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Modeling Tools for SOFC Design and Analysis

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PNNL Modeling Activities: Objectives & Approach

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- Objectives: Develop integrated modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Allow SOFC designers to perform numerical experiments for evaluation of stack electrochemical, thermal, and mechanical performance
  - Aid understanding of materials degradation issues
  - Provide wide applicability for industry teams' to solve key design problems
  - Provide a technical basis for stack design
- Approach: Multiphysics-based analysis tools
  - SOFC-MP: A multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
  - Distributed Electrochemistry (DEC): Cell level multiphysics model to study effects of local properties/conditions on global SOFC performance
  - Reduced Order Models (ROM) to interface with system-level models
  - Micro/meso-scale models to study electrode degradation mechanisms
  - Experimental support to provide necessary material data for the models

PNNL Modeling Tools: Task Overview

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- SOFC-MP Stack Modeling
  - 2D and 3D multi-physics stack model SOFC-MP
  - 2D model benchmarked with literature and experimental data
  - Framework created for high fidelity Reduced Order Model (ROM)
- Electrochemistry & Degradation Modeling
  - Validated 3D multi-physics model of the SOFC electrodes and electrolyte for the investigation of SOFC performance and degradation issues
  - Models for electrode degradation and long term performance
- Interconnect Modeling & Experiments
  - Integrated modeling and experimental approach for prediction of interconnect lifetime
- Seal Modeling & Experiments
  - Investigate the behavior of glass seal material technologies and designs at operating temperatures

SOFC-MP Stack Modeling

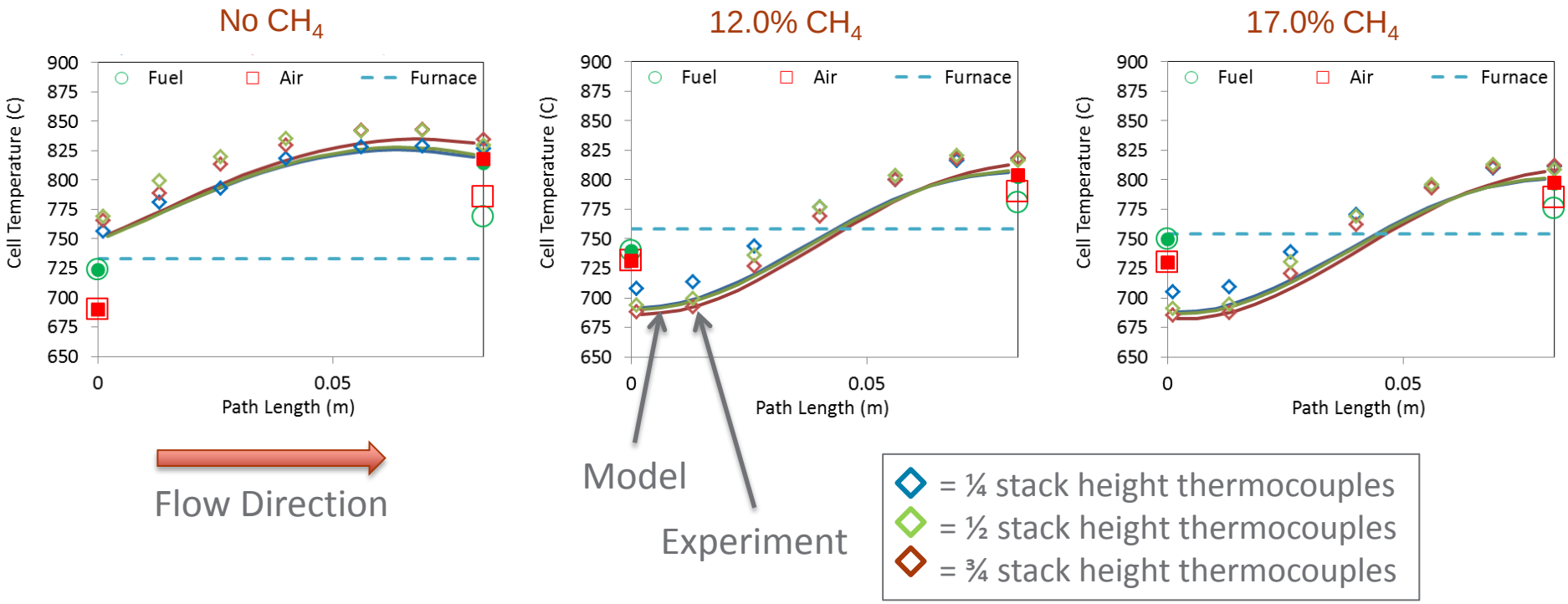
Benchmarking SOFC-MP 2D to Experimental Results

- Model temperature predictions were benchmarked against experimentally measured data
  - SOFC-MP 2D model
  - 30-cell co-flow stack
  - Instrumented 100 cm^2 cells with multiple thermocouples along the flow field
    - @ ¼, ½, ¾ of stack height
  - Ten different cases
  - 30A or 60A current
  - H_2 or CH_4 fuel mixtures
  - Different gas inlet temperatures

- Analyses showed that accurate model predictions of the cell temperature distribution required:
  - Accounting for all relevant structures that affect the lateral heat conduction of the cells
    - Load frame, heat spreading, and measurement plates in the stack
    - Flow channel media geometry
  - Methane steam reformation rate based on the anode used
  - Precise known location of the thermocouples
  - Calculation of realistic convection coefficients

SOFC-MP Benchmarking: Effect of Methane Concentration

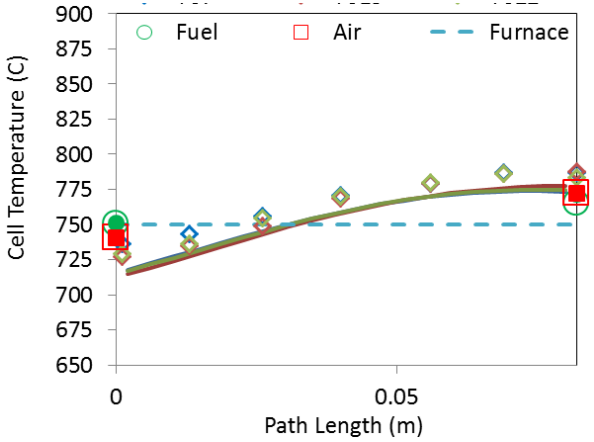
- SOFC-MP 2D model captures the steam-methane reformation effects on the cell temperature distribution for 60A current
  - With no CH_4, heating of the cell along the flow direction
  - With added CH_4, strong endothermic cooling at the inlet



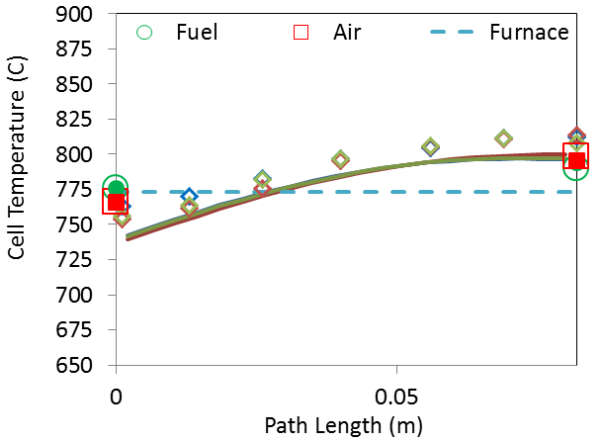
SOFC-MP Benchmarking: Effect of Current and Inlet Temperature

- Reduced current density and reformation for 30A cases make the endothermic cooling at the inlet relatively weaker even with 12.5% CH_4
  - Results in a more uniform cell temperature distribution that is influenced more by the inherent cell heat transfer characteristics
- Higher inlet gas temperatures primarily caused an upward shift of the temperature profile with little change to its shape

