Pacific
Northwest
NATIONAL LABORATORY

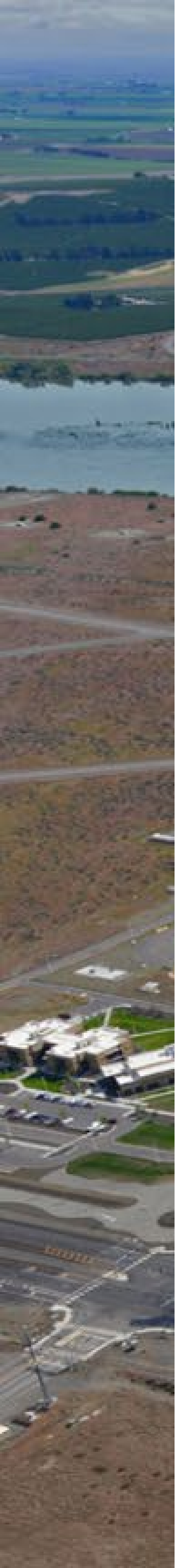
SOFC Development at PNNL: Overview

May 30, 2020

**J. Hardy, B. Koeppel, Y. Chou, C. Coyle,
J. Choi, B. Kirby, Z. Xu, N. Karri, J. Bao,
B. Nguyen, N. Canfield, T. Droubay, D. Wang,
K. Meinhardt, G. Whyatt, J. Davis, C. Fischer,
C. Lowrey, and J. Bonnett**

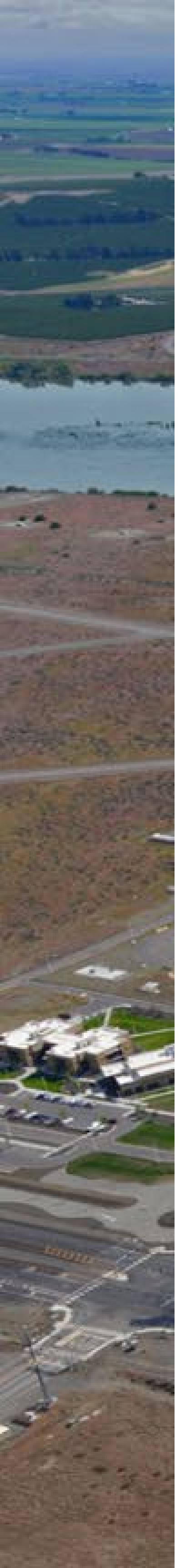
U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy



Scope of Work

- Core Technology Program
  - Materials Development
    - ✓ Cathode materials and interactions
      - Effects of volatile species (Cr, Sr) on cell performance
      - Mitigation of Cr poisoning: Evaluation of Cr capture materials
      - Cathode contact materials: Enhancing reliability of cathode/contact materials interfaces
    - ✓ Interconnects/BOP
      - Co-free protective coatings for metallic interconnects
  - Modeling/Simulation
    - ✓ SOFC Stack and System Modeling Tool Development
    - ✓ Modeling of Stack Degradation and Reliability
- Small-Scale SOFC Test Platform
  - Evaluation of performance and reliability of new stack technologies (1-10 kW)



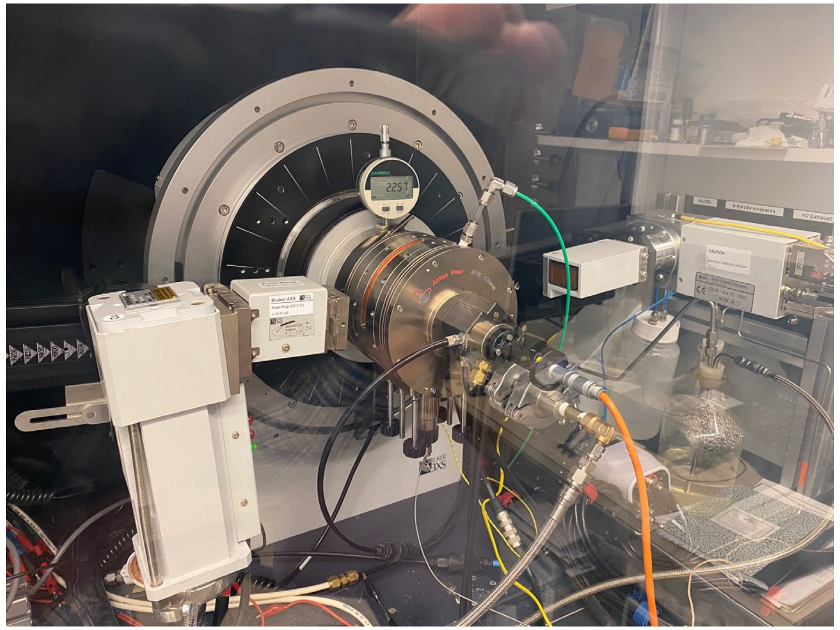
Cr Poisoning

- Challenges
  - Developing an understanding of the effects of Cr poisoning on phase formation in and atomic structure of SOFC cathodes
  - Mitigation of effects of volatile Cr species on cathode performance

- Approaches
  - In-operando XRD of LSM and LSCF-based cathodes with various Cr concentrations in the cathode air stream

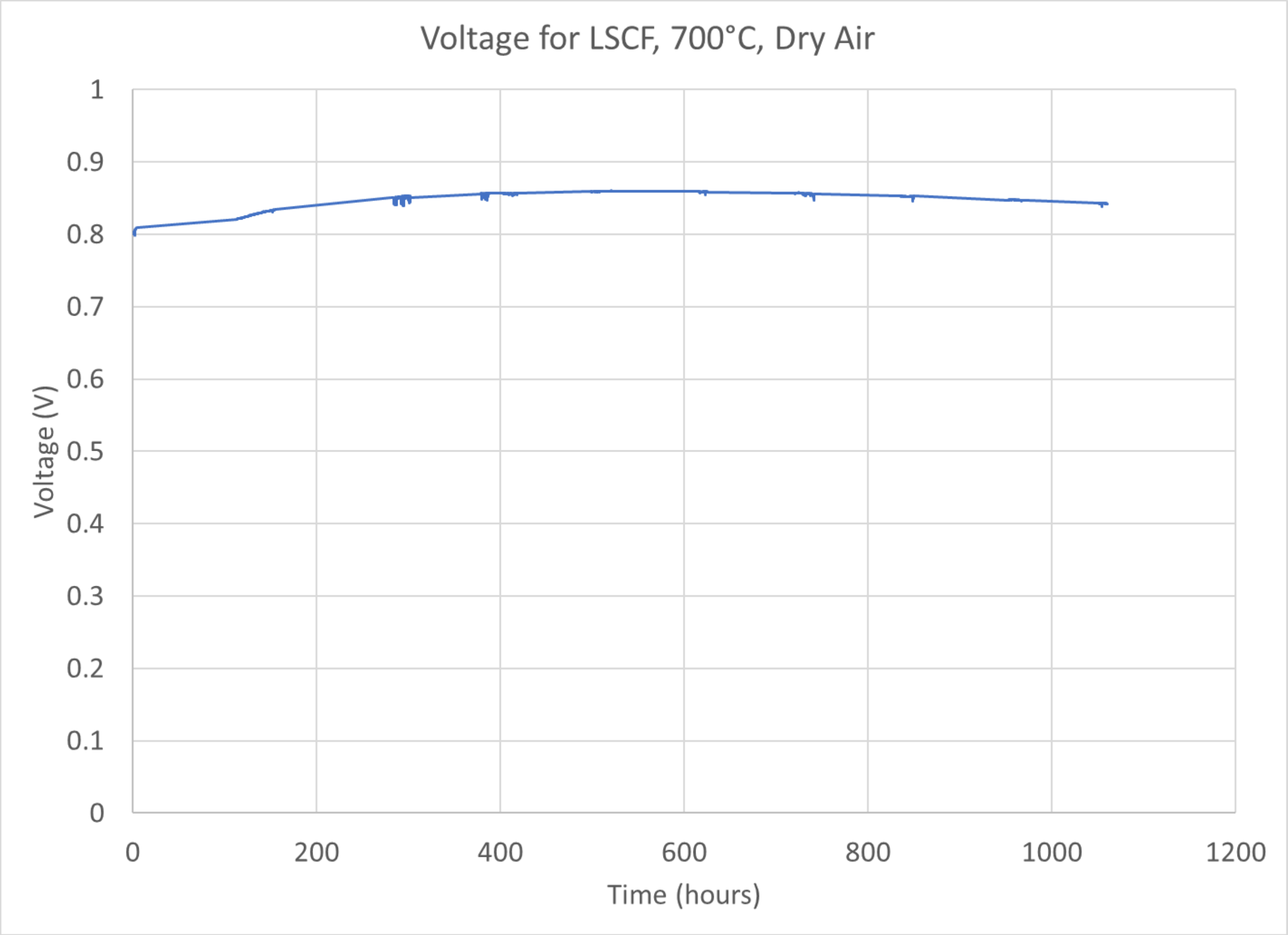
  - Evaluation/optimization of Cr “getter” materials intended to capture volatile Cr species
    - ✓ May be located upstream of stack and/or within stack (“on-cell” capture)
    - ✓ Possibly use upstream getter as primary, and “on-cell” getter as secondary (“polishing”)

Cr Poisoning: In-operando XRD



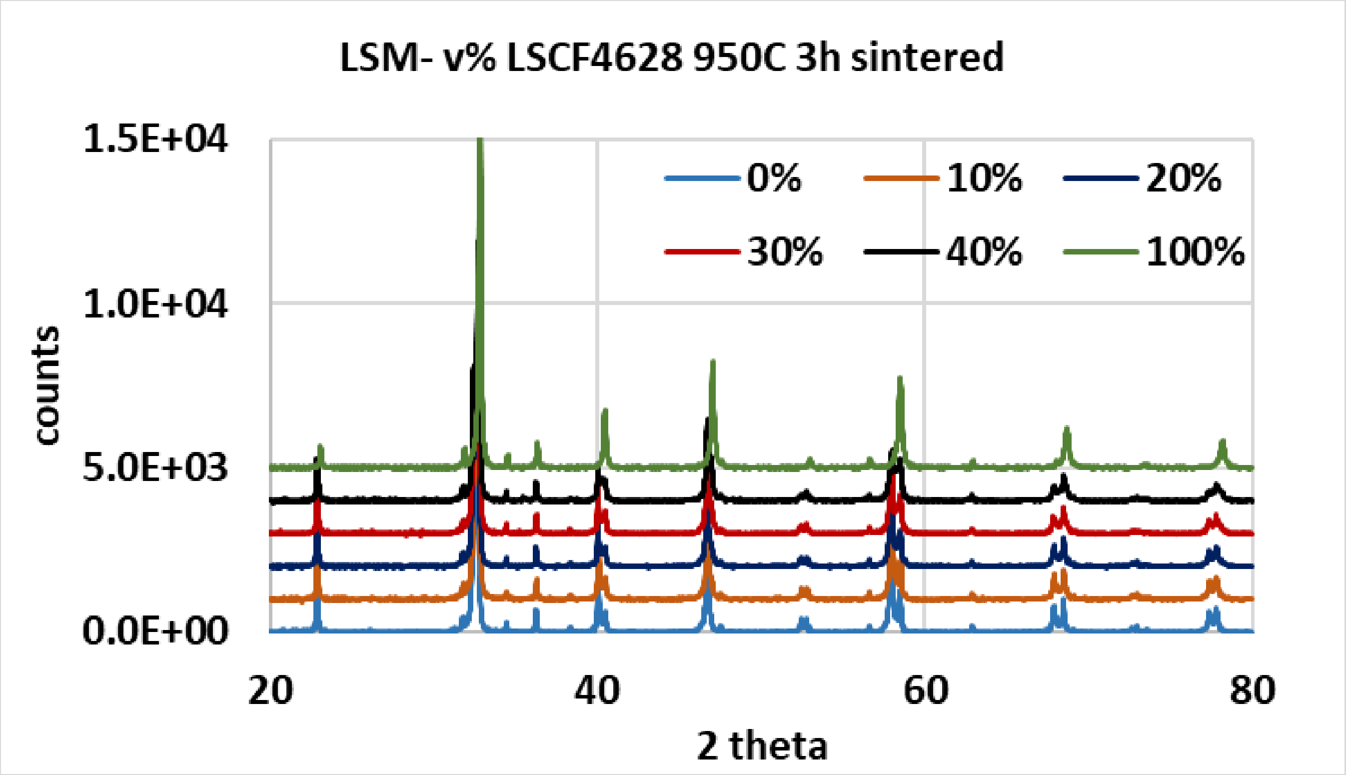
- A hydrogen safety incident at PNNL prompted safety upgrades to all experiments using hydrogen.
- Safety upgrades for in-operando XRD of SOFCs were installed:
  - Metallic lines for flammable gases
  - Over temperature monitoring
  - Fume hood pressure monitoring
  - Flammable gas sensing
  - Automatic shut down

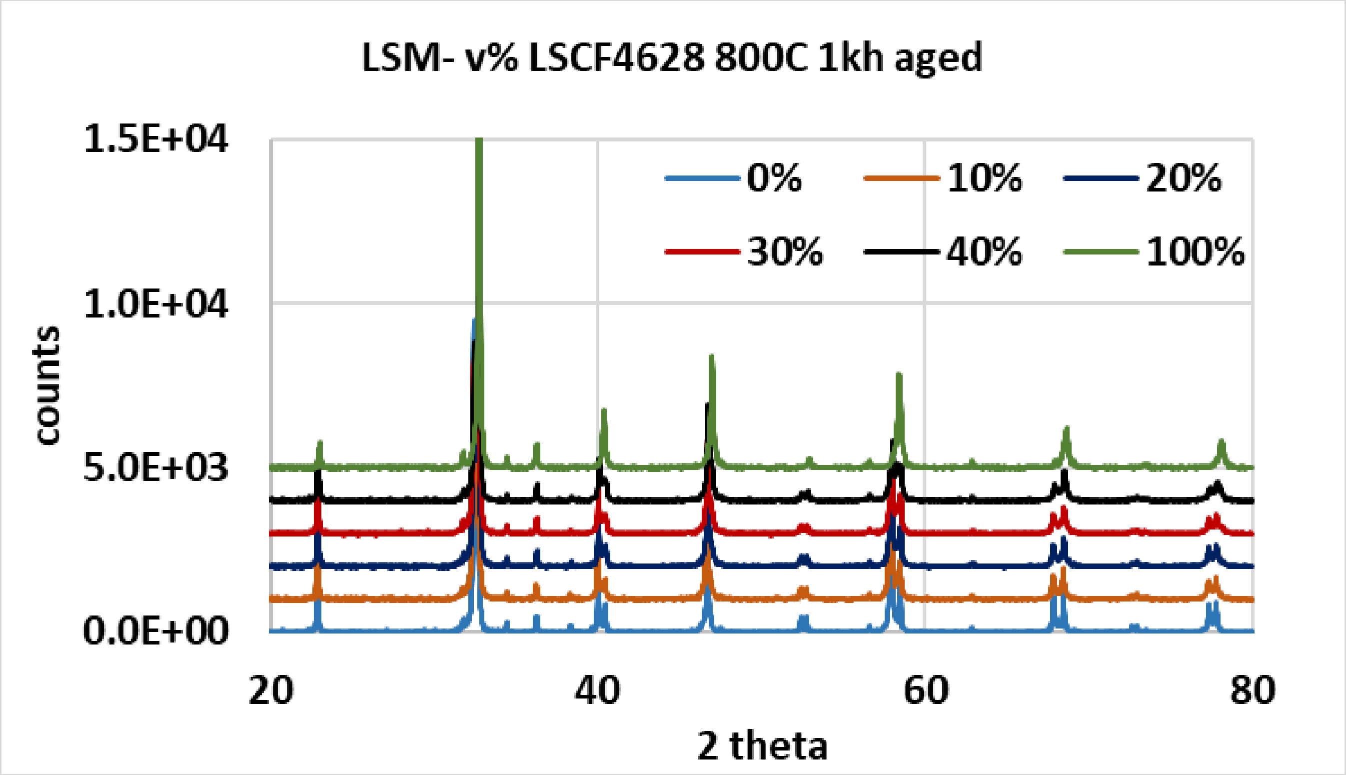
- Baseline test on LSCF cell in dry, clean air was recently completed – XRD analysis pending

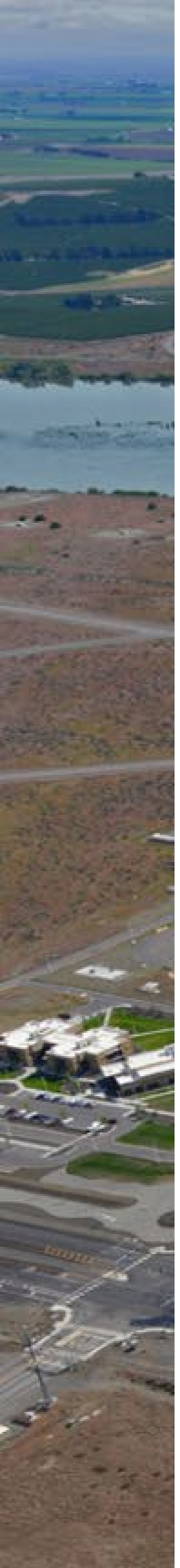


Cr Gettering Materials

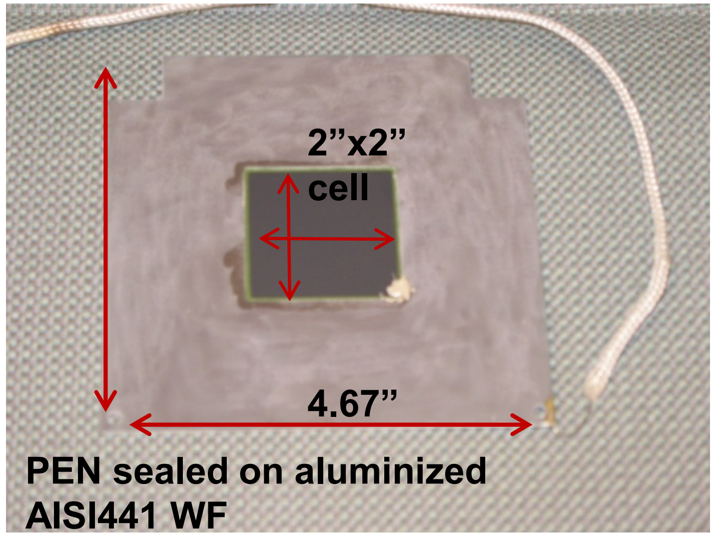
- In previous work, LSCF perovskites with high Sr content were shown to be effective as upstream getters due to high reactivity with Cr vapor species (forming $SrCrO_4$ as reaction product).
- For on-cell applications, Cr-gettering material needs to have matched CTE, high electrical conductivity, chemical compatibility, and thermal stability.
- Approach: Evaluate LSCF/LSM and LSCF/LSCo mixtures as dual purpose cathode contact / Cr getter materials.





