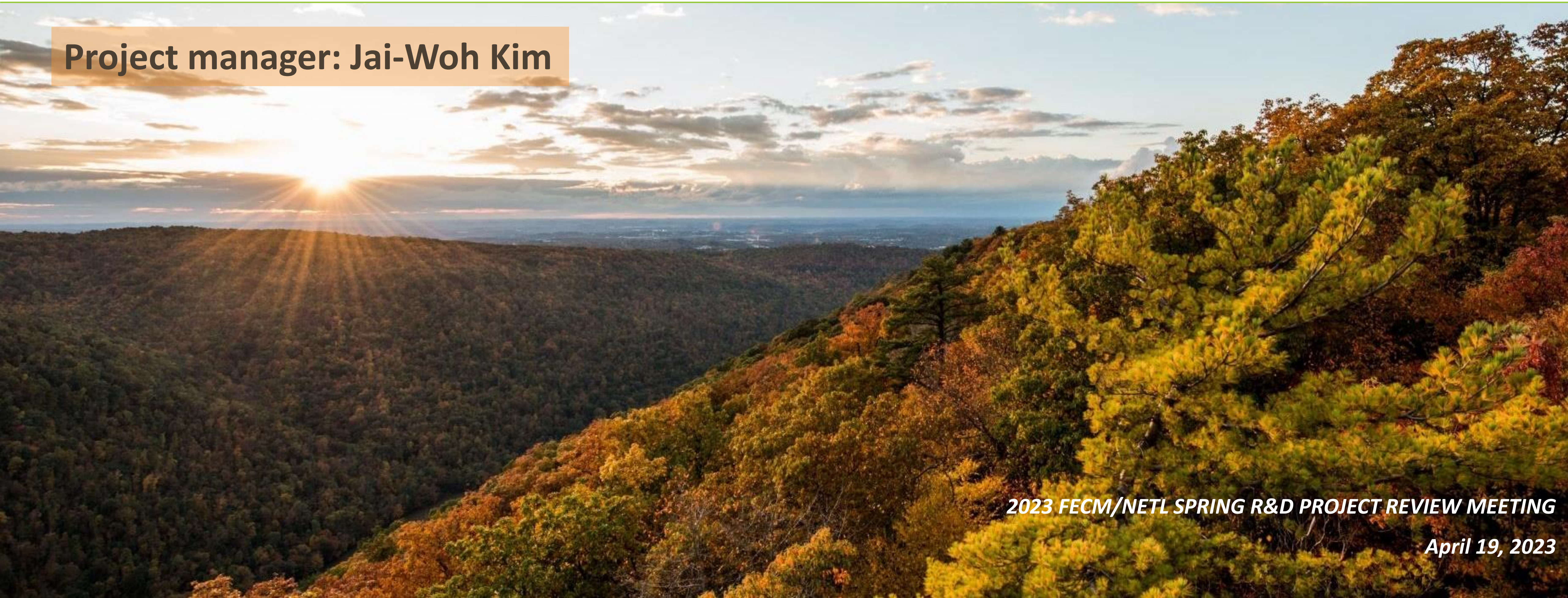
Reversible Solid Oxide Cell Degradation Characterization, Simulation, and Mitigation at NETL

NETL FWP 1022411

Harry Abernathy, Ph.D.
Team Lead, NETL SOC R&D



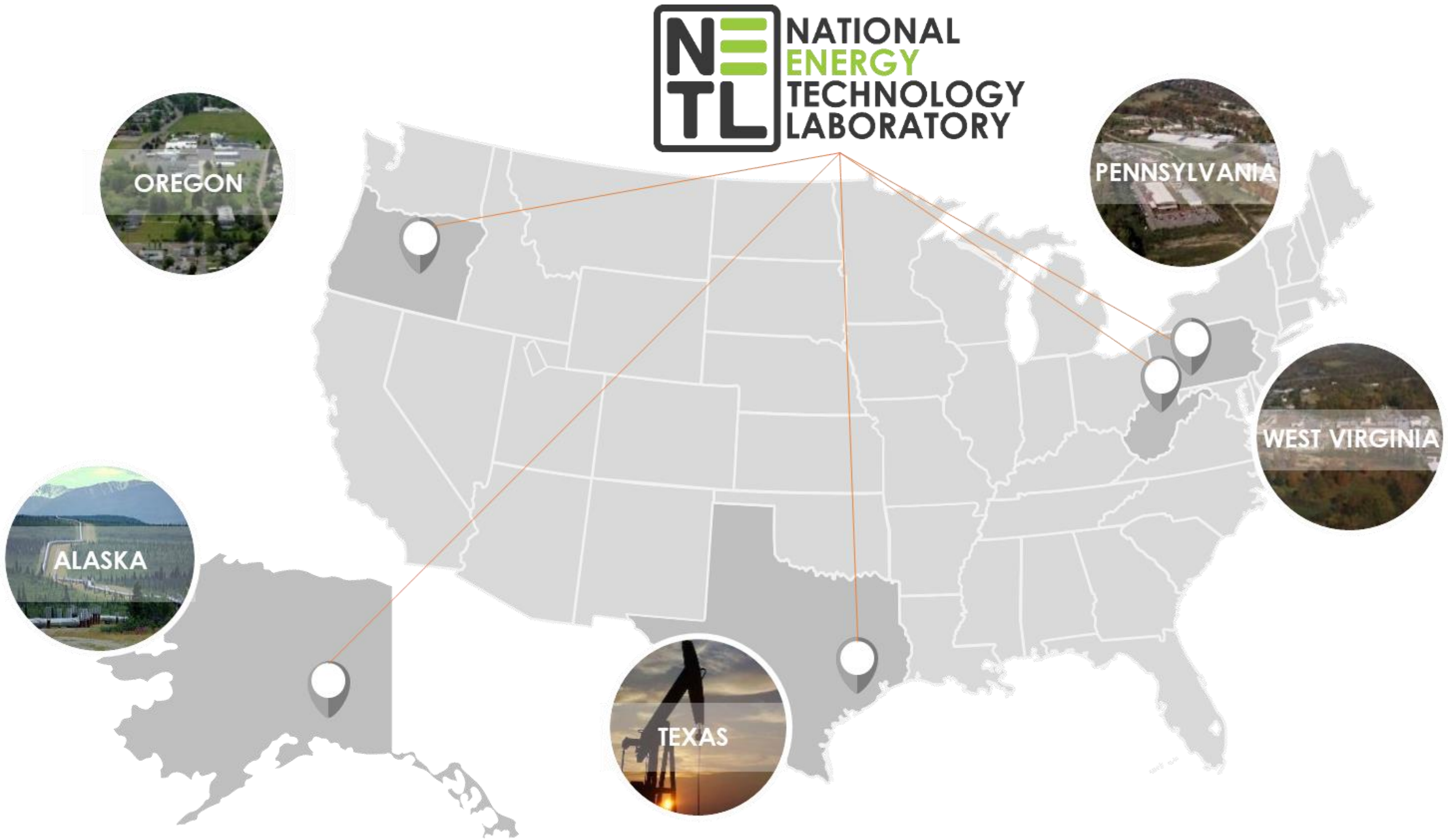
Project manager: Jai-Woh Kim

2023 FECM/NETL SPRING R&D PROJECT REVIEW MEETING

April 19, 2023

Outline

- **Introduction**
- **Recent Progress**
  - Cell and Stack Degradation Modeling and Simulation
  - Electrode Design and Engineering
- **Wrap-Up**



SOFC FY23 FWP Personnel

NETL (Federal Staff)
- Anthony Burgard (PGH)
- Billy Epting (**Task 2 PI**, ALB)
- Gregory Hackett (**Task 4 PI**, MGN)
- Harry Abernathy (**TPL**, MGN)
- Jay Liu (**Task 3 PI**, MGN)
- Rich Pineault (MGN)
- Sam Bayham (**Task 5 PI**, MGN)
- Wissam Saidi (PGH)
- Youhai Wen (ALB)
- Yuhua Duan (PGH)
- Yves Mantz (MGN)

Carnegie Mellon University
- Paul Salvador (MSE)
- William Kent (PhD student)
- Rachel Kurchin (MSE)

Clemson University
- Kyle Brinkman (MSE)
- Jack Duffy (MSE, PhD student)

NETL (Site Support Contracts)
- Alex Noring (KeyLogic/PGH)
- Arun Iyengar (KeyLogic/PGH)
- Biao Zhang (LRST/MGN)
- Bo Guan (LRST/MGN)
- Farida Harun (LRST/MGN)
- Fei Xue (LRST/ALB)
- Kyle Buchheit (KeyLogic/PGH)
- Lynn Fan (LRST/MGN)
- Rick Addis (SOS/MGN)
- Tao Yang (LRST/MGN)
- Tianle Cheng (LRST/ALB)
- Tom Kalapos (**PM**, LRST/PGH)
- Yinkai Lei (LRST/ALB)
- Yoosuf Picard (LRST/PGH)
- Youngseok Jee (LRST/PGH)
- Yueh-Lin Lee (LRST/PGH)

Georgia Southern University
- Hayri Sezer (Eng&Tech)

Penn State University
- Long-Qing Chen (MSE)
- Yanzhou Ji (MSE)

University of Wisconsin-Madison
- Dane Morgan (MSE)
- Ryan Jacobs (MSE)
- Chiyoung Kim (MSE PhD student)

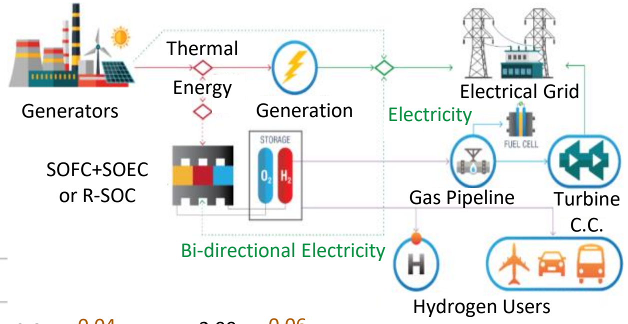
West Virginia University
- Harry Finklea (Chemistry)
- Ed Sabolsky (MAE)
- Joshua Tenney (PhD student)
- Xueyan Song (MAE)
- Xingbo Liu (MAE)
- Yun Chen (WV Research Corp.)

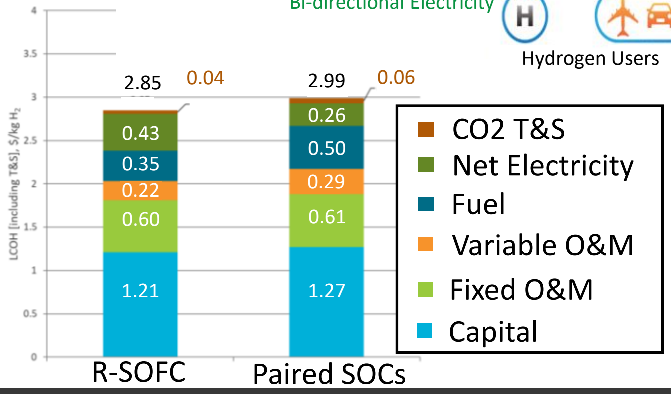
NETL SOC Capability Overview

CHALLENGE: SOC technology is cost prohibitive due to long-term performance degradation
APPROACH: Develop degradation modeling and mitigation tools to improve performance / longevity of SSEC

Systems Engineering and Analysis

- Techno-Economic Analysis
- Hybrid configuration assessment
- R&D Goals Evaluation

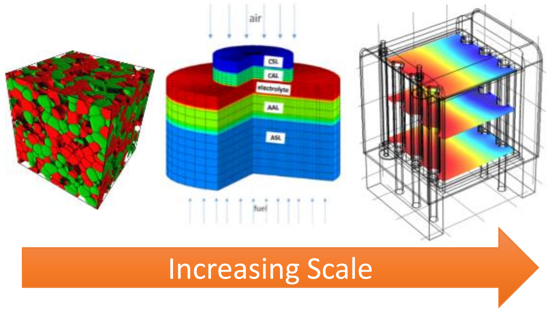


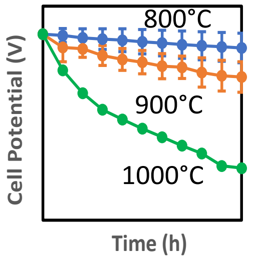


Levelized Cost of H_2 at $20/MWh Electricity

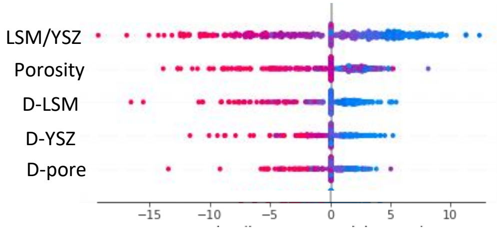
Performance Degradation Modeling

- Degradation prediction tools
- Atoms-to-System scale bridging
- Experimental validation
- Advanced Gas, Temperature Sensors





Machine learning-informed design tools

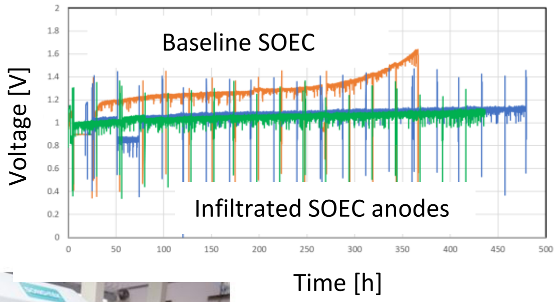


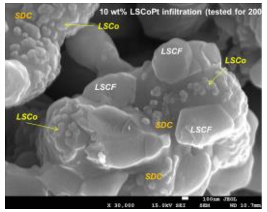
Impact of microstructural features on lifetime performance

Electrode Engineering

- Degradation mitigation
- Microstructure optimization
- Technology transfer to industry
- System demonstrations

