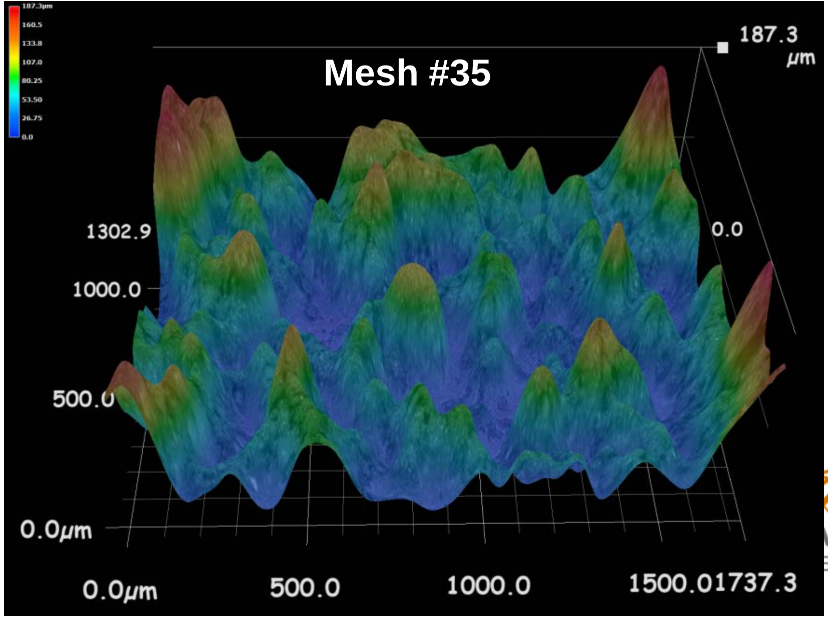
- Deposition of LSM20 granules onto wet 2mil print, dried, and sintered 1100ºC/2h in air



Mesh #100



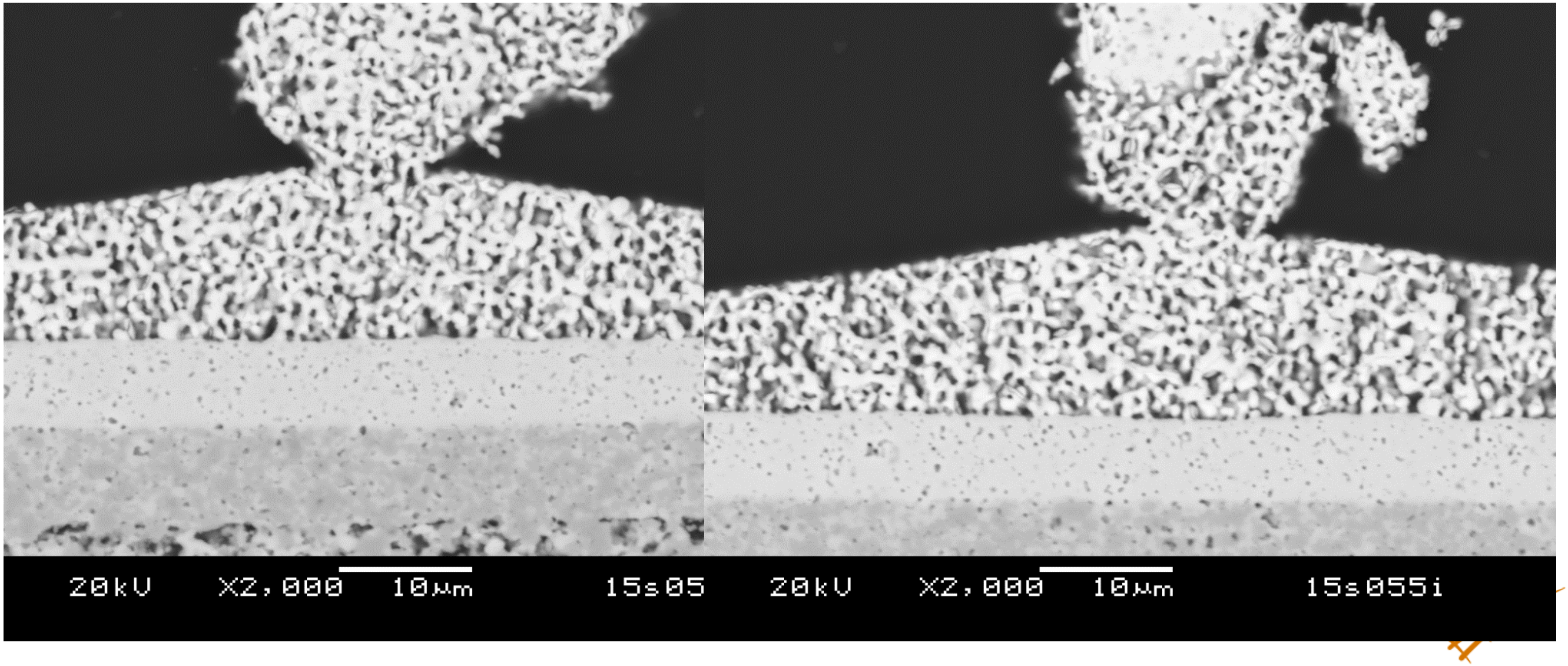
Mesh #60



Mesh #35

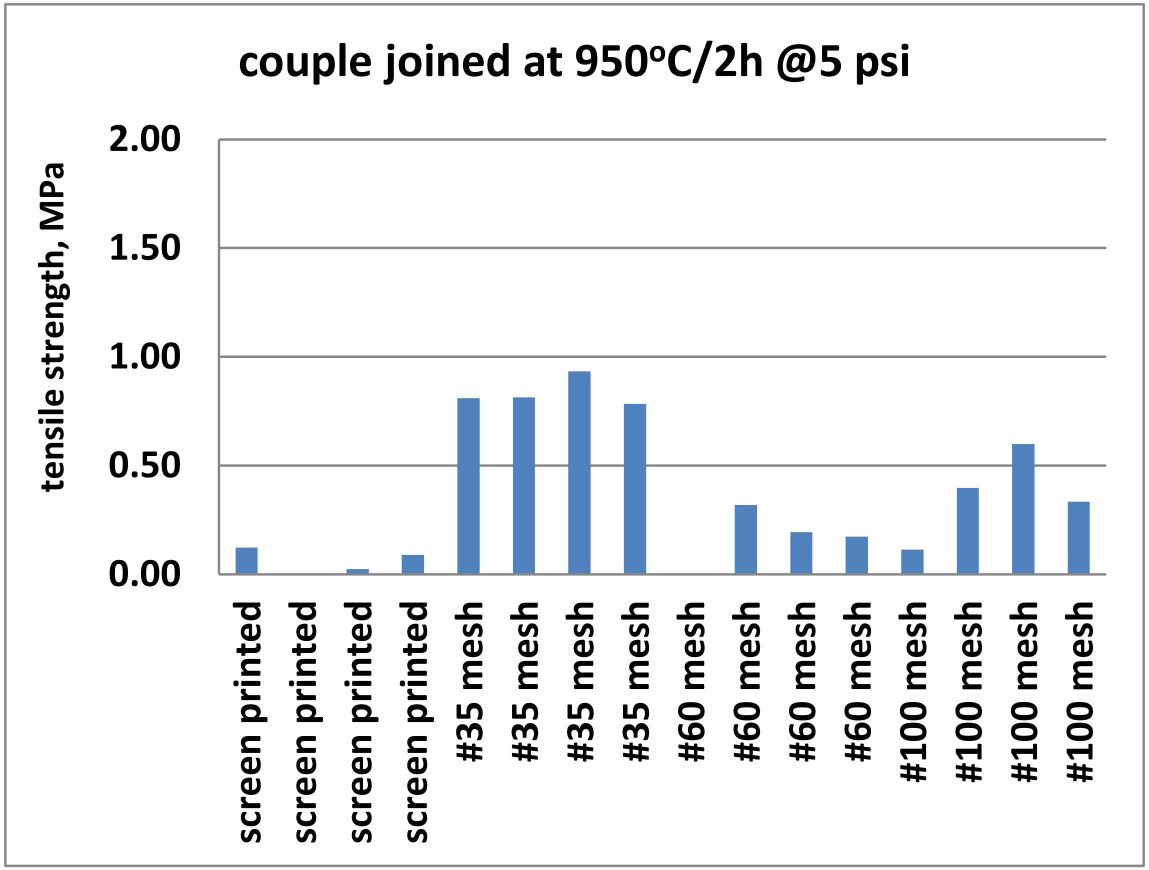
Bonding of deposited granules on cathode

- LSM20 powders (#100 mesh) sintered at 1100^{o}C/2h in air onto LSM20 cathode.
- Solid-state bonding



