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SOFC Development at PNNL: Overview

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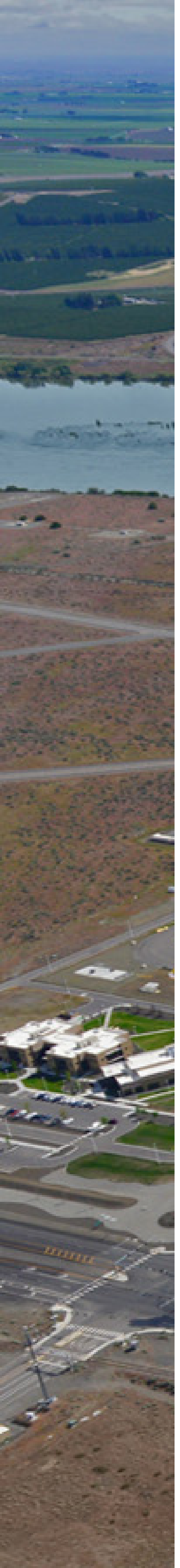
Scope of Work

- 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

- Core Technology Program
  - 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 (3-10 kW)



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Cr Poisoning

- Challenges
  - Quantitative understanding of threshold concentrations and mechanisms for Cr poisoning of SOFC cathodes
  - Mitigation of effects of volatile Cr species on cathode performance

- Approaches
  - Determination of relationship between Cr concentration in cathode air stream and rate of degradation in cathode performance
    - ✓ LSM and LSCF-based cathodes
    - ✓ **Poster: Effects of Cr Concentrations in Air on LSM/YSZ and LSCF Cathode Degradation (John Hardy)**
  - 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”)

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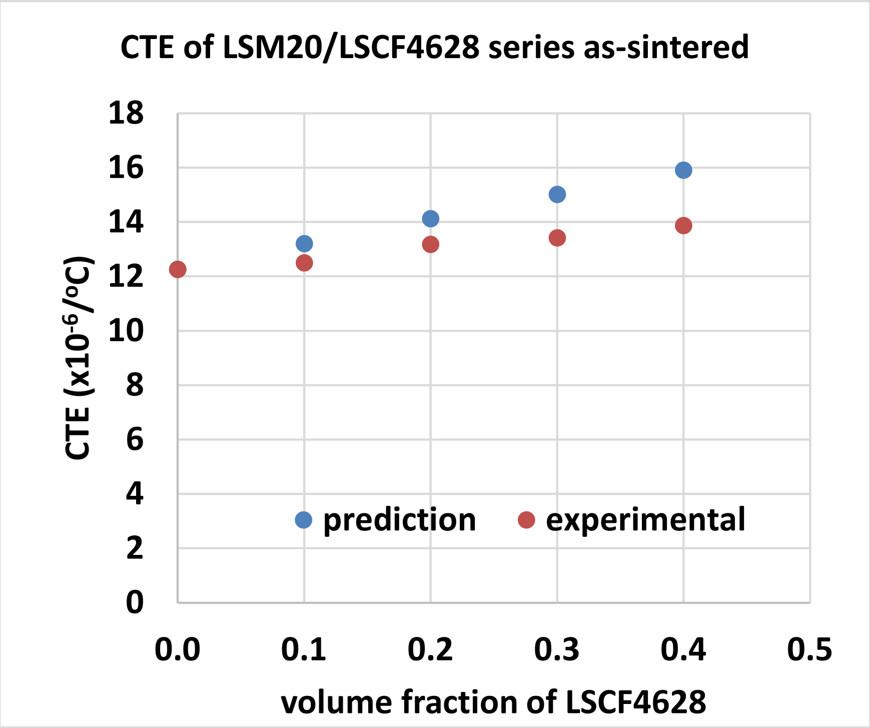
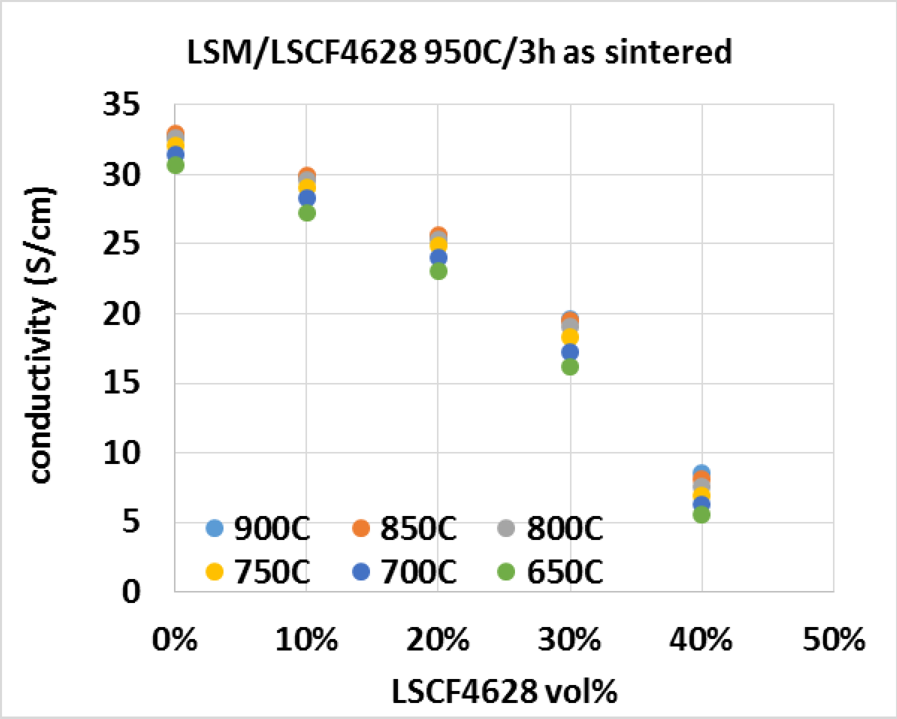
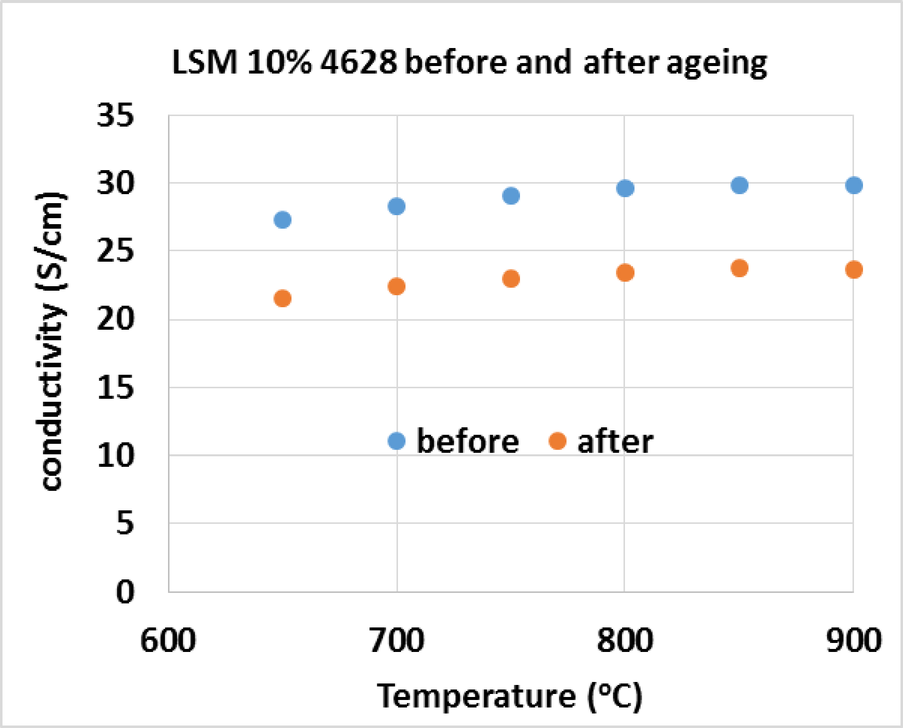
Cr Gettering Materials

- 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 mixtures as dual purpose cathode contact / Cr getter materials.



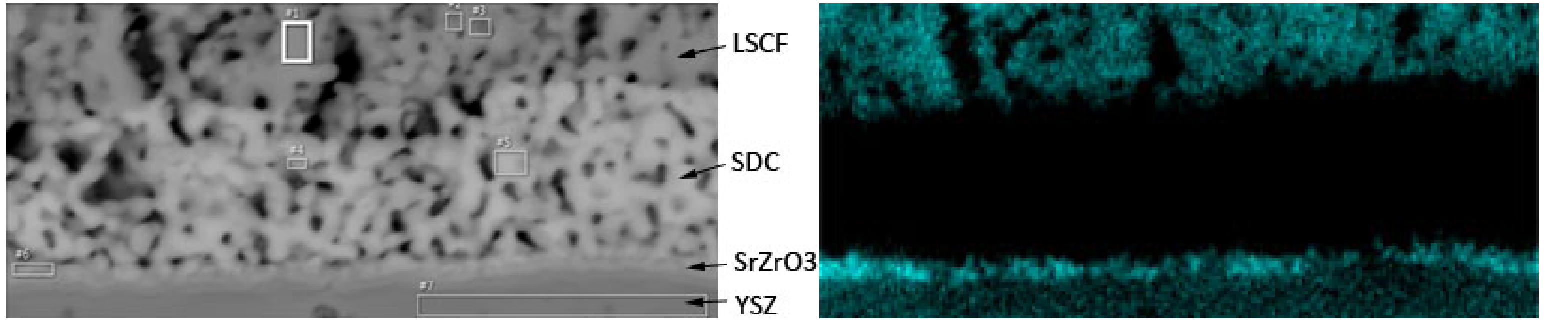




Poster: Cr Mitigation by LSM-LSCF Composites for Solid Oxide Fuel Cells (Matt Chou)

Ceria Barrier Layers: Sr Volatility

- Challenge
  - Increased cell resistance through formation of insulating Sr zirconate at ceria/electrolyte interface during sintering of LSCF-based cathodes with doped ceria barrier layers
  - After cathode sintering, Sr observed in cathode and at YSZ interface, but not in ceria layer



- Approach
  - Investigate likelihood of vapor phase transport of Sr from cathode to ceria/electrolyte interface

Poster: Investigating Sr Vapor Phase Evolution from LSM/YSZ and LSCF Cathodes During and After Sintering (John Hardy)

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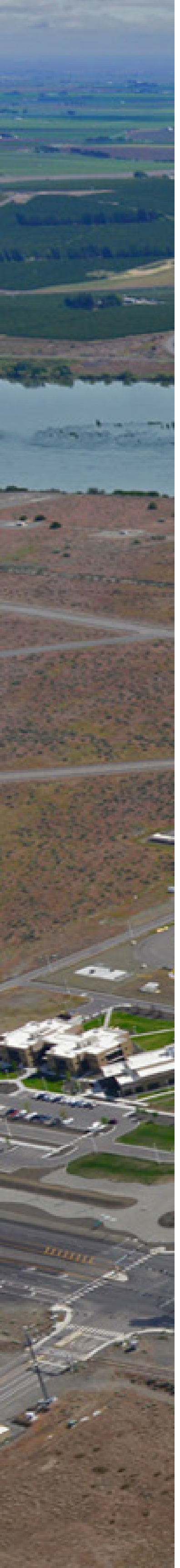
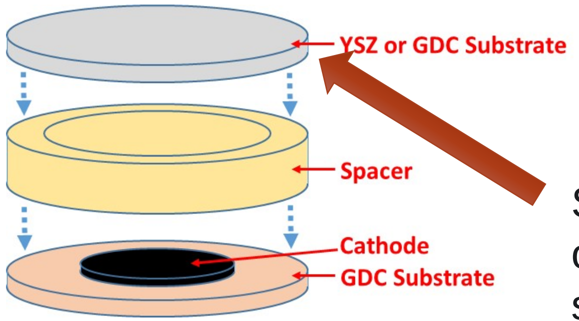
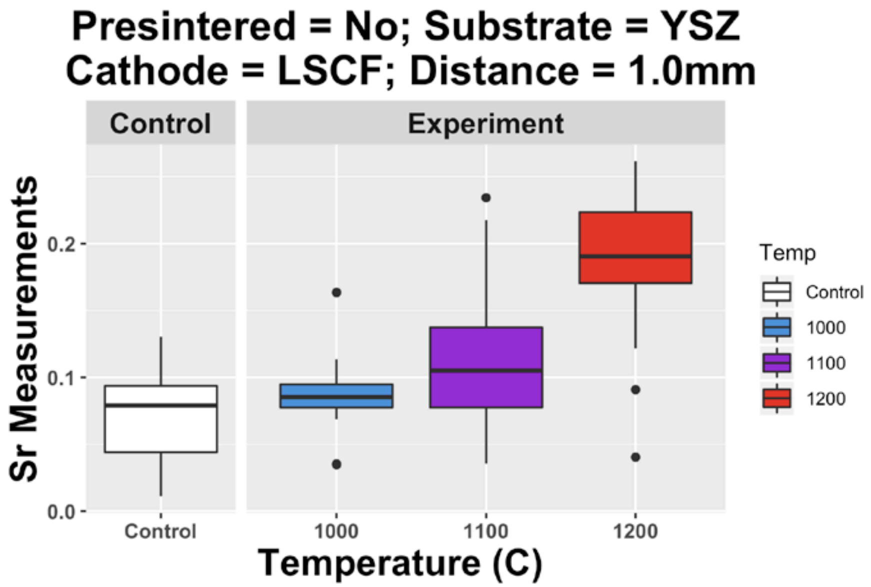
Ceria Barrier Layers: Sr Volatility



- Thermodynamic calculations show that SrO heated to 1100°C can produce Sr vapor pressures of the same order of magnitude as Cr vapor from chromia at 750°C.