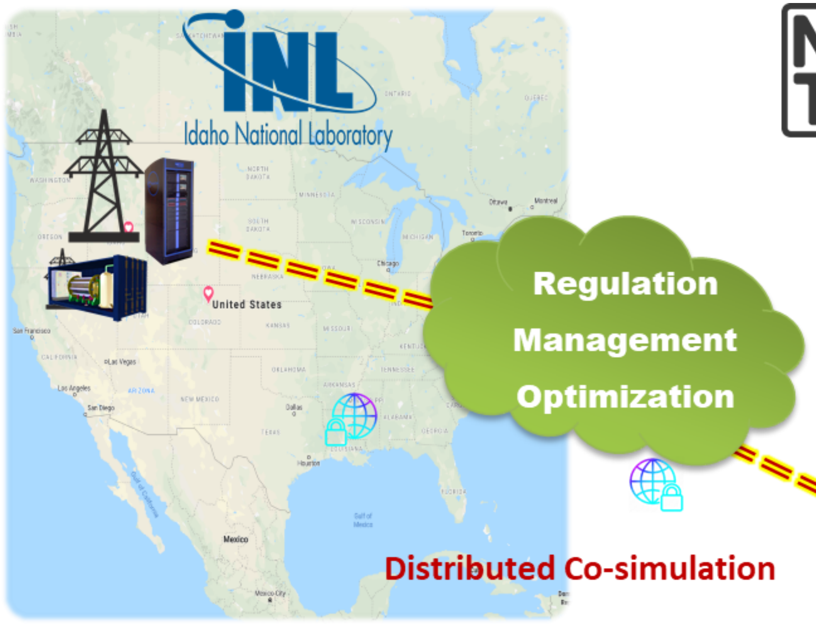
Infiltrated Cells from **6** Partners



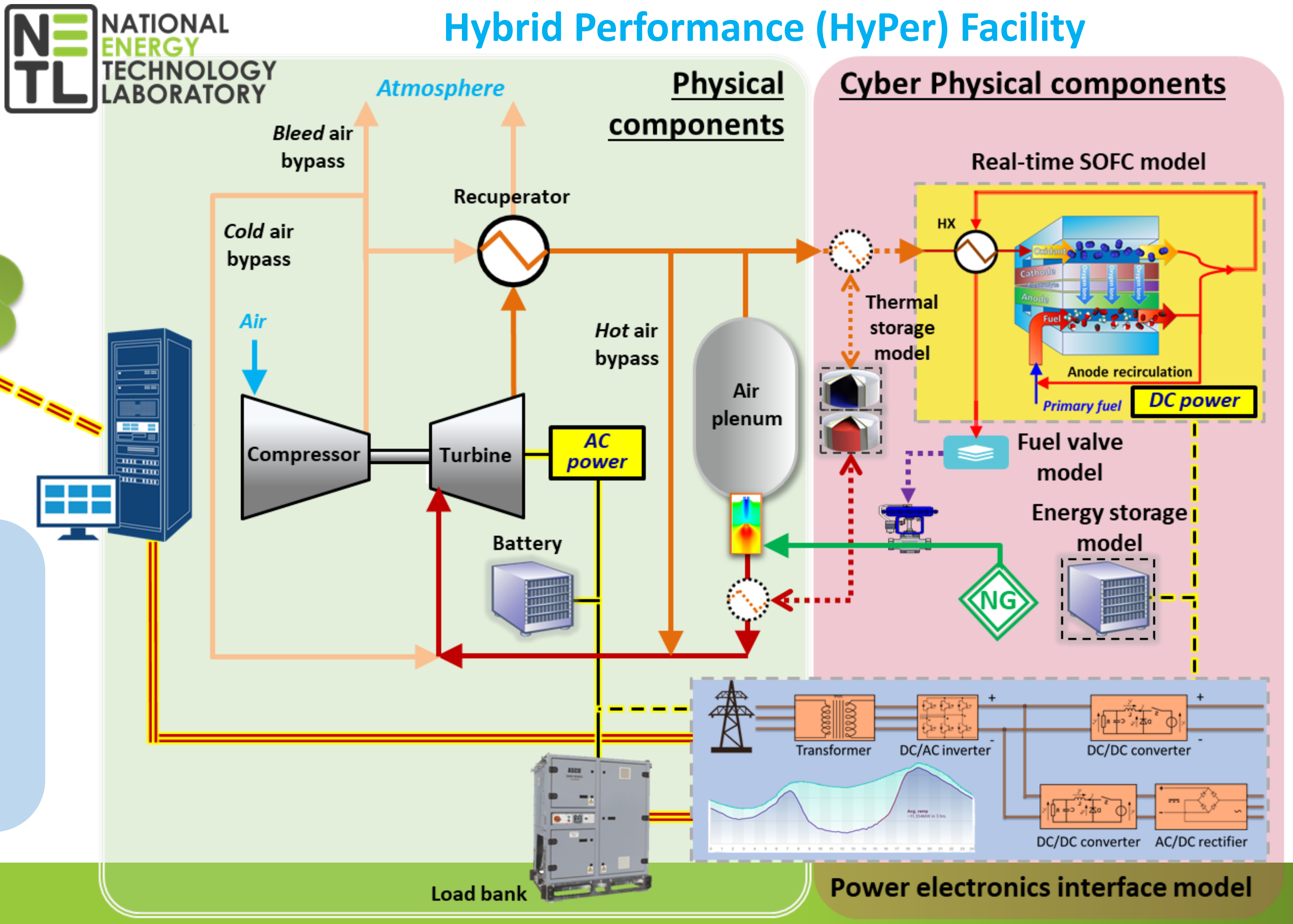


INL/NREL/NETL Grid Simulations

Cyber-physical simulations for systems/controls development

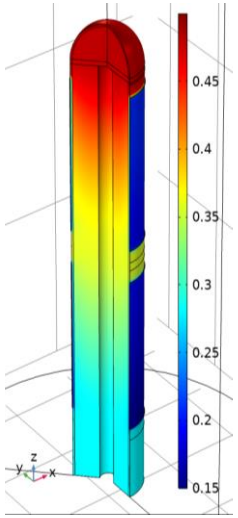


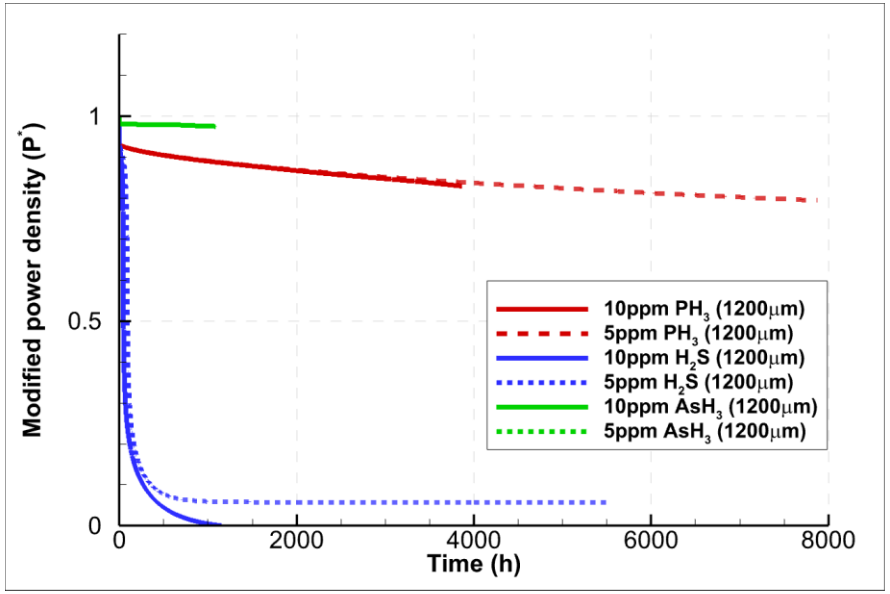
Cyber-physical facility allows for
- More flexible configurations
- Cheaper studies
- Practical, real-time simulations
- Accelerated testing



R-SOFC Program Collaborations

UNDEERC





- Modeling SOFC degradation from coal gas contaminants
- Project: DE-FE31977

Aris Renewable Energy Solutions

- 5.6 kW demonstration in Morgantown
- Project: DE-FE31978

External SOC Collaboration

Applying capabilities outside of R-SOFC Program

OxEon Phase II Air Force STTR

Oxeon

- Using NETL's patented infiltration technology to create advanced electrode designs for fuel-flexible SOFC

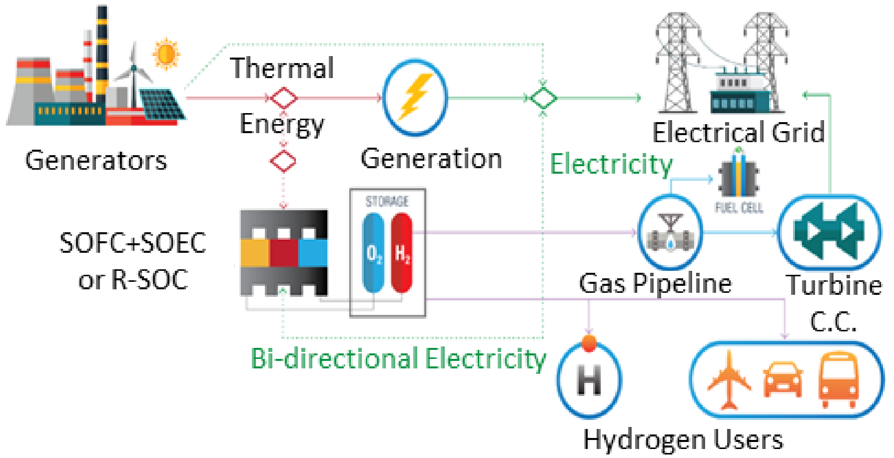
H2NEW Lab Consortium

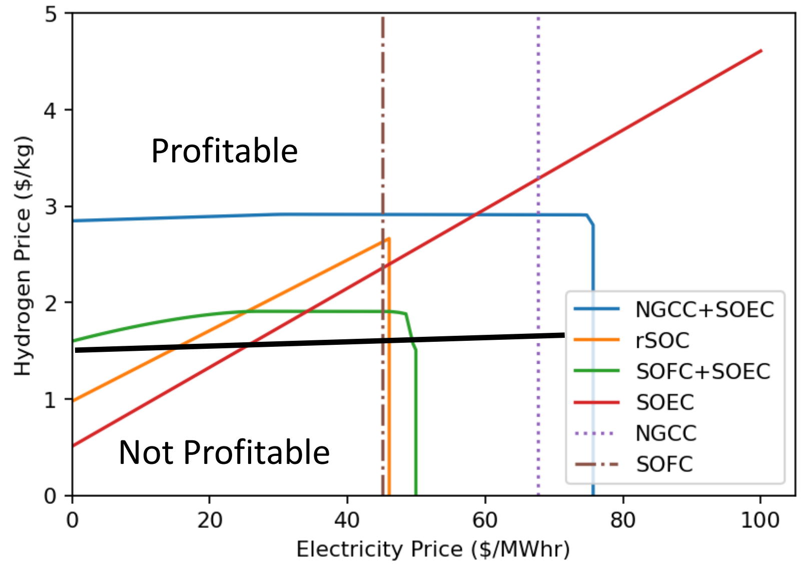
H2NEW
U.S. DEPARTMENT OF ENERGY

- Modeling and characterization of performance degradation of high temperature electrolyzers

NETL Work Plan Tasks

- **Task 2: Cell and Stack Degradation Evaluation and Modeling**
  - Performance and degradation model development
  - Microstructural analysis and analysis methods
  - Machine learning for materials studies, electrode design
  - Optical fiber-based gas/temperature sensor development
- **Task 3: Electrode Engineering**
  - Infiltration for degradation mitigation
  - R-SOC characterization
  - Protonic SOC materials characterization and development
  - Advanced electrode design and manufacturing
  - TEM analysis of cell degradation
- **Task 4: Strategic Systems Analysis and Engineering**
  - R-SOC system configuration studies
  - TEA of H_2-fueled SOFCs
- **Task 5: Cyber Physical Modeling**
  - 1D real-time SOEC stack model development
  - Controls design for dynamic operation of SOC stacks in HyPer Facility





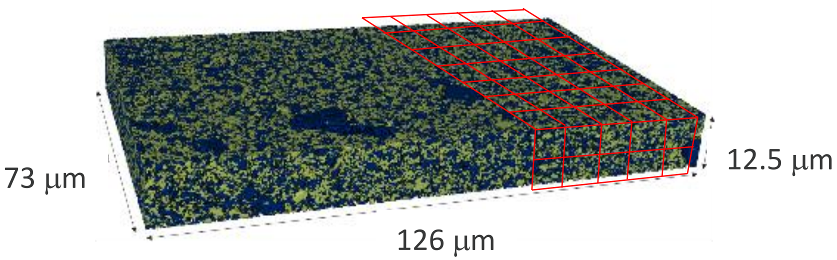
Breakeven curves for H_2/Power Production

Cell and Stack Degradation Modeling

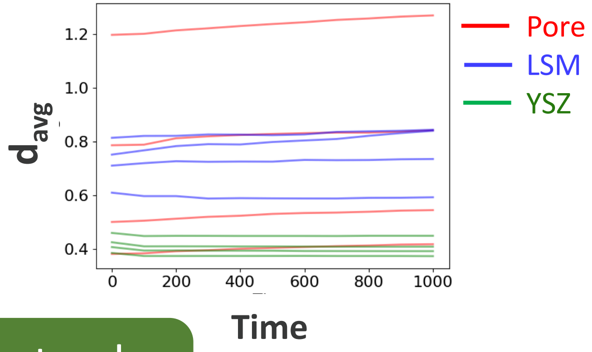
Simulation-driven design of advanced SOCs

Integrated Cell Degradation Model

NATIONAL ENERGY TECHNOLOGY LABORATORY



3D Electrode Microstructures

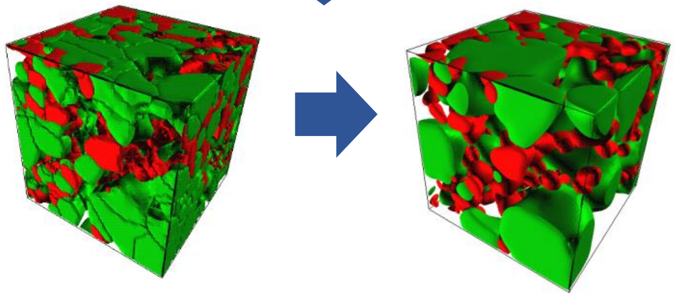


Microstructural Analysis

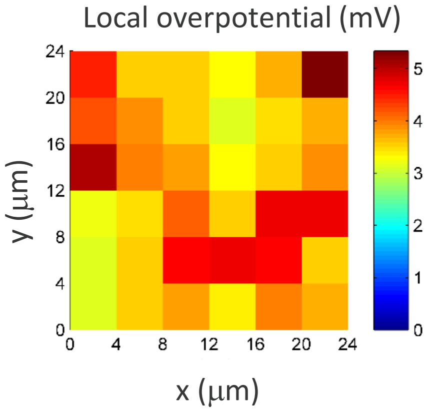
- Particle sizes
- Volume fraction
- Distributions
- Heterogeneity
- Tortuosity

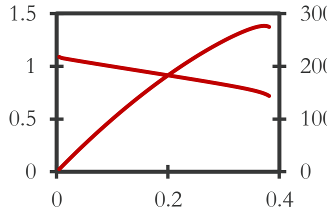
- Coarsening
- Secondary phases
- Poisoning
- Interdiffusion
- Cracking/delamination

Degradation models



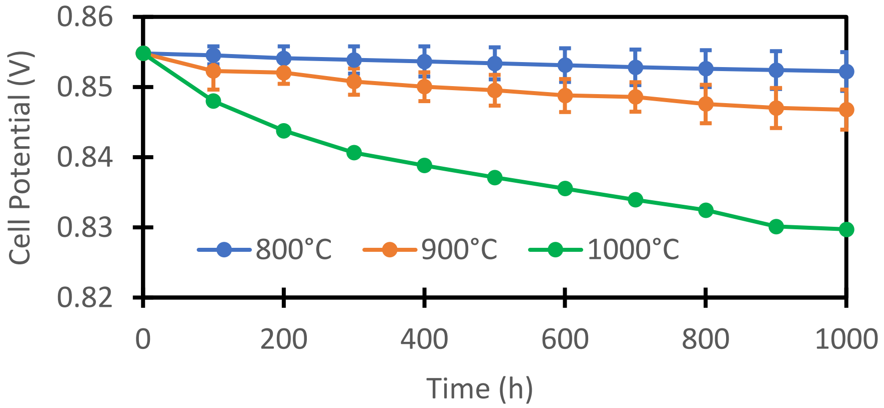
Multiphysics Performance Model





- Polarization curves
- Impedance spectra
- T, P Distributions
- Hotspots

Cell Lifetime Prediction



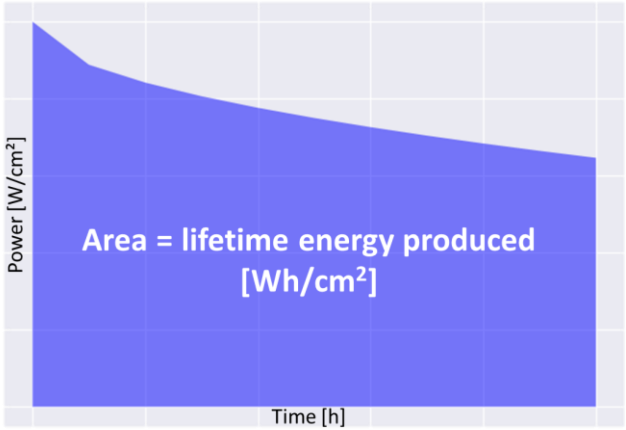
SOFC degradation from **coarsening** shown. Framework can be used in SOFC, SOEC, and r-SOC mode with multiple modes.