Contact strength of joined couples sintered at 950ºC/2h in air

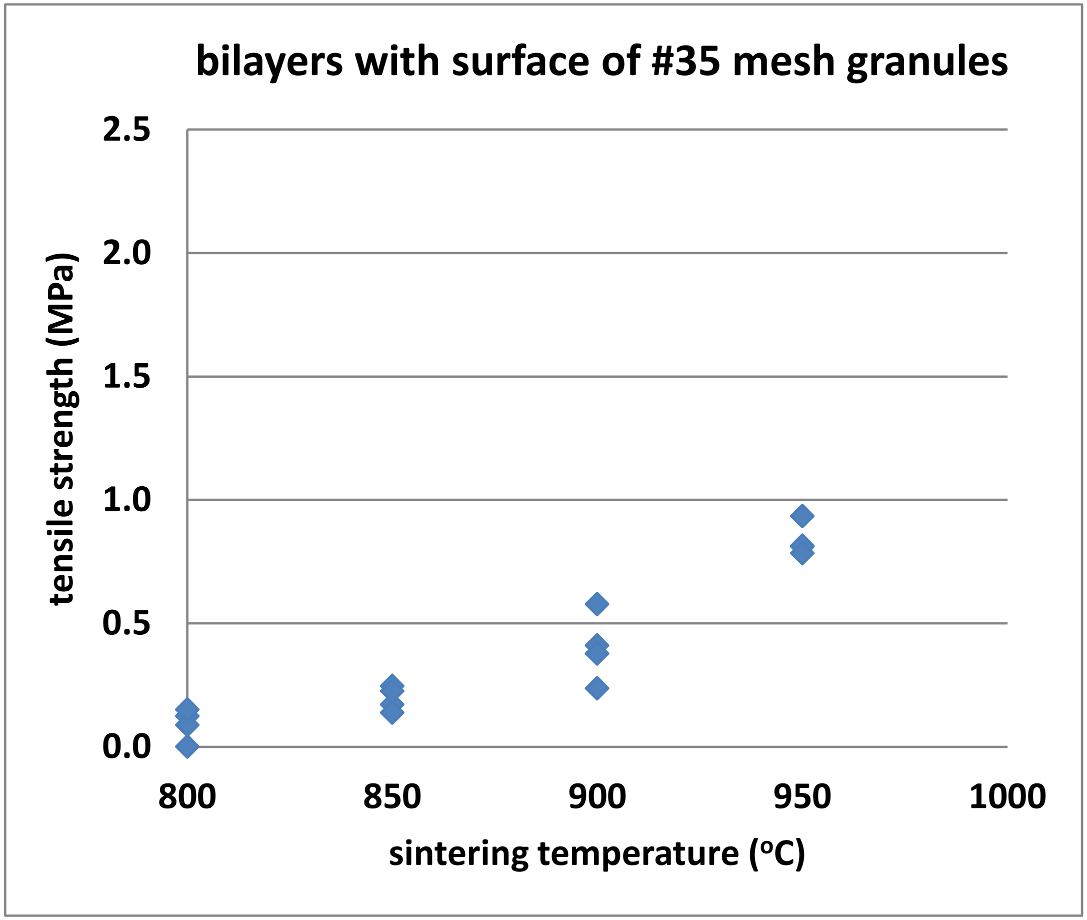
Strength increased ~3-14 times with granules-deposited surfaces



surface condition	MPa	avg
screen printed	0.12	**0.06**
screen printed	0.00	
screen printed	0.02	
screen printed	0.09	
#35 mesh	0.81	**0.84**
#35 mesh	0.81	
#35 mesh	0.93	
#35 mesh	0.78	
#60 mesh	0.00	**0.17**
#60 mesh	0.32	
#60 mesh	0.19	
#60 mesh	0.17	
#100 mesh	0.11	**0.36**
#100 mesh	0.40	
#100 mesh	0.60	
#100 mesh	0.33	

Effect of sintering temperature on contact strength of joined couples

- All sintered at T for 2h in air with granule-deposited (#35 mesh) surfaces

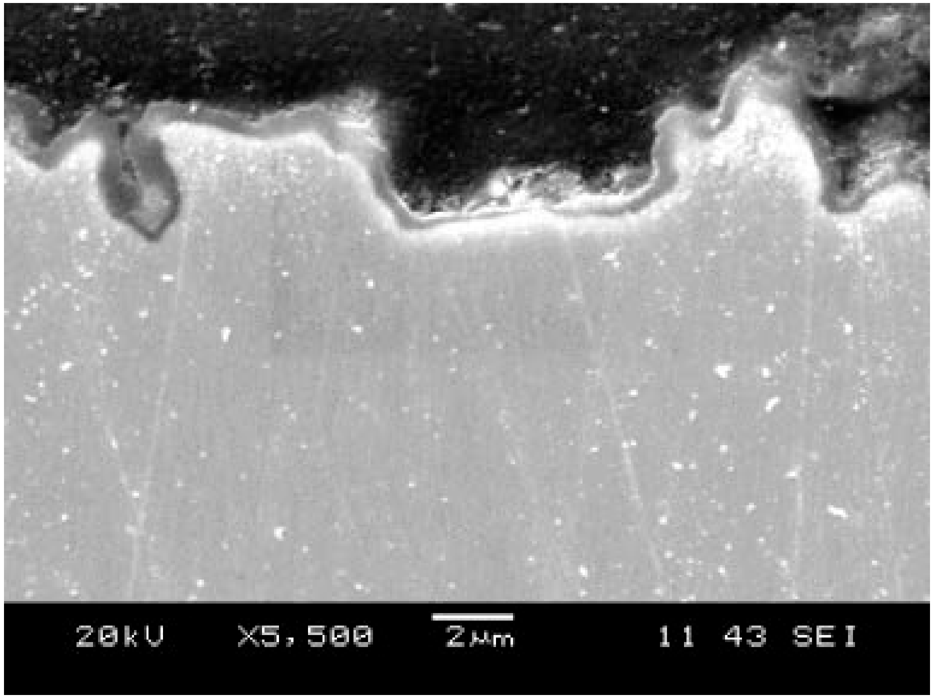


Poster:
“Mechanical Properties of Cathode Contact Materials and Surface Texture Effect on Cathode Contact Strength of Solid Oxide Fuel Cells” (Matt Chou)

Reactive Air Aluminization: Dip Coating

Reactive Air Aluminization (RAA)

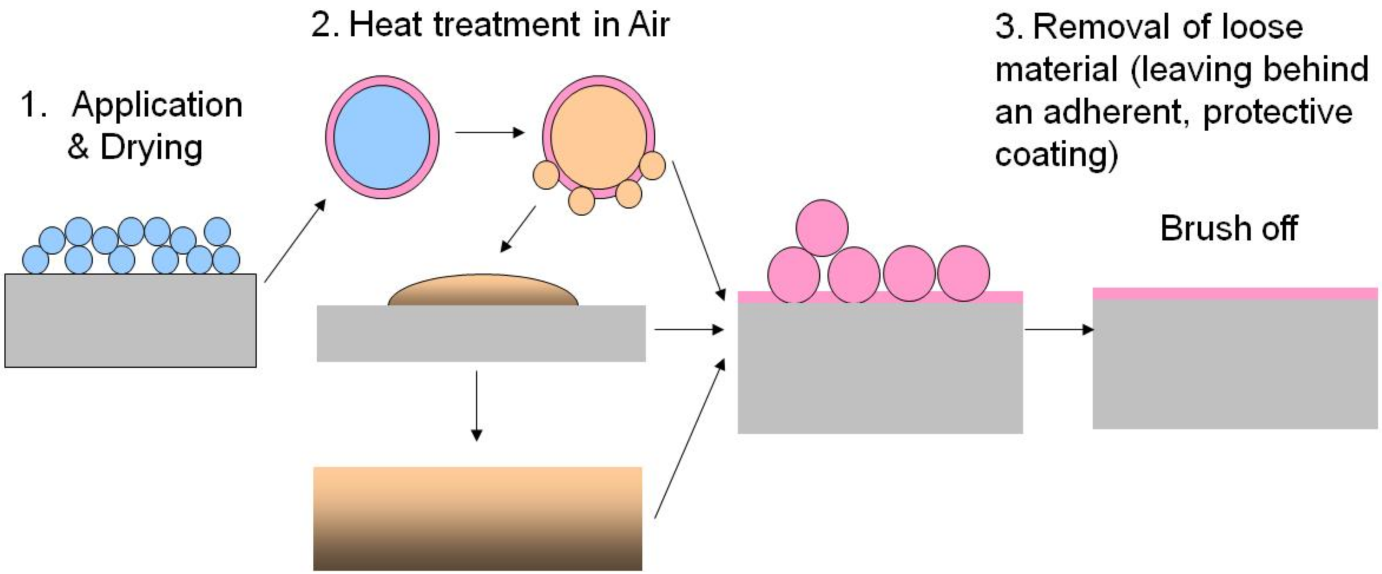
- Reaction between alkaline earths in glass seals and Cr in interconnect steel can form high CTE chromate phases (e.g., $SrCrO_4$), which degrade interfacial strength
- Cr volatility from alloys can poison cathodes
- Reactive Air Aluminization (RAA) offers a simple alternative to controlled atmosphere aluminization of interconnects (and BOP components)



