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Modeling Tools for SOFC Design and Analysis: Recent PNNL Progress

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14th Annual SECA Workshop, Pittsburgh, PA

August 2, 2013

Modeling Objectives & Approach

- **Objectives**: Develop stack modeling tools to:
  - Evaluate the tightly coupled multi-physical phenomena in SOFCs
  - Aid understanding of materials degradation issues
  - Allow SOFC designers to perform numerical experiments for evaluation of electrochemical, thermal, and mechanical stack performance
  - Provide wide applicability for industry teams to solve key design problems

- **Approach**:
  - SOFC-MP 2D/3D: Multi-physics solver for computing the coupled flow-thermal-electrochemical response of multi-cell SOFC stacks
  - Stack reduced order model (ROM) creation for system-level studies
  - Component and material models to improve stack mechanical reliability
  - Micro/meso-scale models to evaluate electrode degradation mechanisms
  - Experimental support to provide necessary material data for the models

Recent Progress

- SOFC-MP Tools
  - Modifications to the 3D tool for use in a more generic graphical user interface (GUI)
  - Development of the reduced order modeling (ROM) tool
- Compliant Seals
  - Constitutive model development and behavior of compliant seal materials in SOFC stacks
- Metallic Interconnects
  - Experimental and modeling approach for scale strength and prediction of interconnect lifetime using interfacial indentation tests
- Electrochemical Degradation
  - Models for cathode degradation under high humidity

Modeling Tools for SOFC Stack Analysis

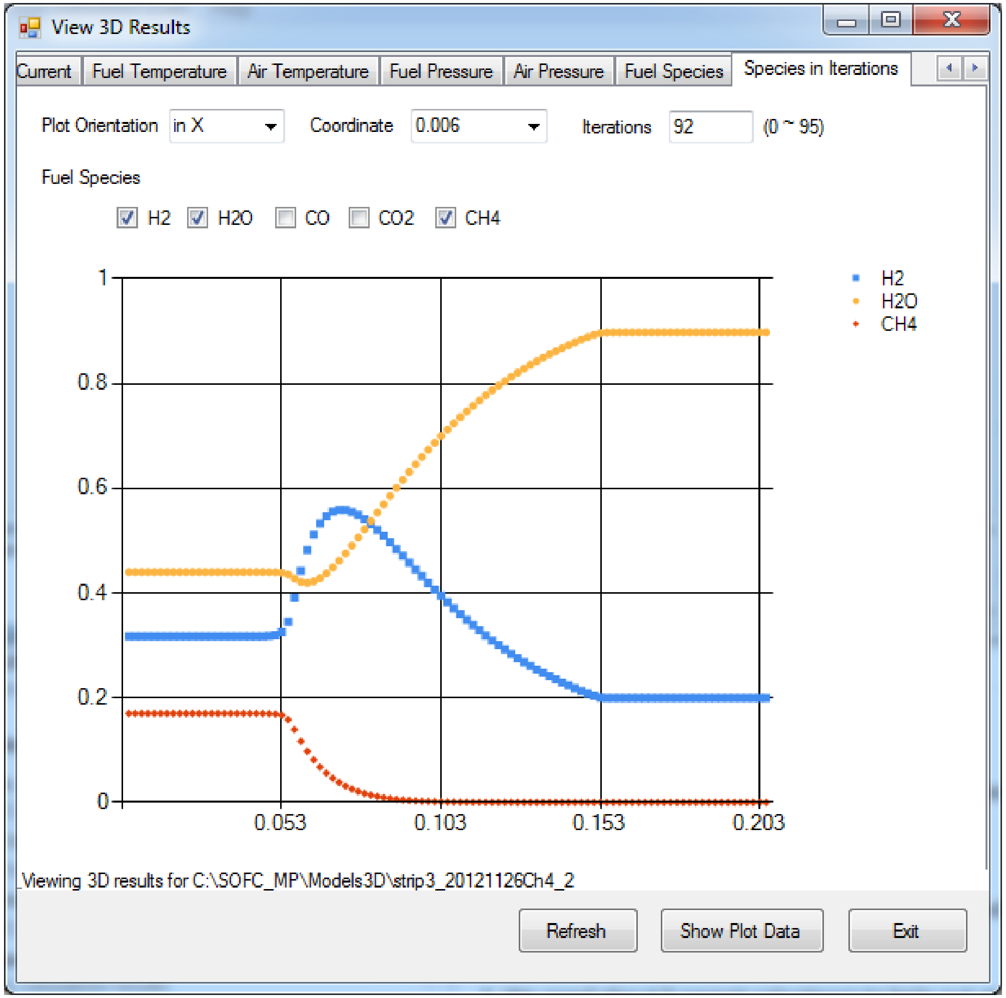
- **Challenge**:
  - SOFC stacks must be designed for high electrochemical performance and mechanical reliability
- **Goal**:
  - Develop numerical modeling tools to aid the industry teams' design and engineering efforts
- **Technical Approach**:
  - SOFC-MP 3D - Evaluates detailed 3D multi-cell stack structures for electrochemical, thermal, and mechanical stress analyses
  - SOFC-MP 2D – Rapid engineering analysis of electrochemical and thermal performance of tall symmetric stacks
  - SOFC-ROM – Creates reduced order models (ROMs) of SOFC stacks using response surface techniques for use in system modeling analyses

SOFC-MP 3D Recent Progress

- Construction of generic framework for SOFC-MP initiated
  - Replaces existing MSC MARC GUI for pre- and post-processing
  - Eliminates costly commercial license requirement
  - Unifies 3D and 2D packages under a common GUI for ease of use
- Pre- and post-processing for 2D tool completed
- Pre-processing for 3D model creation completed
  - Alternate model creation route beyond legacy Mentat-FC GUI
  - Implemented translators for ANSYS and ABAQUS FEA meshes
  - Fully integrated to the common GUI including assignment of operation and control parameters

SOFC-MP 3D Recent Progress (cont'd)

- Results post-processing for 3D tool started
  - Linear plotting of distributions along the flow field for all physics properties completed:
    - Air and fuel temperature
    - Pressure
    - Current density
    - Species concentrations
  - Multi-cell plotting and 3D contour plots using open-source software in progress
- Improved multi-physics solver performance for high methane (+20%) fuel compositions



Plot Orientation: in X
Coordinate: 0.006
Iterations: 92 (0 ~ 95)

Fuel Species

☑ H2 ☑ H2O ☐ CO ☐ CO2 ☑ CH4

Viewing 3D results for C:\SOFC_MP\Models3D\strip3_20121126Ch4_2

SOFC-ROM Motivation

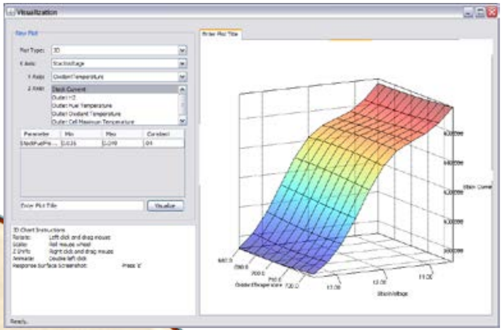
- More studies being performed for SOFC stack block integration and performance in large-scale demonstration systems
  - Understand performance and issues with BOP versus stand-alone testing
- Need a model to represent the stack in system models
  - Thermodynamic or 0-D models have no information about stack internal parameters such as temperature gradients, but such parameters may be critical for safe operation (e.g., maximum cell temperature)
  - Existing high fidelity SOFC-MP models have necessary information, but are too computationally expensive to run in system analyses
- Reduced order models (ROMs) provide approximate representations of such detailed models in O(1) time
- SOFC-ROM leveraged from the REVEAL framework at PNNL
  - REVEAL: a generic, automated framework for building ROMs for scientific simulations

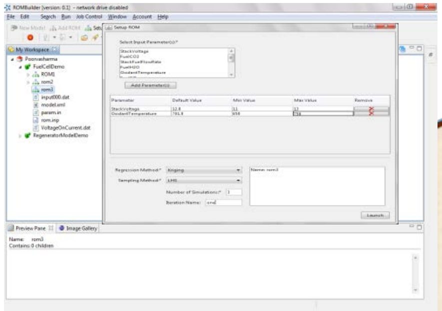
SOFC-ROM Workflow

Base Fuel Cell Model

Identify Design Parameters:
Stack Voltage,
Fuel temperature ,etc.

