SOFC Development at PNNL: Overview

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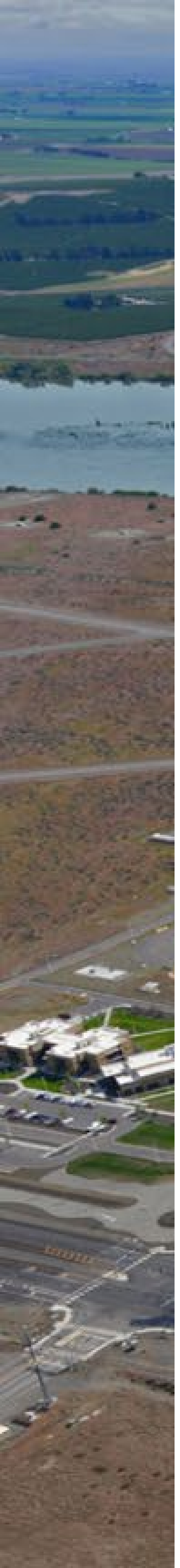


Scope of Work

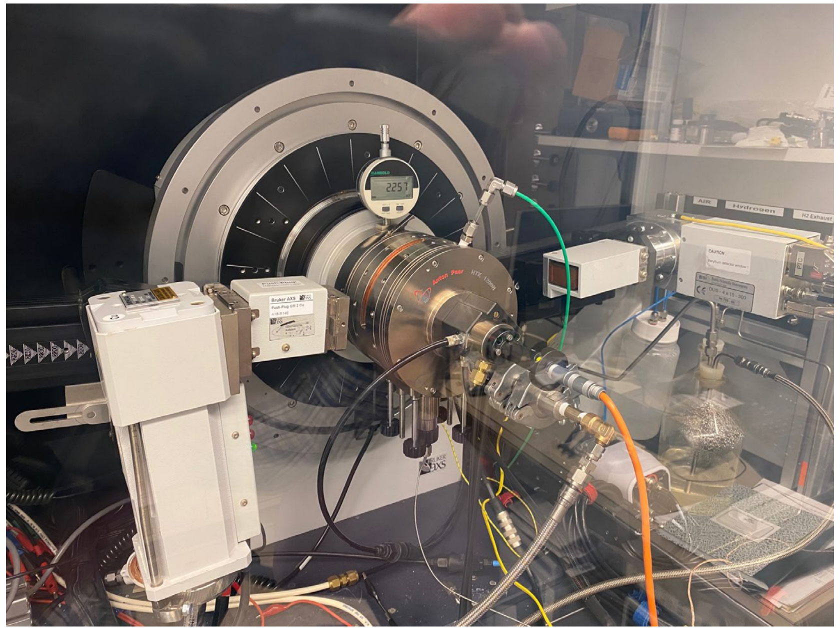
- Core Technology Program
  - Materials Development
    - ✓ Cathode materials and interactions
      - Effects of volatile species (Cr, Sr) on cell performance
      - Mitigation of Cr poisoning: Evaluation of Cr capture materials
      - Cathode contact materials: Enhancing reliability of cathode/contact 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

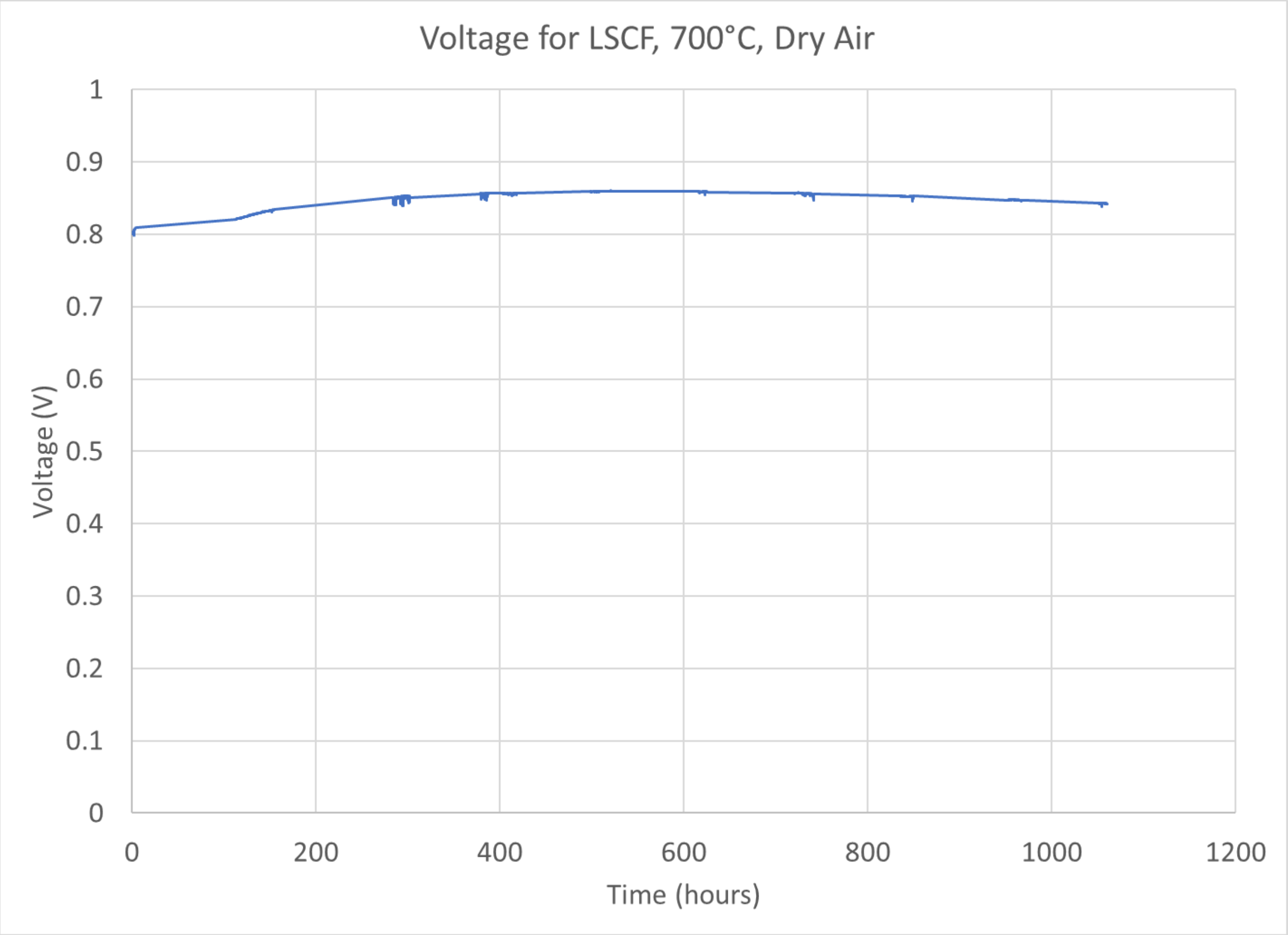
- Approaches
  - In-operando XRD of LSM and LSCF-based cathodes with various Cr concentrations in the cathode air stream
  - Evaluation/optimization of Cr "getter" materials intended to capture volatile Cr species
    - ✓ May be located upstream of stack and/or within stack ("on-cell" capture)
    - ✓ Possibly use upstream getter as primary, and "on-cell" getter as secondary ("polishing")

Cr Poisoning: In-operando XRD



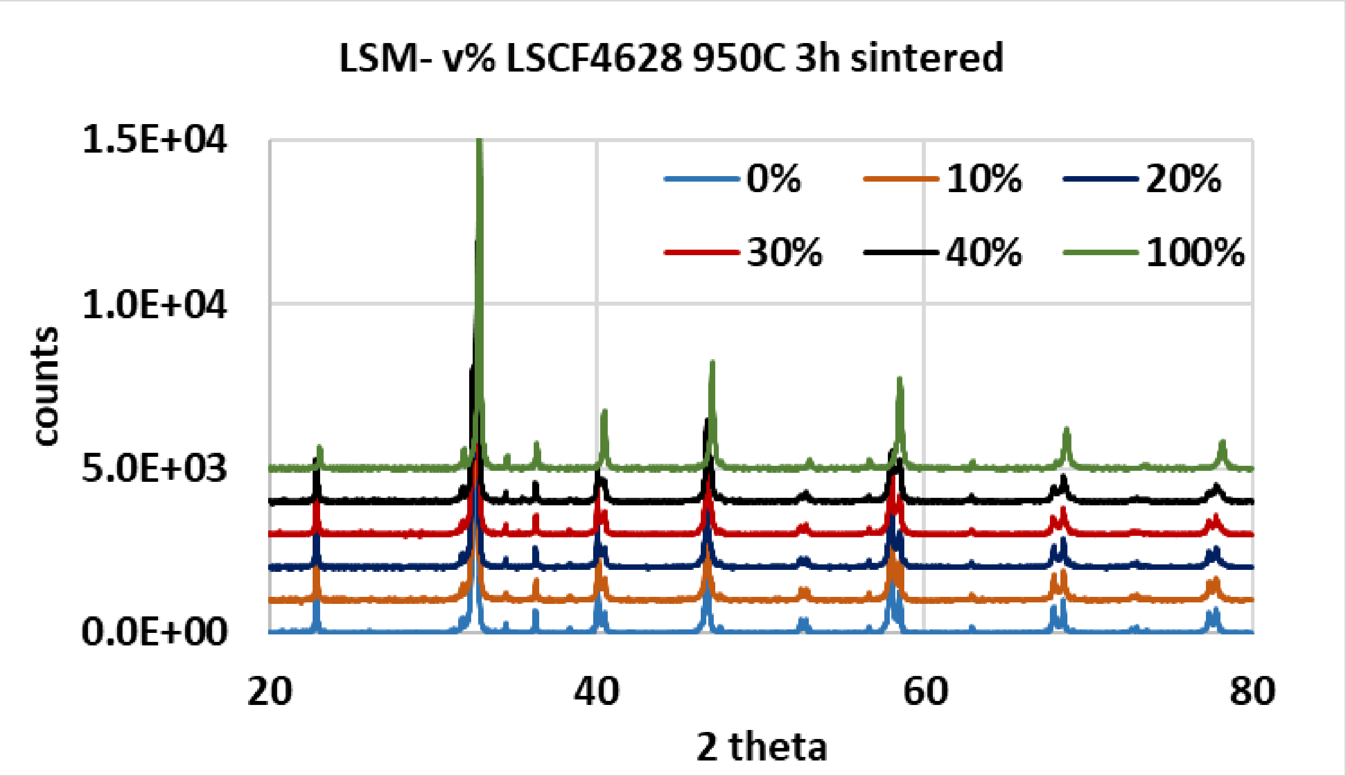
- A hydrogen safety incident at PNNL prompted safety upgrades to all experiments using hydrogen.
- Safety upgrades for in-operando XRD of SOFCs were installed:
  - Metallic lines for flammable gases
  - Over temperature monitoring
  - Fume hood pressure monitoring
  - Flammable gas sensing
  - Automatic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

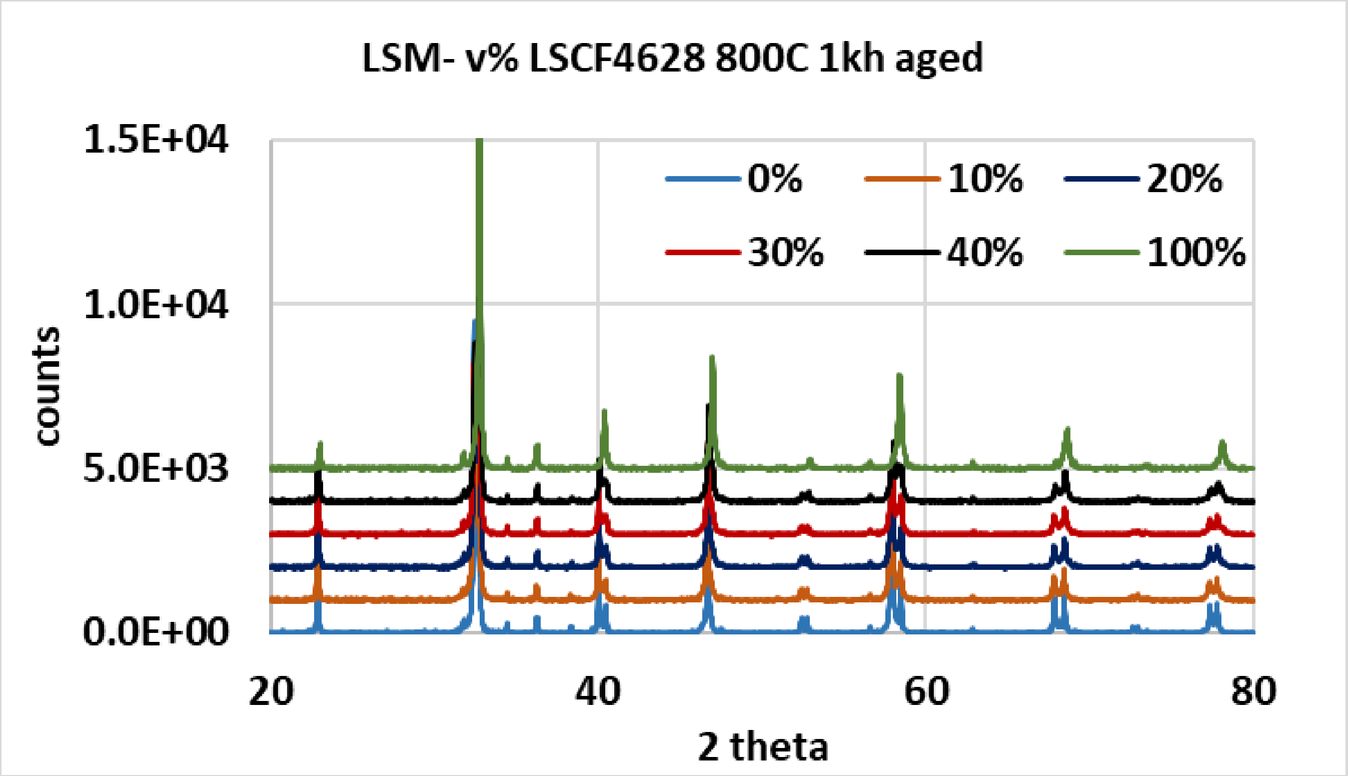
- Baseline test on LSCF cell in dry, clean air was recently completed – XRD analysis pending



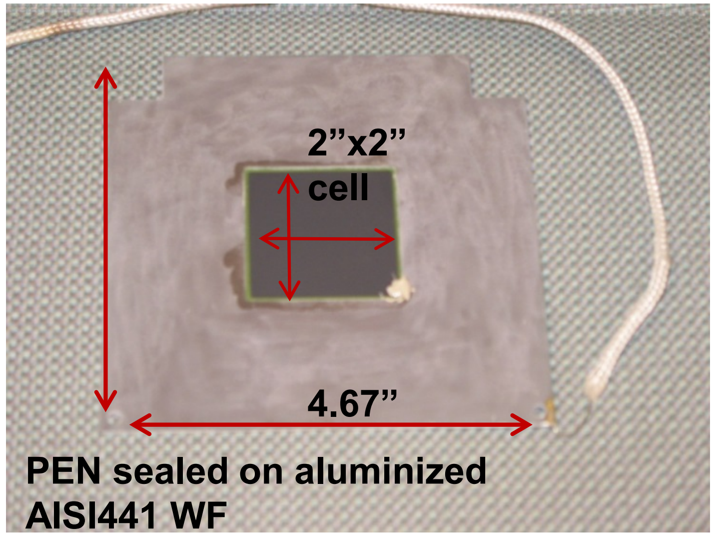
Cr Gettering Materials

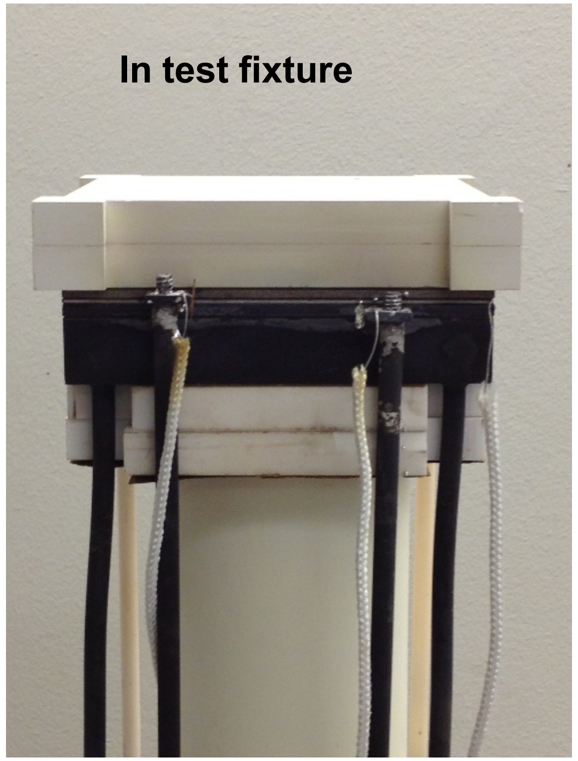
- In previous work, LSCF perovskites with high Sr content were shown to be effective as upstream getters due to high reactivity with Cr vapor species (forming $SrCrO_4$ as reaction product).
- For on-cell applications, Cr-gettering material needs to have matched CTE, high electrical conductivity, chemical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