Current Emphasis

- Development of dip-coating process for coating interior surfaces (e.g., cathode air delivery tubes)
- Alternative to previously developed screen-printing and aerosol spray processes

Reactive Air Aluminizing

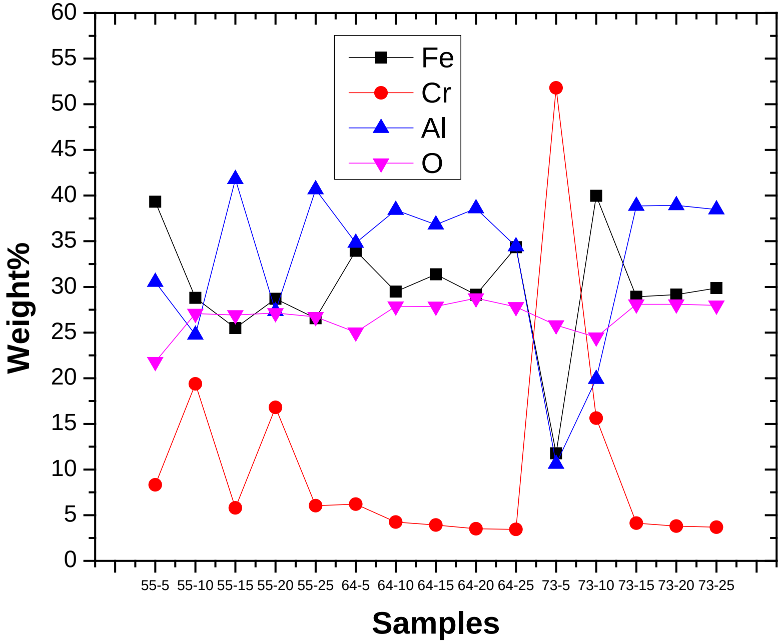


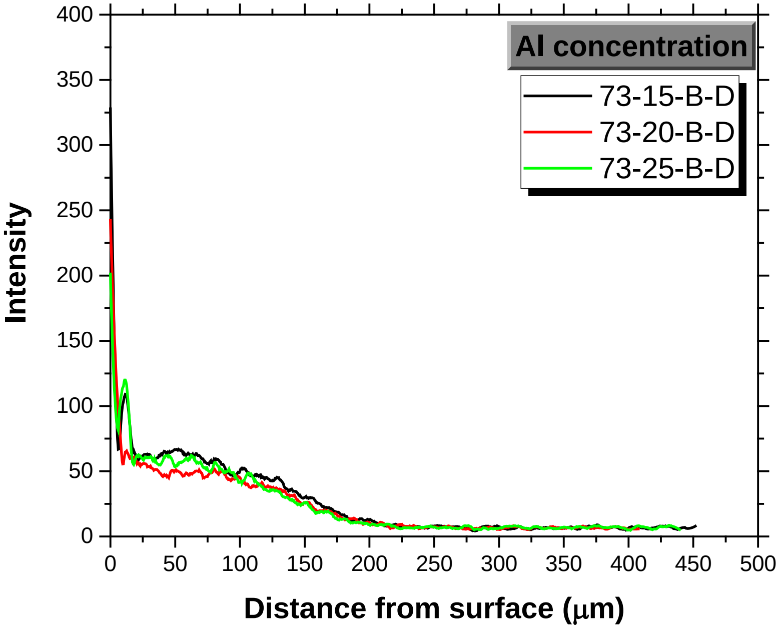
- Aluminum powder slurry-based process
  - Spray, screen-print, dip-coat
- Heat treatment in air
  - 3ºC/min to 1000ºC
  - 1 hour dwell at 1000ºC
  - 3ºC/min cool-down

RAA: Dip-Coating Process

Slurry variables: Solids/Solvent ratio, binder content

5:5	Solid	Solvent	Binder	6:4	Solid	Solvent	Binder	7:3	Solid	Solvent	Binder
#1	47.5	47.5	5	#1	57	38	5	#1	66.5	28.5	5
#2	45	45	10	#2	54	36	10	#2	63	27	10
#3	42.5	42.5	15	#3	51	34	15	#3	59.5	25.5	15
#4	40	40	20	#4	48	32	20	#4	56	24	20
#5	37.5	37.5	25	#5	45	30	25	#5	52.5	22.5	25





Poster: “Dip Coating Reactive Air Aluminization Process for SOFC Components”(Jung Choi)

Modeling of Contact Sintering

Modeling of Contact Sintering: Overview

- **Goal**: Develop computational models to simulate the *in situ* formation and subsequent reliability of the cathode contact layer during fabrication and operation
  - Provide guidance on material properties or modifications necessary for dense, mechanically robust cell interfaces and contact layers
- **Accomplishment**: Developed a three-dimensional thermo-visco-elastically coupled continuum sintering model and implemented in FEA to capture the densification behaviors of the cathode contact materials
  - Porous medium treated as a linear-viscous incompressible fluid containing isotropically distributed voids following Olevsky-Skorohod framework

Elastic Strain

Sintering Strain

$$\varepsilon_{ij} = \varepsilon_{ij}^{E} + \varepsilon_{ij}^{S}$$

Shape Change

Volumetric Change

Capillary Stresses

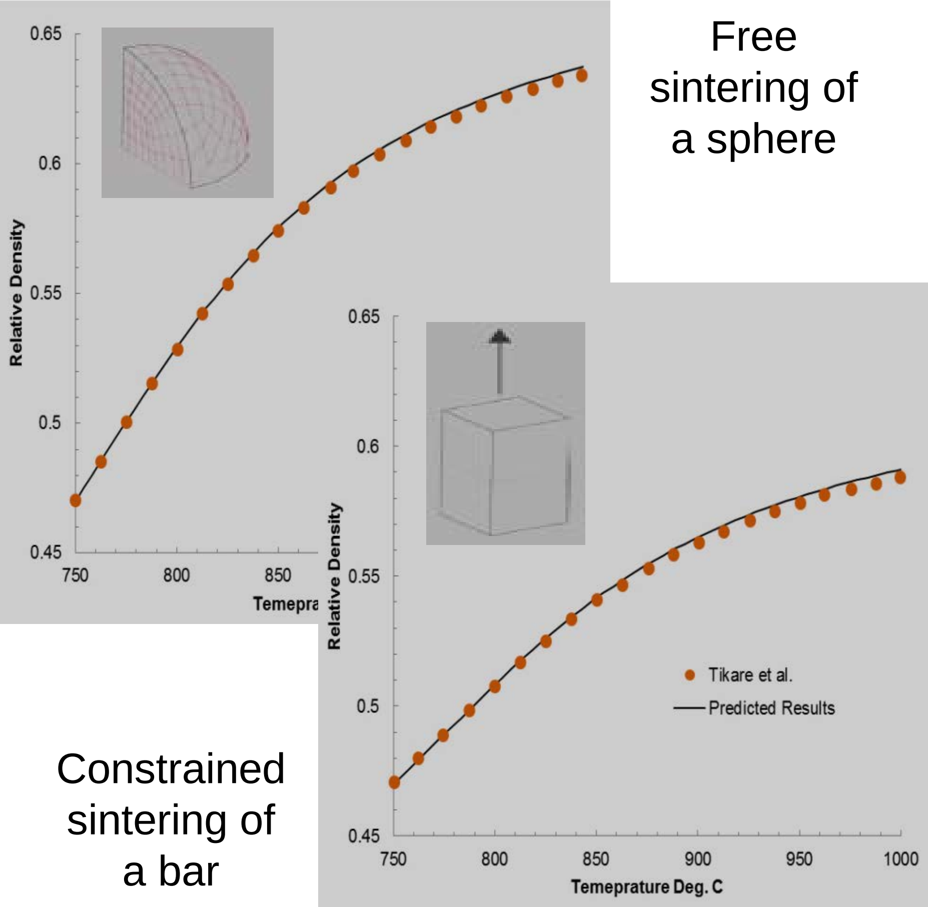
$$\sigma_{ij} = 2\eta_0\left[\varphi\dot{\varepsilon}_{ij}^{S} + \left(\Psi - \frac{1}{3}\varphi\right)\dot{e}^{S}\delta_{ij}\right] + P_L\delta_{ij}$$