Analyzing SOC performance degradation

How to determine what's a good or bad electrode?

- Simulations run on database of 1000s of synthetic microstructure covering large matrix of microstructural parameter combinations (particle sizes, phase fractions, particle size distribution, phase fraction distribution)

Need a single figure-of-merit that captures **both** **initial performance** and **stability**



Lifetime energy production **chosen for SOFC**

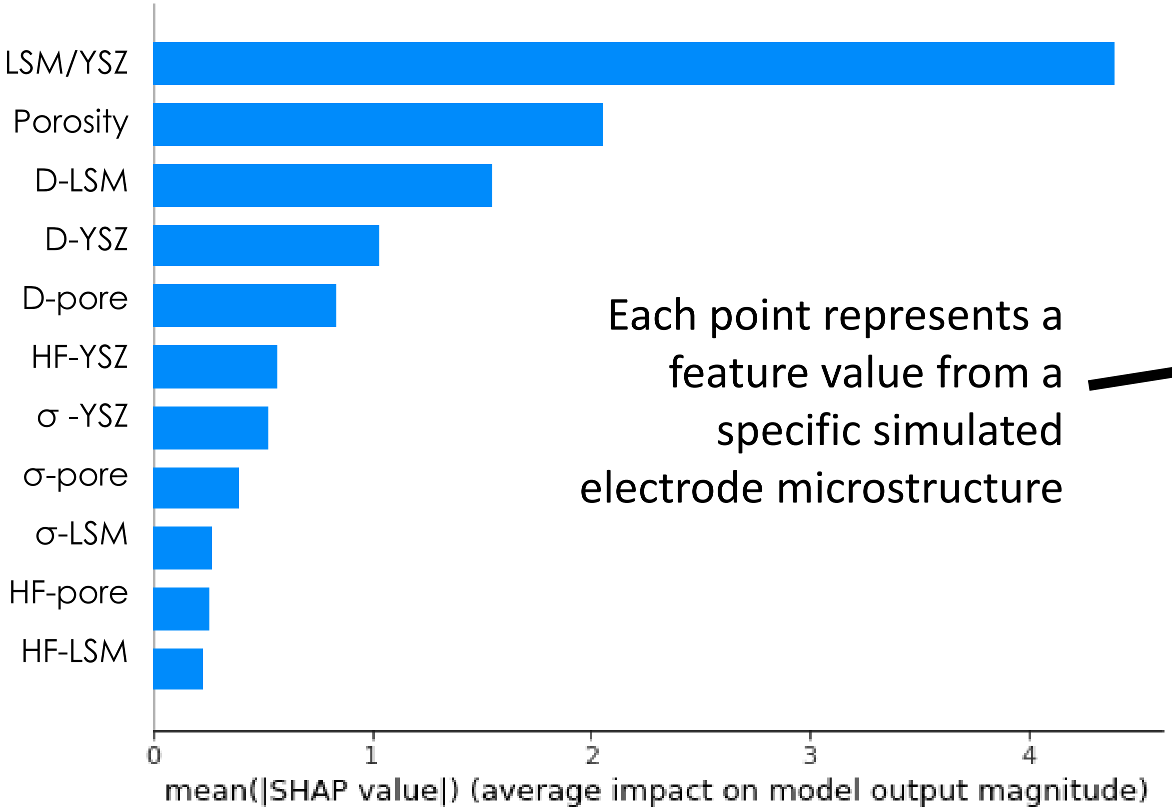
Lifetime H_2 production **chosen for SOEC.**

Presently: Operation at a given current density, up to a given time

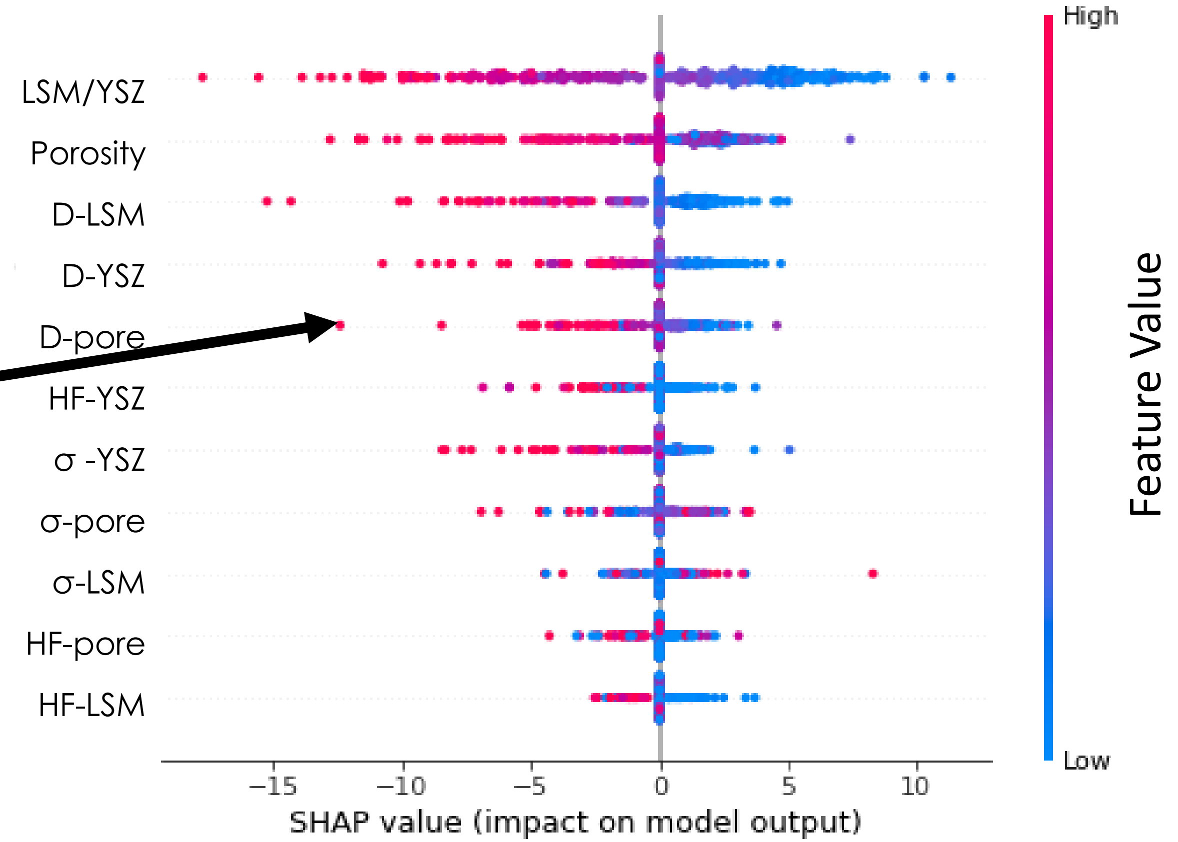
Example: Designing better SOFC cathodes

NATIONAL ENERGY TECHNOLOGY LABORATORY

Each air electrode feature's impact on lifetime energy produced at 400 mA/cm^2



Each point represents a feature value from a specific simulated electrode microstructure



Lower LSM/YSZ ratio, lower porosity, and smaller particle sizes increased lifetime production

Understanding Ni Redistribution in SOCs

Problem: Literature reports various directions of Ni redistribution depending on the operating mode and temperature. No current chemical/physical model can completely explain the variety of the results.

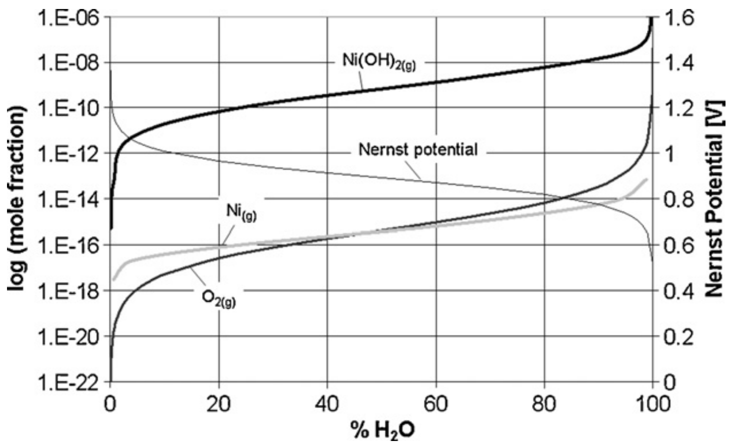
	Mode	Temperature	Current Density	Gas Composition	Operating Time (Sim. time)	Redistribution
Menzler	FC - Stack	700 °C	0.5 A/cm²	$21\%H_2O$-$79\%H_2$	100 kh (100 kh)	Toward Electrolyte
Barfod	FC - Button	850 °C	0.5 A/cm²	$50\%H_2O$-$50\%H_2$	1 kh (10 kh)	Away from Electrolyte
Hauch	EL - Button	950 °C	2.0 A/cm²	$90\%H_2O$-$10\%H_2$	68 h (1 kh)	Toward Electrolyte
Trini	EL - Stack	750 °C	0.7 A/cm²	$45\%H_2O$-$55\%H_2$	8.7 kh (15 kh)	Away from Electrolyte

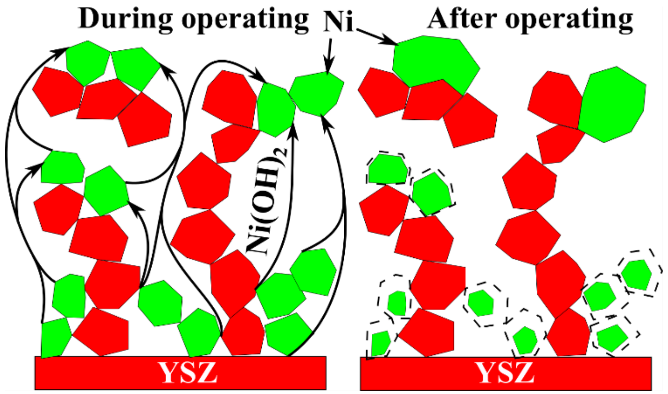
Menzler et al., J. Power Sources, **478** (2020) 228770; Barfod et al., Proc. Electrochem. Soc. PV **2003-7** (2003) 1158;
Hauch et al., J. Electrochem. Soc., **155** (2008) B1194-B1193; Trini et al., J. Electochem. Soc., **166** (2019) F158-F167;

Possible Mechanisms of Ni Redistribution

- Ni(OH)$_x$ formation and diffusion
- Ni-YSZ wettability change
- NiO formation
- O vacancy accumulation

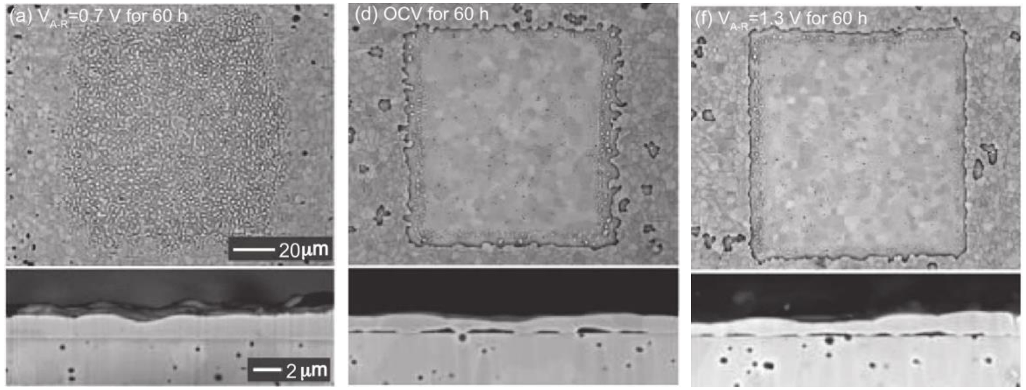
Ni(OH)$_2$ formation and diffusion

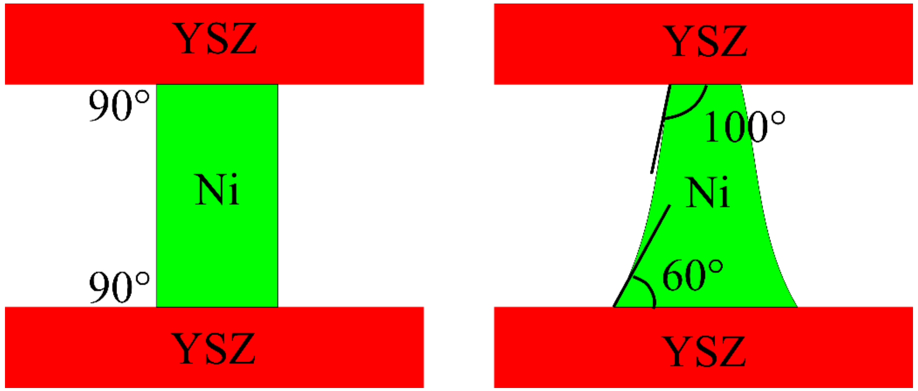




Ni-YSZ wettability change

0.7 V (η~0.2V) OCV 1.3 V





Holzer et al., *J. Power Sources*, **196** (2011) 1279-1294; Jiao et al., *J Power Sources*, **396** (2018) 119-123.
Lei et al., J. Power Sources, **482** (2021) 228971; Lei et al., J. Power Sources, **545** (2022) 231924.

U.S. DEPARTMENT OF ENERGY

Current Ni degradation model includes coarsening, Ni(OH)x diffusion, and Ni-YSZ contact angle change

Initial microstructures

Target:
A set of microstructures that vary one selected property, but are otherwise similar
Varied properties:
Ni-YSZ ratio, Porosity, pore size and pore tortuosity.

Synthetic microstructures are generated by DREAM.3D software.
Reconstructed microstructures are subvolumes selected from a PFIB-SEM 3D reconstruction of a commercial electrode produced by MSRI.

