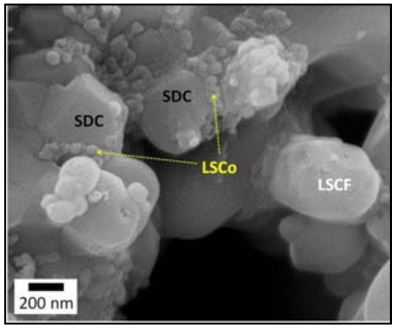
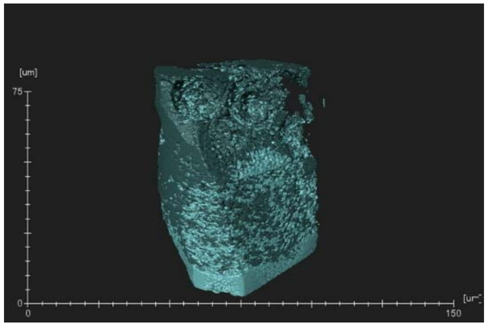
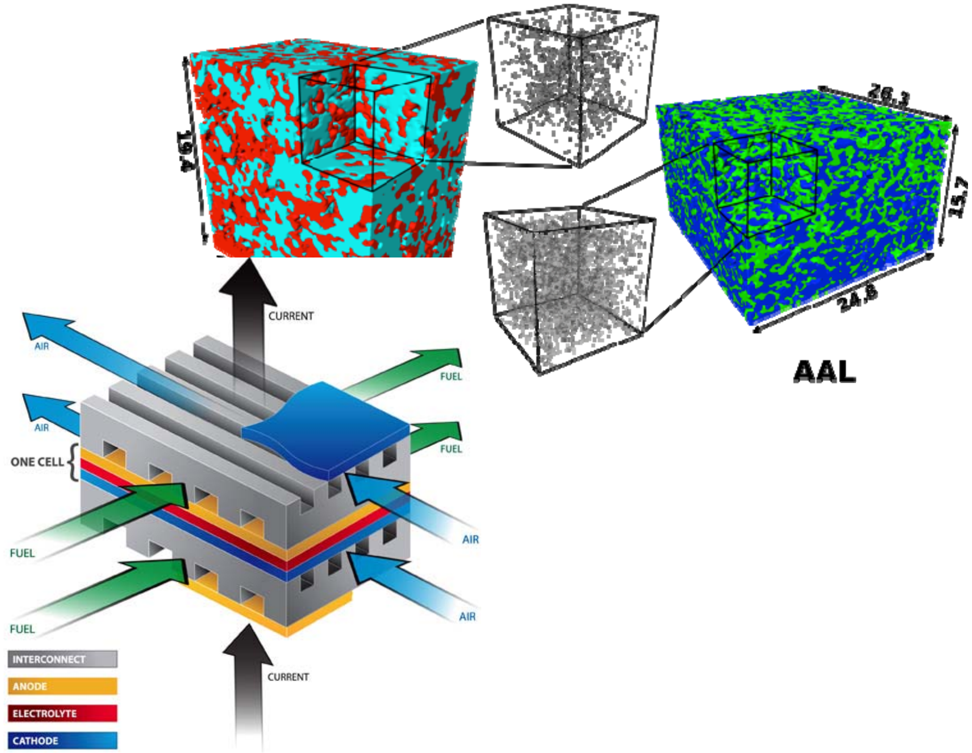
Driving Innovation ♦ Delivering Results







NETL R&D: SOFC Materials Development and Degradation Modeling

Gregory A. Hackett, Ph.D.
Energy Process Analysis Team
Fuel Cells Technical Portfolio Lead
July 20, 2016

U.S. DEPARTMENT OF ENERGY | National Energy Technology Laboratory

Outline

- **NETL R&IC Solid Oxide Fuel Cell Team**
- **Portfolio Research Objectives**
- **Cell and Stack Degradation Research Efforts**
  - 3-D Microstructure Reconstruction
  - Impedance Modeling Tool
  - Non-invasive Sensor Implementation
  - Parameter Estimation via Bayesian Statistics
  - Phase Field Modeling, First Principles Modeling
  - Incorporation of Degradation Models in Multi-Physics Model
- **Electrode Engineering Innovations**
  - Cathode Infiltration
  - Steam Induced Degradation Mitigation
  - Anode Infiltration
- **Future Work**

NETL SOFC Research Team

NETL (Morgantown, WV)
- Gregory Hackett (Energy Process Analysis)
- Rich Pineault (Innovative Energy & Water)
- Harry Abernathy (AECOM)
- Shiwoo Lee (AECOM)
- Lynn Fan (AECOM)
- Jay Liu (ORISE)
- Hunter Mason (ORISE)
- Yves Mantz (Comp. Mat. Eng.)
- Rick Addis (AECOM)

NETL (Pittsburgh, PA)
- Paul Ohodnicki (Functional Materials)
- Yuhua Duan (Comp. Mat. Eng.)
- Slava Romanov (Geo. Geospatial Analysis)
- Tom Kalapos (AECOM)
- Yang Yu (AECOM)
- Yueh-Lin Lee (ORISE)
- Billy Epting (ORISE)
- Giuseppe Brunello (ORISE)
- Grigorios Panagakos (ORISE)
- Miaolei Yan (ORISE)

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- Jason Vielma (ORISE)

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- David Mebane (MAE)
- Ed Sabolsky (MAE)
- Xueyan Song (MAE)
- Yun Chen (WV Research Corp)
- Ismail Celik (MAE)
- Ozcan Ozmen (MAE, Graduate Student)

Carnegie Mellon University
- Paul Salvador (MSE)
- Tim Hsu (MSE, Graduate Student)
- Rubayyat Mahbub (MSE, Graduate Student)
- John Kitchin (ChE)
- Tony Rollett (MSE)

Penn State University
- Long-Qing Chen (MSE)

U. Wisconsin-Madison
- Dane Morgan (MSE)

Currently 36 Research Team Members

NETL SOFC Research Objectives

- **Detailed investigation of fuel cell degradation modes in the anode/electrolyte/cathode facilitates targeted efforts to improve the longevity of the fuel cell, ultimately resulting in decreased system costs.**
  - Develop modeling, analysis, and visualization tools for evaluating and predicting long term performance degradation of relevant SOFC components based on theoretical and experimental evidence (TRL 3-4)

- **Electrode innovations yield improved performance, thereby resulting in increased cell efficiency and ultimately a diminished system cost.**
  - Facilitate testing, scale-up, and transfer of SOFC technology to industrial partners (TRL 5-6)

SOFC Program Mission:

"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."

Cell and Stack Degradation
Motivation/Approach

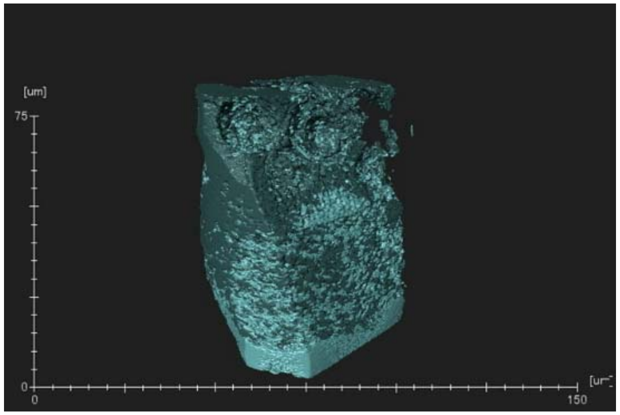
- **Motivation**
  - Comprehensive models predicting SOFC stack degradation do not exist or are not sufficiently descriptive to consider all of the primary degradation modes
    - <u>How does structure correlate to function?</u>
    - <u>How does structure change over time?</u>
- **Approach**
  - Experimental and theoretical results will be incorporated into a computational framework model that will include the most prominent degradation modes, focusing on <u>commercially relevant material sets</u>
    - Microstructural (porosity, particle size)
    - Kinetic (oxygen exchange coefficient, conductivity, cation interdiffusion)
    - Operating Conditions (local overpotential, temperature)

Cell and Stack Degradation
What NETL Offers SOFC Program Partners

- **Products**
  - *Comprehensive Predictive Model* (“Hurricane Model” - FY18/19)
  - Impedance Modeling Tool for deconvolution of cell processes (FY17/18)
  - Visualization Tool for maneuvering through 3-D reconstructions (FY17/18)
- **Services to Offer (Currently)**
  - Testing Facilities
    - Multi-Cell Array for reliable statistical testing, screening
    - Facilities for testing under high steam and other contaminants
    - Test stand capable of testing larger area cells
  - 3-D Microstructural Reconstruction at multiple scales
  - Creation of simulated microstructures for analysis, modeling
  - Bayesian statistical analysis framework tool for finding model parameters and associated uncertainty
  - Reaction and transport modeling for electrochemical performance prediction with impedance simulation

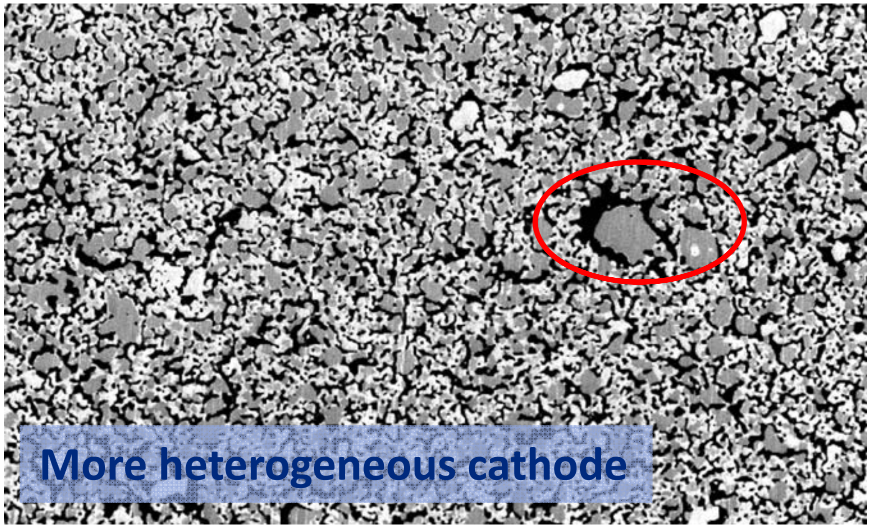
Cell and Stack Degradation
3-D Microstructure Reconstruction

- **Need to inform model with reconstructions of REAL microstructures in order to understand degradation processes**
- **Large volume reconstructions will yield complete distributions to describe**
  - Activity and degradation of activity
  - Heterogeneous cell structures
- **Proper coupling to computations will yield complete multi-scale description of SOFC performance over time in full operational conditions**
- **Proper development of microstructurally-based operational models will accelerate development of commercial SOFCs**

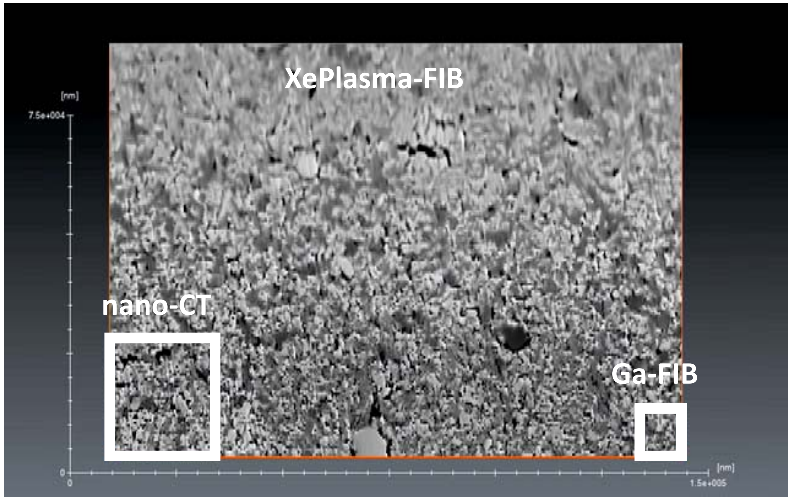


Cell and Stack Degradation
3-D Microstructure Reconstruction

- **Equipment/Approach**
  - Ga^+ Focused Ion-Beam (FIB) SEM (common method, 10×10 µm²)
  - Nano-CT (lower resolution, non-destructive, 50×50 µm²)
  - Xe-Plasma FIB (new, faster, 150×150 µm²)



p-FIB, LSM/YSZ Active Cathode



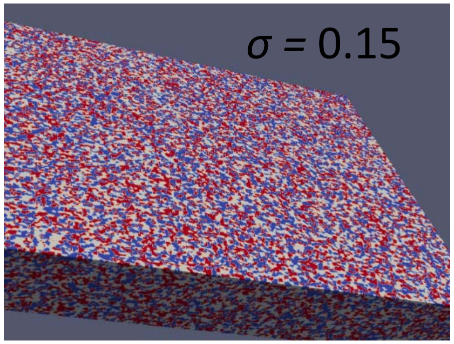
Ongoing work: Simulating effect of heterogeneity and "mixedness" of composite electrode on cell performance and degradation