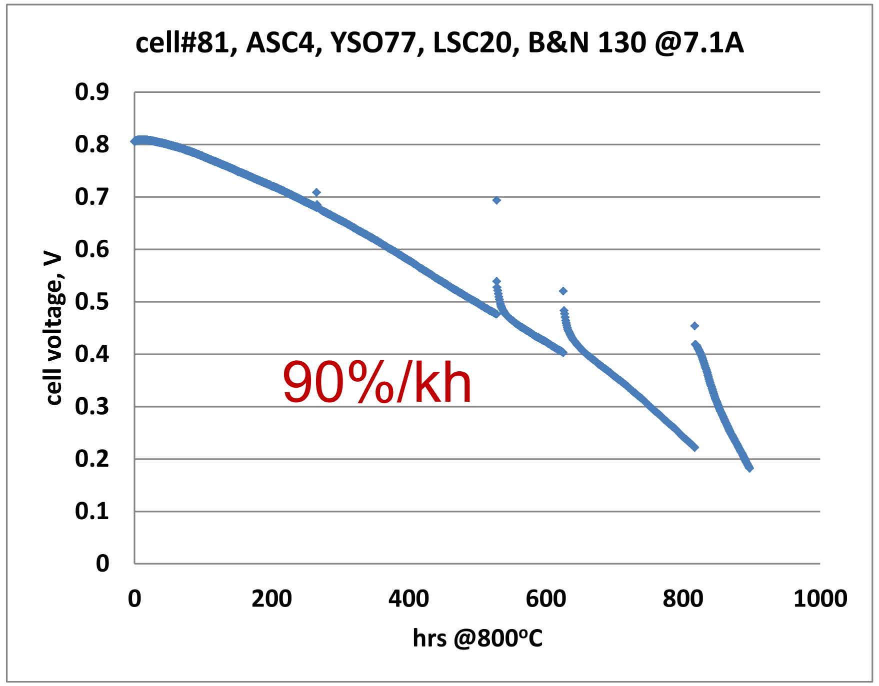


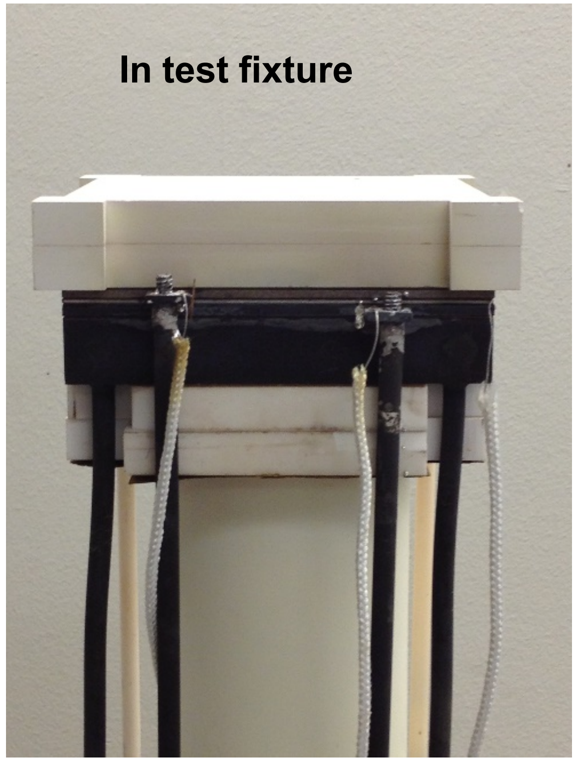
Cr Gettering Materials: LSCF/LSM Validation Testing



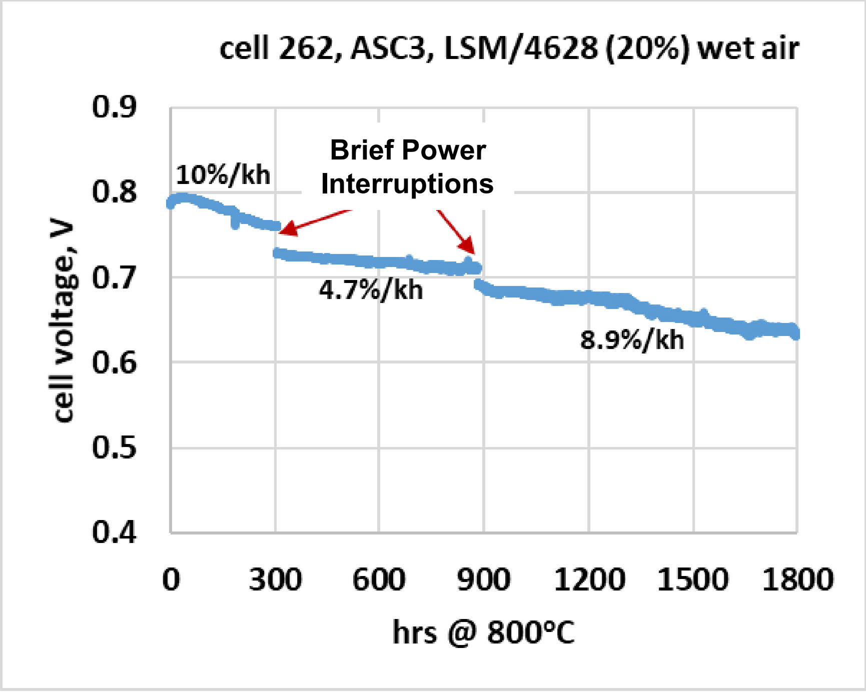
PEN sealed on aluminized AISI441 WF

No Cr Getter:





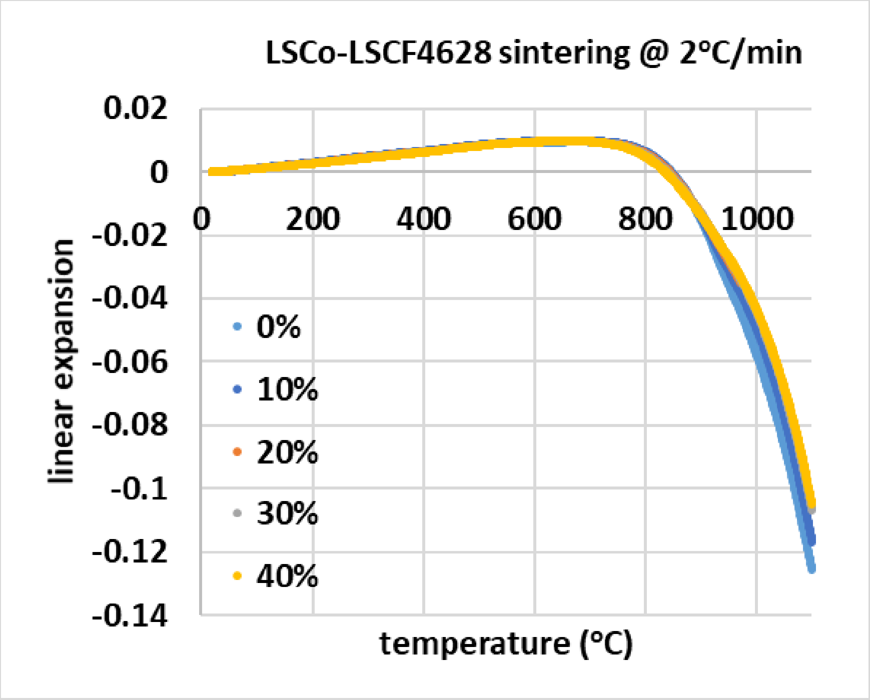
80% LSCF / 20% LSM:
On-cell Getter



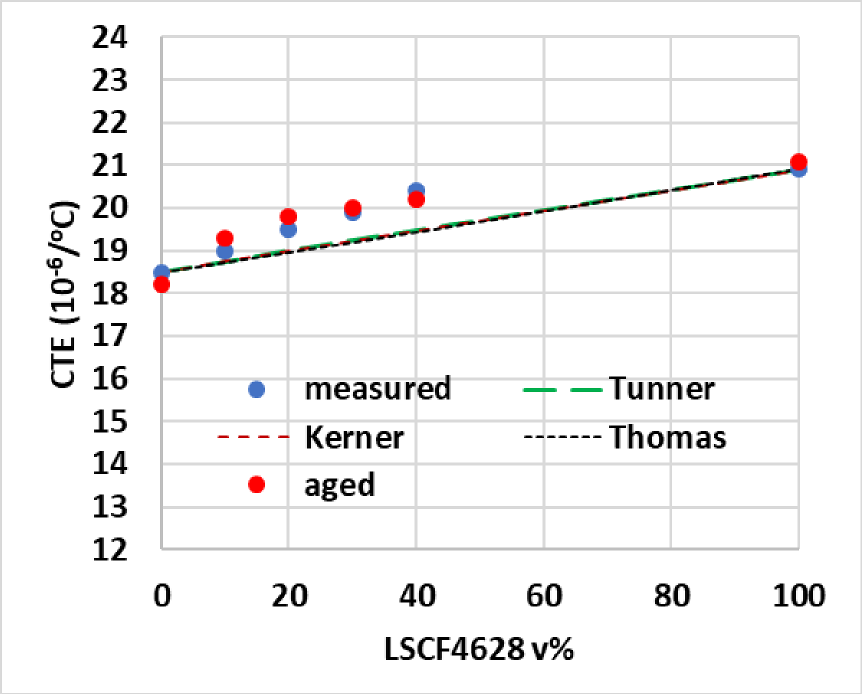
Pacific Northwest
NATIONAL LABORATORY

Cr Gettering Materials: LSCF/LSCo Characterization

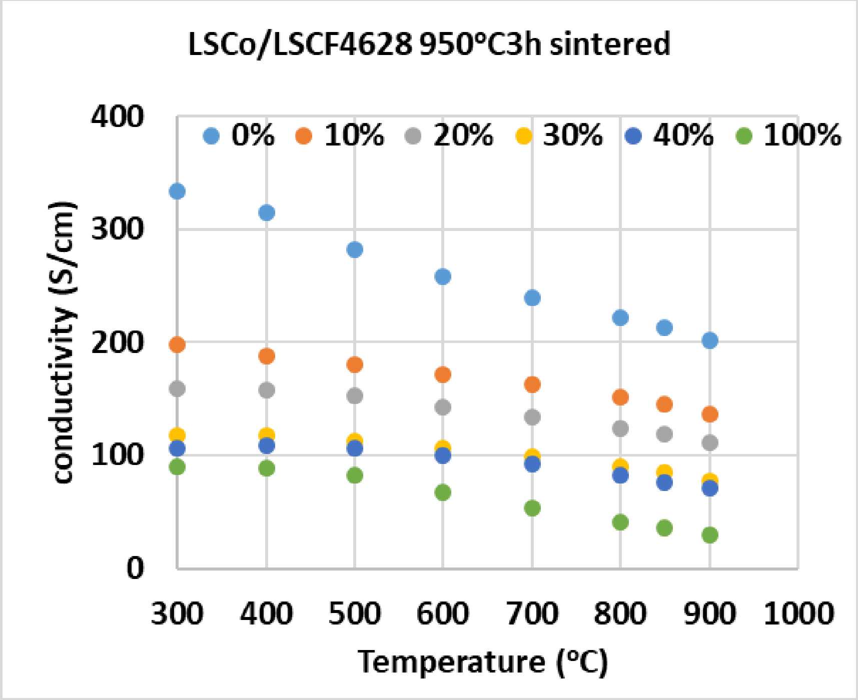
Sintering Curves

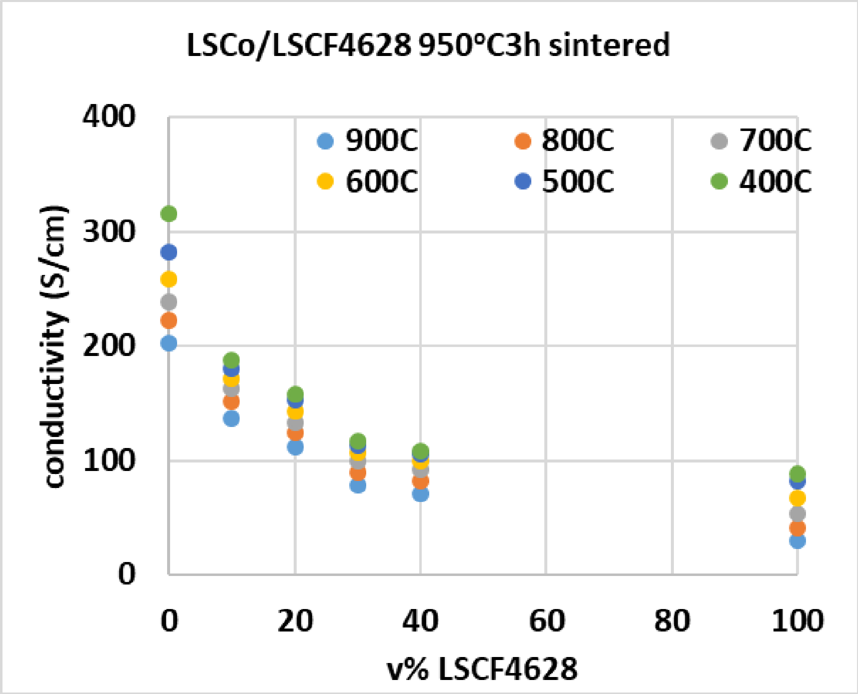


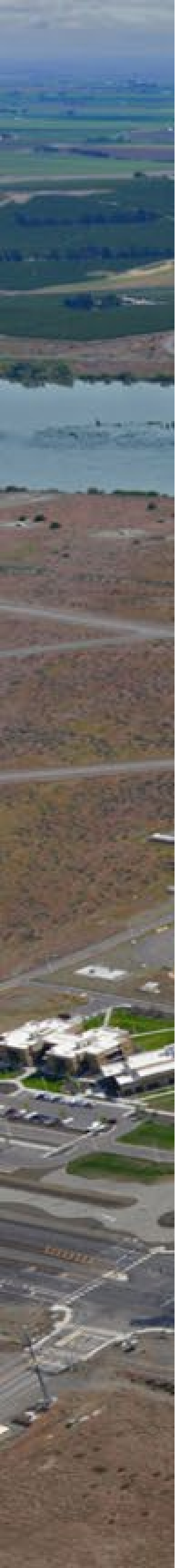
Thermal Expansion



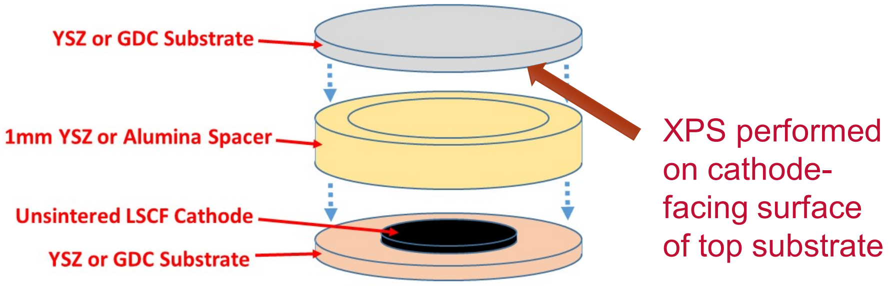
Electrical Conductivity





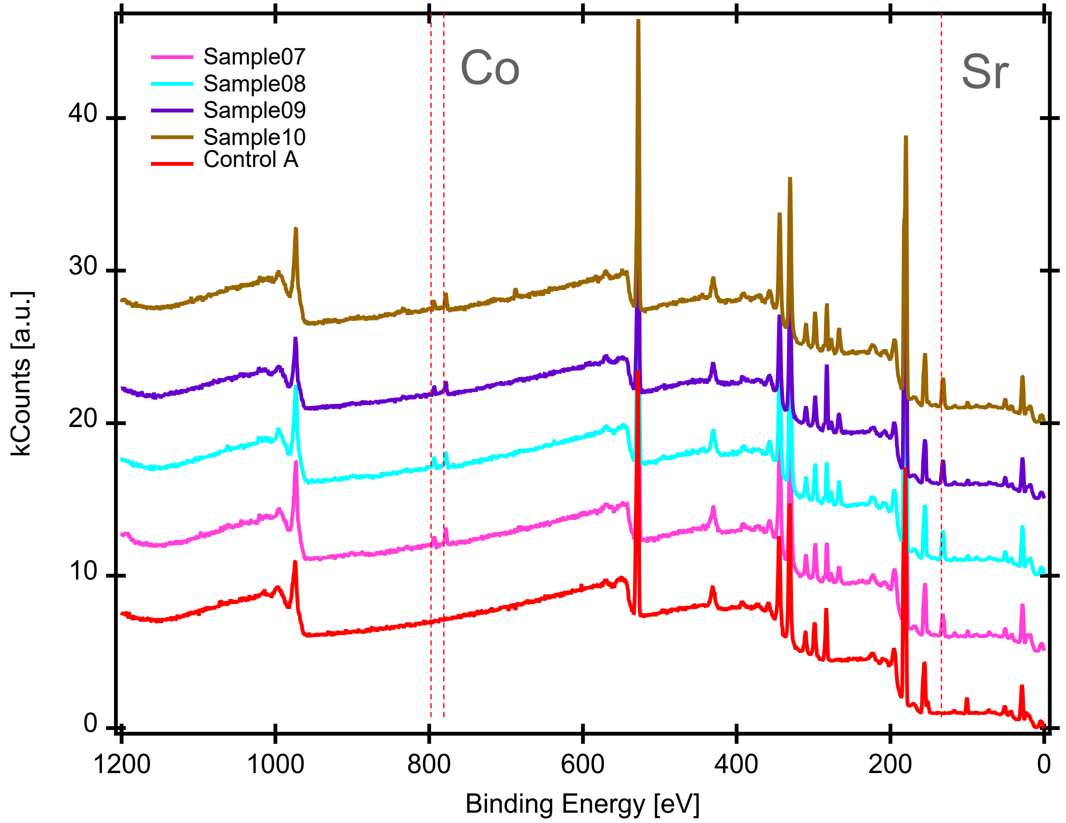


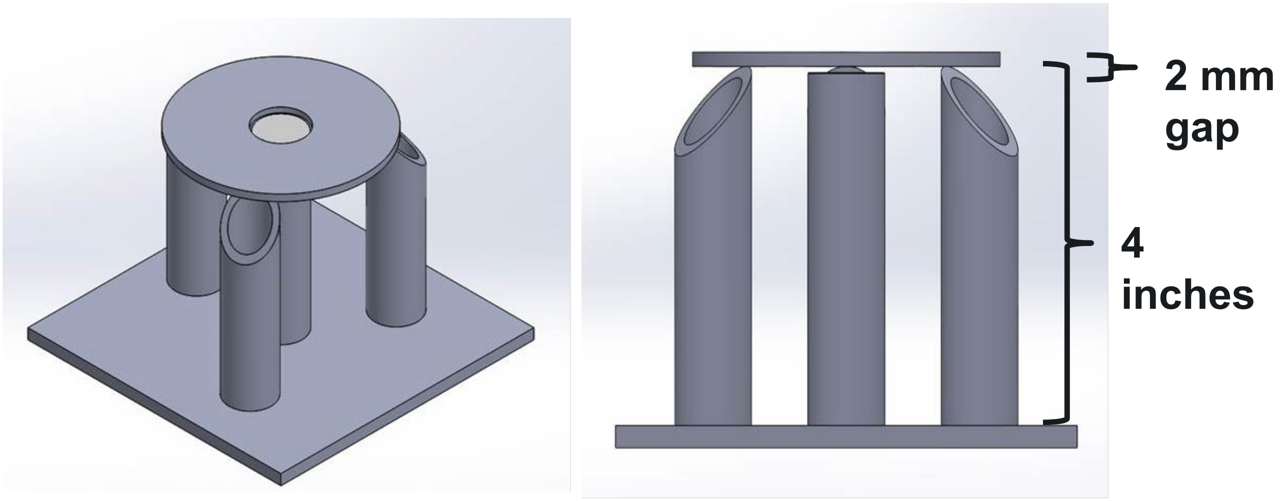
Vapor Transport of Species from LSCF Cathodes