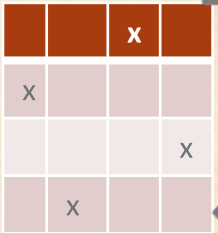
Export ROM
Plug-in for power system simulations



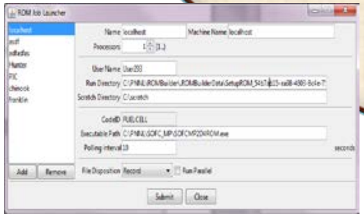


SOFC-ROM
User Environment

Sampling Method
Parameter Ranges
Number of Samples



Sampling: LHS, Norm, QMC



Name: localhost
Machine Name: localhost
Processors: 1
User Name: User233
Run Directory: [illegible]
Scratch Directory: C:\scratch
CodeID: FUEL CELL
Executable Path: C:\PNNL\SOFC_MP\SOFCMP2DROM.exe
Polling interval: 10 seconds
File Disposition: Record
☐ Run Parallel

Job Execution Infrastructure

Model

- Automated Post processing
- Data Management

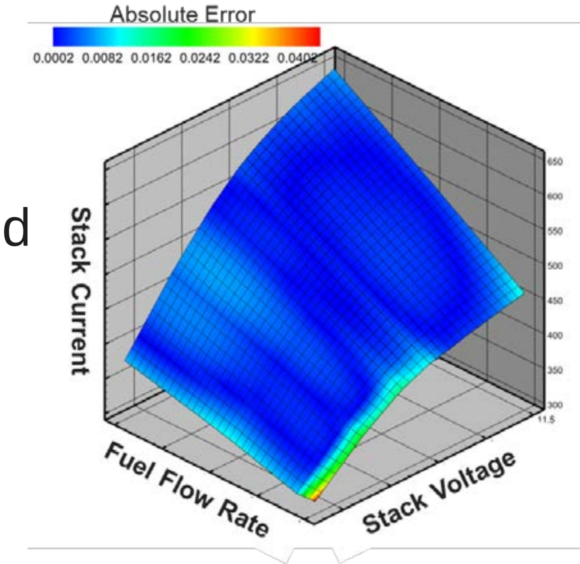
ROM Analysis Tools
- Visualization
- Error Estimation
- Predictive Analysis

Regression
- Kriging
- ANN
- SVM

Sensitivity Analysis
- ANOVA
- SRC

SOFC-ROM Recent Progress

- SOFC-ROM workflow completed
  - SOFC-MP 2D tool integrated as stack input
  - Multiple sampling methods implemented (LHS, QMC, Gaussian)
  - Multiple methods for regression (Kriging, ANN, MARS, SVM) and sensitivity analysis (ANOVA, SRC, MARS) implemented
  - ROM output in ACM or CAPE-Open format added
  - Fuel/air composition added to parameter set
  - Constraints on fuel/air compositions and and parameter dependencies added
  - Error handling added to trap and discard invalid or unconverged cases from the solution set
  - Installation and user manuals prepared



Ongoing and Future Work

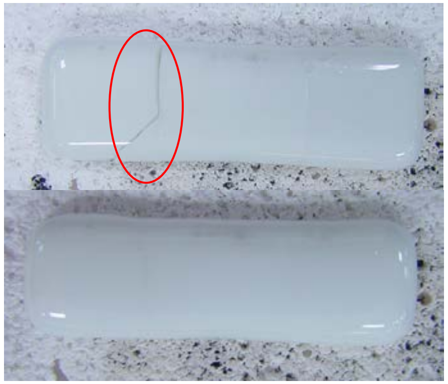
- SOFC-MP 3D
  - Implement post-processing visualization of SOFC-MP 3D results contours in the common GUI
  - Implement FEA stress analysis routines
- SOFC-ROM
  - Evaluate ROM export capabilities and integration with commercial system modeling tools (e.g. ASPEN) for study of SOFC-based power generation systems.
  - Release ROM version with documentation and examples

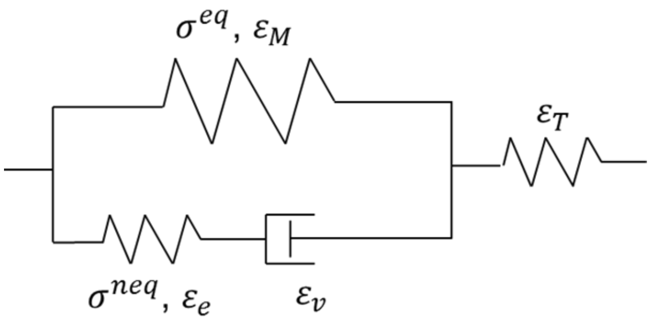
Modeling of Compliant Seals

- **Challenge**:
  - SOFC stacks must have reliable hermetic seals under operating and thermal cycling loads
- **Goal**:
  - Develop constitutive and damage models to design and simulate robust compliant seal materials and concepts for stacks
- **Technical Approach**:
  - Understand the healing and damage mechanisms
  - Combine different length-scale modeling approaches to establish quantitative relationships between material structure and its measured physical properties
  - Perform stack-level thermo-mechanical simulations to determine the effects of material properties and operating conditions
  - Validate the models through comparisons with experimental data

Constitutive Damage/Healing Model

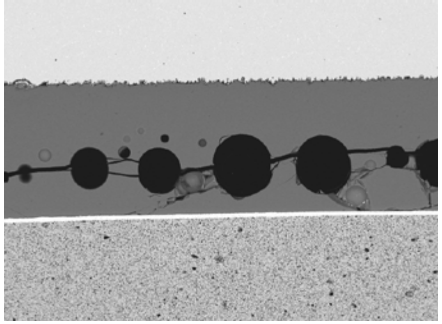
- Continuum thermo-inelastic model for dynamic damage and healing of self-healing glass
  - Includes the crack evolution and internal pore propagation





$$\dot{\sigma}_{ij}^{M} = (1 - \xi)\left(C_{ij}^{eq}\,\dot{\varepsilon}_{ij}^{M} + C_{ij}^{neq}\,\dot{\varepsilon}_{ij}^{e}\right)$$

$$\dot{\xi} = \dot{\xi}^{c} + \dot{\xi}^{p}$$



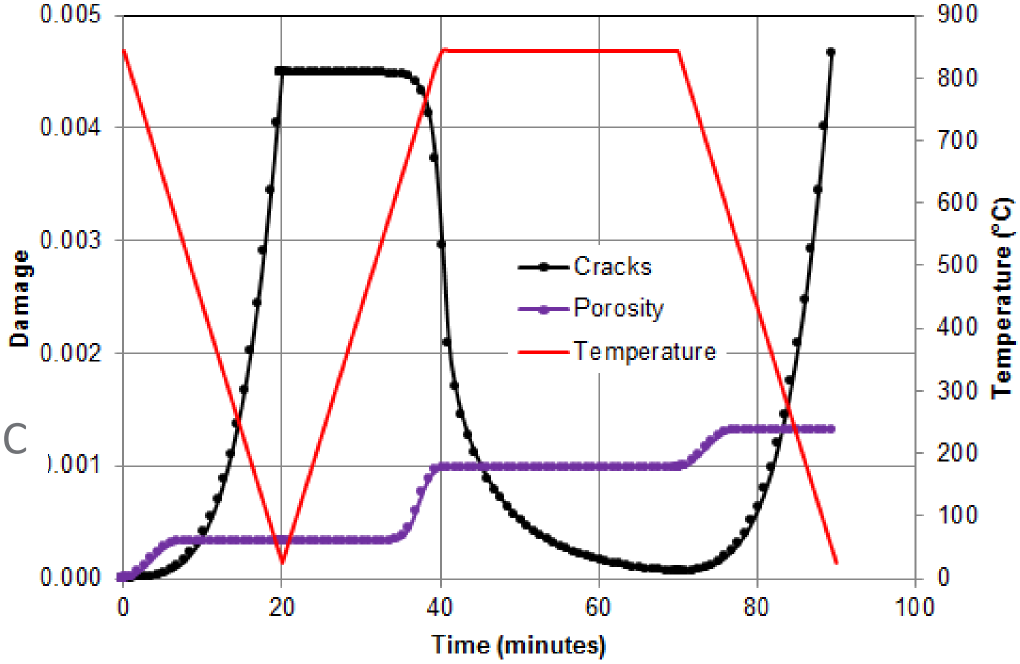
- Consider different underpinning mechanisms
  - Pressure driven crack nucleation
  - Deformation energy driven crack growth
  - Thermal diffusional crack healing
  - Homogenous and heterogeneous pore nucleation
  - Inelastic flow induced pore growth

$$\dot{\xi}^{c} = \dot{\xi}_{n}^{c} + \dot{\xi}_{g}^{c} + \dot{\xi}_{h}^{c}$$

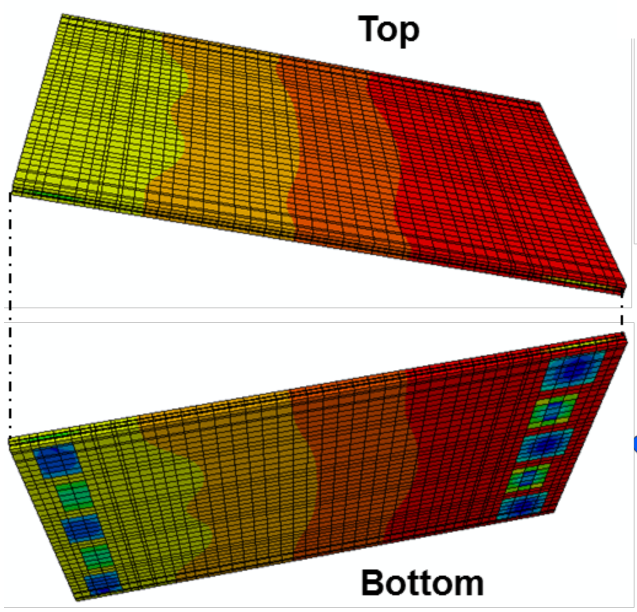
$$\dot{\xi}^{p} = \dot{\xi}_{n}^{p} + \dot{\xi}_{g}^{p}$$

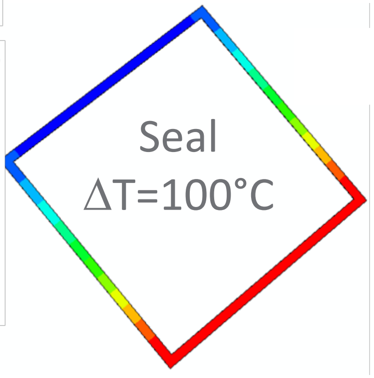
Single-Cell SOFC Stack Simulation

- SOFC single cell simulation predicts the seal mechanical response during rapid thermal cycling
  - Realistic temperature profile from SOFC-MP analysis