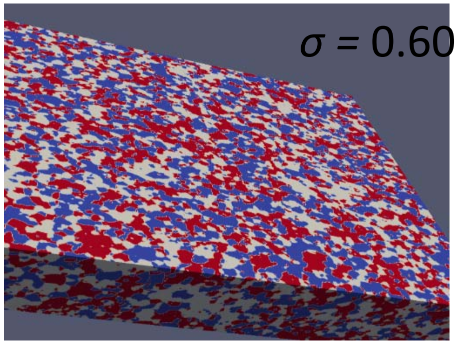
Cell and Stack Degradation

3-D Microstructure Reconstruction

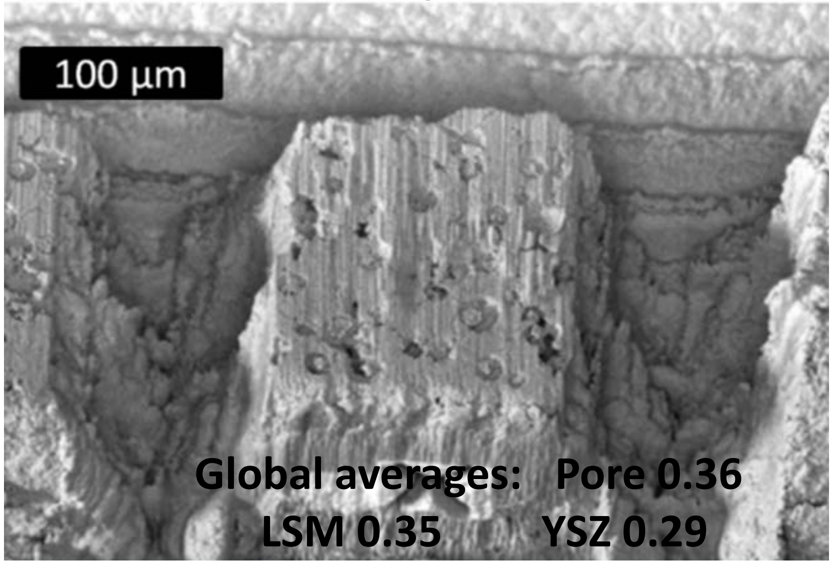
- **Production of synthetic microstructures using Dream 3-D**
- **Identification of representative volume element that statistically describes measured phase fraction with acceptable error**
- **Real SOFC microstructures to overlay modeling degradation processes**

POSTER – "Representative Volumes in Highly Heterogeneous Fuel Cell Materials" – Billy Epting



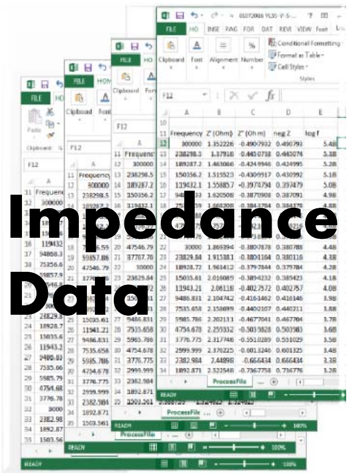


Xe Plasma FIB-SEM dataset, 126 x 73 x 12.5 µm, from Carnegie Mellon



Cell and Stack Degradation
Impedance Analysis Tool

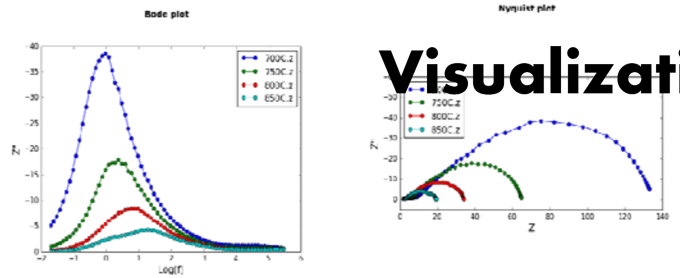
Goal: Analysis of routine EIS measurements



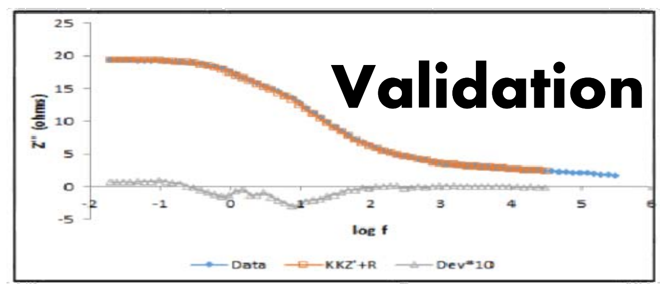
Impedance Data

FY16/17: Excel -> Open source with web interface

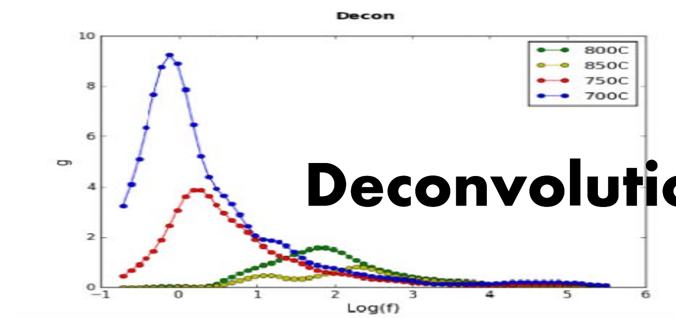
POSTER – "Characterization of SOFC Cathode Impedance under Polarization Using Appropriate Counter Electrode Design" -Jay Liu/Harry Finklea



Visualization



Validation

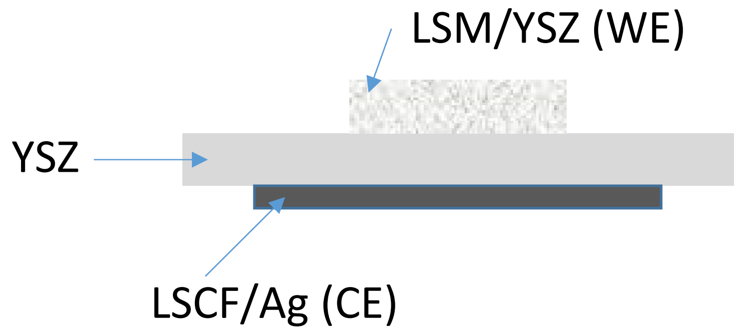


Deconvolution

Cell and Stack Degradation

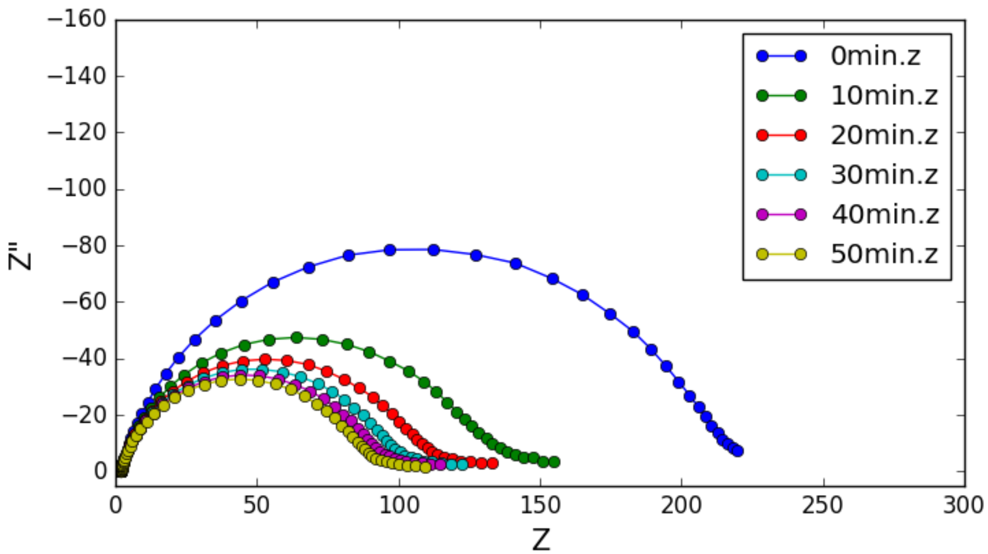
Impedance Analysis Tool

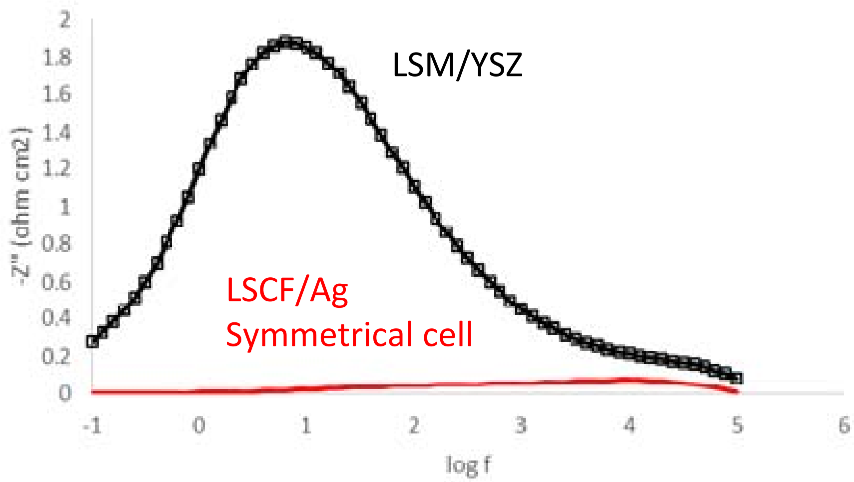
Ideal Counter Electrode Development



Desired properties:

- **Small R_p**
- **Separate frequency domain**
- **Easy to fabricate (<900°C)**
- **Stable**



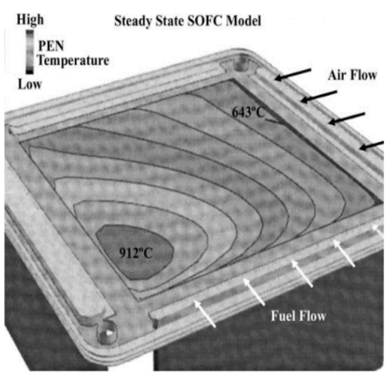


Cell and Stack Degradation
Optical Fiber Temperature/Gas Sensor

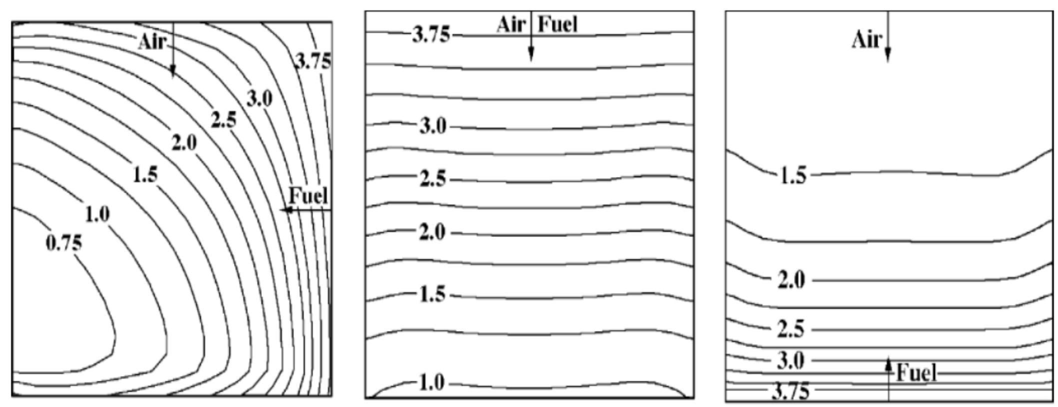
Benefits of in-situ monitoring of temperature, fuel gas gradients:

- Identify effects on the **electrochemical reactions** during operation
- Correlate with **degradation mechanisms**
- Provide instantaneous feedback on **operation control**
- Optimize fuel **utilization rate** and **device efficiency**

Simulated temperature gradient



Simulated H_2 concentration gradient

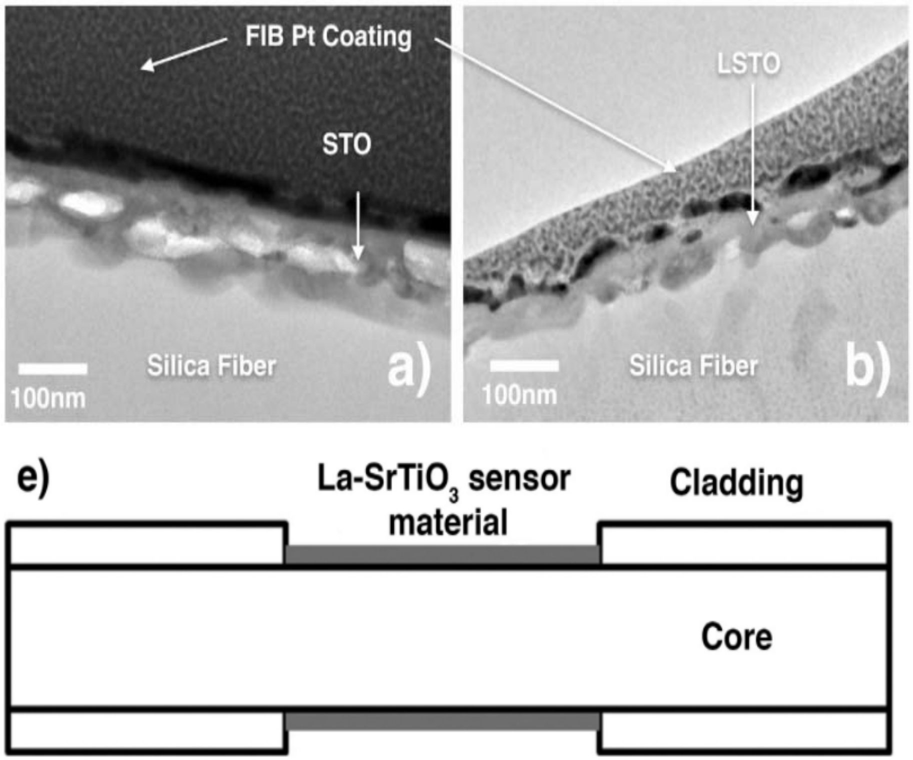


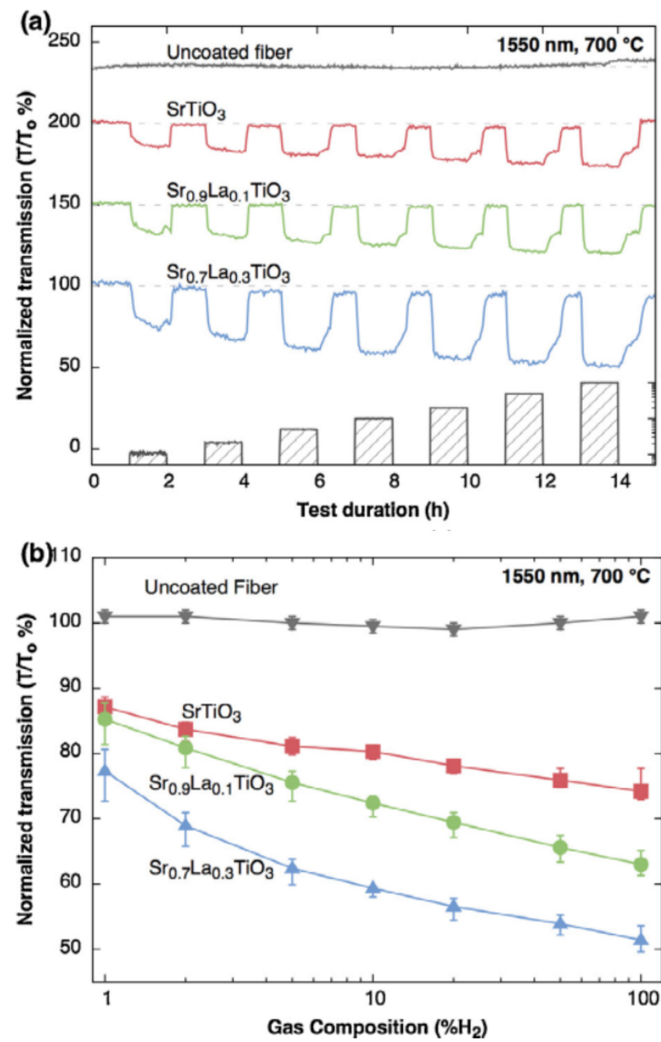
(a) Cross-Flow (b) Co-Flow (c) Counterflow

Recknagle, K. P. et al. J Power Sources 113 (1), 109–114.

Cell and Stack Degradation

La-Doped $SrTiO_3$ on Optical Fiber for H_2 Sensing



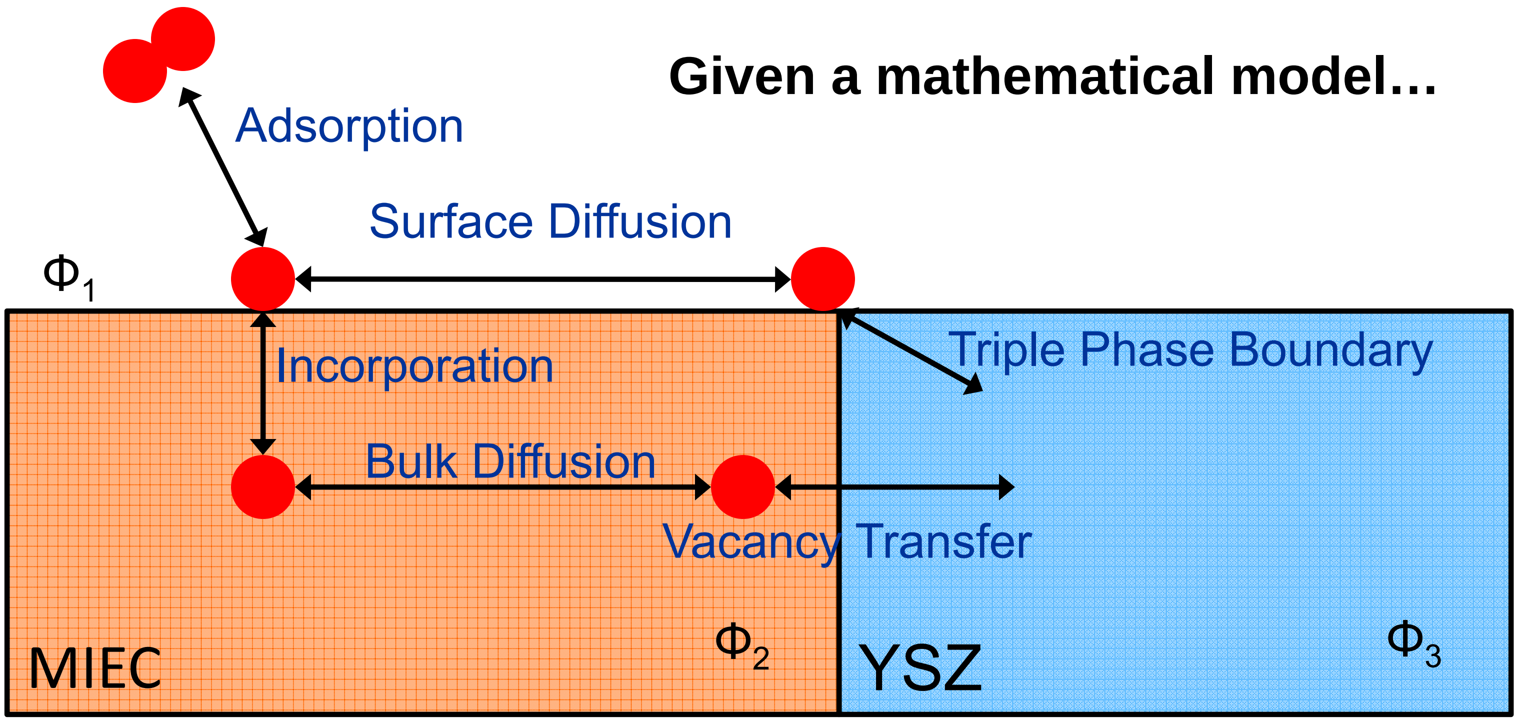


Sensing mechanism:
Changes in H_2 pressure modify free carrier concentrations in LSTO sensing layer, resulting in changing absorption of near infrared radiation by the sensing layer.

Schultz, A. M.; et al. Sensors & Actuators: B. Chemical 221 IS -, 1307–1313.

Cell and Stack Degradation

Parameter Estimation via Bayesian Statistics



Given a mathematical model…

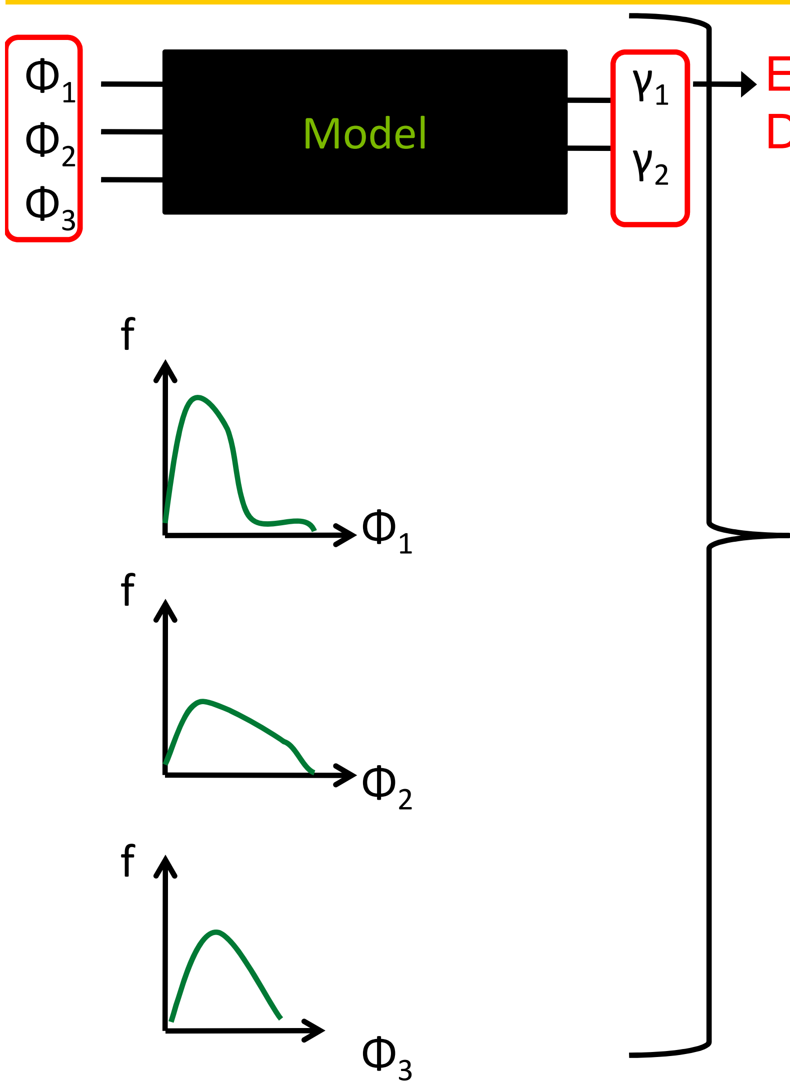
$X_{i,j}=\Phi_i-\Phi_j$

POSTER – "Interpretation of Impedance Spectroscopy Data on Porous LSM Electrodes"
-Giuseppe Brunello