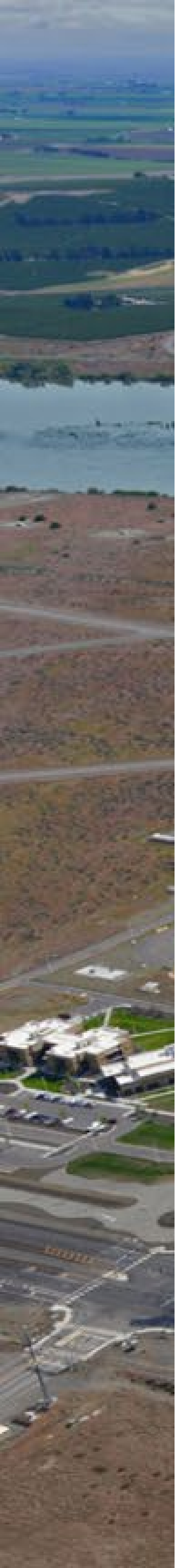
XPS performed on cathode-facing surface of top substrate

- Early tests configured as above indicated transport of Sr and Co





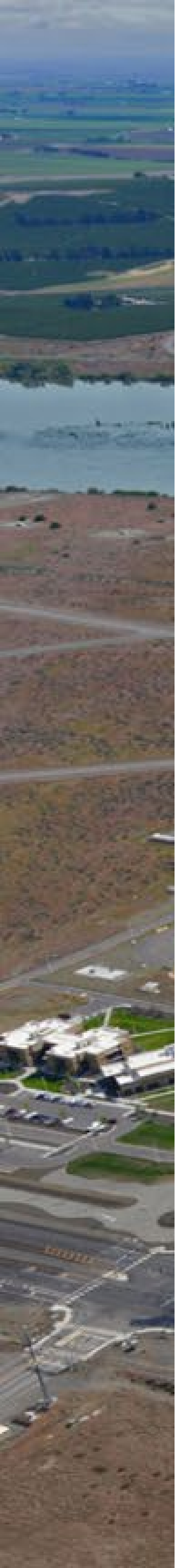
- Subsequent tests designed for long surface diffusion paths (above) between cathode material and substrate sink indicated no appreciable Sr and Co transport
- Open geometry may have limited the concentration of vapor phases, thus new fixture was designed with long surface paths and enclosed chamber
- Next tests are pending



Pacific Northwest
NATIONAL LABORATORY

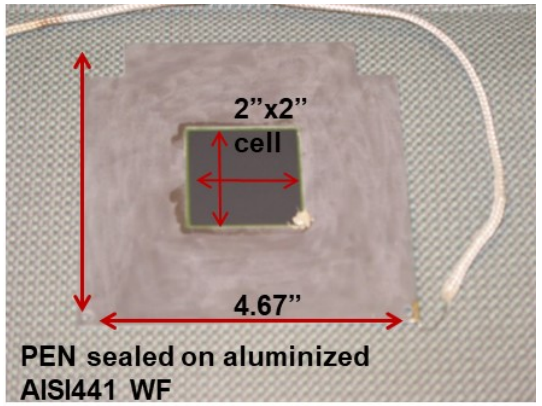
Cathode / Interconnect Contact Materials

- Challenge
  - Electrical contact materials at cathode / interconnect interfaces in planar stacks tend to be mechanical “weak link,” especially during thermal cycling, due to brittle nature of ceramic materials and/or thermal expansion mismatch with adjacent components
    - ✓ Low processing temperatures and constrained sintering conditions during stack fabrication lead to low intrinsic strength and low bonding strength of ceramic contact materials, especially at contact-to-cathode interface
    - ✓ Use of metallic contact materials limited by cost, volatility, and/or electromigration
- Approach
  - Use composite approach to develop ceramic-based contact materials having improved mechanical reliability by reducing thermal expansion mismatch and increasing contact strength/toughness

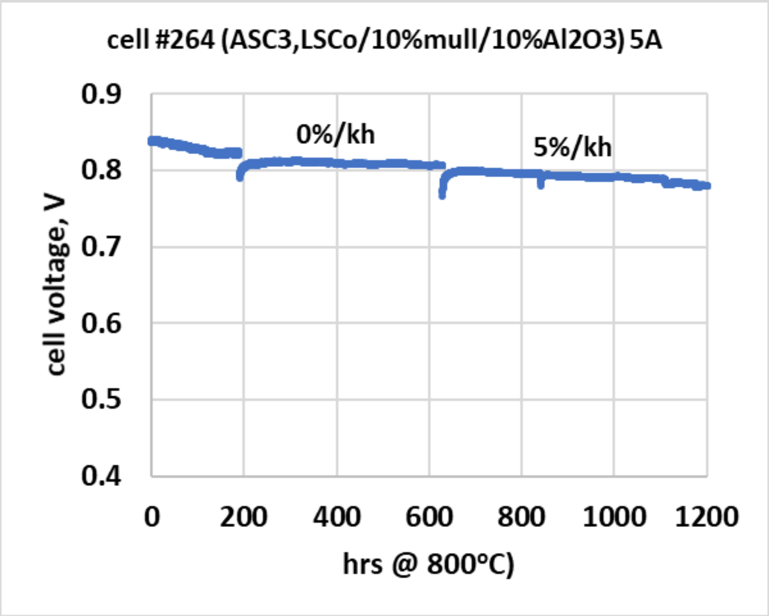


LSCo / mullite / fiber composite contact materials

- LSCo perovskite offers very high electrical conductivity but also has high CTE (~18x10^{-6}/^{o}C) as cathode contact one needs to overcome the large residual stresses by:
- Reduce thermal stresses by adding low CTE phase - mullite (~5.4x10^{-6}/^{o}C)
- Enhance the strength/toughness by reinforcement with strong short Al_2O_3 fibers with high elastic modulus



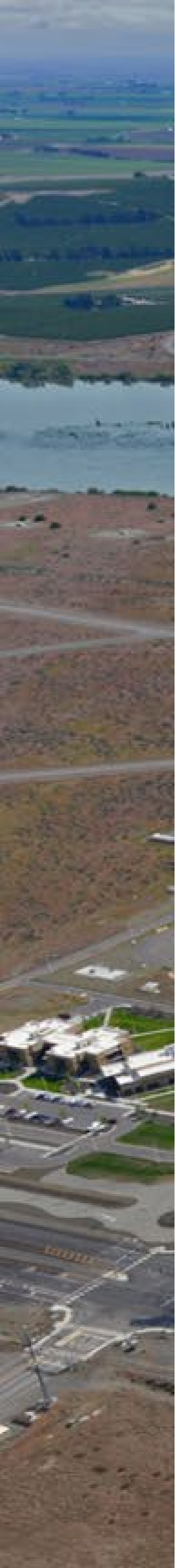
Validation Testing



Issues encountered with LSCo/mullite approach

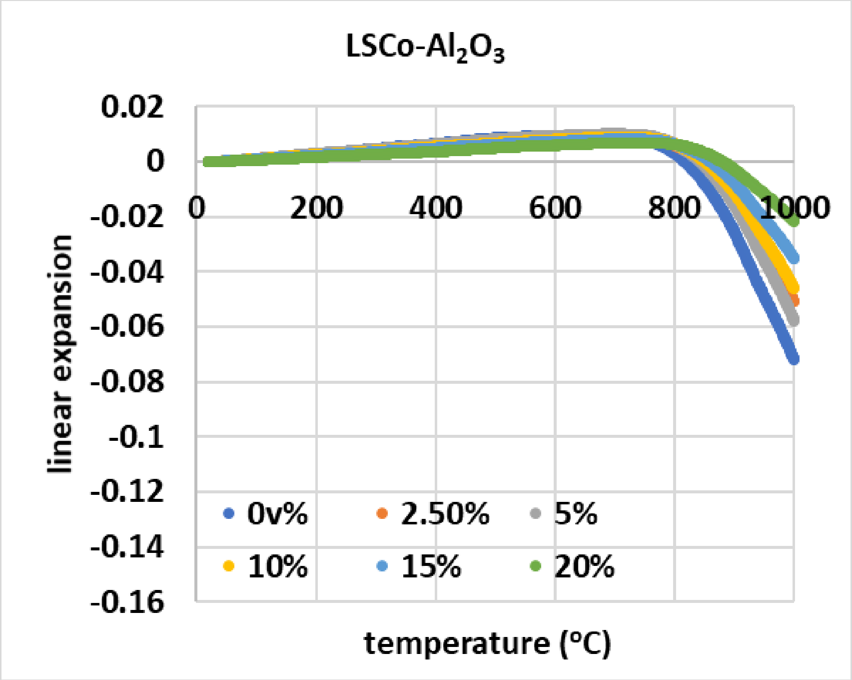
- Needs very high vol. fraction (~0.4) to match CTE in 12-13x10^{-6}/^{o}C
- Poor densification by sintering with rigid inclusions
- Poor strength with mullite at high volume fractions
- Poor conductivity with mullite at high volume fractions
- Potential contamination by Si in presence of moisture?
- Adding 5-10v% Al_2O_3 improved strength and thermal cycle stability

Therefore investigating LSCo/Alumina Fiber composites

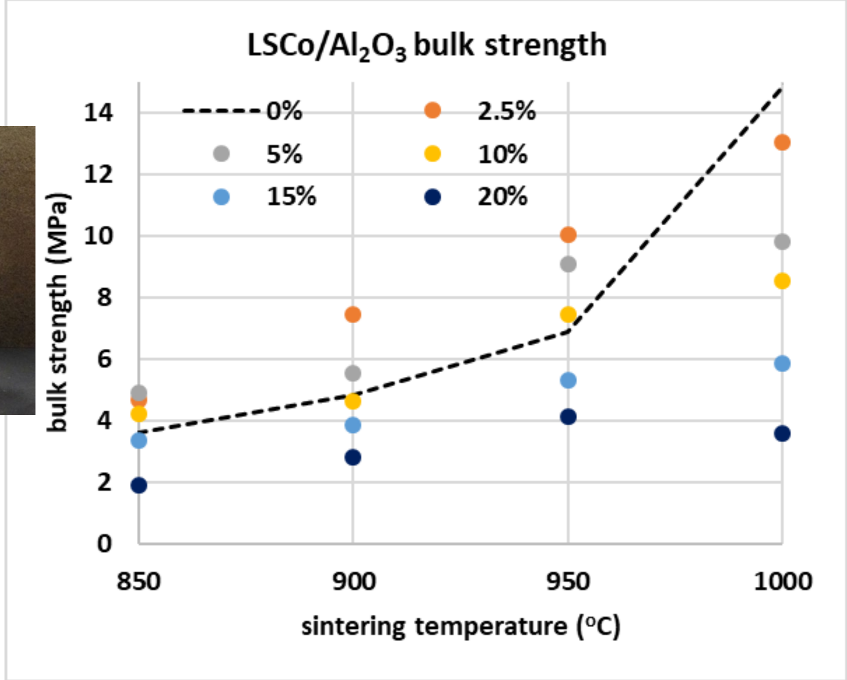


LSCo/Al_2O_3 fiber composite contact materials characterization

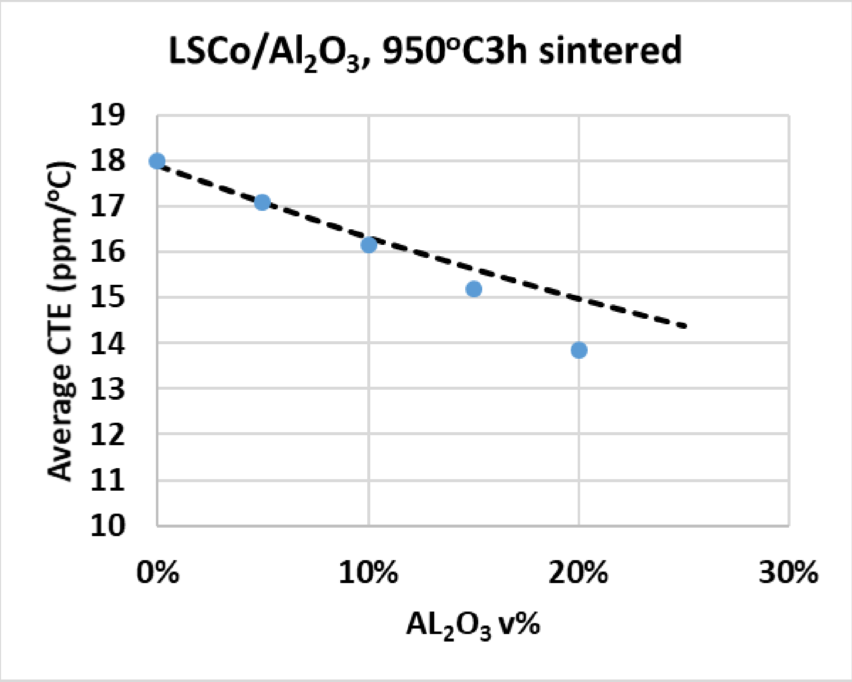
Sintering Study



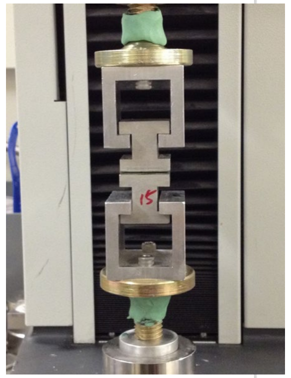
Bulk Strength

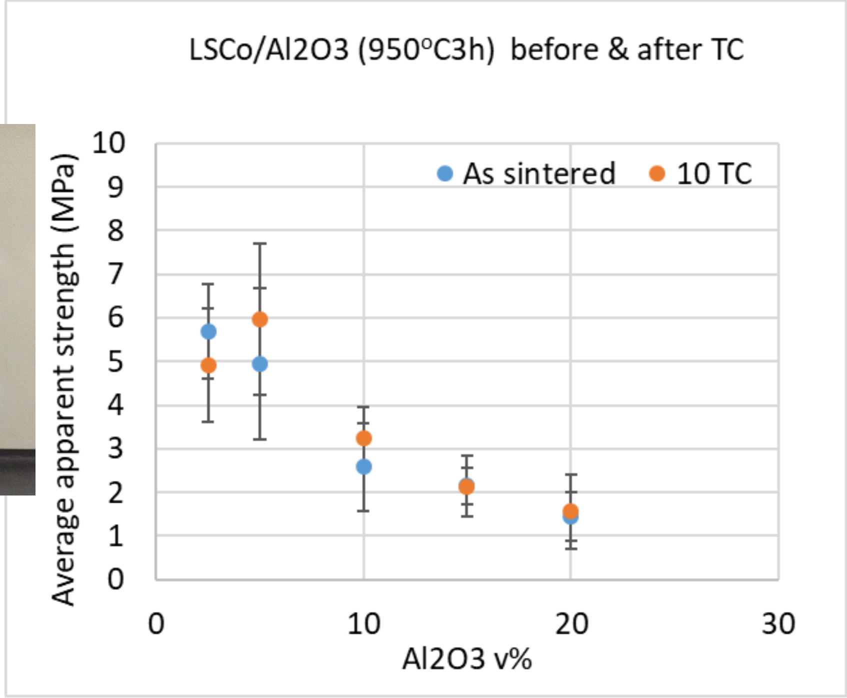


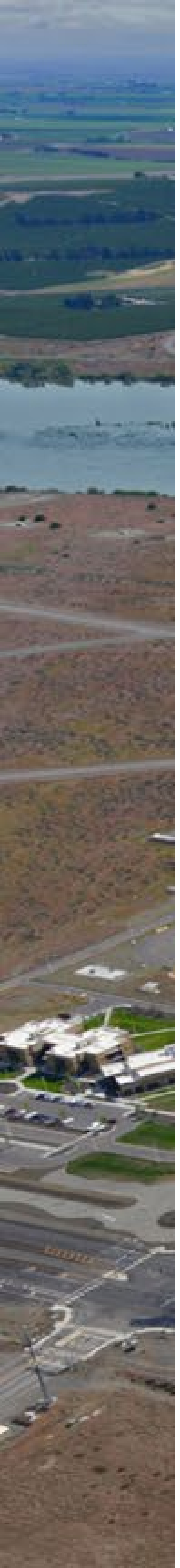
Thermal Expansion



Contact Strength

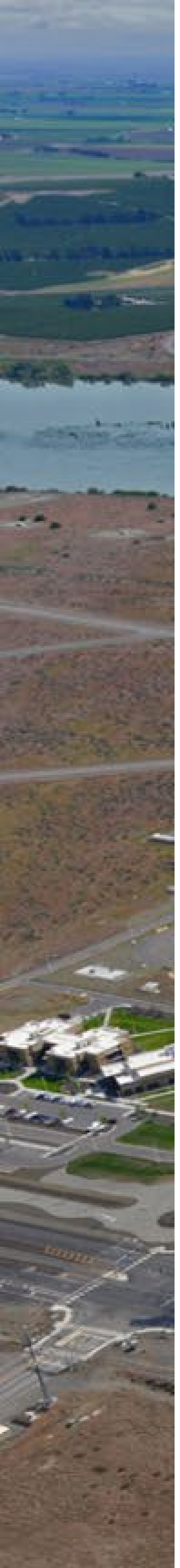






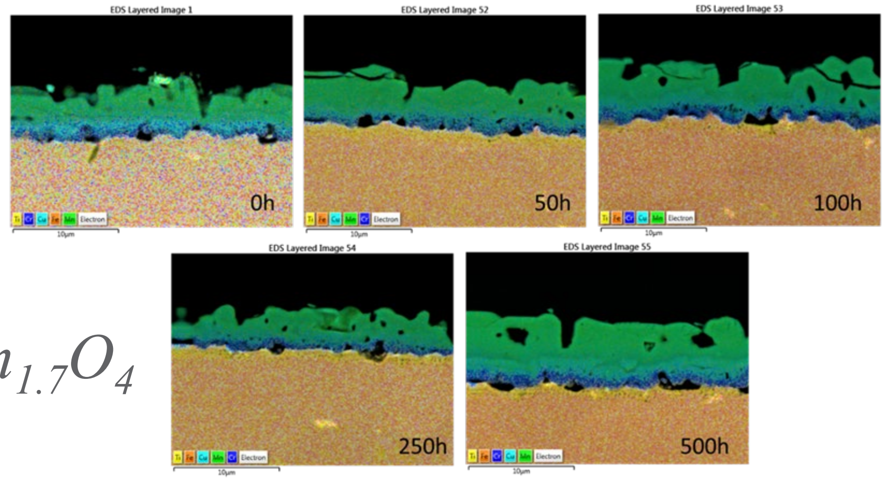
Interconnect / BOP Coatings

- Challenges
  - Metallic interconnects susceptible to oxidation (leading to high electrical resistance), Cr volatilization (leading to Cr poisoning), and reactions with seals (leading to mechanical failure)
  - Other metallic components susceptible to Cr volatilization
- Approaches
  - Electrically conductive Mn-Co spinel coatings exhibit good performance; due to possible issues with Co cost and availability, developing Co-free alternatives
    - Cu-Mn-O; Ni-Mn-O; Cu-Fe-O
  - Reactive air aluminization for applications that don’t require electrical conductivity
    - Simple slurry-based process
    - Fabrication in air at temperatures as low as 900°C