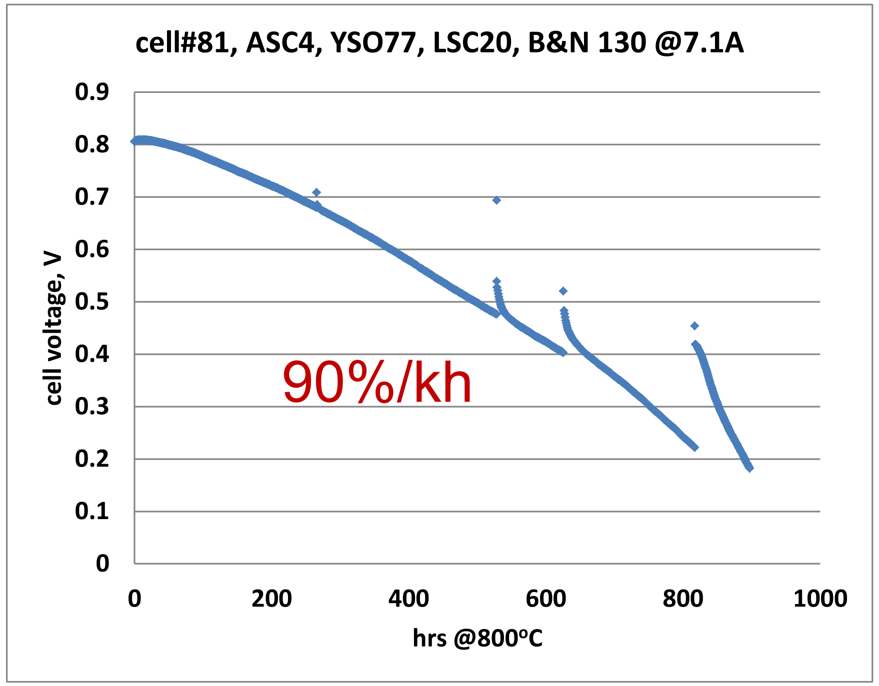


Cr Gettering Materials: LSCF/LSM Validation Testing

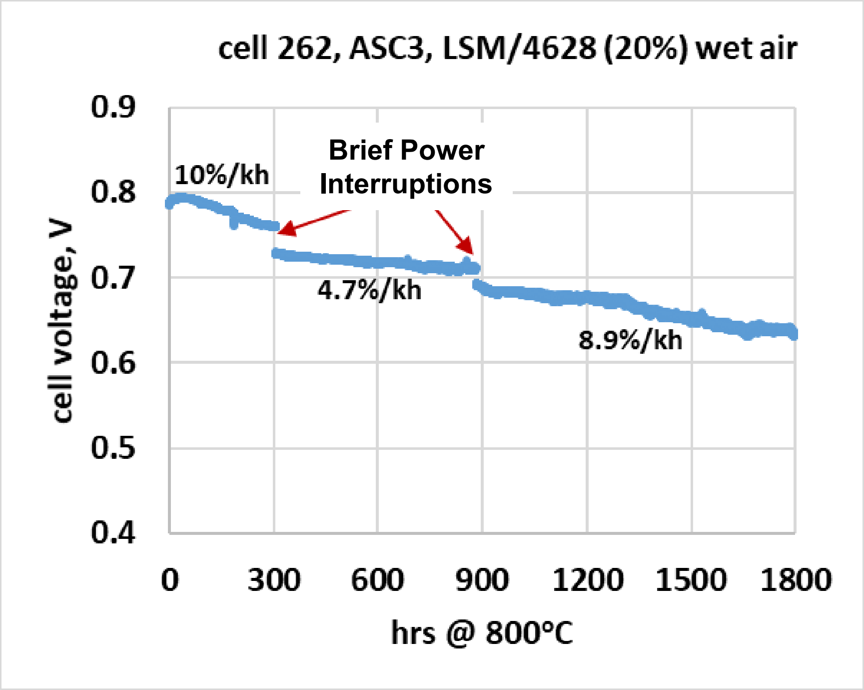


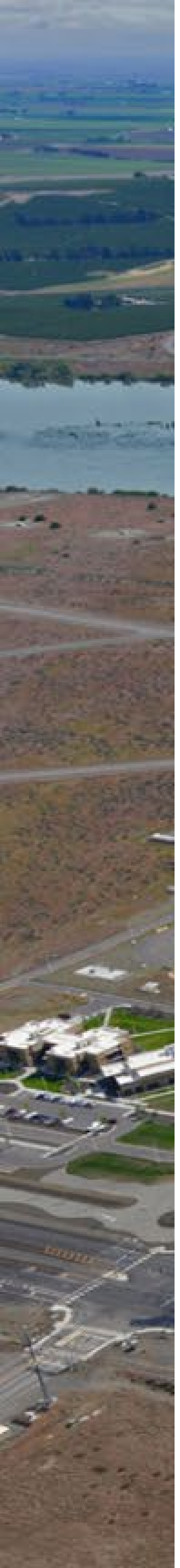


No Cr Getter:



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





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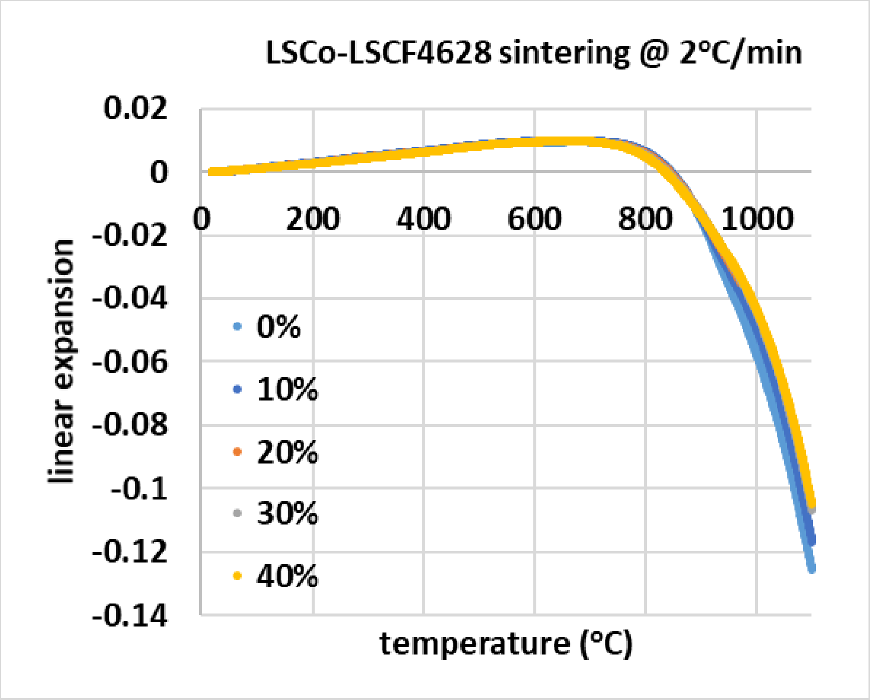
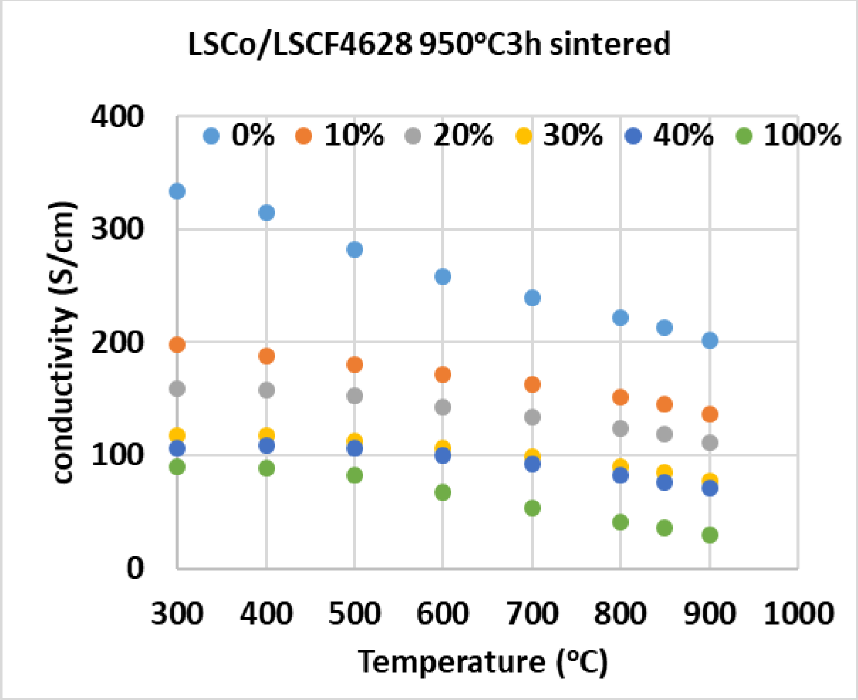
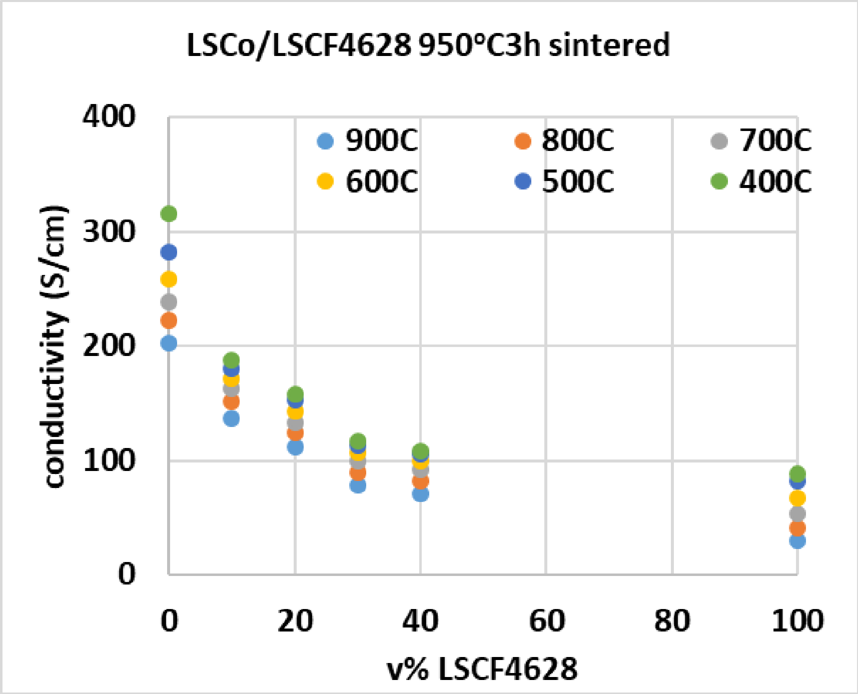
Cr Gettering Materials: LSCF/LSCo Characterization

Sintering Curves

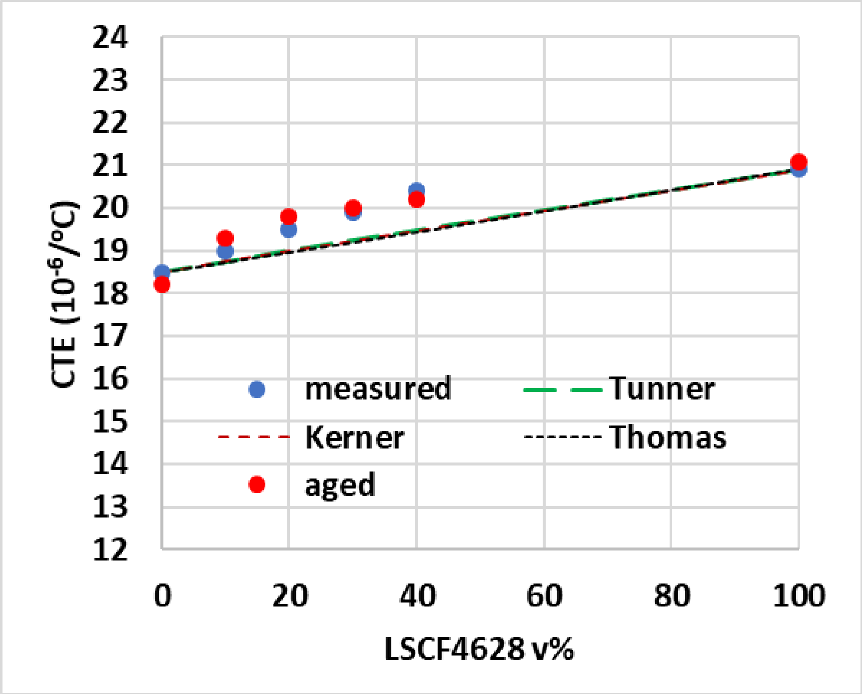


Electrical Conductivity





Thermal Expansion



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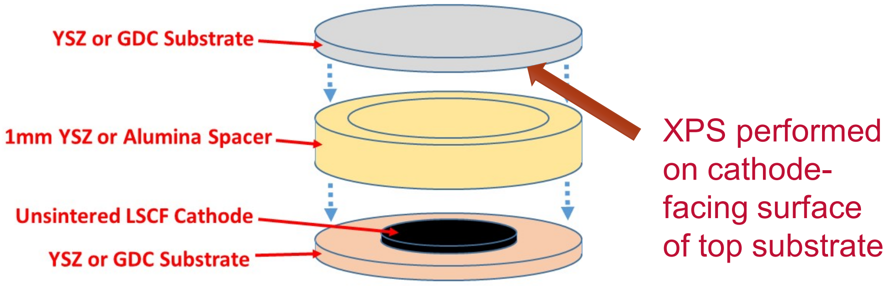
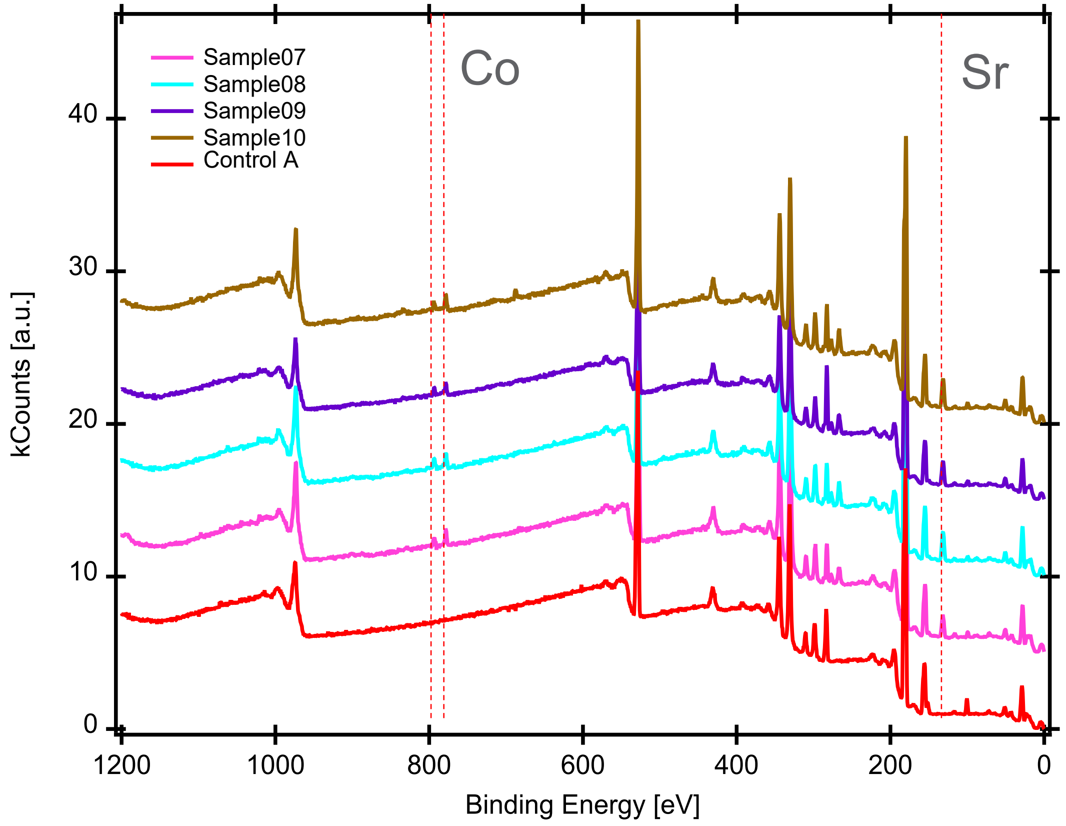
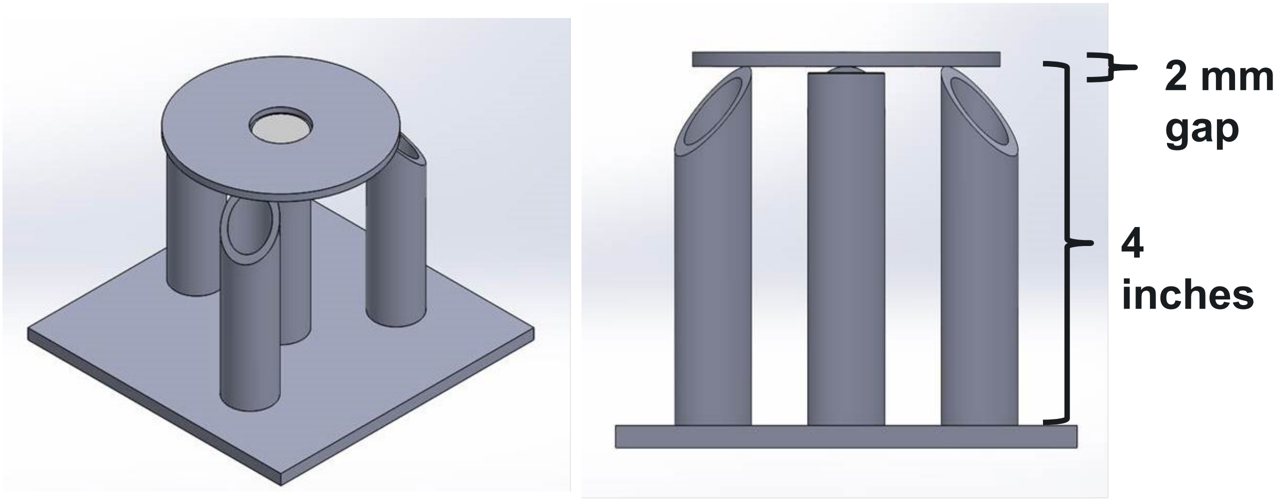
Vapor Transport of Species from LSCF Cathodes



