NETL Research & Development

NATIONAL ENERGY TECHNOLOGY LABORATORY

SOFC Materials Development and Degradation Modeling

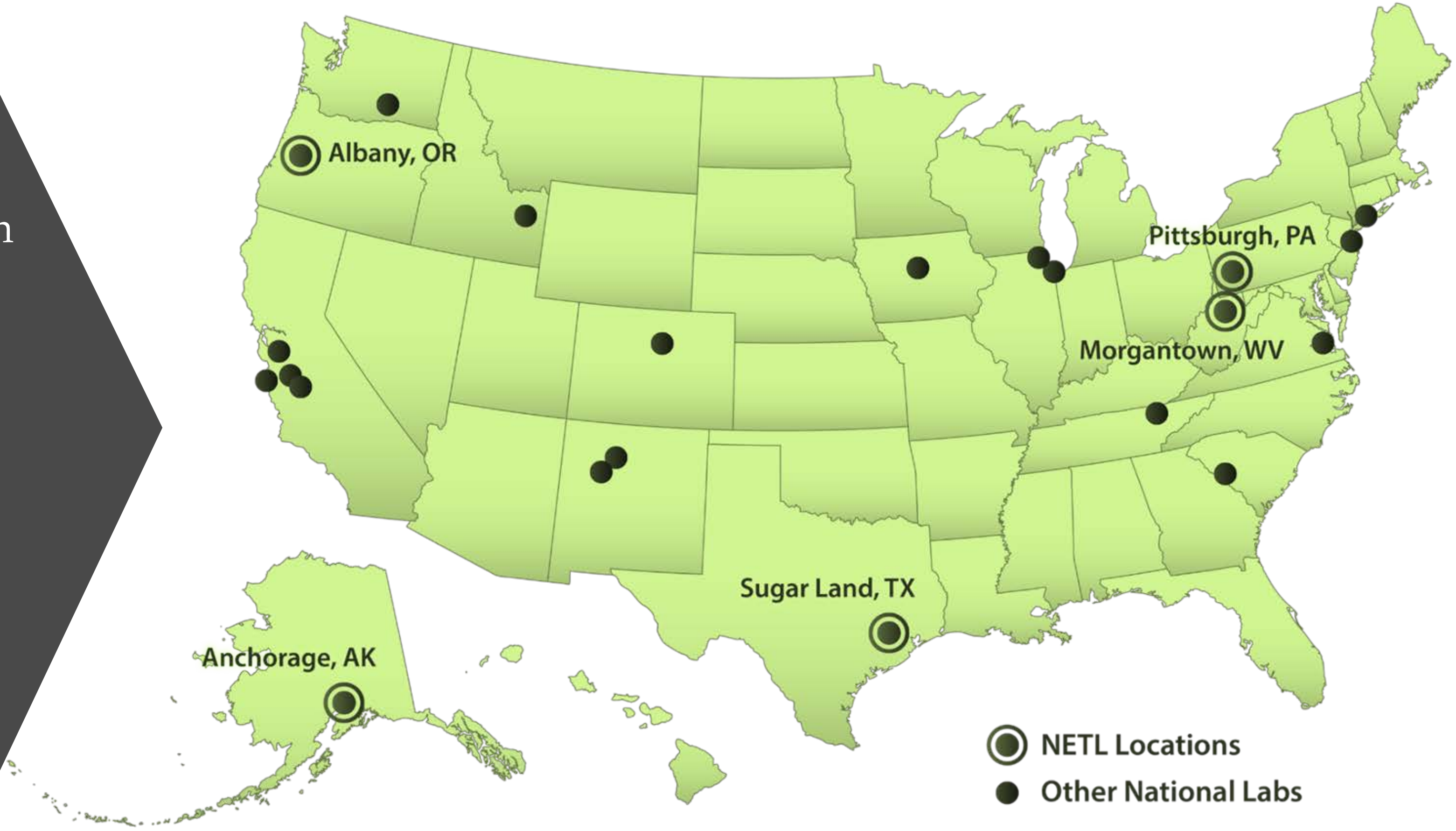
Gregory A. Hackett, Ph.D.

Systems Engineering and Analysis

June 13, 2017

Outline

- **Background**
- **Degradation Modeling Tools**
  - 3-D Microstructure Reconstruction
  - Particle Coarsening Model
  - Materials Interface Evaluation
  - Scale Bridging with PNNL
- **Degradation Mitigation**
  - Electrode Engineering
- **Conclusions**
  - Comprehensive Predictive Modeling Toolset



Background

SOFC Program Mission and R&D Objective

NATIONAL ENERGY TECHNOLOGY LABORATORY

SOFC Program Mission (Grand Challenge):

"To enable the generation of efficient, low-cost electricity with intrinsic carbon capture capabilities for near-term SOFC natural gas distributed generation systems and long-term coal or natural gas central power systems."

A thorough understanding of solid oxide fuel cell operation from the micro- to system scale is needed to improve the performance and durability, ultimately resulting in decreased system costs.

Cell and Stack Degradation

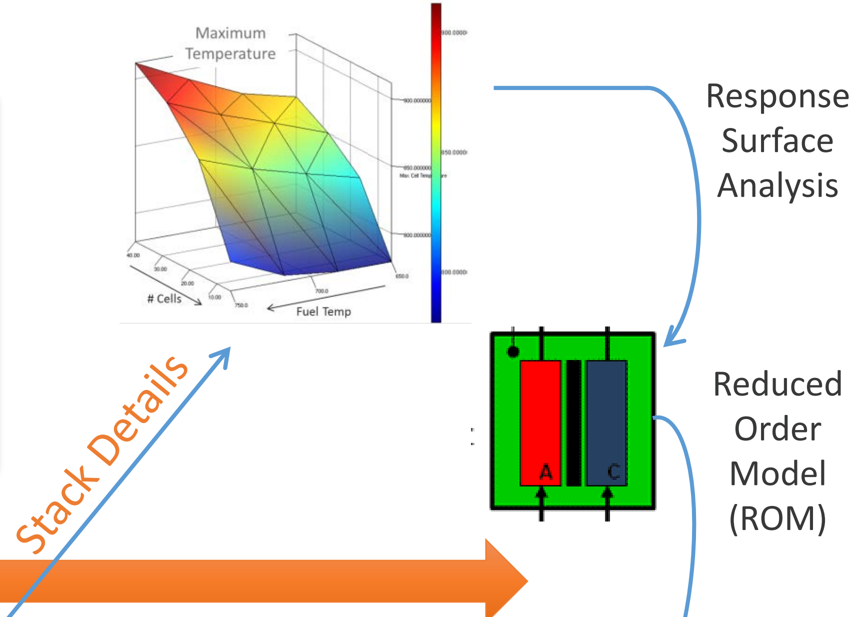
Predictive Modeling Toolset

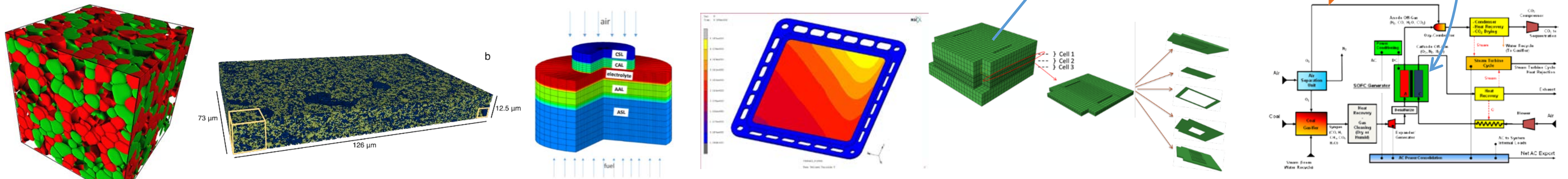
Background

NETL/PNNL Collaboration to Complete Scaling Process

Need design and engineering at several scales to facilitate wide-scale SOFC commercialization

Link NETL and PNNL models at different scales to inform system level and life cycle analyses





Electrode Microstructure

Single Cell

Multi-Cell Stack

IGFC System Model

NETL

NETL

PNNL

Multi-Scale Modeling Approach

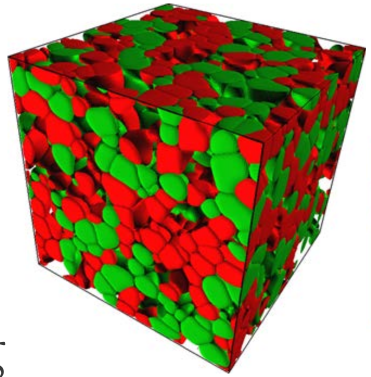
Comprehensive Predictive Modeling Tool Development

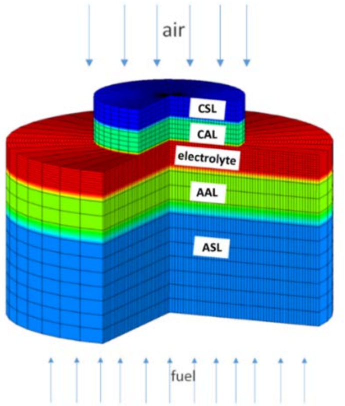
1. **Detailed understanding of degradation modes associated with SOFC electrodes/electrolytes**
   - Electrode coarsening, diffuse interface evaluation, secondary phase formation, contaminants, etc.
2. **Link detailed single cell level model to multi-cell stack model**
   - NETL's multi-physics model to PNNL's SOFC-MP model
3. **Link informed stack model to system model via ROM**
   - PNNL generated ROM to NETL ASPEN Plus system model
4. **Output of system level model used to perform sensitivity studies of utility-scale SOFC plant configurations to minimize cost-of-electricity**

Cell and Stack Degradation Modeling

Approach

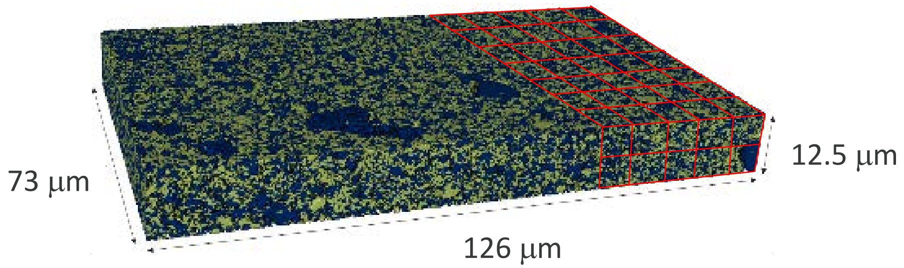
- **Identify Degradation Modes**
  - Particle Coarsening, Secondary Phase Formation, Contaminants
- **Predict Future Behavior**
  - Phase Field Modeling, Density Functional Theory, Scale Bridging
- **Model Validation through Experimentation**
  - Impedance Spectroscopy, Performance Curves, Integrated Sensors
- **Post-experimental Characterization**
  - Microstructure Reconstruction (p-FIB, nano-CT), HR-TEM, SEM
- **Predictive Modeling Tools**
  - "Hurricane" Model, EIS Deconvolution, Visualization, Degradation Analysis, etc.