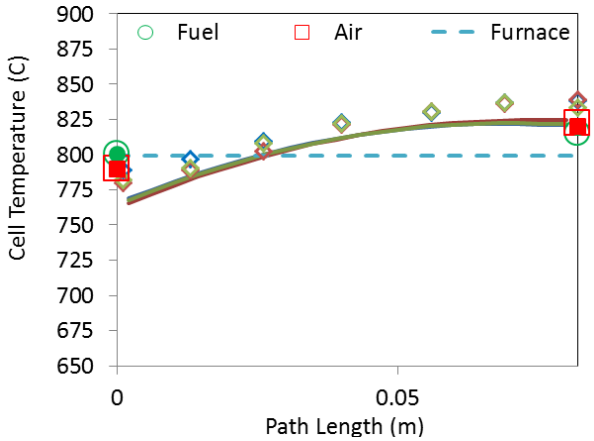
Nominal Tfuel/Tair Inlet



Tfuel/Tair +25°C Inlet



Tfuel/Tair + 50°C Inlet

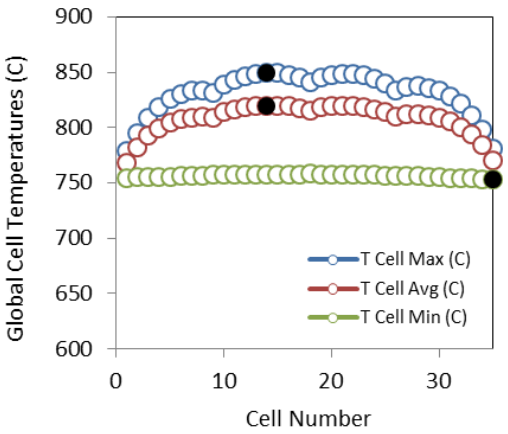


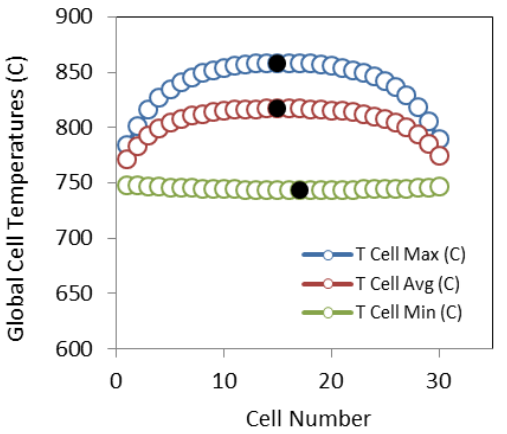
SOFC-MP Benchmarking: Effect of Instrumentation

- The instrumented stack has less temperature variation overall due to better heat spreading
  - Better heat transfer mechanisms in vicinity of non-standard cells are critical for temperature field benchmarking
- The model can predict temperature fields of actual stacks with CH_4 fuel

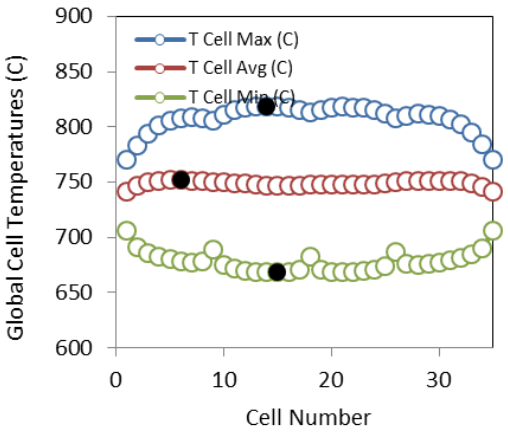
Instrumented Test Stack

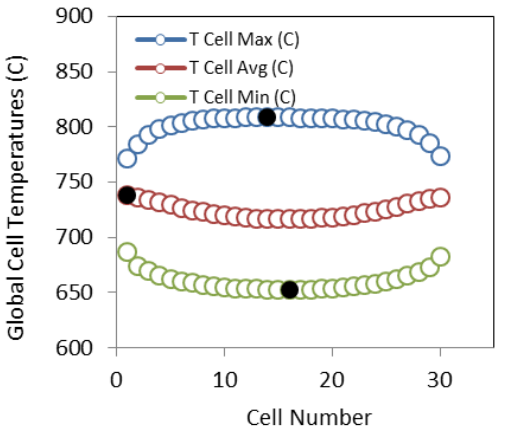
Production Stack





H_2 Fuel Case





CH_4 Fuel Case

Long Term Stack Performance Prediction

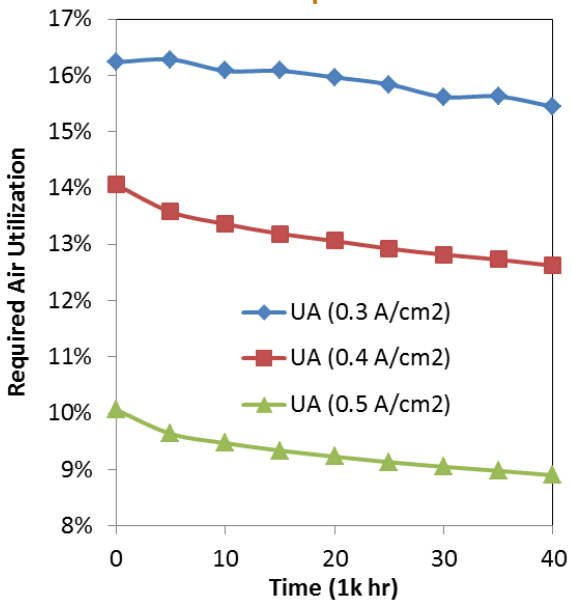
- Ability to simulate long term degradation processes added to SOFC-MP 2D
  - E.g., oxide scale growth on metallic interconnect causes added ohmic loss for the stack
  - The additional heat generation requires reduced air utilization rate to maintain maximum cell temperature
    - Additional BOP losses

Oxide Scale Parabolic Growth

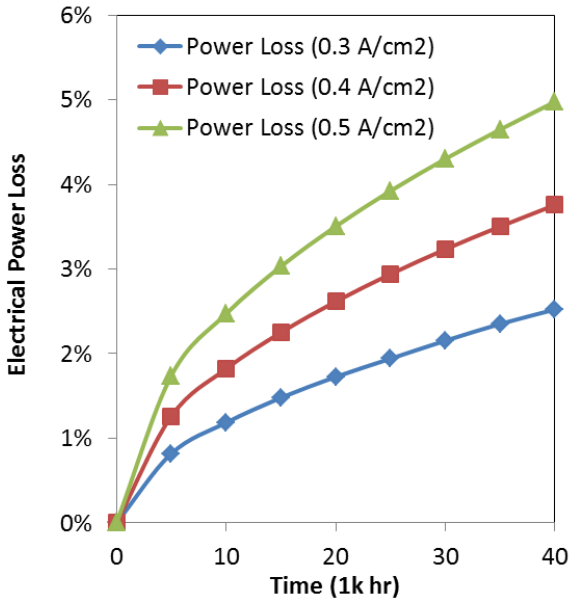
$$\frac{\partial \xi^2}{\partial t} = k_p = k_p^0 e^{\left(\frac{-E_{ox}}{RT}\right)}$$