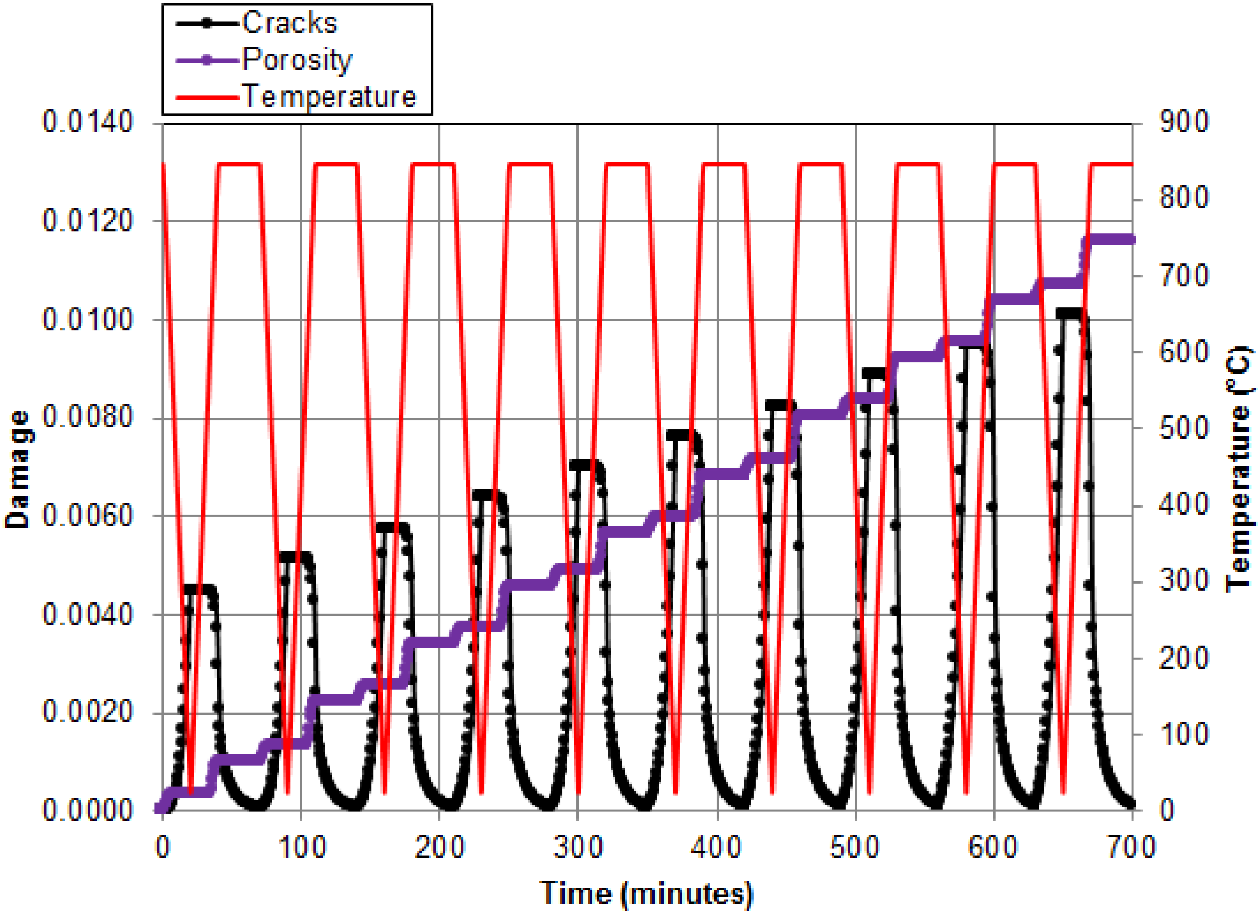
Tmax=860°C





- Cracking damage fully recovered during 30 min high temperature operation
- Pore damage not recovered (based on experimental observations to date)

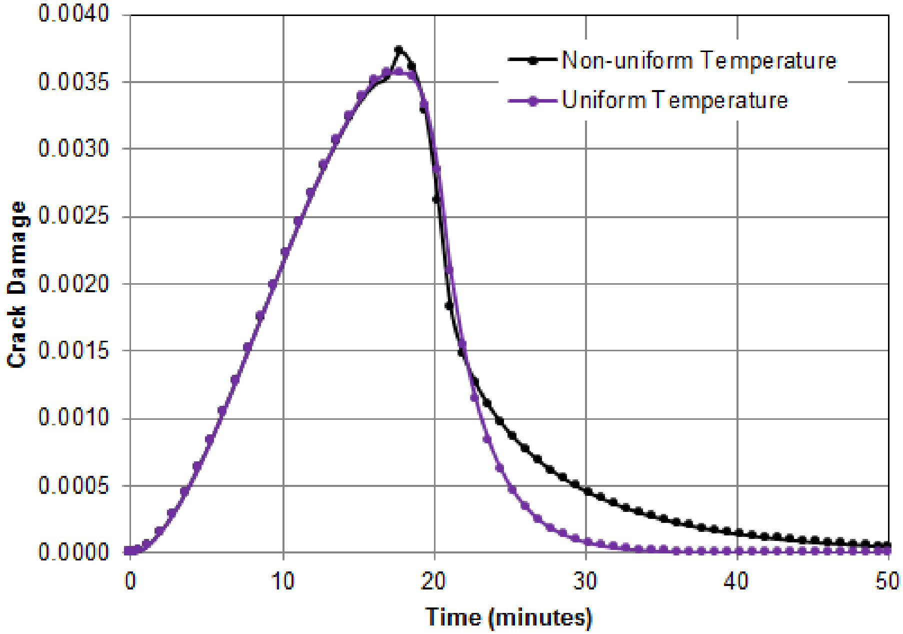
Single-Cell SOFC Stack Simulation (cont'd)

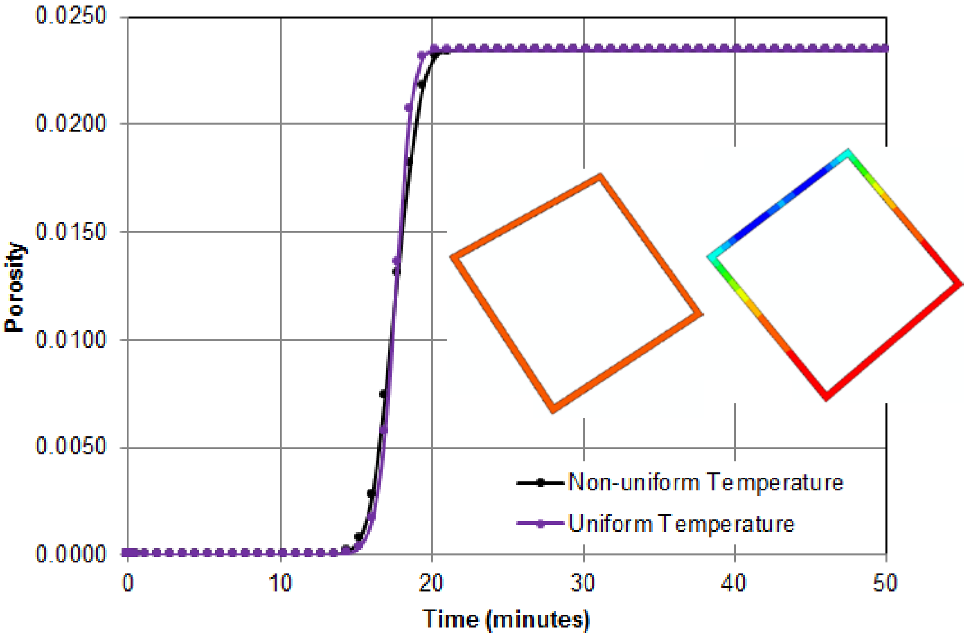


- Can simulate multiple cycles
- Overall damage within the glass seal is still kept within tolerance (<2%)
- Periodic maximum crack damage increases with loading cycles due to porosity accumulation and its effect on the elastic properties

Effect of Temperature Uniformity

- Effects of temperature uniformity in the cell
  - Uniform temperature takes the mean of the non-uniform temperature field
  - Very similar stress distributions in the seal
  - Slightly different damage evolution profiles
  - Temperature variation leads to more non-uniform damage distribution and low temperature regions show slower healing

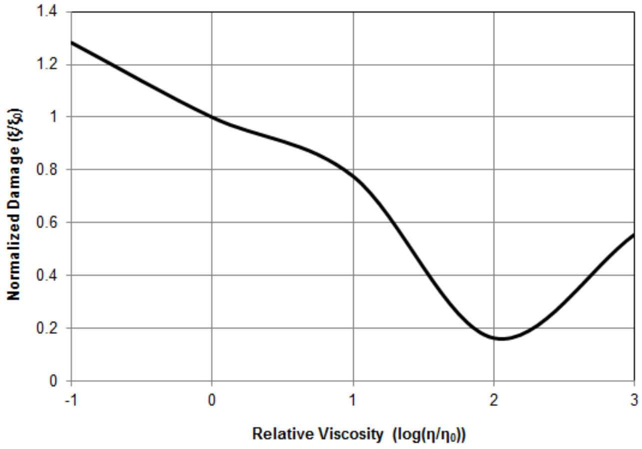




Effect of Dominant Damage Sources

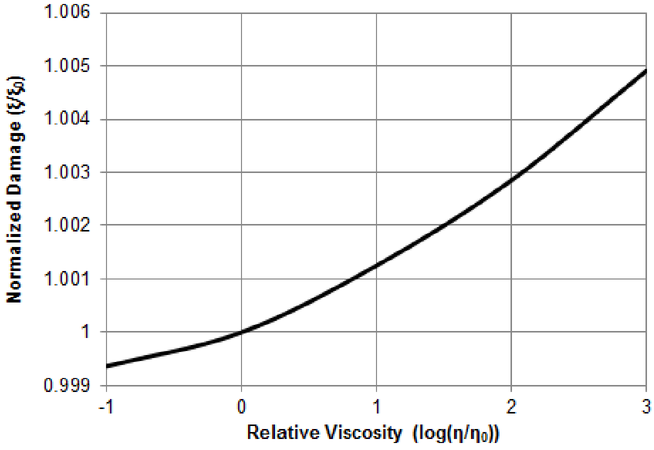
- Depending on which damage sources are dominant, the effects of viscosity on seal glass material behavior may be different