Viscosity

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

Verification of Free/Constrained Sintering

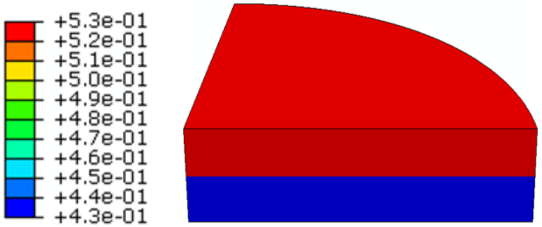
- Analytical solutions for constant heating rate of zinc oxide powder heated at 5°C/min. *(SAND2003-4293)*

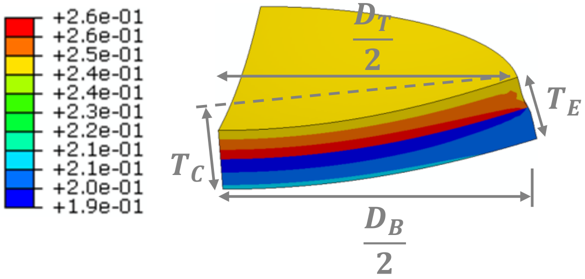


Free sintering of a sphere

Constrained sintering of a bar

- Constrained sintering experiment of zinc oxide bi-layer *(Olevsky, 2006. J.Am.Ceram.Soc.)*

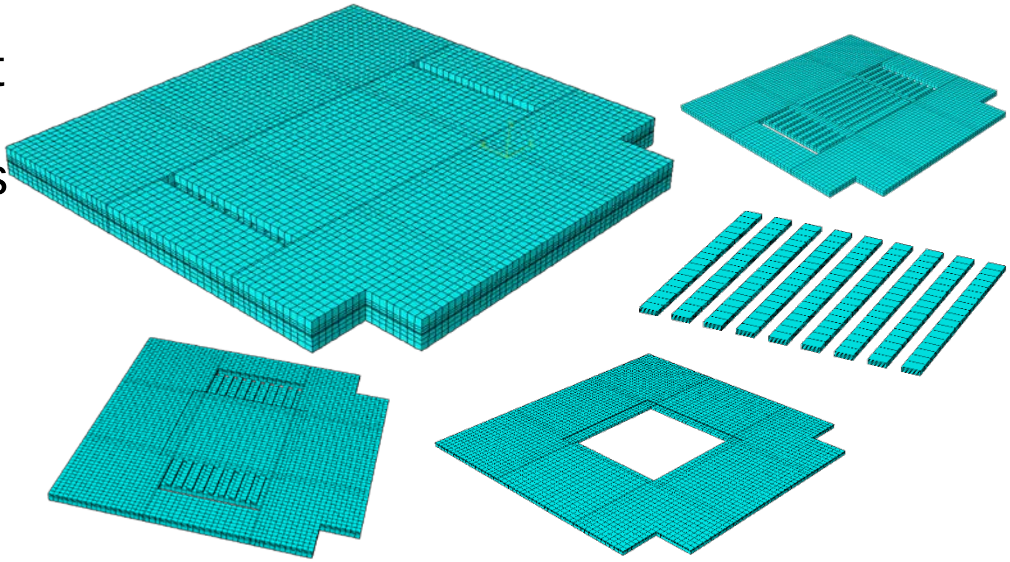


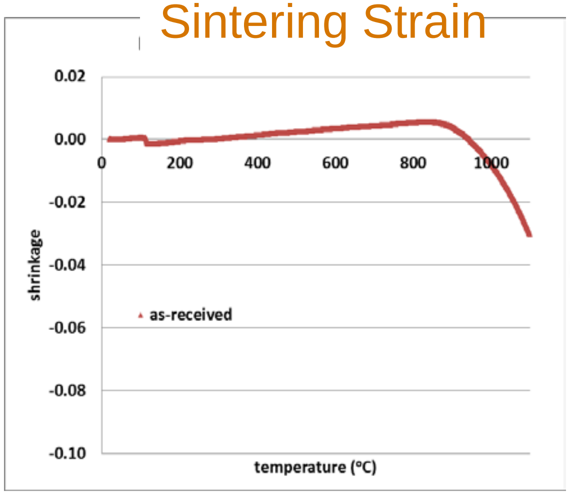


25°C	1000°C		
	Experiment	**Prediction**	**Difference**
L **(8.049 mm)**	**6.7 mm**	**6.98 mm**	**4.2%**
D_T (19.05 mm)	**15.24 mm**	**15.38 mm**	**1.3%**
D_B (19.05 mm)	**15.66 mm**	**16.06 mm**	**2.0%**
T_E (2.00 mm)	**1.63 mm**	**1.68 mm**	**1.1%**
T_C (2.00 mm)	**2.72 mm**	**3.16 mm**	**13.7%**

Cathode Contact Paste Model for SOFC Stack

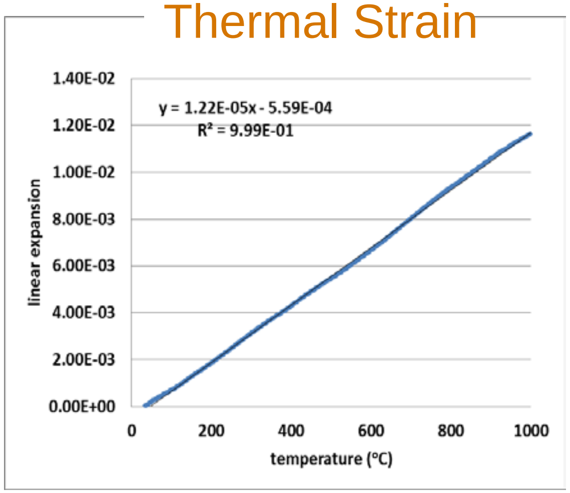
- Extract temperature-dependent viscosity from sintering and thermal expansion experiments for different contact paste materials
- Construct model of PNNL’s stack test fixture with contact paste on the cathode IC ribs