SEM-EDS is performed on cathode-facing surface of top substrate



Variables	Settings
Cathode State	Sintered; Unsintered
Cathode Composition	LSM/YSZ; LSCF
Substrate (Sr Sink) Composition	GDC; YSZ
Spacer Thickness	1 mm; 10 mm
Test Temperature	1000°C; 1100°C; 1200°C
Time at Temperature	0.5 h; 2 h

As compared to unexposed substrates, statistically significant increase in Sr content was measured for tests with:

- No cathode presintering (vs 1100°C for 2 h)
- LSCF cathodes (vs LSM/YSZ)
- 1 mm distance to substrate (vs 10 mm)
- 1100 or 1200°C temperature (vs 1000°C)

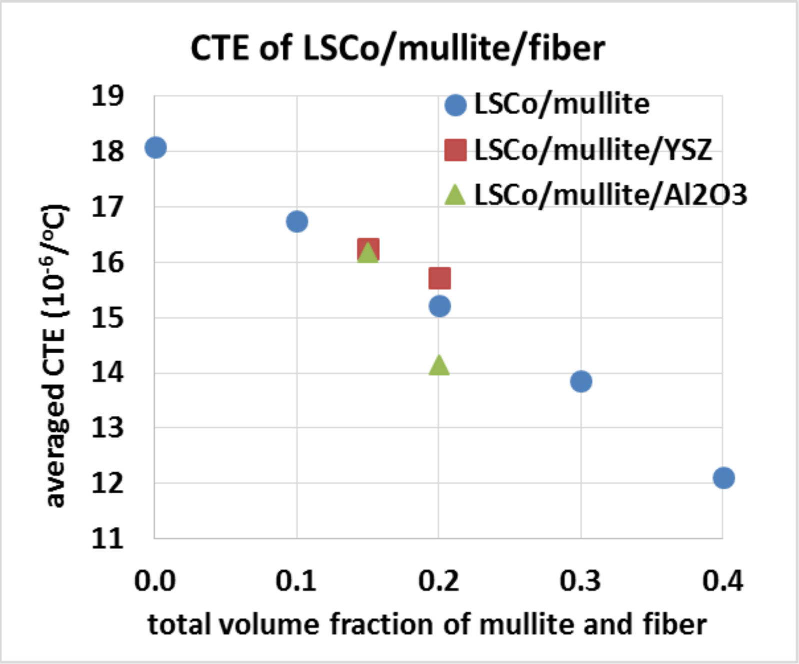
Cathode / Interconnect Contact Materials

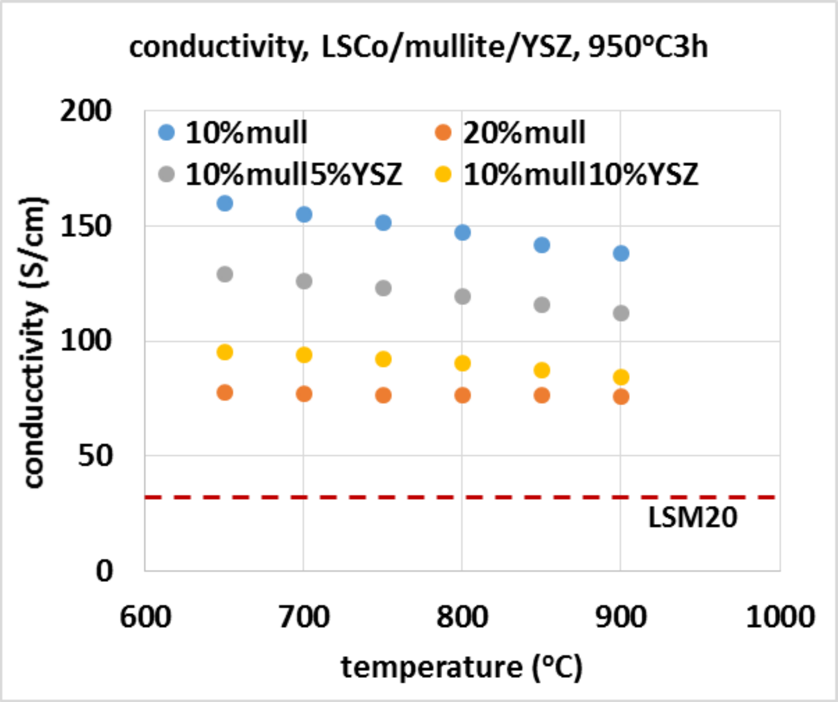
- Challenge
  - Electrical contact materials at cathode / interconnect interfaces in planar stacks tend to be mechanical “weak link,” especially during thermal cycling, due to brittle nature of ceramic materials and/or thermal expansion mismatch with adjacent components
    - ✓ Low processing temperatures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

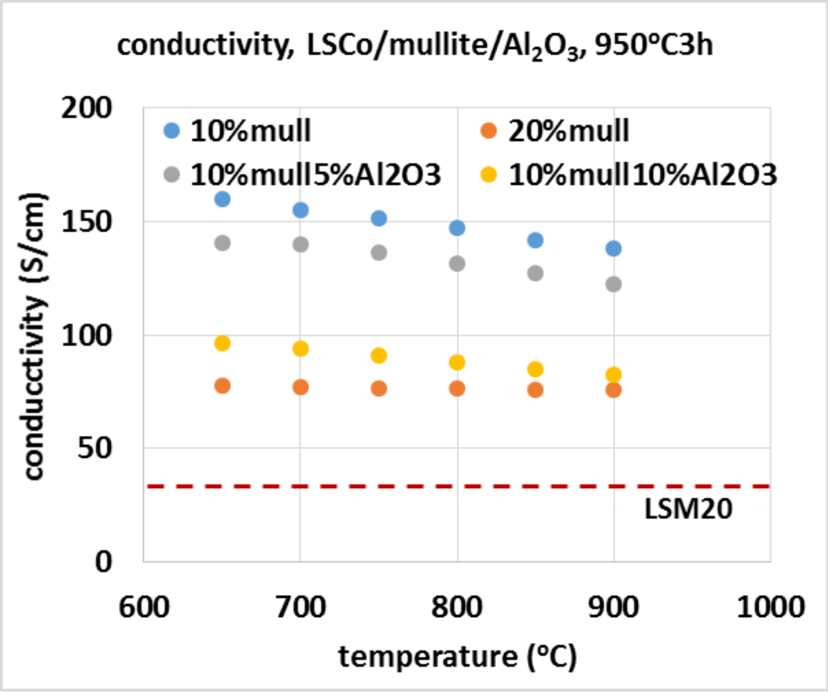
Poster: Composite Cathode Contact Material Development - Validation in Stack Fixture Test and Effect of Strong Fibers (Matt Chou)

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 fibers with high elastic modulus (YSZ or Al_2O_3)

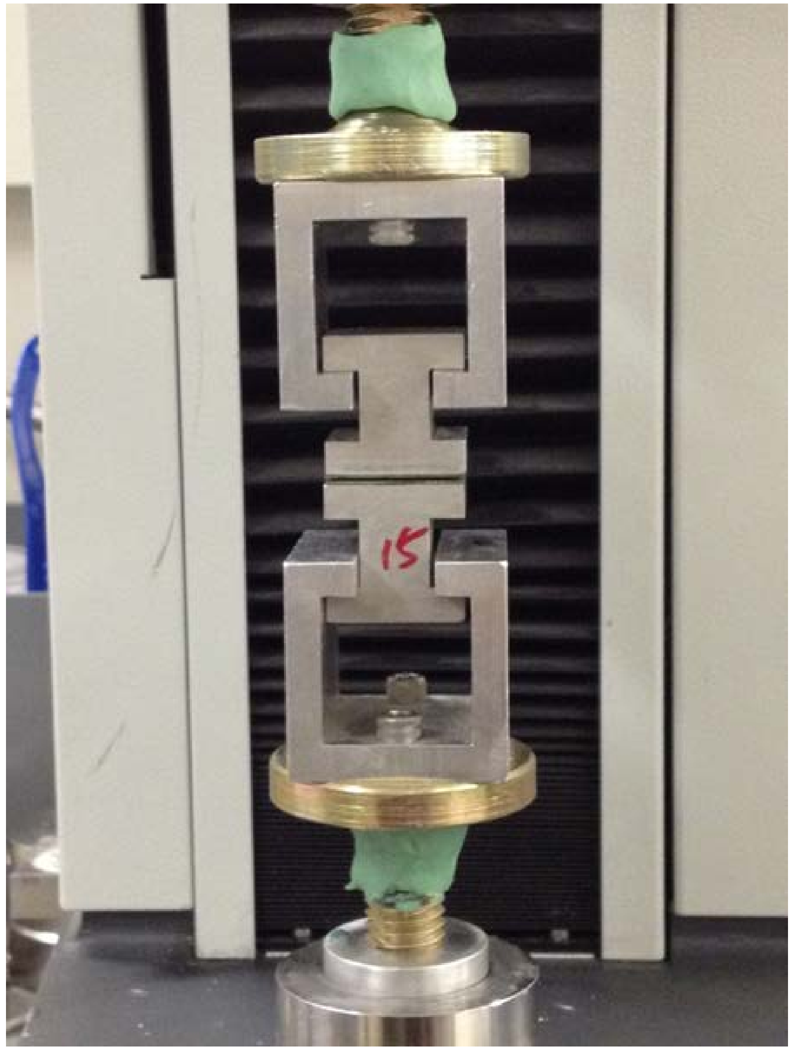






LSCo / mullite / fiber composite contact materials

- Presence of short fibers enhanced the contact bonding strength, initially and after 10 thermal cycles



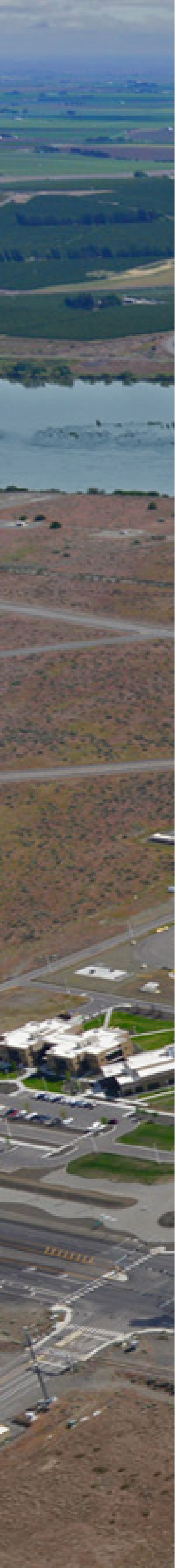
850^{o}C3h sintered	as-sintered		after 10 TC	
Materials	strength (MPa)	stdev (MPa)	strength (MPa)	stdev (MPa)
LSCo	0	na	0	na
LSCo/10%mull	0	na	0	na
LSCo/10/5%Al_2O_3	2.08	0.81	2.11	0.51
LSCo/10%mull/10%Al2O_3	1.74	0.44	1.89	0.56