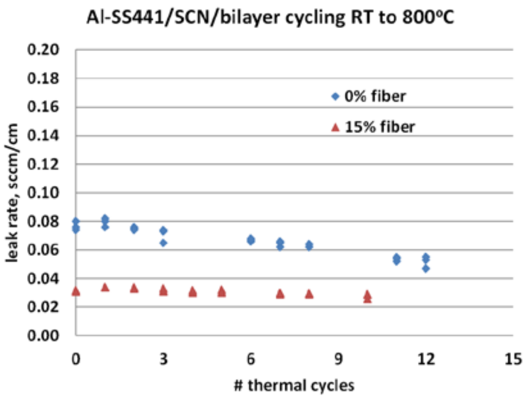
pore dominates



Damage
versus
Viscosity

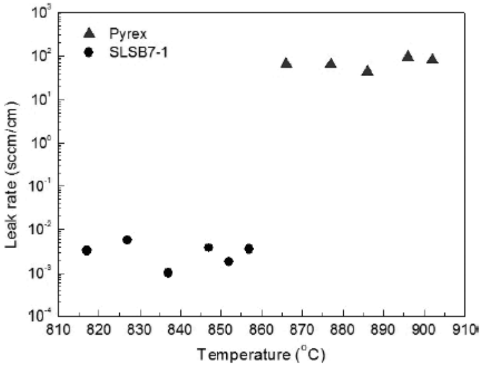
crack dominates





Viscosity ↑
Leak Rate ↓

[Chou, PNNL]

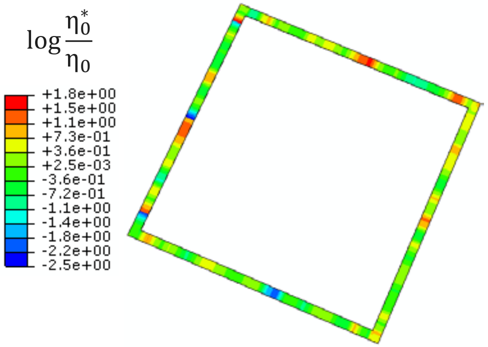


Viscosity ↑
Leak Rate ↑

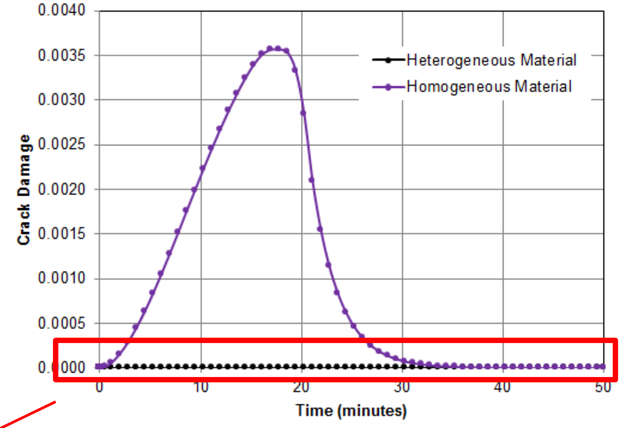
[Kim et al., 2011. Rev. Adv. Mater. Sci. 28]

Effect of Material Heterogeneity

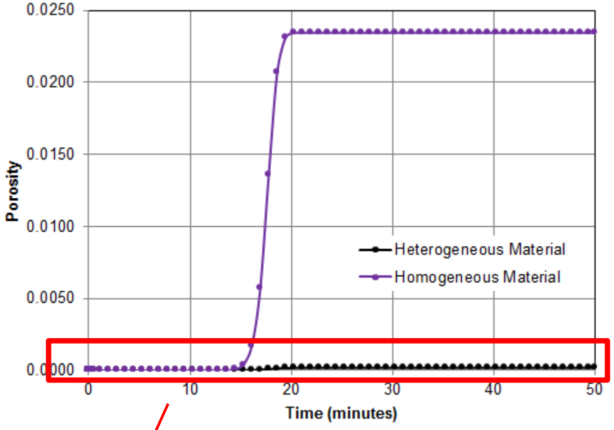
- Reinforcement phases (fibers, particles) can introduce heterogeneity
  - Normal distribution is assumed for the viscosity within the seal geometry
  - Heterogeneous viscosity field greatly reduces the damages
  - Low viscosity regions provide local compliance and stress relief

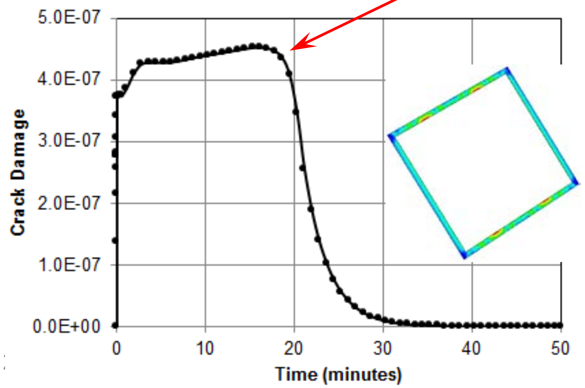


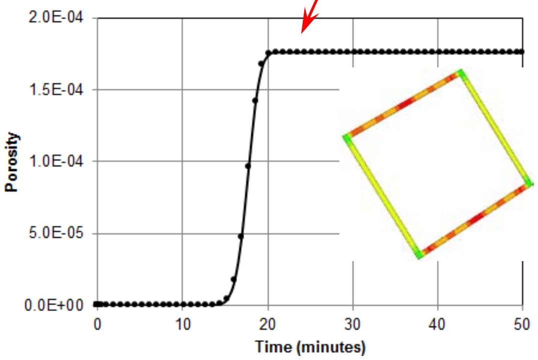
Crack Evolution



Pore Propagation

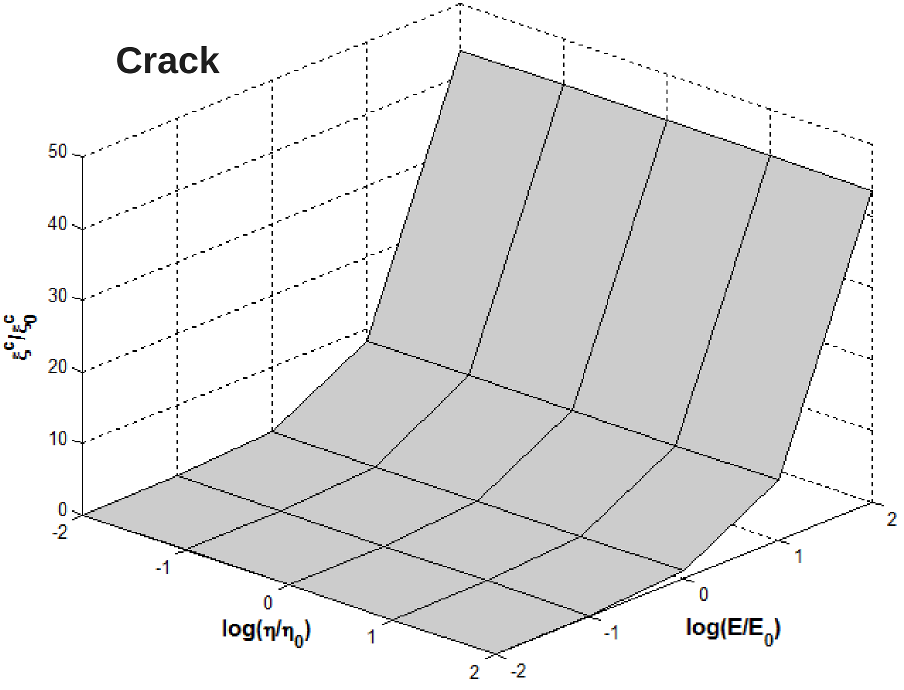


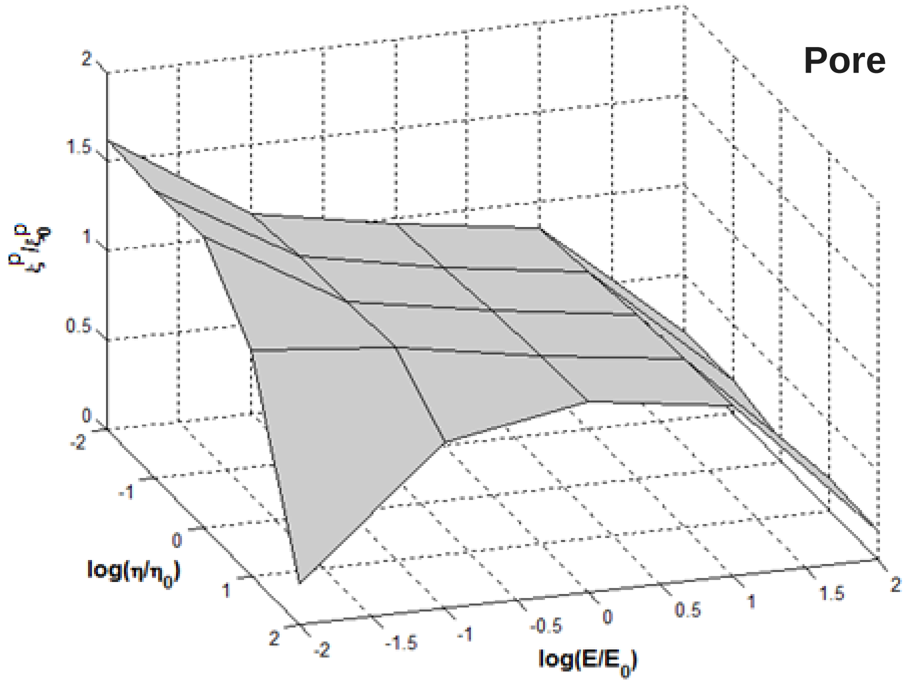




Effect of Material Properties

- Material mechanical response in terms of characteristic material properties, i.e. elastic modulus and viscosity
    - 25 cases to establish the response surface: log(η/η_0): -2:1:2, log(E/E_0):-2:1:2
    - Cracking damage is highly sensitive to stiffness but less affected by viscosity
    - Pore growth is strongly influenced by both properties
    - High viscosity together with low stiffness would lead to the least damage