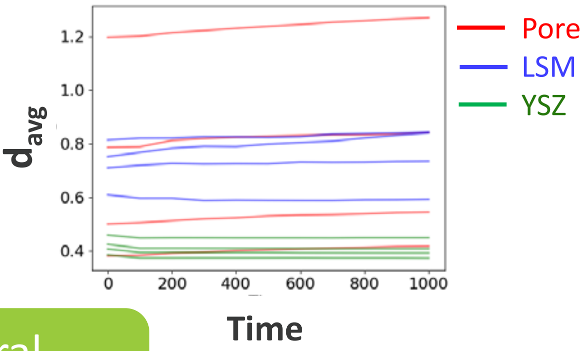
Long-term Performance Prediction

Integrated Cell Degradation Model

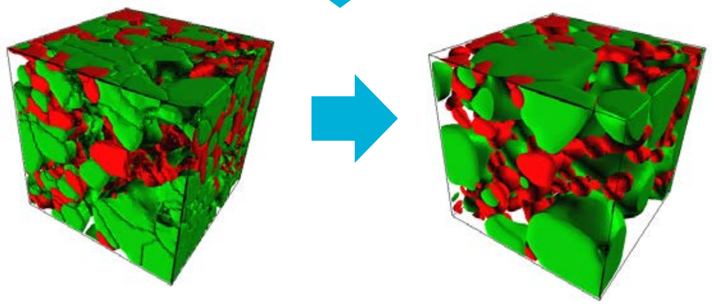


3D Reconstruction of SOFC Electrodes

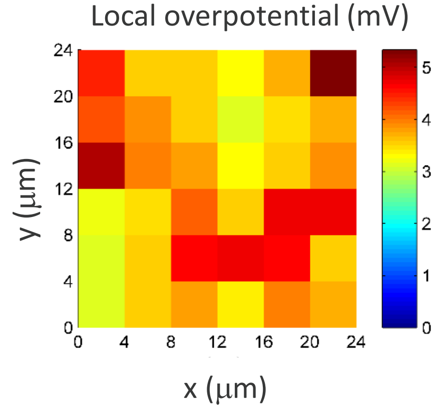
Microstructural Analysis

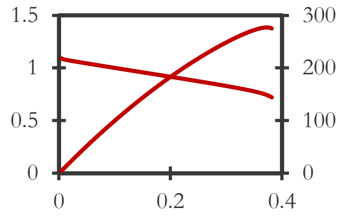


Degradation Models

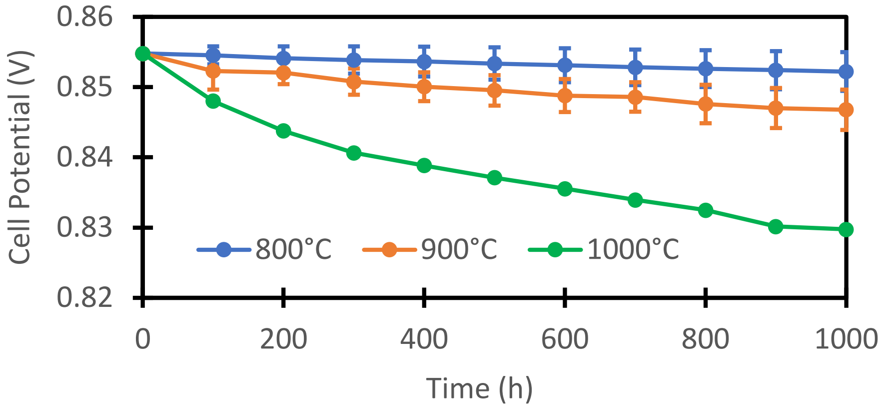


Multiphysics Performance Model





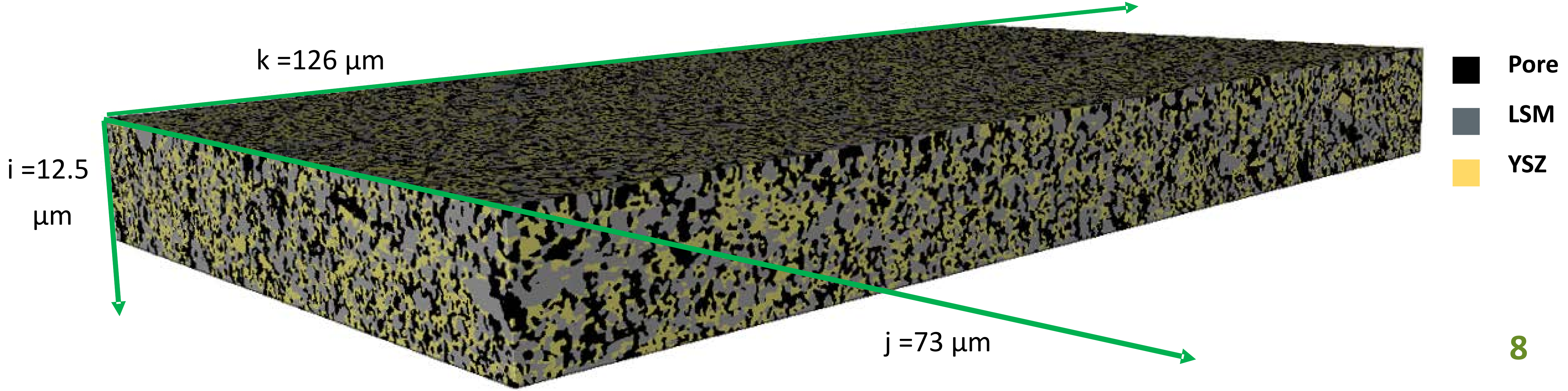
Degradation of Cell Performance



Cell and Stack Degradation Modeling

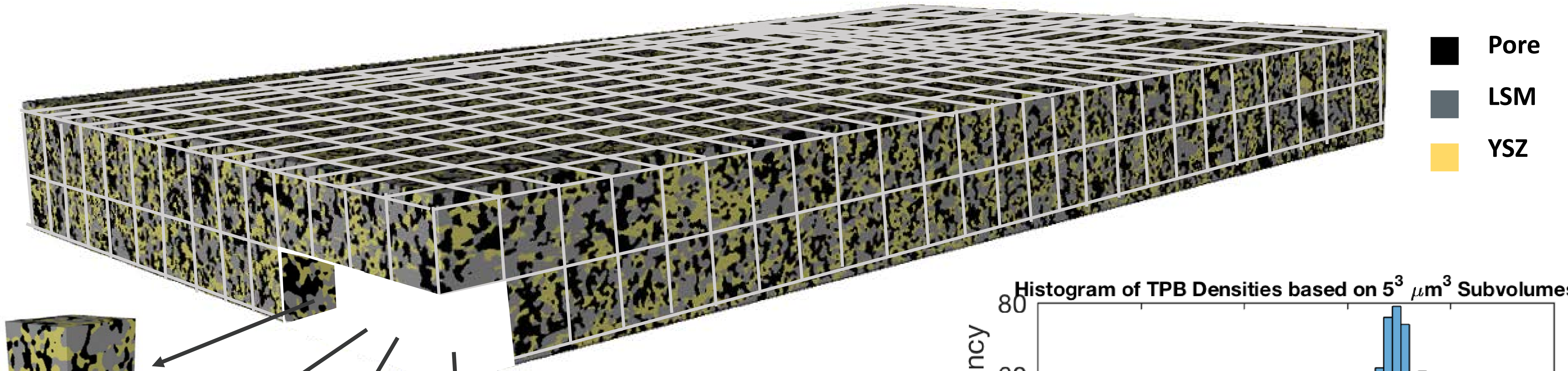
Microstructure Reconstruction

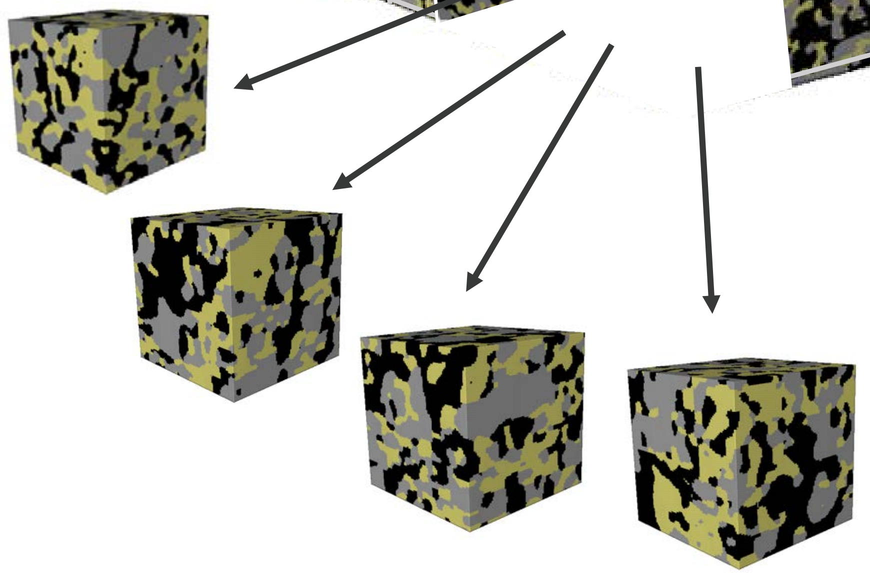
- **Characterization of SOFC Electrodes with High Resolution**
  - Use of plasma-FIB SEM technology to generate world's largest detailed microstructure reconstruction.
    - 150 µm × 150 µm cross-sections possible, 20 nm phase resolution
  - Define real microstructure information to feed into predictive degradation model
  - Validate models with un-operated and long-term operated cells
    - Obtain 20,000+ hour operated cells from commercial developers