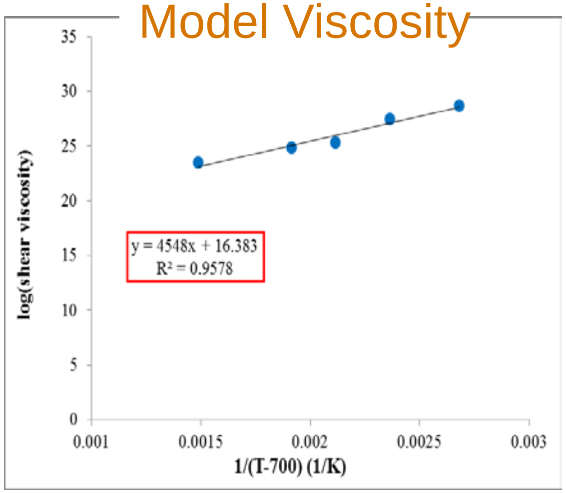
Sintering Strain

+



Thermal Strain

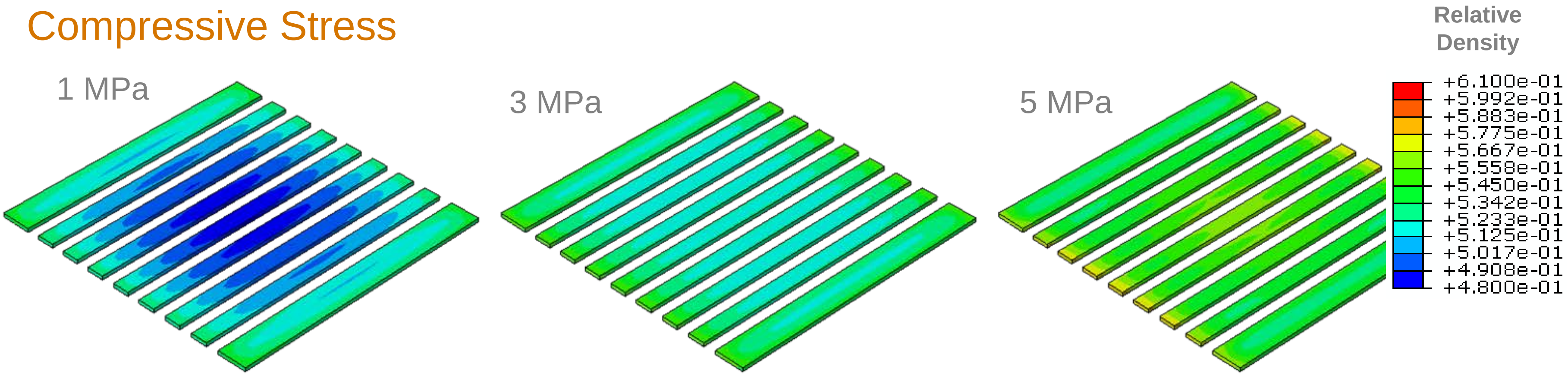
⇨



Model Viscosity

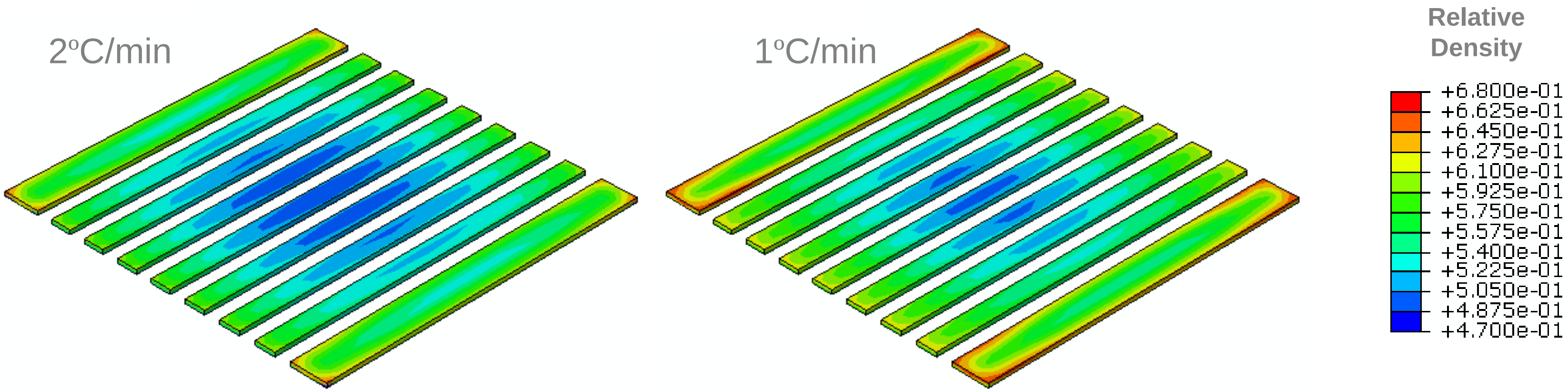
Effects of Fabrication Conditions

Compressive Stress



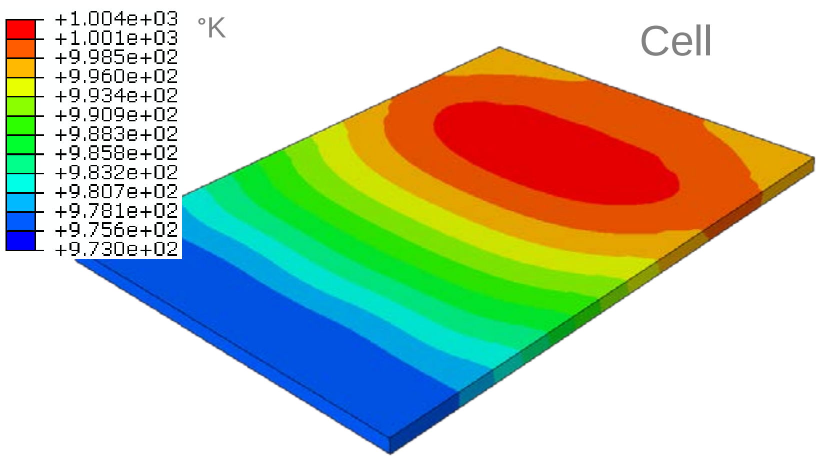
Both compressive load and longer heat treatment aid densification of contact paste

Heating Rate

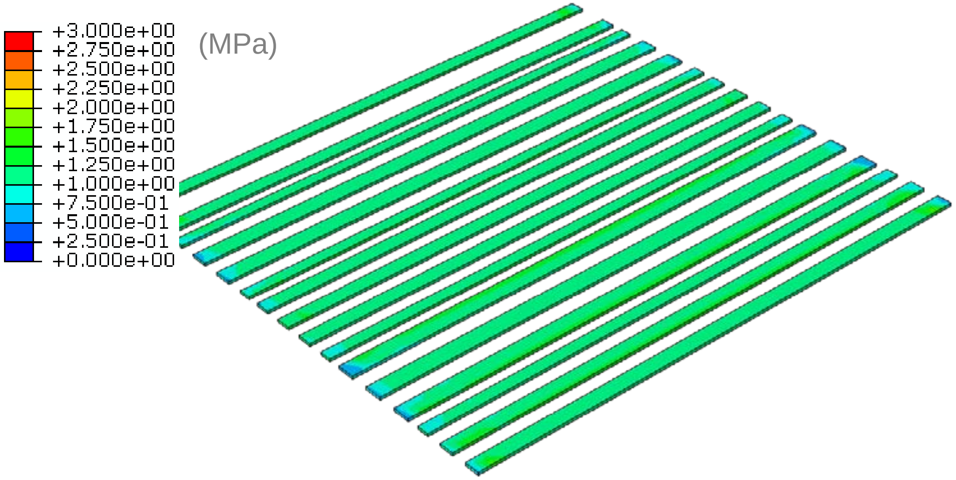


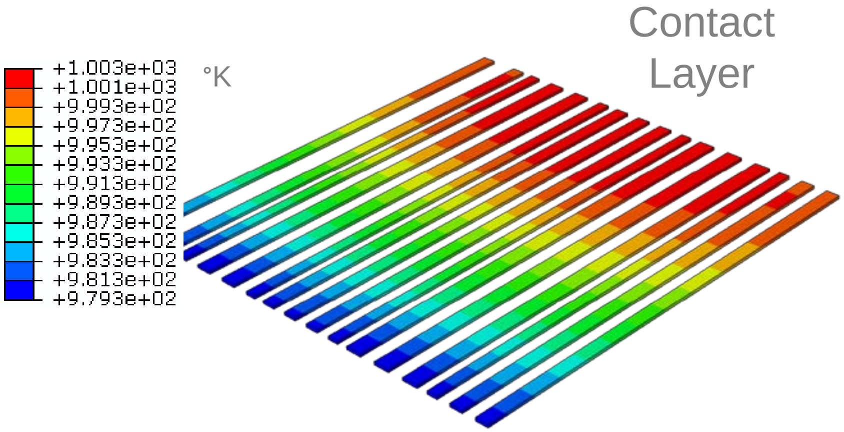
Combined Fabrication and Operating Stresses

Operating Temperature Distribution

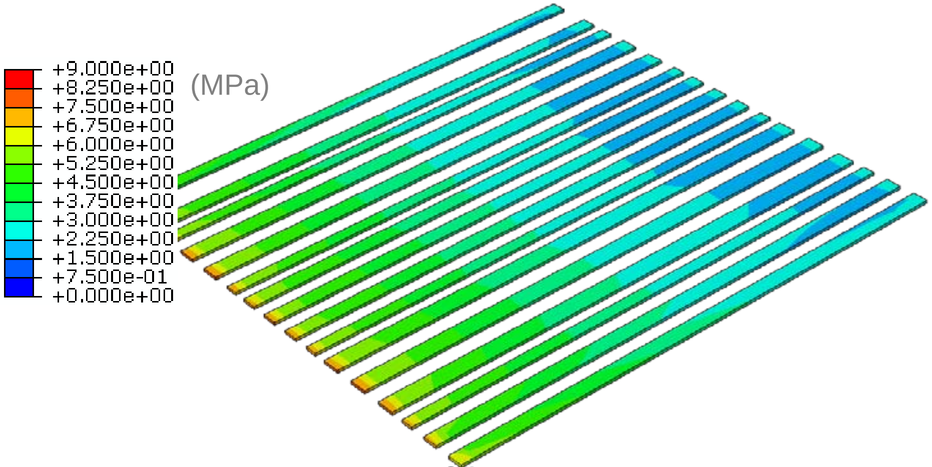


Residual stresses after fabrication





Combined stress state



Next Steps

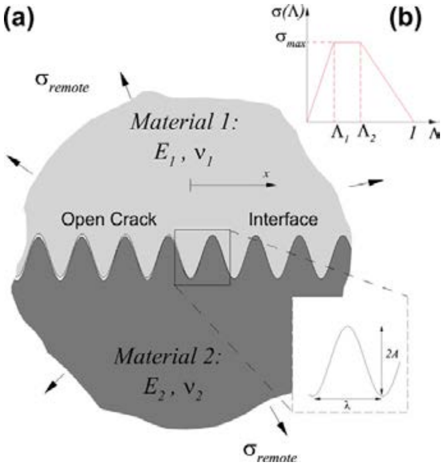
- Currently evaluating the mechanical reliability of the cell as a function of:
  - Combined stress state (residual stresses formed during contact fabrication plus thermal-mechanical stresses due to high temperature operation)
  - Different component material and Weibull strength properties
  - Different stack operating states using SOFC-MP 3D
- Continue to collaborate with materials development team to examine different contact materials and surface modification textures to increase strength and mechanical interlocking

