H2NEW | Hydrogen from Next-generation Electrolyzers of Water

U.S. DEPARTMENT OF ENERGY

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Project ID # P196G

H2NEW HTE: Multiscale Degradation Modeling

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DOE Hydrogen Program

2023 Annual Merit Review and Peer Evaluation Meeting

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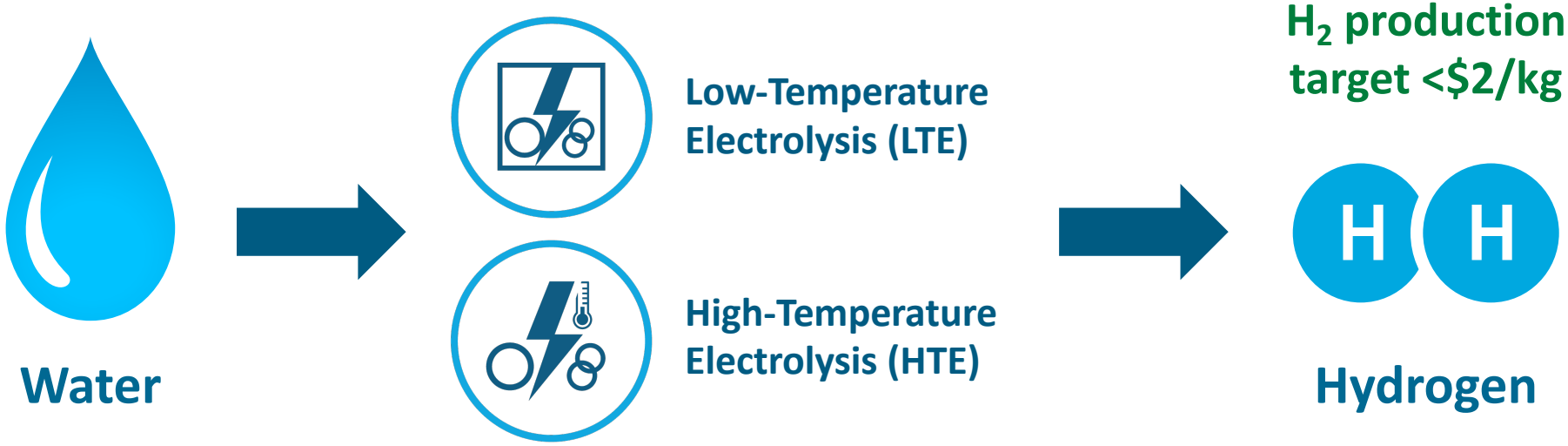
LLNL-PRES- XXXXXX: This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

Project Goals

Goal: H2NEW addresses components, materials integration, and manufacturing R&D to enable manufacturable electrolyzers that meet required cost, durability, and performance targets, simultaneously, in order to enable $2/kg hydrogen.



H2NEW has a clear target of establishing and utilizing experimental, analytical, and modeling tools needed to provide the scientific understanding of electrolysis cell performance, cost, and durability tradeoffs of electrolysis systems under predicted future operating modes

Overview

Timeline and Budget

- Start date (launch): **October 1, 2020**
- Awarded through September 30, 2025
- FY23 DOE funding: **$975k (LLNL) + $1.025M (NETL)**
- Annual budget adjustments anticipated

Barriers

- **F: Capital Cost**
- **G: System efficiency**
- **K: Manufacturing**
- **L: Operations & maintenance**

National Lab Consortium Team

Lawrence Livermore National Laboratory

- Atomistic simulation
- Microstructural / electrochemical degradation modeling

NATIONAL ENERGY TECHNOLOGY LABORATORY

- Microstructural / component / cell modeling

NREL NATIONAL RENEWABLE ENERGY LABORATORY · Pacific Northwest NATIONAL LABORATORY · INL Idaho National Laboratory

- Close coordination w/ Task 7: Advanced Ex-situ and In-operando characterization

Potential Impact

2026 Technical Targets for High-temperature Electrolyzer Stacks	
Performance	1.2 A/cm^2 @ 1.28 V/cell
Electrical efficiency	98% LHV (34 kWh/kg H_2)
Average degradation rate	3.2 mV/kH
Lifetime	40,000 hr
Capital cost	$125/kW

Key factors holding HTE / SOEC technology at current TRL

1. **Degradation limits cost, performance, durability**

   Ni migration, electrode breakdown near the electrolyte, impurity buildup

2. **Need for optimization of fuel electrode micro/nano-structure and chemistry**

   Catalyst infiltration, layer deposition, exsolution, etc.