Ongoing and Future Work

- Evaluate the seal performance within multi-cell SOFC stacks
- Continue model development by including effects such as stress dependent viscosity and material stochastic behavior
- Examine different engineering seal designs to support the seal material development effort

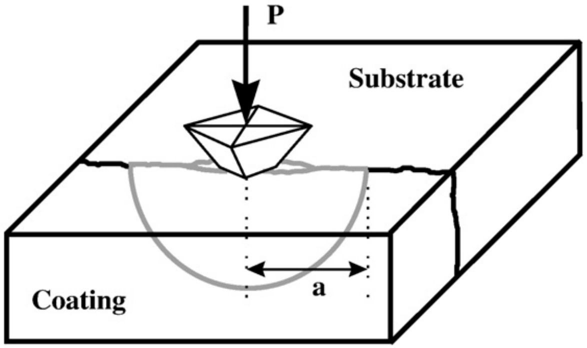
Mechanical Reliability and Life Prediction of Coated Metallic Interconnects

- **Challenge**:
  - IC must meet SECA lifetime requirement
- **Goal**:
  - Use experiments and modeling to predict interconnect life for spinel-coated surface-modified specimens under isothermal cooling and thermal cycling
- **Technical Approach**:
  - Vickers pyramidal nano/micro-indentation performed at the substrate/oxide scale interface to assess apparent fracture toughness and spallation resistance of surface modifications
  - Fracture mechanics and FEA modeling tools to evaluate driving force and energy release rate for spallation to determine the main factors influencing IC degradation
  - Evaluation of IC candidate materials

Interfacial Indentation Testing

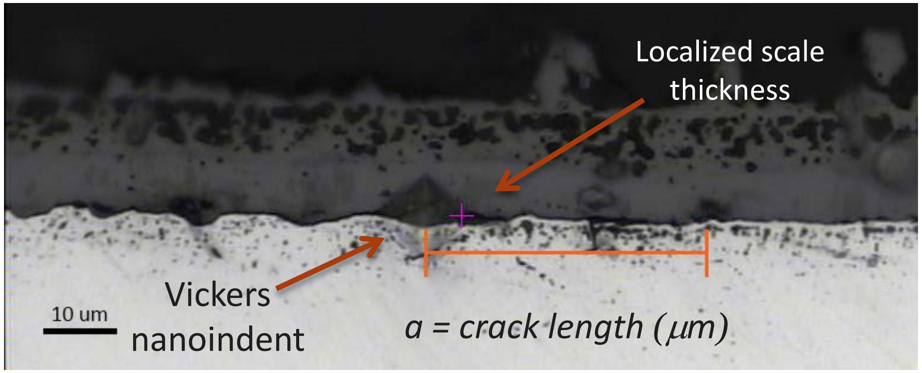
- Apparent interface fracture toughness (K_I) of bimaterial interface may be estimated as [1, 2]:

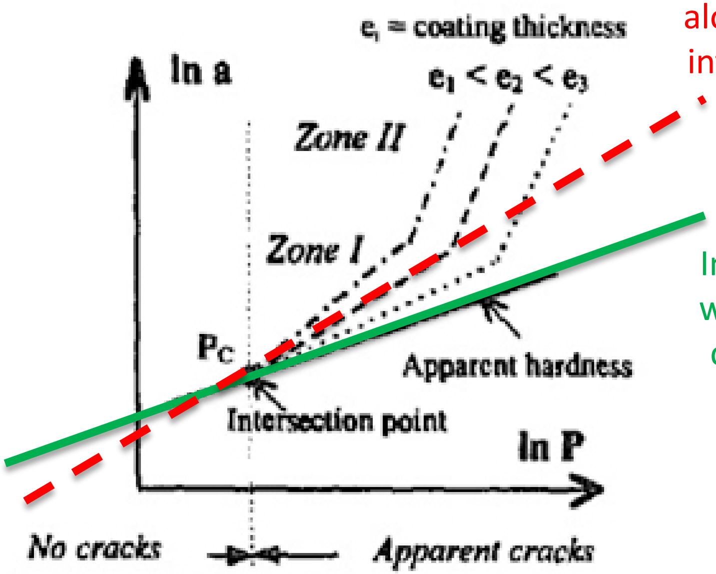
$$K_{in} = 0.015 \boxed{\frac{P_c}{a_c^{3/2}}} \left(\frac{E}{H}\right)_I^{1/2}$$



- Nano/micro indentation performed to propagate crack between substrate and scale to determine the critical load P_c and critical crack length a_c
- Intersection of the indentation data linear fit and the apparent hardness defines the critical load (adaptation of methodology)

Surface ground, 10,000 h, 800 °C





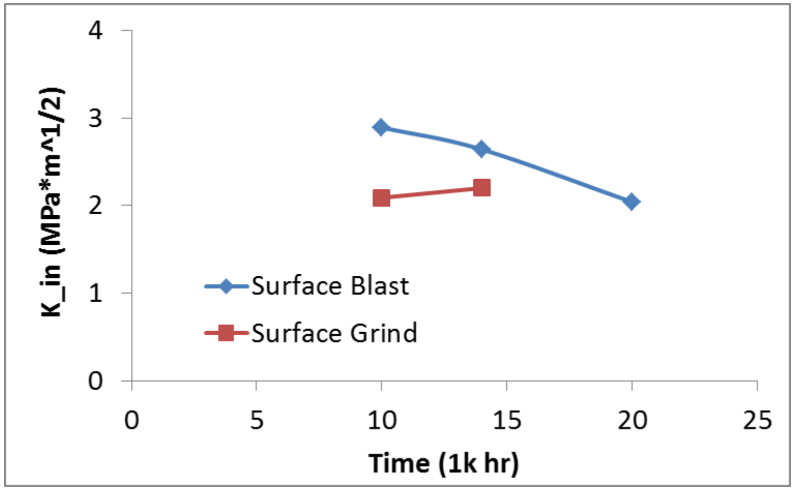
Cracks along the interface

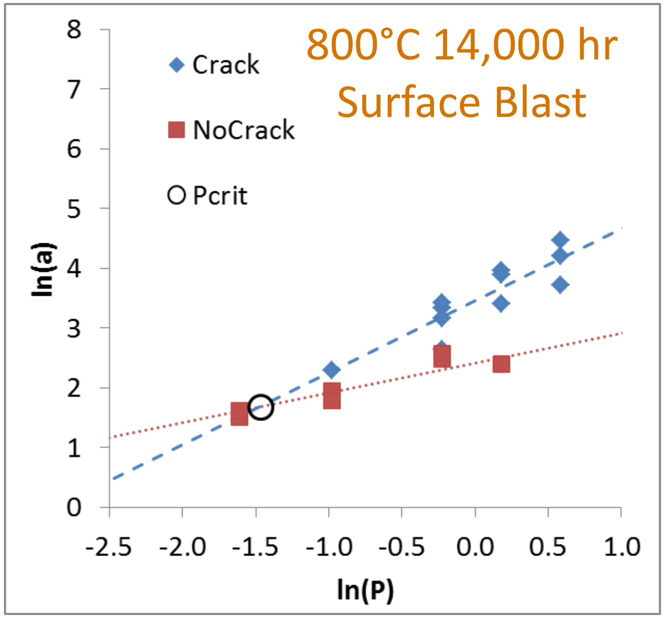
Indents with no cracks

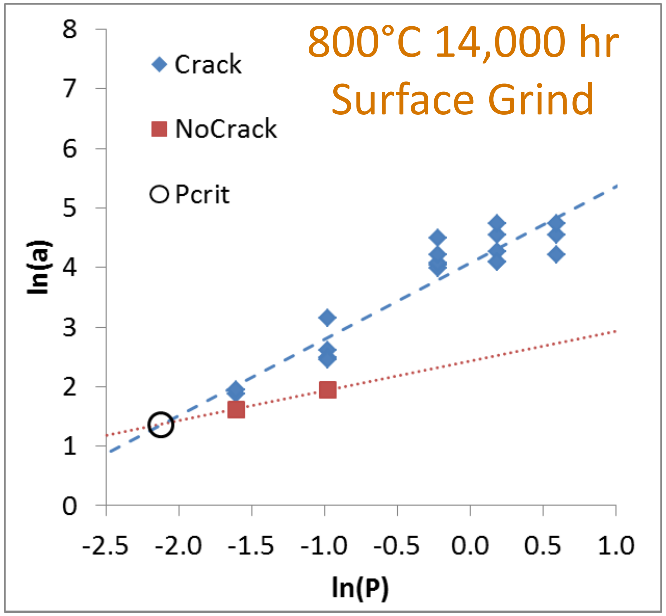
[1]. D. Chicot, et al., Thin Solid Films 283 (1996) 151.
[2]. G. Marot, et al., Surface & Coatings Technology 202 (2008) 4411–4416

Interfacial Indentation Testing Results

- Data collection time intensive
- Initial results indicate indentation tests follow the expected response
- Average stress intensity factor:
  - 441 SB: ~2.5 MPa*m^0.5
  - 441 SG: ~2.0 MPa*m^0.5