Modeling of Rough Interfaces

Interfacial Strength: Benefit of Roughness

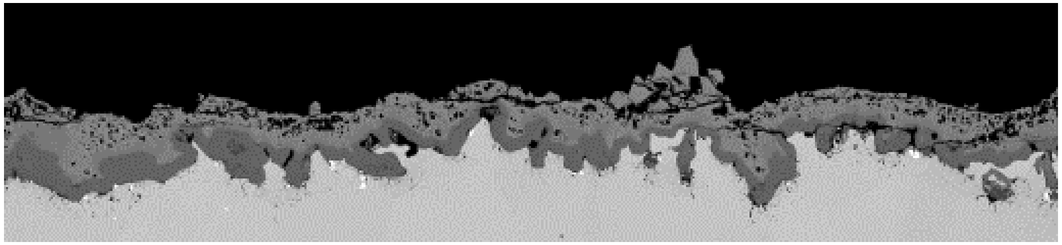
- Physical surface modifications for metallic interconnects (e.g. surface grind, surface blast) were experimentally shown to create a more adherent oxide scale for protection against spallation under long term heat treatment up to 36,000 hr.
- These surface modifications changed the interface roughness profile resulting in improved mechanical behavior and delamination resistance
- Numerical modeling in the literature also suggests an increasing toughness with the interface roughness

- *What is the preferred roughness profile?*



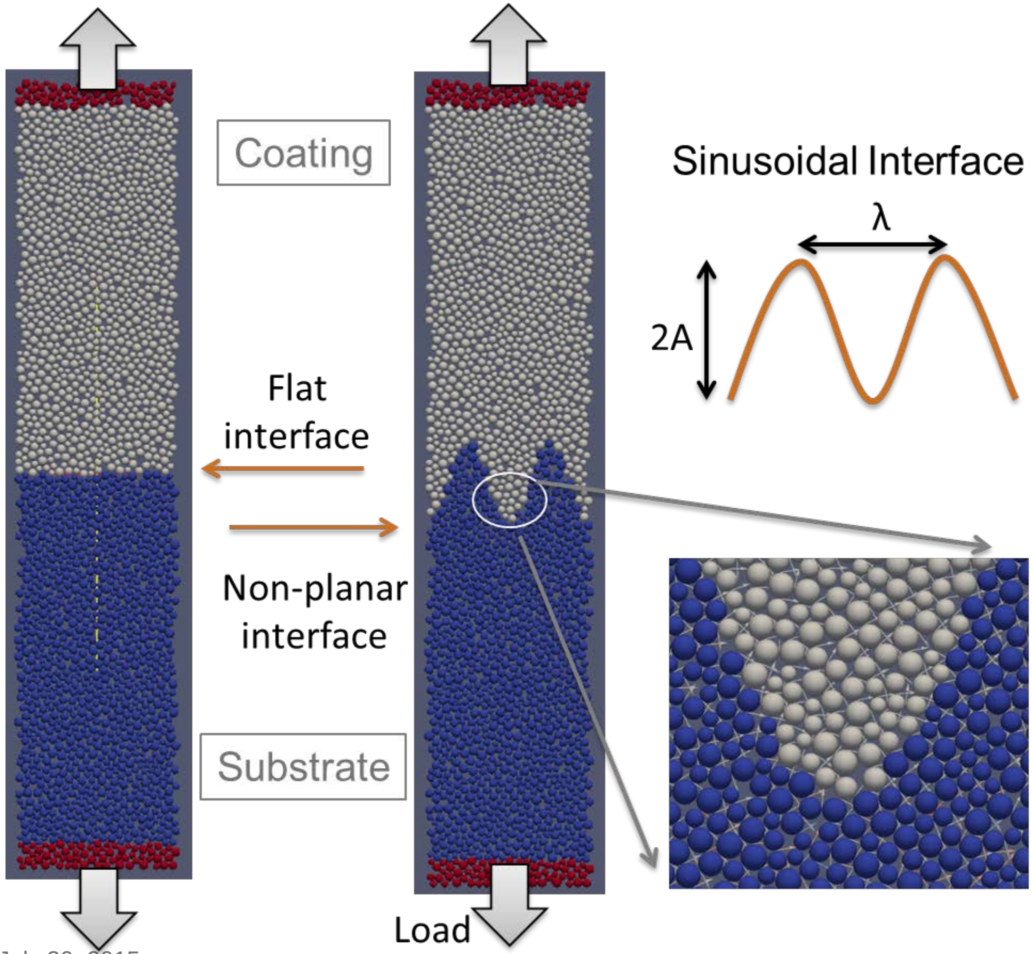
PD Zavattieri, LG Hector Jr, and AF Bower, 2008, “Cohesive Zone Simulations of Crack Growth Along a Rough Interface Between Two Elastic-Plastic Solids,” Engr Fract Mech 75(15):4309-4332.

SS441 interconnect/oxide scale/protective coating



Discrete Element Model (DEM) for Interface Roughness

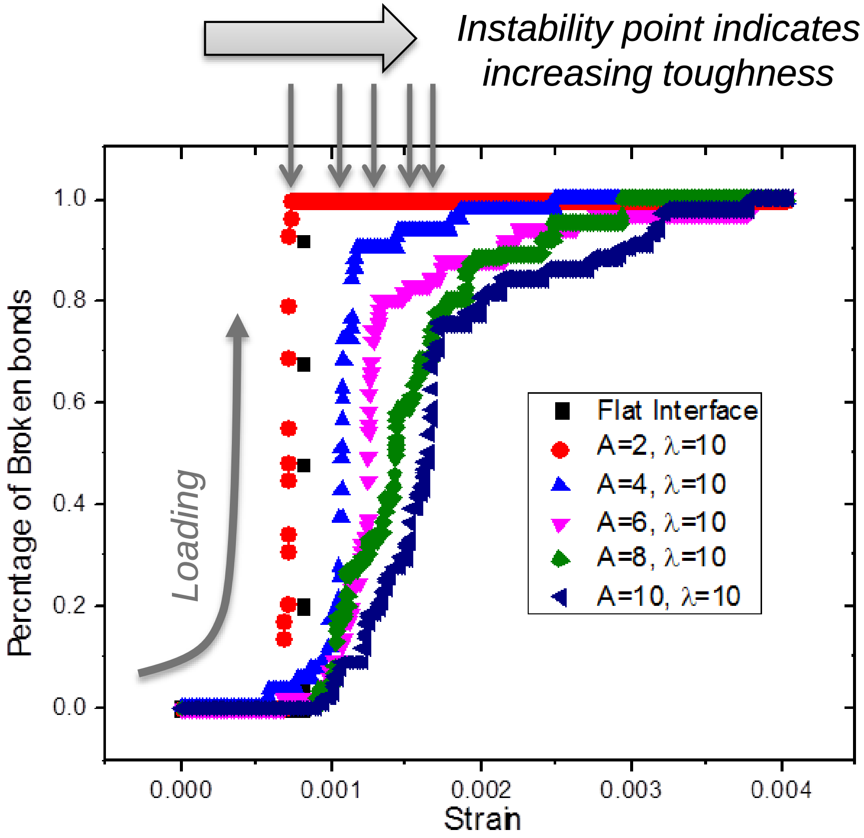
- **Goal**: Quantify the influence of surface roughness on interfacial delamination resistance of dissimilar materials