- 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

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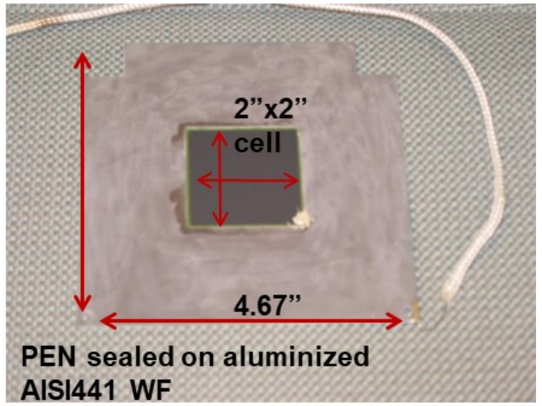
Cathode / Interconnect Contact Materials

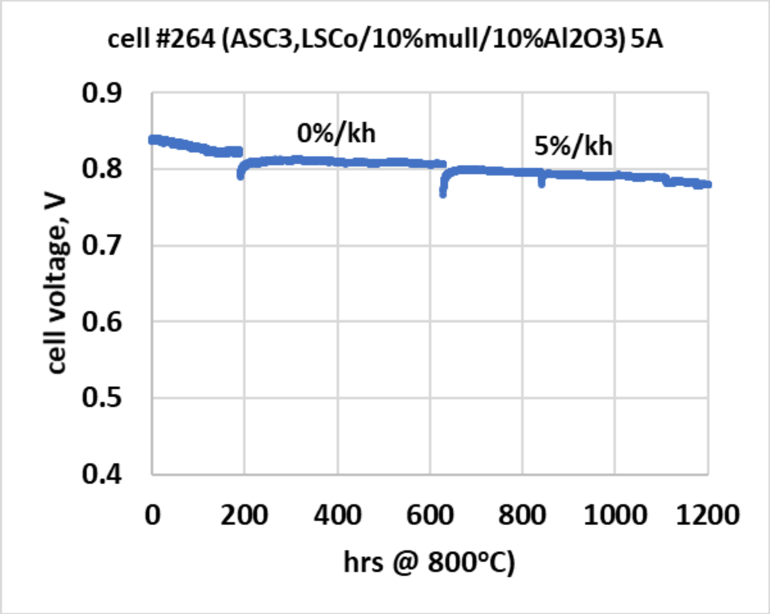
- Challenge
  - Electrical contact materials at cathode / interconnect interfaces in planar stacks tend to be mechanical "weak link," especially during thermal cycling, due to brittle nature of ceramic materials and/or thermal expansion mismatch with adjacent components
    - ✓ Low processing temperatures 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



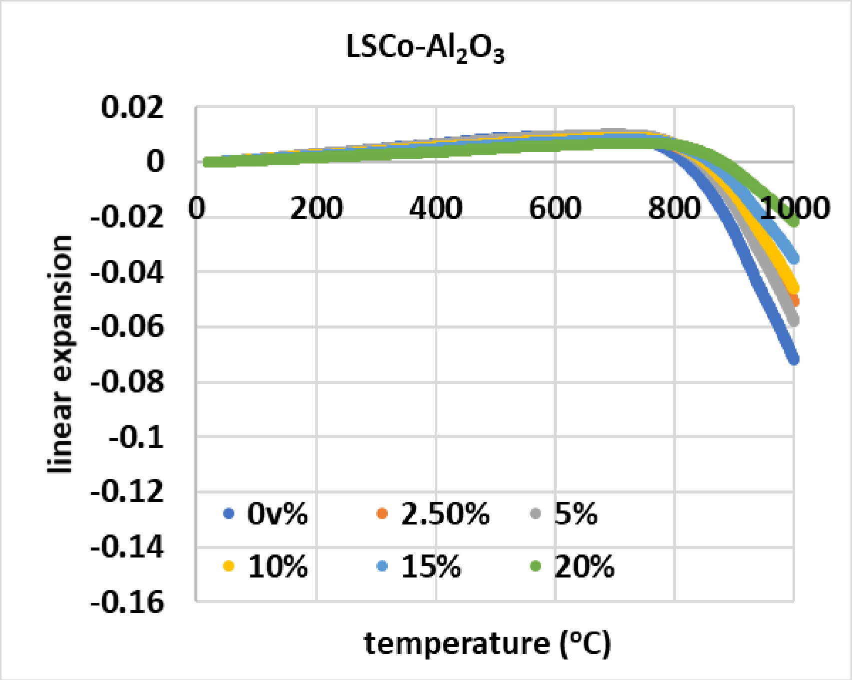
Issues encountered with LSCo/mullite approach

- 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

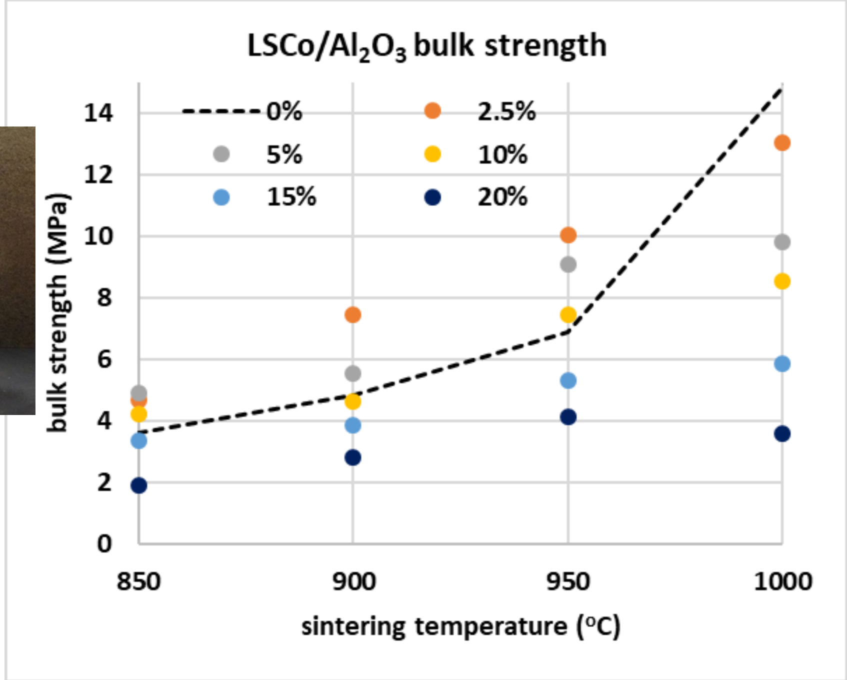
Therefore investigating LSCo/Alumina Fiber composites

LSCo/Al_2O_3 fiber composite contact materials characterization

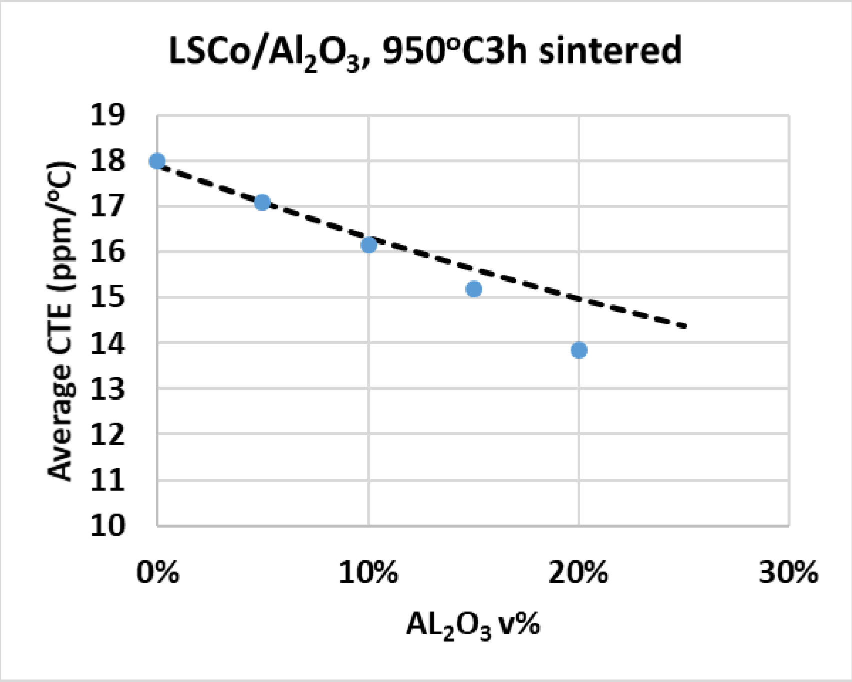
Sintering Study



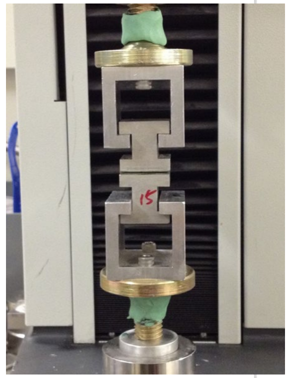
Bulk Strength

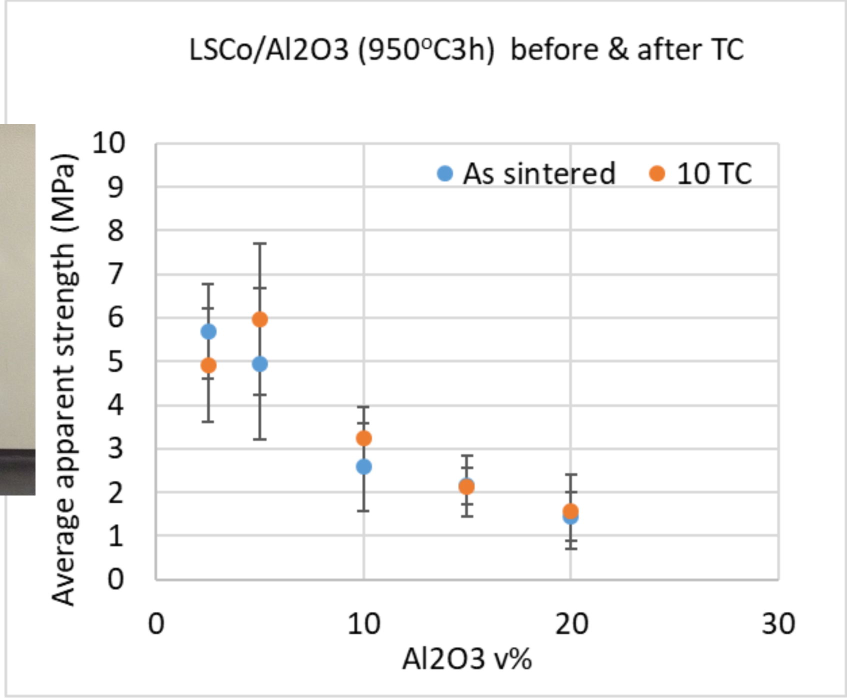


Thermal Expansion



Contact Strength





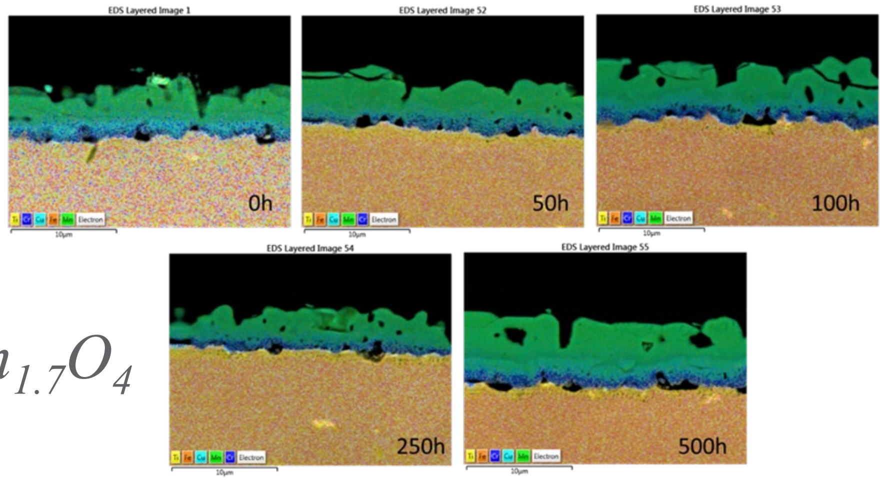
Interconnect / BOP Coatings

- 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

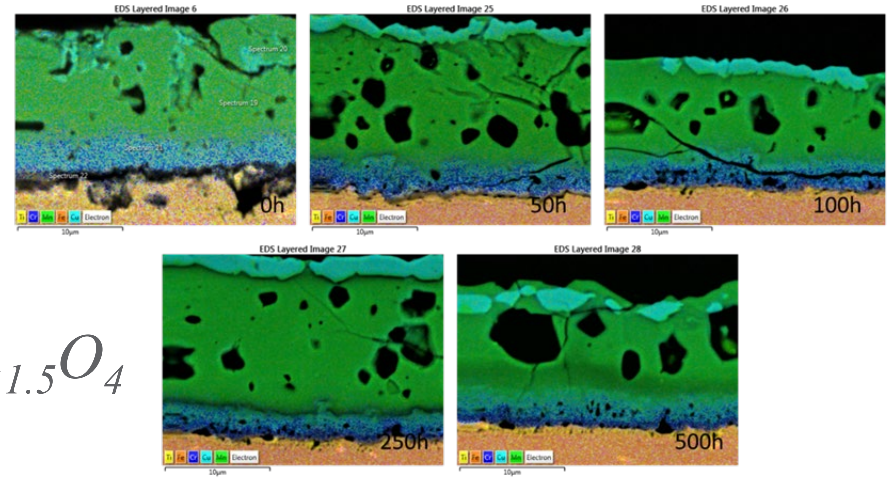
- Approaches
  - Electrically conductive Mn-Co spinel coatings exhibit good performance; due to possible issues with Co cost and availability, developing Co-free alternatives
    - ✓ Cu-Mn-O; Ni-Mn-O; Cu-Fe-O
  - Reactive air aluminization for applications that don't require electrical conductivity
    - ✓ Simple slurry-based process
    - ✓ Fabrication in air at temperatures as low as 900°C