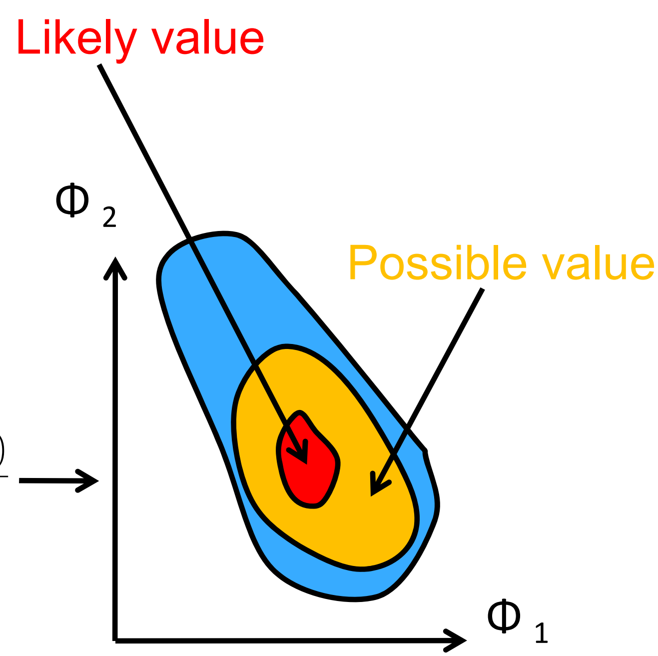
Can we improve the estimates of the parameter values?

Cell and Stack Degradation

Parameter Estimation via Bayesian Statistics



$$\mathcal{P}(\vartheta|Z) = \frac{\mathcal{L}(Z|\vartheta)\mathcal{P}(\vartheta)}{\mathcal{P}(Z)}$$

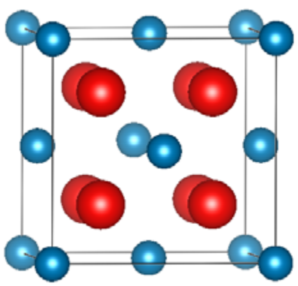


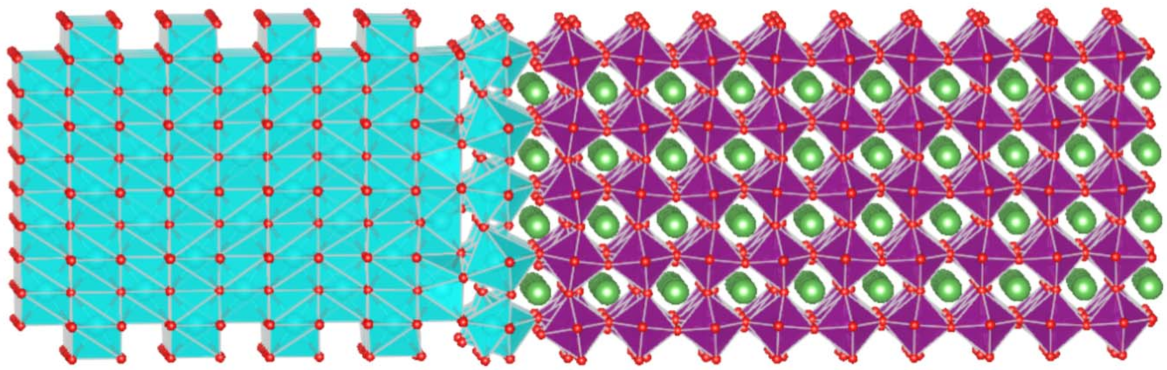
The result of Bayesian calibration is a probability distribution of the model's parameters

Cell and Stack Degradation

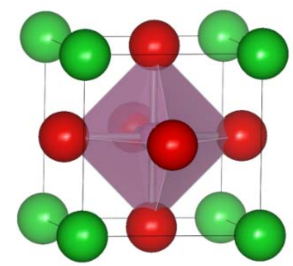
First-Principles Modeling of Cation Diffusion in LSM and YSZ Bulk and Interfaces

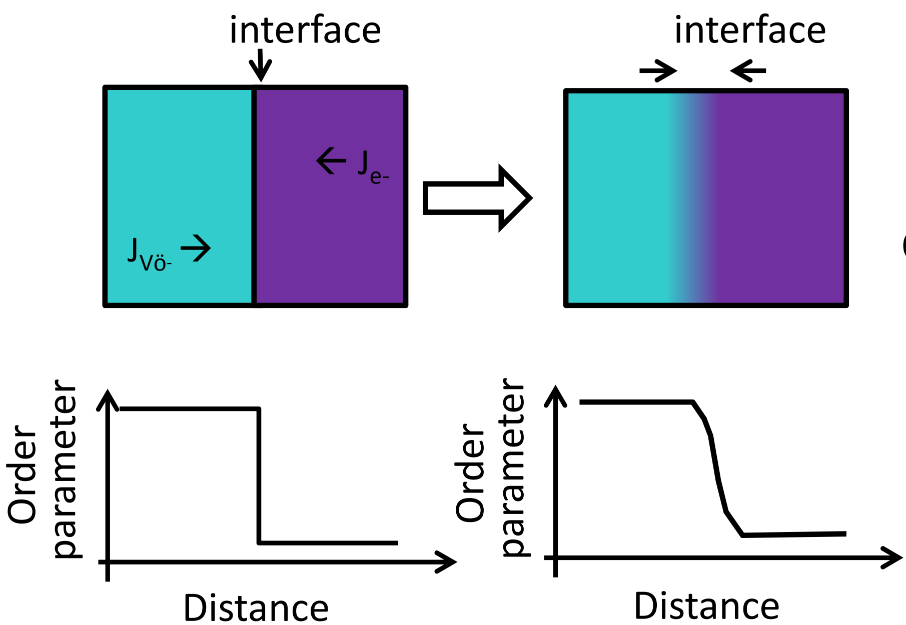
Y doped ZrO_2



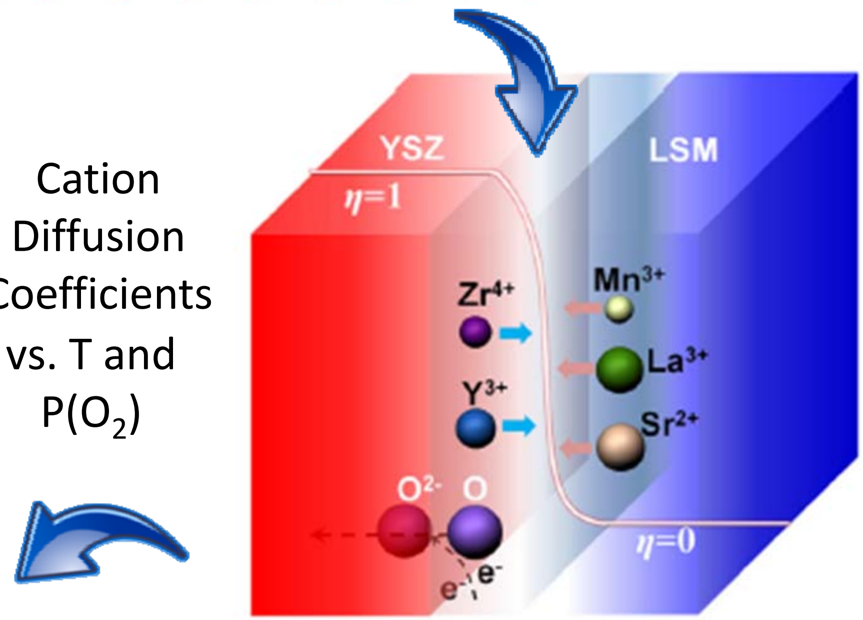


Sr doped $LaMnO_{3\pm\delta}$





Cation Diffusion Coefficients vs. T and $P(O_2)$



Hu et al., Appl. Phys. Lett. (2014)

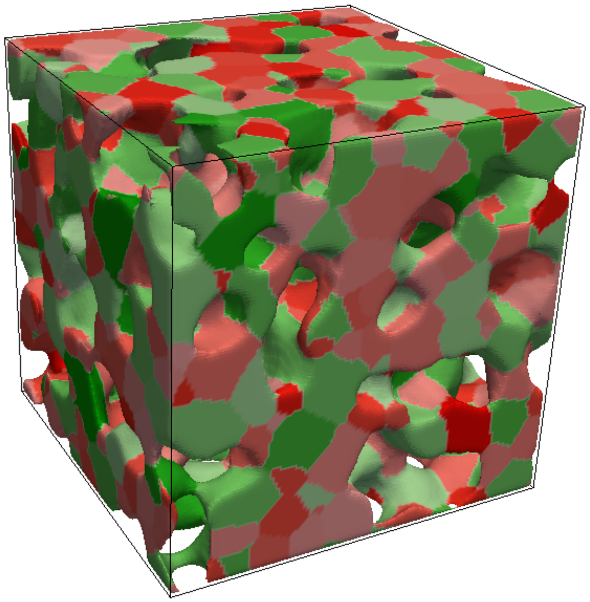
POSTER – "Ab-initio Modeling of Mn Self-Diffusion in LSM for Solid Oxide Electrochemical Cells" -Yueh-Lin Lee

Cell and Stack Degradation
Phase Field Modeling - Coarsening

- **Phenomenological parameters:**
  - Phase fraction C_i
  - Grain orientation η_j^i
- **Free energy density**

$$f = f_b(C_i, \eta_j^i) + \frac{1}{2}\left[\sum_i \kappa_c^{ii}(\nabla C_i)^2 + \sum_{j>i} \kappa_c^{ij}\left(\nabla C_i \cdot \nabla C_j\right)\right] + \frac{1}{2}\sum_{i,j} \kappa_\eta^{ik}(\nabla \eta_k^i)^2$$

  - Bulk free energy density f_{bulk} keeps $\left(C_i, \eta_j^i\right)$ around (0,0) or (1,1)
  - Crossing terms of parameter gradients makes interfacial energy tunable
- **Evolution of C_i: Cahn-Hilliard equation, conservative**



Simulated microstructure of cathode. Red grains: YSZ, Green grains: LSM

POSTER – "Phase Field Modeling of Microstructure and Conductivity Evolution in SOFC Electrodes"
-Youhai Wen

Li *et al*, *Appl. Phys. Lett.* **101**, 033909, (2012)
Liang *et al*, J. Appl. Phys. **117**, 065105, (2015)