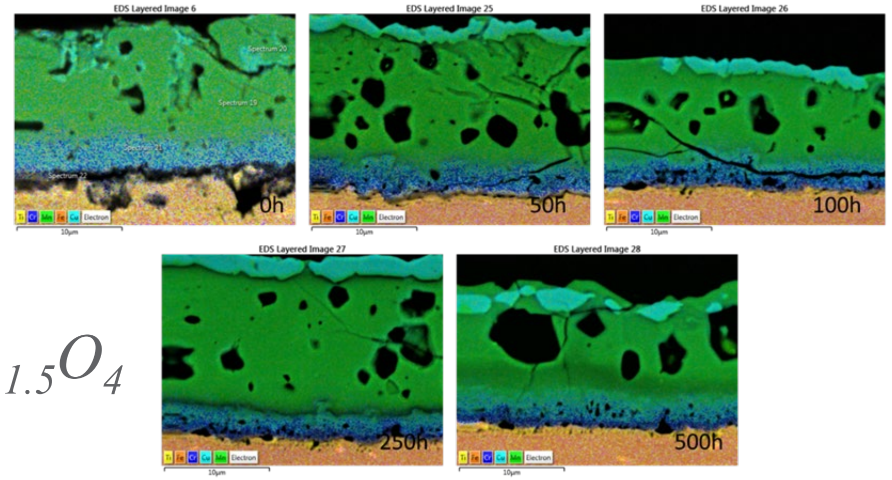


Pacific Northwest
NATIONAL LABORATORY

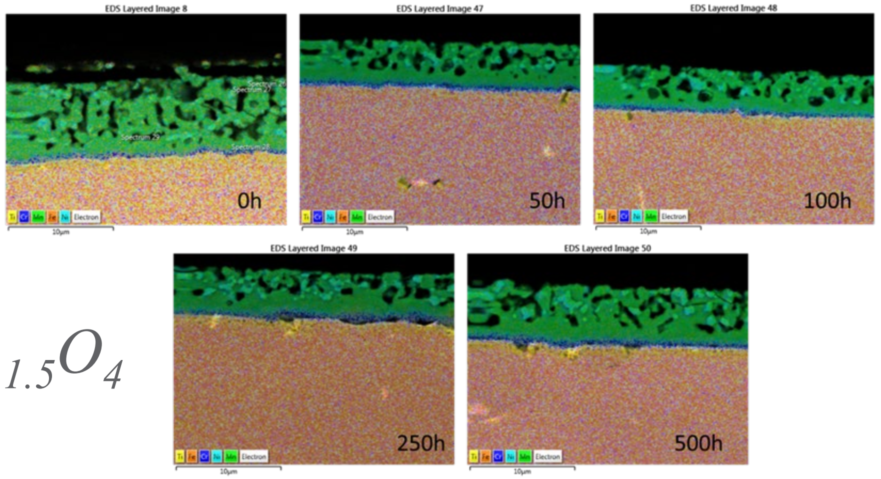
Co-free Electrically Conductive Protective Coatings



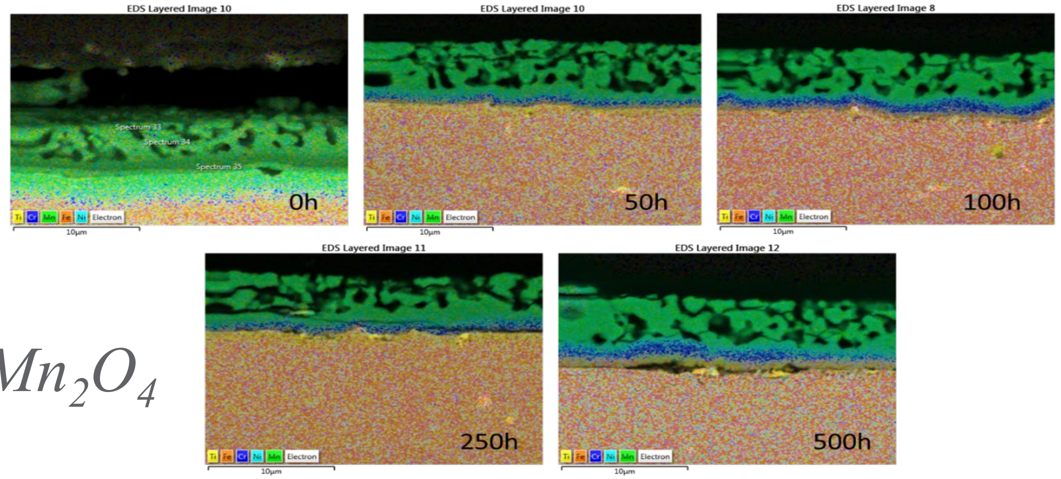
$Cu_{1.3}Mn_{1.7}O_4$



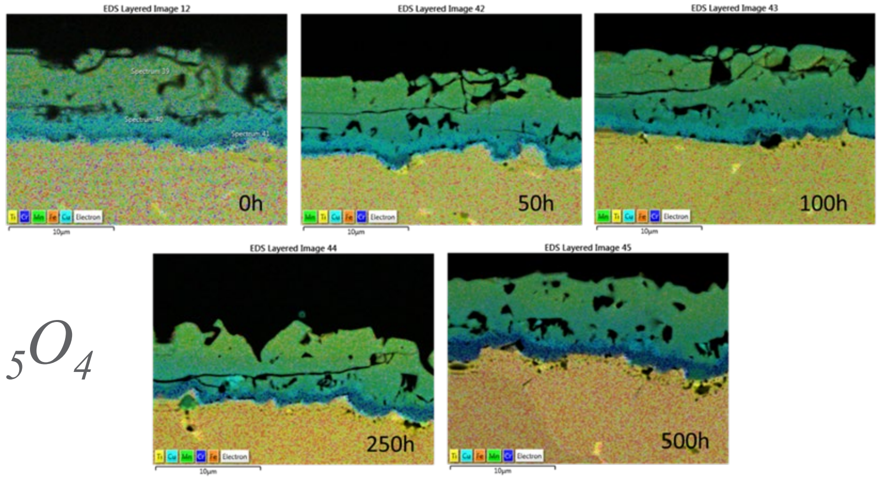
$Cu_{1.5}Mn_{1.5}O_4$



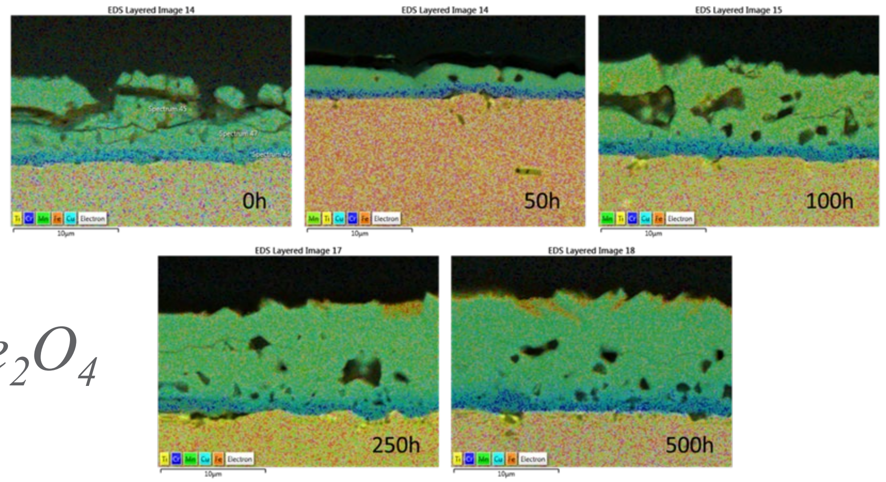
$Ni_{1.5}Mn_{1.5}O_4$



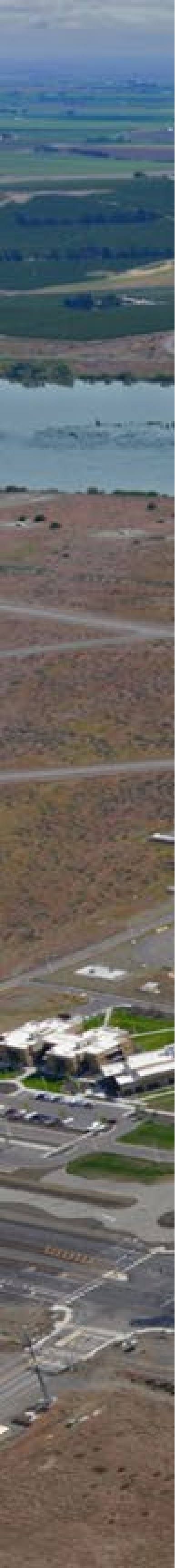
$NiMn_2O_4$



$Cu_{1.5}Fe_{1.5}O_4$



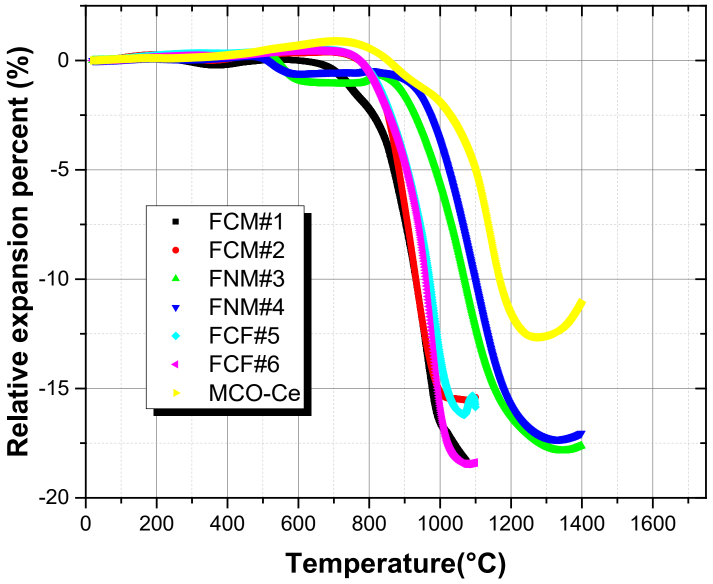
$CuFe_2O_4$



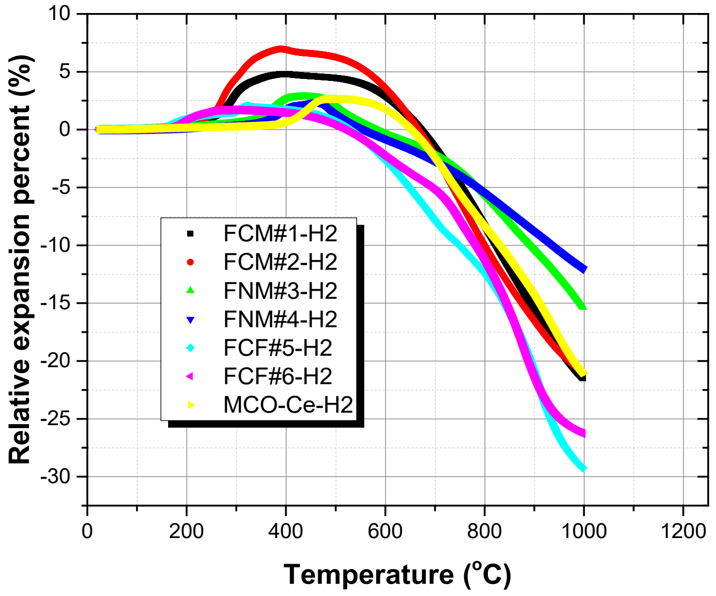
Co-free Electrically Conductive Protective Coatings