Co-free Electrically Conductive Protective Coatings

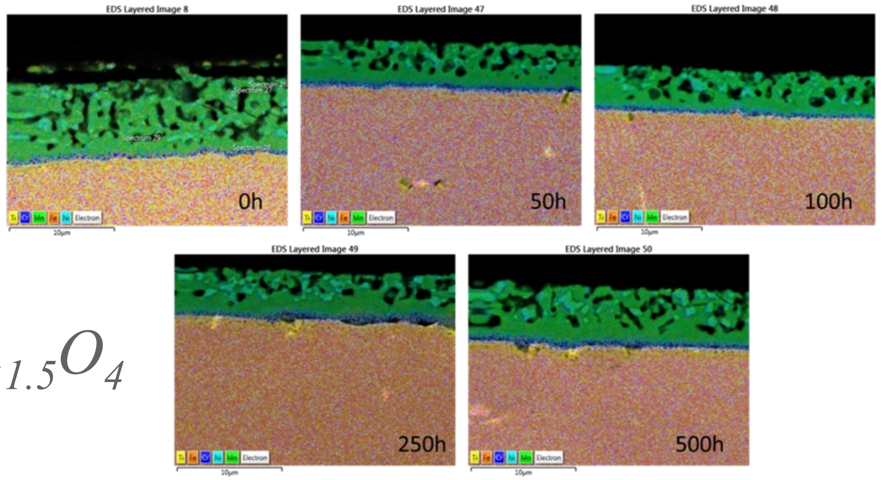
$Cu_{1.3}Mn_{1.7}O_4$



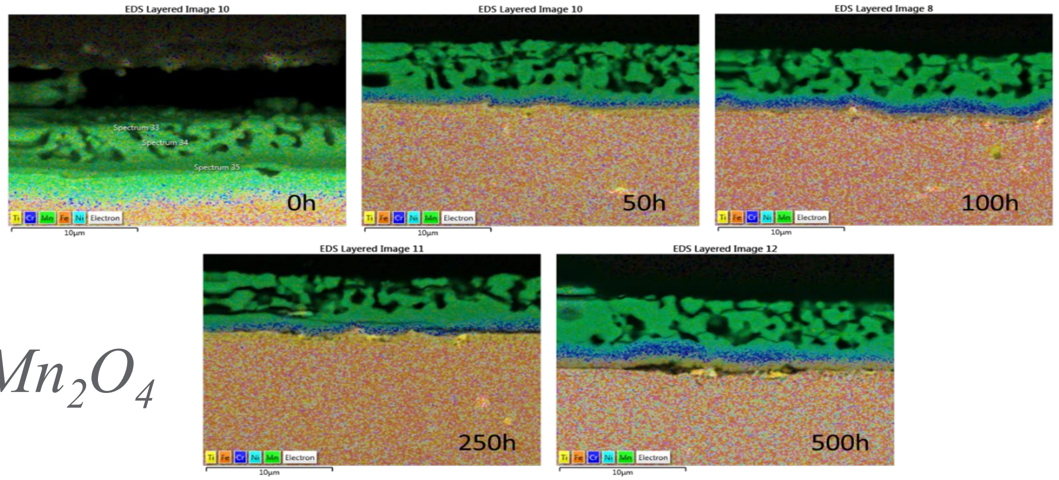
$Cu_{1.5}Mn_{1.5}O_4$



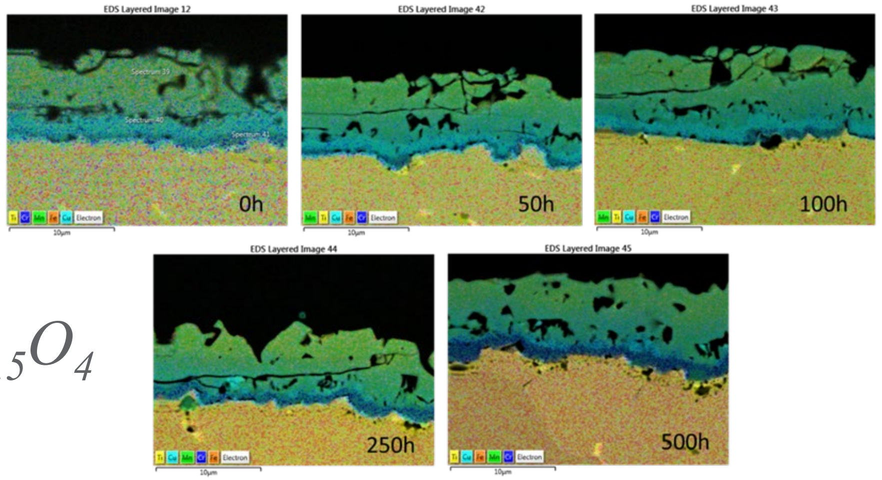
$Ni_{1.5}Mn_{1.5}O_4$



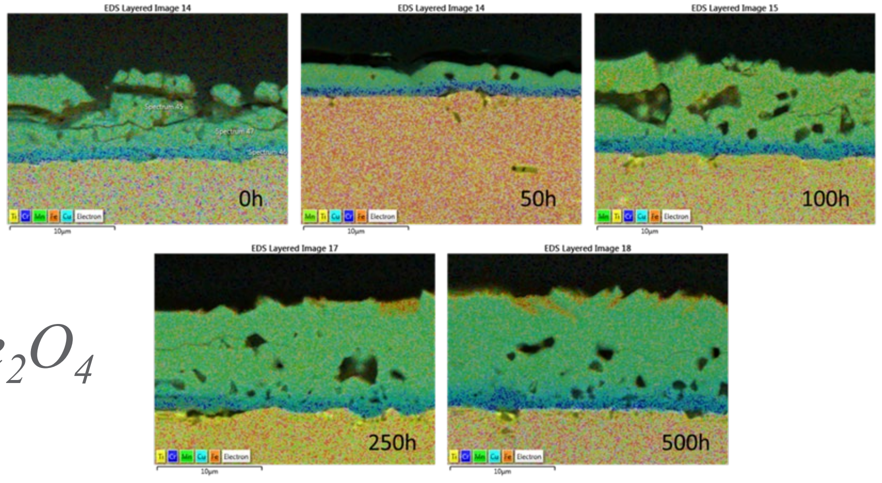
$NiMn_2O_4$

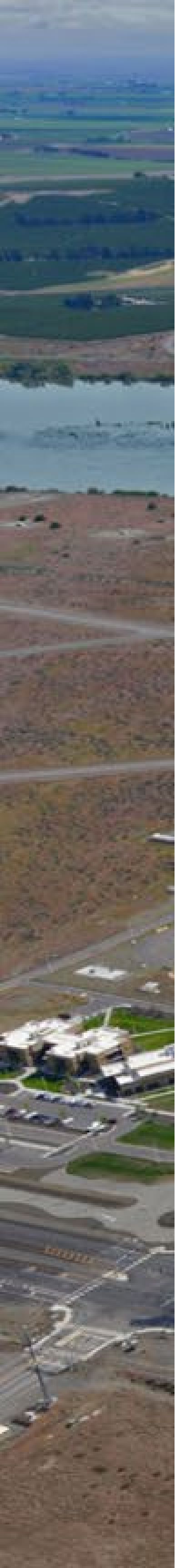


$Cu_{1.5}Fe_{1.5}O_4$



$CuFe_2O_4$

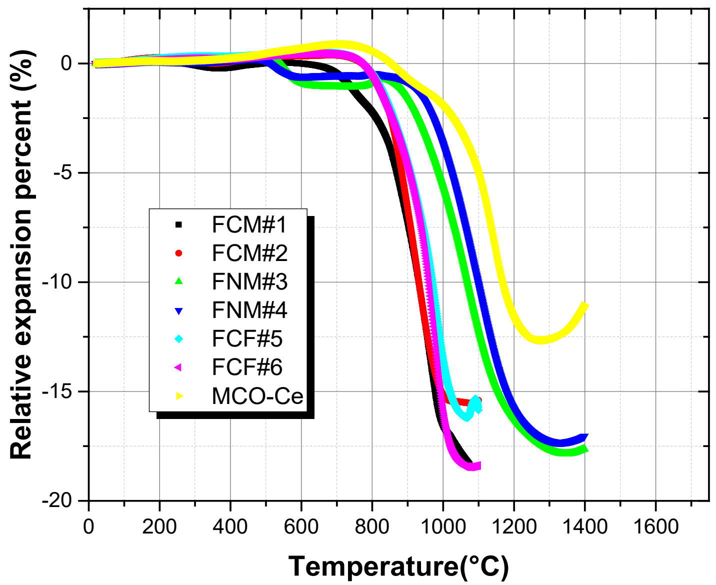




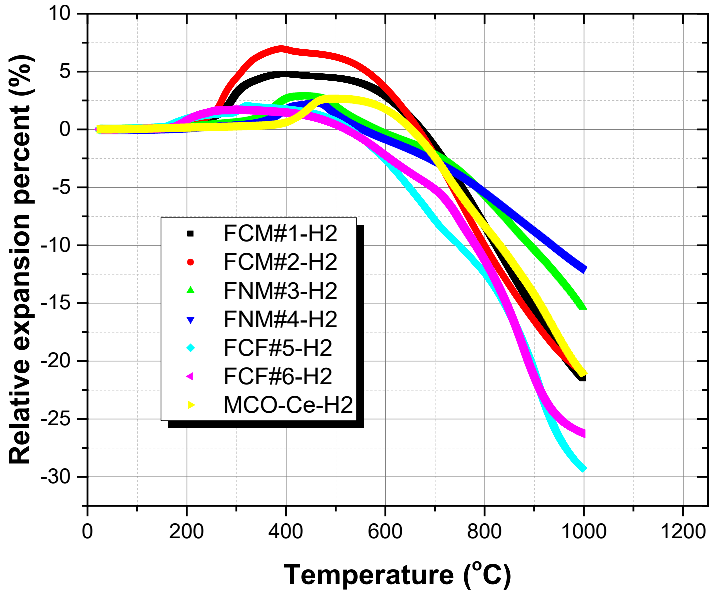
Co-free Electrically Conductive Protective Coatings