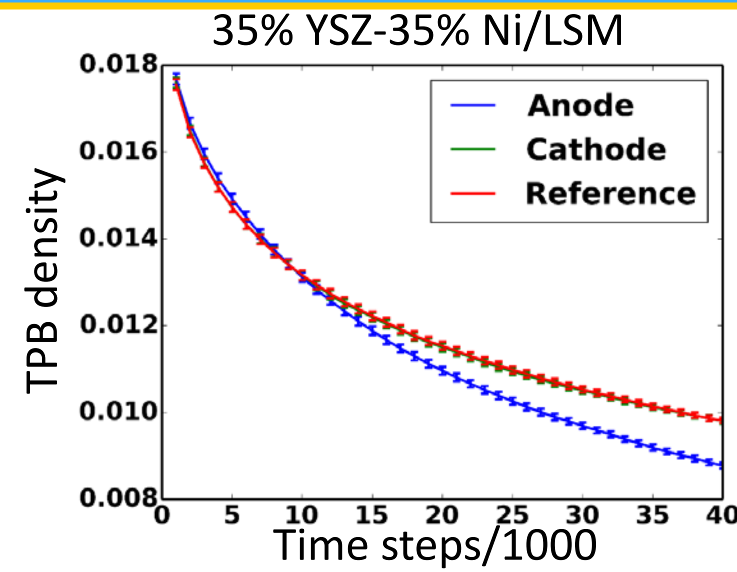
Cell and Stack Degradation
Time Evolution of Microstructure

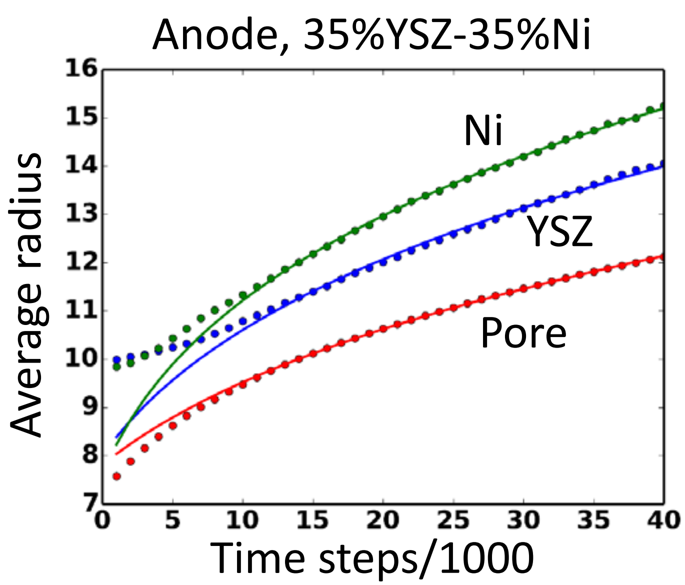
- **Grain growth**

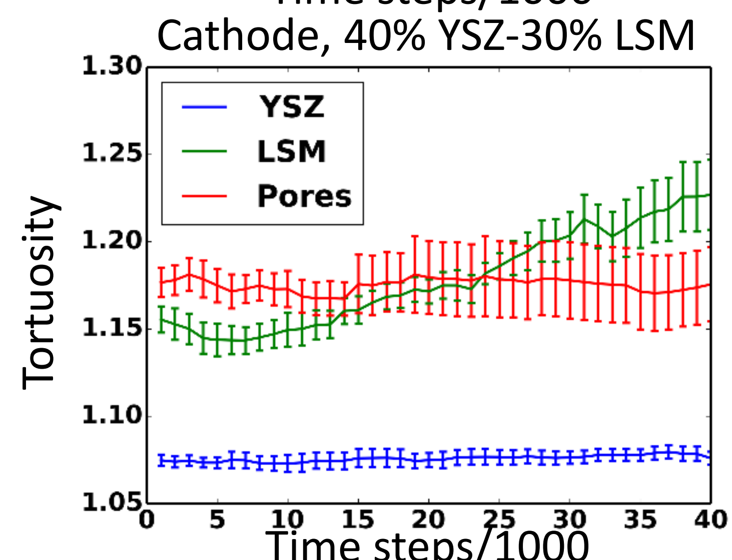
$$R^n - R_0^n = kt$$

n~4, surface diffusion controlled coarsening.

- **TPB degradation faster in anode than cathode.**
- **Tortuosity of Ni/LSM increases with time**







Cell and Stack Degradation

Time Evolution of Conductivity

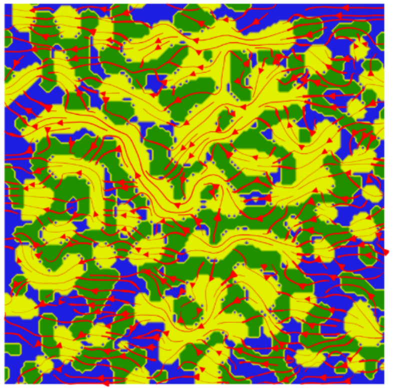
- **Conductivity calculated by solving steady-state Poisson's equation using bound charge successive approximation (BCSA) algorithm.**

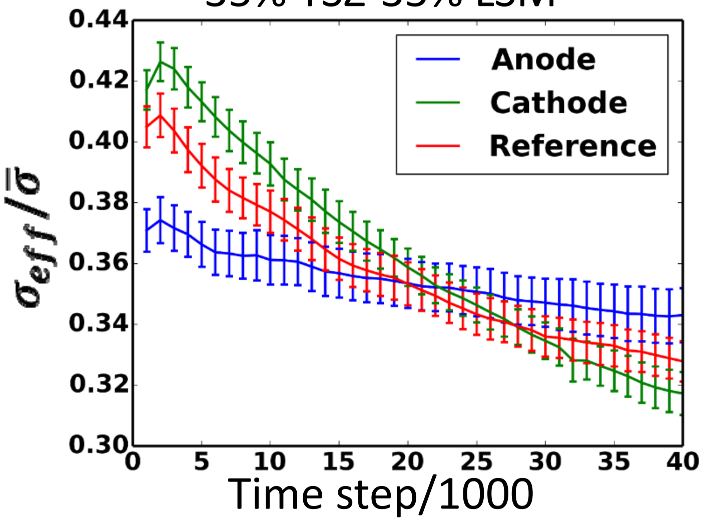
$$\nabla \cdot \left(\sigma(\vec{r})\vec{E}\right) = -\frac{\partial \rho}{\partial t} = 0$$

- **Conductivity evaluated as a function of phase fraction of YSZ and LSM.**
- **Consistent with increasing of tortuosity for the electrode phase.**
- **Degradation slower in anode**

Cheng *et al*, *Phys. Rev. E*, **91**, 055307 (2015)

$\vec{E}$ distribution throughout a simulated 2D microstructure



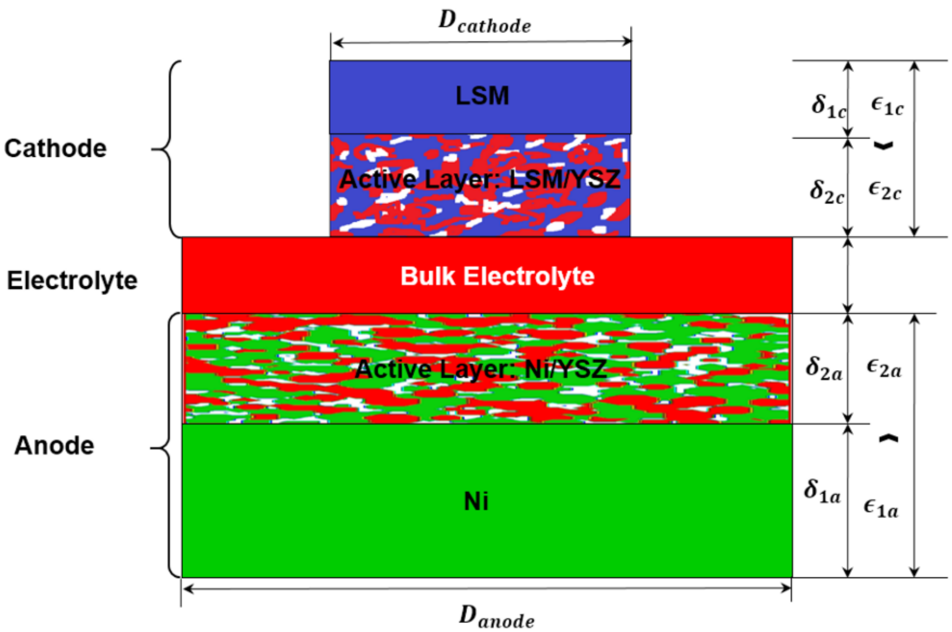


Cell and Stack Degradation

Modeling Degradation due to Grain Coarsening

- A simple degradation model is applied to the cathode of a SOFC with dimensions and operating conditions given below
- The microstructure properties are updated as a function of time in order to study the effect on cell performance

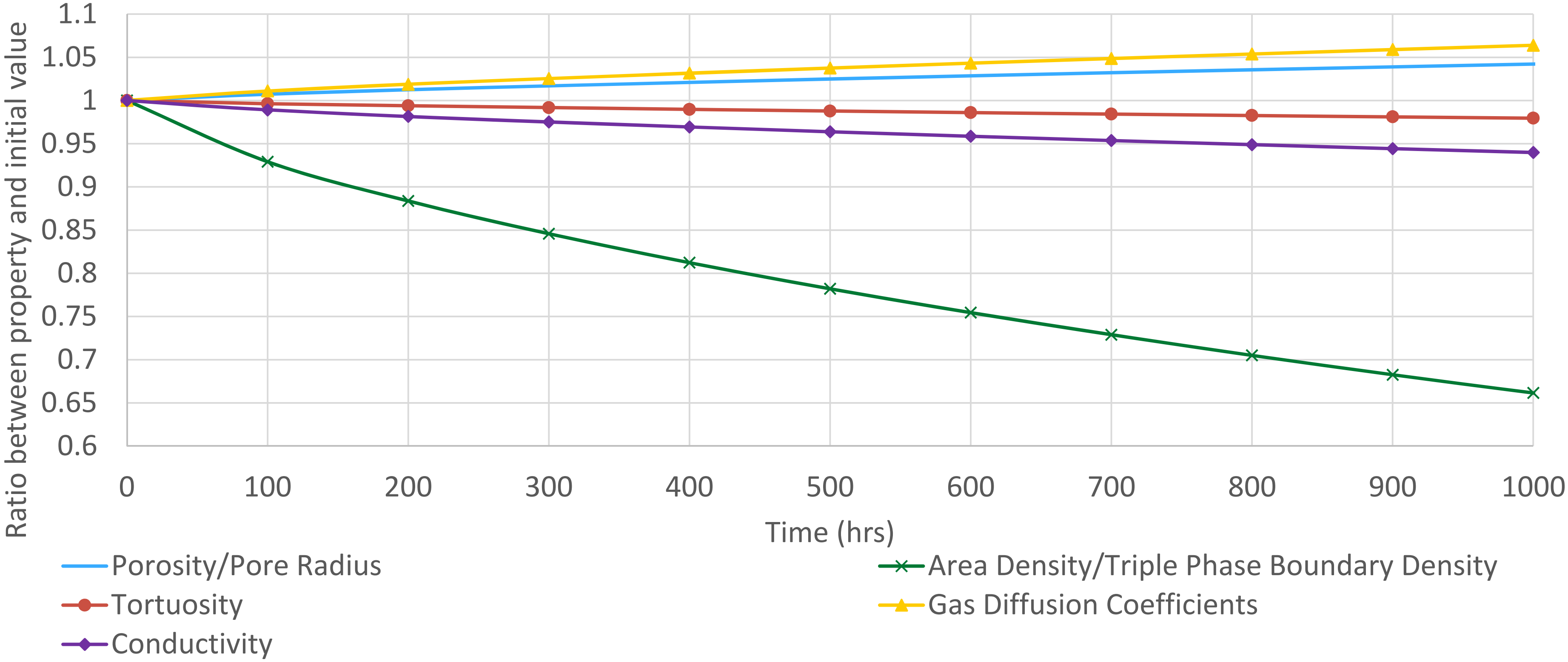
Parameter	Value
Cathode Diameter	$1.7\ cm$
Anode Diameter	$2.54\ cm$
Cathode thickness	$50\ \mu m$
Cathode active layer thickness	$30\ \mu m$
Anode thickness	$900\ \mu m$
Anode active layer thickness	$30\ \mu m$
Electrolyte thickness	$10\ \mu m$
Cell Temperature	$800\ °C$



Cell and Stack Degradation

Modeling Degradation due to Grain Coarsening

- Property models are developed using a combination of physics and empirically fit equations
- For this preliminary study, only the properties in the cathode are modified