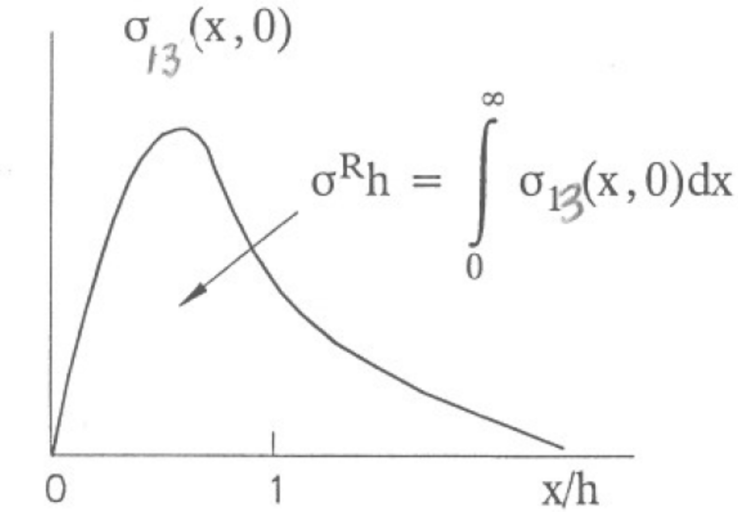






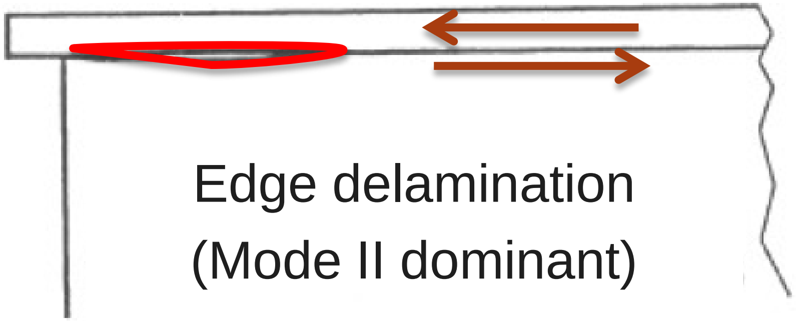
Failure Modes for Coatings

Shear stress distribution



$$\sigma_{13}(x,0)$$

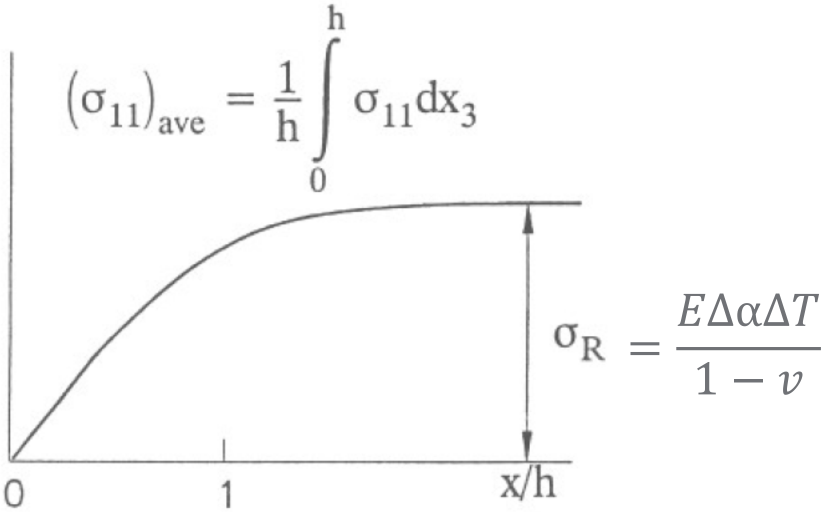
$$\sigma^R h = \int_0^\infty \sigma_{13}(x,0)\,dx$$



Edge delamination

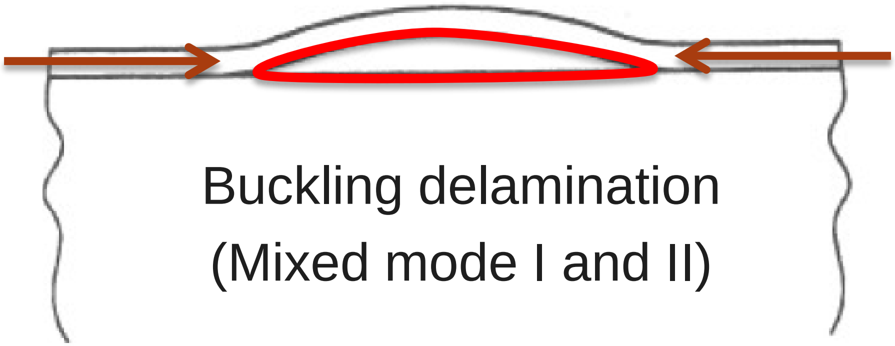
(Mode II dominant)

Compressive stress distribution



$$(\sigma_{11})_{ave} = \frac{1}{h}\int_0^h \sigma_{11}\,dx_3$$

$$\sigma_R = \frac{E\Delta\alpha\Delta T}{1-v}$$



Buckling delamination

(Mixed mode I and II)

Failure Criteria for Critical Thickness h_c

Energy release rate:

$$G = \frac{\left(1-\nu^2\right)h\sigma^2}{2E}\left(1-\frac{\sigma_c}{\sigma}\right)\left(1+3\frac{\sigma_c}{\sigma}\right)$$

Thermal stress:

$$\sigma = \frac{E\Delta\alpha\Delta T}{1-\upsilon}$$

Critical buckling stress:

$$\sigma_c = \frac{\pi^2}{12}\frac{E}{1-\nu^2}\left(\frac{h}{b}\right)^2$$

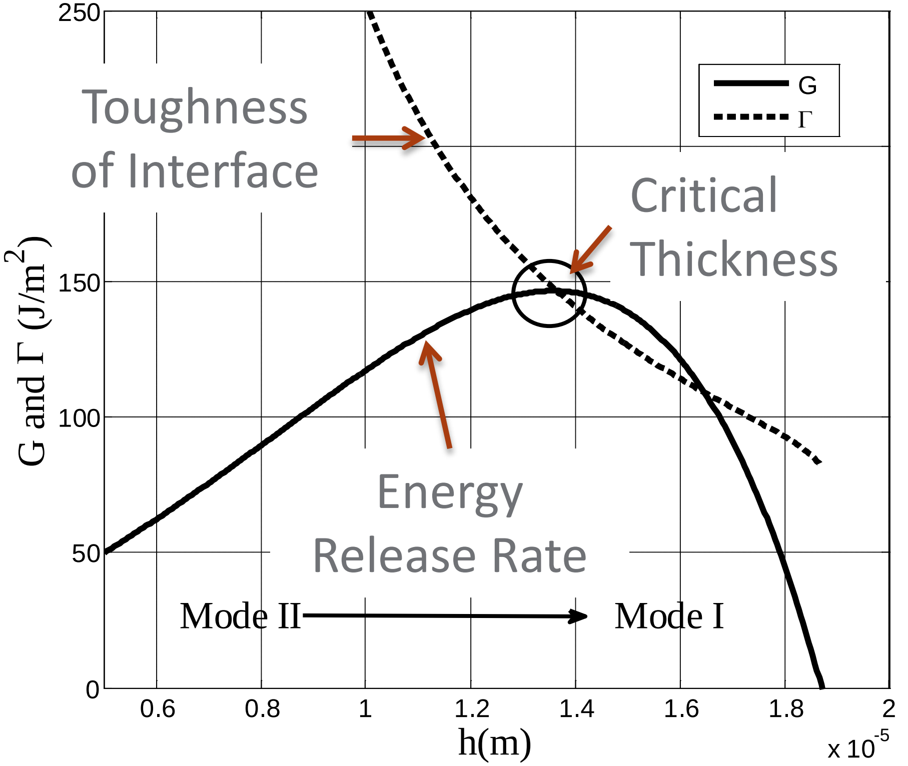
Fracture toughness:

$$\Gamma\left(\Psi\right) = \Gamma_I\left(1+\tan^2\left[\left(1-\lambda\right)\Psi\right]\right)$$

$$\Gamma_I = \frac{1-\nu^2}{E}\bigcirc\!\!\!\!\!\!\; K_I^2 \rightarrow$$

From interface indentation experiment

Failure Criterion: $G\left(h,\sigma,b\right) > \Gamma\left(\Psi\left(h\right)\right)$



Toughness of Interface

Critical Thickness

Energy Release Rate

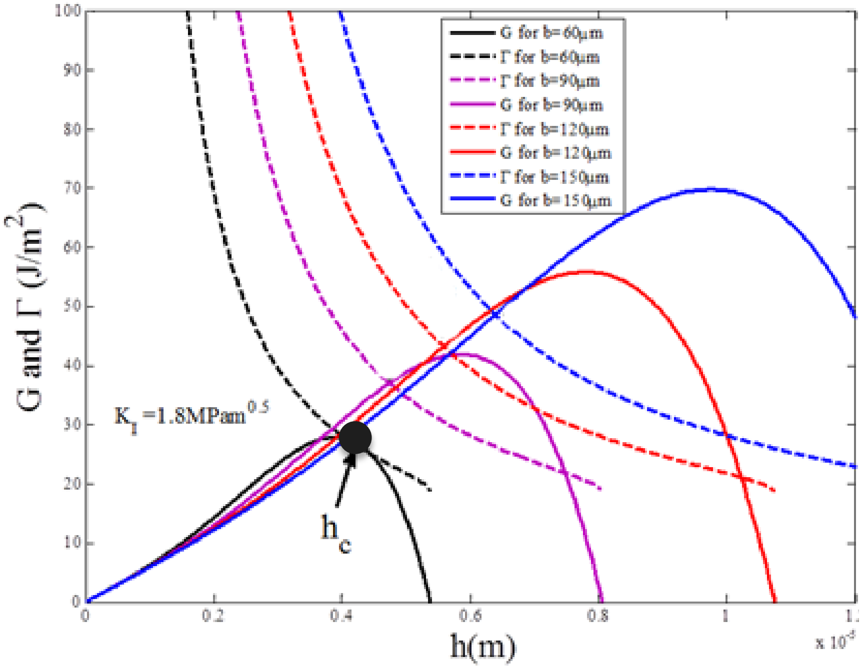
If h > h_c : coating will fail under cooling