Hauch et al (2020). Recent advances in solid oxide cell technology for electrolysis. *Science*, *370* (6513)

Potential Impact

Overall modeling objectives:

1. Identify operating conditions under which different degradation mechanisms become active

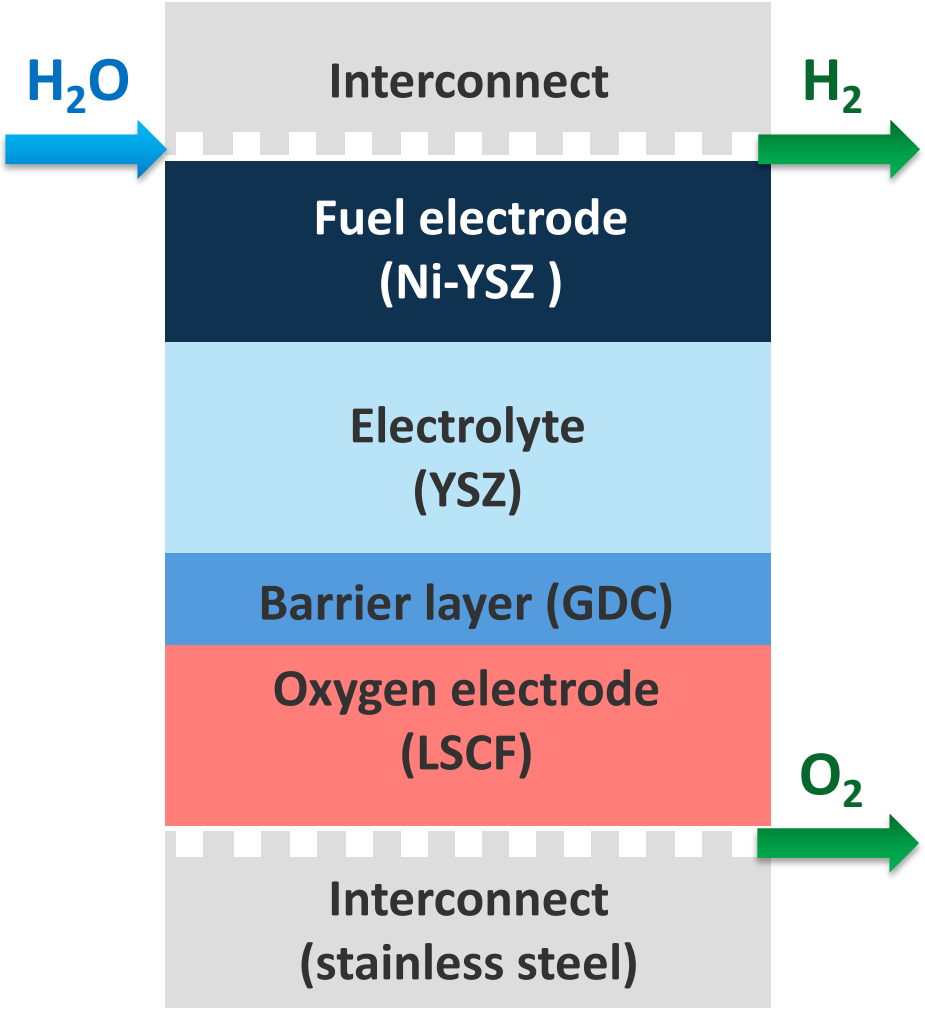
2. Provide a framework to enable longer-time durability and lifetime predictions

3. Guide selection of appropriate accelerated stress testing (AST) conditions and verify that AST protocols are representative of long-term degradation under normal operating conditions

Validated via tie-ins with experimentally measurable quantities. Leverages advanced simulation capabilities and codes developed through HydroGEN and complementary DOE-funded activities at partner labs.