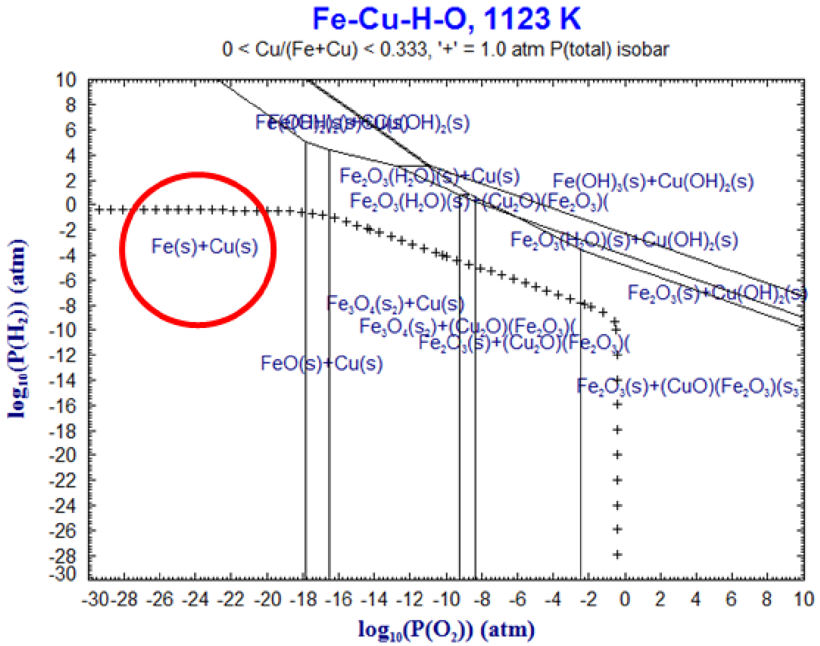
Sintering Study

In air



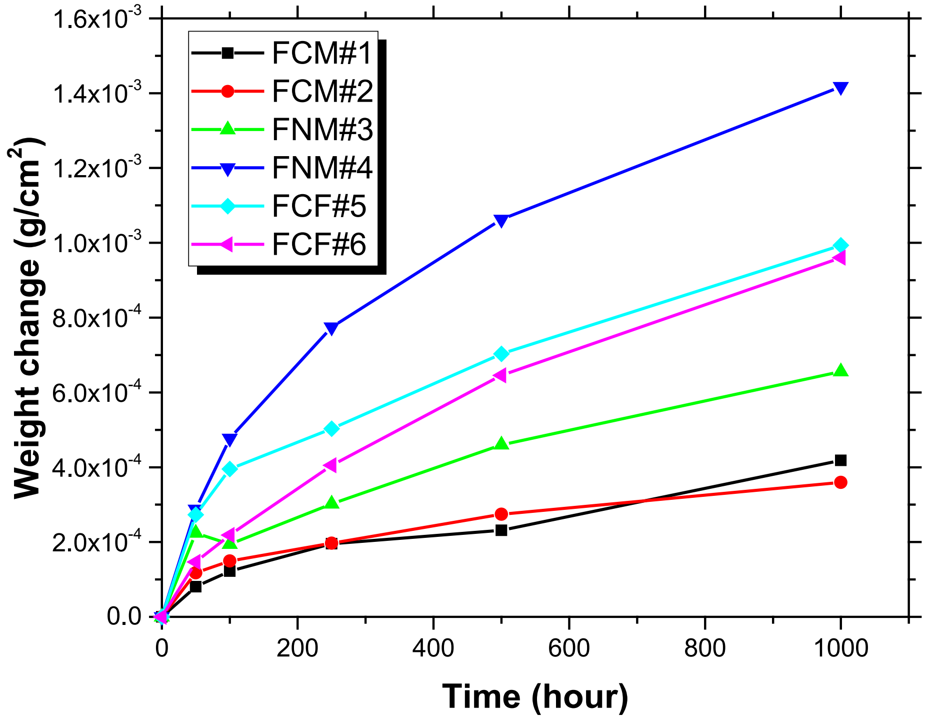
In hydrogen



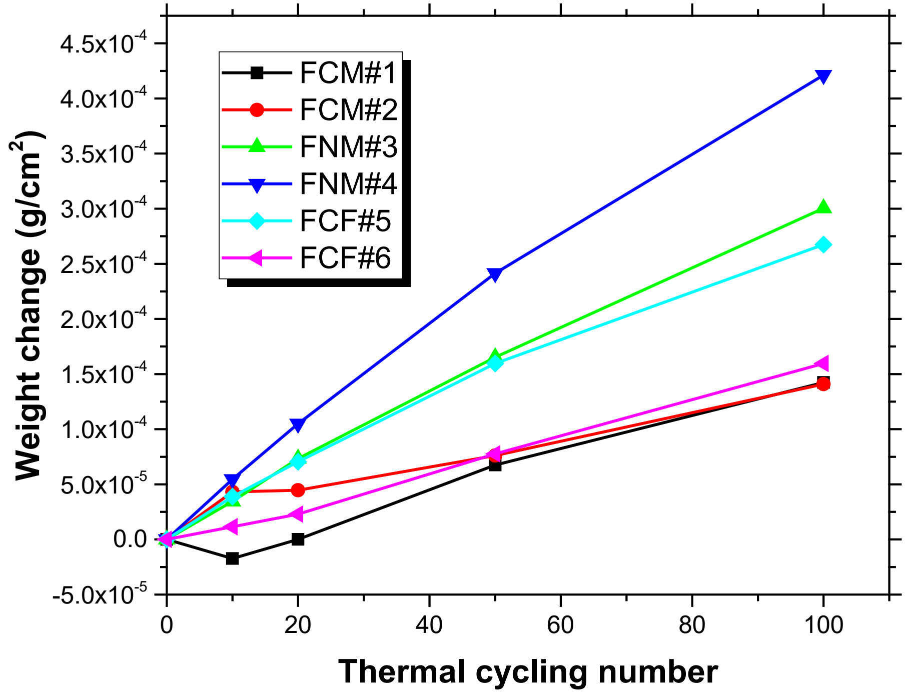


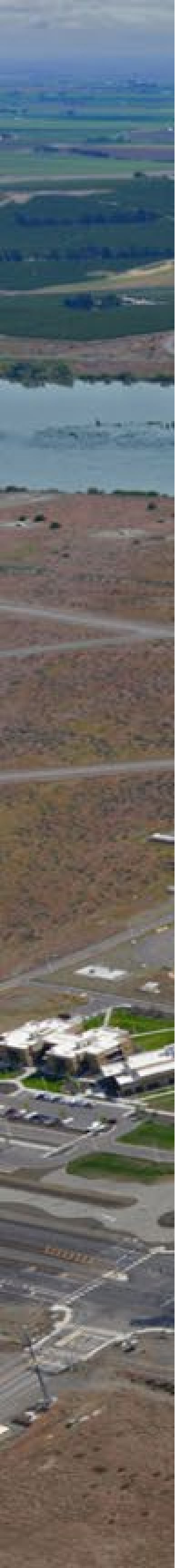
Oxidation Study

Isothermal



Thermal Cycling

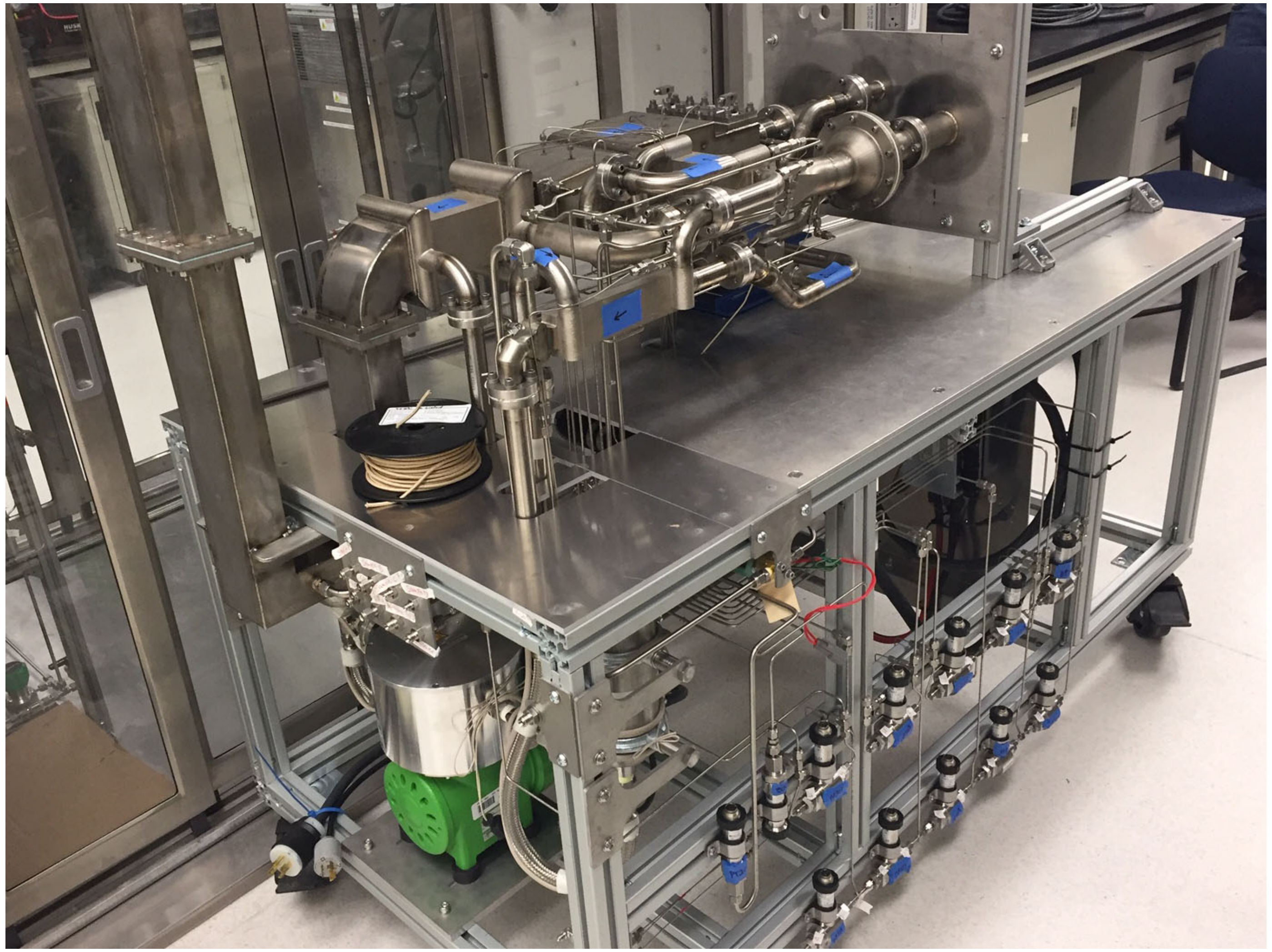




Designed & Built Small-Scale SOFC Test Platform

- Purpose:
  - Evaluate performance and reliability of emerging stack technologies (2-10 kW) under realistic operating conditions

- Test capabilities:
  - Steam-reformed methane
  - Steady-state isothermal tests
    - ✓ Variables: temperature, current, voltage, fuel
  - Thermal cycling
  - E-stop cycles (redox tolerance)
  - Variable anode recycle rates

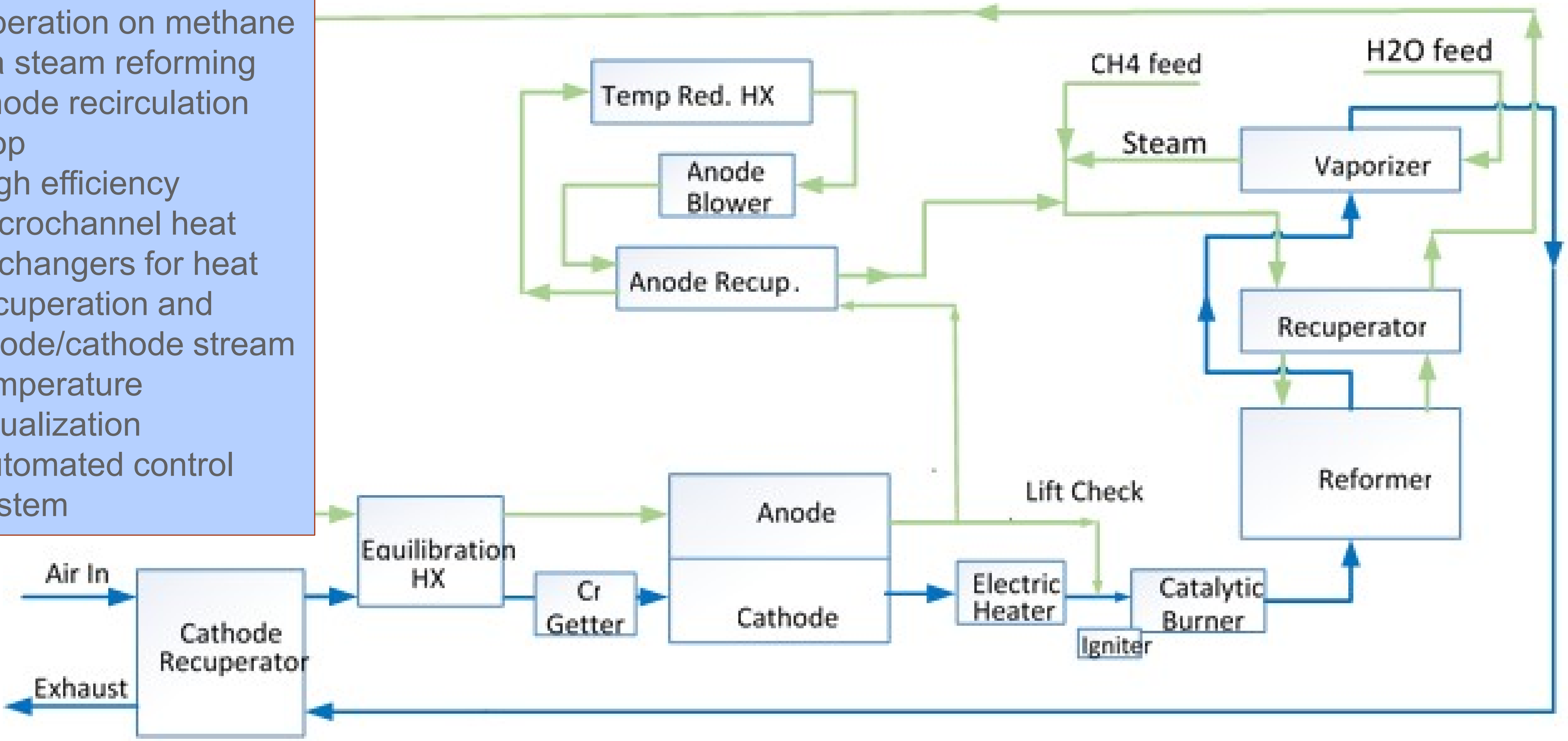


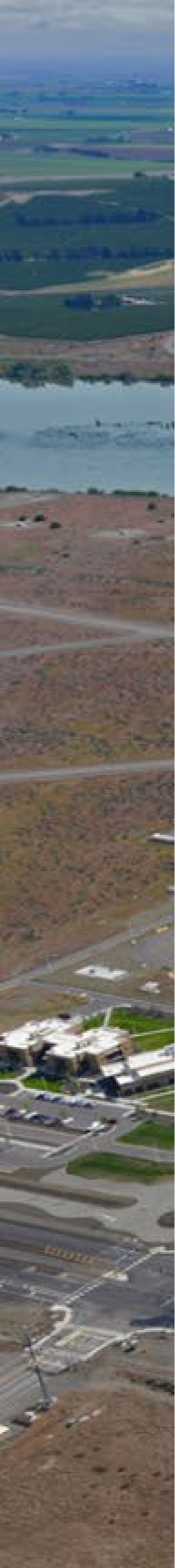
- Validated the test platform in 500 hour test on reformed methane with 40% anode recycling – operated a 3.7 kW stack at 62% gross LHV efficiency
- Thereafter, various recycle rates were tested for effects on efficiency

Small-Scale SOFC Test Platform

Key features:

- Operation on methane via steam reforming
- Anode recirculation loop
- High efficiency microchannel heat exchangers for heat recuperation and anode/cathode stream temperature equalization
- Automated control system





Overview: Stack Modeling Tools

Technical Challenge

- SOFC stacks must be designed for high *electrochemical performance* and *mechanical reliability*

Modeling Objective

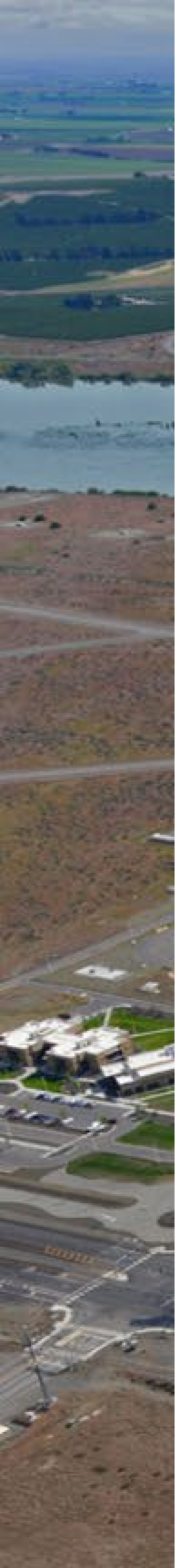
- Develop numerical modeling tools to aid the industry teams' design and engineering efforts at the *cell/stack scale*

Technical Approach

- **SOFC-MP 2D** – Analysis of electrochemical and thermal performance of tall symmetric stacks
- **SOFC-MP 3D** - Detailed 3D multi-cell stack structures for electrochemical, thermal, and stress analyses
- **SOFC-ROM** – Reduced order models (ROMs) of SOFC stacks for use in system modeling analyses
- **GUI** – Common interface for the modeling tools with pre-processing and post-processing capabilities

Recent Accomplishments

- Implemented high-pressure operation in SOFC-MP
- Developed complete ROM generation tool
- Improved ROM exhaust species predictions through use of DNN and data normalization techniques
- Demonstrated dual mode degradation for prediction of end-of-life (EOL) performance
- Demonstration of SOFC tools for electrolysis mode

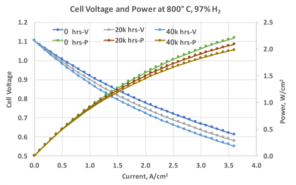


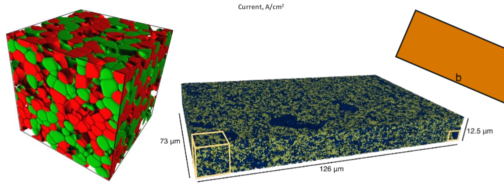
Program Modeling Objective:
Linking Models Across Different Length Scales

- Recent modeling activity has focused on ***linking model results across length scales***
  - Utilize a ***Reduced Order Model (ROM)*** approach to improve the accuracy of power system models

Micro/Meso-Scale Models

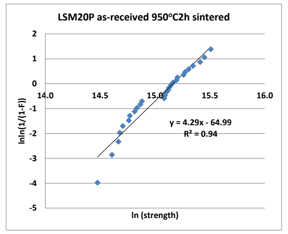
I-V Performance



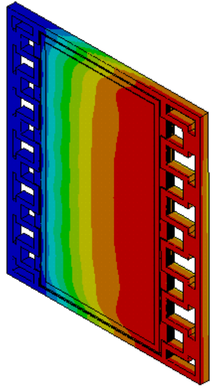


Cell Material Testing

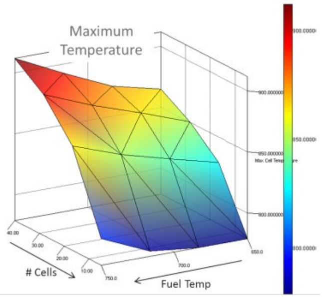
Property Data



Cell/Stack Models

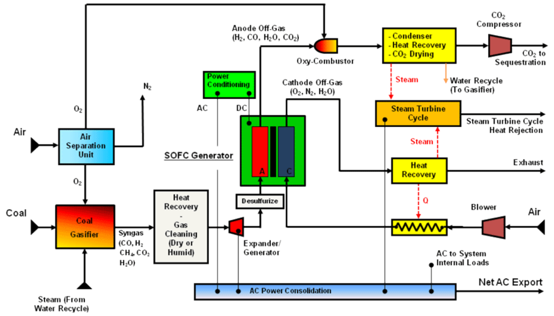


Response Surface Analysis

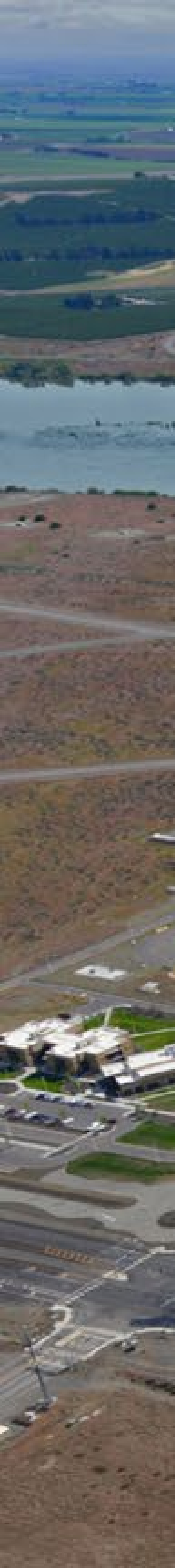


Performance:
Electrical
Thermal
Mechanical

System Models



Reduced Order Model (ROM)



Pacific Northwest
NATIONAL LABORATORY

Overview: Reduced Order Model (ROM)

Technical Challenge

- SOFC systems must be designed for high *efficiency* and low *capital costs*

Modeling Objective

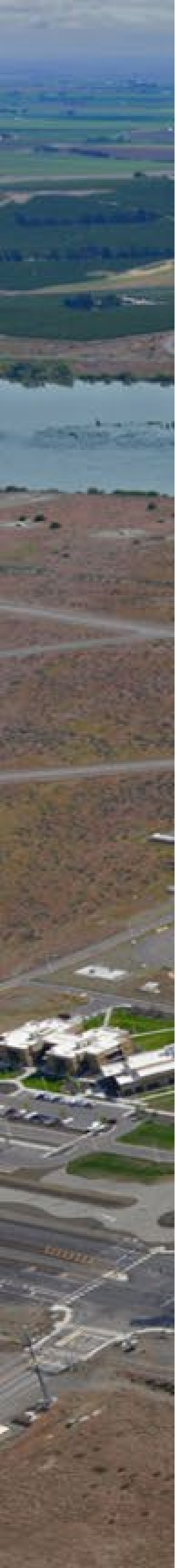
- Improve accuracy and capability of *SOFC systems analyses* used for design and *cost of energy* (COE) predictions

Technical Approach

- Integrate the PNNL SOFC-MP 2D model into NETL's system model as a *reduced-order model* (ROM)
  - Develop ROM that improves accuracy of the SOA SOFC analysis with reduced computational time and complexity
- Investigate machine learning (ML) approaches to *improve accuracy* and sensitivity of generated ROMs

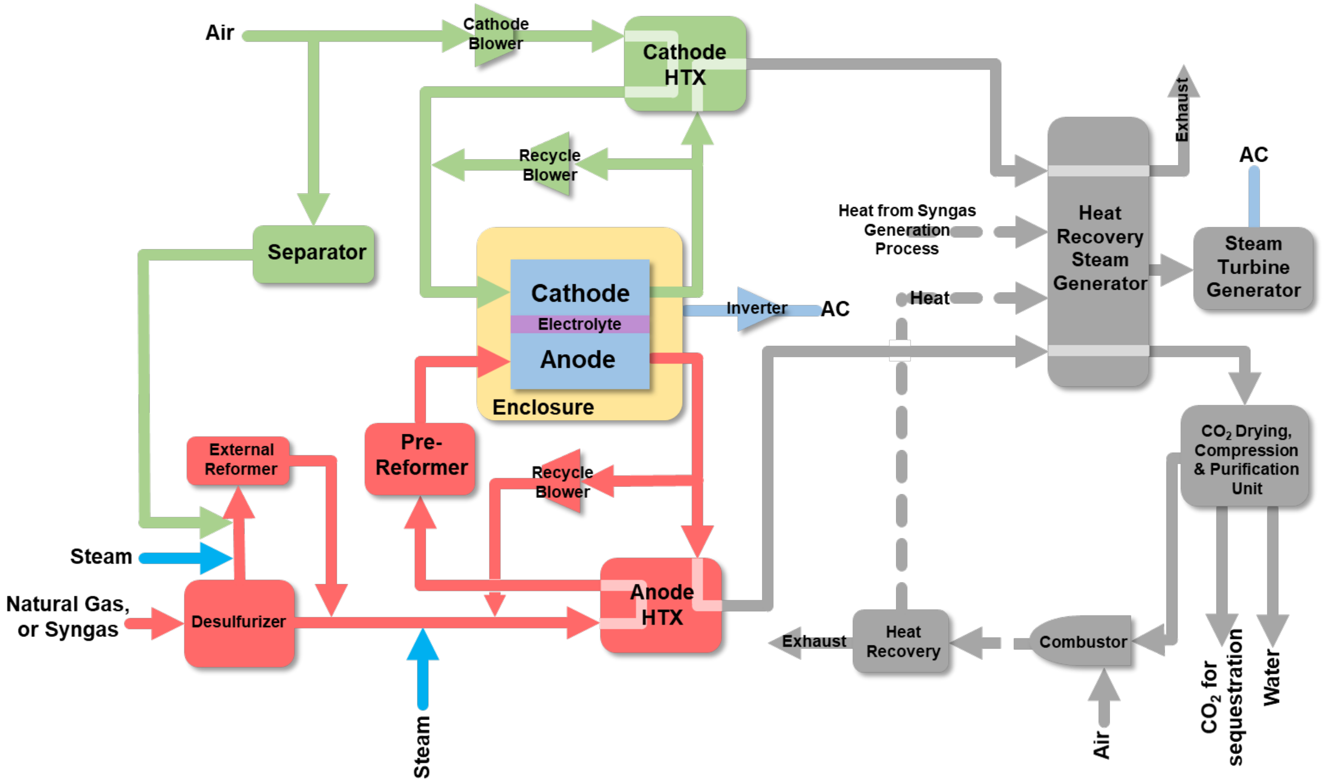
Recent Accomplishments

- Delivered numerous ROMs for different power system architectures to NETL collaborators
- Developed automated ROM construction tool and GUI to support local and remote solution on HPC cluster
  - Included error quantification for 95% confidence interval and sampling tool for high-dimensional parameter space
- Used machine learning methods to improve the prediction accuracy of stack exhaust species composition and classify case results
- Reviewed SOA electrochemical performance



ROM Generation

- General process diagram for NGFC or IGFC power system
- Evaluated stack performance and thermal gradient for wide range of potential operating conditions
- Provided NETL collaborators with 27 ROMs for various configurations to support pathway studies
  - NGFC
  - IGFC (conventional, enhanced, catalytic)
  - SOA and future stack performance
  - System w/ or w/o carbon capture
  - System w/ or w/o vent gas recirculation concept