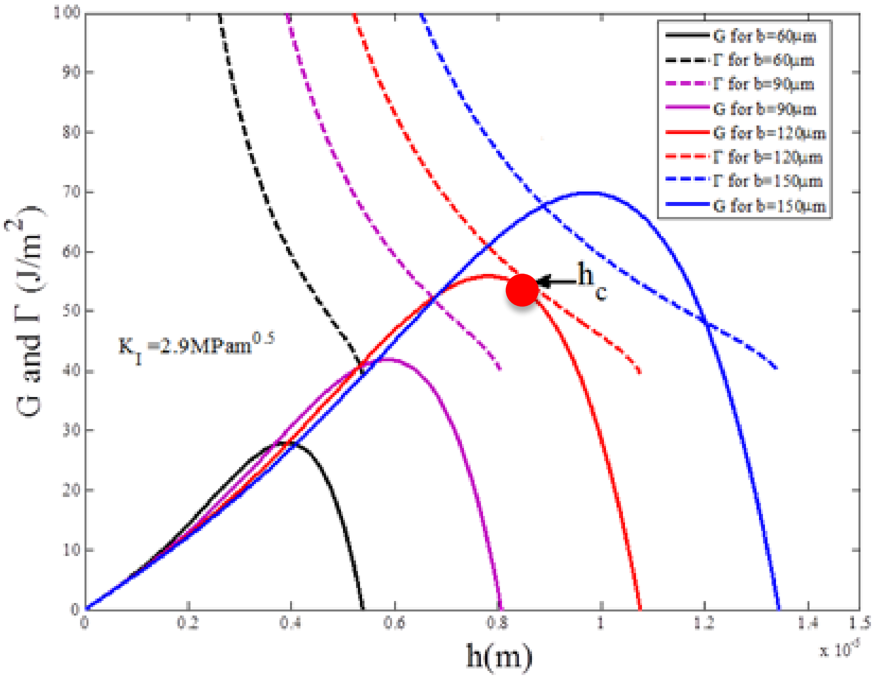
If h < h_c : coating will survive cooling

Failure Analysis Results

Based on the measured stress intensity factor, a threshold blister size is predicted for which no buckling delamination failure is expected

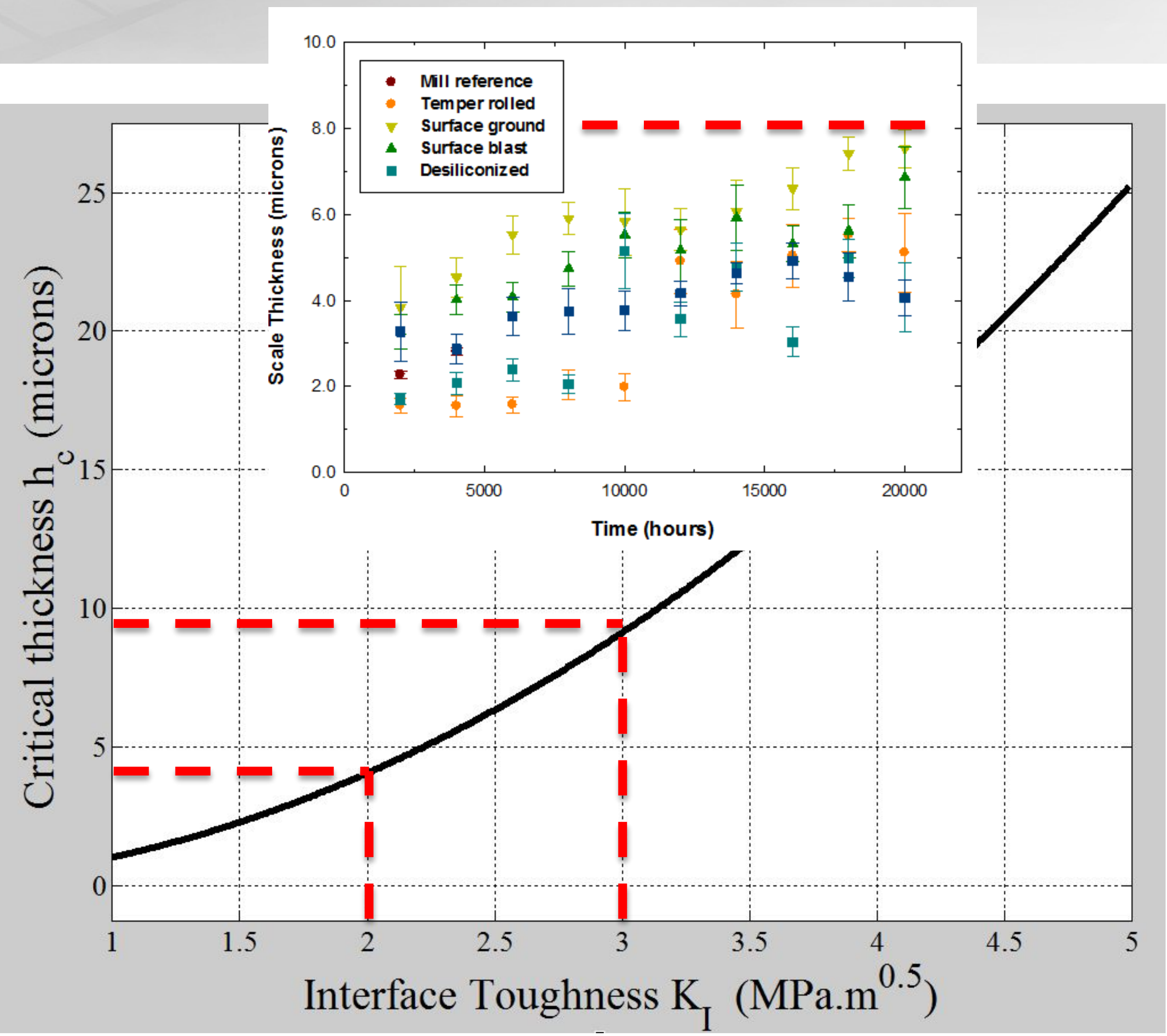
- K_I = 1.8 MPa-m$^{0.5}$, b=60 μm, h_c ~ 4.4 μm
- K_I = 2.9 MPa-m$^{0.5}$, b=120 μm, h_c ~ 9.2 μm





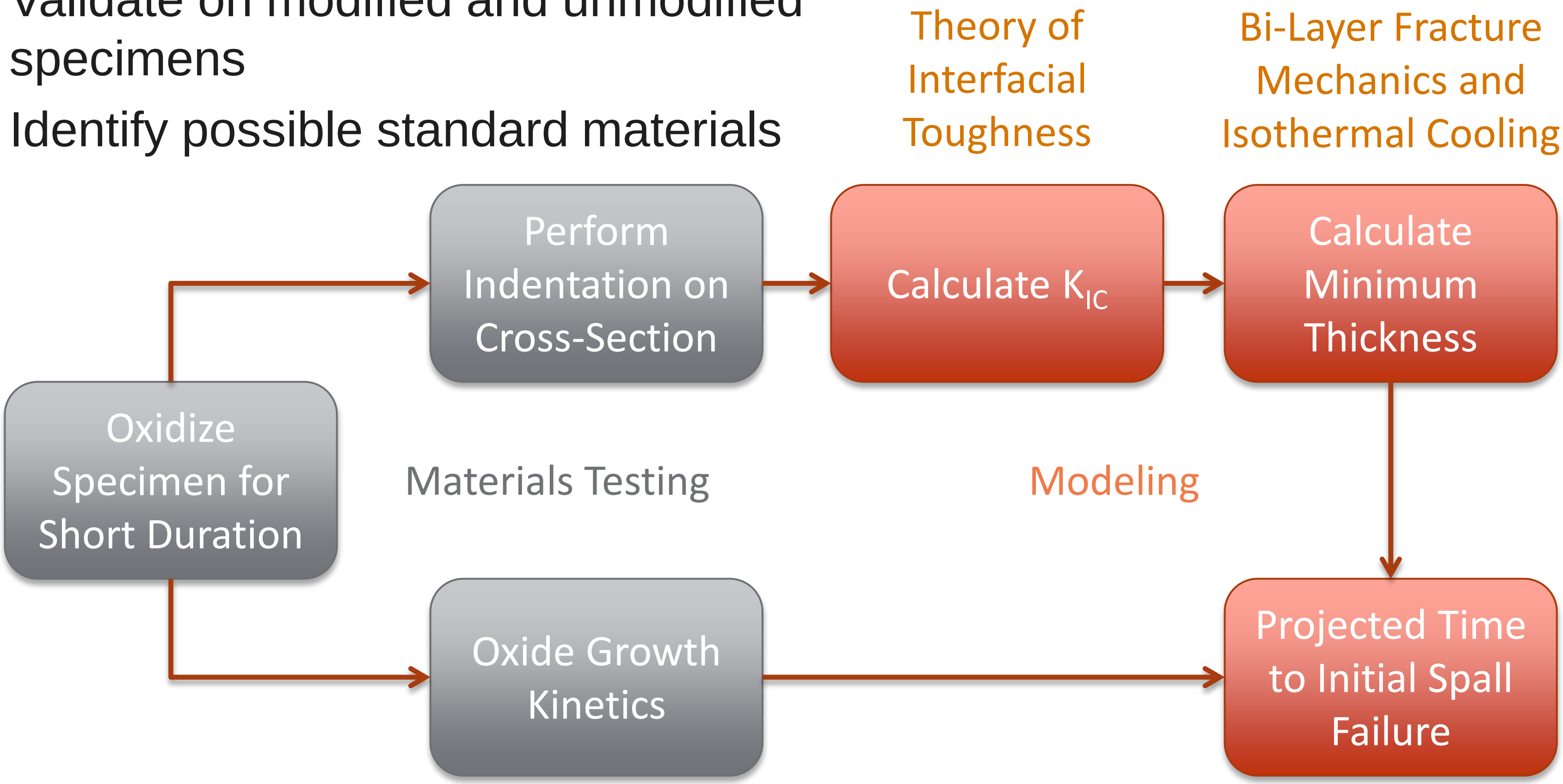
Failure Analysis Results (cont'd)