Goeber & Jackson, Integr. Mater, Manuf. Inov. **3** (2014) 56-72
R. Mahbub, *et al.*, J. Electrochem. Soc., **167** (2020) 054506

Porosity

Ni	YSZ	Pore	Pore size (µm)	Pore Tort. factor	TPB (μm^{-2})
42.4%	42.5%	15.1%	0.50	1.98	4.58
39.9%	40.0%	20.1%	0.48	2.00	5.69
37.7%	37.3%	25.0%	0.50	1.92	6.10
35.0%	35.1%	29.9%	0.50	1.44	6.41

Tortuosity (Reconstructed)

Ni	YSZ	Pore	Pore size (µm)	Pore Tort. factor	TPB (μm^{-2})
38.5%	42.6%	18.9%	0.51	1.35	7.78
39.4%	43.2%	17.4%	0.52	2.08	6.99
39.3%	43.0%	17.7%	0.50	2.99	7.51
38.8%	43.8%	17.4%	0.50	4.04	7.41

Ni-YSZ Ratio Impact on Redistribution

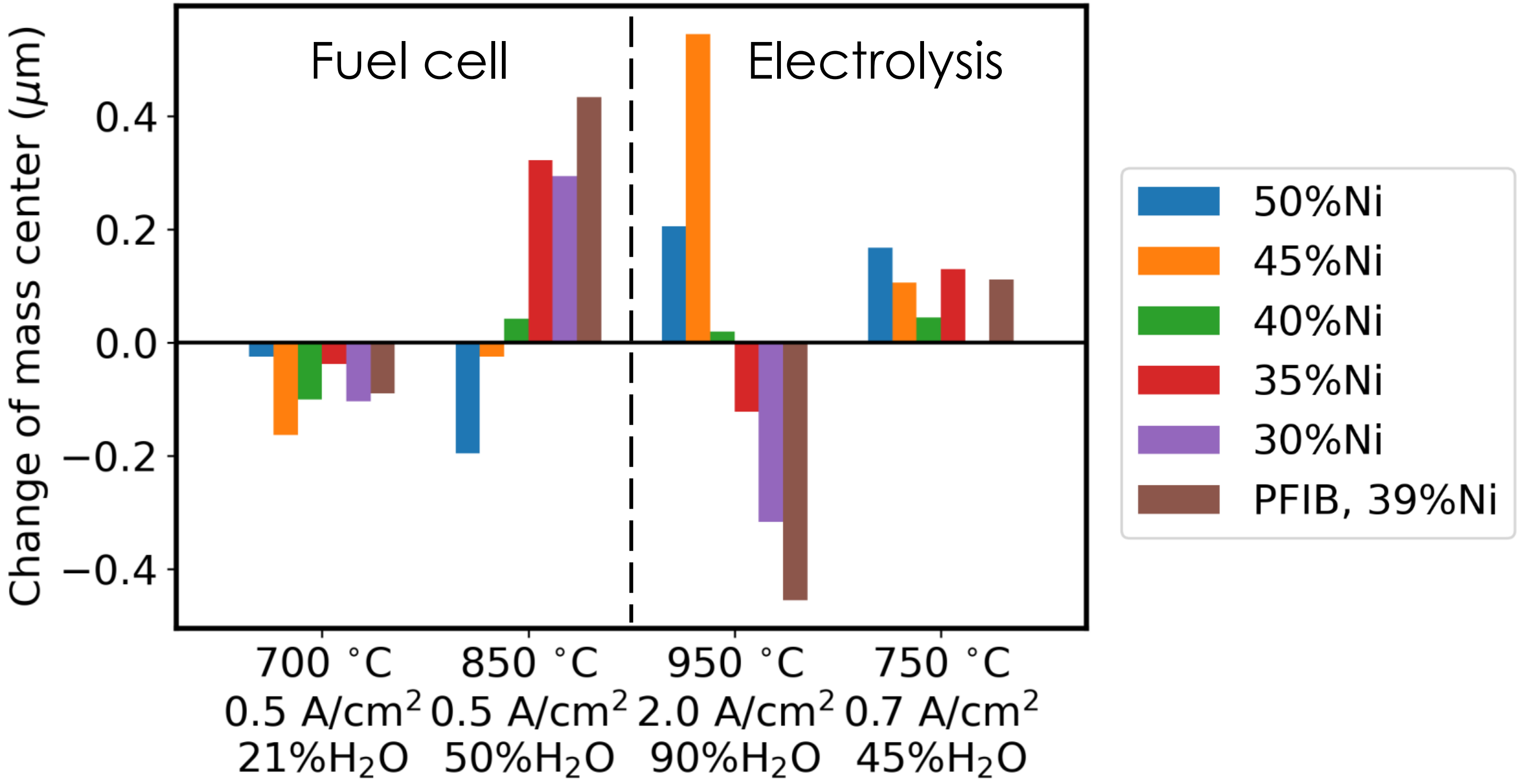
Not just **operating conditions**, but also **microstructural features** can impact the direction of Ni redistribution

Synthetic

Ni	YSZ	Pore
49.6%	30.0%	20.3%
44.5%	35.3%	20.2%
39.9%	40.0%	20.1%
34.5%	45.8%	19.7%
30.0%	50.1%	19.9%

PFIB Reconstructed

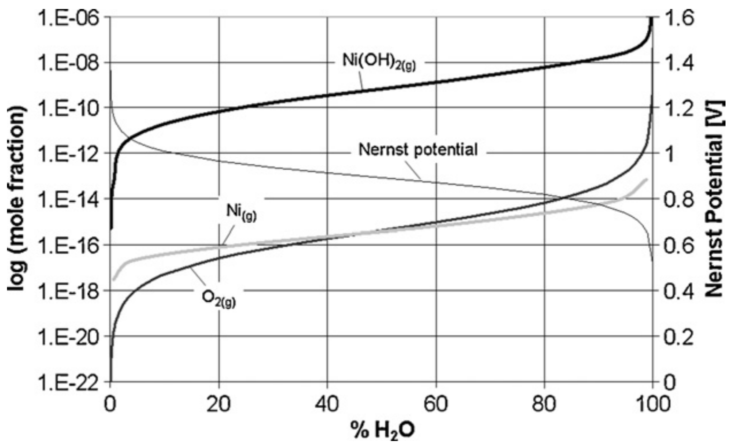
Ni	YSZ	Pore
39.4%	43.2%	17.4%

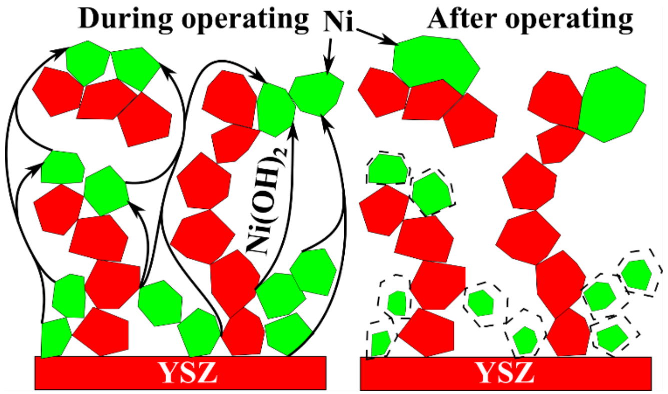


Possible Mechanisms of Ni Redistribution

- $Ni(OH)_x$ formation and diffusion
- Ni-YSZ wettability change
- NiO formation
- O vacancy accumulation

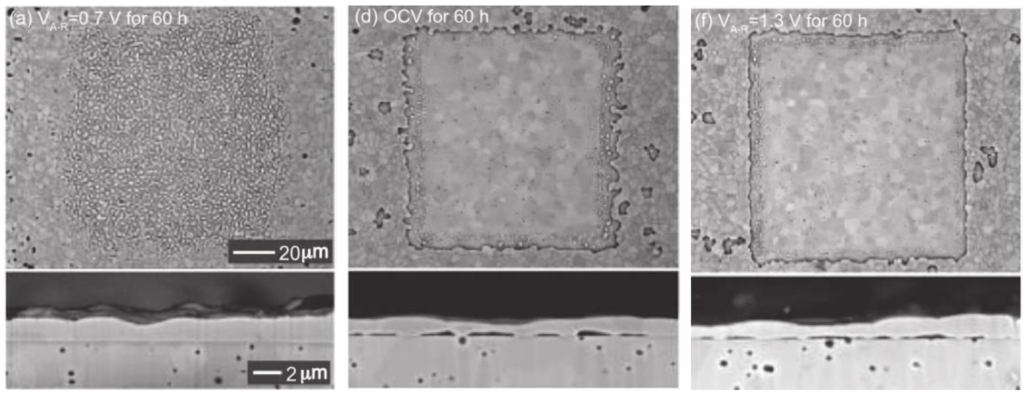
$Ni(OH)_2$ formation and diffusion

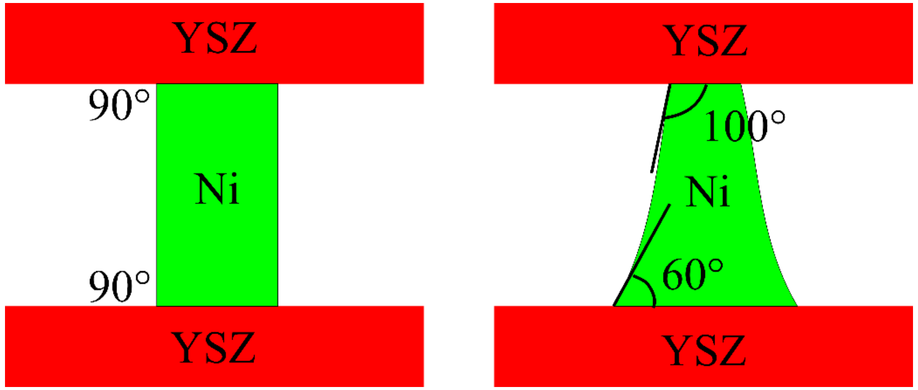




Ni-YSZ wettability change

0.7 V (η~0.2V) OCV 1.3 V





Holzer et al., *J. Power Sources*, **196** (2011) 1279-1294; Jiao et al., *J Power Sources*, **396** (2018) 119-123.
Lei et al., J. Power Sources, **482** (2021) 228971; Lei et al., J. Power Sources, **545** (2022) 231924.

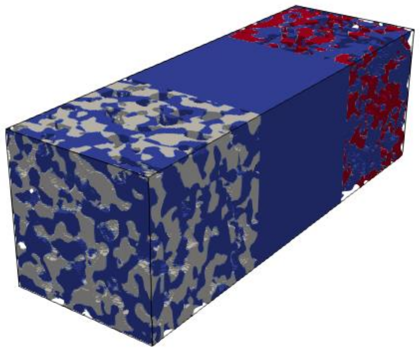
U.S. DEPARTMENT OF ENERGY

Current Ni degradation model includes coarsening, Ni(OH)x diffusion, and Ni-YSZ contact angle change

P(O_2) distribution and NiO formation

- **Multiphysics model used to simulate P(O_2) distribution throughout cell under SOFC, SOEC operating conditions.**
  - Model includes limited e^- transport in YSZ per Virkar, **Int. J. Hydrog. Energy** 35(18) 9527, 2010.

	Mode	Temperature	Cell Voltage	Gas composition
Cell-1	Fuel cell	750 °C	0.77 V	3% H_2O, 97% H_2
Cell-2	Fuel cell	750 °C	0.60 V	3% H_2O, 24% H_2, 73% N_2
Cell-3	Electrolysis	850 °C	1.32 V	50% H_2O, 50% H_2
Cell-4	Electrolysis	850 °C	1.50 V	50% H_2O, 50% H_2

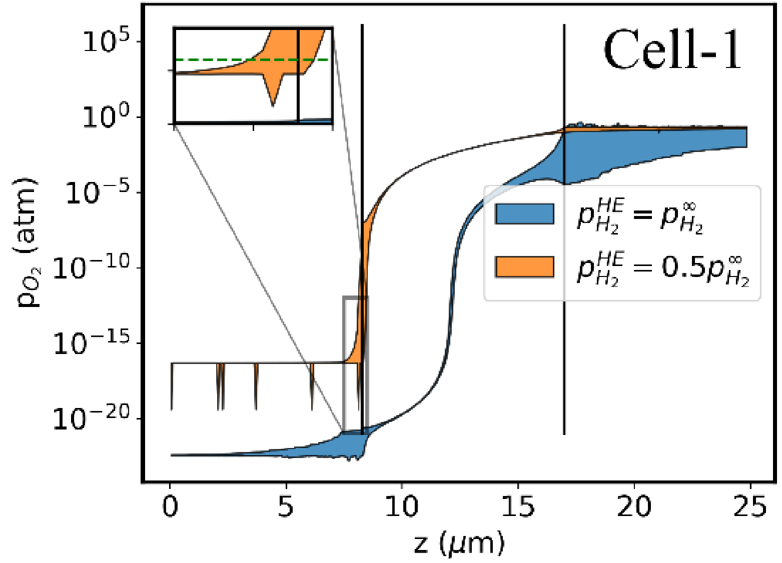


T.L. Cheng, et al., **Journal of Power Sources** 569, 232991, 2023
Y. Lei, et al., submitted to **ECS Transactions** Vol. 111 for SOFC XVIII, 2023.

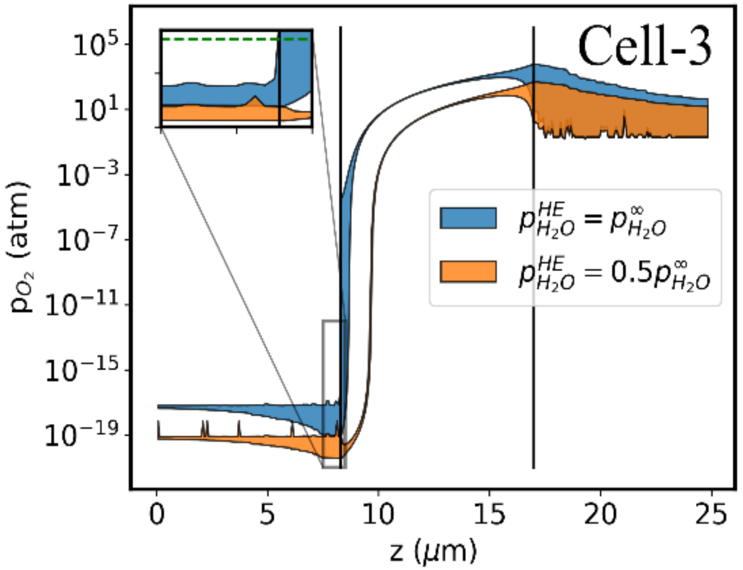
18

$P(O_2)$ distribution and NiO formation

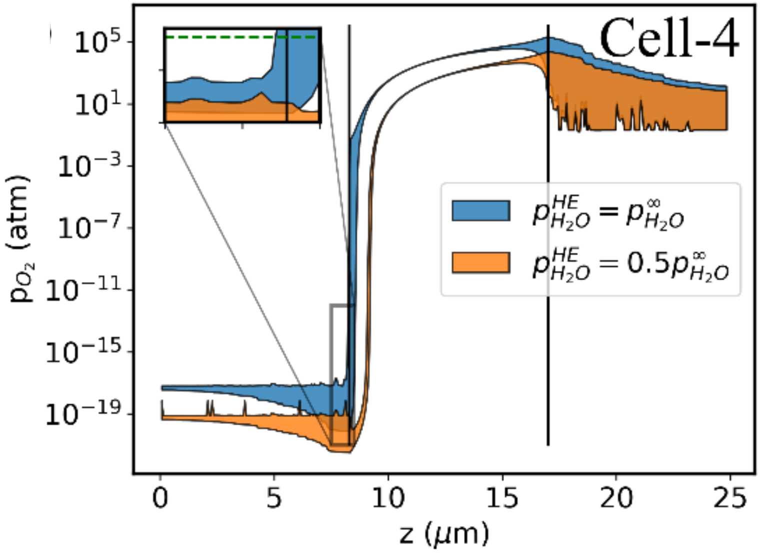
- Even though nominal electrode $P(O_2)$ is too low, it can increase above Ni oxidation threshold near the electrolyte



SOFC, 750°C, 0.77 V



SOEC, 850°C, 1.32 V



SOEC, 850°C, 1.50 V

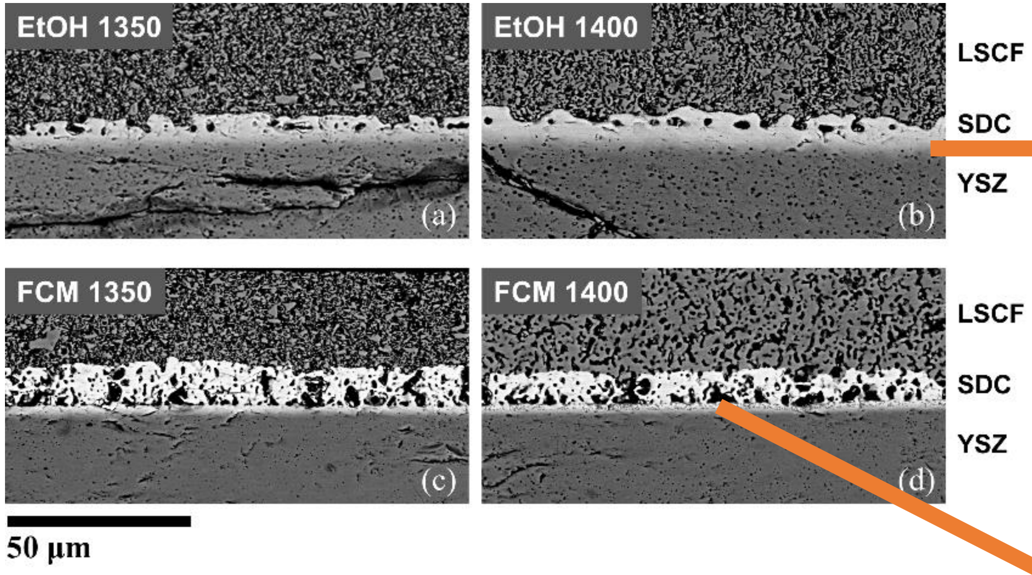
Bands represent spread in $P(_{O2})$ across 2D slice. **Blue bands** are low utilization. **Orange bands** are high utilization. **Green dashed line** represents $P(O_2)$ at which NiO forms.