Input parameters	Range
Average current density (A/m^2)	2000-6000
Fuel temperature (C)	15-600
Internal reforming (NA) *	0-1
Oxidant temperature (C)	550-800
Oxidant recirculation (NA)	0-0.8
Oxygen to carbon ratio (NA)	1.5-3
Stack fuel utilization (NA)	0.4-0.95
Stack oxidant utilization (NA)	0.0833-0.833
System pressure (ATM)	1-5
VGR temperature (C) **	15-204
VGR rate (NA) **	0.3-0.97

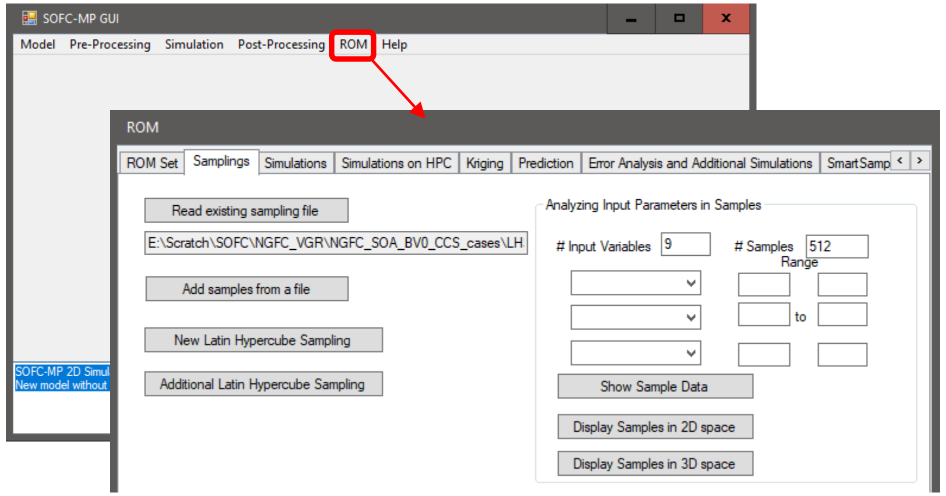
* Only available in NGFC
** Only available in VGR

Pacific Northwest
NATIONAL LABORATORY

ROM Graphical User Interface (GUI)

- Created a graphical user interface (GUI) and manual to allow a general user to more easily create a ROM using SOFC-MP stack results

1. Sampling

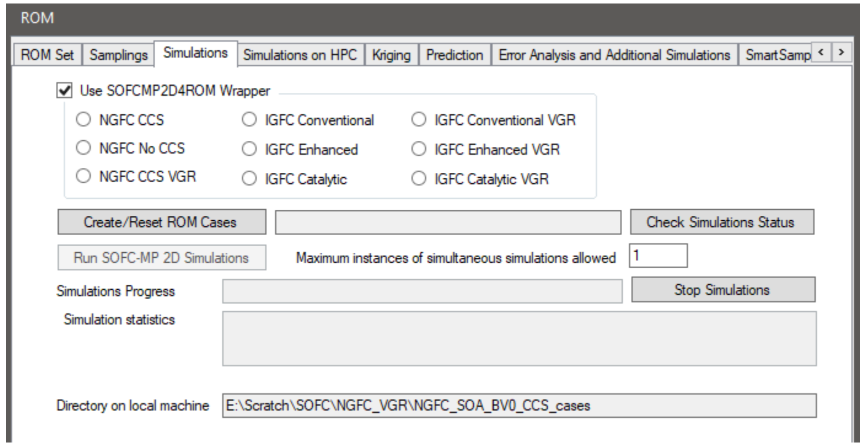


E:\Scratch\SOFC\NGFC_VGR\NGFC_SOA_BV0_CCS_cases\LH

Input Variables 9

Samples 512

2. Create Cases and Solve

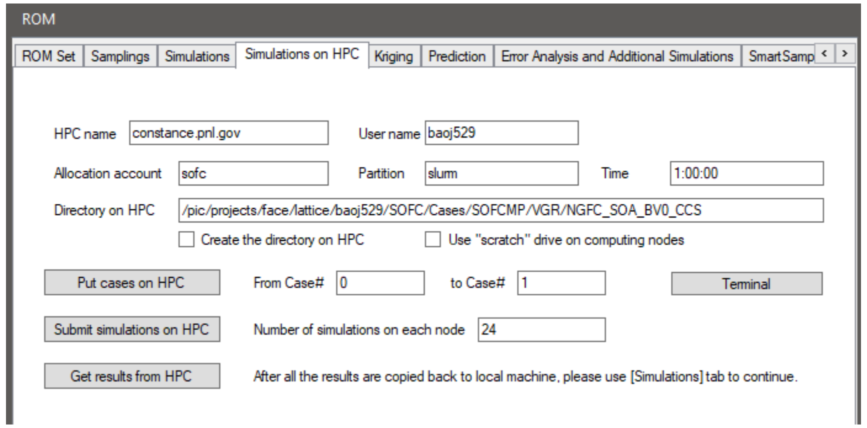


☑ Use SOFCMP2D4ROM Wrapper

○ NGFC CCS ○ IGFC Conventional ○ IGFC Conventional VGR
○ NGFC No CCS ○ IGFC Enhanced ○ IGFC Enhanced VGR
○ NGFC CCS VGR ○ IGFC Catalytic ○ IGFC Catalytic VGR

Maximum instances of simultaneous simulations allowed 1

Directory on local machine E:\Scratch\SOFC\NGFC_VGR\NGFC_SOA_BV0_CCS_cases



HPC name constance.pnl.gov

User name baoj529

Allocation account sofc

Partition slurm

Time 1:00:00

Directory on HPC /pic/projects/face/lattice/baoj529/SOFC/Cases/SOFCMP/VGR/NGFC_SOA_BV0_CCS

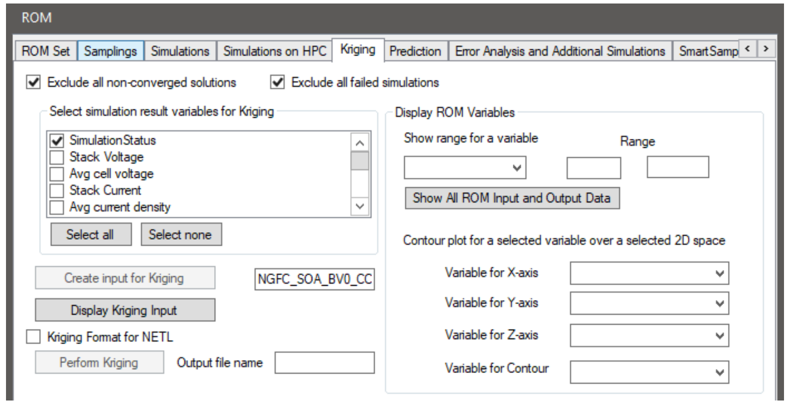
☐ Create the directory on HPC ☐ Use "scratch" drive on computing nodes

From Case# 0 to Case# 1

Number of simulations on each node 24

After all the results are copied back to local machine, please use [Simulations] tab to continue.

3. Build Kriging ROM



☑ Exclude all non-converged solutions ☑ Exclude all failed simulations

Select simulation result variables for Kriging

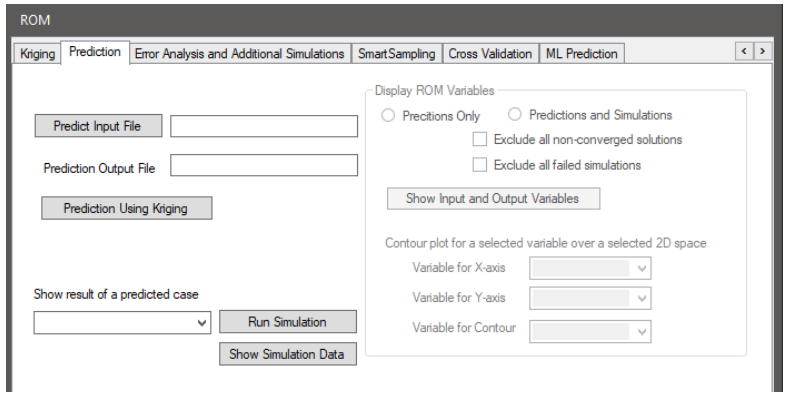
☑ SimulationStatus
☐ Stack Voltage
☐ Avg cell voltage
☐ Stack Current
☐ Avg current density

NGFC_SOA_BV0_CC

☐ Kriging Format for NETL

Output file name

4. ROM Prediction

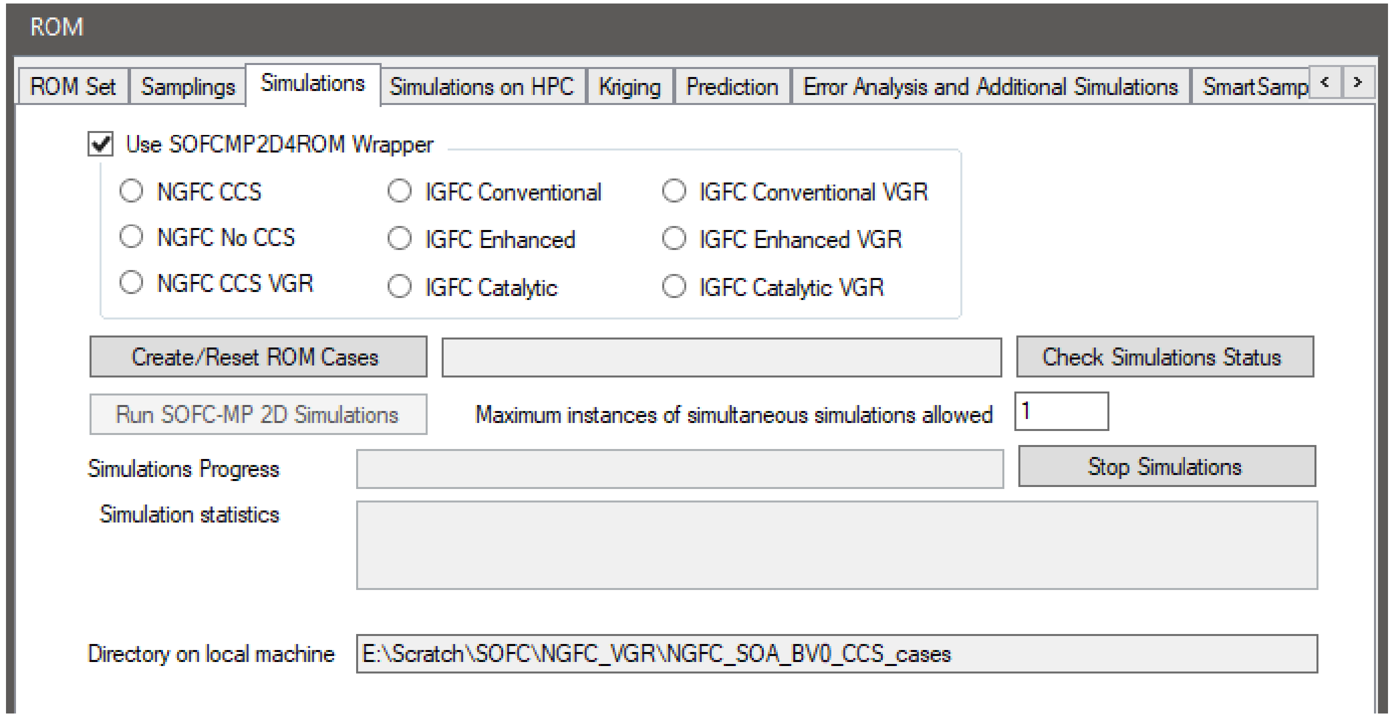


○ Precitions Only ○ Predictions and Simulations

☐ Exclude all non-converged solutions
☐ Exclude all failed simulations

ROM GUI Features

- Simplified creation of ROMs for different NGFC and IGFC system configurations w/ or w/o carbon capture and storage (CCS) and vent gas recirculation (VGR) options
- Smart sampling of more cases in regions of high mean square error
    - Local solution on PC
    - Remote solution on high performance computer (HPC)
- Cross validation of results to determine confidence interval of prediction
- Deep neural network (DNN) prediction option in addition to the standard Kriging prediction



☑ Use SOFCMP2D4ROM Wrapper

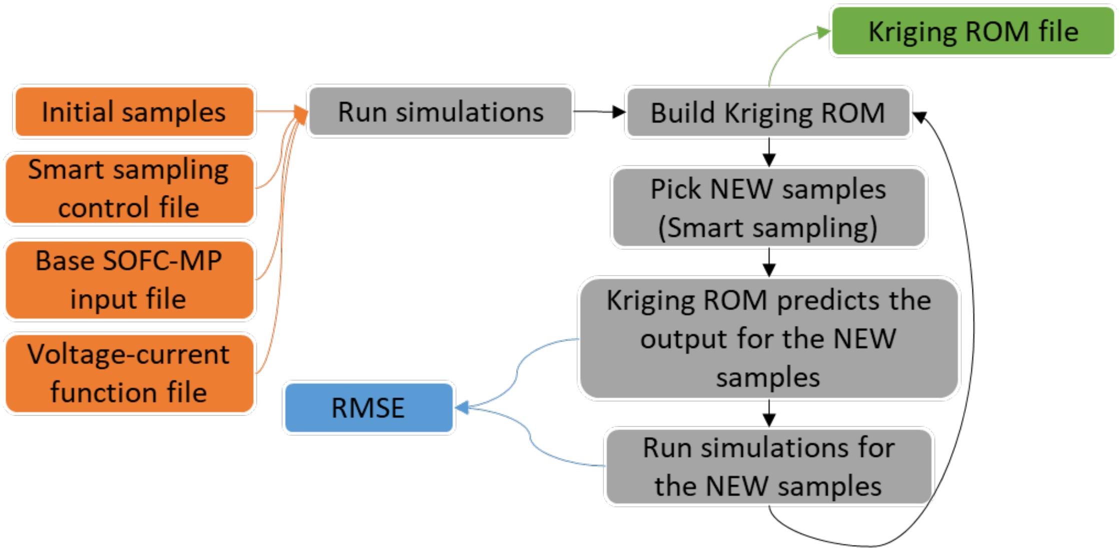
○ NGFC CCS
○ NGFC No CCS
○ NGFC CCS VGR
○ IGFC Conventional
○ IGFC Enhanced
○ IGFC Catalytic
○ IGFC Conventional VGR
○ IGFC Enhanced VGR
○ IGFC Catalytic VGR

Maximum instances of simultaneous simulations allowed: 1

Simulations Progress

Simulation statistics

Directory on local machine: E:\Scratch\SOFC\NGFC_VGR\NGFC_SOA_BV0_CCS_cases



Kriging ROM file

Initial samples

Smart sampling control file

Base SOFC-MP input file

Voltage-current function file

Run simulations

Build Kriging ROM

Pick NEW samples (Smart sampling)

Kriging ROM predicts the output for the NEW samples

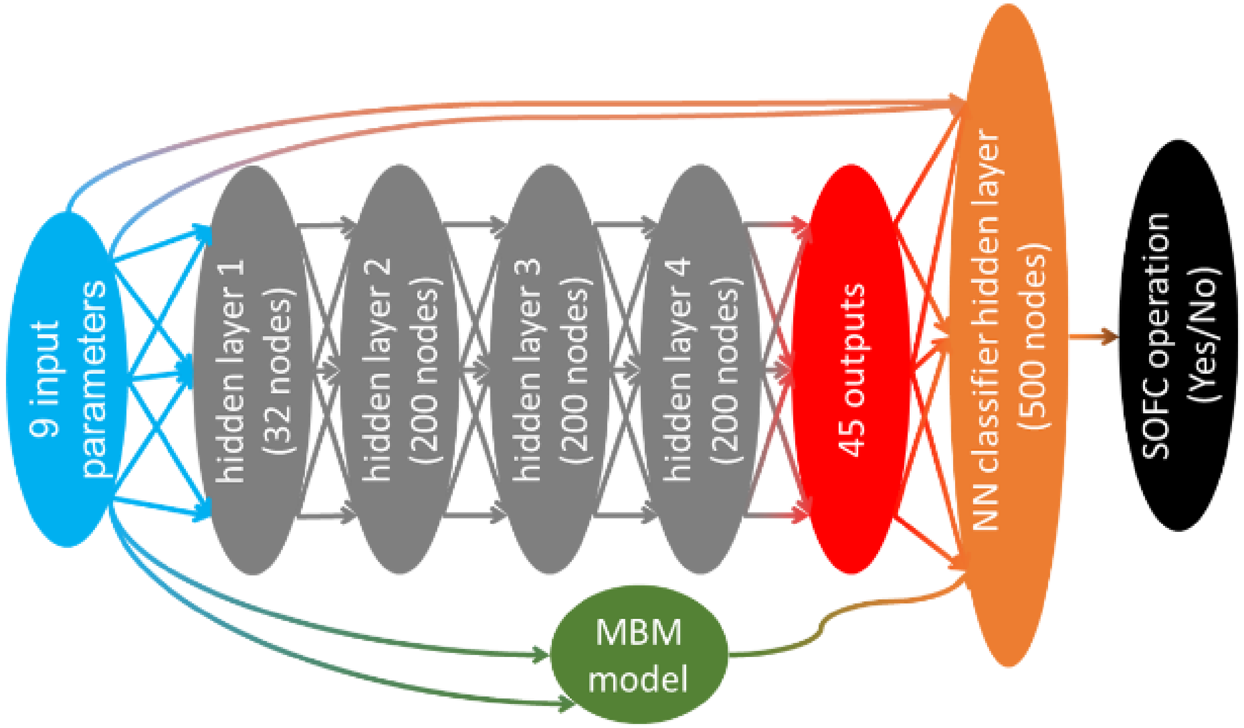
Run simulations for the NEW samples

RMSE

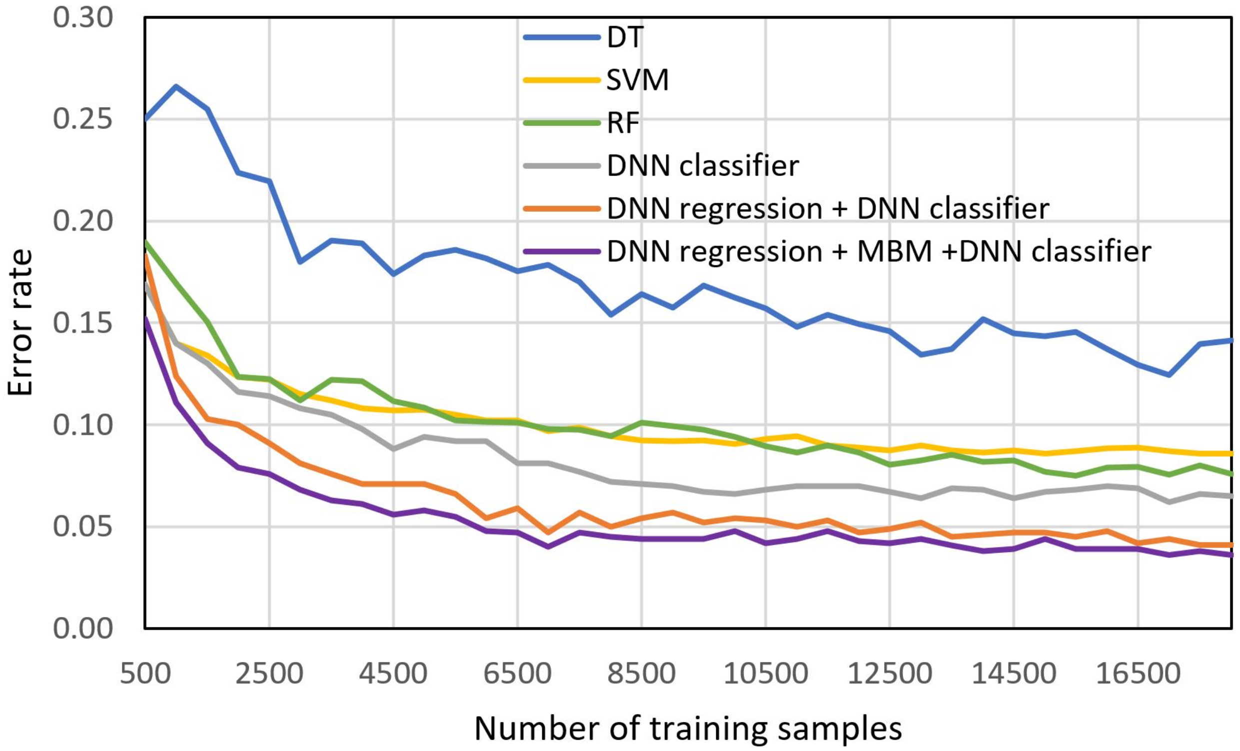
ROM w/ Machine Learning: Result Classification