- For range of stress intensity factor of ~2-3 MPa-m$^{0.5}$, a critical thickness of 4-9 μm is predicted for SB/SG materials
- Present long-term experiments with average thickness of almost 8 μm for SB/SG materials are still running



Proposed Predictive Methodology

- Use short duration oxidized specimens for long-term predictions
- Validate on modified and unmodified specimens
- Identify possible standard materials



Theory of Interfacial Toughness

Bi-Layer Fracture Mechanics and Isothermal Cooling

Oxidize Specimen for Short Duration

Perform Indentation on Cross-Section

Calculate K_{IC}

Calculate Minimum Thickness

Oxide Growth Kinetics

Projected Time to Initial Spall Failure

Materials Testing

Modeling

Ongoing and Future Work

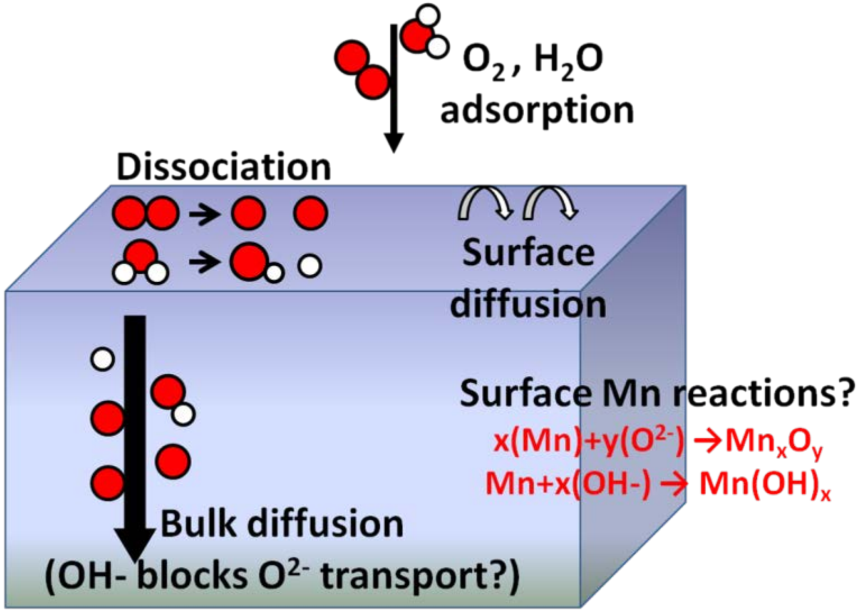
- Indentation measurements on 850°C specimens
- Evaluation of experimental/analytical methodology as screening method for life-prediction
  - Life predictions of surface modified specimens exposed to 800°C
  - Determine K_{in} for 2000 h, 800°C, unmodified, coated 441 specimens
  - Benchmarking of methodology with known standards if available
  - Effect of surface roughness on methodology and data scatter

Electrochemical Degradation Under High Cathode Humidity Conditions

- **Challenge**:
  - Long-term electrochemical performance degradation must be low
- **Goal**:
  - Use modeling to identify cathode degradation mechanisms and characterize electrochemical impact for high humidity conditions
- **Technical Approach**:
  - <u>Micro-scale</u> – Investigate the surface level kinetics and thermodynamics of H_2O with LSM using molecular dynamics modeling of H_2O, O_2 and LSM in the presence of an applied field
  - <u>Meso-scale</u> – Resolve the reactive transport in the cathode and at the cathode-electrolyte interface using SPH porous media model
  - <u>Macro-scale</u> – Cell and stack level modeling of the effects of degradation on stack performance using SOFC-MP

Micro-Scale Modeling Results

- Want to evaluate O_2 and H_2O competitive adsorption and diffusion on LSM
- $La_{0.8}Sr_{0.2}MnO_3$ periodic solid structure model built (density, cohesion energy, and O_2 adsorption activation energy) consistent with experiment
- H_2O adsorption activation energy predicted and passed up to the meso-scale model



O_2, H_2O adsorption

Dissociation

Surface diffusion

Surface Mn reactions?

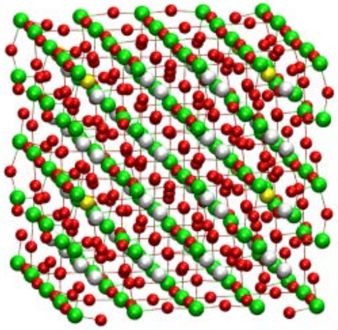
$x(Mn)+y(O^{2-}) \rightarrow Mn_xO_y$

$Mn+x(OH-) \rightarrow Mn(OH)_x$

Bulk diffusion

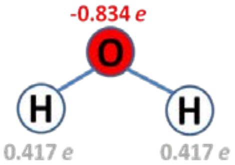
(OH- blocks O^{2-} transport?)

Property	Calculated	Experiment
density at 1000 K (g/mL)	5.77	5.99[2]
cohesion energy at 1000 K (eV)	26.55	31.0 [3]
O_2 adsorption activation energy (eV)	0.97±0.02	1.09±0.01 [1]
H_2O adsorption activation energy (eV)	1.32±0.07	n/a



Sr-doped LSM model

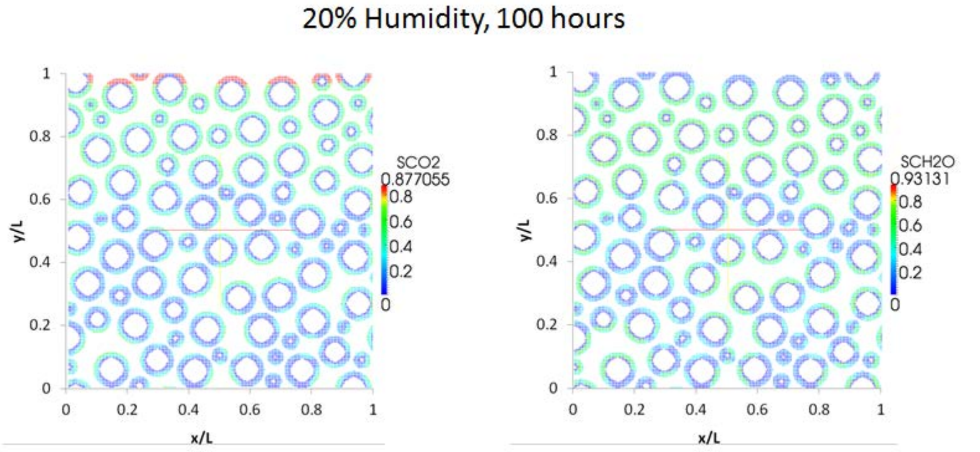
Quadrupole O_2 model



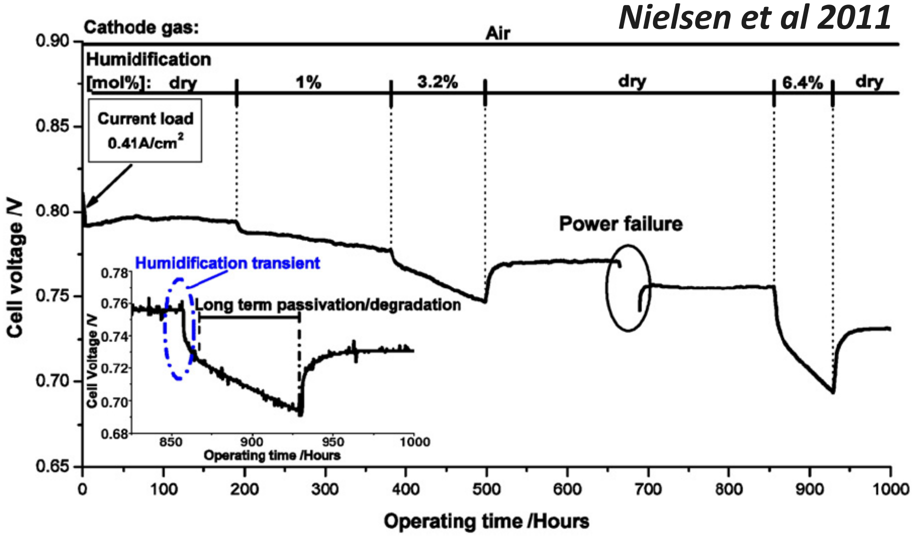
TIP3P water model

Meso/Macro-Scale Modeling Results

- SPH model for 2D porous cathode structure created
- Langmuir model for competitive adsorption
- Simulated accelerated testing with higher humidity levels (10%, 20%, 40%) for 100 hr to accelerate rate of degradation
  - **Adsorption site competition alone cannot explain the degradation results of PNNL or Nielsen (2011)**
- Electrochemical degradation captured as damage factor and applied to the cathode exchange current density in the macro-scale I-V curve



20% Humidity, 100 hours



Nielsen et al 2011

Ongoing and Future Work

- Expand micro-scale model to consider possible reactions with Mn or Sr
- Evaluation of PNNL long-term test data for identification of possible mechanisms at low humidity

Acknowledgements

- The work summarized in this presentation was funded by the U.S. Department of Energy’s Solid-State Energy Conversion Alliance (SECA) Core Technology Program

- The authors wish to thank Shailesh Vora, Briggs White, Rin Burke, Joe Stoffa, and Travis Shultz for their valuable technical discussions and guidance.