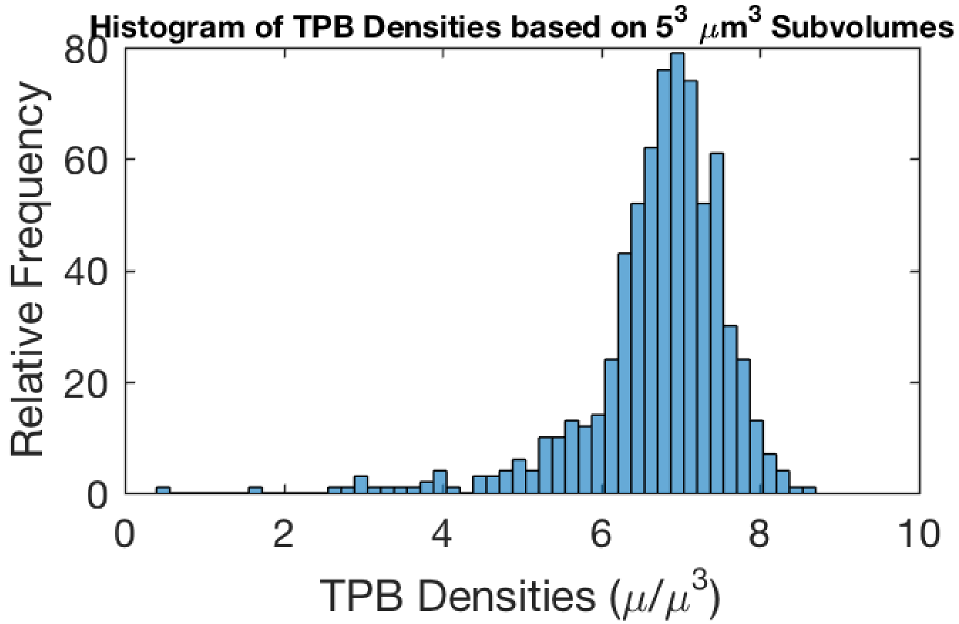
Cell and Stack Degradation Modeling

Microstructural Property Evaluation





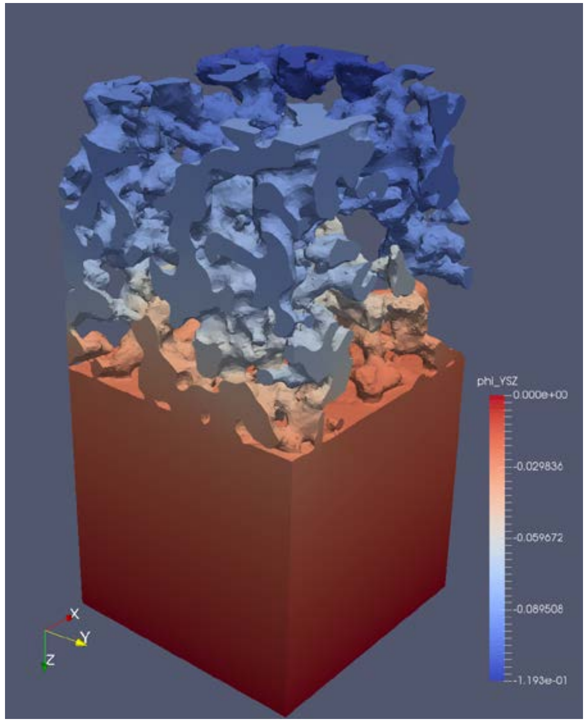
Phase Fraction
Average Particle Size
Standard Deviation
TPB Density
Tortuosity



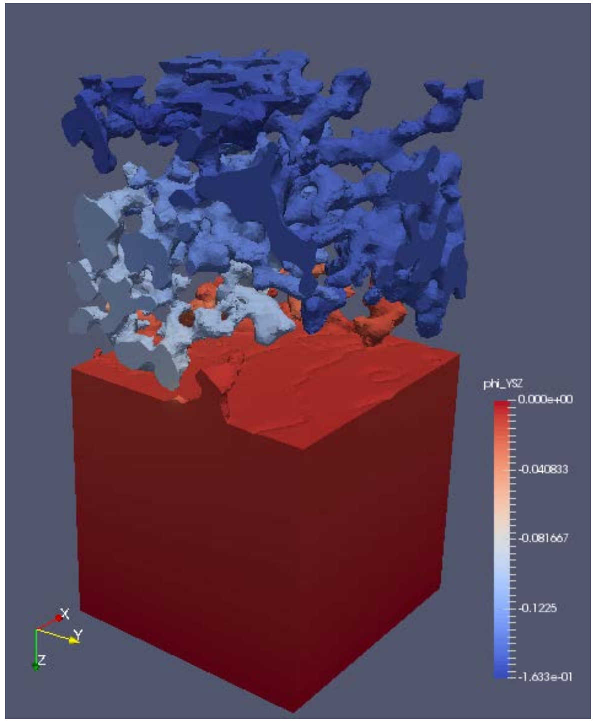
Cell and Stack Degradation Modeling

Sub-volume Analysis

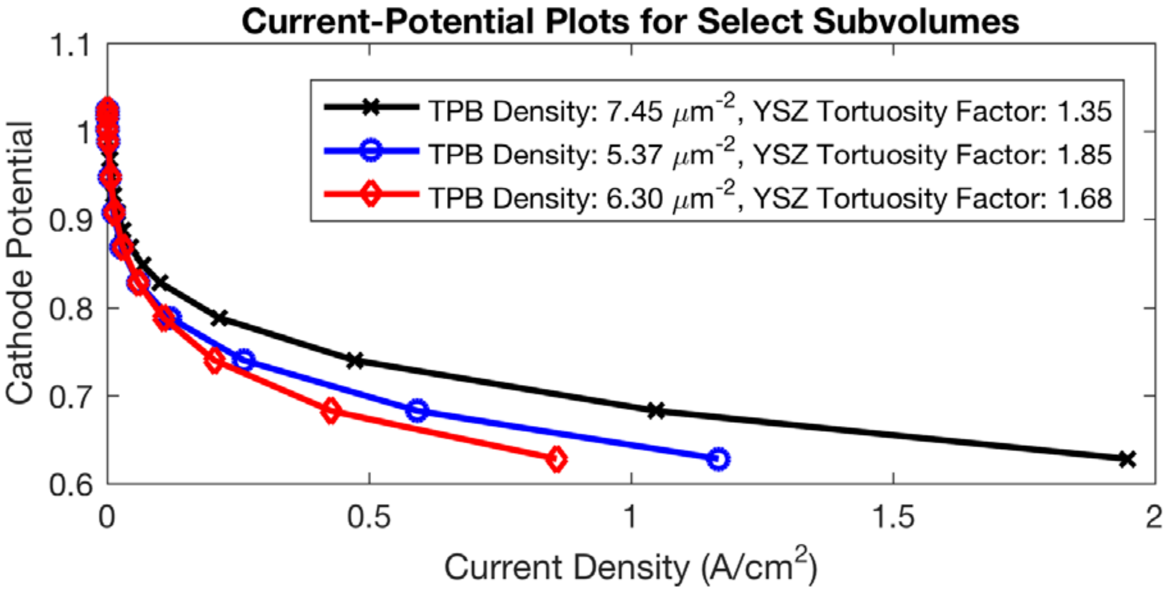
- **Using an electrochemical reaction model developed within MOOSE framework, sub-volume performances are evaluated**