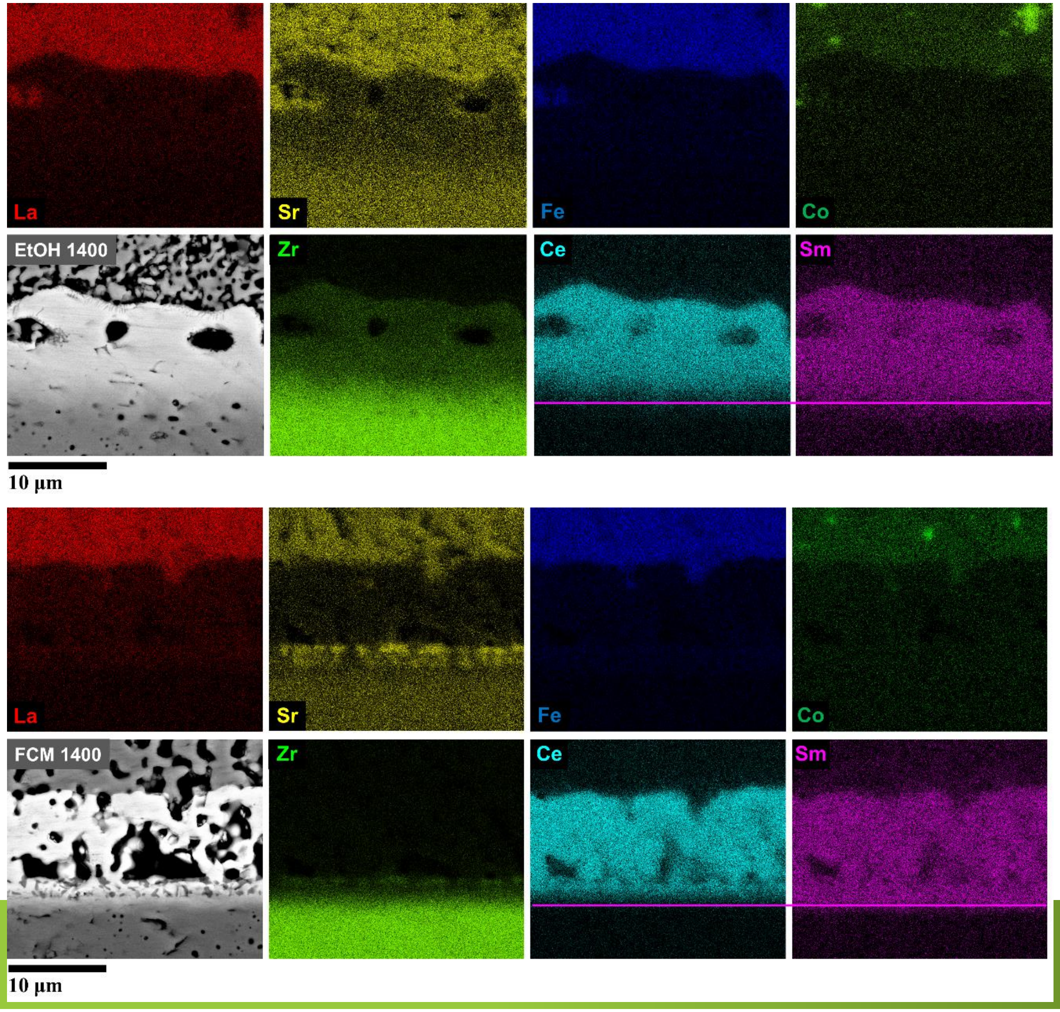
T.L. Cheng, et al., **Journal of Power Sources** 569, 232991, 2023
Y. Lei, et al., submitted to **ECS Transactions** Vol. 111 for SOFC XVIII, 2023.

Cation diffusion through barrier layer

Cation transport during sintering and operation

- Density of barrier layer varied with choice of ink vehicle (Commercial vs. Homemade) and sintering temperature (1350°C vs. 1400°C)





Denser reduces Sr transport, but makes for easier Zr transport

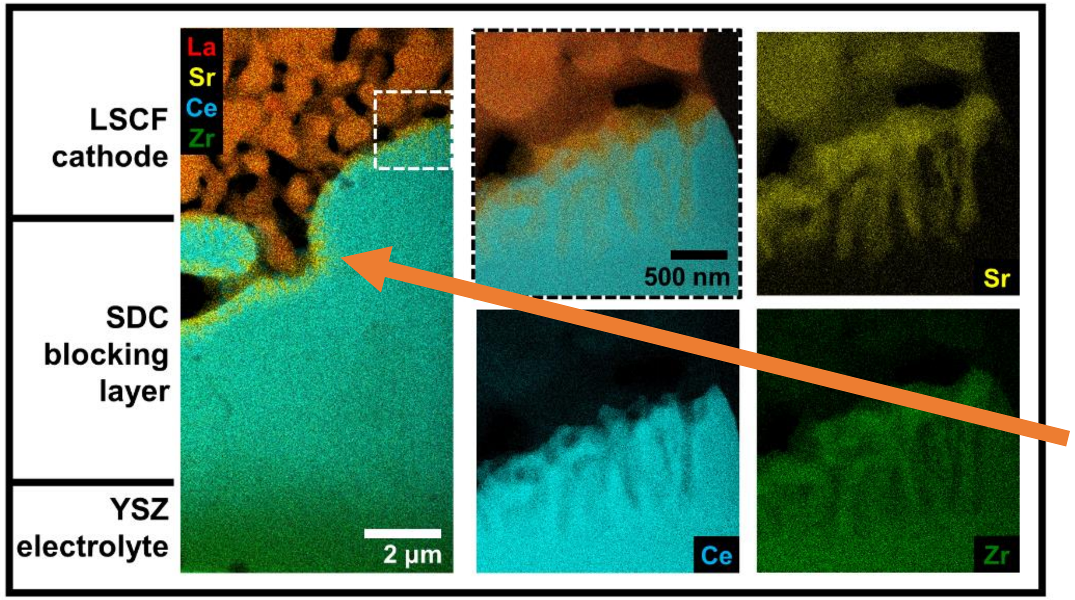
Cation diffusion through barrier layer

Cation transport during sintering and operation

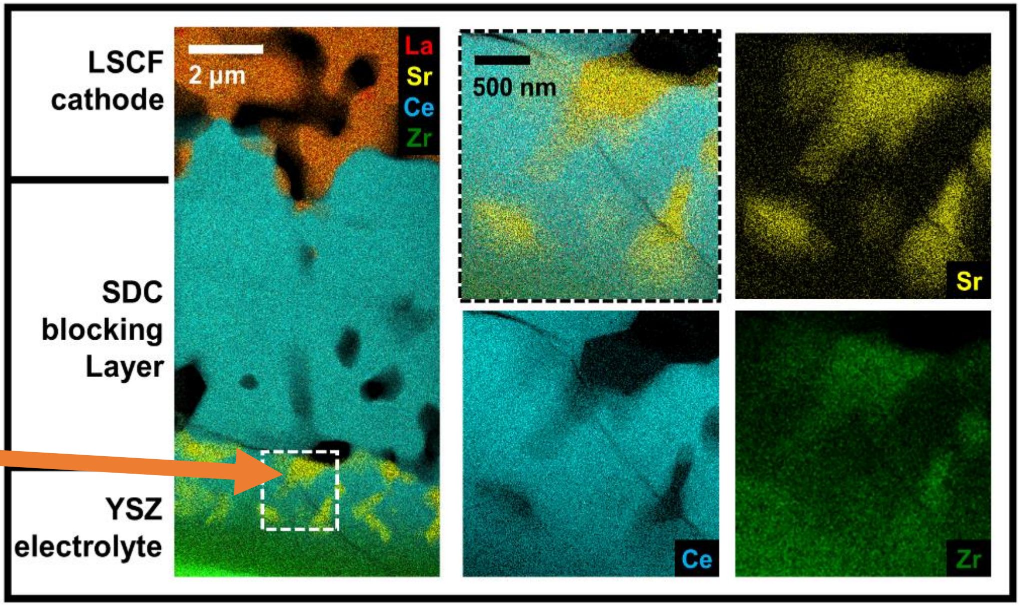
- $SrZrO_3$ location impacted by quality of barrier layer

See Poster: Yoosuf Picard

EtOH 1400



FCM 1400



$SrZrO_3$

Ongoing: Determining the impact of cathodic/anodic overpotential on cation profiles

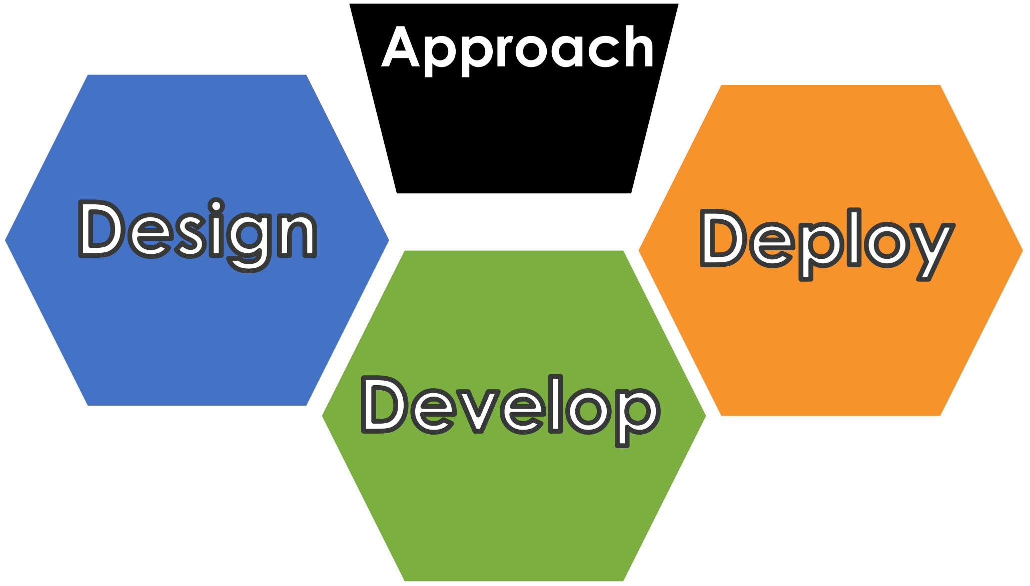
Electrode Design and Engineering

Building better performing, longer lasting electrodes

SOC Electrode Design and Engineering

Objectives

- Enhancement of performance and longevity
- Materials engineering
- Microstructure engineering



Benefits

- Cell/stack cost reduction
- Cell overpotential reduction
- Increased thermo-chemical/thermo-mechanical stability
- Reduced cost-of-electricity and/or cost of hydrogen

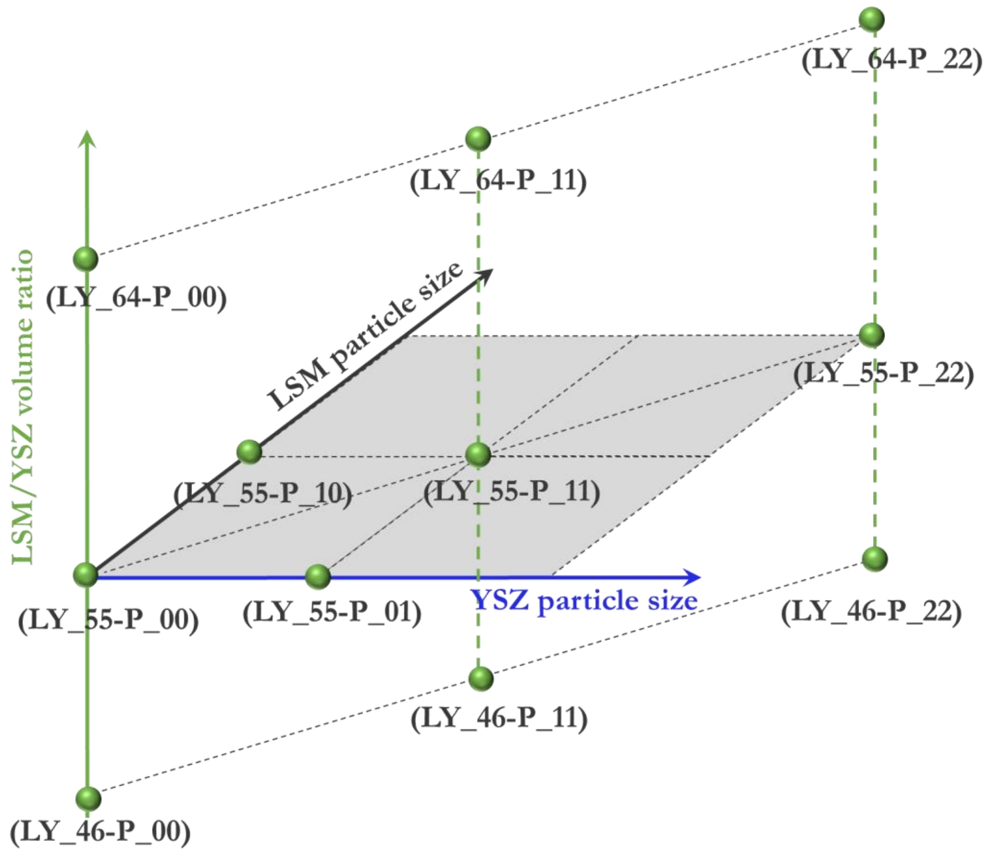
DESIGN new materials and structures

DEVELOP tailored electrode designs

DEPLOY in commercial SOC systems

Simulating infiltrated electrodes: Full cells

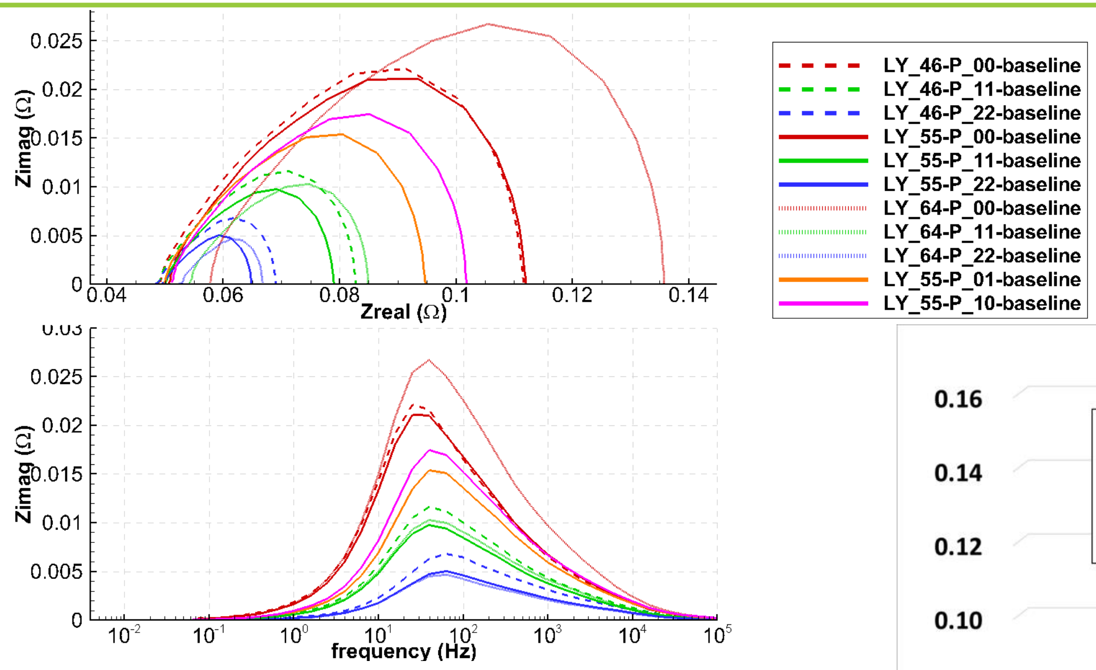
- Using in-house multiphysics code to optimize cathode performance by controlling infiltration and backbone structure
  - Optimal catalytic properties for a given backbone composition/structure
  - Optimal backbone composition/structure for given catalytic properties
  - Optimal lifetime performance based on backbone/infiltrated particle degradation