950^{o}C3h sintered	as-sintered		after 10 TC	
Materials	strength (MPa)	stdev (MPa)	strength (MPa)	stdev (MPa)
LSCo	0	na	0	na
LSCo/10%mull	0	na	0	na
LSCo/10/5%Al_2O_3	3.25	1.09	3.44	1.19
LSCo/10%mull/10%Al2O_3	2.72	0.8	2.68	0.46

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



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Co-free Electrically Conductive Protective Coatings: DoE Optimization of Spray Coating Parameters

Table of Factors and Levels for DoE Optimization

Factors	Level 1	Level 2	Level 3	Level 4
Viscosity	37cP	17cP	9cP	5cP
Coating speed	40mm/sec	60mm/sec	80mm/sec	100mm/sec
Head height	15mm	25mm	35mm	45mm
Ink feeding rate	0.5ml/sec	1ml/sec	1.5ml/sec	2ml/sec
Air flow rate	30ml/sec	40ml/sec	50ml/sec	60ml/sec

Optimized Conditions for each Candidate Composition

Composition	Viscosity	Coating speed	Head height	Ink feeding rate	Air flow rate
($Cu_{1.3}Mn_{1.7}O_4$)	3	4	1	1	2
($Cu_{1.5}Mn_{1.5}O_4$)	3	3	4	1	2
($NiMn_2O_4$)	4	4	1	3	2
($Ni_{1.5}Mn_{1.5}O_4$)	4	4	2	3	2
($Cu_{1.5}Fe_{1.5}O_4$)	4	4	2	2	2
($CuFe_2O_4$)	4	4	4	3	1

Preliminary coating characterization has been completed

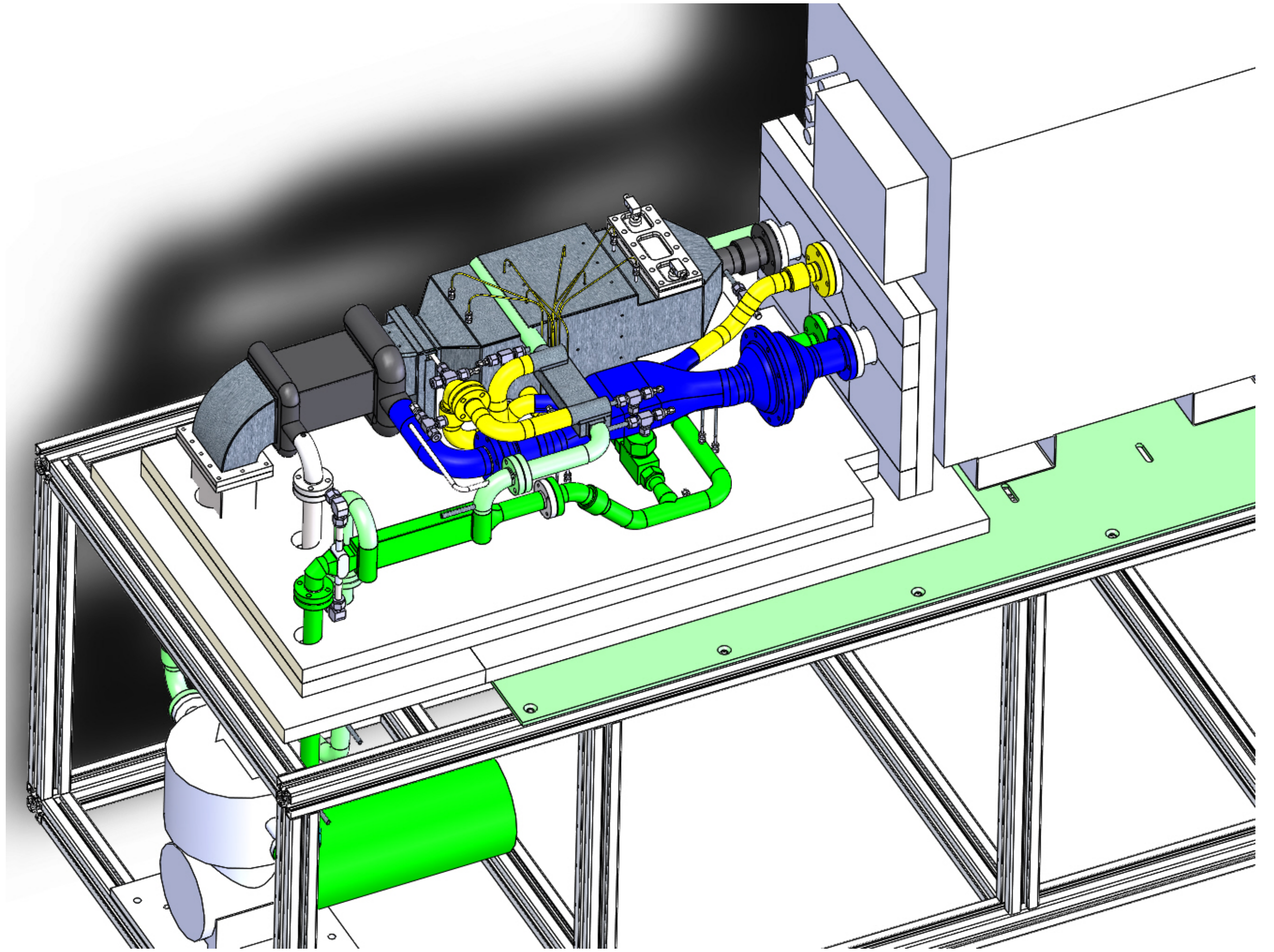
Isothermal (800 and 900°C) and thermal cyclic testing is in progress

Poster: (M, Mn or Fe)$_3$O$_4$ spinel for Advanced Electrical Conductive Layer for SOFC Stacks (Jung-Pyung Choi)

Small-Scale SOFC Test Platform

- Purpose:
  - Evaluate performance and reliability of emerging stack technologies (3-10 kW) under realistic operating conditions
  - Estimated completion: May, 2019

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

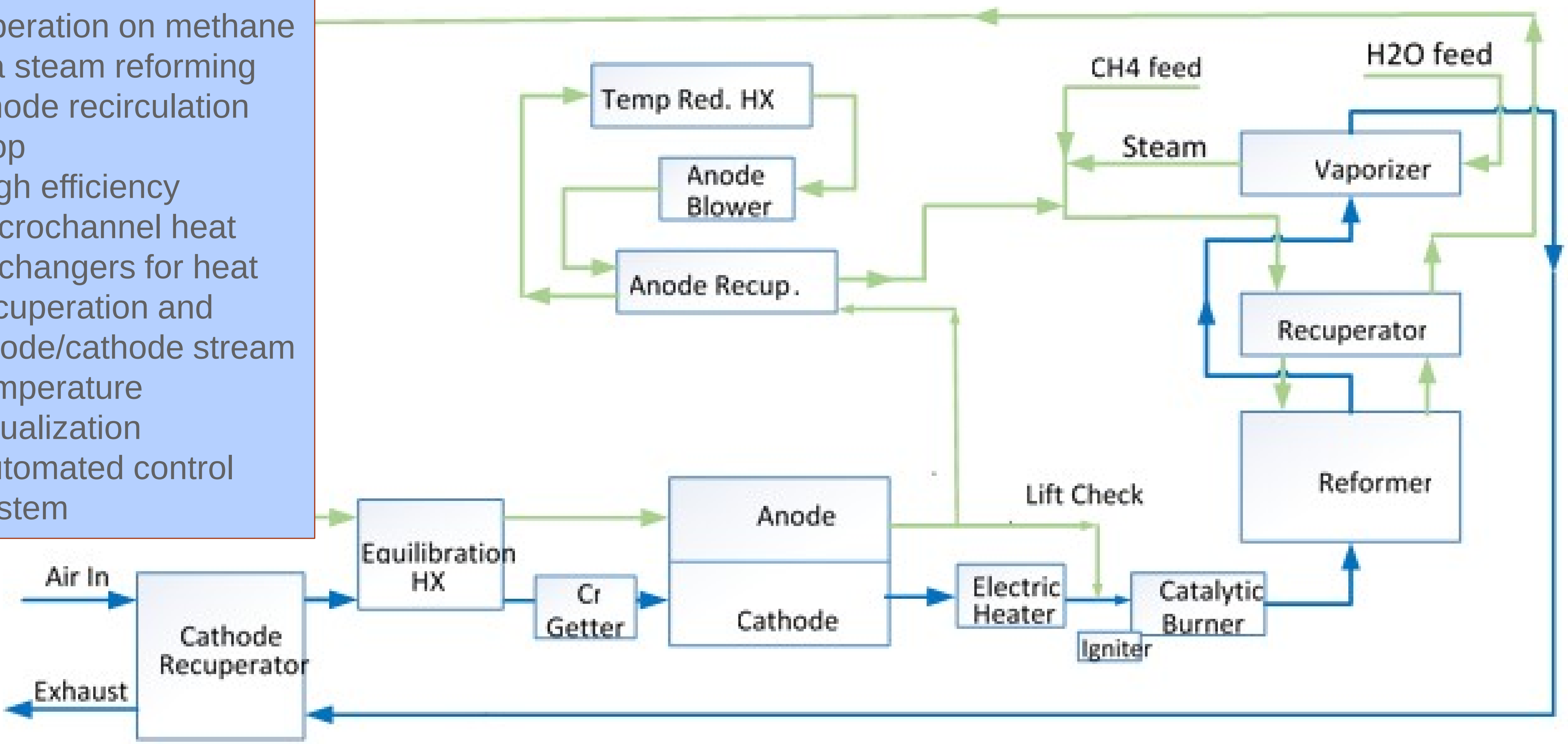


Poster: Small-Scale SOFC Test Platform (Brent Kirby)

Small-Scale SOFC Test Platform

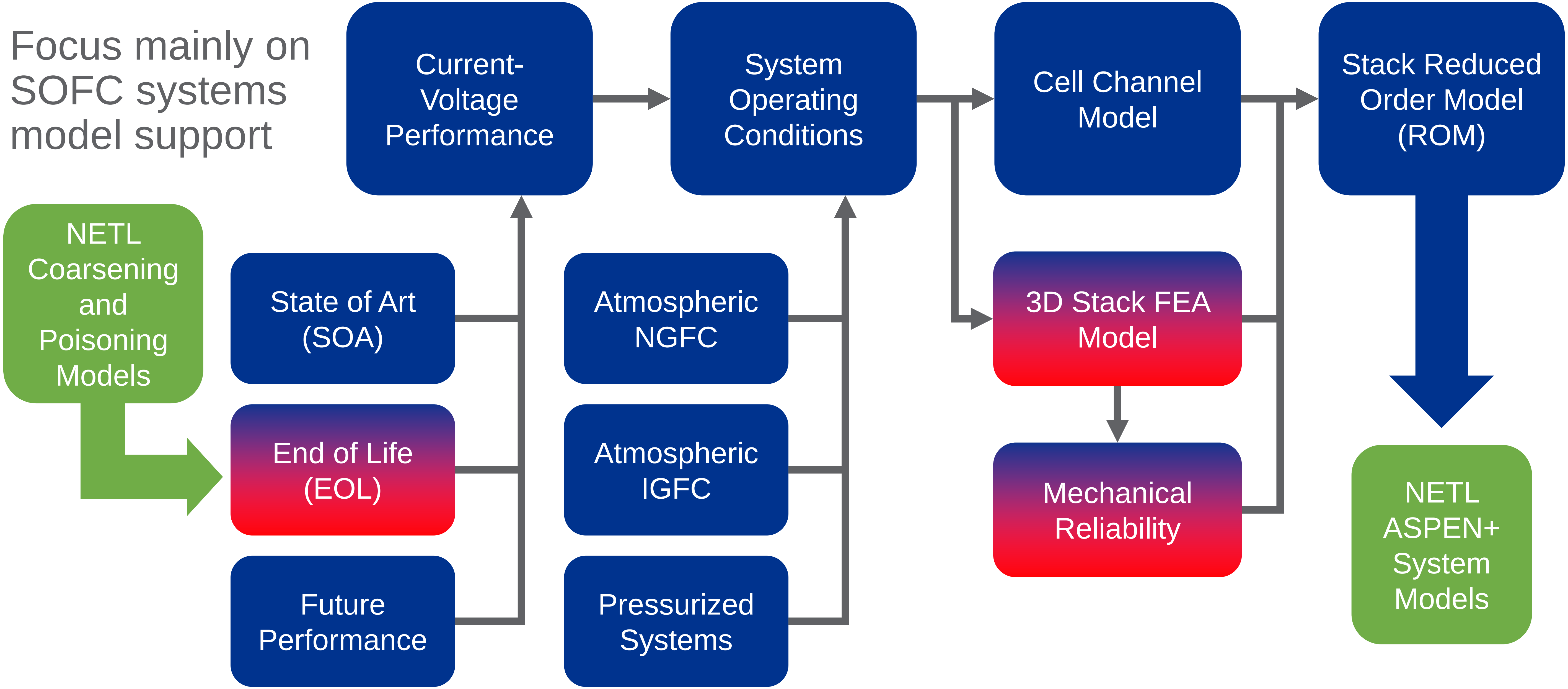
Key features:

- 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



Focus of Current PNNL Modeling Efforts

Focus mainly on SOFC systems model support



Modeling Tools and Analysis Overview

Challenges:

- Develop modeling **tools** to evaluate SOFC behavior
- Integrate modeling results at different **scales** to improve design
- Understand performance **degradation** mechanisms and control strategies

FY19 Approach:

1. Develop ROMs to support NETL system evaluations
   - ✓ Provides more accurate stack representation for system design
   - ✓ **Poster: Use of Reduced Order Models (ROMs) to Predict SOFC Stacks Performance (Jie Bao)**
2. Evaluation of Cr poisoning
   - ✓ Incorporate NETL model to understand long-term performance impacts at the stack level
3. Evaluation of creep
   - ✓ Use FEA to understand time-dependent deformation on mechanical reliability of the stack
   - ✓ **Poster: Influence of Anode Creep on the Structural Reliability of SOFCs (Brian Koeppel)**
4. Evaluation of metal-supported cells

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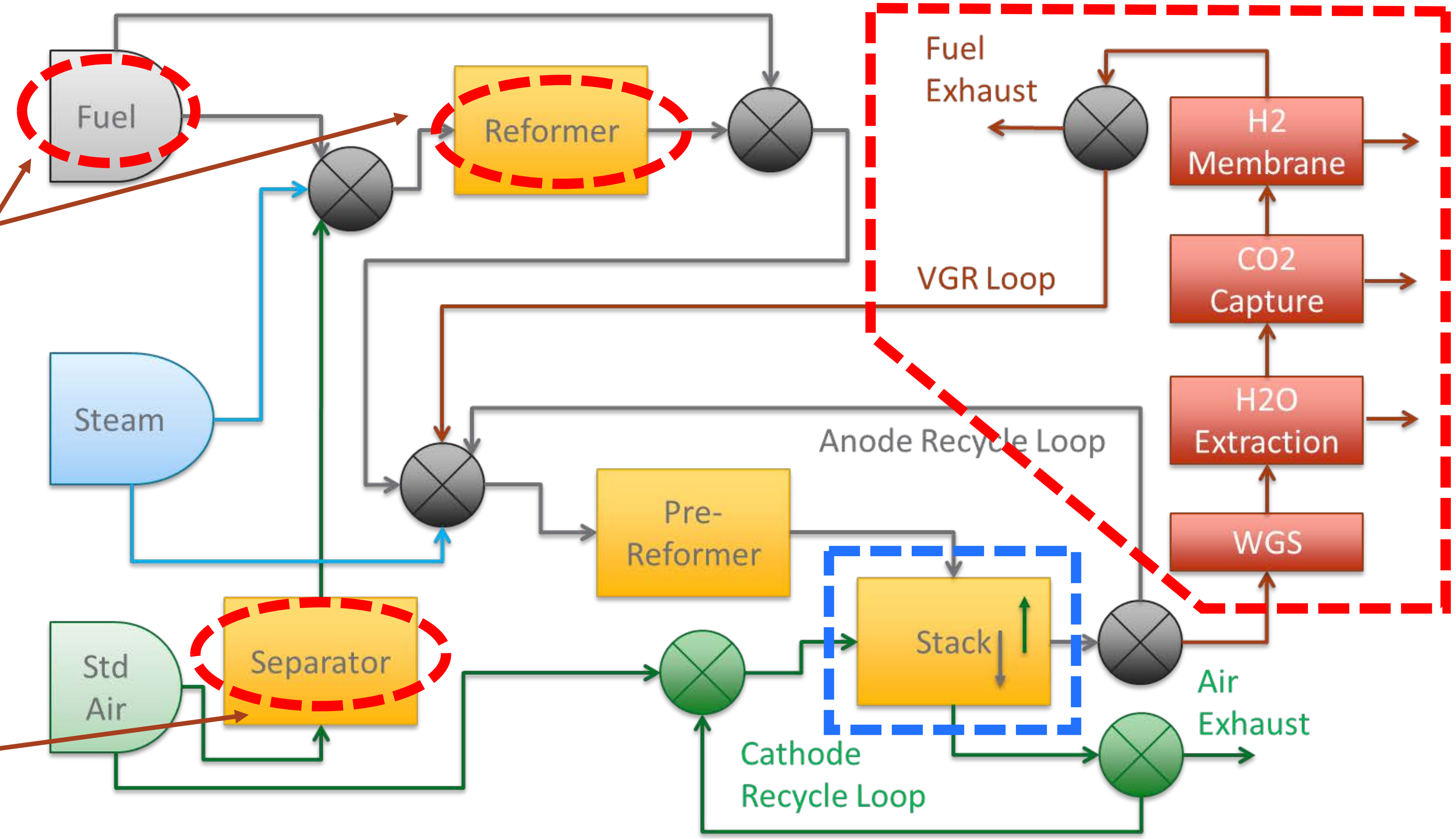
1A. Generic Material Flowchart for ROM

***NGFC**: Natural gas fuel w/ external reformer*

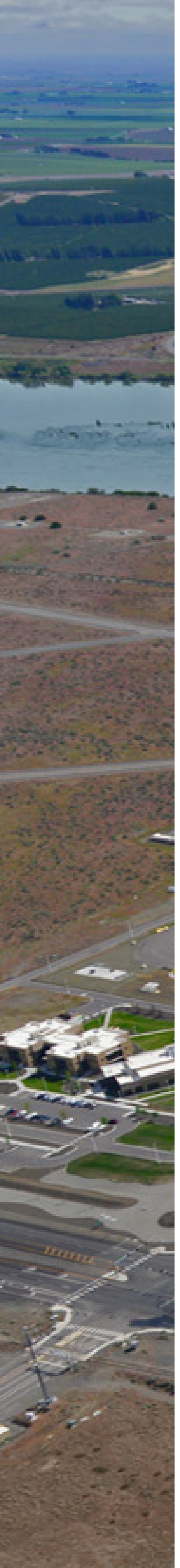
***IGFC**: Syngas fuel w/o external reformer*

***CCS**: w/ O_2 separator*

***No CCS**: w/o O_2 separator*



***VGR**: vent gas recirculation concept*



1A. ROMs Generated for Various SOFC Systems

- Provided 23 ROMs to NETL for supporting Pathway Studies
  - **Type**: Natural gas fuel cell (**NGFC**), integrated gasification fuel cell (**IGFC**-conventional, enhanced, and catalytic);
  - **Pressure**: atmospheric or pressurized;
  - **Performance**: state-of-art (SOA), future performance with reduced cell losses;
  - **Configuration**: with or without carbon capture (**CCS or w/o CCS**), inclusion of vent gas recirculation (**VGR**).

Average Current Density	2000-6000 A/m^2
Internal Reforming	0-100%
Oxidant Recirculation	0-80%
Oxygen-to-Carbon Ratio Target @ Stack Inlet	1.5-3.0
Fuel Utilization (including recirculation loop)	40-95%
Oxidant Utilization (including recirculation loop)	12.5-83.3%
Oxidant Stack Inlet Temperature	550-800^{o}C
Fuel Loop Inlet Temperature	15-600^{o}C
System Pressure	1-5 atm
Vent Gas Recirculation	30-97%

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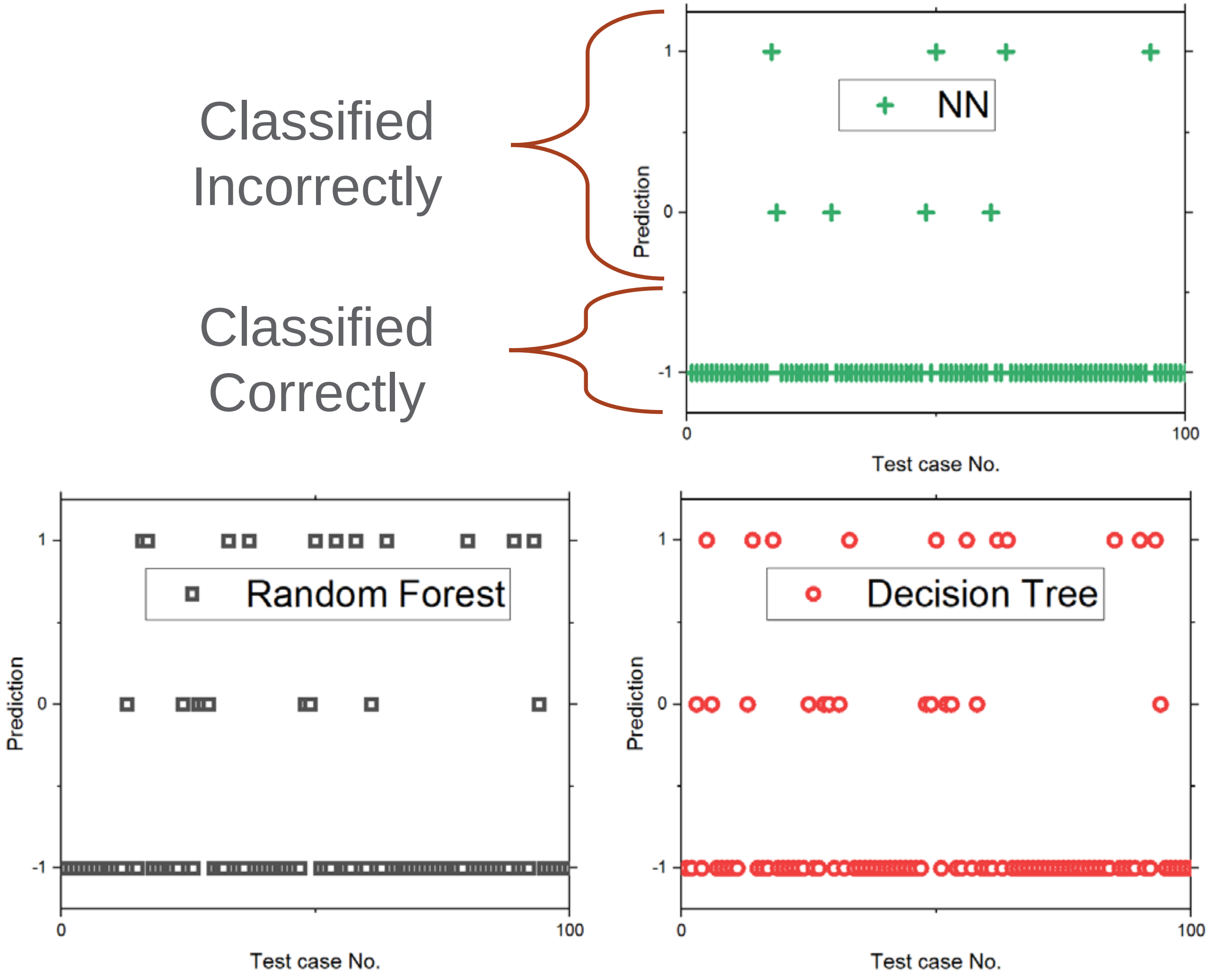
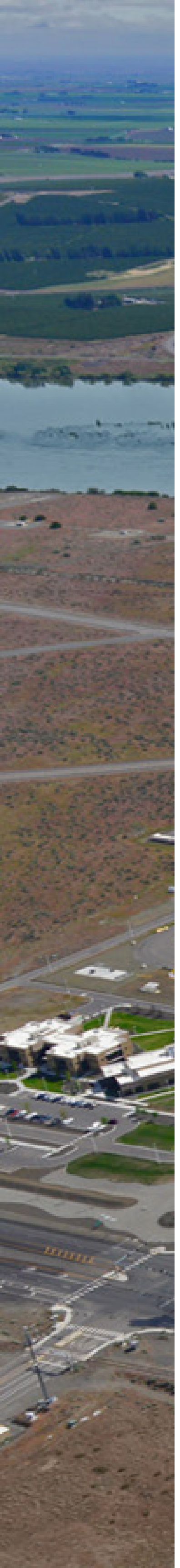
1B. Machine Learning (ML) Classification