Black Curve



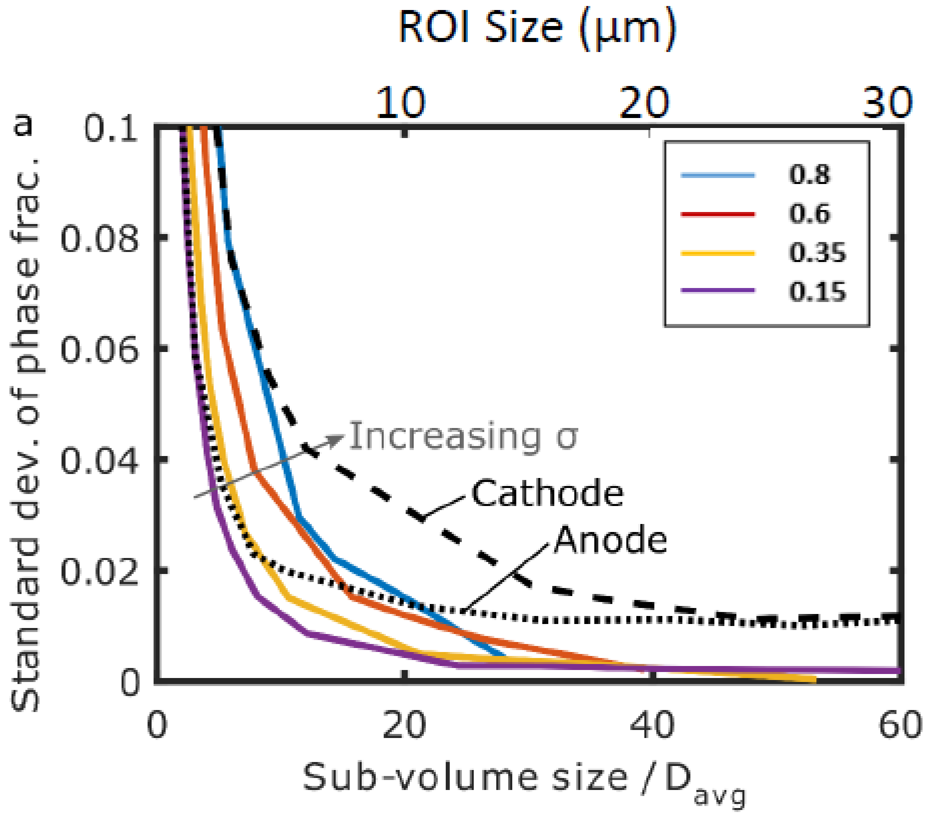
Red Curve



Cell and Stack Degradation Modeling

Region of Interest Analysis

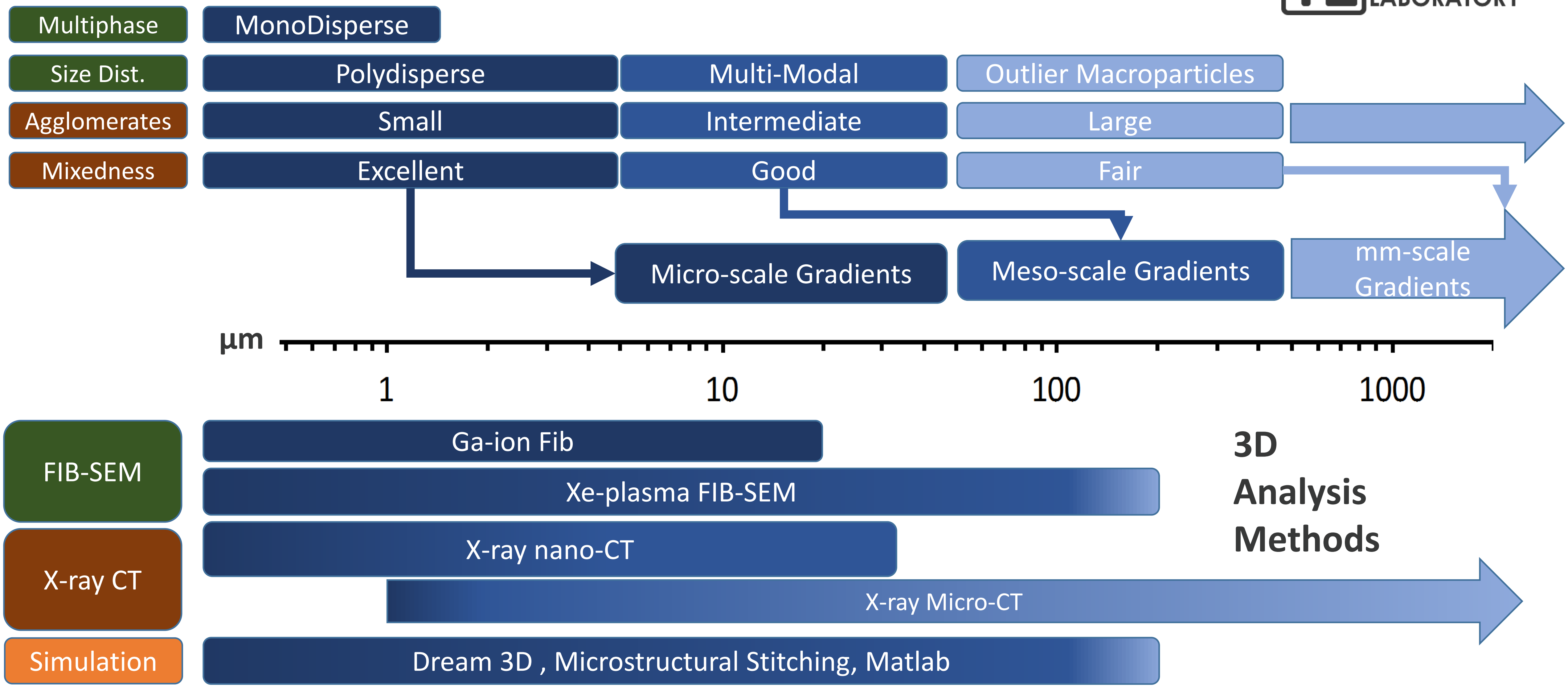
- **Real electrodes are not as homogeneous as synthetic ones created in Dream3D**
- **Heterogeneity exists beyond particle size variations between the phases**
- **Have developed procedure for creating and measuring the level of "mixedness" within the electrode**
  - Mixing combinations of sub-volumes with different microstructural parameters that generate same expected average parameters



Solid curves of from synthetic microstructures with known particle size distributions. Dashed lines are from real anode, cathode pFIB data.

Multiscale Heterogeneities from Feedstock

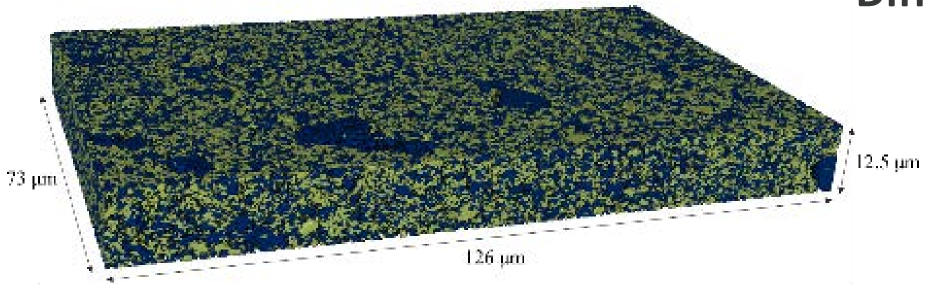
NATIONAL ENERGY TECHNOLOGY LABORATORY



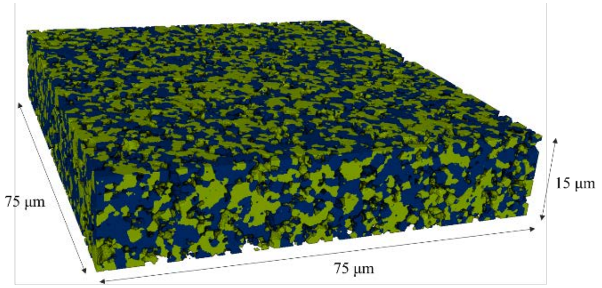
Characterizing Multiscale Heterogeneities

NATIONAL ENERGY TECHNOLOGY LABORATORY

Xe-PFIB-SEM Commercial



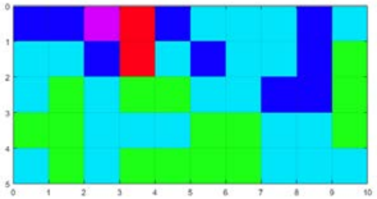
Stitched Dream3D Simulations of Polydisperse Powders



Polydisperse

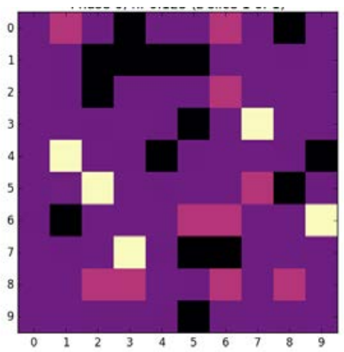
Outlier Macroparticles

12.5 µm Partitions of Different Volume Fractions



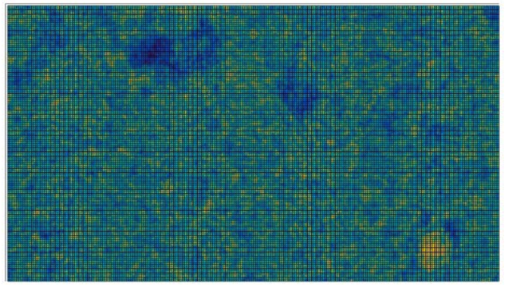
Experimental

Simulated

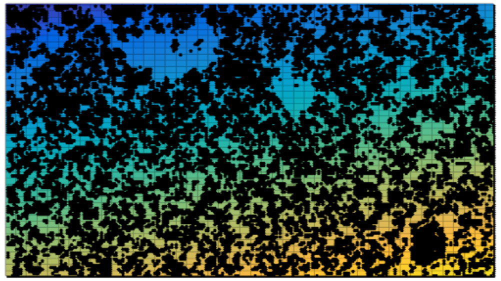


V_f Variations : 10s µm

5 µm bins Volume Fractions



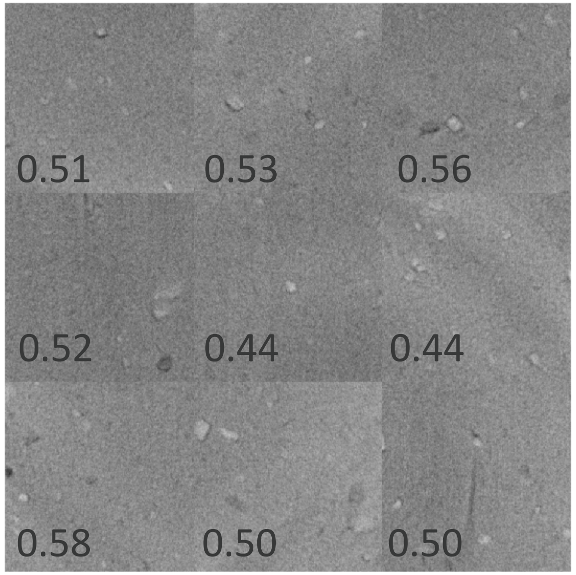
Planar Gradient



V_f Gradients: 50s µm

V_f Variations : 100s µm

APS µCT Commercial 2D Cathode Images Stitched



V_f Variations : 50s µm

V_f Variations : 100s µm

Outlier Macroparticles

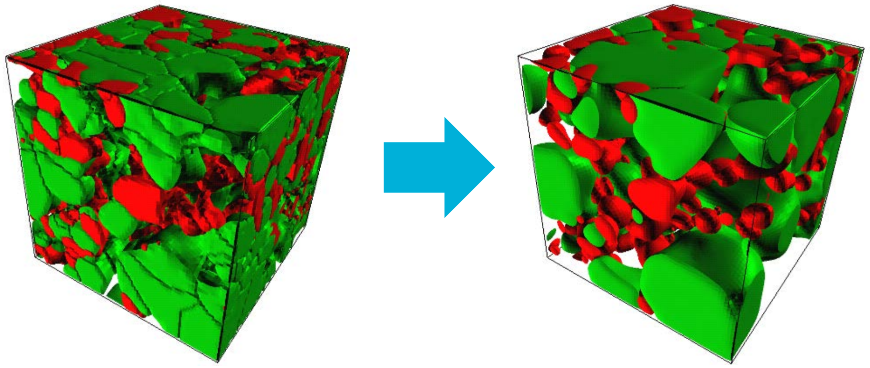
1 10 100 1000

Micro-scale | Meso-scale | mm-scale

Cell and Stack Degradation Modeling

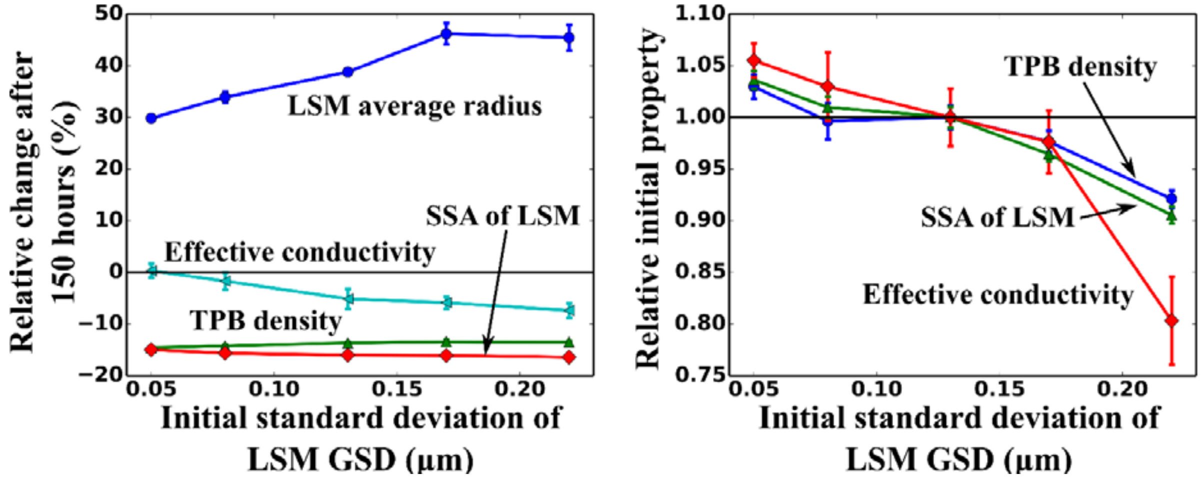
Identification of Intrinsic Degradation Modes