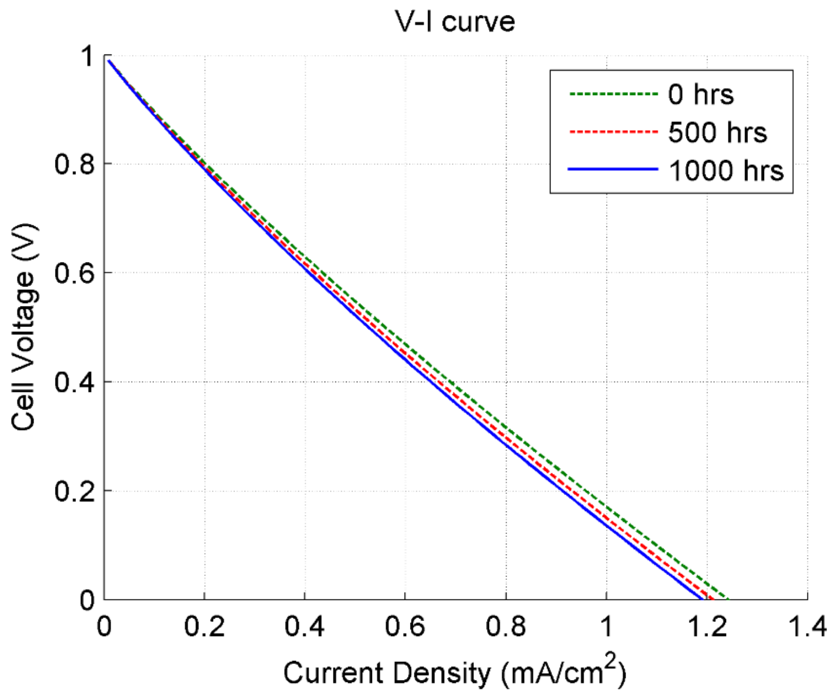


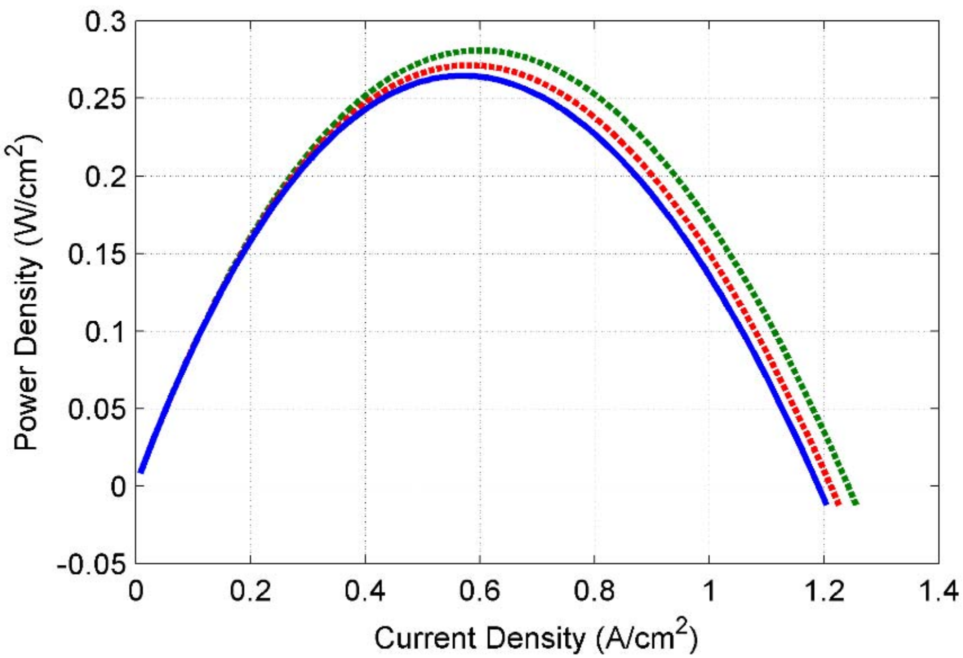
References: Kennouche et al, J. Power Sources, 307 (2016) 604; Pihlatie et al, Solid State Ionics, 189 (2011) 82-90; Simwonis et al, Solid State Ionics, 132 (2000) 241-251; Preliminary data analysis from Yinkai Liu and William Epting

Cell and Stack Degradation

Modeling Degradation due to Grain Coarsening

- Predicted polarization and power density both exhibit degradation

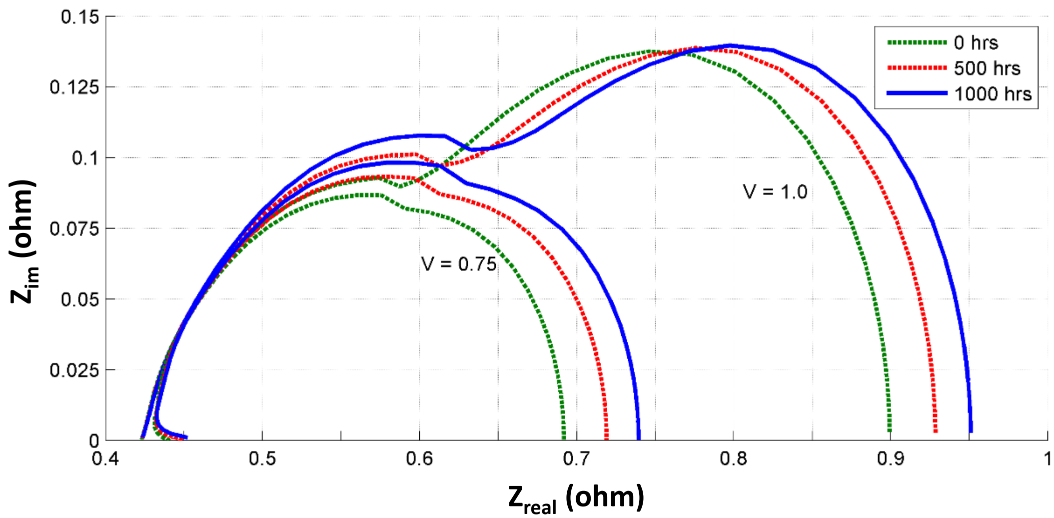


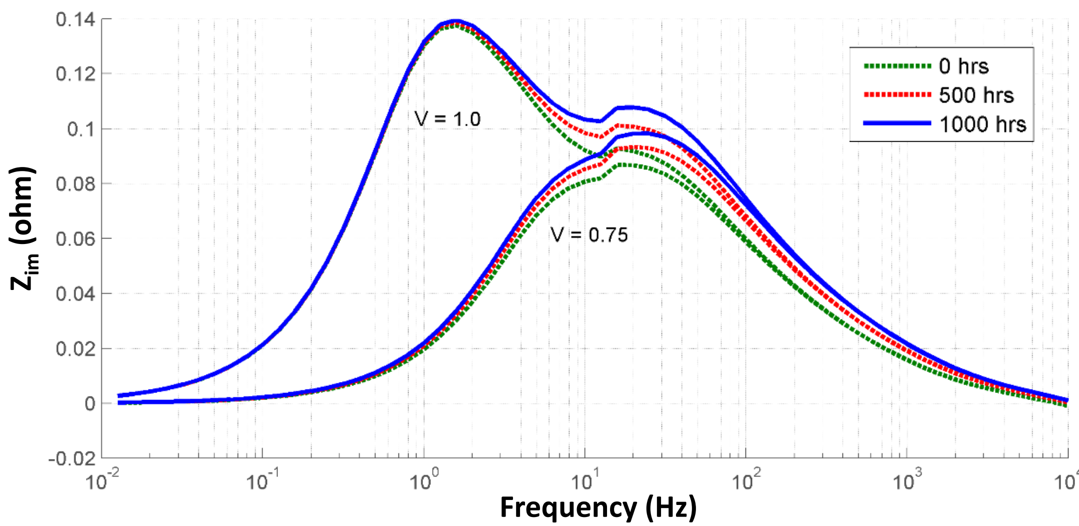


Cell and Stack Degradation

Modeling Degradation due to Grain Coarsening

- **Impedance analysis clearly indicate degradation**
- **Only the impedance due to the cathode changes**
  - Cathode arc peaks between ~10^1 and 10^2 Hz

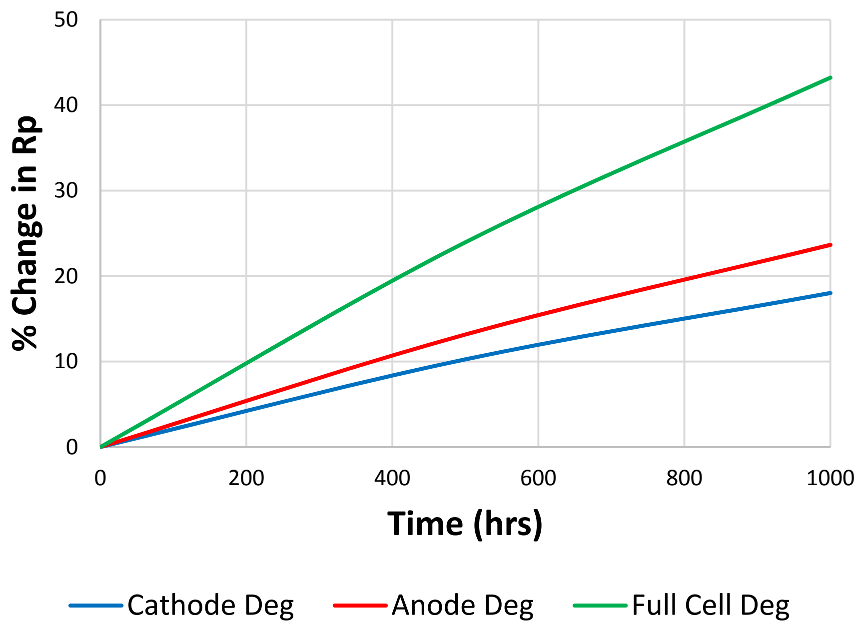


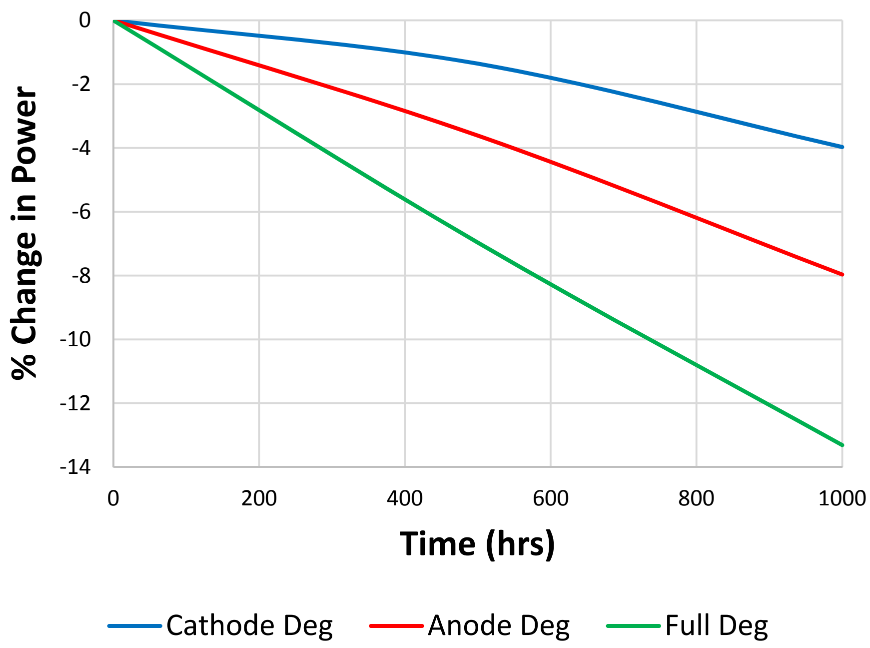


Cell and Stack Degradation

Modeling Degradation due to Grain Coarsening

- Impact of individual degradation modes can be compared to overall cell degradation