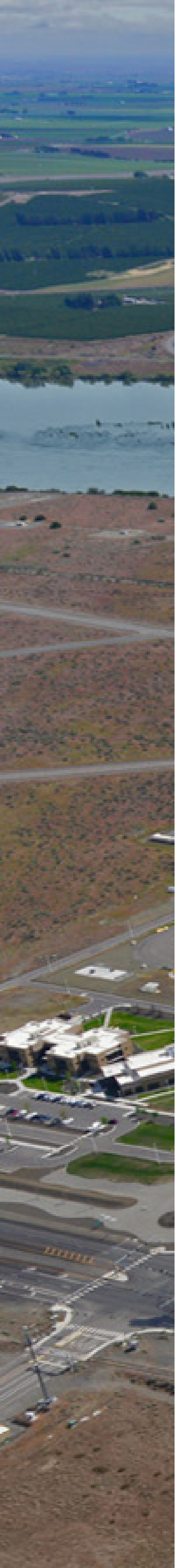
- **Issue**: ROM will provide a result for non-physical parameter combinations
- **Goal**: Identify true operating domain
- **Approach**:
  - Implement ML methods: support vector machine (SVM), random forest, decision tree, and neural network (NN)
  - Apply cross-validation to determine prediction accuracy
- **Results**:

ML Method	Prediction Accuracy
NN	93.0%
SVM	91.4%
Random Forest	89.0%
Decision Tree	82.6%

Evaluation of 100 Non-Physical Cases



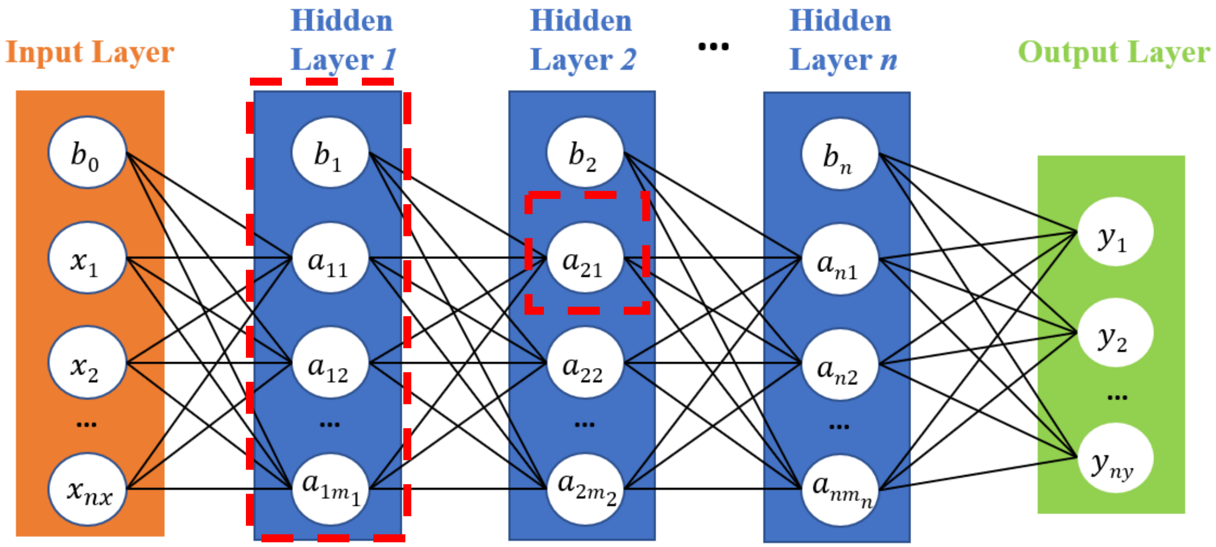




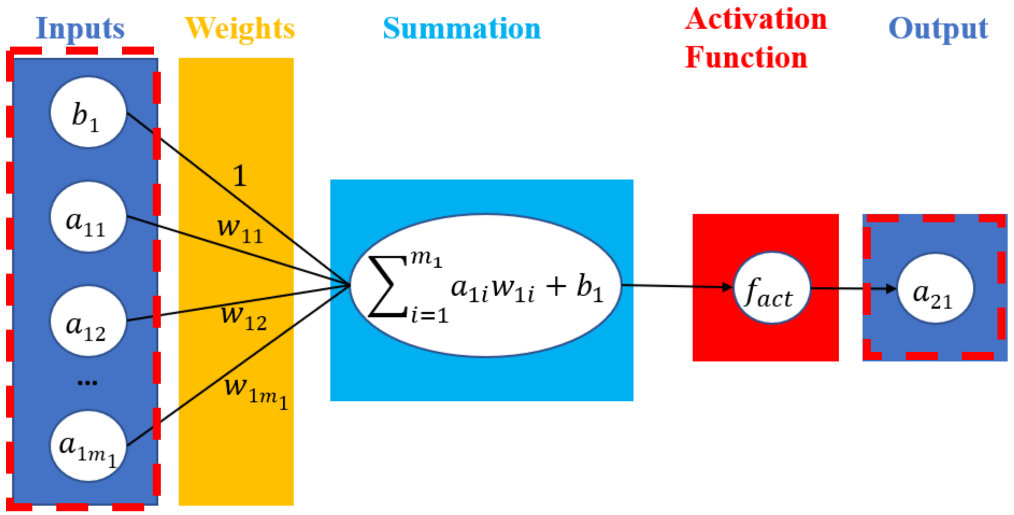
1C. Use of ML for ROM Generation

- **Goal**: Evaluate deep learning regression-based ROM as alternative to the Kriging regression-based ROM to predict SOFC stack performance
- **Approach**: Built a deep neural network (**DNN**)-based ROM
- **Results**: DNN ROM can provide **better prediction accuracy and reduce the prediction error by a factor of 2-3** compared with existing Kriging ROM

General DNN Framework

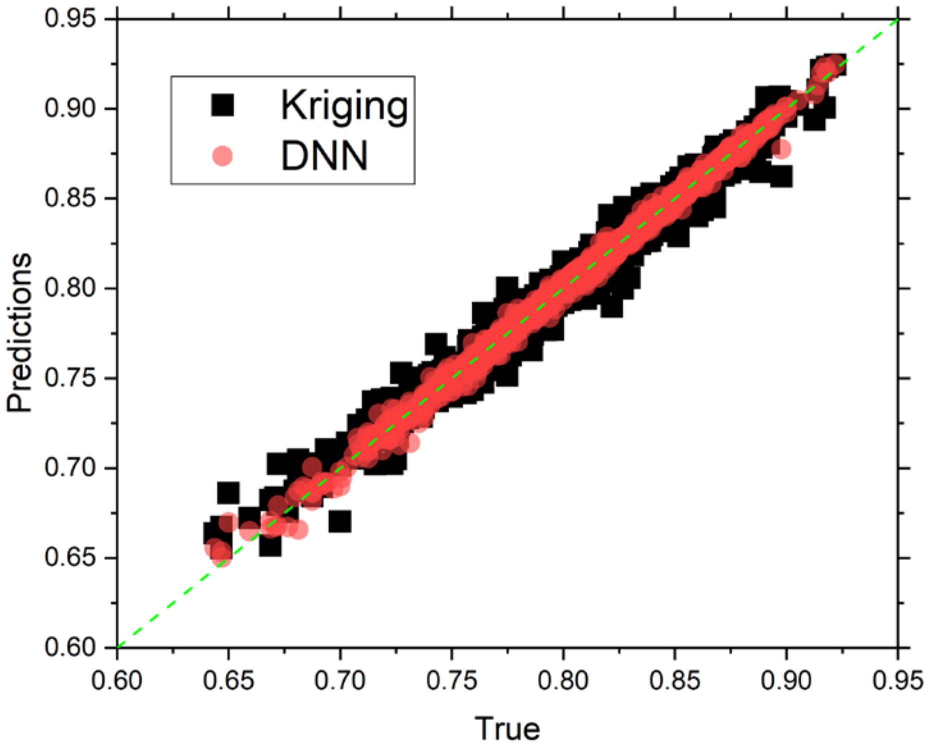


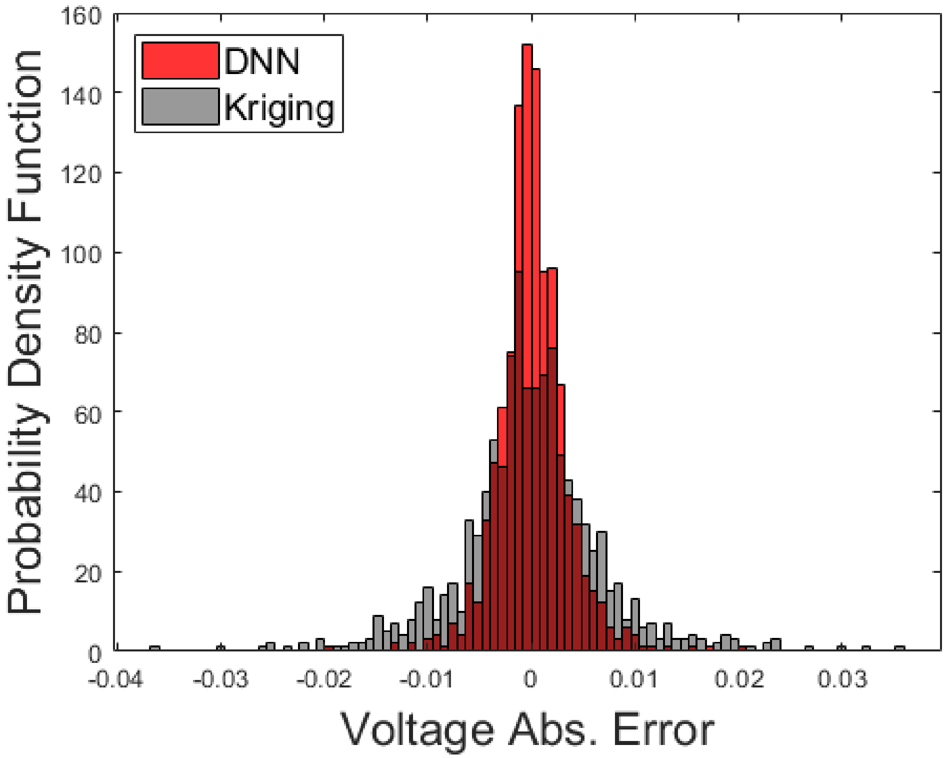
Algorithm of Individual Neuron



1C. Deep Learning (DL) vs. Kriging ROM Results

Voltage Prediction Results





Parameters from PDF	DNN	Kriging	Improvement Ratio
UB for 95% CI	0.0057	0.0135	**2.36**
LB for 95% CI	-0.0060	-0.0136	**2.27**
Max Error	0.0130	0.0354	**2.72**
Min Error	-0.0140	-0.0362	**2.59**

2. Modeling of Stack Performance Degradation

Objective:

Collaborate with NETL and university partner modelers to bridge the scales of degradation from microstructure to stack.