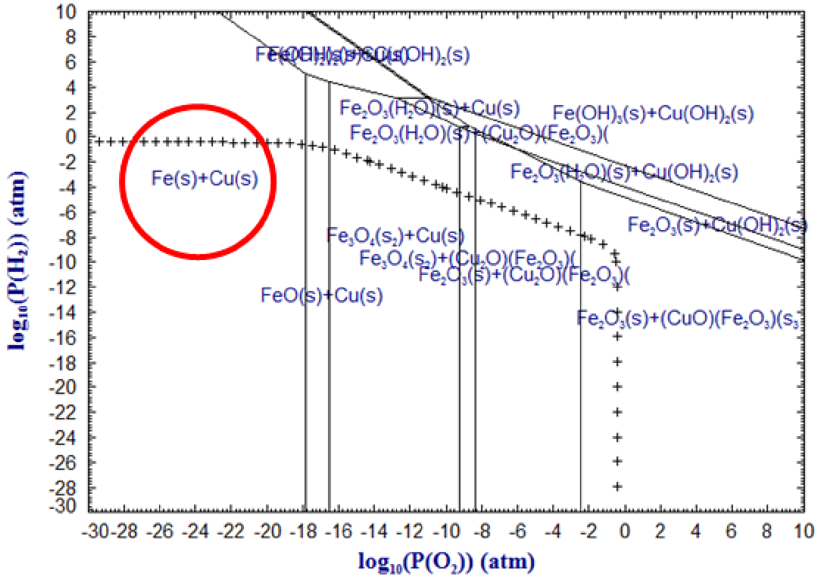
Sintering Study

In air



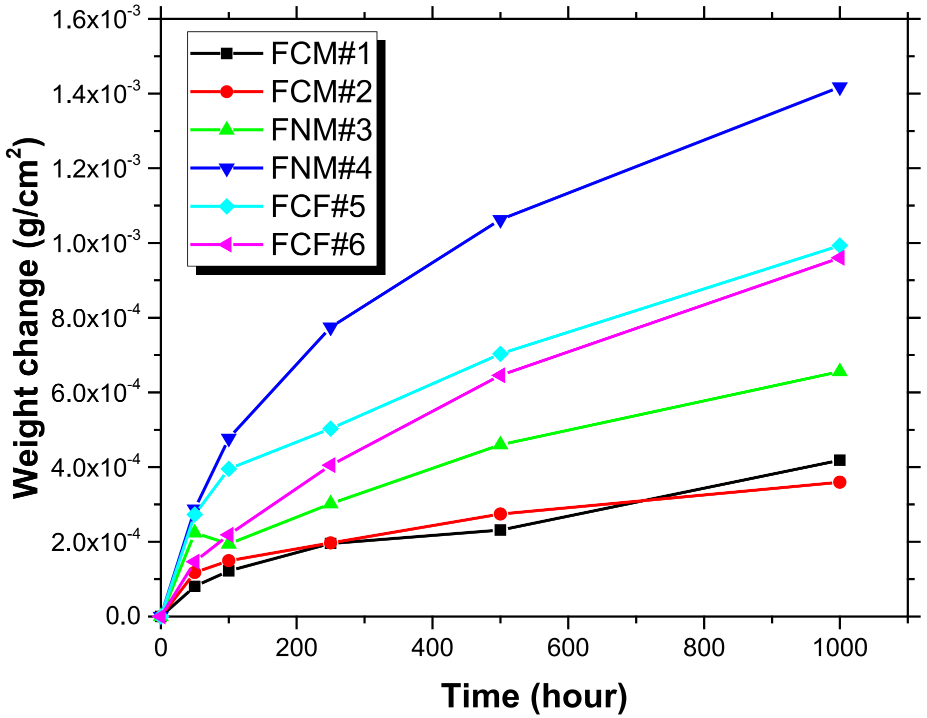
In hydrogen



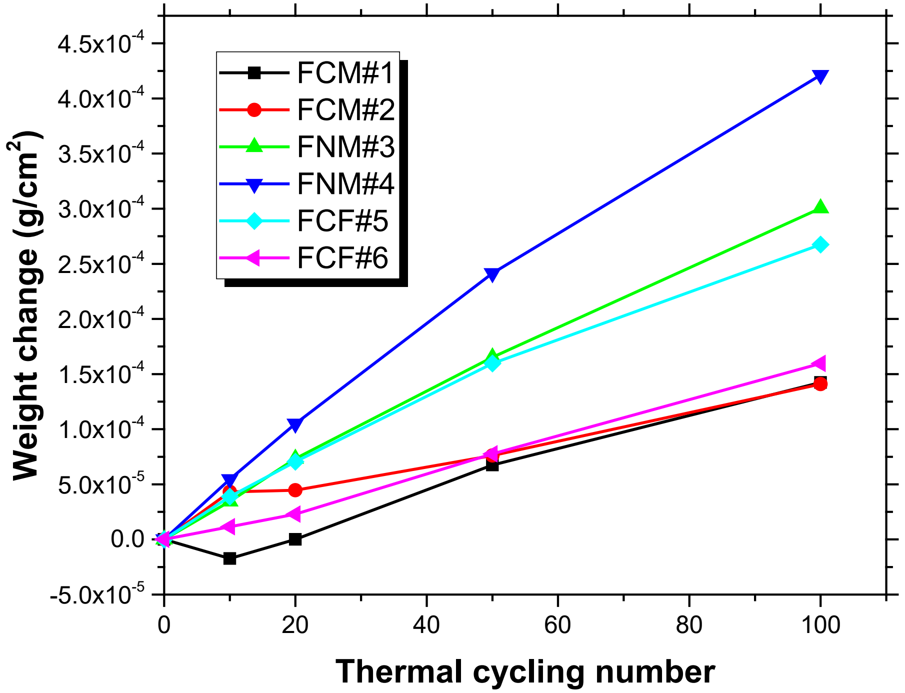


Oxidation Study

Isothermal



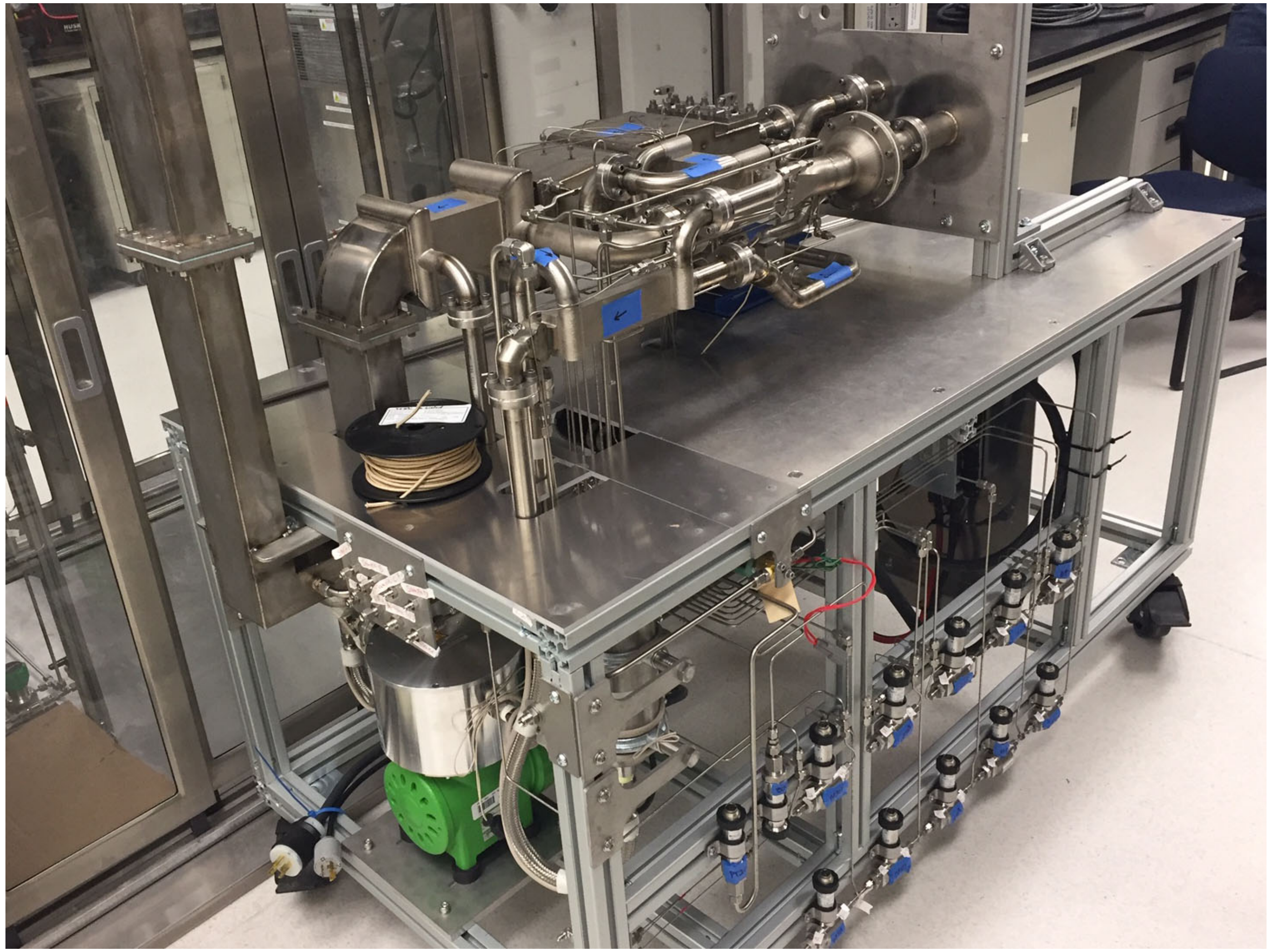
Thermal Cycling



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

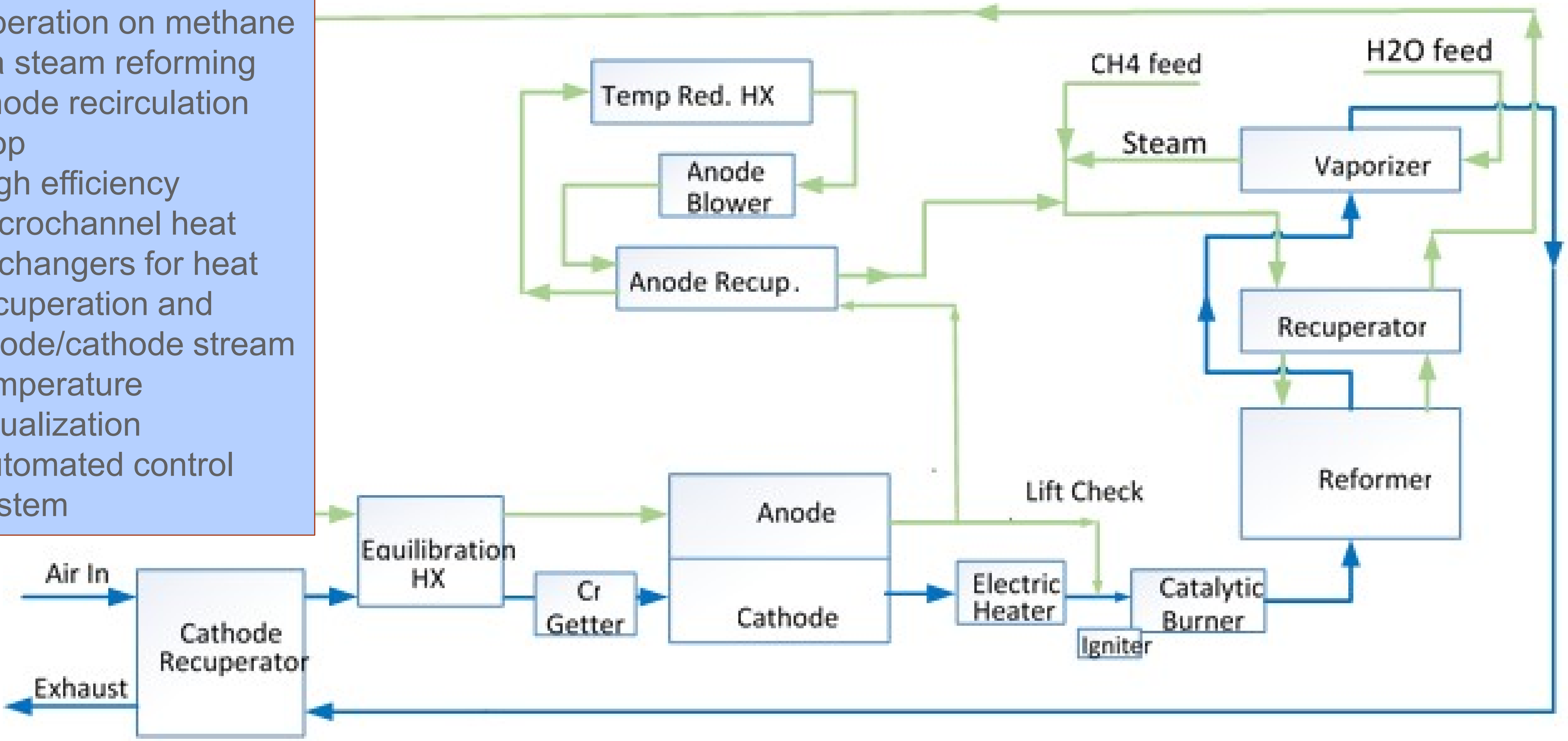


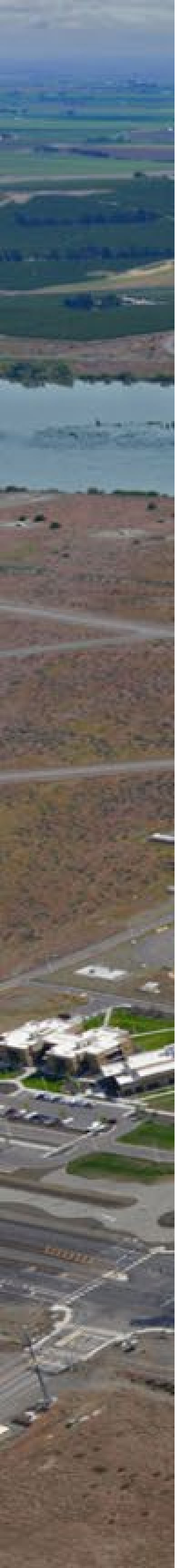
- Validated the test platform in 500 hour test on reformed methane with 40% anode recycling – operated a 3.7 kW stack at 62% gross LHV efficiency
- Thereafter, various recycle rates were tested for effects on efficiency

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





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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

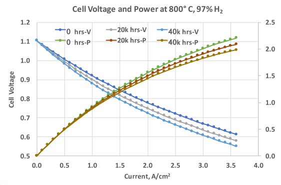
- Implemented high-pressure operation in SOFC-MP
- Developed complete ROM generation tool
- Improved ROM exhaust species predictions through use of DNN and data normalization techniques
- Demonstrated dual mode degradation for prediction of end-of-life (EOL) performance
- Demonstration of SOFC tools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

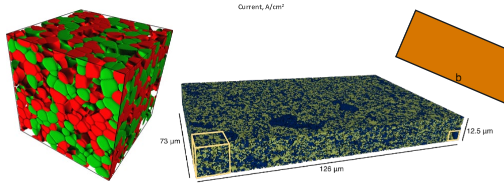
Program Modeling Objective: Linking Models Across Different Length Scales

- 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

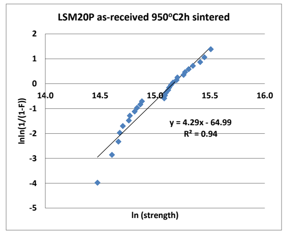
I-V Performance



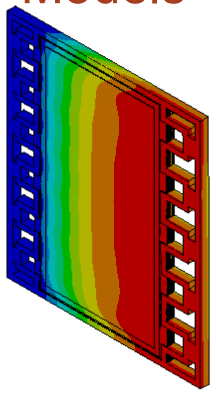


Cell Material Testing

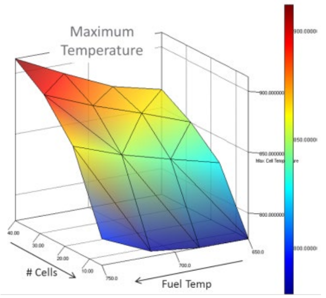
Property Data



Cell/Stack Models

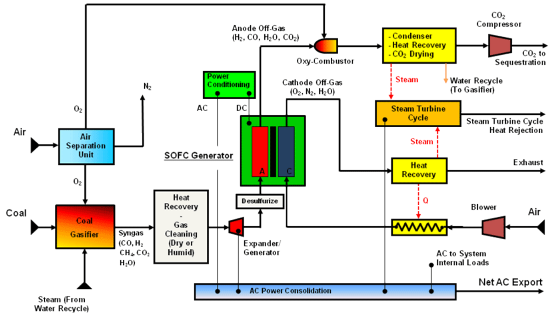


Response Surface Analysis

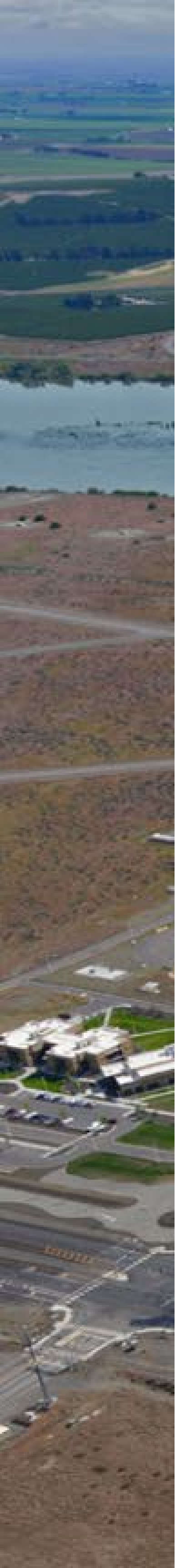


Performance: Electrical Thermal Mechanical

System Models



Reduced Order Model (ROM)



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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

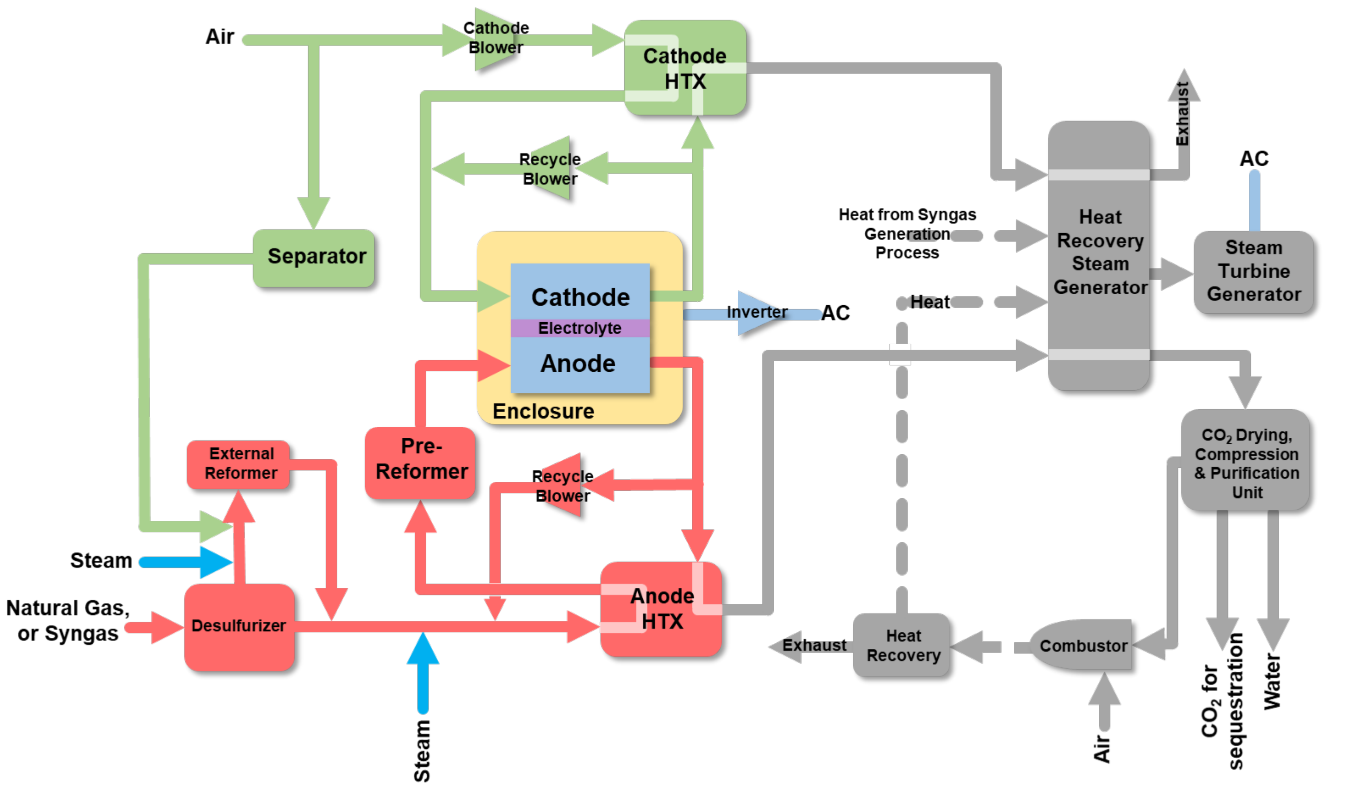
- Integrate the PNNL SOFC-MP 2D model into NETL's system model as a *reduced-order model* (ROM)
  - Develop ROM that improves accuracy of the SOA SOFC analysis with reduced computational time and complexity
- Investigate machine learning (ML) approaches to *improve accuracy* and sensitivity of generated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

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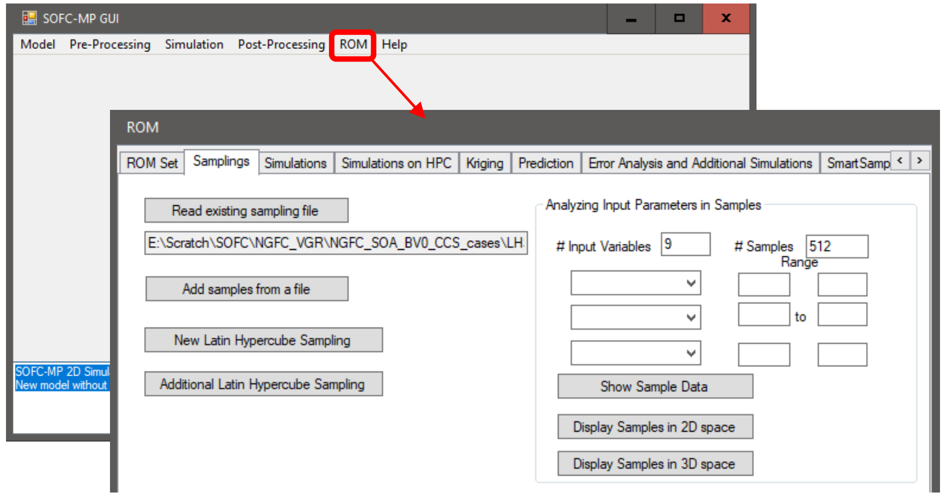
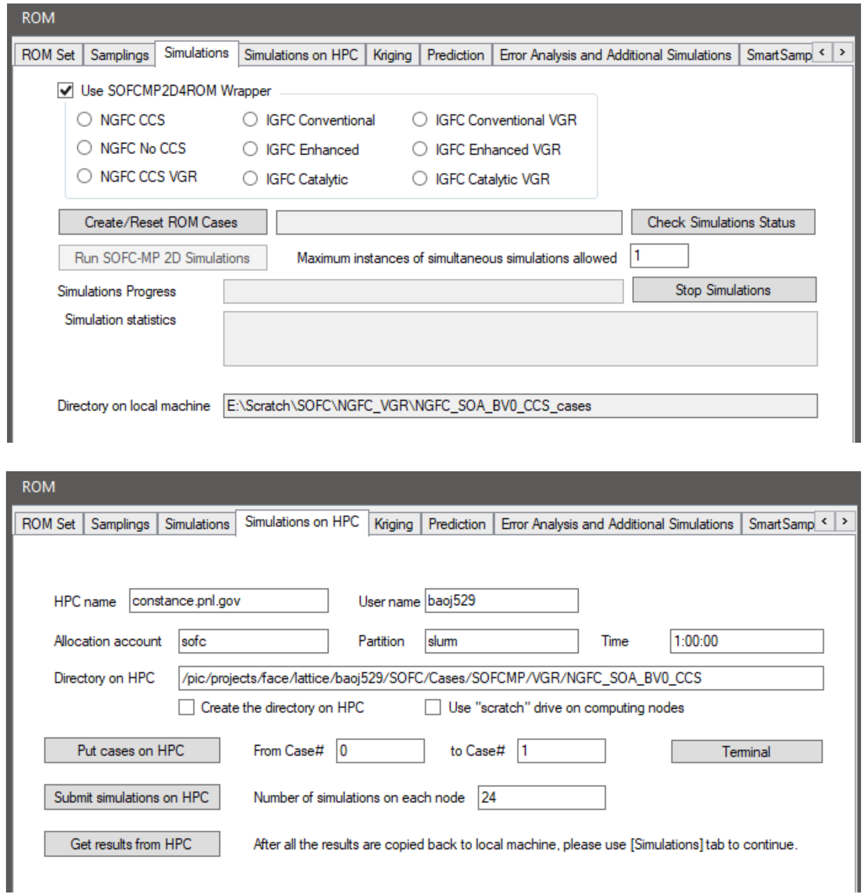
ROM Graphical User Interface (GUI)