$$\sigma_{ox} T = \sigma_{ox}^0 e^{\left(\frac{-E_{el}}{RT}\right)}$$

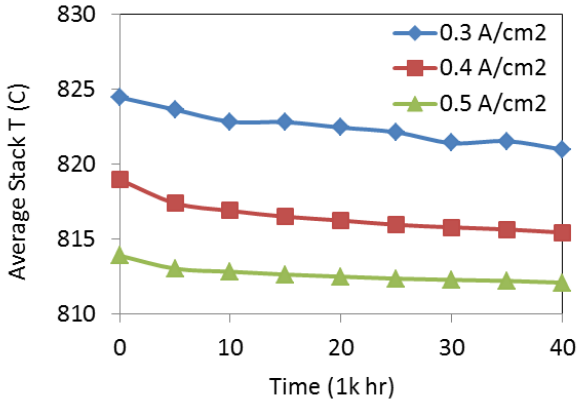
Air Required



Power Loss



Average Stack Temperature



Reduced Order Modeling (ROM): Overview

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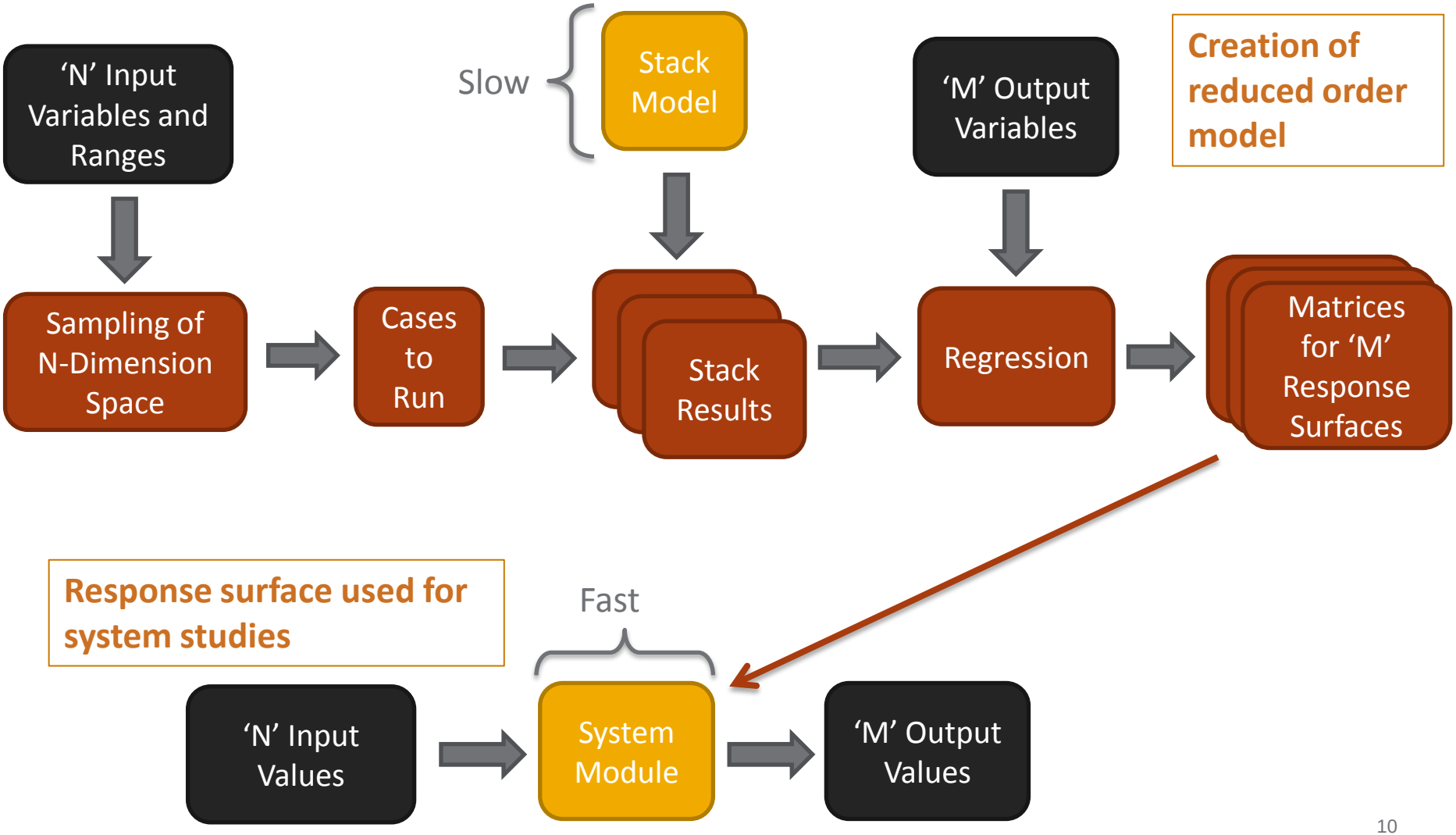
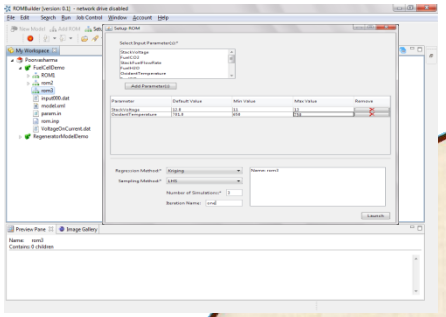