Approach

Modeling addresses key degradation modes in HTE components



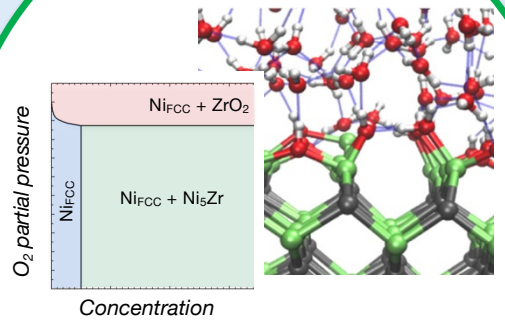
- Interconnect corrosion
- Ni redistribution & coarsening
- Secondary phase formation & particle breakdown
- Cation migration and interdiffusion among electrode, electrolyte, and barrier layer
- Electrode decomposition & secondary phase formation
- Interconnect / electrode interactions (Cr poisoning)
- Air electrode mechanical failure

Approach

"Bottom-up"

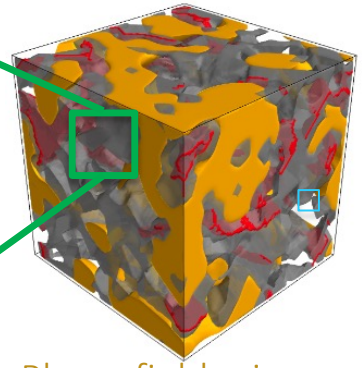
Multiscale physics-based modeling of mechanisms

Atomistic



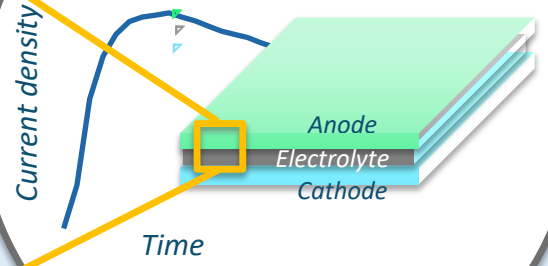
Ab initio transport & thermodynamics

Microstructural



Phase-field micro-structure evolution

Component/cell



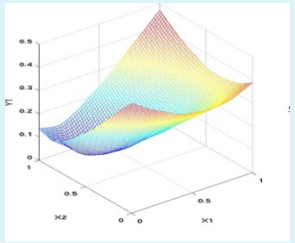
Electrode architecture & performance

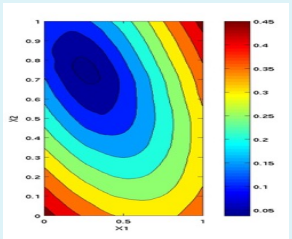
Models are linked across scales, correlated to testing data, and accelerated with ML/AI

"Top-down"

Performance analysis

test matrix → correlations → inferences





Relevant degradation modes

Materials/ components/ cells

Operating conditions

Accomplishment: Predicted thermodynamic conditions for common pathways of LSCF electrode decomposition

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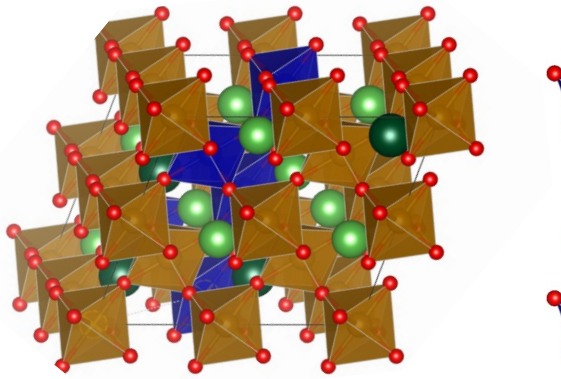
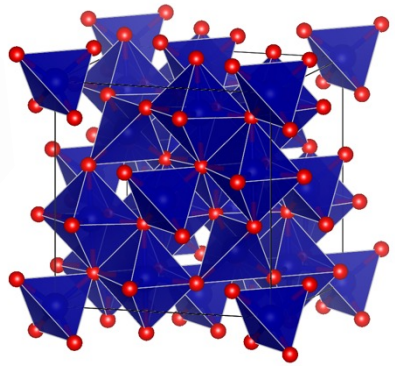
Ab initio thermodynamics predict that local heating can promote LSCF decomposition to La_2O_3, $(Co,Fe)_3O_4$ spinel, and SrO