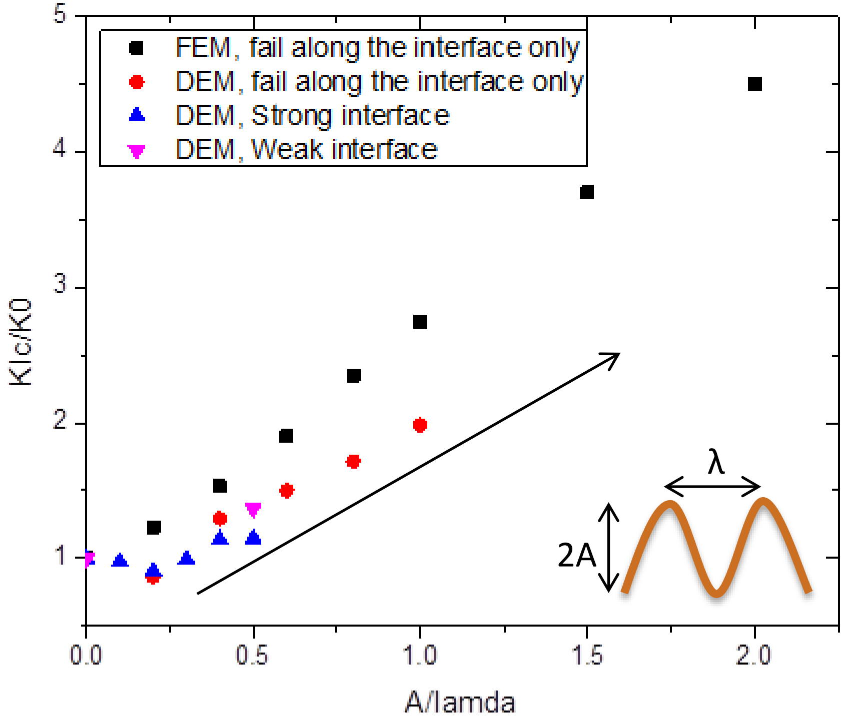
- DEM represents a body as a packed array of bonded particles:
  - Random particle size
  - Interaction via bonds and friction
  - Can assign material failure as a function of shear and/or normal stress
  - Can easily define an interface between two materials with its own property set
  - Can study failure propagation paths

Effect of Increasing Roughness

- Increasing the amplitude of the sinusoidal interface (i.e. roughness) increases the strain/load at which unstable delamination occurs
- Interface toughness predicted to increase similar to the literature data



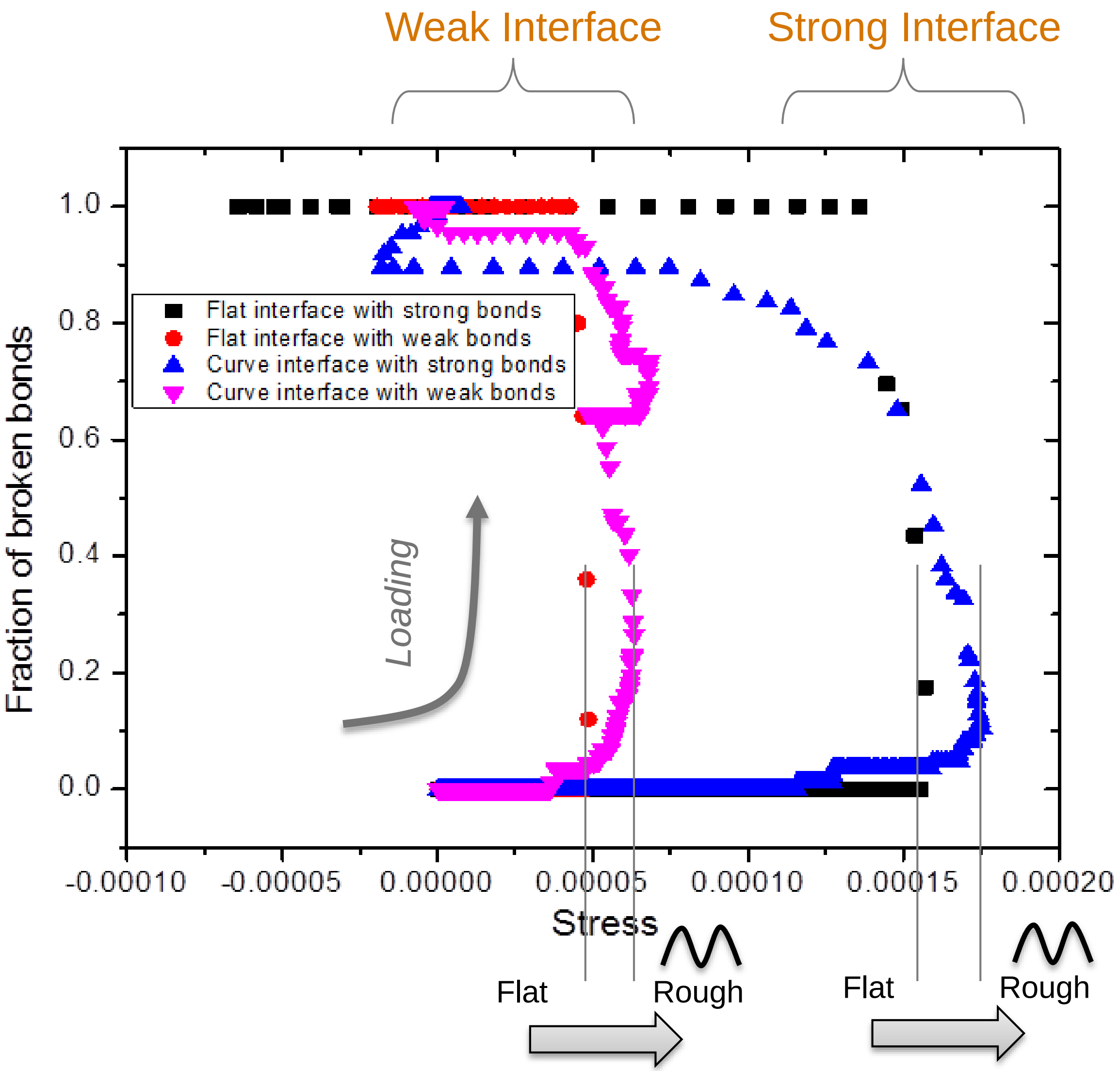
Instability point indicates increasing toughness



Fracture Toughness Ratio

Effect of Coating and Interface Failure

- Including the option for coating and interface fracture, the roughness is still beneficial to increase the effective strength of the interface
  - ~30% for the ‘weak’ interface and ~15% for the ‘strong’ interface definition
- Local mechanical interlocking further increases load carrying capacity of the interface



Next Steps

- Currently, evaluating the interconnect oxide scale structure and compare to previously obtained experimental data to verify the model predicts improved interface strength due to surface modification and realistic roughness profiles.
- Evaluate the cathode contact layer and potential surface modifications to provide guidance on surface roughness for enhancement of interfacial strength.

Poster:
“A Discrete Element Model (DEM) for
Fracture Toughness of Rough Interfaces”
(Zhijie Xu)

SOFC-MP and SOFC-ROM Modeling Tools

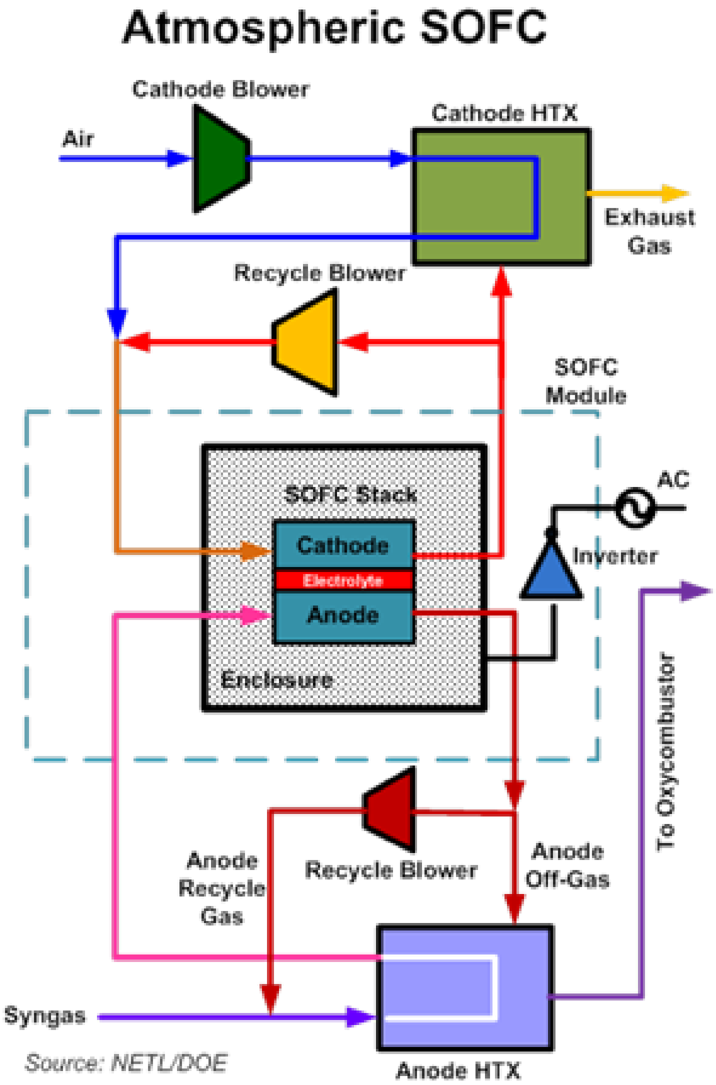
Reduced Order Model (ROM) Demonstration

- **Goal**: Demonstrate an analysis procedure to leverage high fidelity stack model performance information for use in system-level modeling tools
- **Approach**: Collaborate with ESPA/NETL modelers to define, generate, implement, and demonstrate use of an SOFC stack ROM in the NETL power generation system models
- **Accomplishments**:
  - Ensured use of state-of-art SOFC stack current-voltage performance
  - Implemented material flow sheet to define stack operating parameters based on key parameters relevant to the SOFC-based power system
  - Utilized the SOFC-MP 2D stack model for sampled cases
  - Performed error analysis for ROM output parameters of interest
  - Collaborated with ESPA/NETL system modelers to implement the exported ROM and demonstrate its use in NETL ASPEN+ system models for an NGFC system (*to be presented by NETL*)