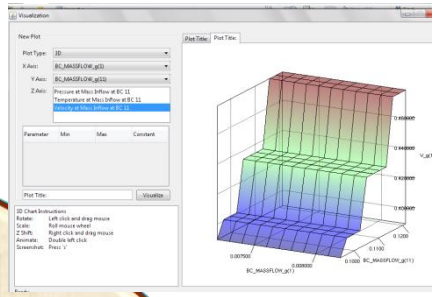
Design of the ROM Framework

Base Fuel Cell Model

Identify Design Parameters:
Stack Voltage
Fuel temperature

Export ROM
-Plugins in 'larger scale' simulations

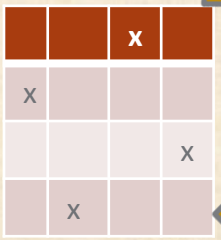




Generic Parser

ROM Analysis Tools
- Visualization
- Error Estimation
- Predictive Analysis

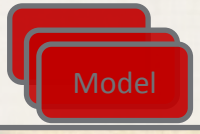
ROM Content Manager



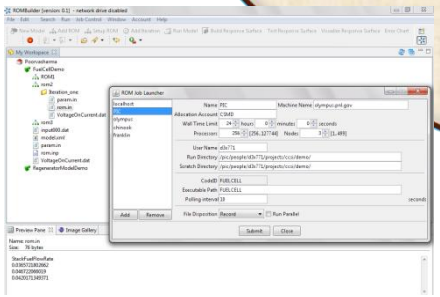
Sampling

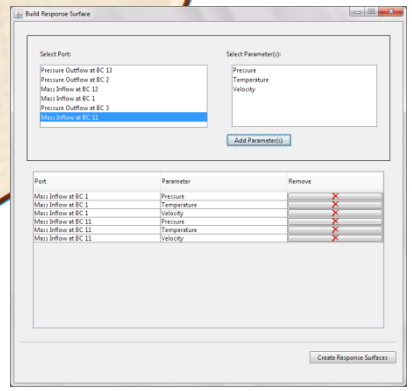
Regression
- Kriging
- FANN
- SVM

Job Execution Infrastructure



- Automated Post processing
- Data Management - Velo

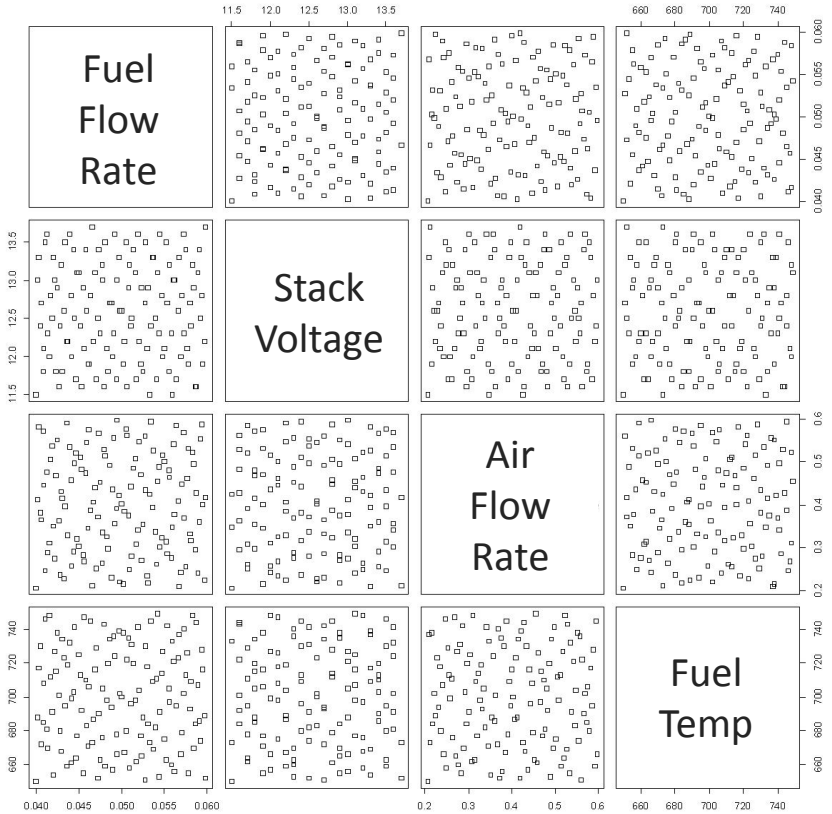




Advanced Mathematics for ROM Efficiency and Accuracy

- Check applicability and sensitivity of sampling/regression methods for the nonlinear SOFC model
  - 16-cell co-flow stack w/ H_2 fuel
- Input parameters
  - Air/fuel temperature
  - Air/fuel flow rate
  - Air/fuel composition
  - Stack voltage
- Output variables
  - Air/fuel species
  - Air/fuel outlet temperature
  - Cell maximum temperature
  - Stack current

Uniform Sampling in 4-D Space using QMC



ROM Parameter Sensitivity and Applicability of Regression Method

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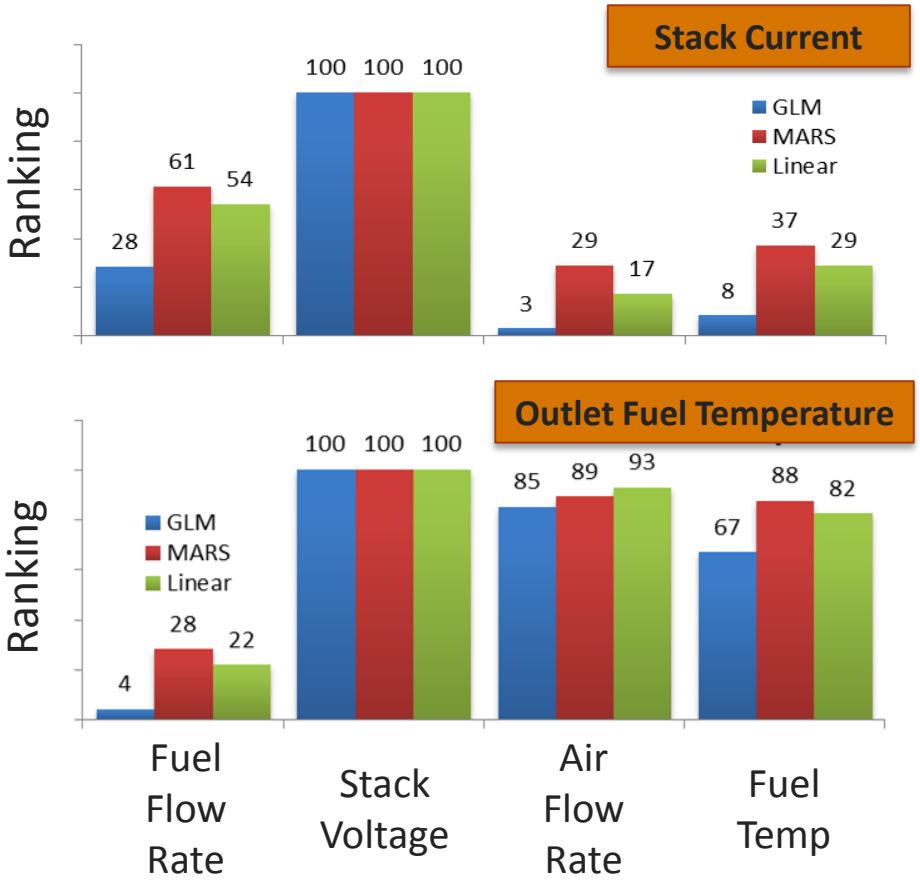
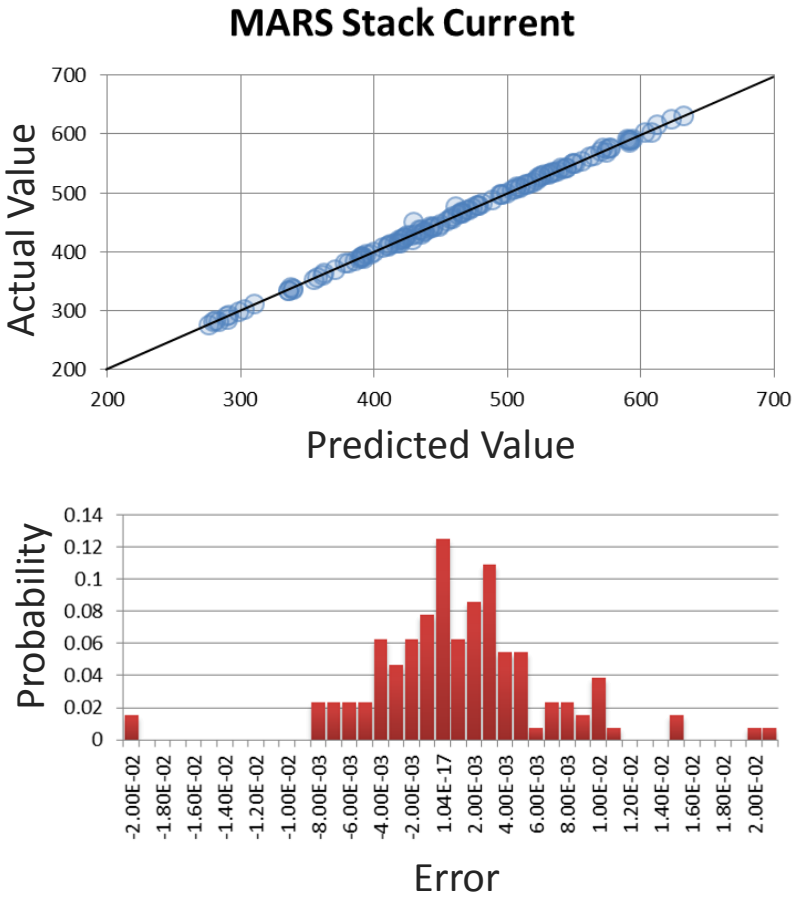
Sensitivity of Output to Input Parameters