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

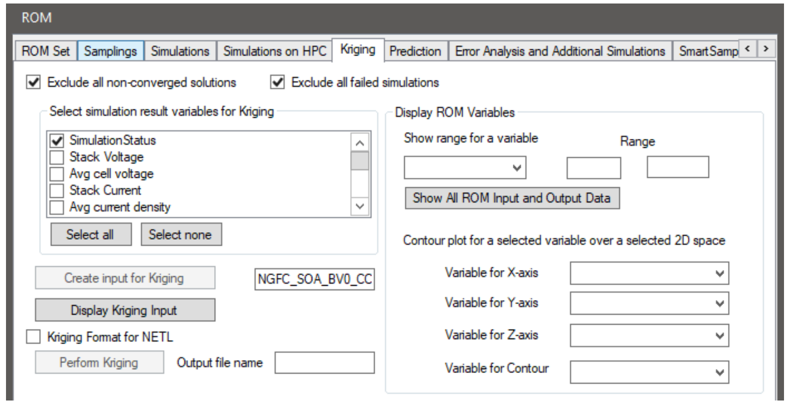
1. Sampling



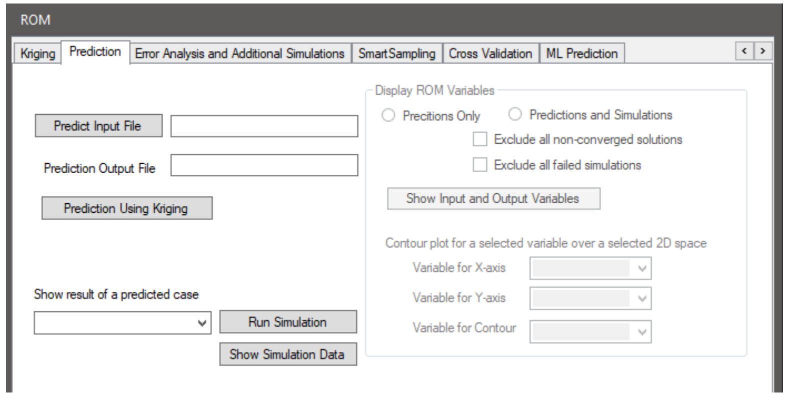
2. Create Cases and Solve

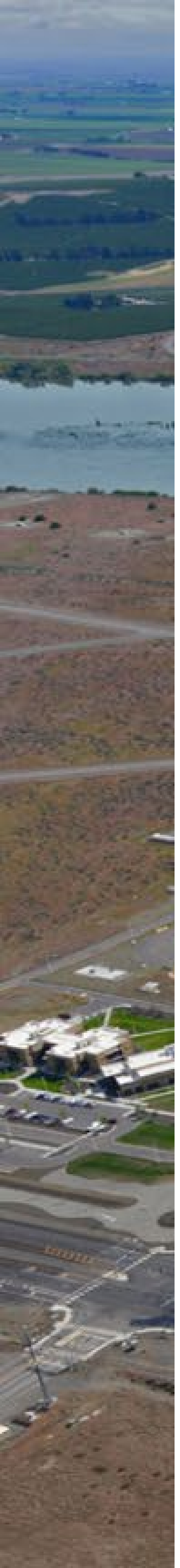


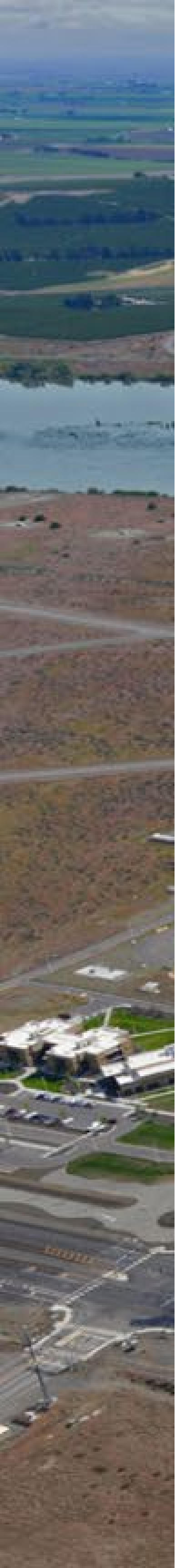
3. Build Kriging ROM



4. ROM Prediction

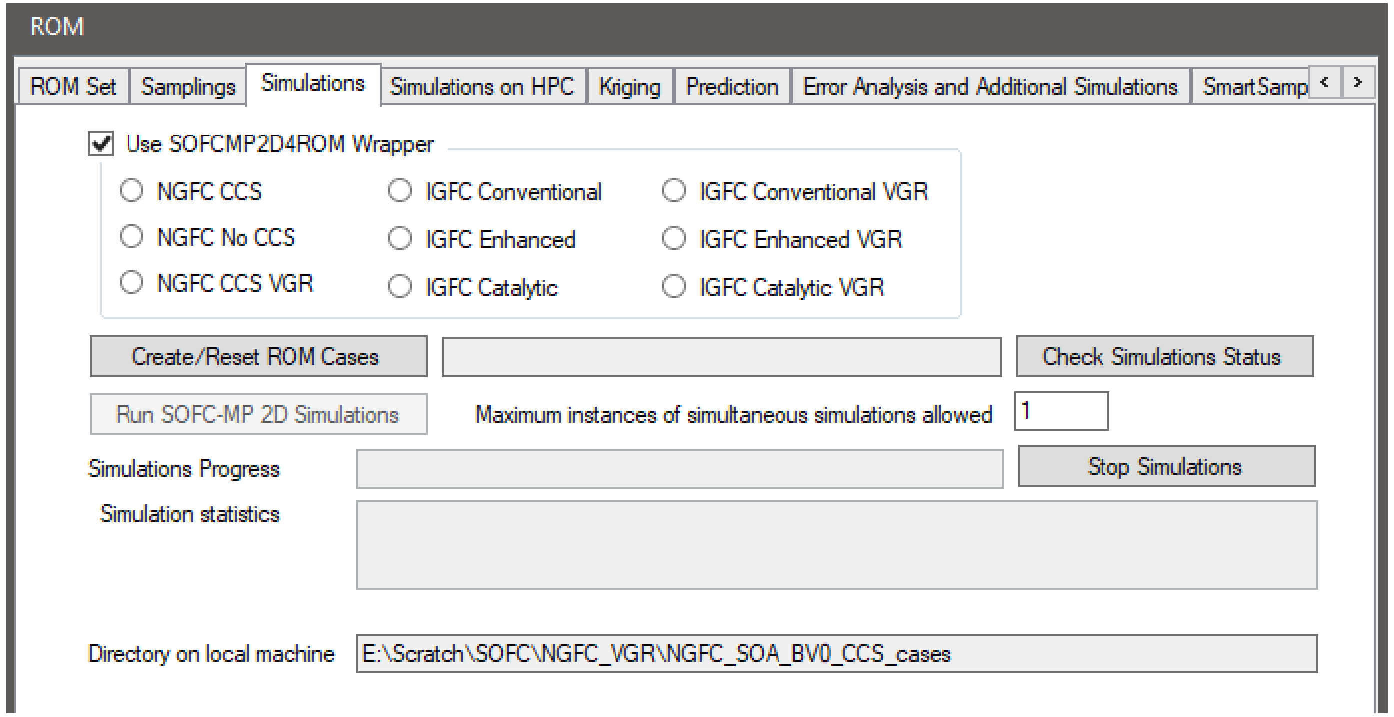


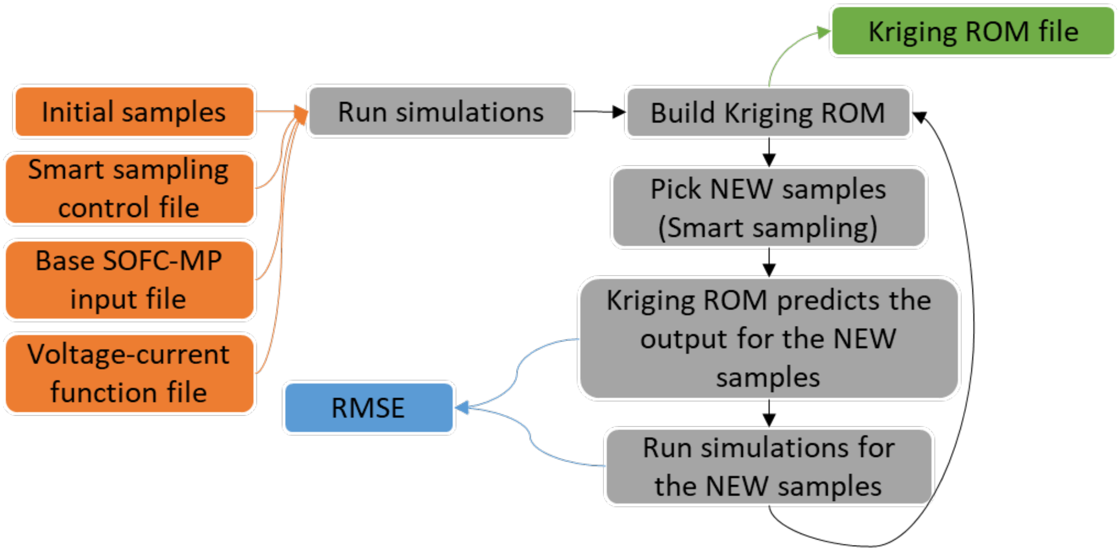




ROM GUI Features

- 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

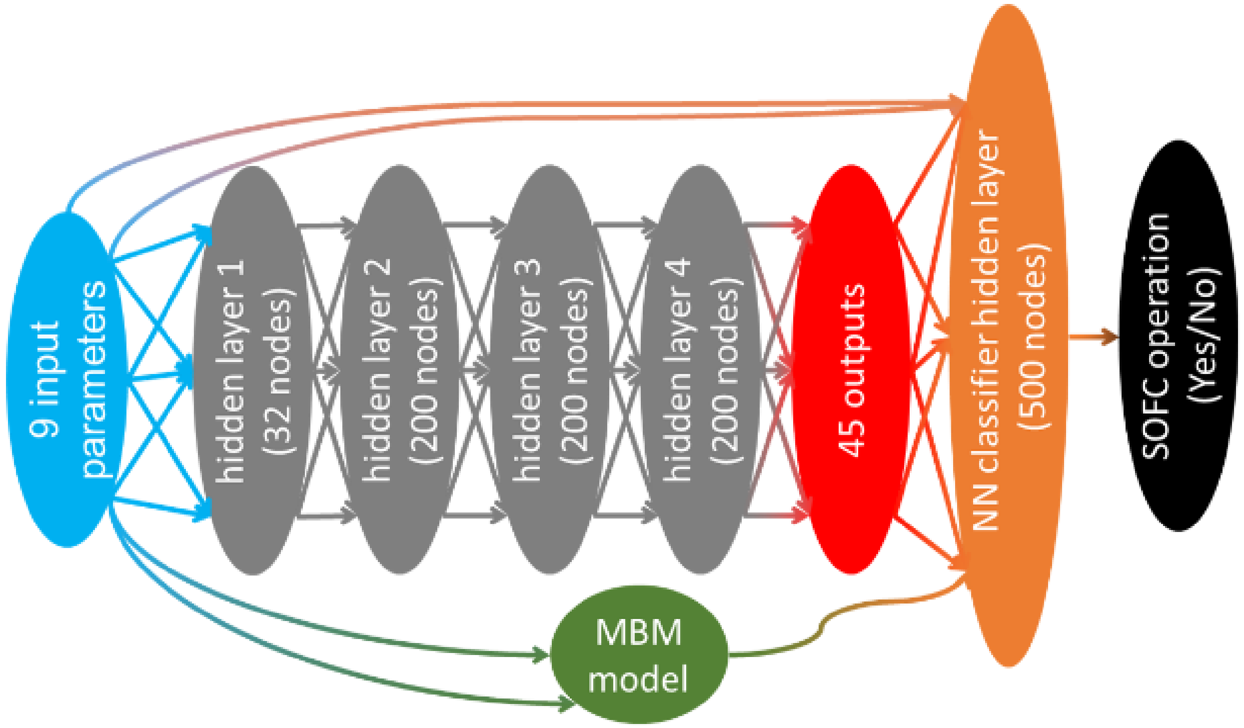




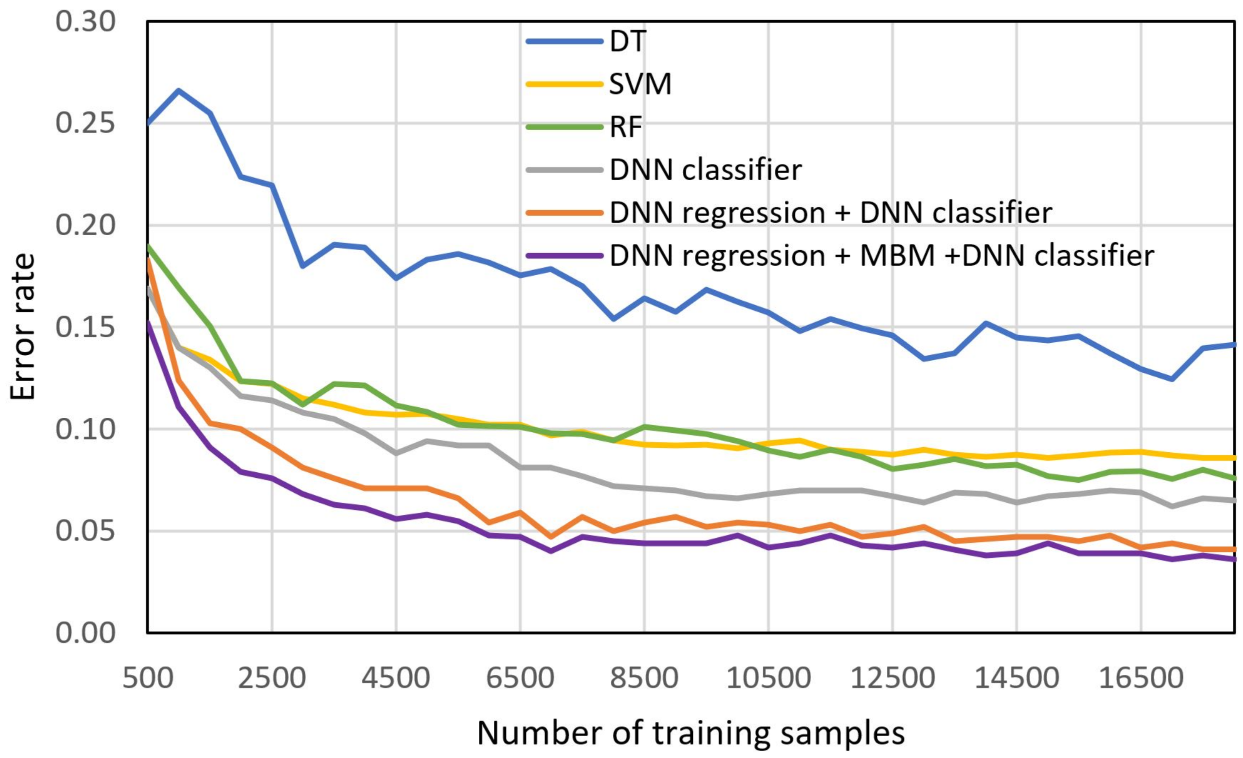
ROM w/ Machine Learning: Result Classification