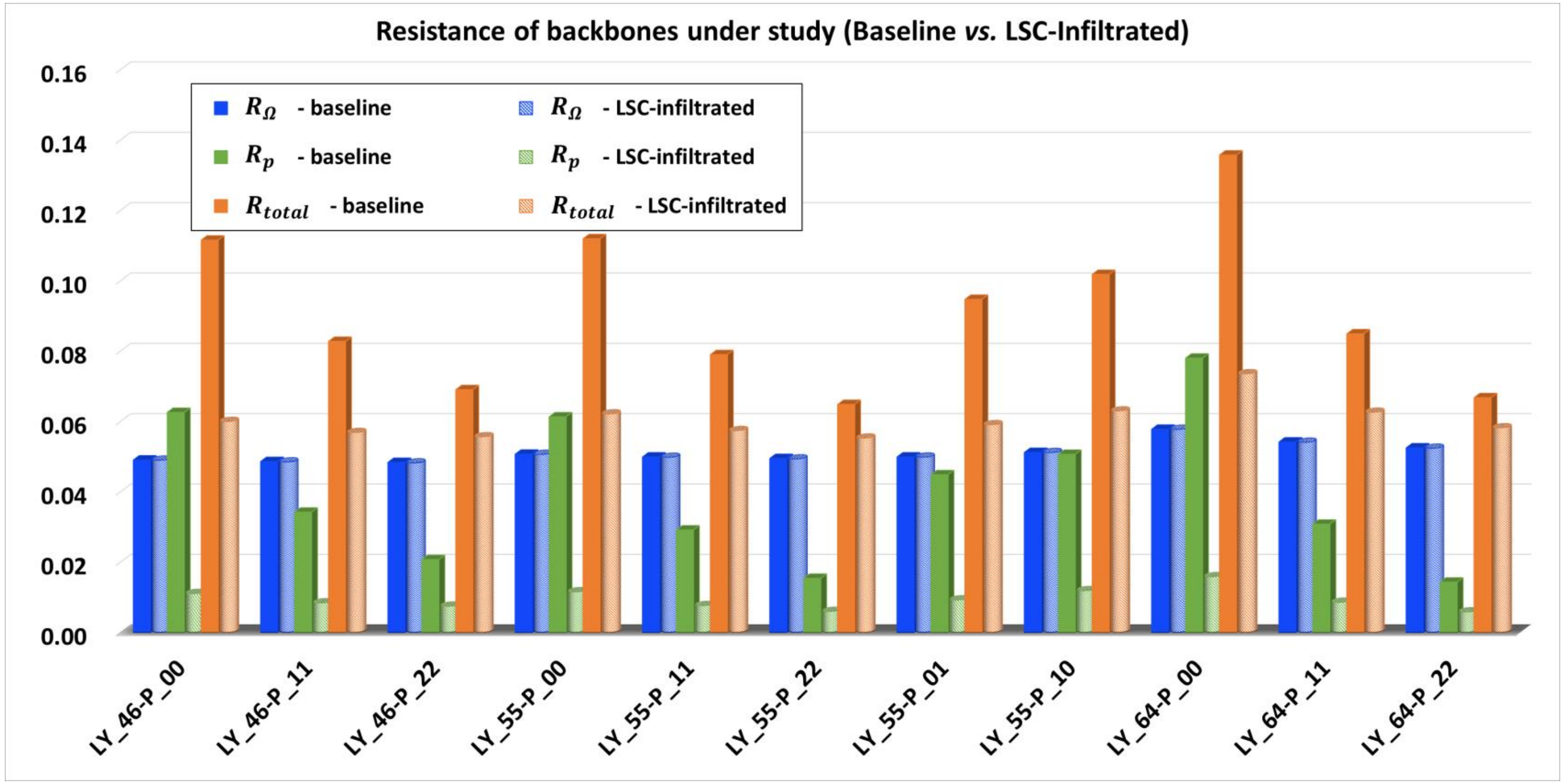


Volume fractions:	Particle size:
40:60	-1,0,1,2,3,4
50:50	0 = Baseline
60:40	-1 = Coarser
	1-4 = Finer

Notation: Backbone_LSM:YSZ-LSM/YSZ Particle size

Simulating infiltration onto LSM/YSZ





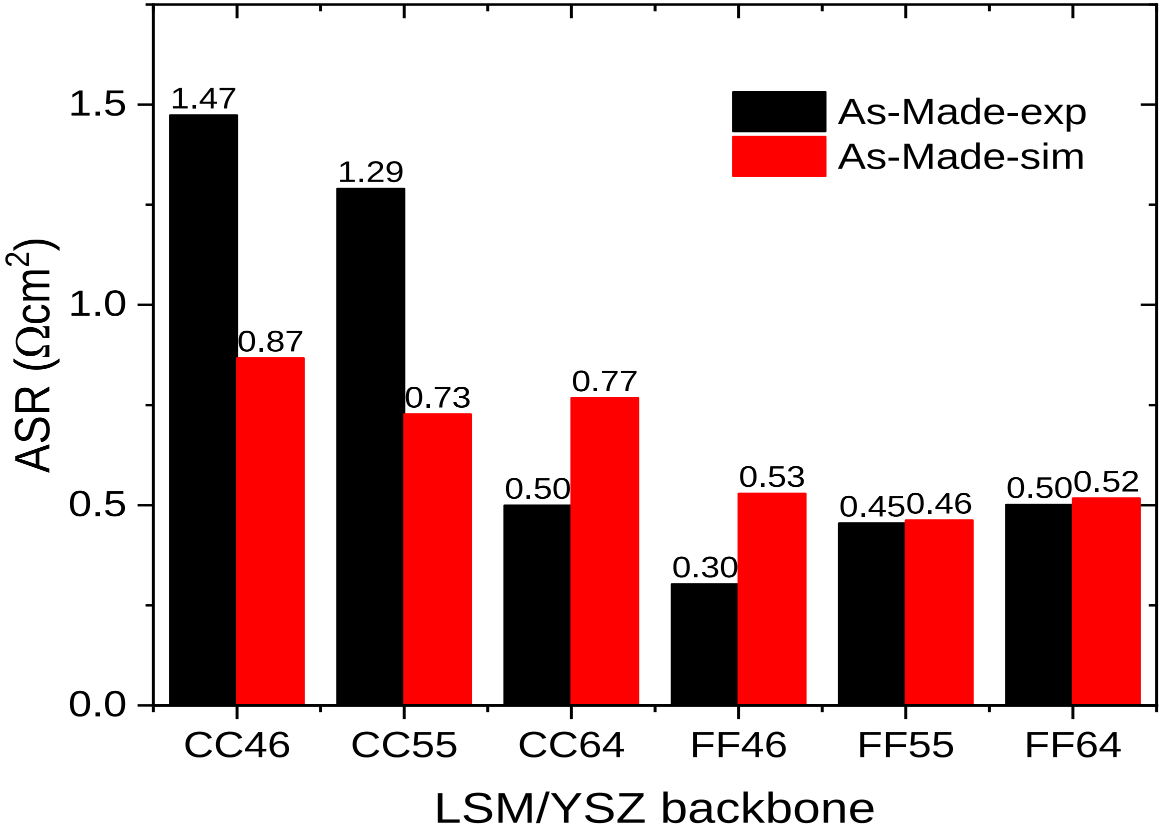
Finer particle sizes increase performance, but infiltration can make coarser backbones acceptable.

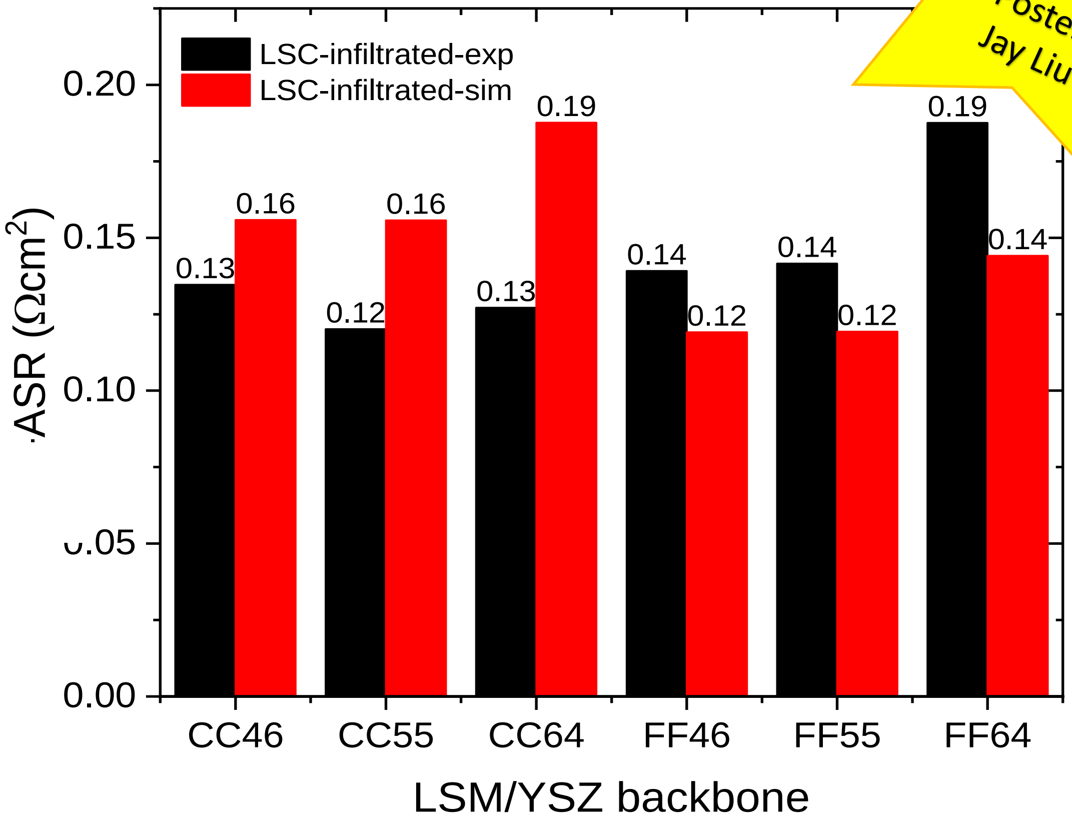
Notation: Backbone_LSM:YSZ-LSM/YSZ Particle size

Experiments vs. Simulations

- There is qualitative agreement; however, the microstructural parameters for each of the samples are being measured, post-sintering, to adjust simulations.