Approach:

- Incorporate mechanisms affecting cell microstructure and electrochemical performance into PNNL stack modeling tools (SOFC-MP)

Accomplishments:

- Thermal coarsening of the electrodes was added in FY17
- Chromium poisoning of the cathode was added in FY19
- Demonstrated simulation of multi-mode stack performance degradation

2. Chromium Poisoning Mechanism

- Chromium poisoning begins with interconnects and components upstream of the stack containing chromium
- When the components are exposed to inflowing cathode air (including humidity), chromium oxide ($Cr_2O_{3(s)}$) scale is formed on the surface which results in **chromium vapor species** $CrO_2(OH)_{2(g)}$ in the air stream

$$P_{\mathrm{CrO_2(OH)_2},eq} = 4.15 \times 10^{-3} a^{0.5}_{\mathrm{Cr_2O_3}} P^{0.75}_{\mathrm{O_2}} P_{\mathrm{H_2O}} \exp\left(-\frac{5.35 \times 10^4}{RT}\right)$$

- The gas reacts with the cathode at the triple-phase-boundary (TPB) reaction sites depositing a solid chromium oxide ($\mathrm{Cr_2O_3}$) with a **deposition reaction current** ($i_{D,\mathrm{Cr_2O_3}}$)

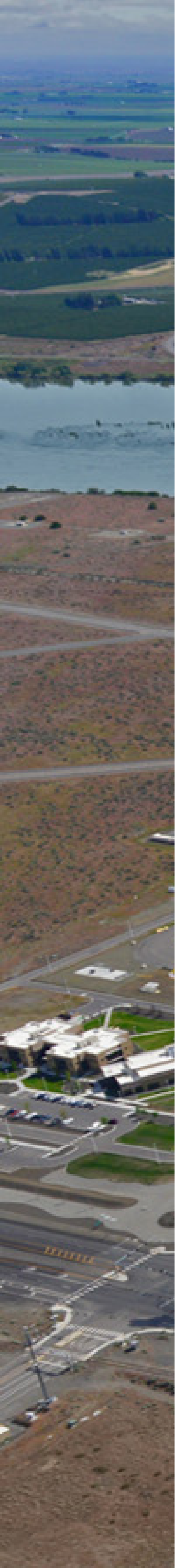
$$2\mathrm{CrO_2(OH)_2}(g) + 6\mathrm{e}^- \rightarrow \mathrm{Cr_2O_3}(s) + 2\mathrm{H_2}O(g) + 3\mathrm{O}^{2-}$$

$$i_{D,\mathrm{Cr_2O_3}} = i_{0D,\mathrm{Cr_2O_3}} l_{TPB} w_{TPB} P_{\mathrm{CrO_2(OH)_2}} P_{\mathrm{H_2O}} \left[\exp\left(\frac{F}{2RT}\eta\right) - \exp\left(-\frac{F}{2RT}\eta\right)\right]$$

- The oxide irreversibly covers the TPB area ($\theta_{TPB,\mathrm{Cr}}$) such that $\mathbf{L_{TPB}}$ **is decreased** and the oxygen reduction reaction is diminished over time causing the electrochemical performance to degrade

$$\theta_{TPB,\mathrm{Cr}}(t + \Delta t) = \theta_{TPB,\mathrm{Cr}}(t) - \Delta t \frac{1}{2F} \frac{M_{Cr_2O_3}}{\rho_{Cr_2O_3} h_{TPB}} * \frac{i_{D,\mathrm{Cr_2O_3}}}{l_{TPB} w_{TPB}}$$

$$l_{TPB} = l_{TPB,0}\left(1 - \theta_{TPB,\mathrm{Cr}}\right)$$



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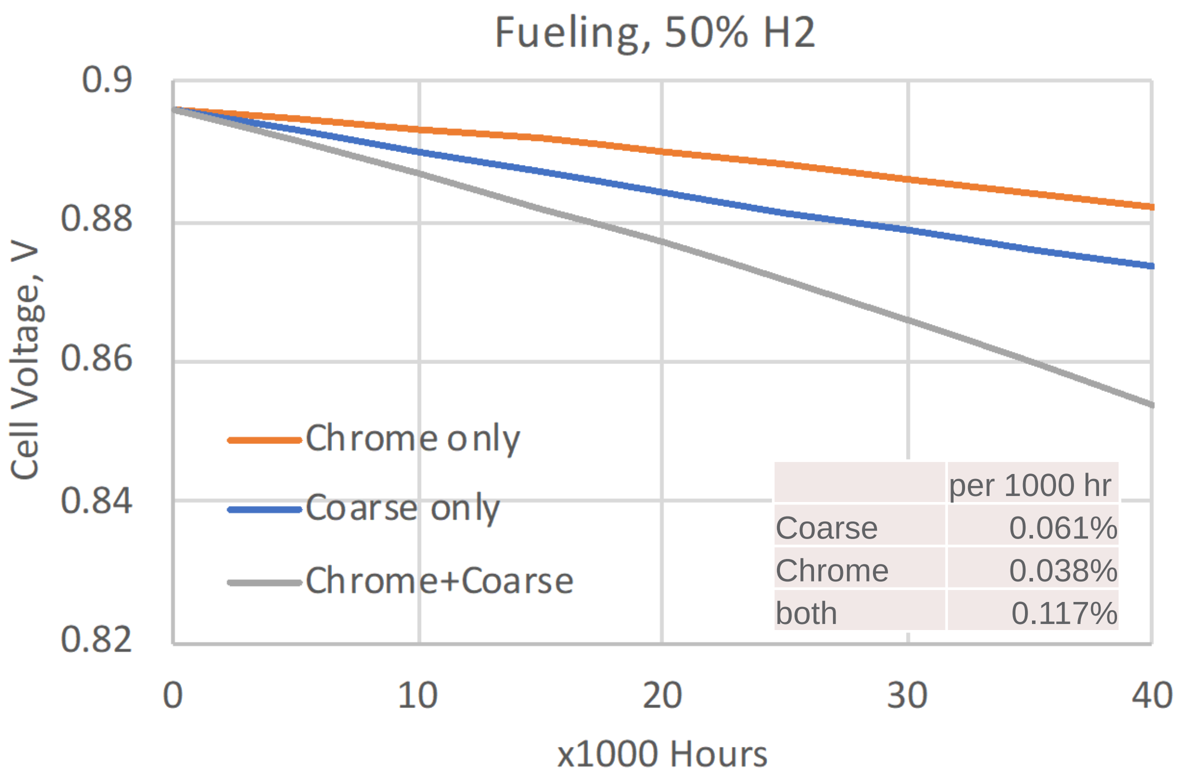
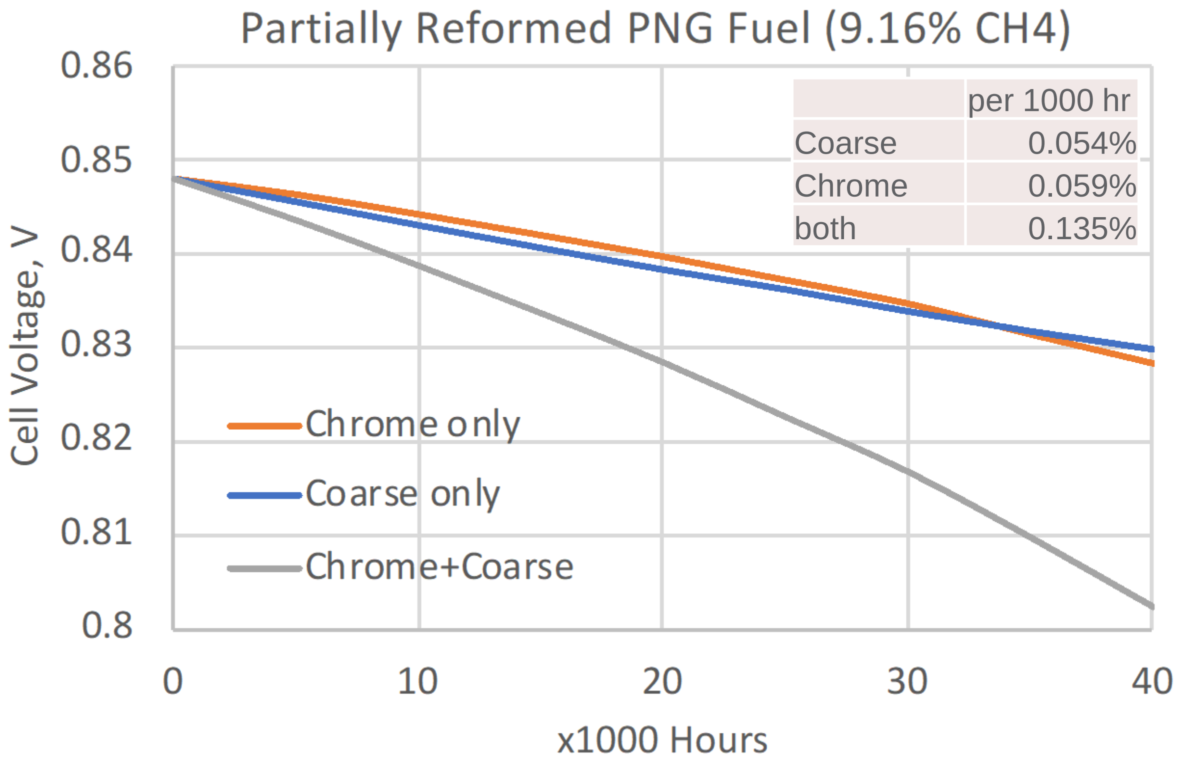
2. Effect of Fuel on Long-Term Performance

- Example case operating at 800°C and 0.5 A/cm^2, 1% H_2O in air.
  - <u>On H_2 fuel</u> degradation due to coarsening is greater than that of chromium poisoning
    - ✓ Coarsening is a large factor at 800°C
  - <u>On partially reformed natural gas</u> degradation due to chromium poisoning is increased
    - ✓ Due to increased activation polarization (η) and chromium oxide deposition rate (i_{D,Cr_2O_3})
  - <u>For both fueling scenarios</u> the degradation is larger with both modes together than the sum of each mode occurring separately
    - ✓ L_{TPB} is decreased by both mechanisms accelerating the degradation

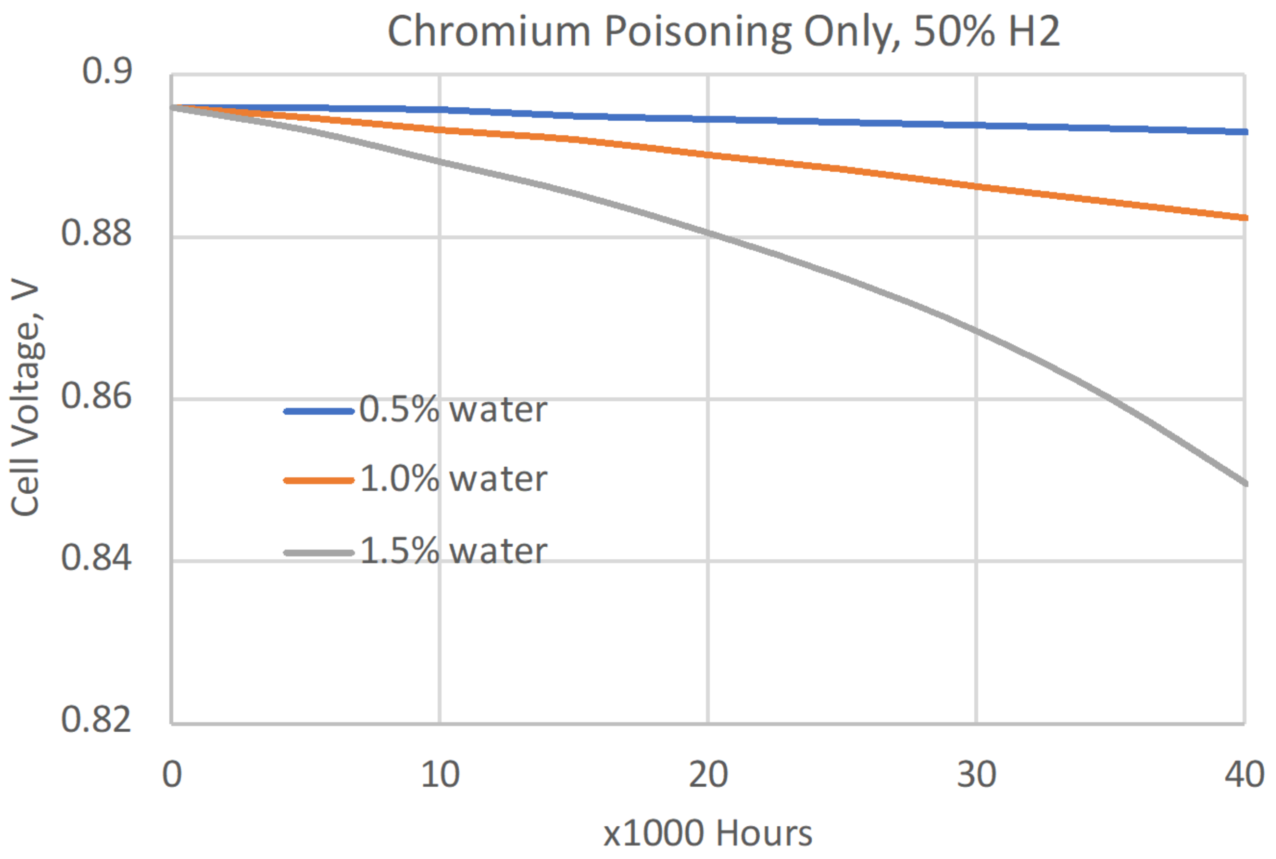




2. Effect of Cathode H_2O on Long-Term Performance

- Example case operating at 800°C and 0.5 A/cm^2
- Baseline: 1% H_2O in air resulted in <u>0.038%</u> per 1khr
- When the cathode H_2O is increased to 1.5% the degradation is more than tripled to <u>0.129%</u> per 1khr.
  - Equilibrium partial pressure of chromium vapor species and deposition reaction current is first order with steam
- If the H_2O is decreased to 0.5% the degradation decreases to less than a quarter of the baseline at <u>0.008%</u> per 1khr