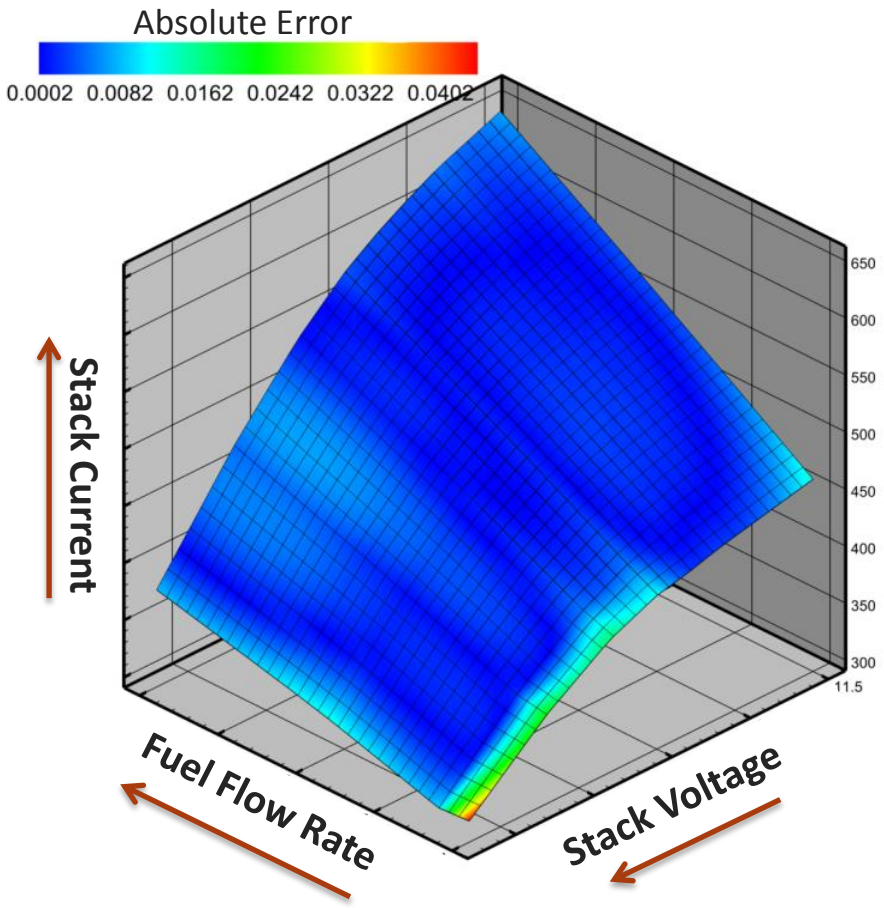
Assessment of Regression Method



ROM Response Surface Evaluation

- Response surfaces computed and visualized by 3D contours
  - E.g., 128 samples sufficient to reduce stack current error to less than 1% (maximum of 4% on extremities of the chosen design space)
- Response surface relationships implemented into a calculator
- Multi-Element Probabilistic Collocation Method used to identify regions of highest sensitivity that can be augmented with additional samples to achieve high accuracy
- Principal Component Analysis-based mapping has also been investigated to reduce the number of required regressions for prediction of stack temperature distributions

Response Surface for Stack Current



Benefits of the ROM Framework

- Provides an automated system to build Reduced Order Models for SOFC stacks
  - Generic: Configurable for any domain
  - Portable: Windows, Linux
  - Extensible: Multiple sampling, regression, and analysis tools
  - Cost Efficient: Open source packages
  - Time Efficient: Automated job submission, post-processing, error analysis, augmented sampling, and data management tools
  - Data Sharing
  - Metadata Management
  - Rich client on desktop
    - Wiki interface through web can be available

Electrochemistry & Degradation Modeling

Electrochemistry and Electrode Degradation Modeling

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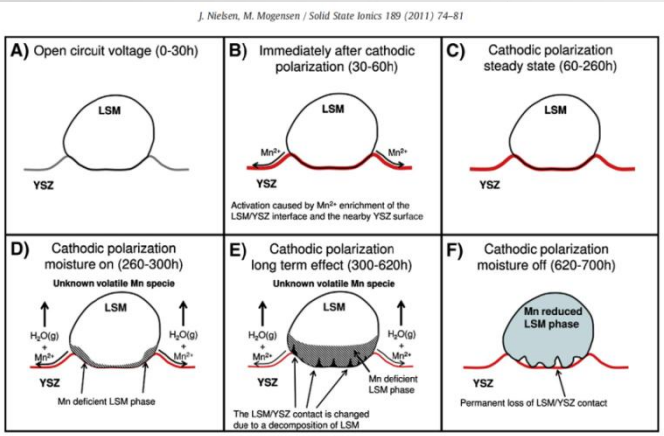
Technology Challenges

- Investigate degradation issues in the electrodes of the SOFC
- Understand degradation processes in electrodes
  - Investigate the effect of microstructure and local conditions within the electrodes on cell performance
  - Confidently predict global cell performance for a range of conditions

Objectives

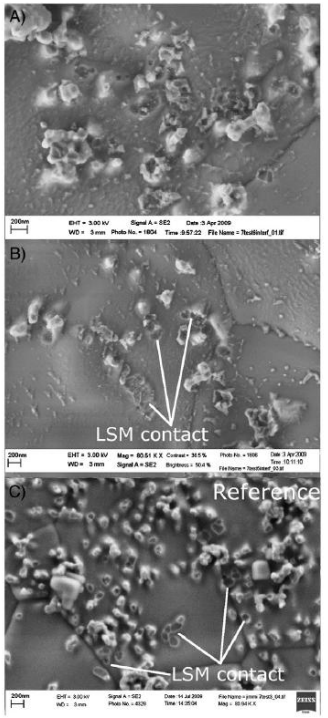
- Develop models to predict cell performance and to investigate degradation
  - Calculations based on operating conditions and microstructure within the electrodes
  - Dependent on coupled electric potential, charge transfer, and reactive transport
  - Use different modeling approaches for specific problems
  - Validate the models by comparison with experimental data
  - Simulate microstructural and operational effects on cell performance