Simulated 3D microstructure evolution



- **Particle Coarsening**
  - Caused by long-term thermo/electrochemical operation
  - Results in decreased reaction area (TPB)
  - Phase field modeling technique used to predict coarsening
- **Effect on Cost-of-Electricity**
  - Cathode material grain size distribution results in varied coarsening and degradation rates
  - Quality control
  - Optimization potential

Effect of LSM grain size distribution on coarsening/degradation rate (left) and initial property (right)

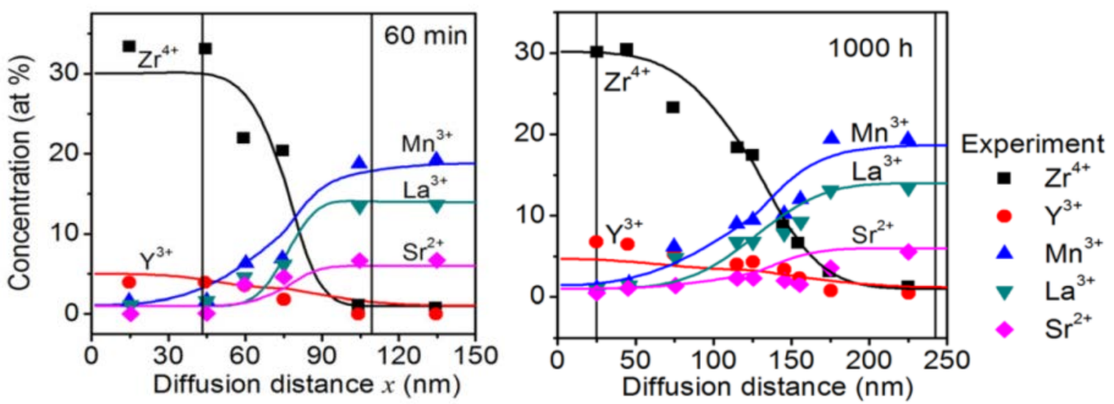


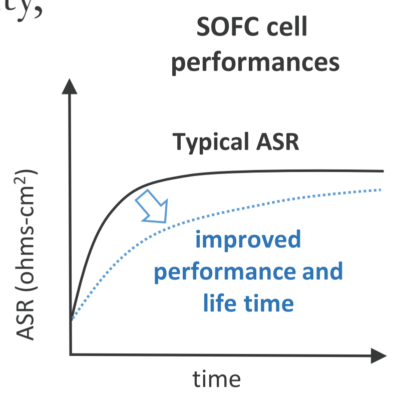
Cell and Stack Degradation Modeling

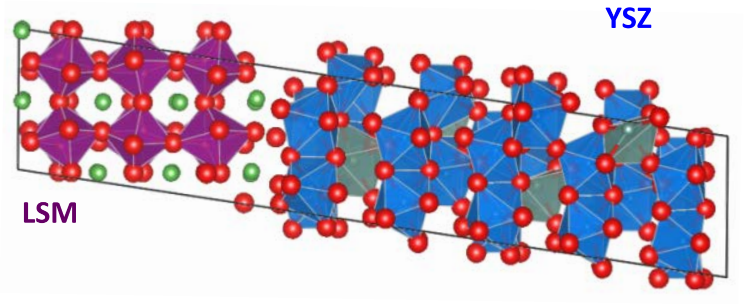
Identification of Intrinsic Degradation Modes

- **Diffuse Interface and Secondary Phase Formation**
  - Caused by interdiffusion of electrolyte and electrode materials due to thermochemical and/or electrochemical operation
  - Results in changes in reaction kinetic parameters
  - Density functional theory used understand effects
    - Transport kinetics, defect chemistry, phase stability, surface reactions, and electronic structure
- **Effect on Cost-of-Electricity**
  - Target ASR reduction, improving performance and lifetime

Predicted Diffusion Profile of Cations over Time







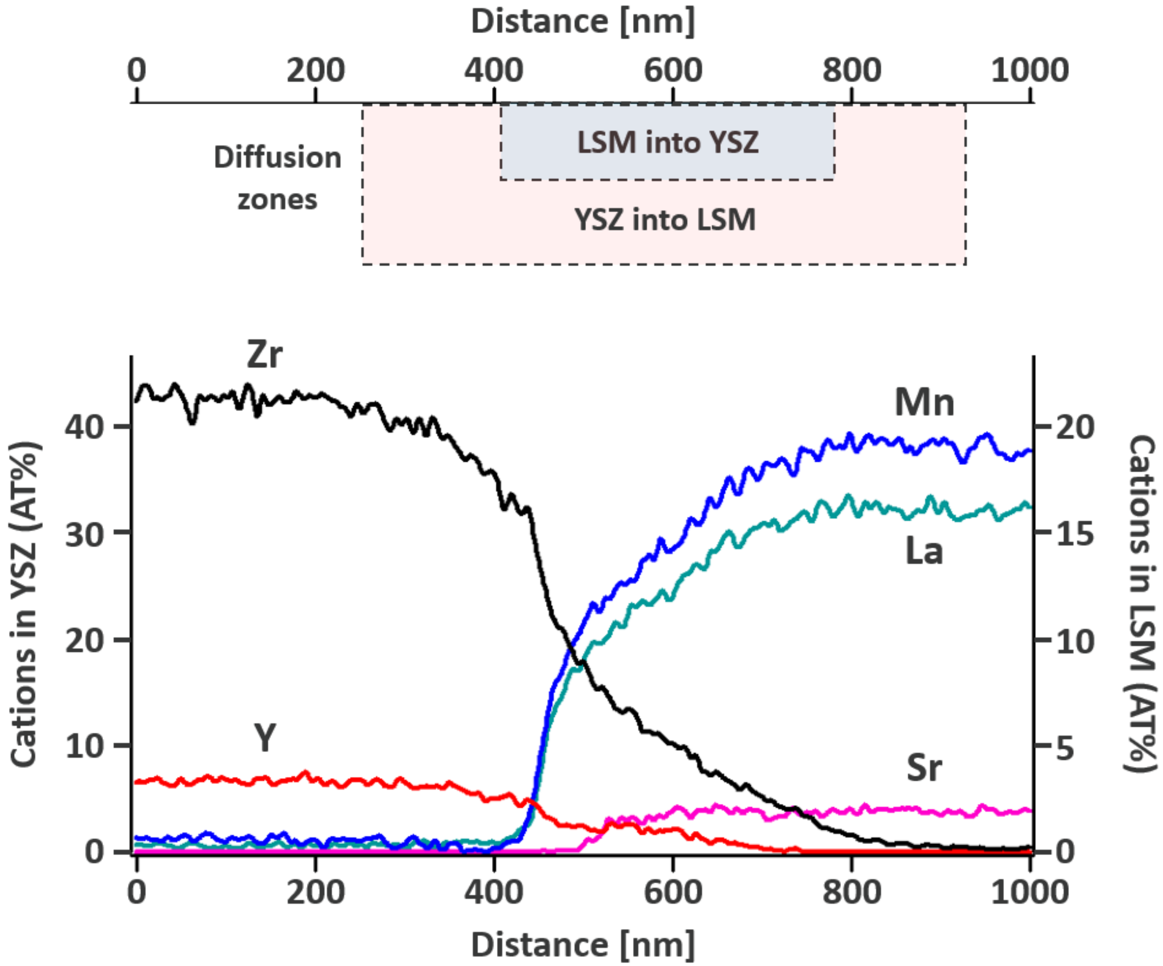
Oxygen vacancy stability of ideal LSM/YSZ interface

Cell and Stack Degradation Modeling

Identification of Intrinsic Degradation Modes

- **Cation Segregation Analysis**
  - Needed to validate diffuse interface predictions from DFT
  - Use of HR-TEM to quantify the interdiffusion of cations between the electrolyte and electrode material
    - Varied temperature and oxygen partial pressures
  - Calculate cation diffusion coefficients
    - Used to model the composition of the electrode/electrolyte interface

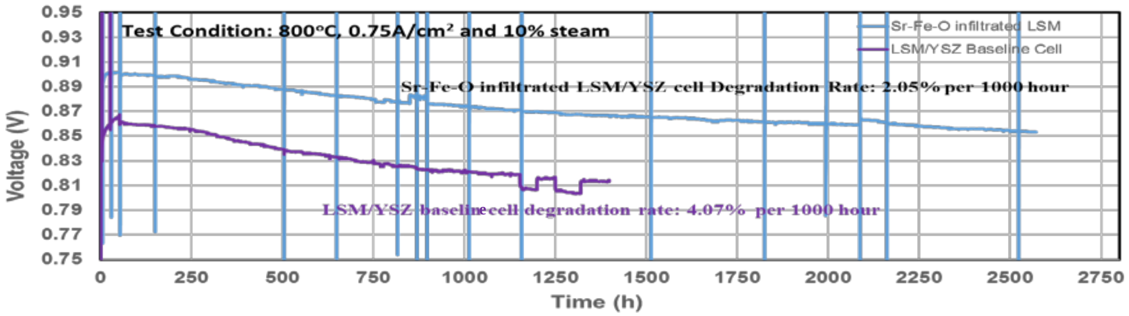
Operation at 750 °C, dry air, 0.25 A/cm^2 for 408 hours



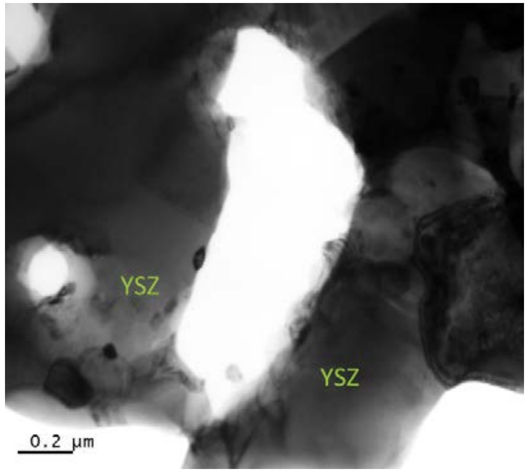
Cell and Stack Degradation Modeling

Identification of Extrinsic Degradation Modes

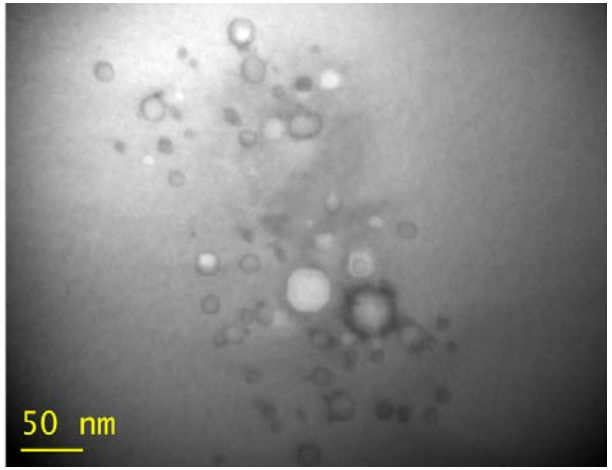
- **Fuel/Air Contaminant Interactions**
  - Coal trace species contaminant research has been well-documented in literature
  - Current contaminants of interest include chromium and water
  - Elevated steam content in cathode air results in performance loss
  - Use of HR-TEM to investigate degradation
- **Effect on Cost-of-Electricity**
  - Infiltrate identification to mitigate extrinsic degradation and improve lifetime