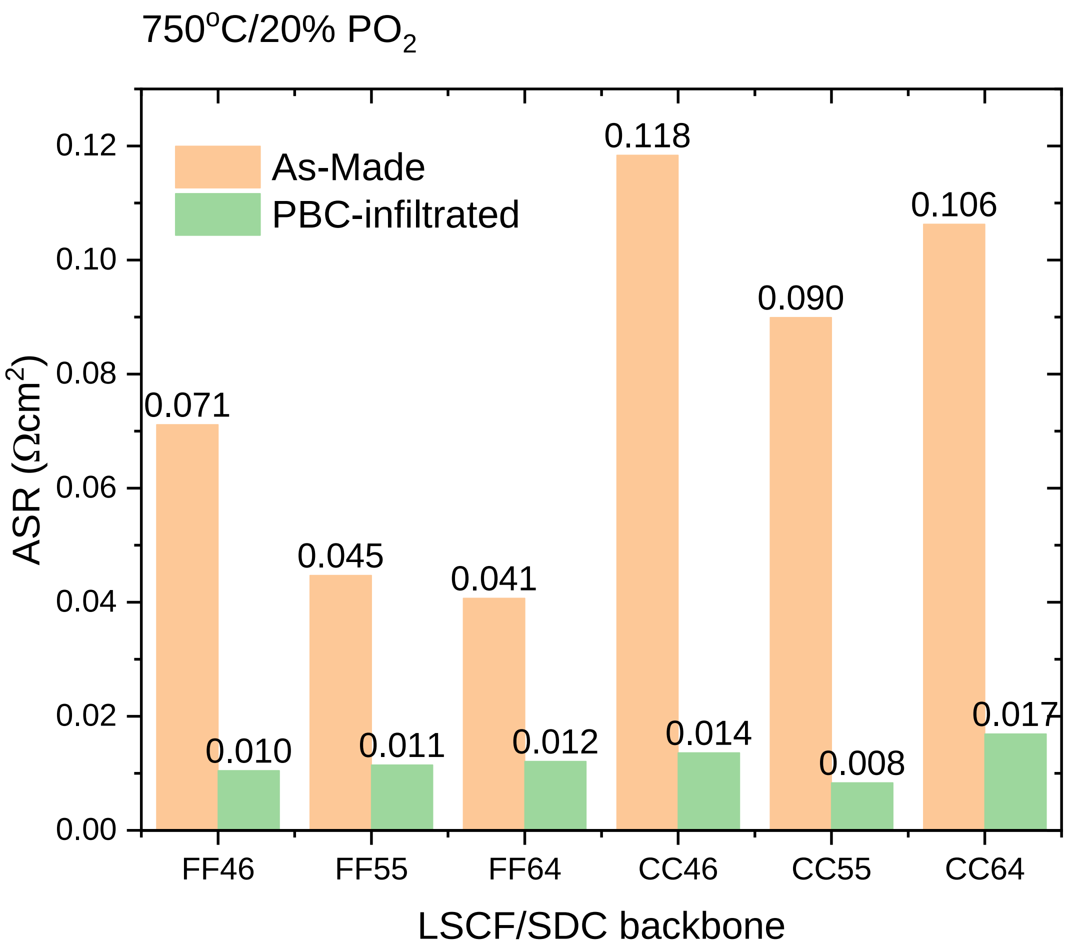
See Poster: Jay Liu





Ongoing: Expanding to LSCF

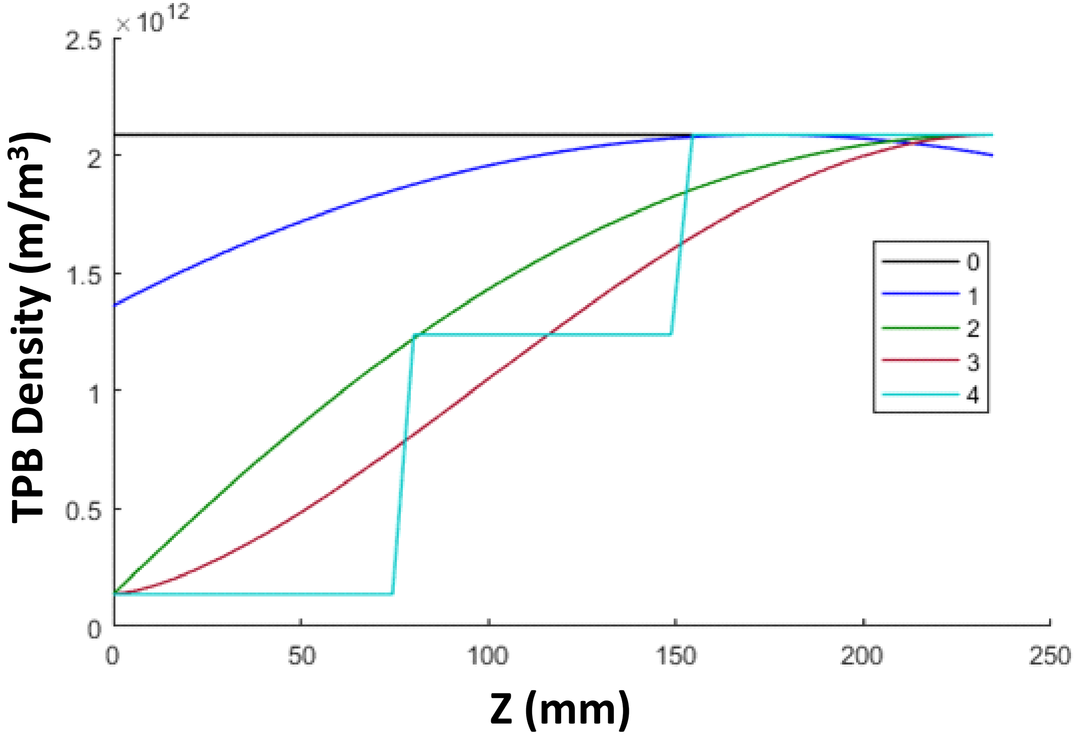
- LSCF/SDC backbones fabricated, infiltrated, and tested
- PBC infiltrated as a more active material
- LSCF reaction model undergoing calibration based on new 3D reconstruction data

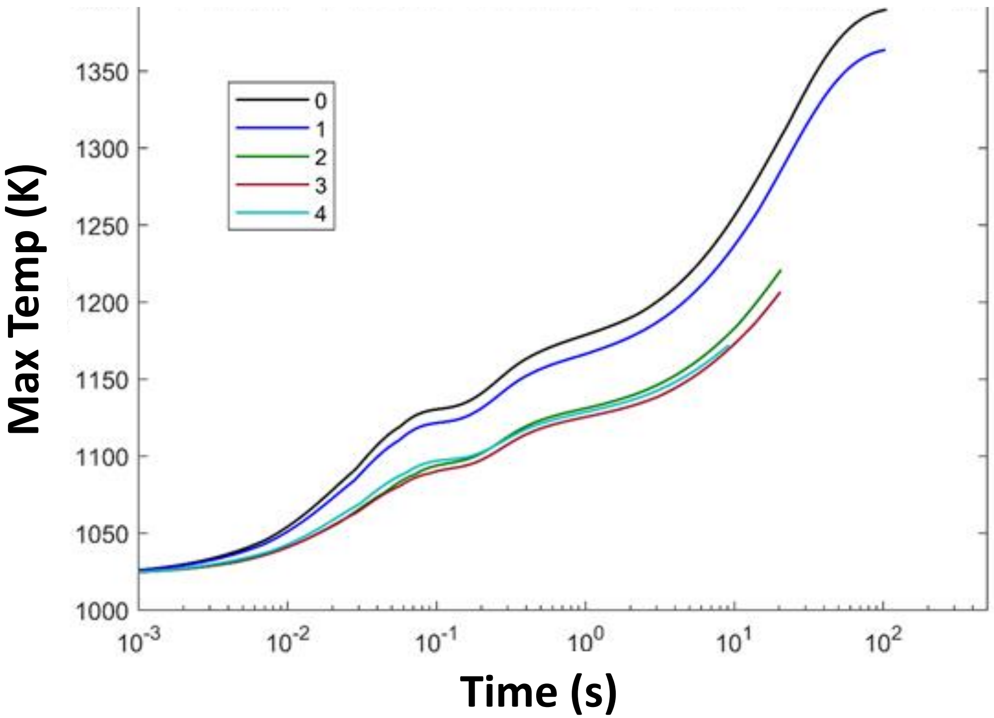


Motivation: Reducing gradients in planar cells

Mitigating long-term degradation through advanced electrode design

- TPB density varied by adjusting Ni:YSZ ratio from inlet to outlet
- Temperature gradient can be reduced by varying microstructure across planar cell



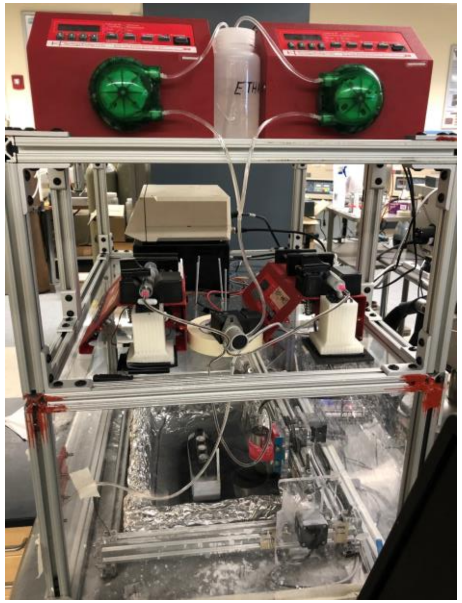


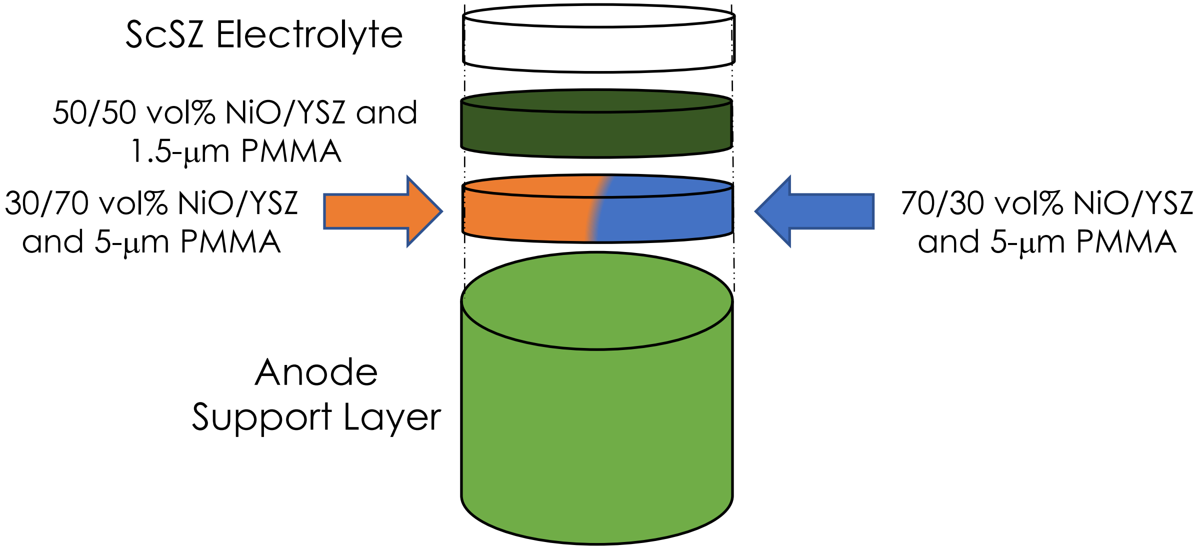
Additive manufacturing of SOC electrodes

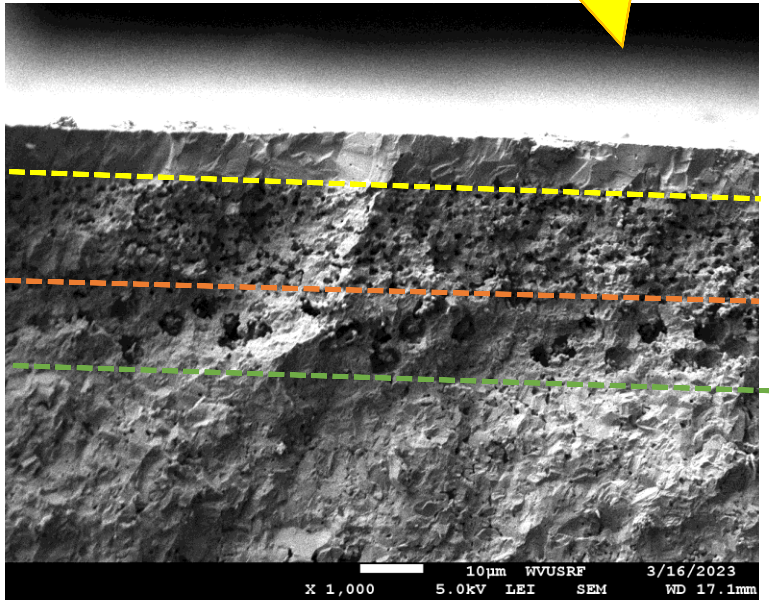
Creating 3D gradients in composition, microstructure

- Automated aerosol spray deposition system built at WVU to fabricate SOC electrodes and electrolytes
  - Feedstocks provide precursors with varying compositions, particle sizes
  - In situ mixing system for wider range of possible compositions
- System coupled with simulations to optimize stability in planar cells by reducing T, V gradients.
  - Can also be paired with gradients in infiltrated catalysts using NETL's spray infiltration system

See Poster: Ed Sabolsky



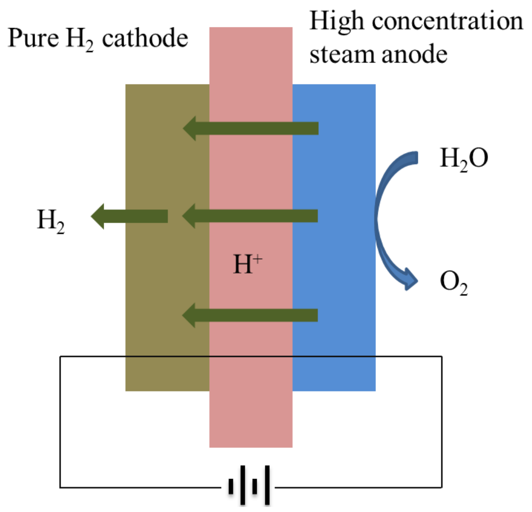




Proton-conducting SOCs

Expanding the degradation modeling framework's material sets

- **Proton-conducting SOCs can help lower operating temperatures, increase operational stability, and don't have a diluted H_2 stream**
- **Materials needs:**
  - More active electrodes
  - Electrolytes with higher σ, higher H^+ transference number
  - Less expensive thermal processing
- **SOEC, SOFC performance model code options created for proton-conducting systems**

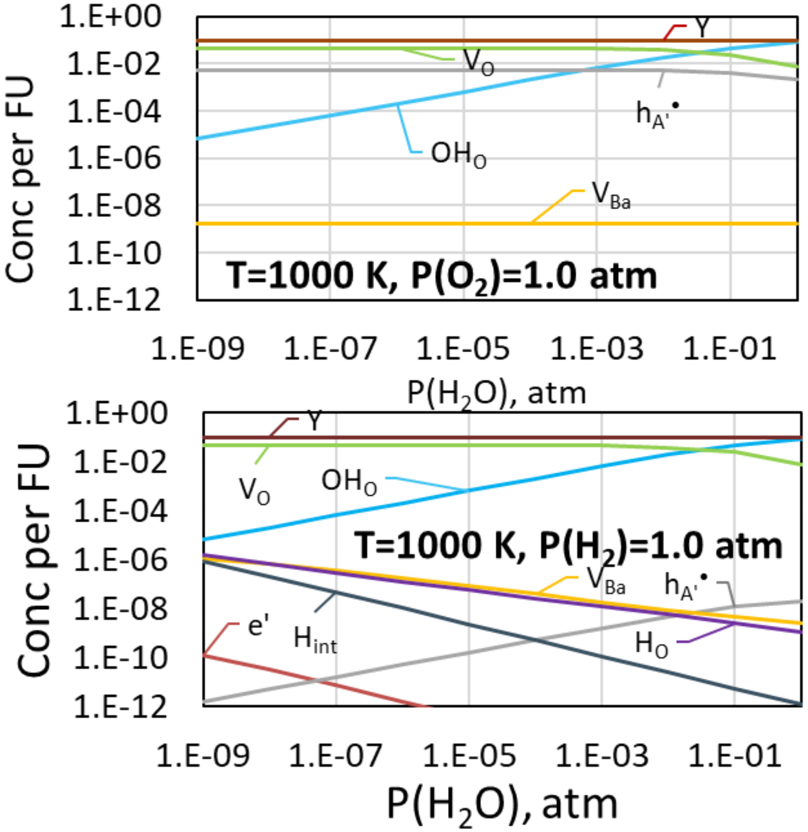


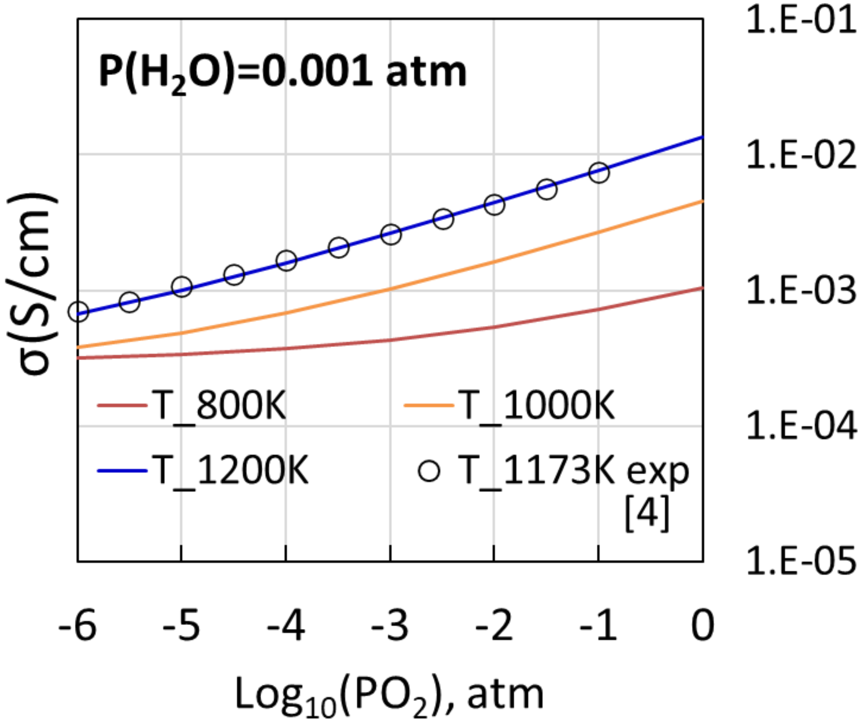
Proton-conducting SOEC

Proton-conducting materials studies

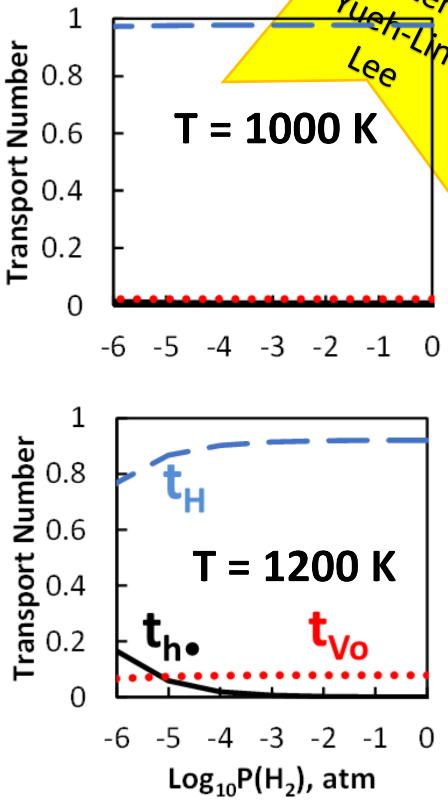
Electrolyte materials

- Defect Thermodynamics and Transport Properties of Proton Conducting Oxide Electrolyte $BaZr_{1-x}Y_xO_{3-\delta}$ (x≤0.1) based on first principles