Humidity in the Cathode



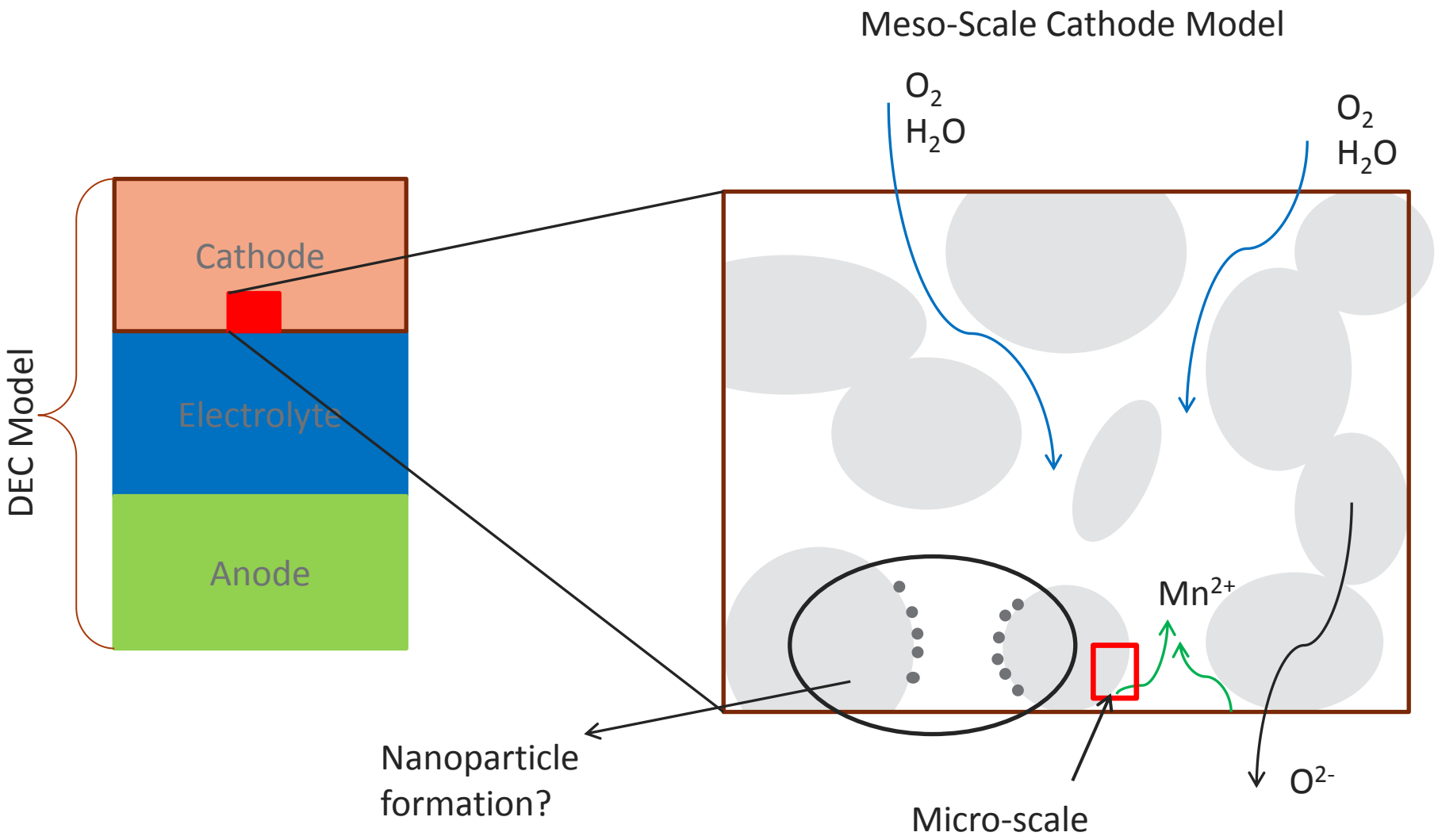
Nielsen et al 2011

- Two stage degradation
  - Immediate decrease in performance
  - Slower, steady degradation over long term operation
- Reactions with LSM
  - Testing with LSCF shows little to no degradation
  - LSM-YSZ and LSM-CGO show similar degradation
    - Not YSZ reactions → LSM reactions
  - Theories
    - Formation of La_2O_3
      - Nano-particles on surface
    - Reaction of H_2O with Mn^{2+} ions
    - Reduction of active interface



Nielsen et al 2010

Current Work: Development of Micro- and Meso-Scale Cathode Models



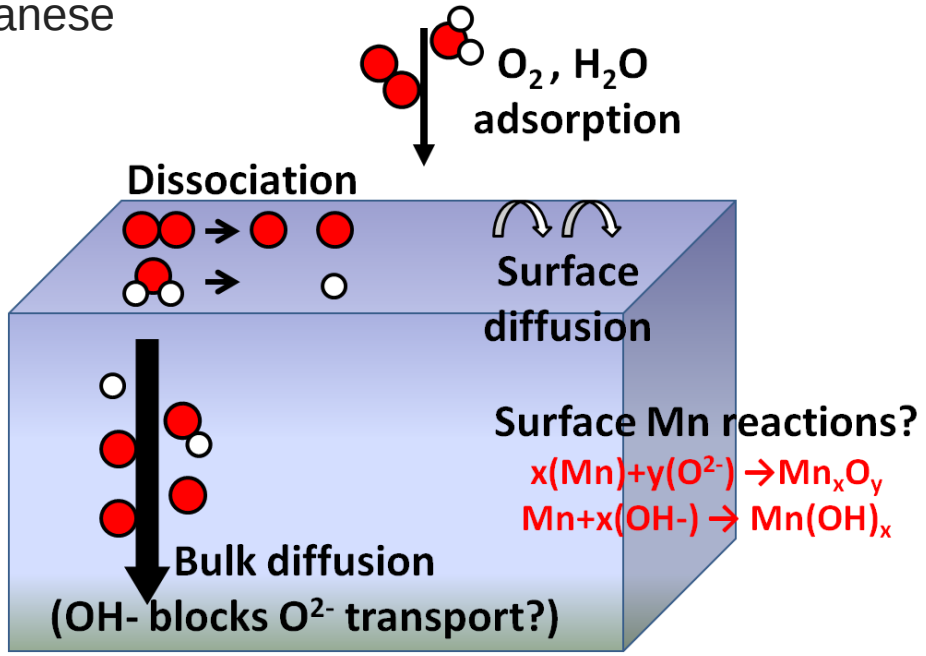
Note: Not to scale

Meso-Scale Cathode Model

- Smoothed particle hydrodynamics model of the cathode microstructure
  - Includes the reactive transport in the gas (O_2, H_2O, etc.) and solid (O^{2-}), charge transfer reactions
- Considers possible reaction mechanisms of H_2O with LSM
  - Nanoparticle formation (precipitation)
  - Mn^{2+} removal
- Experimentally it is difficult to know what is happening during operation vs. shut down
  - Model will help to narrow down possible physical phenomena of H_2O in the cathode

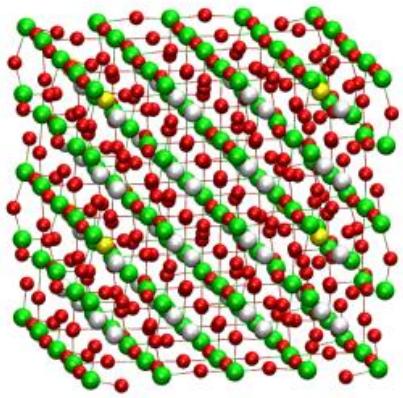
Micro-scale modeling of the Cathode

- Molecular modeling of Sr-doped LSM in presence of H_2O.
- What are the possible interactions between LSM and water and how do they interfere with cathode operation?
  - Use molecular modeling techniques to simulate and compare possible reaction mechanisms
- Approach:
  - Adsorption and diffusion simulations using classical molecular dynamics
  - Formation thermodynamics of manganese oxides and hydroxides using density functional theory
  - H_2O, O_2 dissociation thermodynamics on LSM surface using density functional theory



Micro-scale modeling of the Cathode

- Current research:
  - Build $La_xSr_{1-x}MnO_3$ atomistic slab structure
  - Develop and test classical potential energy function describing slab structure, motion and intermolecular interactions at any temperature or pressure
  - Adsorption, surface and bulk diffusion simulations based on atomistic structure and inter-atomic potentials
- Preliminary Results:
  - Created 4x4 rhombohedral $La_{0.8}Sr_{0.2}MnO_3$ slab structure
  - Developed and tested initial classical potential energy function
    - PE function correctly reproduces experimental structural parameters
  - Adsorption, surface diffusion simulations of O_2, H_2O, OH- are underway



Next Steps and Future Work

- Continue implementation of degradation models
  - Validation with experimental data
- Couple micro- and meso-scale cathode models
  - Use fundamental reaction information gained from micro-scale modeling to develop reaction parameters of meso-scale modeling.
- Investigate mitigation strategies for humidity in the cathode

Seal Modeling & Experiments

Seal

- Motivation: To quantify the healing capability of the self-healing seal materials under various thermo-mechanical operating conditions
- Goal: To assist the development of the reliable stack-level SOFC design integrated with the self-healing glass sealing system
- Technical Approach: Develop time and temperature dependent mechanistic based healing models as building blocks in stack-level seal performance simulations to predict the healing behaviors under different conditions

Mechanistic Based Crack Healing Model

- A two-stage diffusion driven self-healing mechanism
  - 1st: Creep-driven crack closure

$$\dot{\varepsilon} = \frac{1}{\eta}\sigma \quad \eta = \eta_0 \exp\left(\frac{Q_V}{RT}\right)$$