- 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



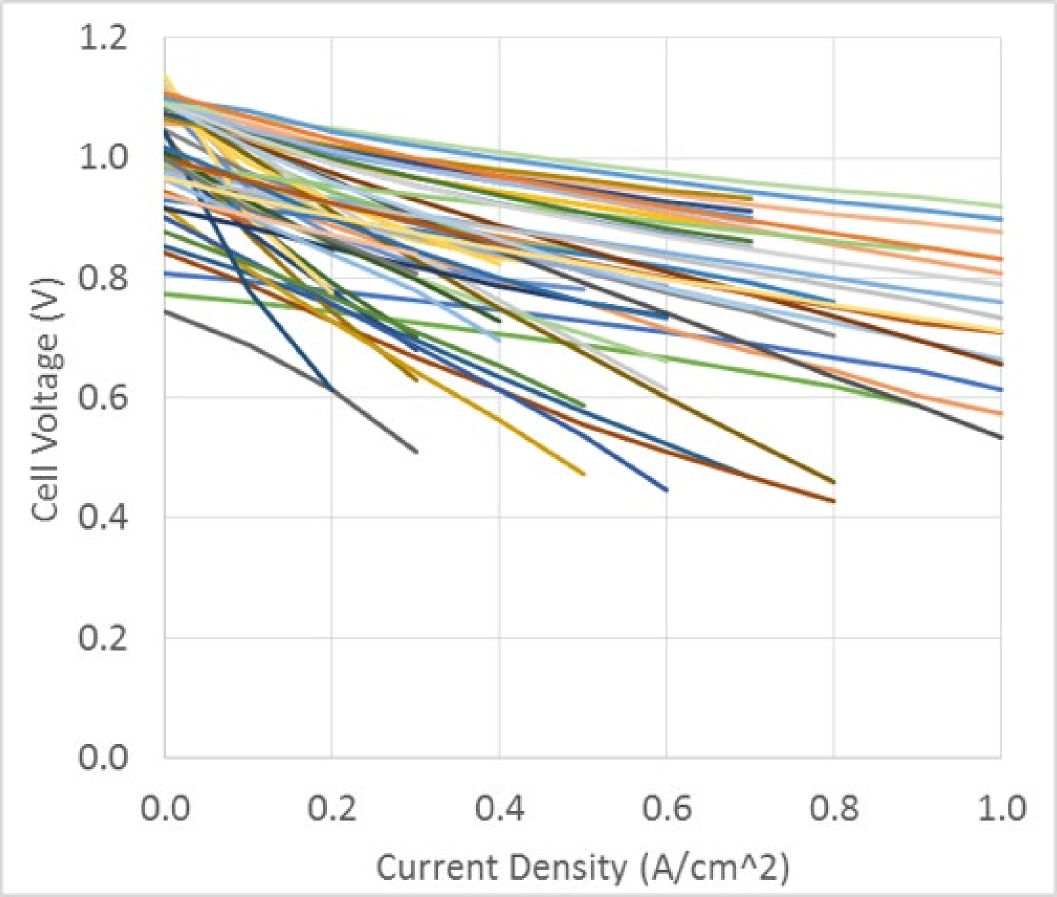
Comparison of Different Classifiers

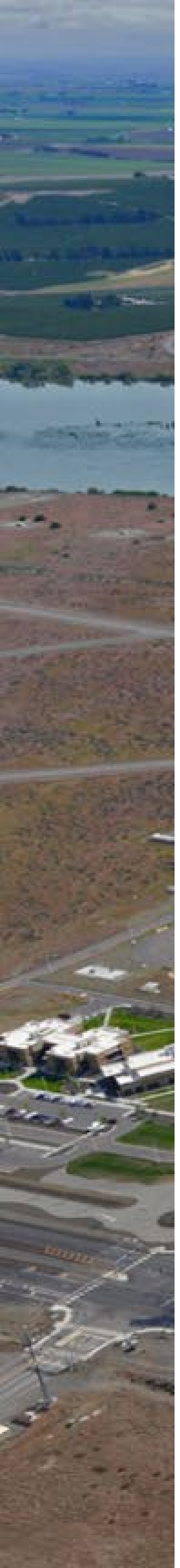


Stack State-of-Art Electrochemical Performance

- 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





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Overview: Short Term Reliability

Technical Challenge

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

Modeling Objective

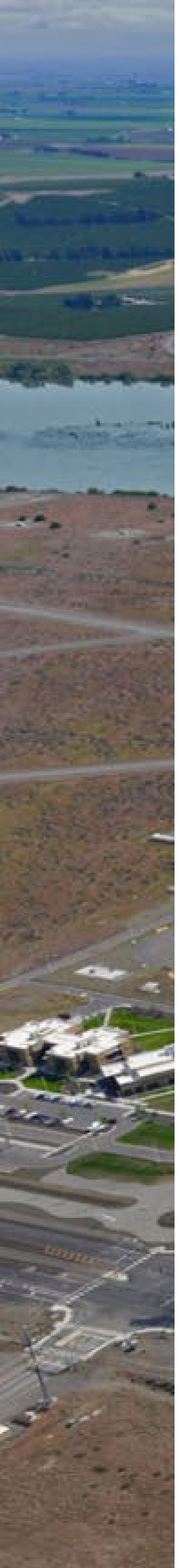
- Investigate influence of stack design, geometry, fuel composition and *identify conditions for high reliability*

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



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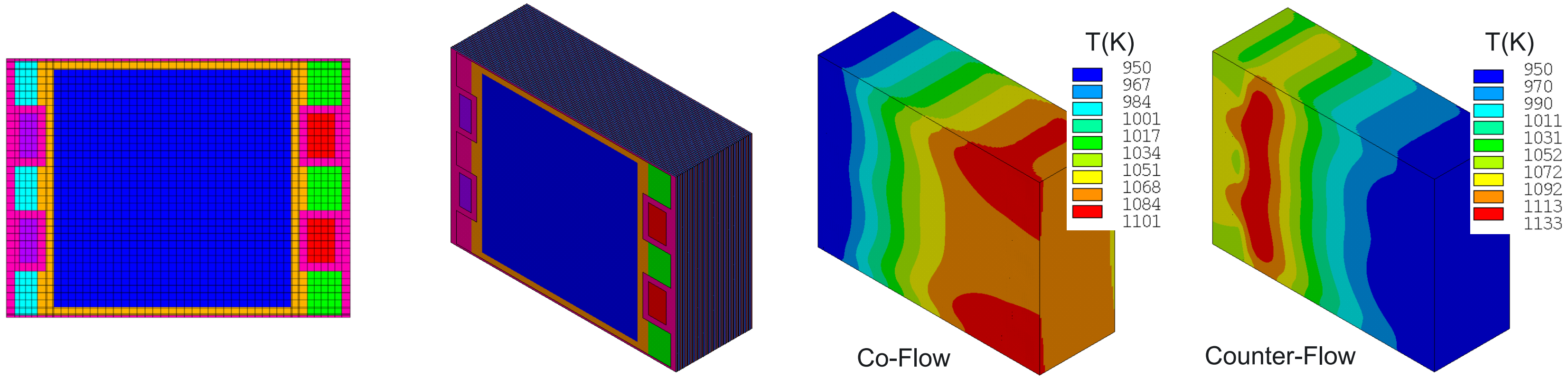
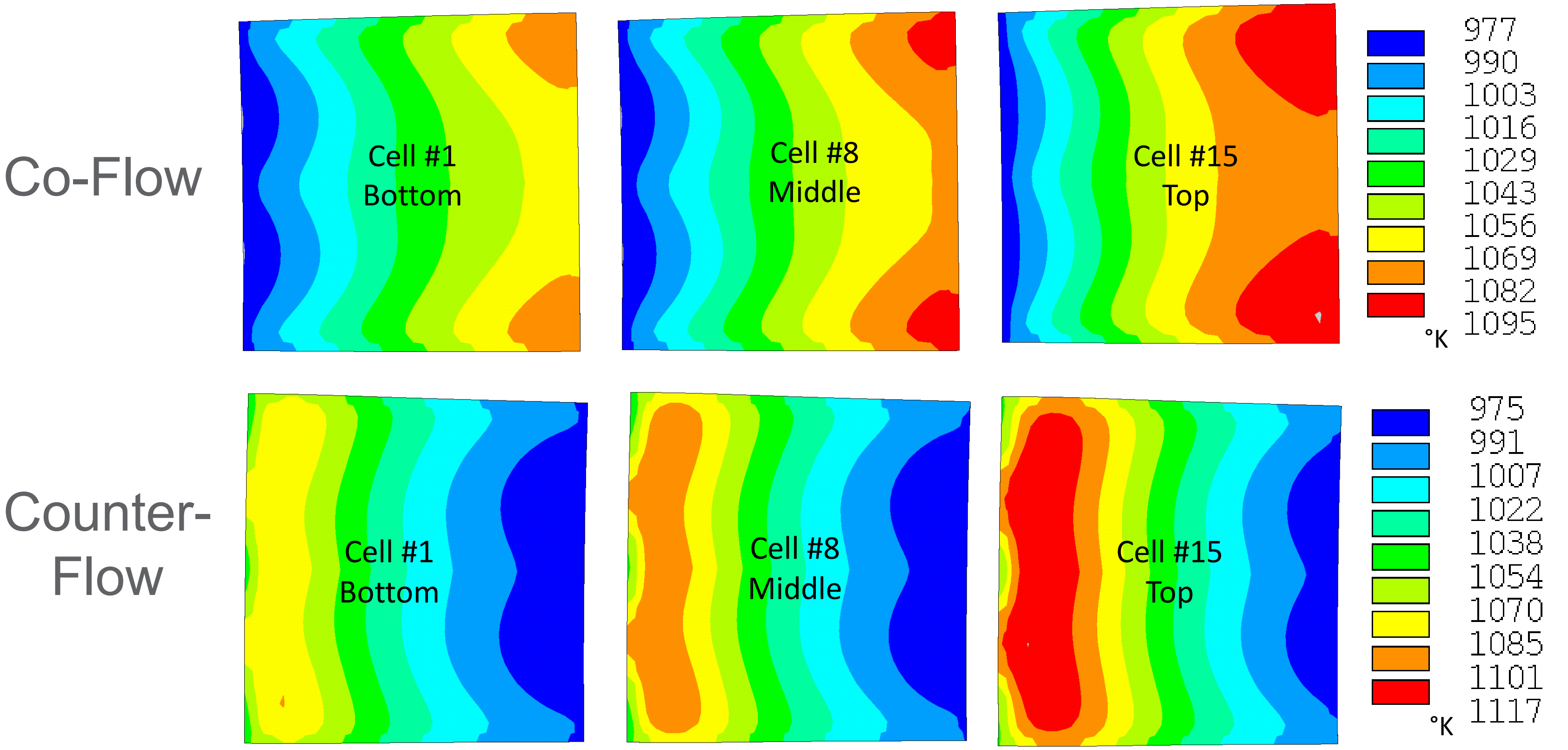
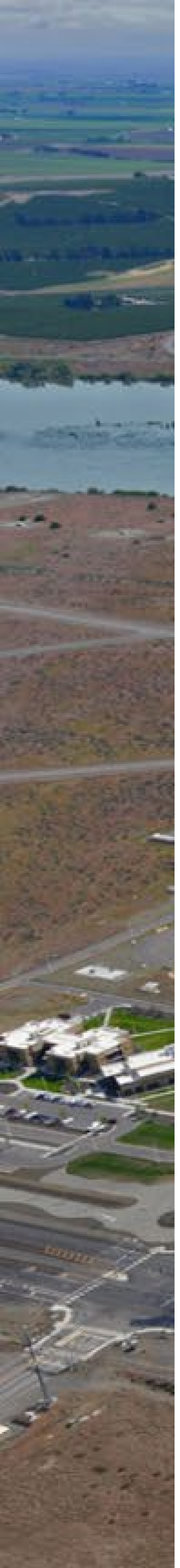
Beginning of Life (BOL) 3D Stack Evaluations

- 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







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Overview: Long Term Degradation

Technical Challenge

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

Modeling Objective

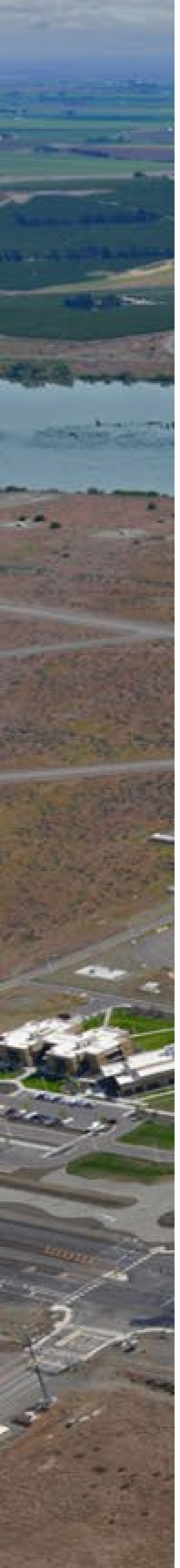
- Identify operating conditions for *optimal initial performance* and *minimal degradation*
- Investigate effect of creep on SOFC mechanical reliability

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.

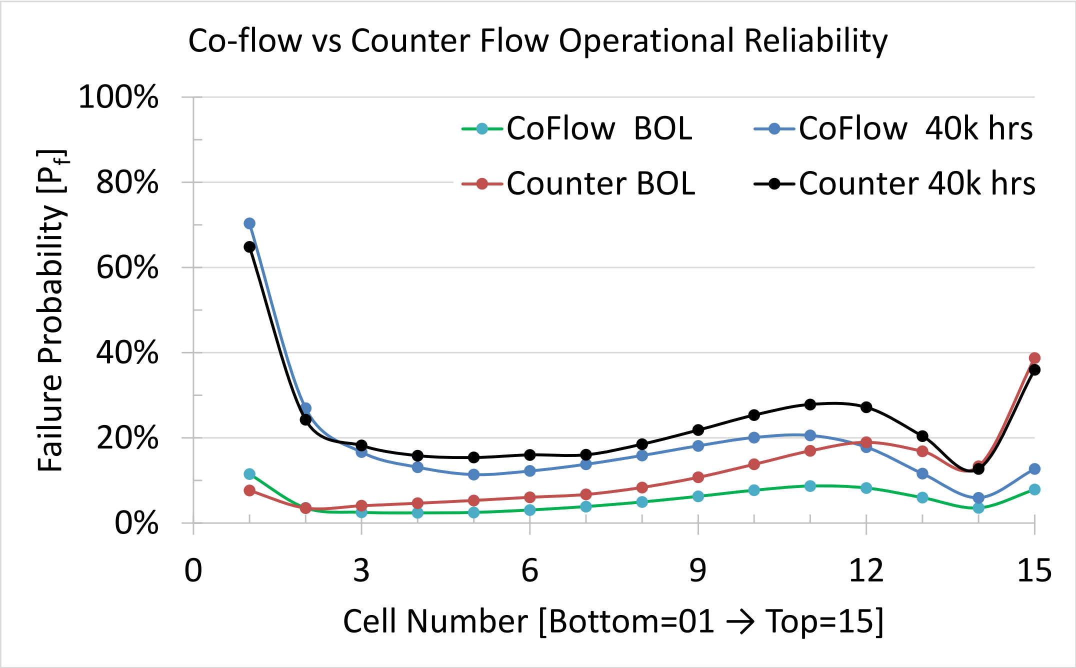
Recent Accomplishments

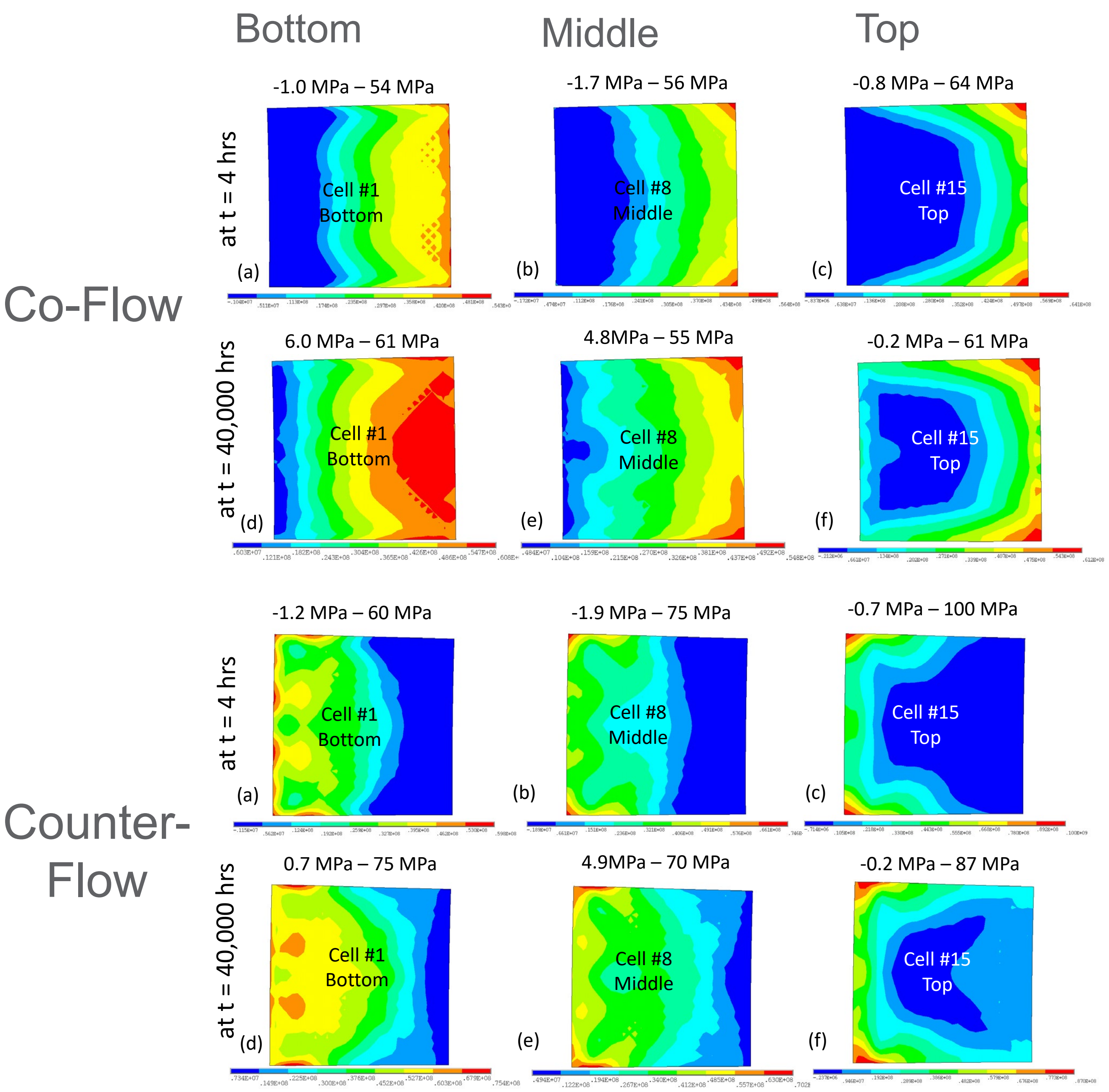
- Evaluated the performance and reliability of single and multi-cell SOFCs stacks under one or more degradation mechanisms
- Material creep model parameters were identified for the SOFC operational range (700 – 800°C)
- Evaluated influence of creep on stresses and reliability of generic multi-cell stack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