Long-term performance loss of infiltrated versus baseline LSM cell



Secondary phase formation on electrolyte surface

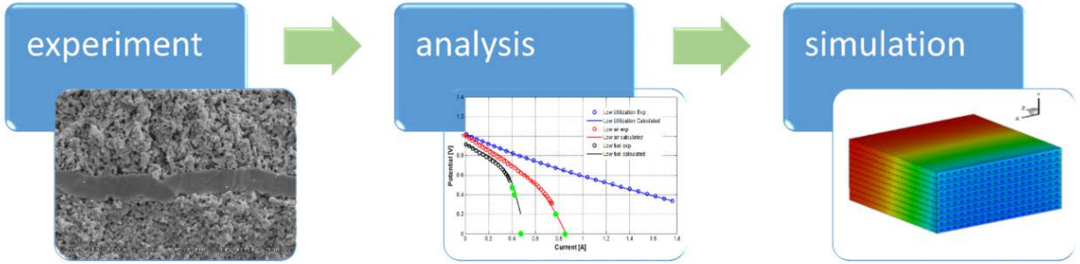


Formation of “nano-voids” in electrolyte

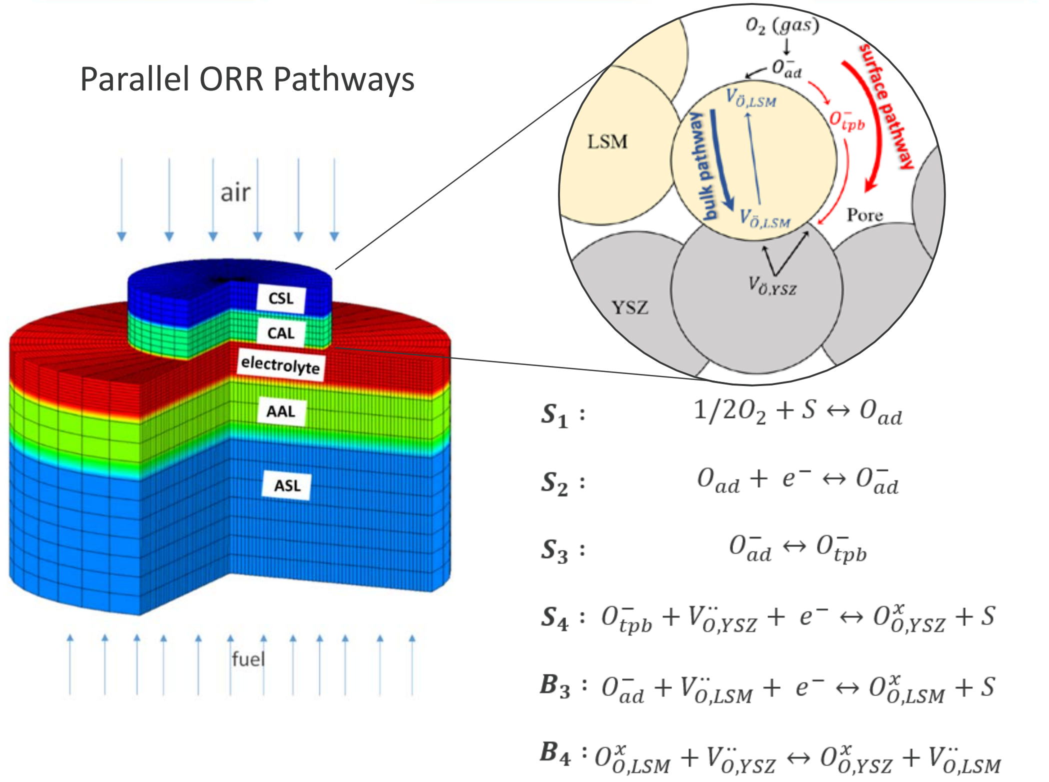
Cell and Stack Degradation Modeling

Bringing It All Together

- **Multi-physics Model**
  - Continuum level multi-physics simulation for SOFC performance analysis
  - Optimize cell performance through in-depth understanding of electrochemical reaction mechanisms via impedance analysis
  - Parameter determination/error analysis via Bayesian statistical analysis
  - Incorporate detailed reduced-order models for oxygen reduction reaction and hydrogen oxidation reaction



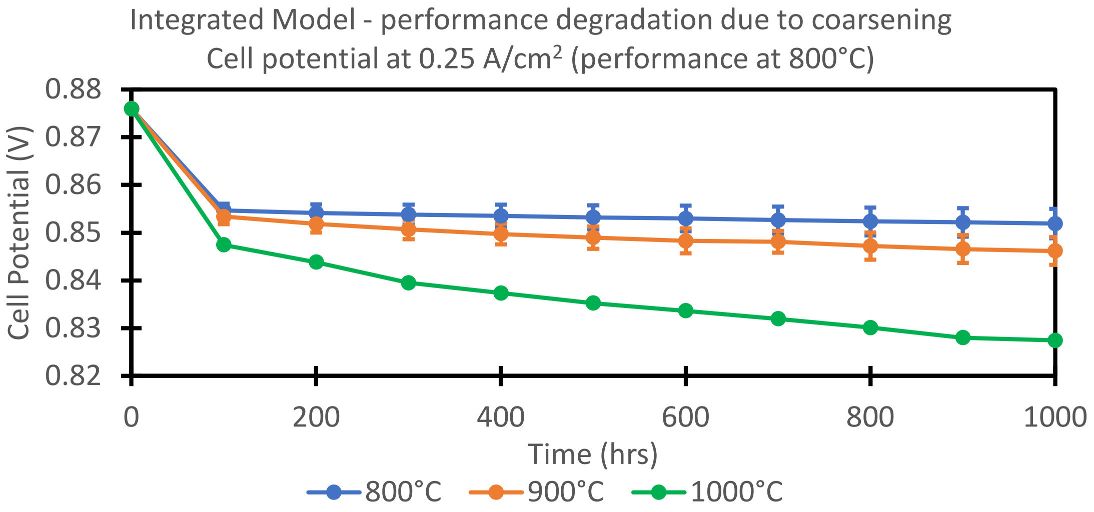
Parallel ORR Pathways

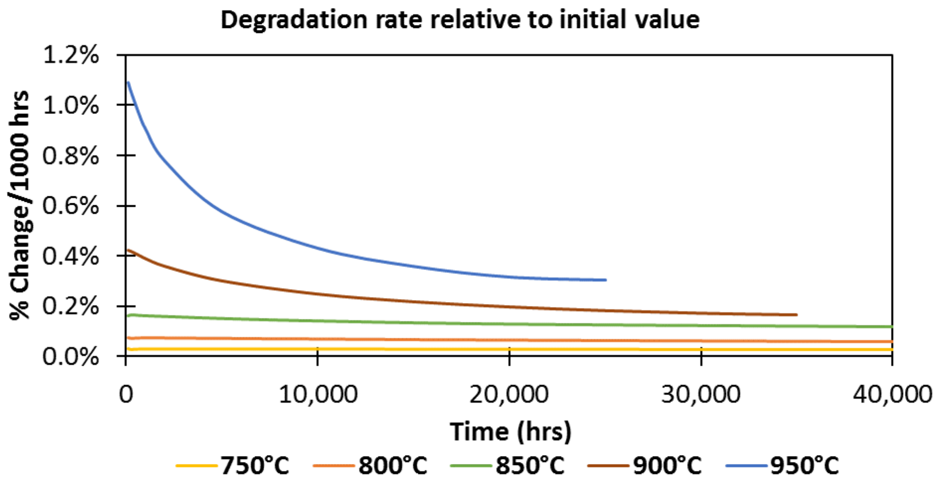


Cell and Stack Degradation Modeling

Incorporating Cell Level Degradation and Modeling Tools

- **Complete Cell Level Model**
  - Model single cells to predict performance based on cell properties and operating conditions
  - Develop and apply models for certain degradation modes and predict cell performance degradation
  - Integration of multi-physics model with phase field model and microstructure analysis tool has been demonstrated

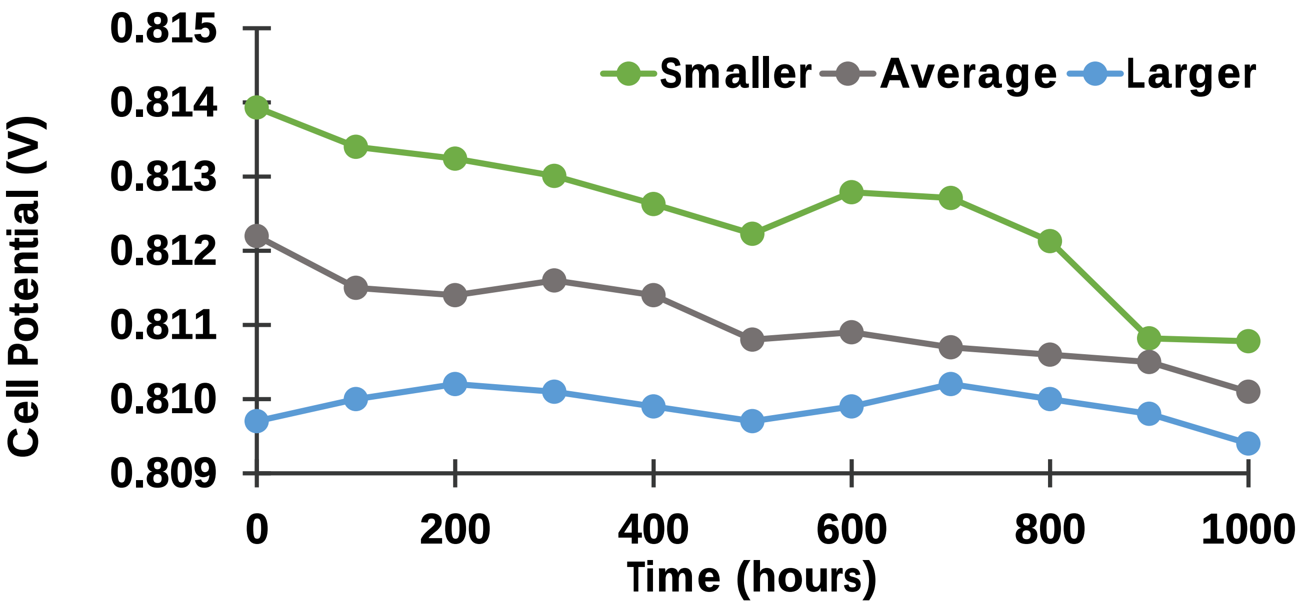




Cell and Stack Degradation Modeling

Parametric studies

- **Tested integrated model with 24x24x8 μm^3 active layer anode, cathode**
  - Used calibrated Butler-Volmer model for both electrodes
  - Generated synthetic microstructures based on pFIB data subvolume
  - Varied average Ni, LSM particle by ~±25%