  - 2nd: Interdiffusion-driven bond formation - a characteristic dwelling time τ is needed for molecular transportation to establish sufficient links on contact area

$$\tau = \tau(T) = \alpha \exp(\frac{\beta}{T})$$

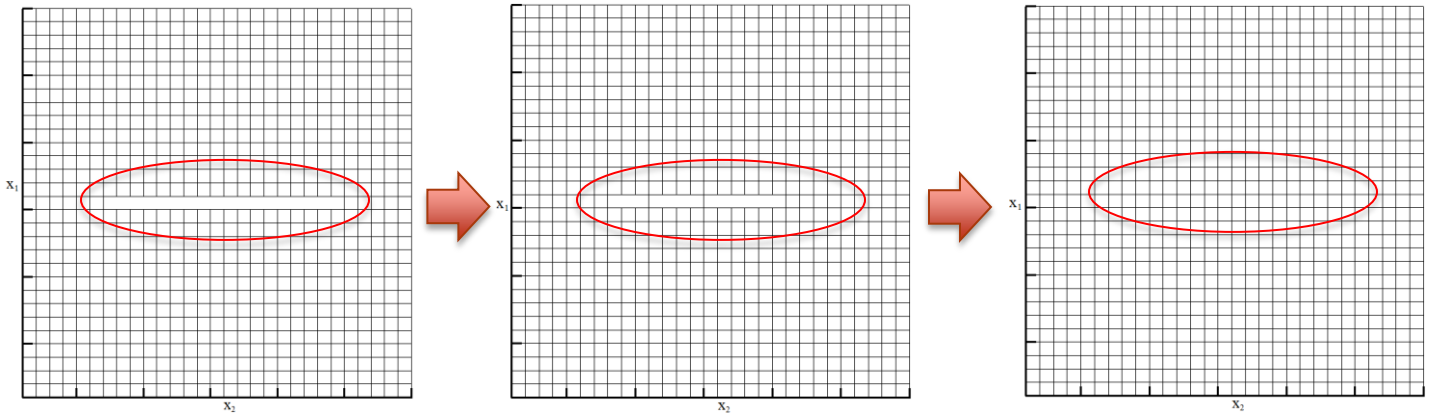
- Performed multi-scale simulation, using both Kinetic Monte Carlo and Finite Element Method, to investigate the stress and temperature dependent healing behavior from different scales
  - The healing path and temperature dependence is fully driven by the proposed mechanism without any prerequisites

Simulation of the Self-healing Process

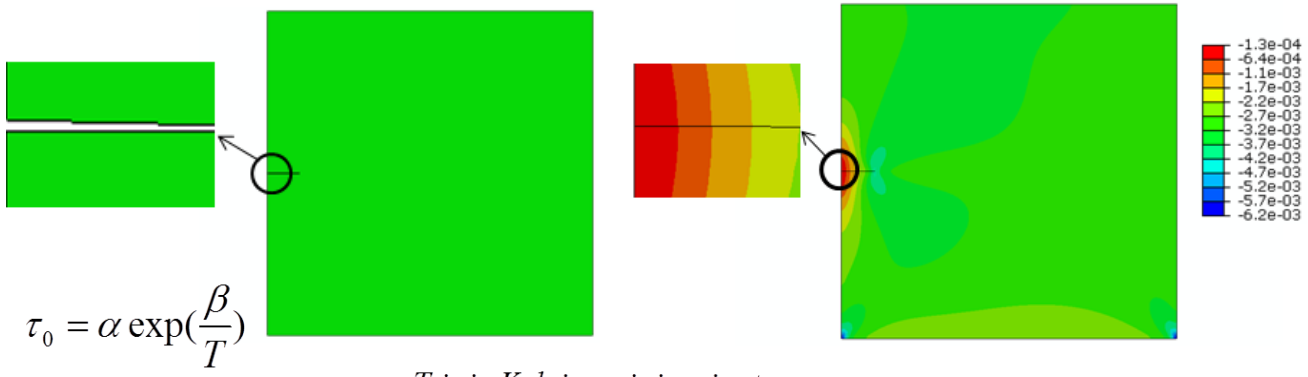
- kMC simulation

$$P = w_h \times \exp(-\frac{E_h}{kT}) \quad w_h = 6.02E9Hz \quad E_h = 2.555eV$$

(*k*: Boltzmann constant)



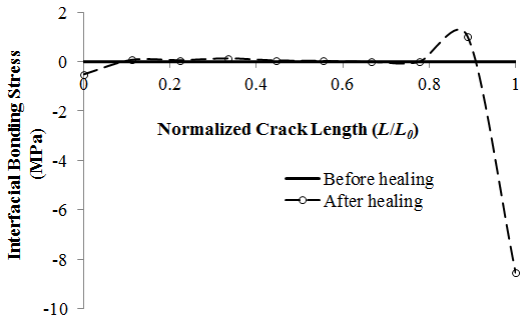
- Finite Element Analysis



$$\tau_0 = \alpha \exp(\frac{\beta}{T})$$

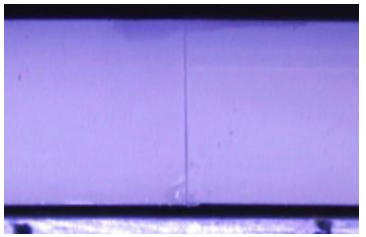
$\alpha = 2.4082E-9 \quad \beta = 24890$ *T is in Kelvin,* τ_0 *is in minute.*

Interfacial Bonding Stress



Experimental Calibration of the Characteristic Dwell Time

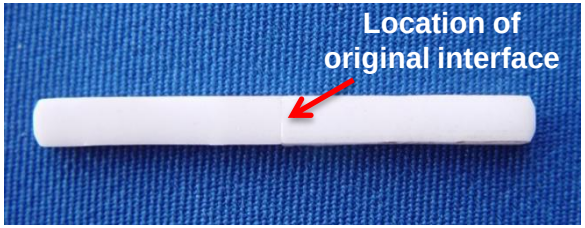
- Controlled experiments were performed to mimic the healing process. The measured flexural strength recovery was used to calibrate the healing probability function of the kMC model.



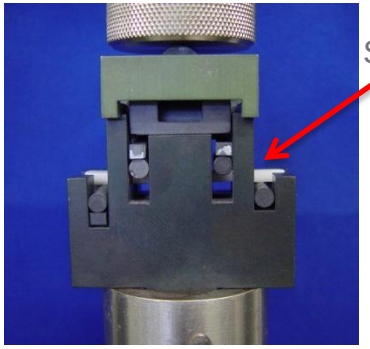
Pre-test specimen illustrating no gap between glass bars.

Flexural tests results summary for specimens exposed to elevated test temperatures with no gap at the interface and no load.

Specimen	Test Temperature (°C)	Time at Test Temperature (min.)	RT Flexural Strength (MPa)
700-6	700	40	23.0
700-7	700	60	51.7
700-9	700	120	79.8
800-5	800	5	10.5
800-3	800	10	66.8
800-6	800	20	75.5



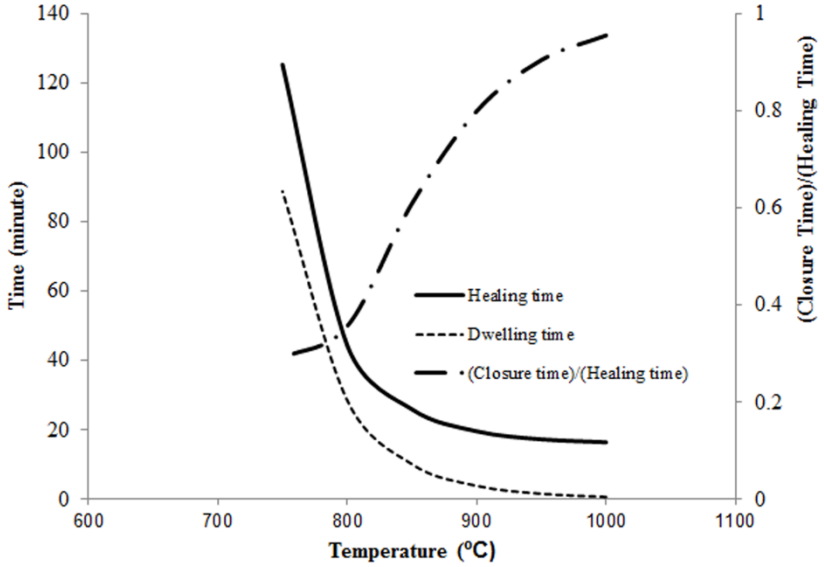
Post-test specimen exposed to 700°C for 60 minutes.



Four-point bend test fixture.