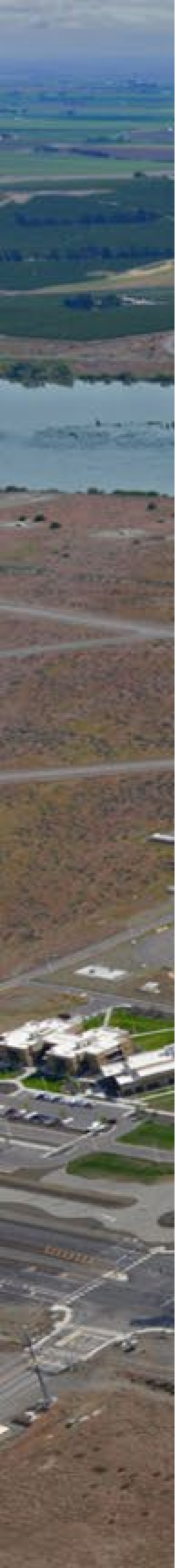


End of Life (EOL) 3D Stack Evaluations

- 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







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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

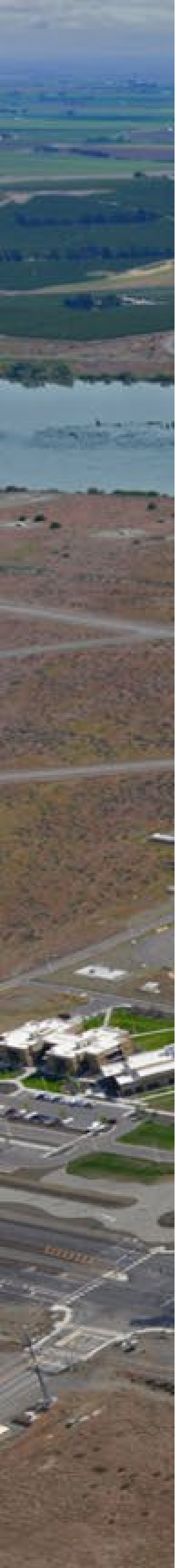
- *Predict progressive damage* of SOFC electrode and evaluate long-term reliability

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

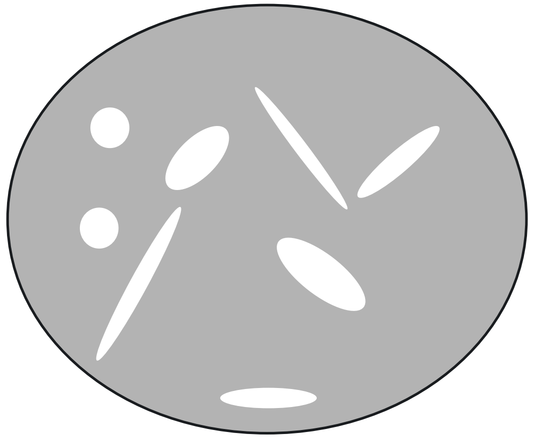
Recent Accomplishments

- 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

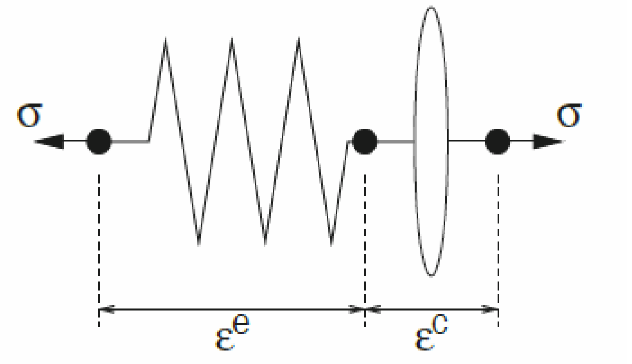


Damage Models for SOFC Cell Materials

- 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

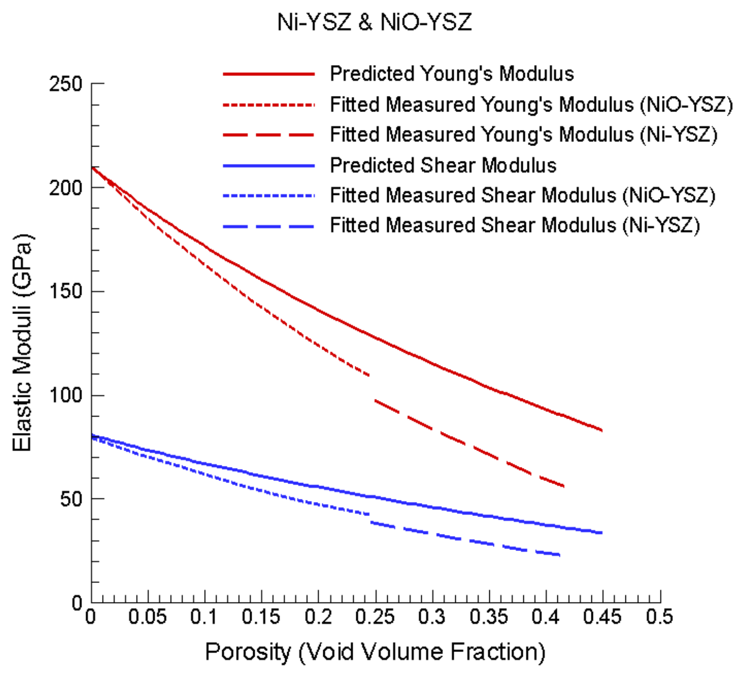


$\sigma = E\varepsilon^e \qquad \varepsilon = \varepsilon^e + \varepsilon^c$

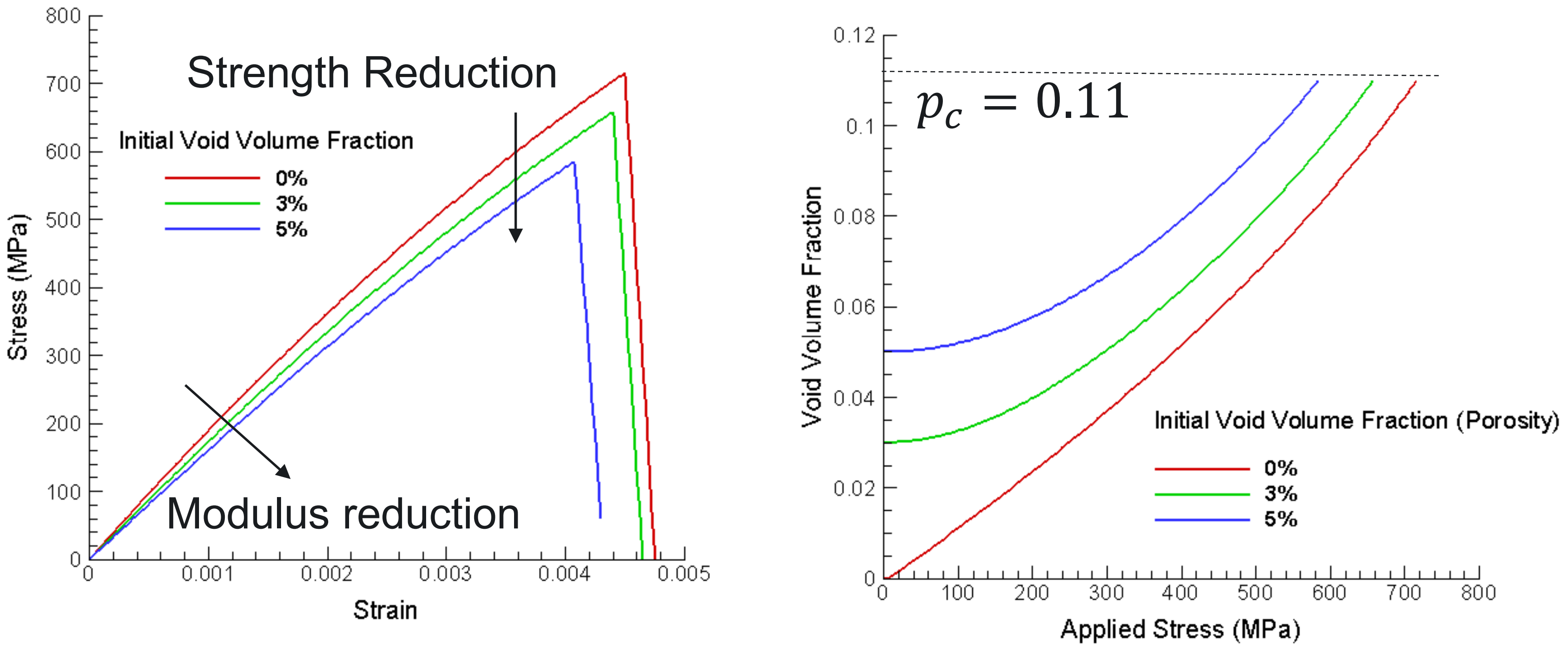
Continuum Damage Mechanics (CDM) Model

- 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



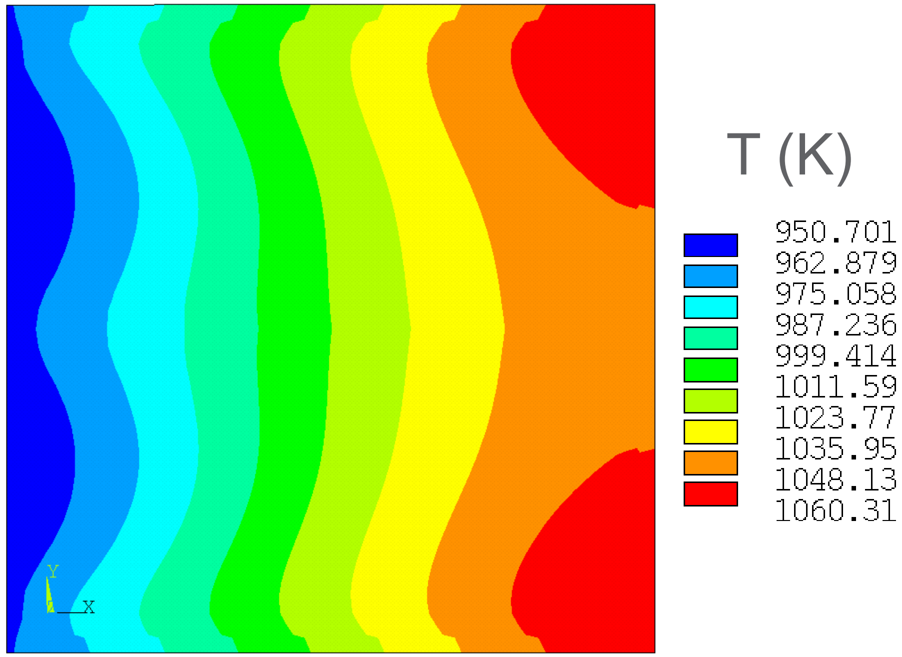
Strength Reduction Due to Damage



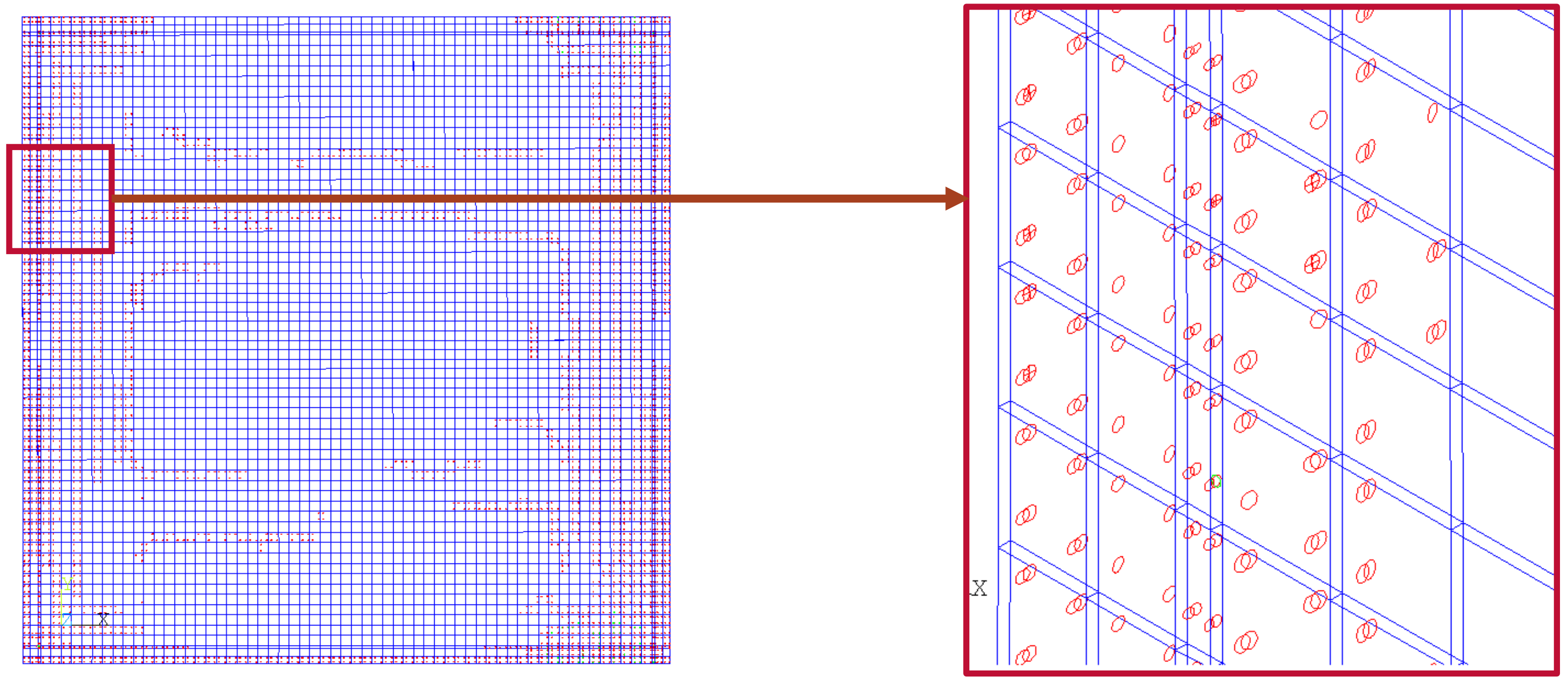
Smeared Crack Model (SCM)

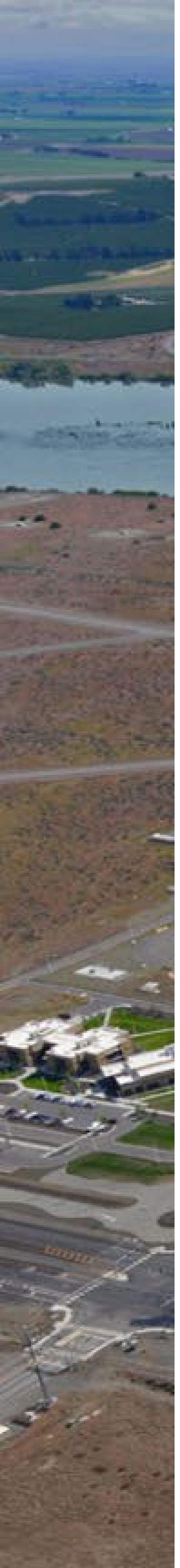
- Degradation due to cracking represented without discrete crack modeling
- Considers reduced strengths in compression, tension and shear after cracking
- Easy to implement with fewer material parameters than the CDM model, this model is used often for modeling brittle damage in concrete structures

Predicted Temperature



Anode Crack Density





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Thank you