Degradation of each electrode combination at 800°C, 0.25 A/cm² (%/1000hrs)

		Cathode		
		Smaller	Average	Larger
Anode	Smaller	-0.39%	-0.33%	-0.31%
	Average	-0.32%	-0.19%	-0.24%
	Larger	-0.12%	-0.06%	-0.08%

Cell and Stack Degradation Modeling

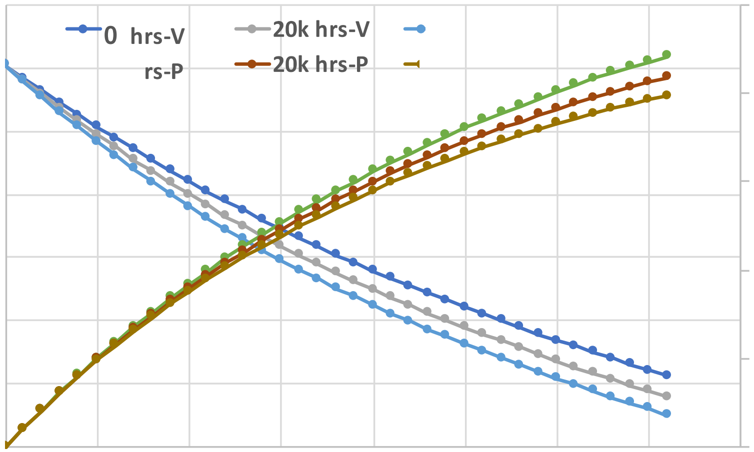
Ongoing parametric studies FY17-FY18

- Larger electrode volumes to capture wider distributions and heterogeneities
- Vary particle size, size distribution, temperature, phase fraction, and mixedness
- Incorporate oxygen reduction mechanism to measure impact on 2PB and 3PB pathways
- Incorporate water-mediated nickel coarsening in anode coarsening model
- Create navigable database for partners to use
- Complete GUI development for EIS Deconvolution Tool

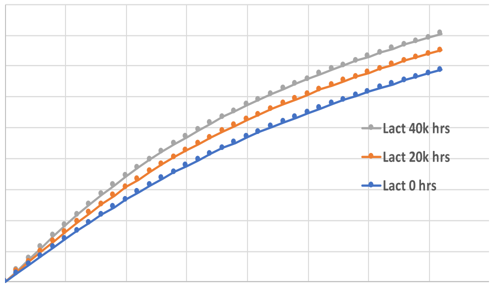
Scale Bridging

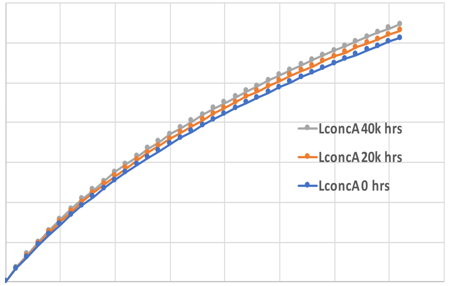
NETL Cell Level Model to PNNL SOFC-MP Stack Model

- **Integration with PNNL SOFC-MP stack model**
  - Empirical model for degradation due to coarsening has been applied at the cell level and passed to PNNL to be used at the stack level



- **Initial Results**
  - Voltage and power decrease 11% @ 800°C
  - Electrochemistry model power loss:
    - 94% due to loss of TPB
    - 5.5% due to anode concentration polarization
    - 0.5% due to ohmic losses and cathode concentration polarization

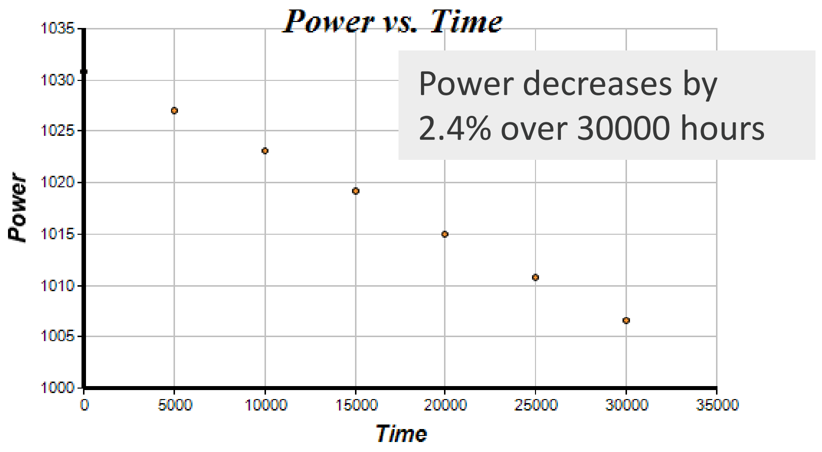




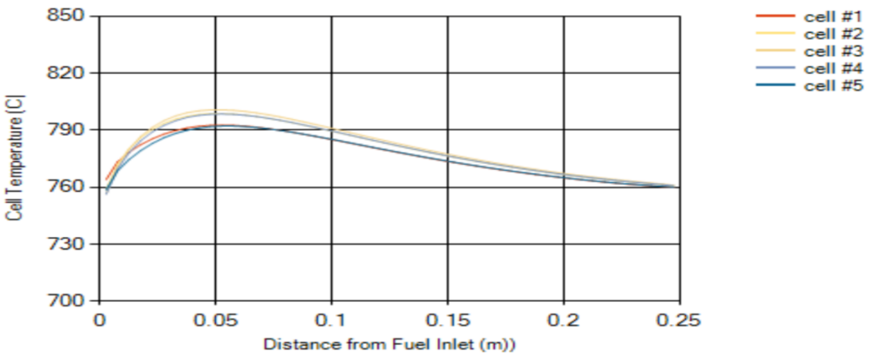
PNNL SOFC-MP & NETL Degradation Model

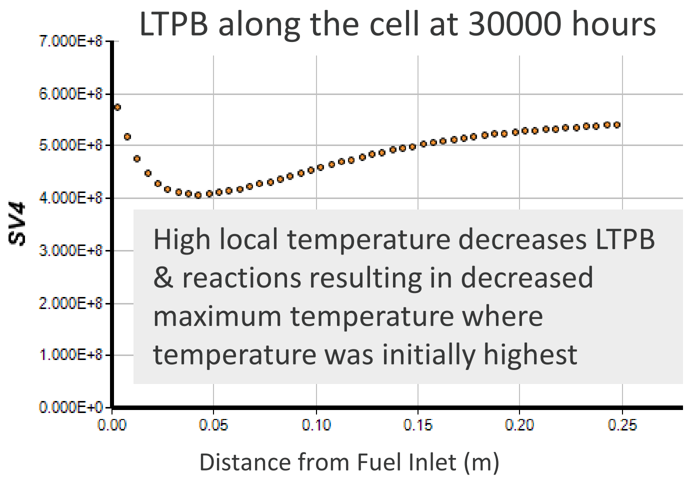
Results from Preliminary Demonstration

- **Stack Details**
  - 5 cell co-flow stack, 25×25 cm²
  - 750°C
  - Wet hydrogen fuel (3% water)
  - Target cell voltage - 0.81 V