See Poster: Yueh-Lin Lee

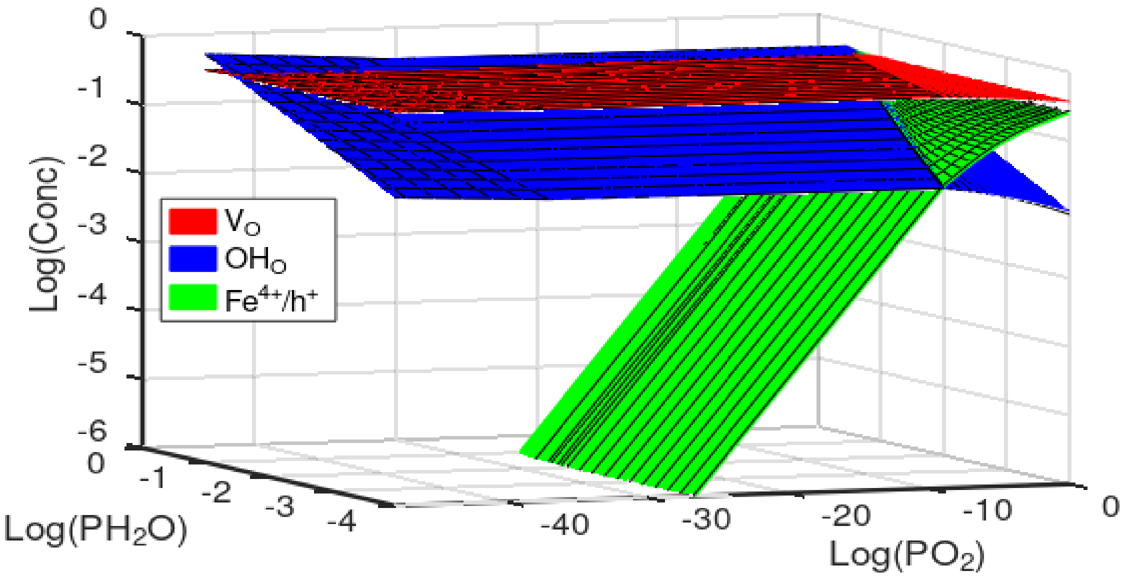


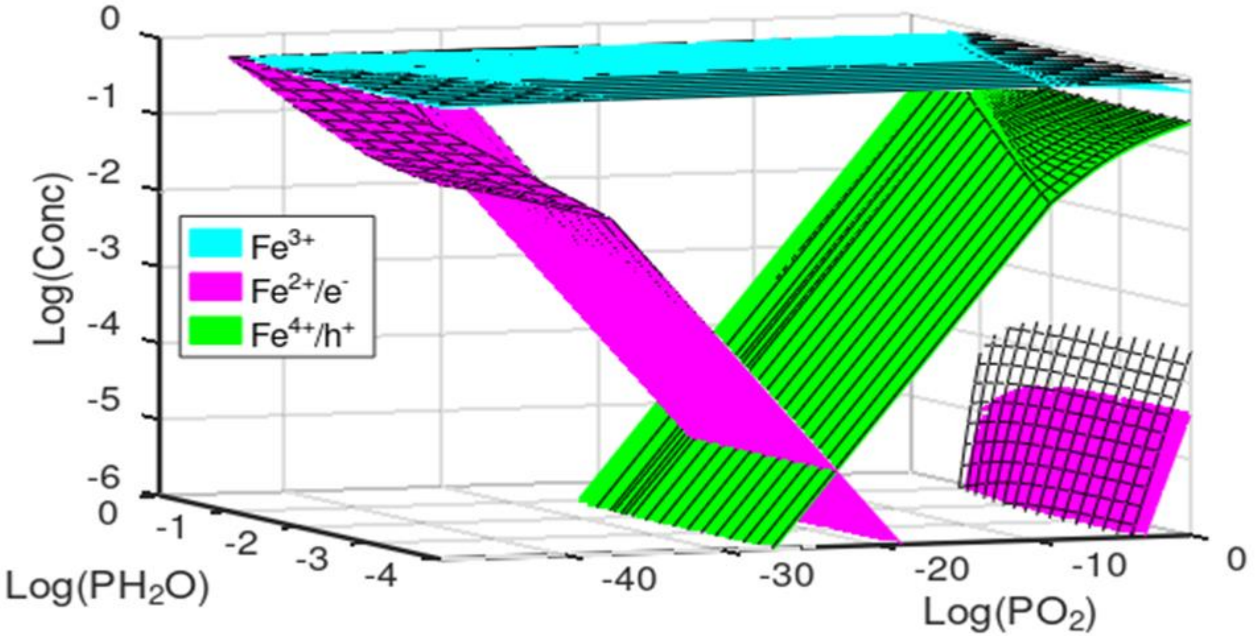
Y.L. Lee, et al., **JOM** 74, 4506-4526, 2022.

Proton-conducting materials studies

Electrode materials

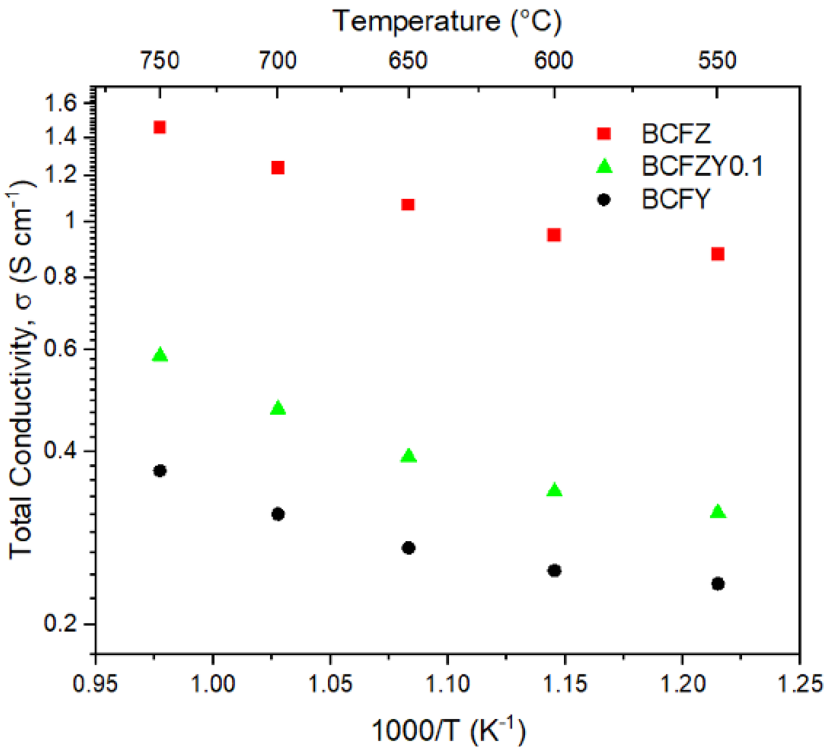
- Defect thermodynamic modeling of $BaFe_{0.9}Y_{0.1}O_{3-\delta}$
- A defect model solver was developed to allow incorporation of nonlinear δ-dependent defect reaction energies and entropies for calculating defect concentration of the triple-conducting perovskites $(La,Ba)Fe_{1-x}MxO_{3-\delta}$ **(Public release of model script *pending*)**

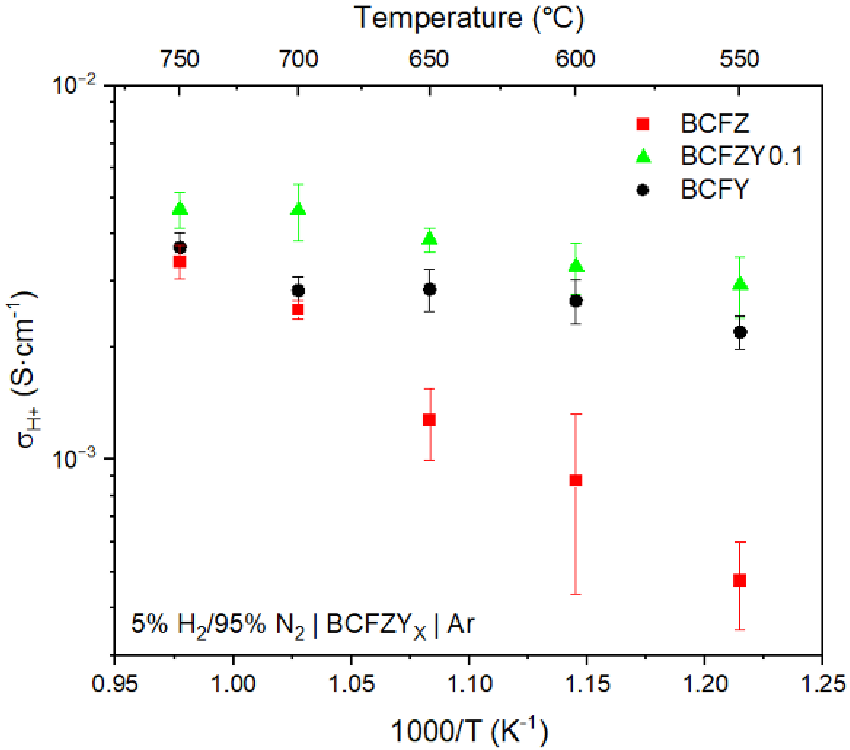




Triple-conducting oxide materials studies

- Computational study of H+ transport in Ba(Co, Fe, Zr, Y)$O_{3-\delta}$ based on [$V_O^{\cdot\cdot}$], cation arrangement, and amount of Y substitution
- Experimental measurement of conductivities, H_2/O_2 permeation, and transference numbers of BCFZ/Y compositions





J.H. Duffy, et al., Accepted by **Journal of Materials Chemistry A** 2023.

Strategic Systems Analysis and Engineering

Defining SOEC, SOFC, and R-SOC operation in the modern grid

See the 9:30 AM presentation by Gregory Hackett, **“Status Update of NETL Techno-Economic Analysis of Solid Oxide Cells”**

See the 4:00 PM presentation by Anthony Burgard/Steve Zitney, **“Multi-Scale Modeling and Optimization Using IDAES”**

Wrap-Up

Key Points

- Integrated degradation modeling framework expanded with more materials, more degradation modes, more data analysis
- Access to degradation framework available through collaboration
  - Help interpret impedance data
  - Move beyond correlation
  - Get recommendations on how much your cell can be improved
- Additive manufacturing and infiltration capabilities developed and available to create electrodes with engineered gradients
- Computational methods developed to characterize, develop proton-conducting SOC materials

Output: 2023 Project Review Posters

- **Tao Yang**, **Harry Abernathy,** “Investigation of Long-Term Performance for Solid Oxide Fuel Cells with Multiple Degradation Mechanisms”
- **Jay Liu**, “Microstructure Optimization of LSM/YSZ Air Electrodes for Catalyst Infiltration”
- **Ed Sabolsky,** “Advanced Manufacturing of Unique Solid Oxide Fuel Cell Electrode and Electrolyte Microstructures through Aerosol Deposition”
- **Yun Chen,** “Sr Surface Segregation & Grain Boundary Degradation of LSCF/SDC Oxygen Electrode Operated in Both Fuel Cell and Electrolysis Mode”
- **Yueh-Lin Lee**, “Defect Thermodynamics and Transport Properties of Proton Conducting Oxide $BaZr_{1-x}Y_xO_{3-\delta}$ ($x \leq 0.1$) and $BaFe_{0.9}Y_{0.1}O_{3-\delta}$ Evaluated Based on Density Functional Theory Modeling”
- **Yoosuf Picard**, “Cation Migration in SOC Electrodes Investigated by Transmission Electron Microscopy”

Output from past 12 months

NATIONAL ENERGY TECHNOLOGY LABORATORY

1. J.H. Duffy, H. Abernathy, K. Brinkman, "Tuning Proton Kinetics in $BaCo_{0.4}Fe_{0.4}Zr_{0.2-X}Y_XO_{3-\delta}$ Triple Ionic-Electronic Conductors via Aliovalent Substitution" Accepted by **Journal of Materials Chemistry A** 2023.
2. T.L. Cheng, Y. Lei, Y. Chen, Y. Fan, H. Abernathy, X. Song, Y.H. Wen, "Oxidation of nickel in solid oxide cells during electrochemical operation: Experimental evidence, theoretical analysis, and an alternative hypothesis on the nickel migration," **Journal of Power Sources** 569, 232991, 2023.
3. X. Fei et al., "Phase-field modeling of crack growth and mitigation in solid oxide cells", **International Journal of Hydrogen Energy** 48, 9845, 2023.
4. T. Yang, et al., "Multiphysics modeling of SOFC performance degradation caused by interface delamination and active layer cracking," **International Journal of Hydrogen Energy** 47(97), 41124-41137, 2022**.**
5. Y.L. Lee, et al., "Defect Thermodynamics and Transport Properties of Proton Conducting Oxide $BaZr_{1-x}Y_xO_{3-\delta}$ ($x \leq 0.1$) Guided Based on Density Functional Theory Modeling," **JOM** 74, 4506-4526, 2022**.**
6. Y. Lei, et al., "Modeling Ni redistribution in the hydrogen electrode of solid oxide cells through $Ni(OH)_2$ diffusion and Ni-YSZ wettability change," **Journal of Power Sources** 545, 231924, 2022.
7. Y. Chen, et al., "Space charge layer evolution at yttria-stabilized zirconia grain boundaries upon operation of solid oxide fuel cells," **Acta Materialia** 237, 1188179, 2022.
8. T. Hsu, et al., "High performance finite element simulations of infiltrated solid oxide fuel cell cathode microstructures," **Journal of Power Sources** 541, 231652, 2022.
9. R. Jacobs, et al., "Unconventional Highly Active and Stable Oxygen Reduction Catalysts Informed by Computational Design Strategies," **Advanced Energy Materials**, 2201203, 2022.

- 8 presentations (1 invited), 1 poster at 20th International Symposium on Solid Oxide Cells, part of ICACC 2023

Acknowledgement

NATIONAL ENERGY TECHNOLOGY LABORATORY

- This work was performed in support of the U.S. Department of Energy's (DOE) Fossil Energy and Carbon Management's Solid Oxide Fuel Cell Research Program and executed through the National Energy Technology Laboratory (NETL) Research & Innovation Center's Solid Oxide Fuel Cell FWP 1022411 .

NETL Resources

VISIT US AT: **www.NETL.DOE.gov**

@NETL_DOE

@NETL_DOE

@NationalEnergyTechnologyLaboratory

CONTACT:
Harry Abernathy
Harry.Abernathy@netl.doe.gov
304-285-4632