- Not all input parameter combinations are physically viable for the system
  - Developed classifier network to identify physically operational cases
  - Deep neural network (DNN) regression + DNN classifier + mass balance model (MBM) to improve prediction accuracy and reduce RMS error by 2-3X

Classification Network



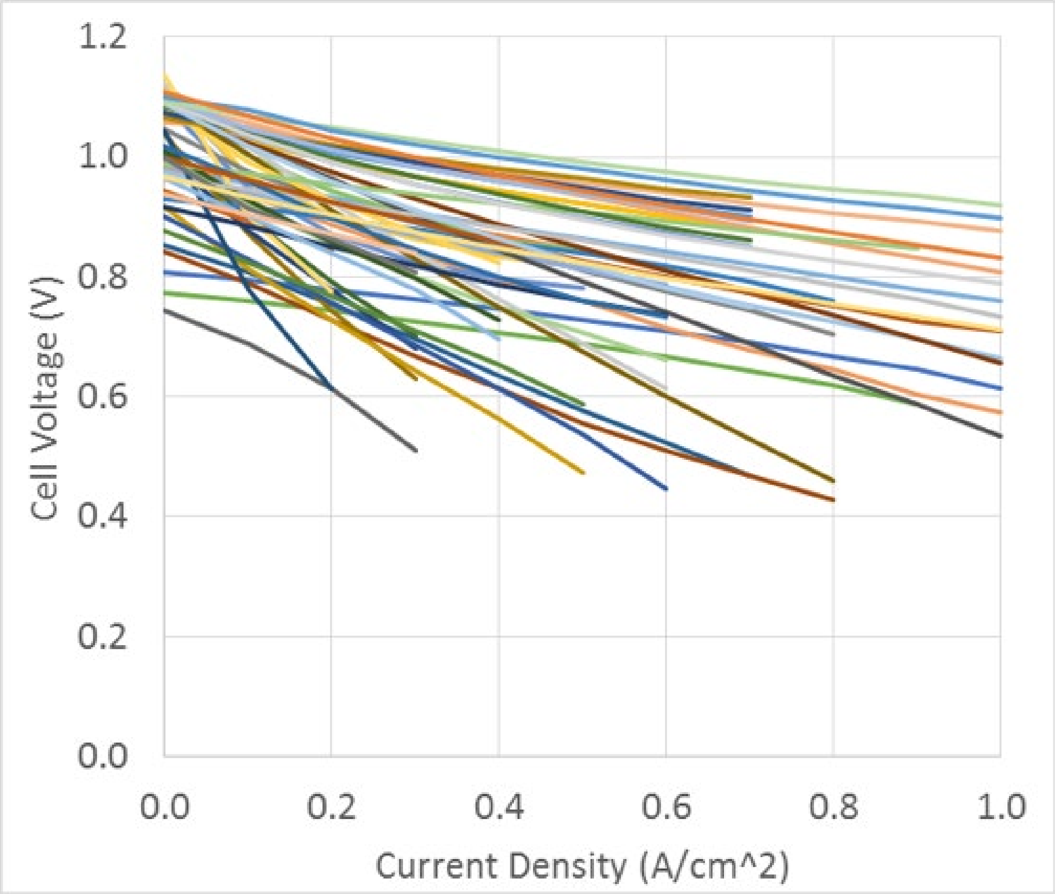
Comparison of Different Classifiers

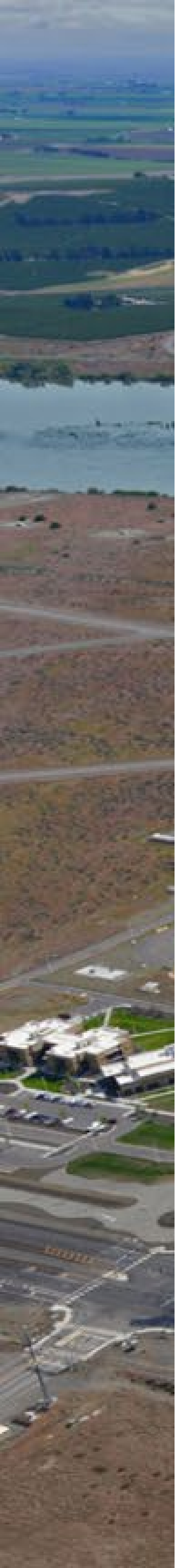


Stack State-of-Art Electrochemical Performance

- Reviewed voltage-current density (V-J) data within and outside the DOE SOFC program to ensure the best state-of-art (SOA) performance is being used for modeling simulations
- Challenges
  - Teams often report performance but do not provide enough data (i.e., stack details, conditions) to fully identify the V-J curve
  - Difficult to make ‘apples-to-apples’ comparisons
- Observations
  - Multi-cell stacks not as good as single cells due to ohmic losses
  - All-ceramic cells not as good as planar anode-supported cells
  - For the SOFC program, FCE and Delphi stacks are top performers
  - Wide range of activation losses due different material sets
  - The best metal-supported cells are approaching performance of best anode-supported cells, so purported advantages in lower temperature operation and higher durability may drive it to be the prominent architecture
  - V-J data used for ROM activity is representative of current stacks

Voltage-Current Density Plots





Pacific Northwest
NATIONAL LABORATORY

Overview: Short Term Reliability

Technical Challenge

- Stack *operating stresses dependent* on design, flow configuration, operating conditions and affect reliability

Modeling Objective

- Investigate influence of stack design, geometry, fuel composition and *identify conditions for high reliability*

Technical Approach

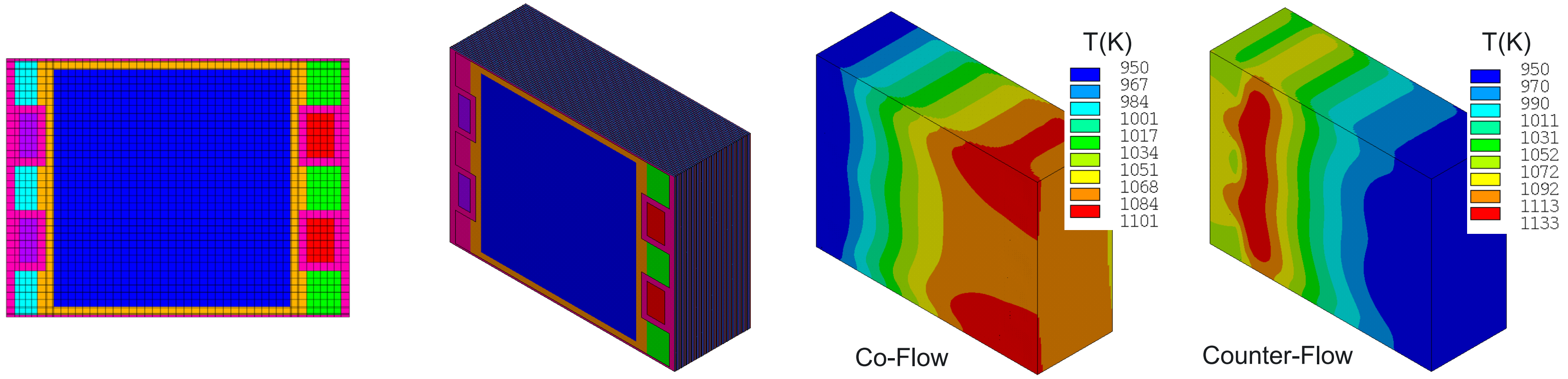
- Predict *stack temperature distribution* with different designs, geometry, flow configuration, and fuel compositions for NGFC systems using SOFC-MP
- Perform FEA stress analysis to predict *operating and shutdown stresses* and evaluate *mechanical reliability*
- Identify *optimal operating conditions* using design-of-experiments approach with desirability function

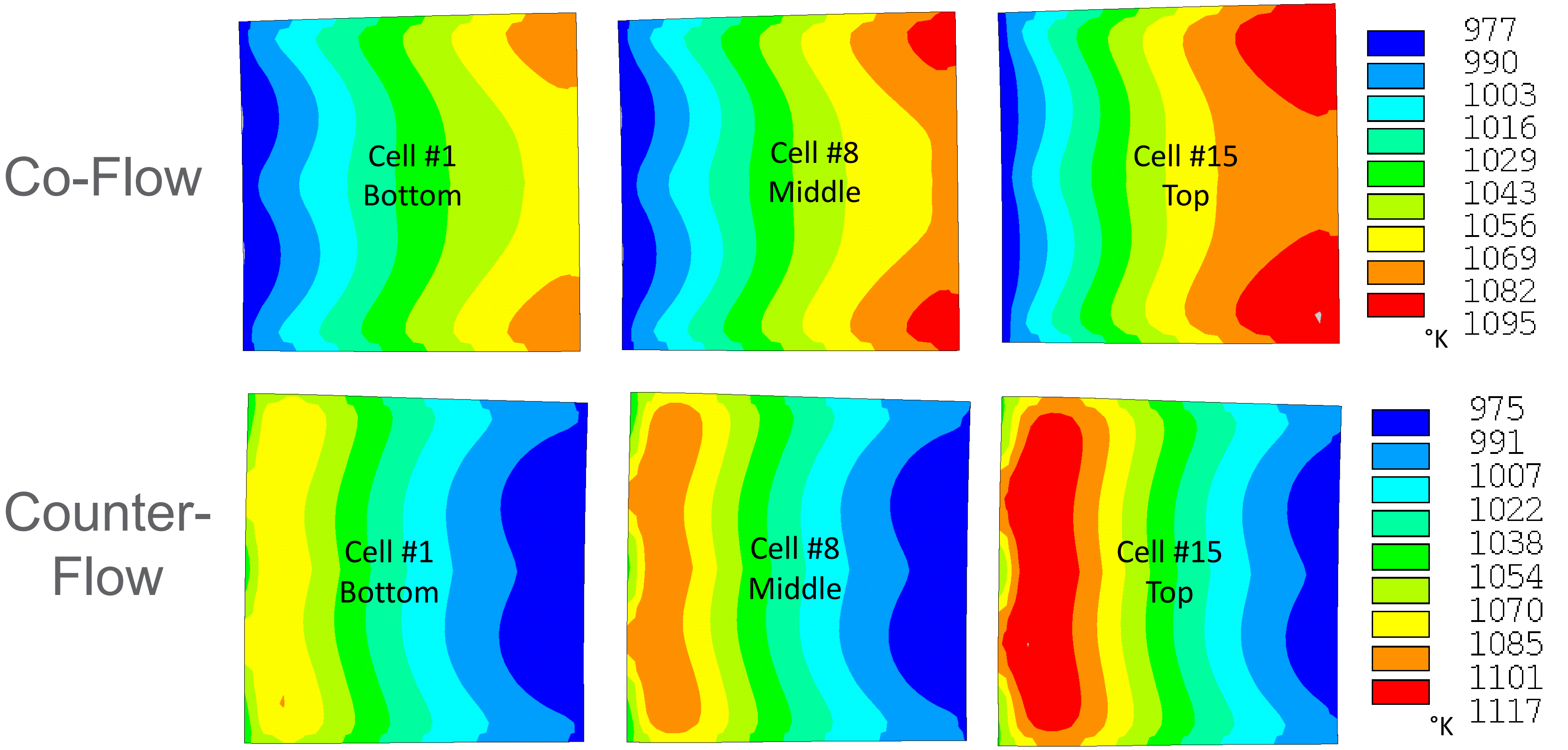
Recent Accomplishments

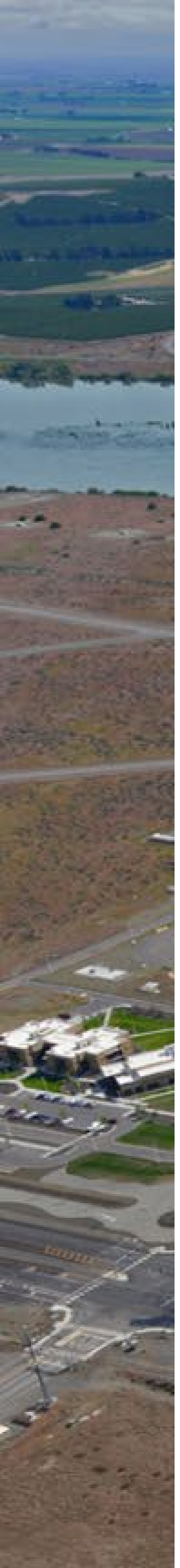
- Evaluated electrochemical/thermal performance and mechanical reliability of co- and counter-flow configurations for multi-cell stacks under similar operating conditions

Beginning of Life (BOL) 3D Stack Evaluations

- Evaluated 15 and 45 cell large area stacks to understand the benefits of flow configuration and operating conditions on the relative performance at beginning of life (BOL)
- Counter-flow stacks generally had higher power and peak temperature but also higher temperature difference for similar operating states and average cell temperature
- Local peak temperatures at corners induced high stresses and predicted high local failure probability
- This was more influential than the actual flow configuration effect
  - Reinforces importance of the sensitivity to realistic geometries and adequate fuel/oxidant manifold design







Pacific Northwest
NATIONAL LABORATORY

Overview: Long Term Degradation

Technical Challenge

- *Bridge scales* of degradation from microstructure to stack
- Understand effect of *creep*

Modeling Objective

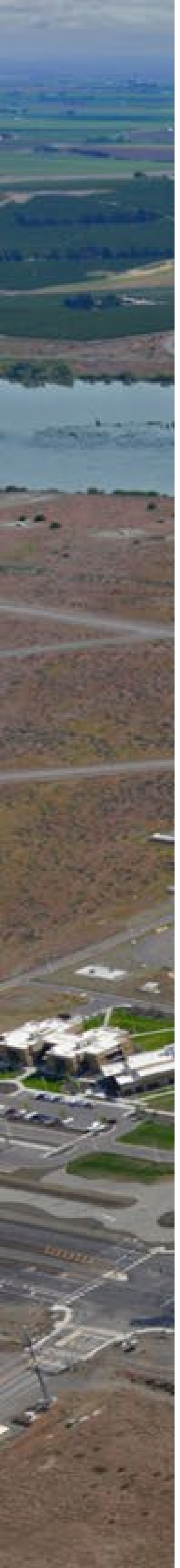
- Identify operating conditions for *optimal initial performance* and *minimal degradation*
- Investigate effect of creep on SOFC mechanical reliability

Technical Approach

- Evaluate stack performance with *multiple degradation mechanisms* acting independently and simultaneously
  - E.g., grain coarsening, Cr poisoning, scale growth, mechanical creep
- Evaluate BOL and *long-term reliability* of single and multicell stacks under realistic operating conditions.

Recent Accomplishments

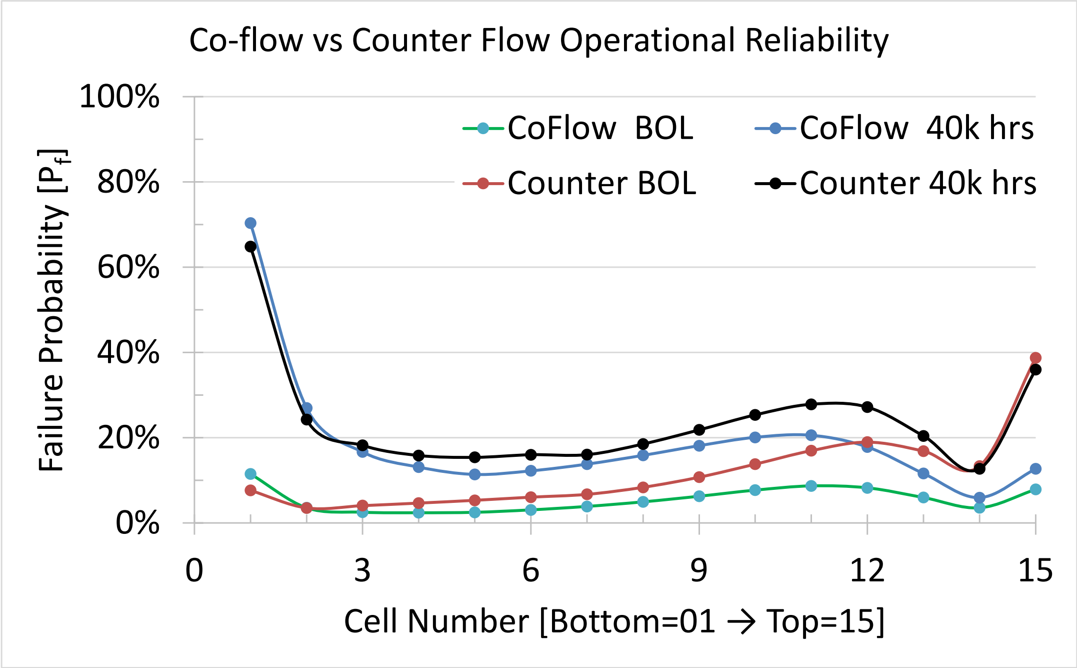
- Evaluated the performance and reliability of single and multi-cell SOFCs stacks under one or more degradation mechanisms
- Material creep model parameters were identified for the SOFC operational range (700 – 800°C)
- Evaluated influence of creep on stresses and reliability of generic multi-cell stack designs for realistic operating temperatures