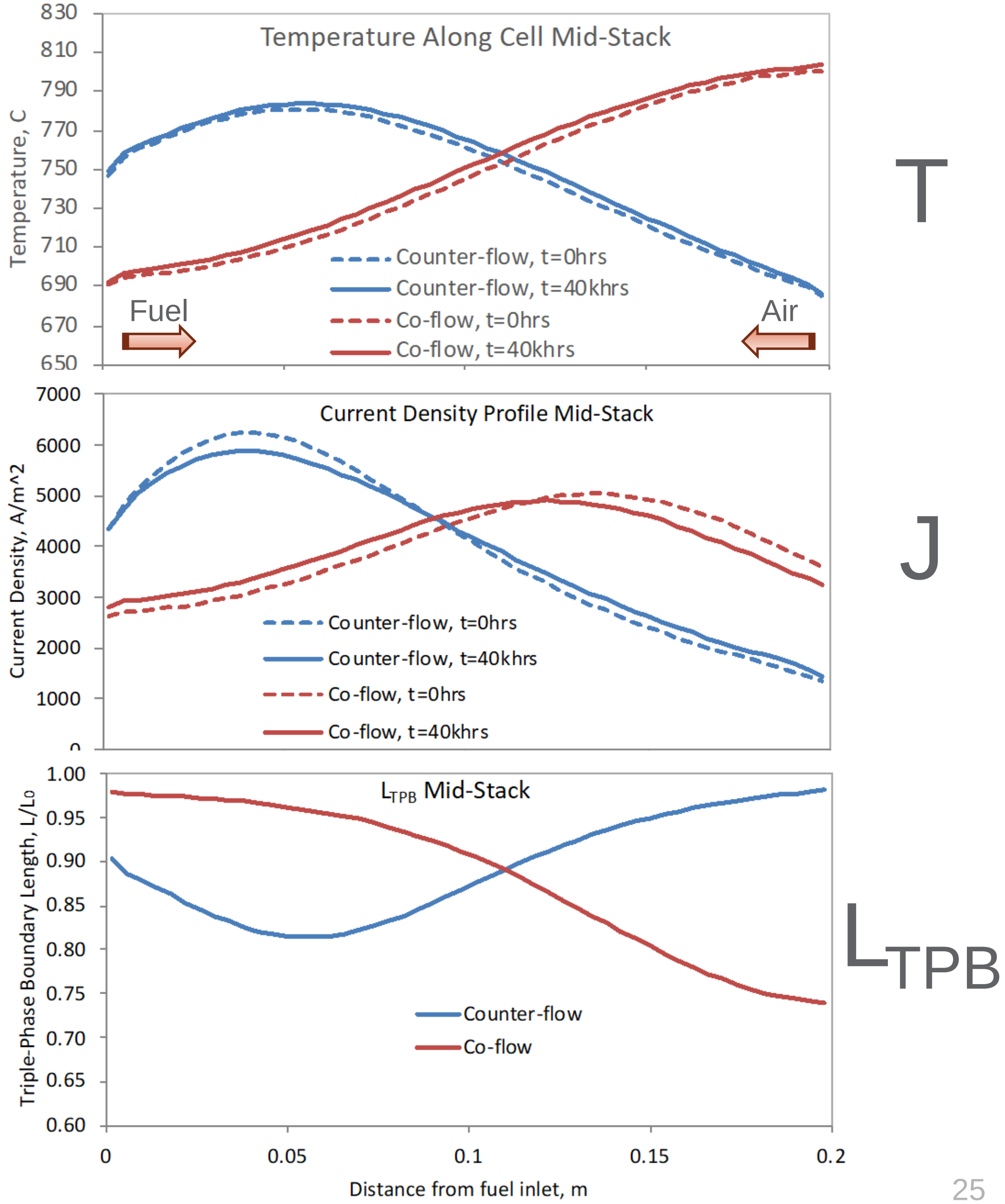
Effect of Steam on Cr Poisoning



2. Effect of Geometry on Long Term Performance

Flow Configuration	Degradation Mechanism		
	Chromium Only Degradation (per 1khr)	Coarsening Only Degradation (per 1khr)	Chromium & Coarsening Degradation (per 1khr)
Co-flow	0.0402%	0.0253%	0.0664%
Counter-flow	0.0428%	0.0203%	0.0705%

- Operating on Natural Gas with 60% IR at 750°C and 0.4 A/cm^2 at 70% Fuel Utilization
- "Coarsening only" degradation is greater for co-flow
  - For co-flow much of power is generated on 2nd half of cell where temperature and current density values are highest
  - Coarsening and **decrease of L_{TPB} is greatest where temperature was highest** (maximum 19°C higher for co-flow)
- "Chromium only" degradation is greater for counter-flow
  - For counter-flow much of power is generated on 1st half of cell where temperature and current density values are highest
  - Locally high temperature increases deposition current (i_{D,Cr_2O_3}) and L_{TPB} coverage ($\theta_{TPB,Cr}$) **degrading L_{TPB} most where power generation is highest**
- "Chromium & Coarsening" mechanisms together are **synergistic** and degradation is greater for counter-flow
  - Activation polarization (η) is decreased toward fuel exit thus deposition rate is decreased such that synergetic coarsening and coverage of L_{TPB} is not present for this co-flow case (at this temperature)



3. Modeling of Stack Reliability under Creep

Objective:

Investigate effect of creep on long-term operational reliability of SOFC stacks.

Approach:

- Implement creep models and study the influence on reliability using FEA .

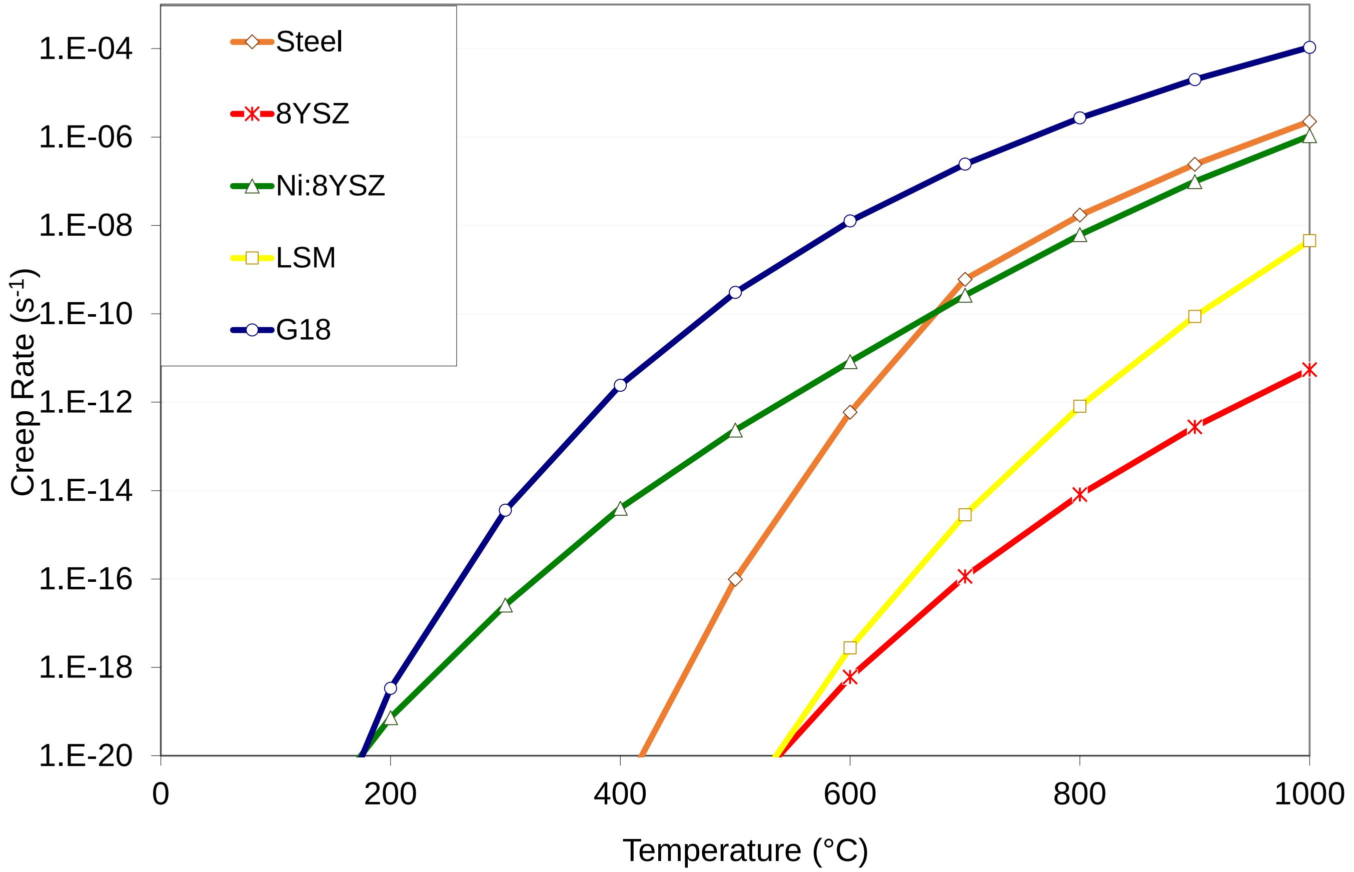
Accomplishments:

- Material creep model parameters were identified for the SOFC operational range (700 – 800°C)
- Simulations were carried out for realistic operating temperatures for generic multi-cell stack designs