Poster:
“Reduced Order Model Creation for SOFC
Power System Models” (Kevin Lai)

Recirculation Capability for SOFC-MP 2D

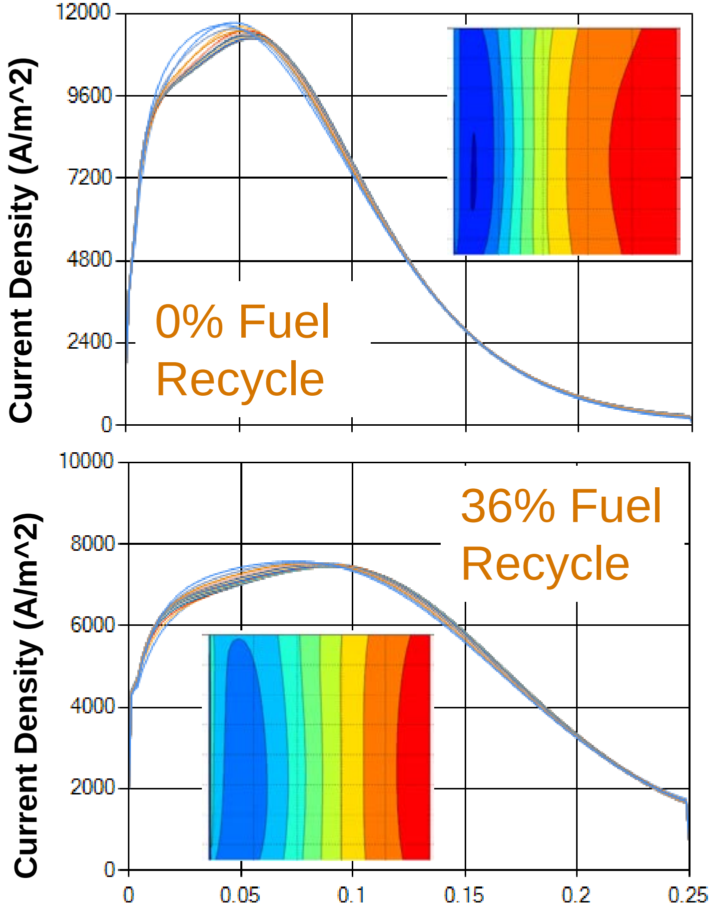
- Air and fuel recirculation loops added to SOFC-MP 2D module to benefit the ROM/system modeling activity
  - Air and fuel recirculation loops with heat exchangers (HTX)
  - Air side: cold inlet air heated in HTX by stack exhaust prior to mixing with recirculated fraction of air
  - Fuel side: cold inlet fuel mixes with stack exhaust prior to heating by anode off-gas
- This approach provides preferable access to the operating metrics useful from the system modeling perspective rather than the usual stack perspective
  - E.g., heat exchanger effectiveness, recirculation fraction, etc.



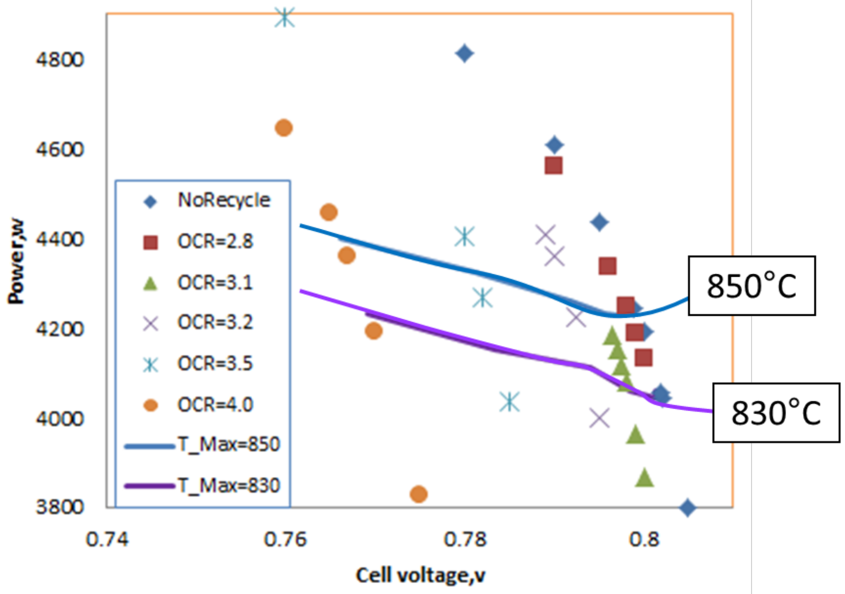
Source: NETL/DOE

Example: Fuel Recycle Benefit

- Recycle of fuels with high CH_4 content provides smaller ΔT and smoother current density profile



- Tradeoffs in power for different recirculation fractions can be identified with respect to the cell temperature state



- Next Step: Test ROM generation procedure and evaluate approximation error using 2D stack input with recirculation capability

SOFC-MP 3D Support for ROM

- The ROM tool presently utilizes SOFC-MP 2D only for detailed stack model sampled inputs
- Integration of SOFC-MP 3D module to the ROM tool in progress
  - Beneficially, the 3D provides more accurate results and detailed distributions of the performance quantities of interest
  - 3D simulations are more computationally intensive, but permit analysis of the cross-flow cell configuration
- Supports ROM variables to mimic the 2D module implementation

ROM Input Parameters	Salient ROM Output Parameters*
Average current density (J)	Cell voltage (V)
Fuel utilization (FU)	Cell temperature profile (including T_{max}, T_{min}, and ΔT)
Inlet NG composition - fixed	Stack air outlet conditions
Inlet air composition	Air outlet temperature ($T_{air\text{-}out}$)
Fuel inlet temperature ($T_{fuel\text{-}in}$)	Species (N_2, O_2, Ar, CO_2, H_2O) mole flows
Air inlet temperature ($T_{air\text{-}in}$)	Stack fuel outlet conditions
Anode inlet gas oxygen to carbon ratio (OTC)	Fuel outlet temperature ($T_{fuel\text{-}out}$)
Cathode gas recirculation fraction (RF_{cath})	Species (CH_4, H_2, CO, H_2O, CO_2, N_2) mole flows
Internal reformation fraction ($X_{int\text{-}ref}$)	Current density profile (J_{max}, J_{min}, J_{avg})
Air utilization (AU) or Air Stoichs	

Future Work

- Cathode materials and interactions
  - Effects of volatile Cr species on cathode performance
    - Quantitative assessment of Cr dosing/Cr update
  - Mitigation of Cr poisoning (Evaluate/optimize Cr gettering materials)
  - Improve the sintered density of doped ceria barrier layers
- Cathode contact materials
  - Further improve the mechanical strength/bonding at cathode-to-interconnect interfaces through fibrous inclusions and sintering aids
- Interconnects and BOP
  - Develop reduced temperature RAA process
- Modeling tools
  - Extend ROM tool for the IGFC system and improve ROM procedure for simplified Aspen+ integration
  - Continue evaluation of cathode contact material improvements and cell reliability
  - Collaborate with NETL and ORNL to use electrochemical performance and degradation models/data developed at different scales

Summary

- PNNL is using experimental and computational capabilities to accelerate the commercialization of SOFC power systems.
- Cathodes
  - Electrochemical performance of both LSCF and LSM-based cathodes is impacted by the presence of moisture (3% water) in the cathode air stream.
  - CO_2 (up to 12%) may impact initial cell performance, but has negligible effect on degradation rates.
- Cathode Contact Materials
  - Texturing of cathode surfaces results in increased bond strength between cathodes and contact materials, but further improvement is desirable.
- Interconnects/BOP
  - A dip coating process has been developed to allow for reactive air aluminization of inner surfaces (e.g., cathode air delivery tubes)
- Stack Modeling Tools
  - Demonstrated use of a reduced order model (ROM) to more accurately represent the stack in power system models

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