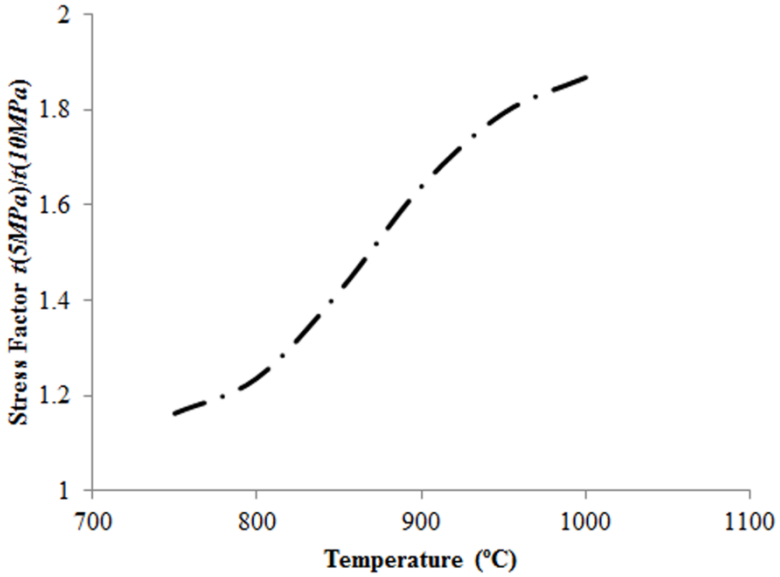
Effects of Operating Conditions

Effects of temperature



Dwelling time only counts the time for the interdiffusion-driven healing stage.

Effects of confining pressure

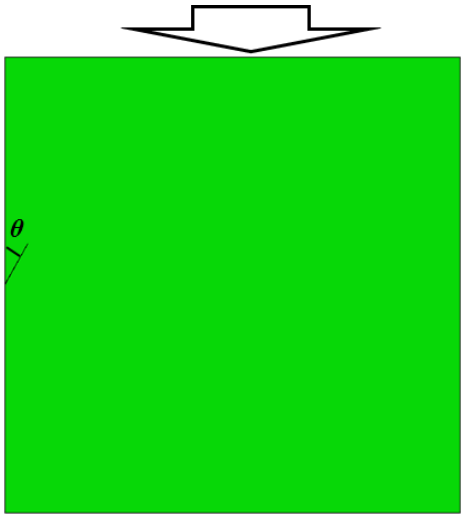


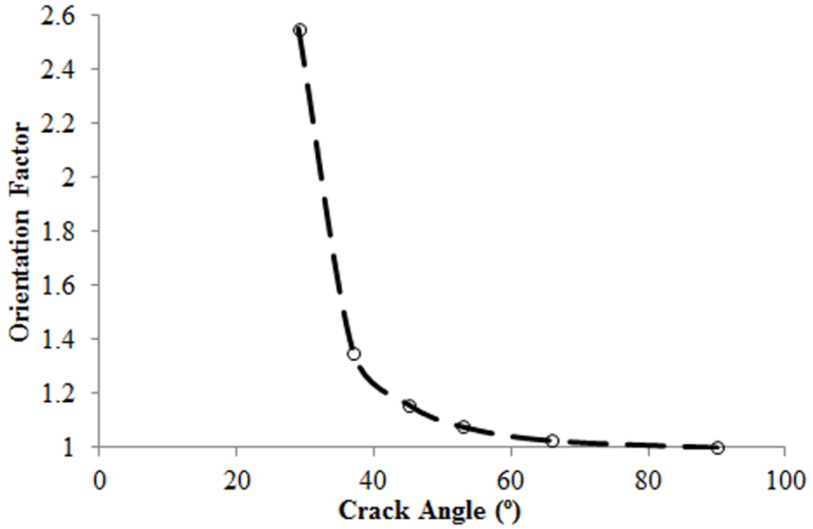
Stress factor: the total healing time under a pressure of 5MPa divided by the total healing time under 10MPa

Effects of Crack Morphology

Crack Orientation:

Orientation factor:
the total healing time of a crack with arbitrary orientation of θ divided by the total healing time of the specimen with a crack of θ=90°

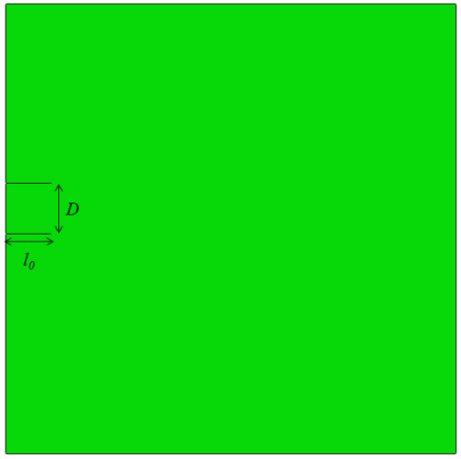


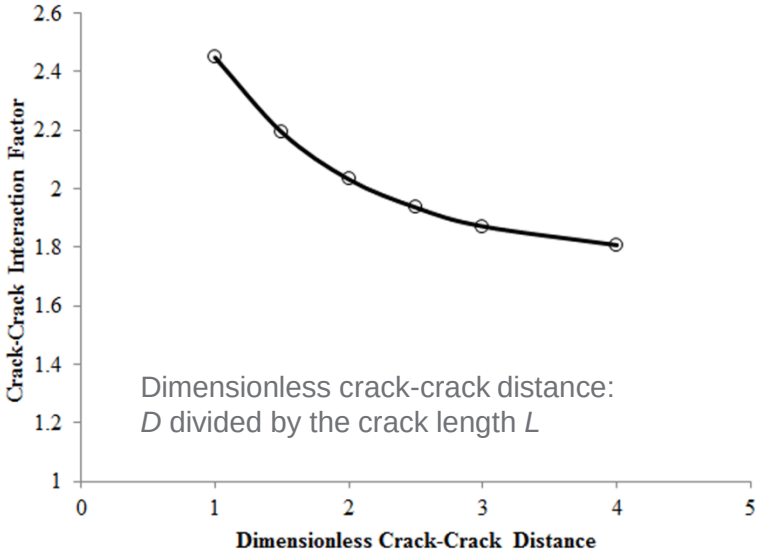


Crack Interaction:

Crack-Crack Interaction Factor:
the total healing time divided by the healing time of the specimen with a single crack.

Two identical edge cracks separated by distance of *D*





Dimensionless crack-crack distance:
D divided by the crack length *L*

PNNL Modeling Summary

- Stack Modeling
  - SOFC-MP 2D successfully benchmarked against experimental temperature data
  - Capability added to SOFC-MP 2D to simulate generic degradation behaviors over time and maintain suitable stack operating temperature
  - Framework developed to generate reduced order models (ROM) for stacks
- Electrochemistry & Degradation Modeling
  - Simulated anode Ni volatilization rate for high humidity/fuel utilization case
  - Began construction of micro/meso-scale models to predict cathode and anode degradation mechanisms under high humidity conditions
- Interconnect Modeling & Experiments
  - Modeling tools are being extended to implement new experimental methodologies and quantitative measurements to quantify and predict IC life
  - Interfacial analysis of surface modified IC specimens in-process
- Seal Modeling & Experiments
  - Developed a two-step, mechanistic-based self-healing model to quantitatively capture and predict the crack healing behavior of SCN-1 glass

Future PNNL Modeling Activities

- Simulation of long-term and transient performance behaviors of stacks
  - Evaluation of high humidity conditions on long-term anode/cathode performance
  - Evaluation of high fuel utilization on long-term anode performance
  - Implement micro/meso-scale performance results into higher-level stack models
- Improved accessibility to software tools
  - Release ROM and apply approach to fuel cell-based power system models
  - Transfer SOFC-MP to a more flexible framework for integration with other FEA solvers and a license-free user interface
- Interconnect Modeling & Experiments
  - Quantification of interfacial strength for varying surface modified SS441
  - Life prediction for coated and surface modified SS441
- Seal Modeling & Experiments
  - Develop a continuum damage-healing model to accommodate stack-level simulations
  - Comparative prediction and optimization of seal designs: compliant seal vs. rigid seal