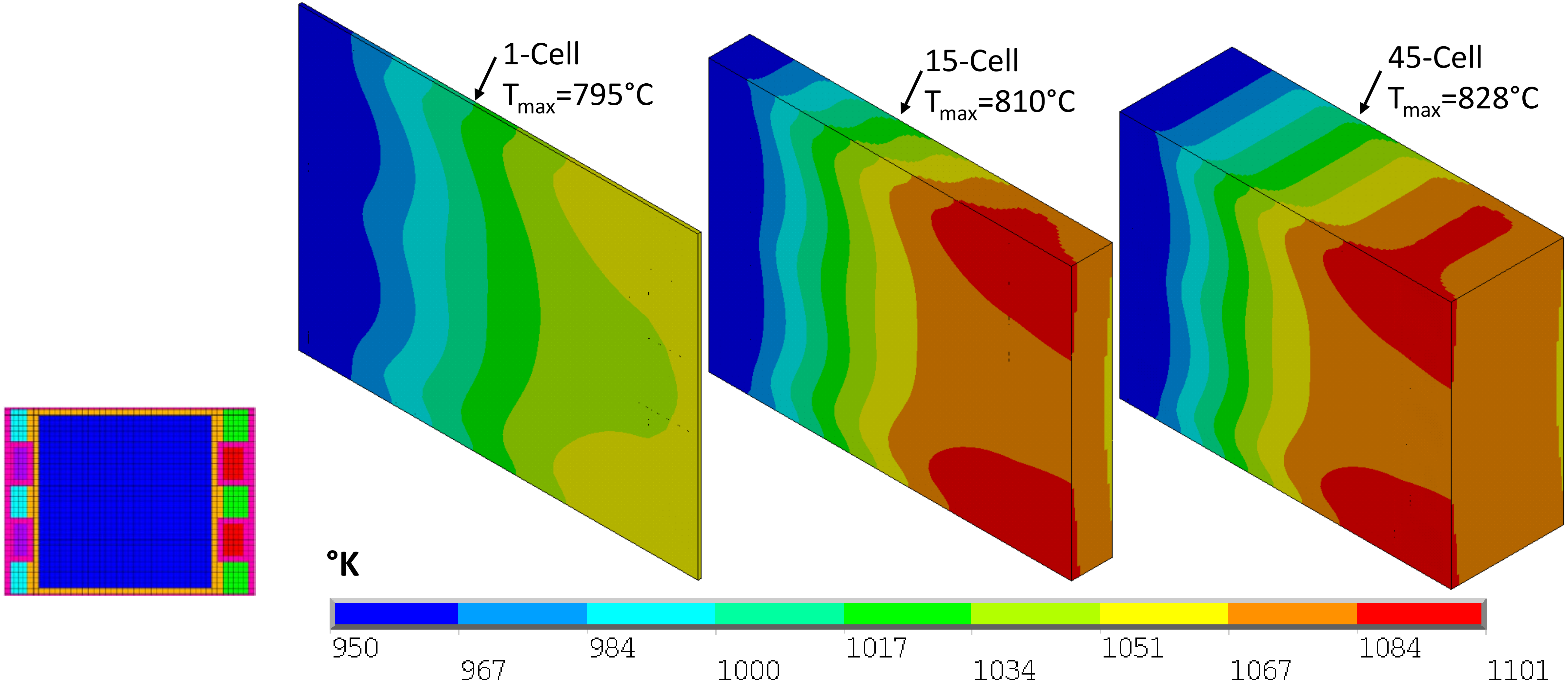
Sample creep strain rates for SOFC materials under 10 MPa stress

$$\dot{\varepsilon}_{cr} = C_1 \sigma^{C_2} e^{-C_3/T}$$

C_1 – Creep constant
C_2 – Stress Exponent
C_3 – the ratio Q/R



3. Temperatures from SOFC-MP 3D Tool



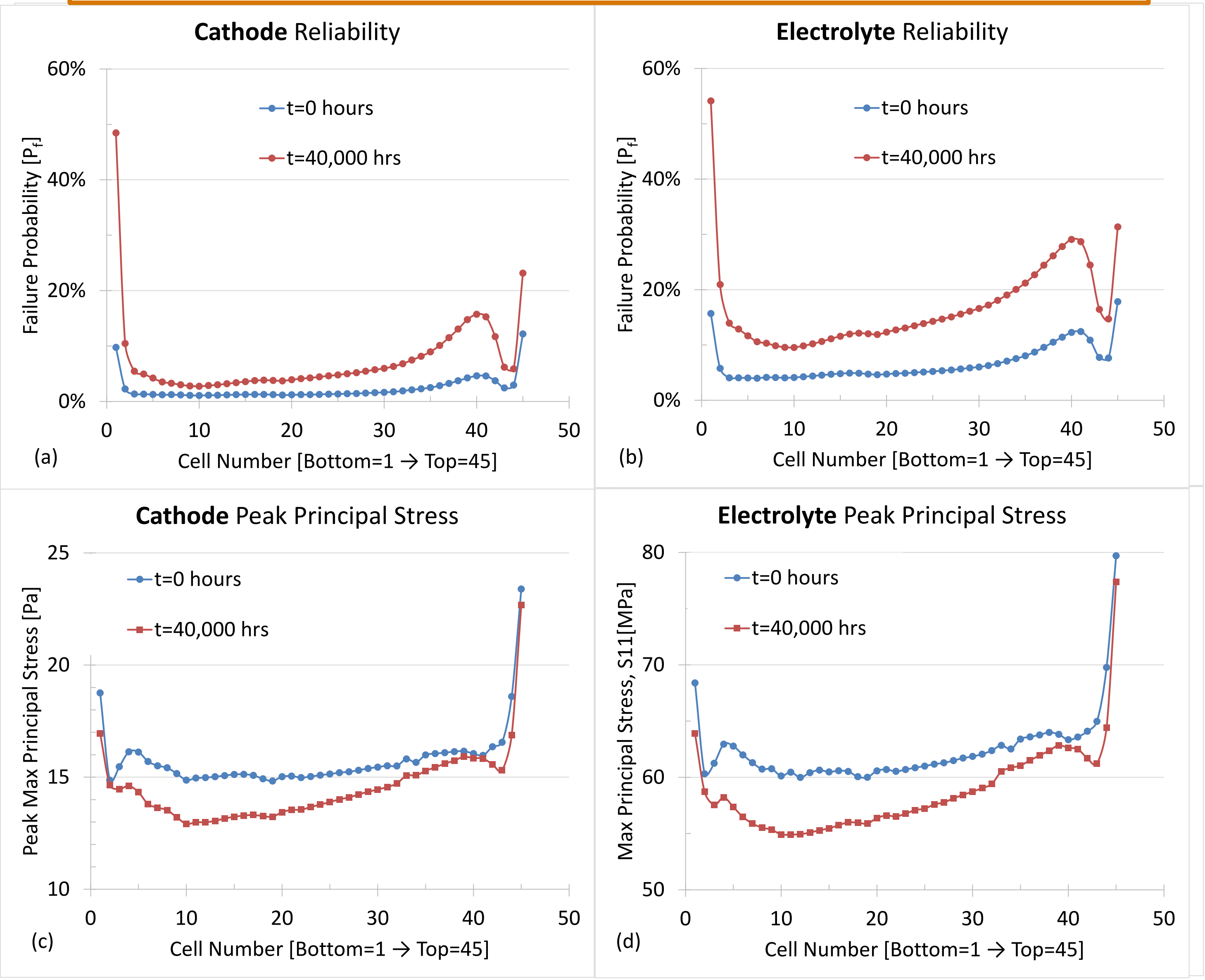
Operating Temperature Contours in 1, 15, and 45-cell Stack Models

(T_{avg}≈750°C, FU=86%, AU=16.4% (V=0.7908×NCELL, I_{dens}=0.4 A/cm^2)

3. 45-Cell Stack Results and Conclusions

- Creep increases failure probabilities of cathode and electrolyte
- Creep typically relaxes peak stresses in the PEN assembly however, the redistributed stresses produce higher net tension regions in electrolyte and cathode leading to higher failure probabilities.
- Effect is more pronounced in the cells near stack end (load frame).
- Pre-load significantly alters creep influence.

Stack Failure Probabilities / Peak Stresses



4. Evaluation of Metal-Supported Cells

Objective: Advance modeling capability of the PNNL SOFC-MP codes to include a generic metal-supported cell (MSC)

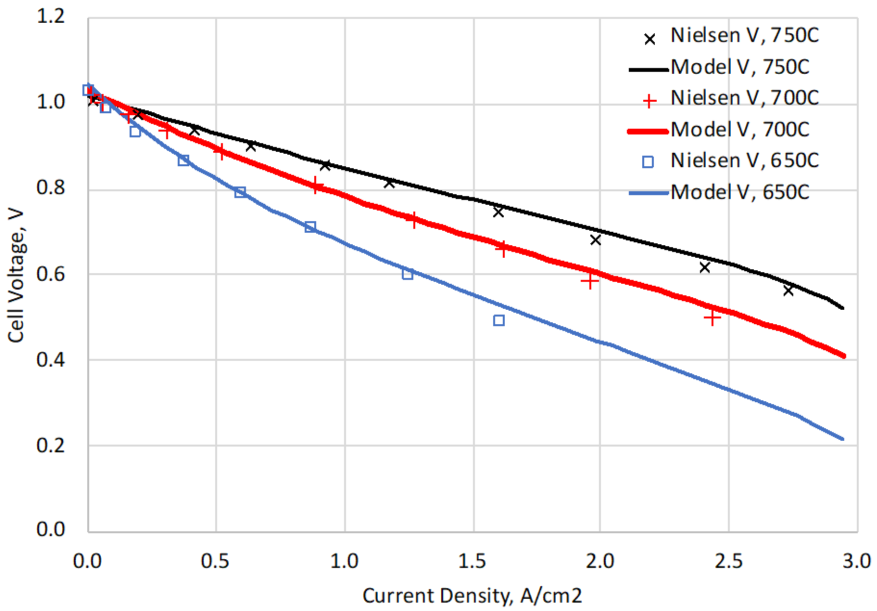
Approach:

- Identify SoA MSC performance and implement in PNNL EC model
- Simulate performance with SOFC-MP and evaluate structural reliability w/ FEA.

Accomplishments:

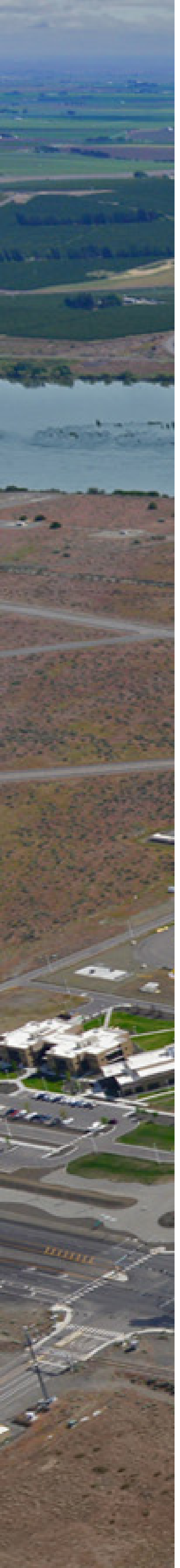
- MSC performance was validated
- Compressive preload and metal support porosity showed significant effect on mechanical reliability

SOFC-MP 2D solution for 400 cm^2, 1-cell 2-D stack model compared to Nielsen* MSC data (Fuel: 80% H_2, 20% H_2O) at 13% FU, 3% AU.



[#] Jimmi Nielsen, Asa H. Persson, Thuy Thanh Muhl, and Karen Brodersen. Towards High Power Density Metal Supported Solid Oxide Fuel Cell for Mobile Applications, Journal of the Electrochemical Society 2018 165: F90-F96

Source	Inflow Temp, °C	Average Stack Temp, °C	Current Density, A/cm^2	Cell Voltage (V)	Cell ΔT, C°
Test Data	N.A.	700	0.4	0.921	N.A.
Model	674	701	0.4	0.923	24.9



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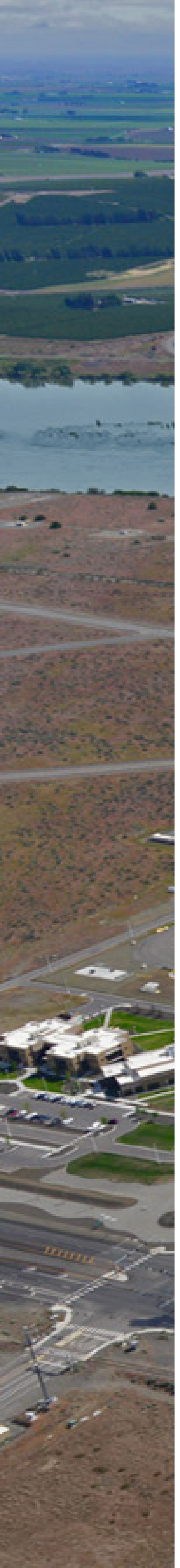
Summary

- **PNNL is using experimental and computational capabilities to extend the knowledge base in order to accelerate the commercialization of SOFC power systems.**

- **Posters**
  - **Effects of Cr Concentrations in Air on LSM/YSZ and LSCF Cathode Degradation (John Hardy)**
  - **Investigating Sr Vapor Phase Evolution from LSM/YSZ and LSCF Cathodes During and After Sintering (John Hardy)**
  - **Cr Mitigation by LSM-LSCF Composites for Solid Oxide Fuel Cells (Matt Chou)**
  - **Composite Cathode Contact Material Development: Validation in Stack Fixture Test and Effect of Strong Fiber (Matt Chou)**
  - **(M, Mn or Fe)$_3$O$_4$ spinel for Advanced Electrical Conductive Layer for SOFC Stacks (Jung-Pyung Choi)**
  - **Use of Reduced Order Models (ROMs) to Predict SOFC Stacks Performance (Jie Bao)**
  - **Influence of Anode Creep on the Structural Reliability of SOFCs (Brian Koeppel)**
  - **Small-Scale SOFC Test Platform (Brent Kirby)**



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