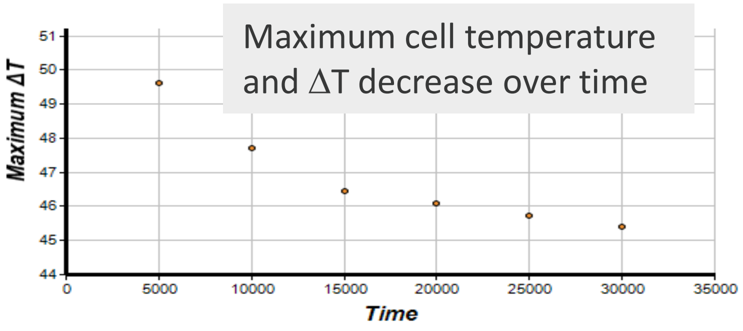


Initial Temperature along the cell





Maximum ΔT vs Time



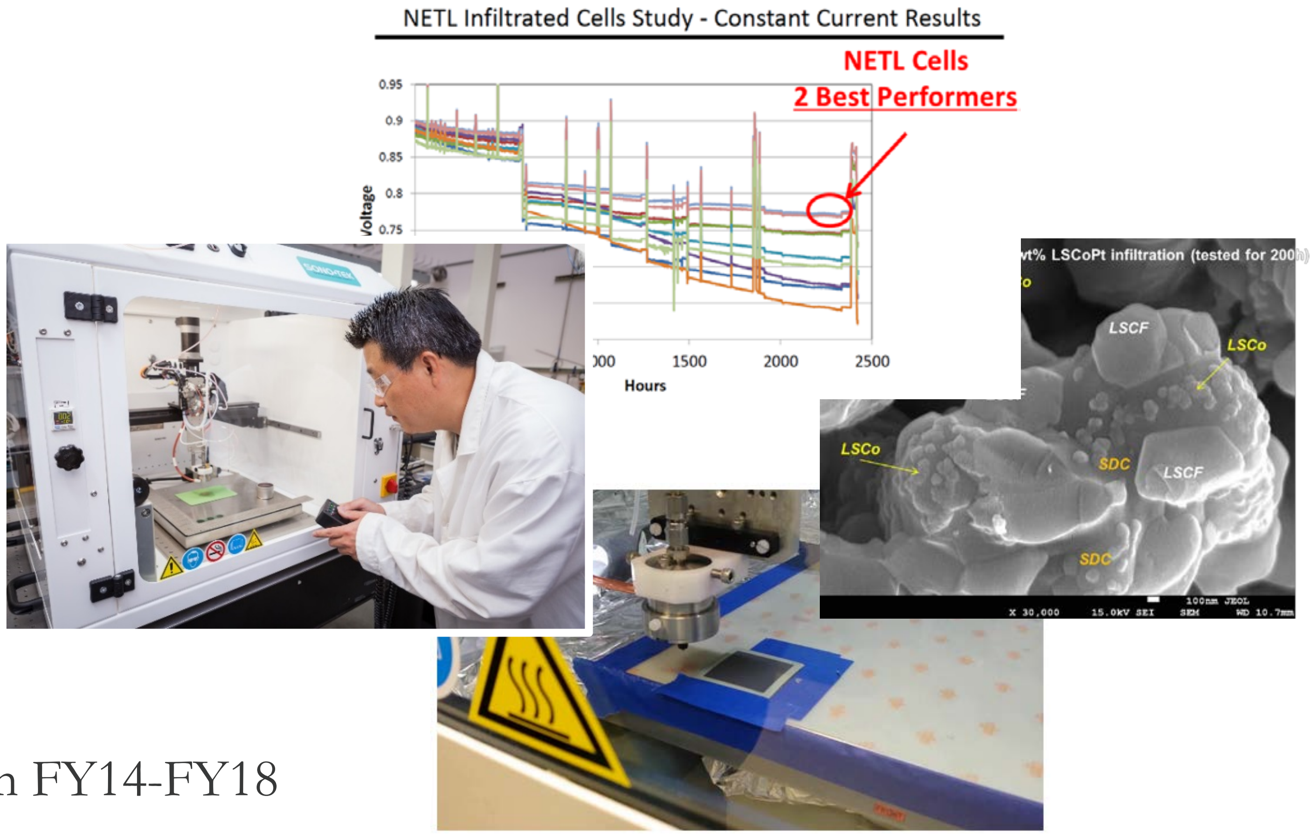
Degradation Mitigation

Electrode Engineering

Degradation Mitigation

SOFC Electrode Engineering

- **NETL has developed and patented* a single-step cathode infiltration technique that can be utilized by commercial SOFC manufacturers to improve state-of-the-art technology reliability at the cell level**
  - Improved oxygen reduction efficiency
  - Increased triple-phase boundary length
  - Increased catalytic activity at TPB
  - Proven performance gains of
    - 10% peak power increase
    - 33% reduction is degradation rate
    - Resulting in a 200% lifetime increase
  - Low-cost
    - \$0.006/cm² (Adds ~0.4¢ on the dollar)
  - Scalable
    - Testing on full-scale commercial cells from FY14-FY18



Degradation Mitigation

SOFC Electrode Engineering

Collaboration with SOFC Commercial Developers

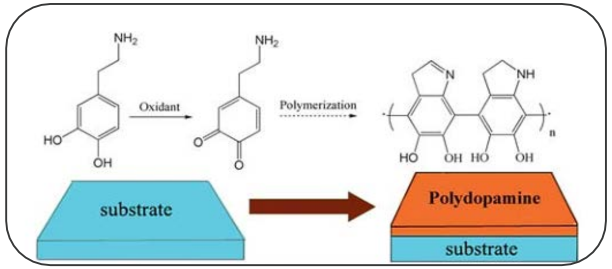
- **NETL has been selected for a Technology Commercialization Fund Award for FY17/18 to scale up the single-step infiltration technology to commercially relevant scales**
  - Industry Partner: Atrex Energy
  - Infiltration of multiple cells for an integrated stack test
  - Successful demonstration of the technology at this scale may lead to commercialization
- **NETL has and is continuing to demonstrate the technology with other SOFC commercial developers**
  - Previously completed work under an NDA
  - Currently working with other developer under an NDA

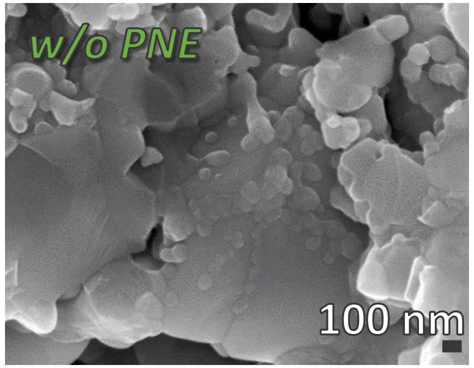
Degradation Mitigation

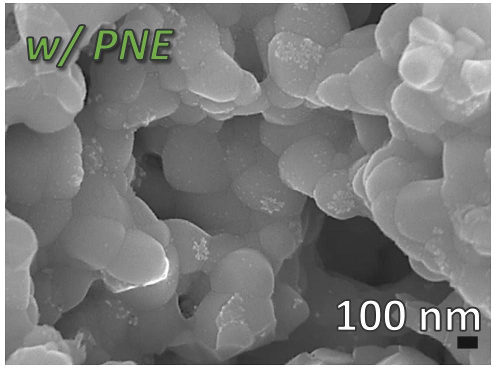
SOFC Electrode Engineering

Expansion of Infiltration Technology to SOFC Anodes

- **Infiltration of nano-catalysts on the anode electrode of SOFC are of interest**
  - To reduce performance losses associated with redox cycling of the system
  - To improve on-cell reforming of hydrocarbon fuels (greatly reducing costs)
- **An investigation of bio-surfactant (e.g. polydopamine/polyepinephrine) application to improve infiltration of the dense anode microstructure is ongoing**
  - This method can also be used to improve cathode electrode infiltration by sonic spraying
  - Additional patents pending







Active layer after 120 h operation

NETL SOFC Predictive Modeling Tool

Conclusions

- **How can SOFC technology deployment be accelerated?**
  - Performance and durability enhancement greatly reduces cost
  - Need a thorough understanding of what causes performance loss and durability issues
    - Intrinsic/extrinsic degradation modes are being investigated at the microscale and the results are being passed up multiple scales to system level
    - Understanding how materials properties (particle size distribution, etc.) change the cost-of-electricity can lead to optimization studies from the micro- to the system scale
  - Detailed, comprehensive modeling tool can extend lifetime of operating SOFC systems by providing real-time feedback, greatly reducing operation costs
    - Real-time impedance analysis, sensor data
    - Course corrective actions
    - Planned shutdowns with sufficient advanced notice

Long-term Performance Prediction

Acknowledgments

NETL

Shailesh Vora

Kirk Gerdes

Joe Stoffa

Heather Quedenfeld

Steve Richardson

PNNL

Brian Koeppel

Kurt Recknagle

Kevin Lai

Gregory Hackett
Technical Portfolio Lead – NETL Solid Oxide Fuel Cells R&D
Systems Engineering and Analysis, Energy Process Analysis Team
Gregory.Hackett@netl.doe.gov

NETL SOFC Research Team (FY17)

NETL (Morgantown, WV)
- Gregory Hackett (NETL)
- Travis Shultz (NETL)
- Rich Pineault (NETL)
- Yves Mantz (NETL)
- Harry Abernathy (AECOM)
- Shiwoo Lee (AECOM)
- Lynn Fan (AECOM)
- Rick Addis (AECOM)
- Jay Liu (ORISE)
- Hunter Mason (ORISE)
- Tao Yang (ORISE)
- Ye Lin (ORISE)
- Navjot Sandhu (ORISE)

University of Wisconsin-Madison
- Dane Morgan (MSE)

Clemson University
- Kyle Brinkman (MSE)

NETL (Pittsburgh, PA)
- Paul Ohodnicki (NETL)
- Yuhua Duan (NETL)
- Slava Romanov (NETL)
- Tom Kalapos (AECOM)
- Yang Yu (AECOM)
- Youngseok Jee (AECOM)
- Yueh-Lin Lee (ORISE)
- Billy Epting (ORISE)
- Giuseppe Brunello (ORISE)
- Grigorios Panagakos (ORISE)

Carnegie Mellon University
- Paul Salvador (MSE)
- John Kitchin (ChE)
- Shawn Litster (MechE)
- Tony Rollett (MSE)
- Tim Hsu (MSE, grad. student)
- Rubayyat Mahbub (MSE, grad. Student)

NETL (Albany, OR)
- Youhai Wen (NETL)
- Tianle Cheng (AECOM)
- Yinkai Lei (ORISE)
- Jason Vielma (ORISE)

West Virginia University
- Harry Finklea (Chemistry)
- Ismail Celik (MAE)
- David Mebane (MAE)
- Ed Sabolsky (MAE)
- Xueyan Song (MAE)
- Xingbo Liu (MAE)
- Yun Chen (WV Research Corporation)
- Ozcan Ozmen (MAE, grad. student)

Penn State University
- Long-Qing Chen (MSE)

Currently 44 SOFC Team Members

NETL SOFC Group Posters

- Multi-physics Modeling of Solid Oxide Fuel Cells with Parallel Oxygen Reduction Reaction Pathways, Tao Yang
- Density-Functional Study of the $La_2Zr_2O_7$ Low-Index Faces, Yves Mantz
- Nanostructure Degradation of LSM/YSZ Interface from the Active Layer of the SOFC Cathode Operated with Elevated Steam Content, Xueyan Song
- Noninvasive Optical Sensor Development for Real-Time Solid Oxide Fuel Cell Monitoring Applications, Youngseok Jee
- High Performance Computation of Local Electrochemistry via TPB and MIEC Pathways in SOFCs based on Morphology-Preserving Microstructural Meshes, Tim Hsu
- Quantitative Mesoscale Analysis of SOFC Electrodes Based on 3D Reconstructions Using Xe-Plasma Focused Ion Beam (pFIB) Coupled with SEM, Rubayyat Mahbub
- Capacitance and Electrochemical Impedance Spectroscopy of a Solid Oxide Fuel Cell Interface using Phase Field Theory, Yinkai Lei
- Nano-Catalyst Infiltration by Bio-Surfactant Modification of Anode Supported SOFC Electrodes, Özcan Özmen
- Bayesian Calibration of Models of SOFC Electrode Materials, Giuseppe Brunello
- Phase Field Modeling on Initial Microstructure Effect on Grain Coarsening and Concomitant Property Degradations in SOFC Electrodes, Yinkai Lei
- Classifying Heterogeneity in SOFC Electrodes, Billy Epting
- Atomistic Modeling of Cation Diffusion in Transition Metal Perovskite $La_{1-X}Sr_XMnO_{3\pm\delta}$ for Solid Oxide Fuel Cell Cathode Applications, Yueh-Lin Lee
- Cation Segregation Analysis in SOFC – a Transmission Electron Microscope Based Study, Yang Yu
- Prediction of Performance Degradation Due to Grain Coarsening Effects in Solid Oxide Fuel Cells, Hunter Mason
- Improved Performance Stability of Solid Oxide Fuel Cells Achieved through Sr-Fe-O Infiltration of LSM/YSZ Cathode, Lynn Fan
- The Electrochemical Performance of LSM with A-site Non-Stoichiometry Under Cathodic Polarization, Jay Liu