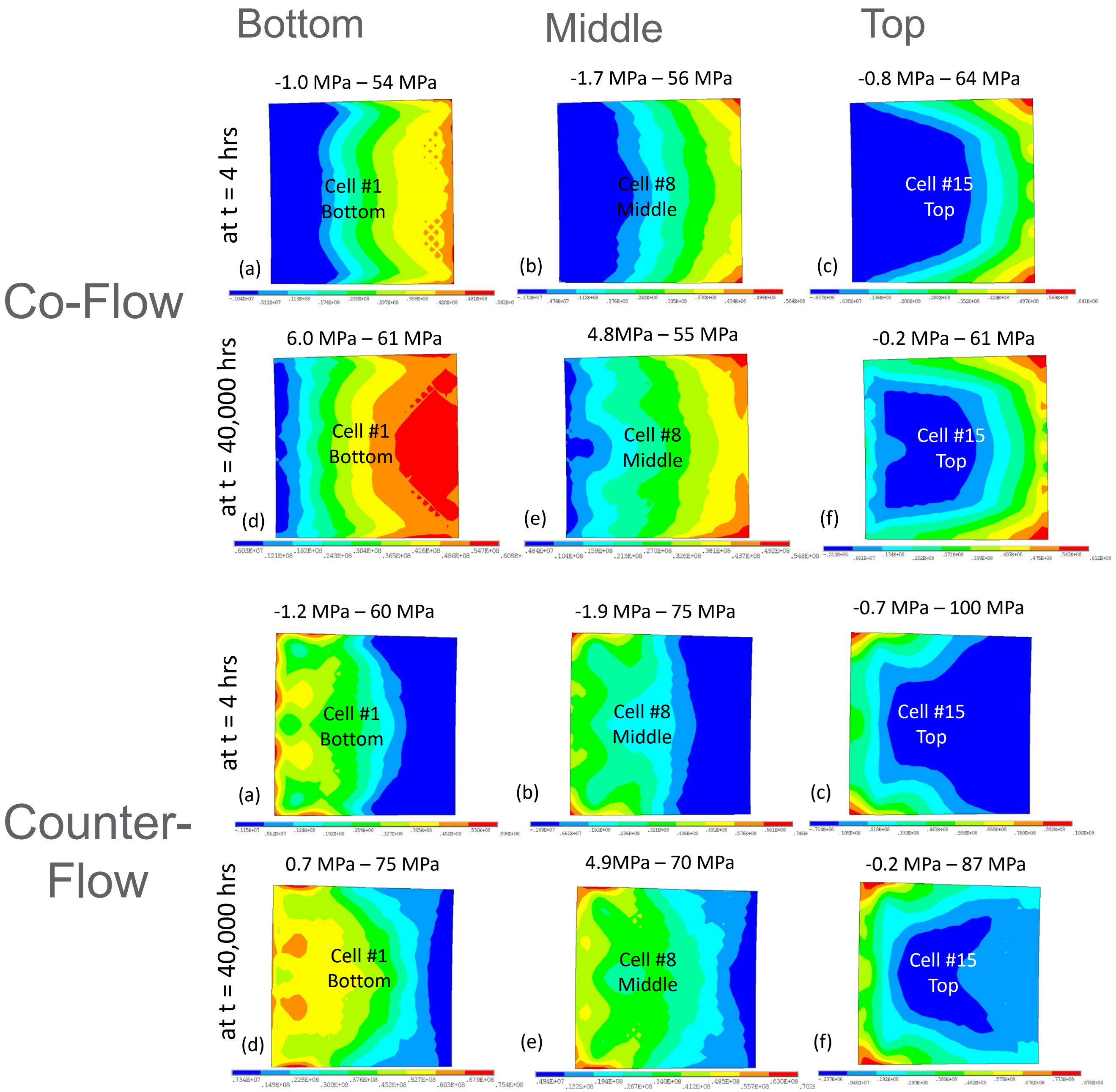


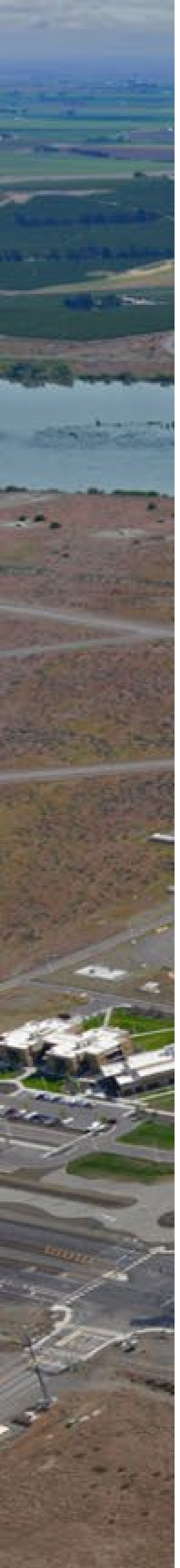
Pacific Northwest
NATIONAL LABORATORY

End of Life (EOL) 3D Stack Evaluations

- Evaluated 40k hour end of life (EOL) condition and mechanical reliability of 15 cell co- and counter-flow stacks experiencing mechanical creep
- Creep relaxation caused redistribution of stresses for both flow configurations that increased failure probabilities at the bottom cells of the stack
    - Potential for long-term damage in end cells nearest the load frame







Pacific Northwest
NATIONAL LABORATORY

Overview: Damage Progression

Technical Challenge

- Weibull analysis predicts 100% failure probability for components with localized (corner, edge) rupture. A *better evaluation is needed* for reliability predictions

Modeling Objective

- *Predict progressive damage* of SOFC electrode and evaluate long-term reliability

Technical Approach

- Investigate progressive damage models in literature and commercial FEA
- Develop and implement a *continuum brittle damage mechanics* constitutive model and validate with literature or experimental data.
- Evaluate progressive damage of electrodes in single and multicell stacks for reliability

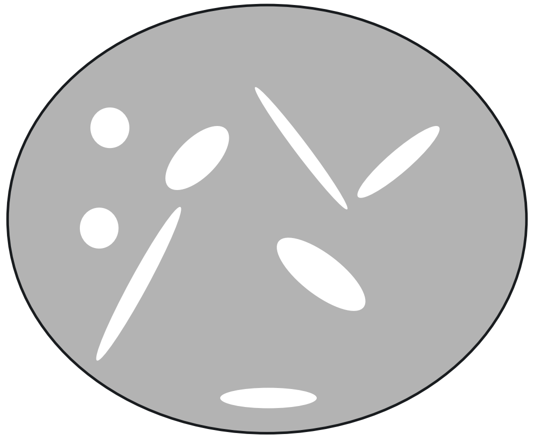
Recent Accomplishments

- Reviewed literature damage models for SOFC materials
- Implemented prediction of mechanical properties as a function of porosity
- Implemented a continuum damage mechanics model in FEA to evaluate damage evolution in the anode
- Implemented a smeared crack model in FEA to evaluate damage evolution in the anode

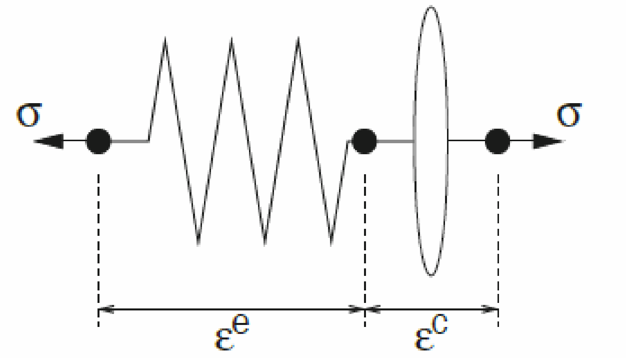
Pacific Northwest
NATIONAL LABORATORY

Damage Models for SOFC Cell Materials

- Continuum Damage Mechanics (CDM)
  - Constitutive theory that describes the progressive loss of material integrity due to the propagation and coalescence of micro-cracks, micro-voids, and similar defects
  - Voids, microcacks and pores are modeled as ellipsoidal inclusions and negligible stiffness in an Eshelby-Mori-Tanaka approach (EMTA) formulation averaged over all possible orientations
  - Typically phenomenological but focusing on *mechanistic* approach



- Smeared Crack Model (SCM)
  - Accounts for highly oriented nature of cracking (anisotropic nature of the damaged stiffness and compliance matrices)
  - Considers both Mode-I (normal) and Mode-II (shear) resistances
  - Appropriate for quasi-brittle materials such as concrete or rock under predominantly tensile loading
  - Typical crack initiation based on maximum principal stress

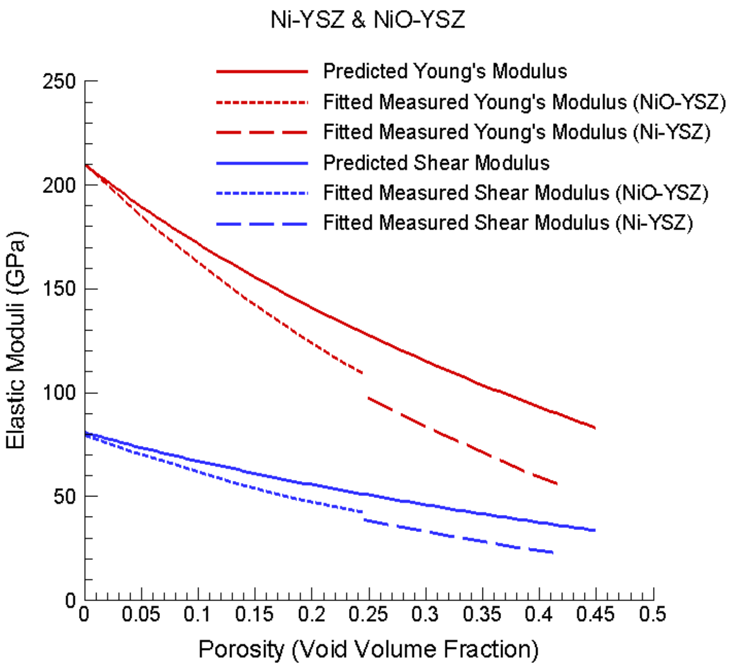


$\sigma = E\varepsilon^e$ $\quad \varepsilon = \varepsilon^e + \varepsilon^c$

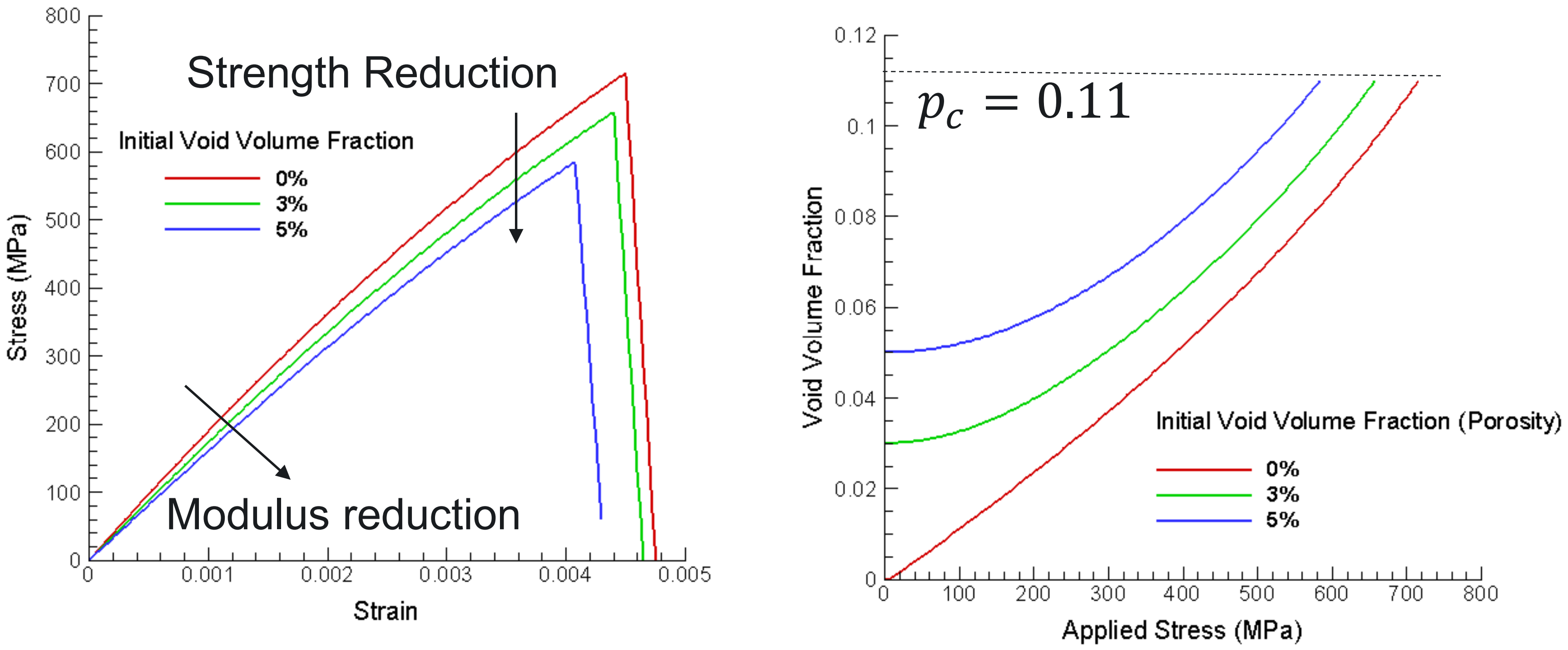
Continuum Damage Mechanics (CDM) Model

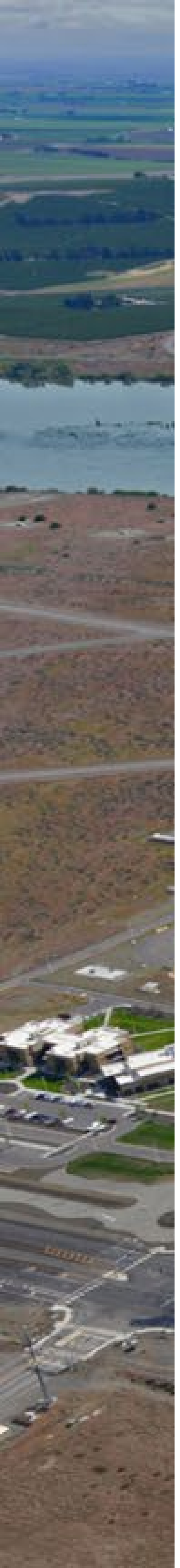
- Stiffness reduction law as a function of the void volume for porous material
- Develop constitutive relations and damage evolution laws
- Implement in FEA with stiffness reduction technique at a critical damage level

Porosity Effect on Elastic Moduli



Strength Reduction Due to Damage

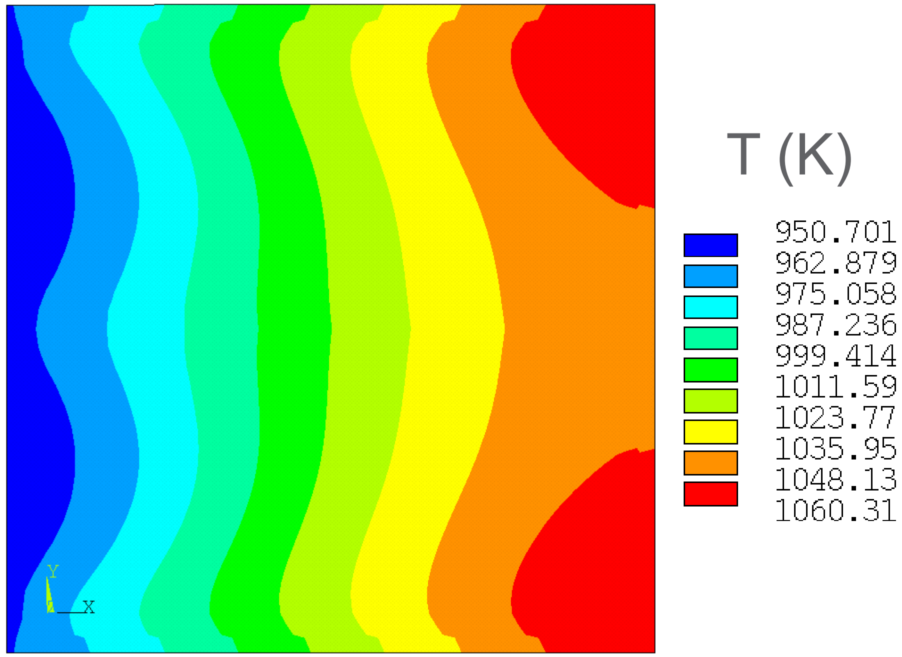




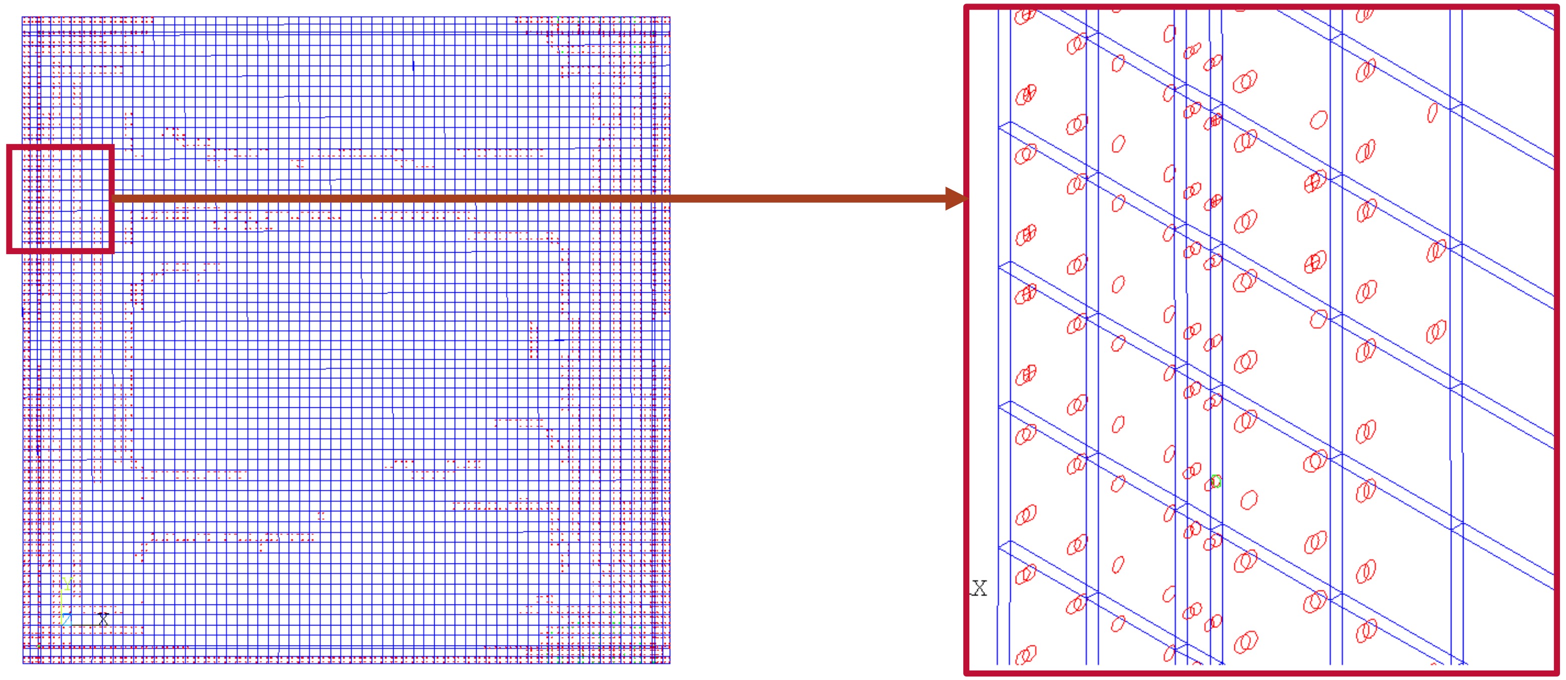
Smeared Crack Model (SCM)

- Degradation due to cracking represented without discrete crack modeling
- Considers reduced strengths in compression, tension and shear after cracking
- Easy to implement with fewer material parameters than the CDM model, this model is used often for modeling brittle damage in concrete structures

Predicted Temperature



Anode Crack Density



Pacific Northwest
NATIONAL LABORATORY

Thank you