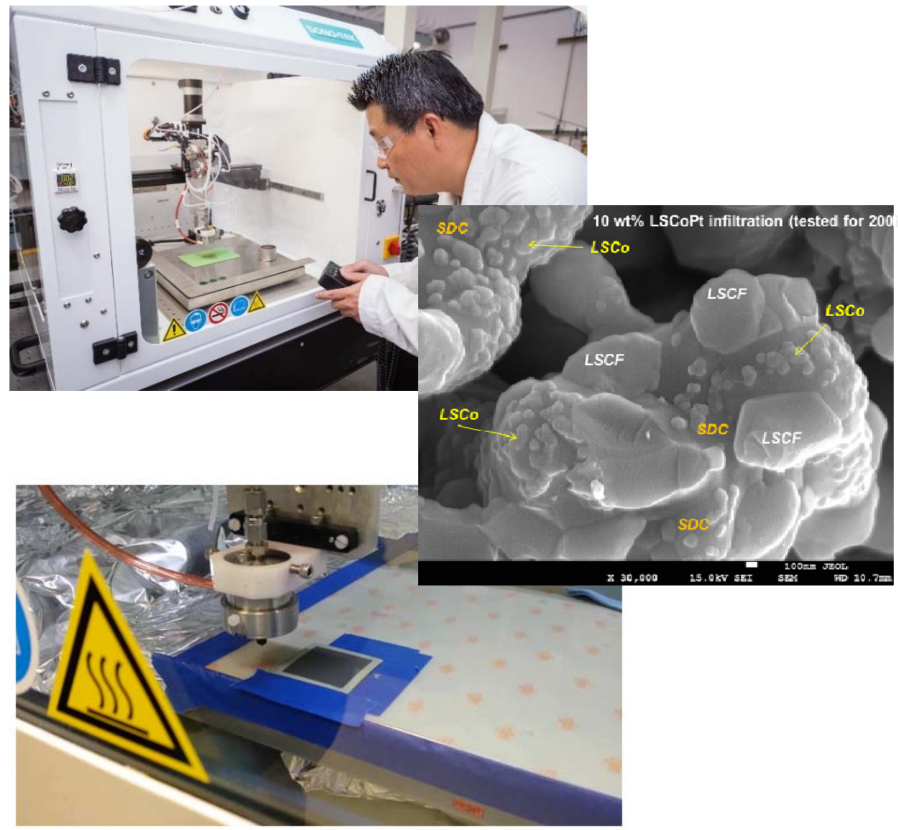
Electrode Engineering Innovation
Motivation/Approach

- **Motivation**
  - Novel materials and production methods may be available to increase efficiency and reduce cost at the cell level, but this may not be feasible to commercial providers producing large volumes with well-established methods
  - Need to identify a simple/low cost method to modify current SOFC production methods/material sets

- **Approach**
  - Tailor electrode infiltration techniques to improve performance and endurance of commercially available cells
  - Direct collaboration with SOFC Program Industrial Partners

Electrode Engineering Innovation
Cathode

- **NETL has developed and patented* a single-step cathode infiltration technique that can be utilized by commercial SOFC manufacturers to improve their cell performance and durability**
  - Proven performance gains of
    - 10% peak power increase
    - 33% reduction is degradation rate
    - 200% lifetime increase
  - Low-cost ($0.006/cm²)
  - Scalable
  - Ready for technology transfer
    - Collaboration with industry
  - Ready for any cell geometry



- K.Gerdes, S. Lee, R. Dowd, "Methods of forming catalyst layer by single step infiltration," (US Prov. Patent Appl. No. 62191548 (2015)).
- K. Gerdes, S. Lee, “Functionally grading of cathode infiltration for spatial control of activity,” (US Appl. No. 14/804,492, PCT Appl.No. is 62/026,876 (2015))

Electrode Engineering Innovation
Cathode

Materials (Electrocatalyst) Identification

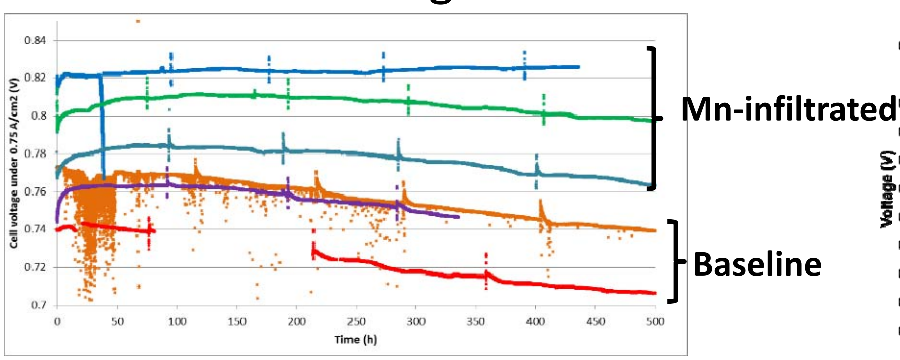
Classification	Composition	Conduction type
Perovskite cobaltite (ferrite, manganite)	LSCo, PSCo, SSCo (LSF, LSM)	MIEC
Pt-substituted perovskite	LSCoPt, PSCoPt	MIEC / Electronic
Perovskite-related (K_2NiF_4)	$(LaSr,)_2CoO_4$, $(PrSr,)_2CoO_4$, La_2NiO_4	MIEC / Electronic
A-site alkaline earth cation(s) perovskite	BSCF, SCF	MIEC / Electronic
Fluorite structure oxide	SDC	Ionic
Spinel oxides	$SrFe_2O_4$, $BaFe_2O_4$ etc.	Electronic
Precious metal	Pt, Pd, Rh	Electronic
Single component	Co, Sr, Fe, Mn	Electronic / insulator
Combination	LSM-LSC	

Electrodе Engineering Innovation

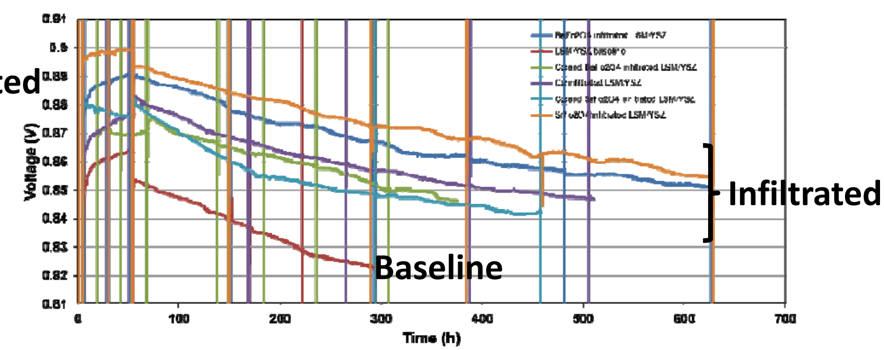
Cathode

Mitigation of Water Induced Degradation

- Use of cathode infiltrate materials in order to reduce steam-induced degradation
  - Elevated steam content investigated on LSM cathode: 3-20%
  - Infiltrate materials include:
    - Single component (Mn, Co),
    - Spinel ferrites ($SrFe_2O_4$, $BaFe_2O_4$)
  - Appropriate nanomaterial infiltration improves performance and mitigates water induced degradation of an LSM cathode



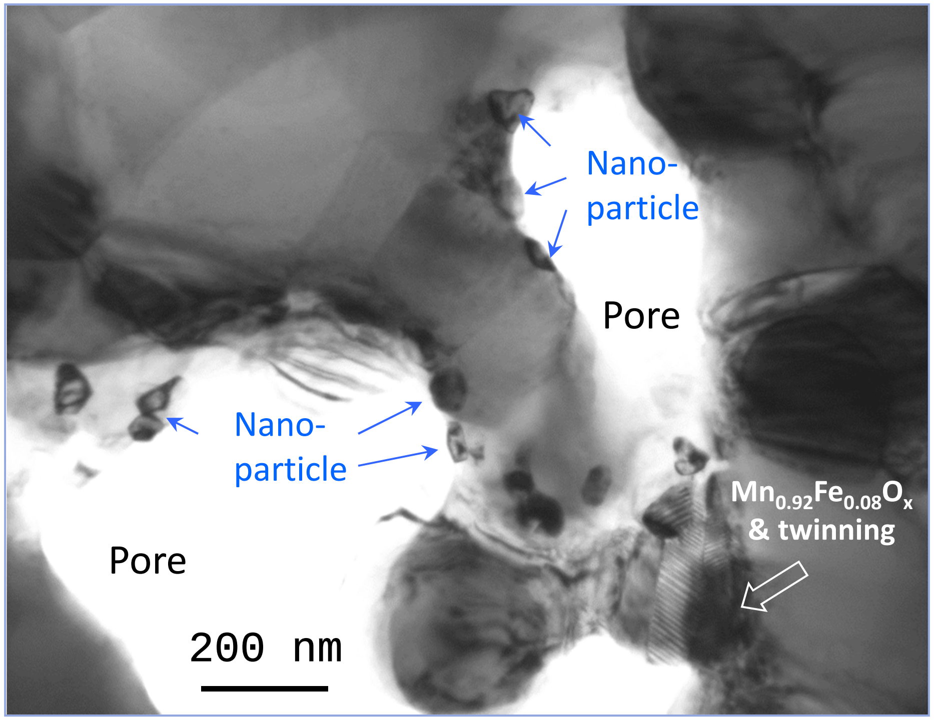
Voltage vs time, 10% steam, 0.75 A/cm^2

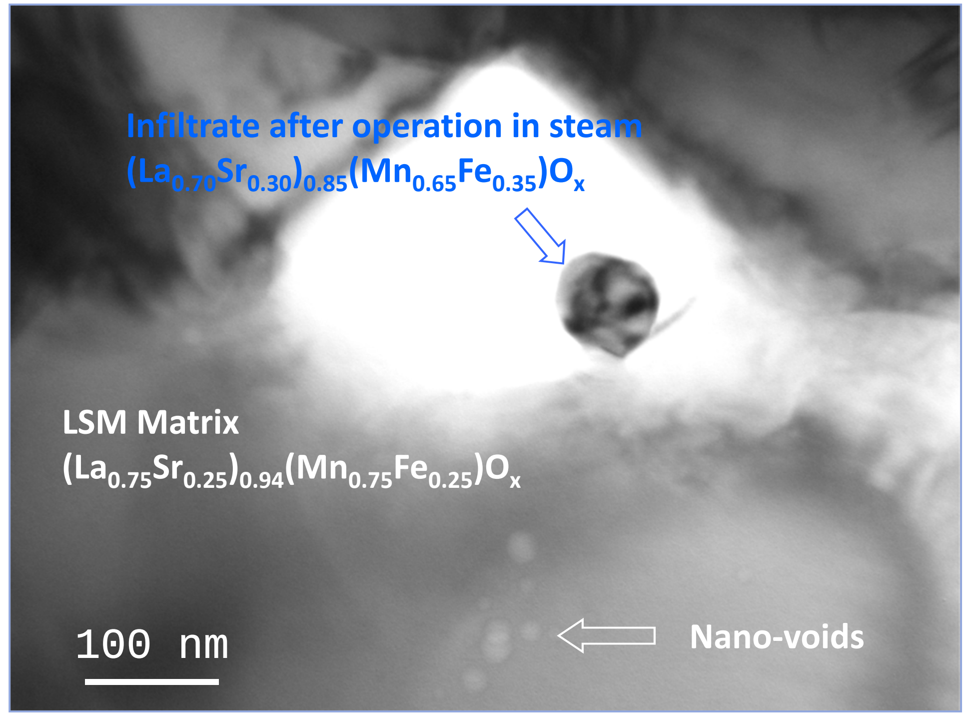


Voltage vs. time, 20% steam, 0.75 A/cm^2

Electrode Engineering Innovation

Effect of $SrFe_2O_4$ Infiltrate and Water





$SrFe_2O_4$ infiltrated LSM/YSZ, 800°C, 10% steam for ~800 hours

- No original $SrFe_2O_4$ nano grains were found after operation.
- Existence of Fe-doped LSM nano-crystals/particles on the backbone.
- Fe diffused into the LSM backbone
- Existence of Mn oxide nano-grains.
- Occurrence of "nano-voids" in the LSM backbone.

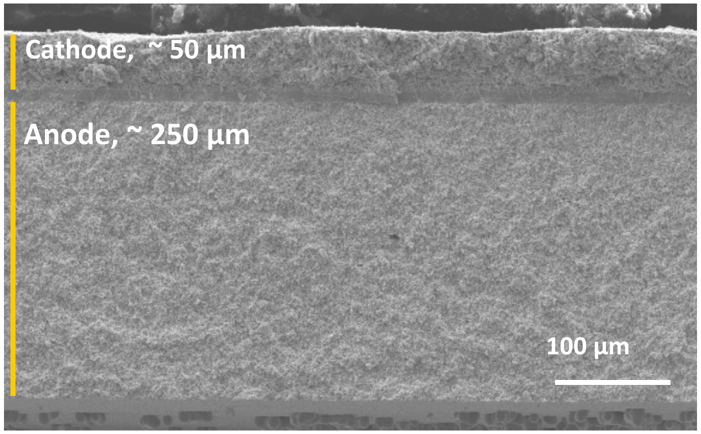
POSTER – "Effects of Humidity on Degradation of Sr-Fe-O Infiltrated SOFC" –Lynn Fan

POSTER – "Evidence of Charge Layer Evolution at the YSZ Grain Boundaries" –Xueyan Song

Electrode Engineering Innovation
Anode

- **Prefer to enhance existing commercial anodes before reduction**
  – NiO/YSZ-support contains <25% porosity *(difficult to impregnate)*
  – Industry does not want to modify their developed anode-microstructure after decades of development
  – Pre-reduced anode-supported SOFCs show very low strength

- **Prefer to eliminate multiple infiltration steps**
  – Eliminate days of processing
  – Eliminate inconsistent deposition from uncontrolled deposition rate and drying

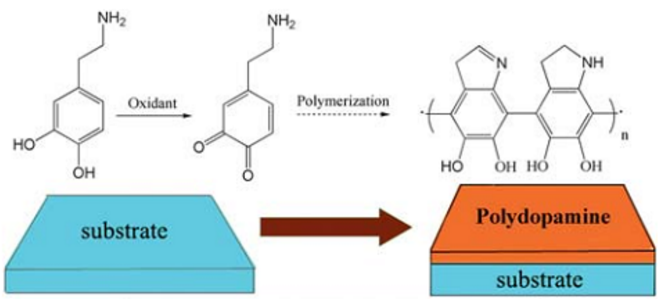


POSTER – "Catalyst Infiltration of SOFC Electrodes Assisted by a Bio-surfactant" –Ozcan Ozmen

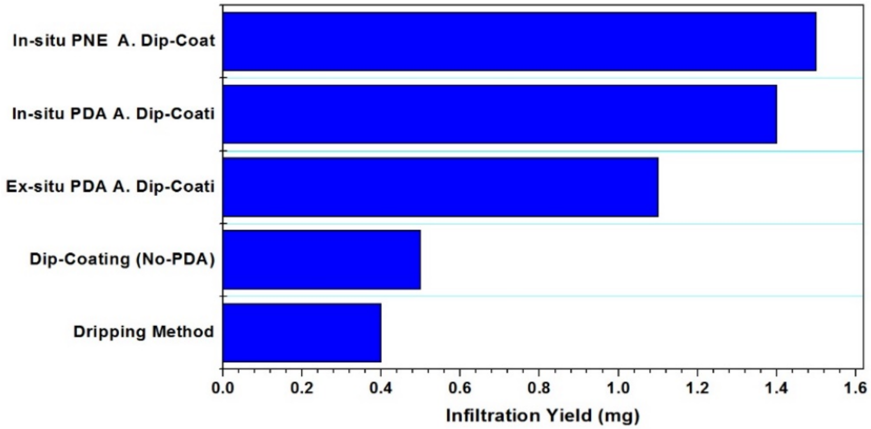
Electrode Engineering Innovation
Anode

Mussel Inspired Bio-surfactant SOFC Electrode Infiltration*

- Enhance wetting of the electrode surface, target deposition of nanoparticles by chelating infiltrated metal cations with surfactant



Polymerized catechols, such as dopamine and nor-epinephrine used as bio-adhesive surfactant for electrode backbone.



Electrode dip-coated by poly-dopamine (PDA) and poly-epinephrine (PNE) trap up to 3 times more nanoparticles per step. CeO_2 infiltration chosen as a representative catalyst system

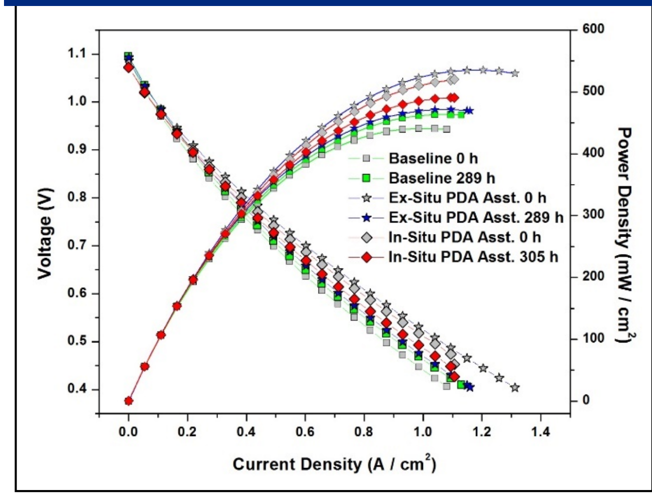
Z. Qin, M. et al., ***J Mech Phys Solids***, 62, 2014
J.H. Waite, ***Nature Materials***, 7, 2008

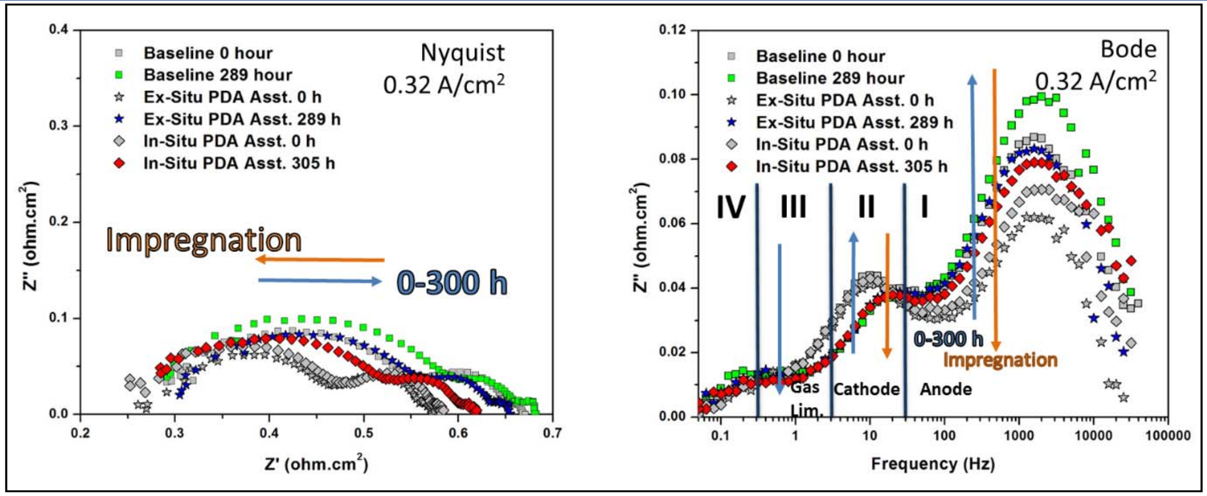
* US Patent Application No. 14/963,564
O.Ozmen et al., Material Letters 164, 2015

Electrodê Engineering Innovation

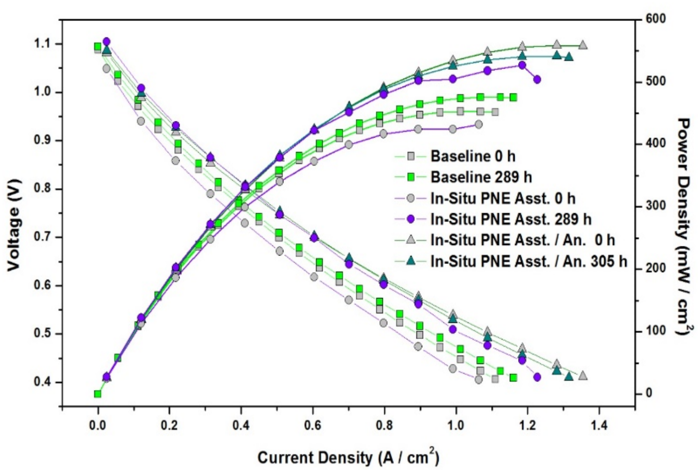
Anode

PDA/PNE Assisted CeO_2 Infiltrated Cells @ 300 h Operation

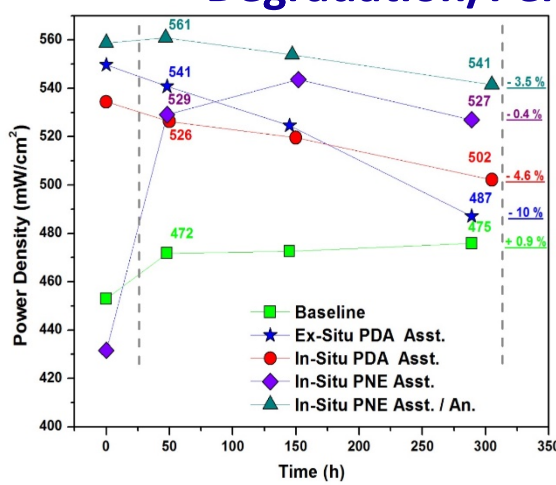




PNE Assisted Infiltration



Degradation/Performance Summary



- PNE-assisted infiltrated cells retained higher power density (10-14%) with lower degradation after 300 h
- PDA-PNE modified infiltration process produced finer and more discrete nano-catalyst deposits.

Future Work

- **Continued collaboration with Industry/SOFC Core Teams**
- **Cell and Stack Degradation**
  - Continued integration of degradation models into Comprehensive Predictive Model
  - Finalization of Impedance Modeling Tool
  - Finalization/release of Microstructure Visualization Tool
- **Electrode Innovation Engineering**
  - Evaluation of new set of materials for infiltration identified by DFT
  - Characterization of infiltrates that mitigate steam induced degradation
  - Build upon success of anode infiltration
    - Graded methane reforming reaction
    - Redox tolerant anodes
  - Transfer of single-step cathode infiltration technique to industry

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- Geo Richards
- Kirk Gerdes

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NETL SOFC Group Posters

- “Phase field modeling of microstructure and conductivity evolution in SOFC electrodes” – **Youhai Wen**
- “Effects of Humidity on Degradation of Sr-Fe-O Infiltrated Solid Oxide Fuel Cells” – **Lynn Fan**
- “Catalyst Infiltration of SOFC Electrodes Assisted by a Bio-surfactant” – **Ozcan Ozmen**
- “Characterization of SOFC Cathode Impedance under Polarization Using Appropriate Counter Electrode Design” – **Jay Liu**
- “Interpretation of Impedance Spectroscopy Data on Porous LSM Electrodes” – **Giuseppe Brunello**
- “Representative Volumes in Highly Heterogeneous Fuel Cell Materials” – **Billy Epting**
- “Ab Initio Modeling of Mn Self-Diffusion in $La_{1-x}Sr_xMnO_3$ (X=0 and 0.25) for Solid Oxide Electrochemical Cells” – **Yueh-Lin Lee**
- “Evidence of the Space Charge Layer Evolution at the YSZ Grain Boundaries” – **Xueyan Song**