$La_{1-x}Sr_xCo_yFe_{1-y}O_3$ → $La_2O_3 + Co_{2.96}Fe_{0.04}O_4 + O_2$

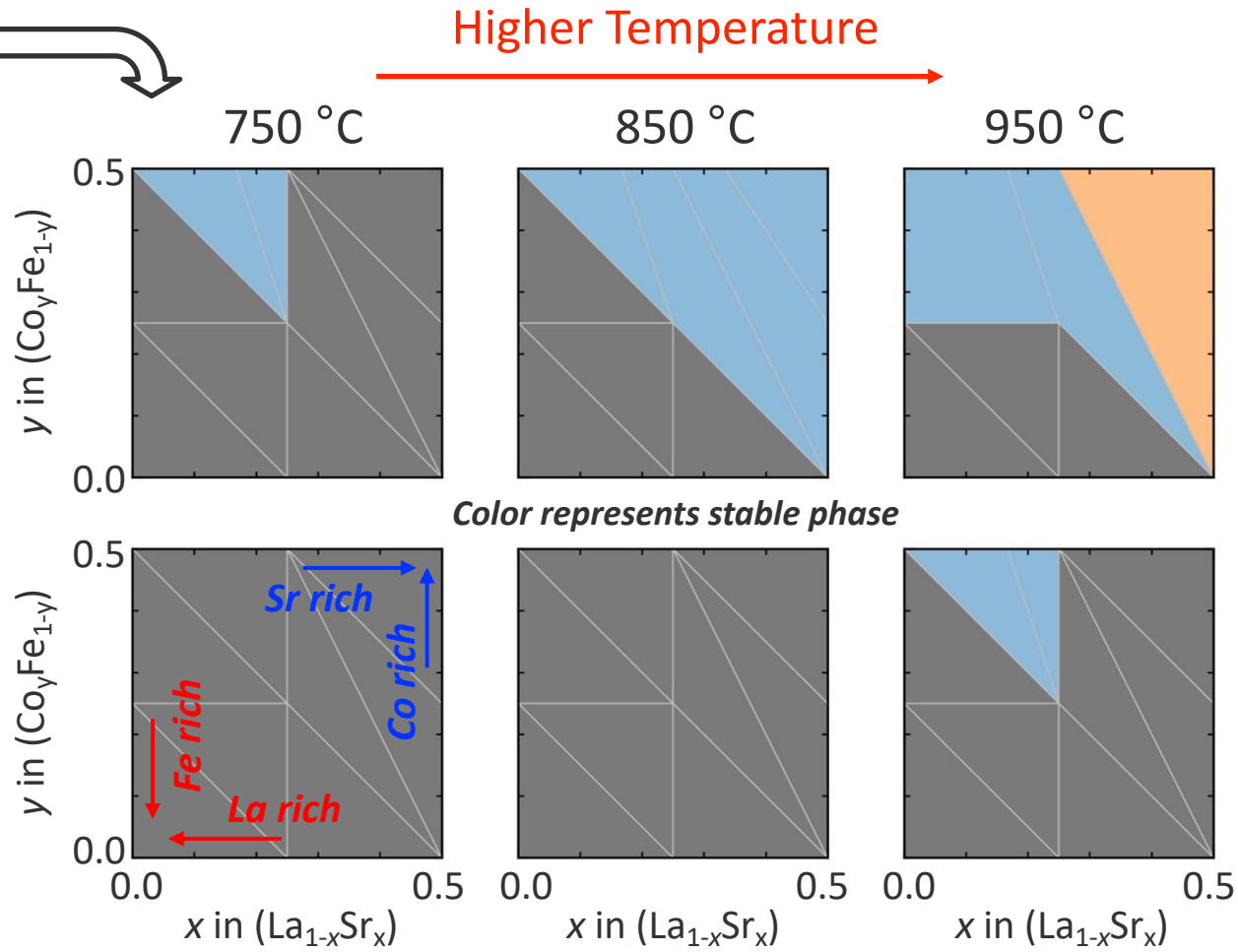
$La_2O_3 + SrO + Co_{2.96}Fe_{0.04}O_4 + O_2$



LSCF perovskite



Co_3O_4 spinel



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Accomplishment: Parameterization of models for cation impurity diffusion through GDC interlayer

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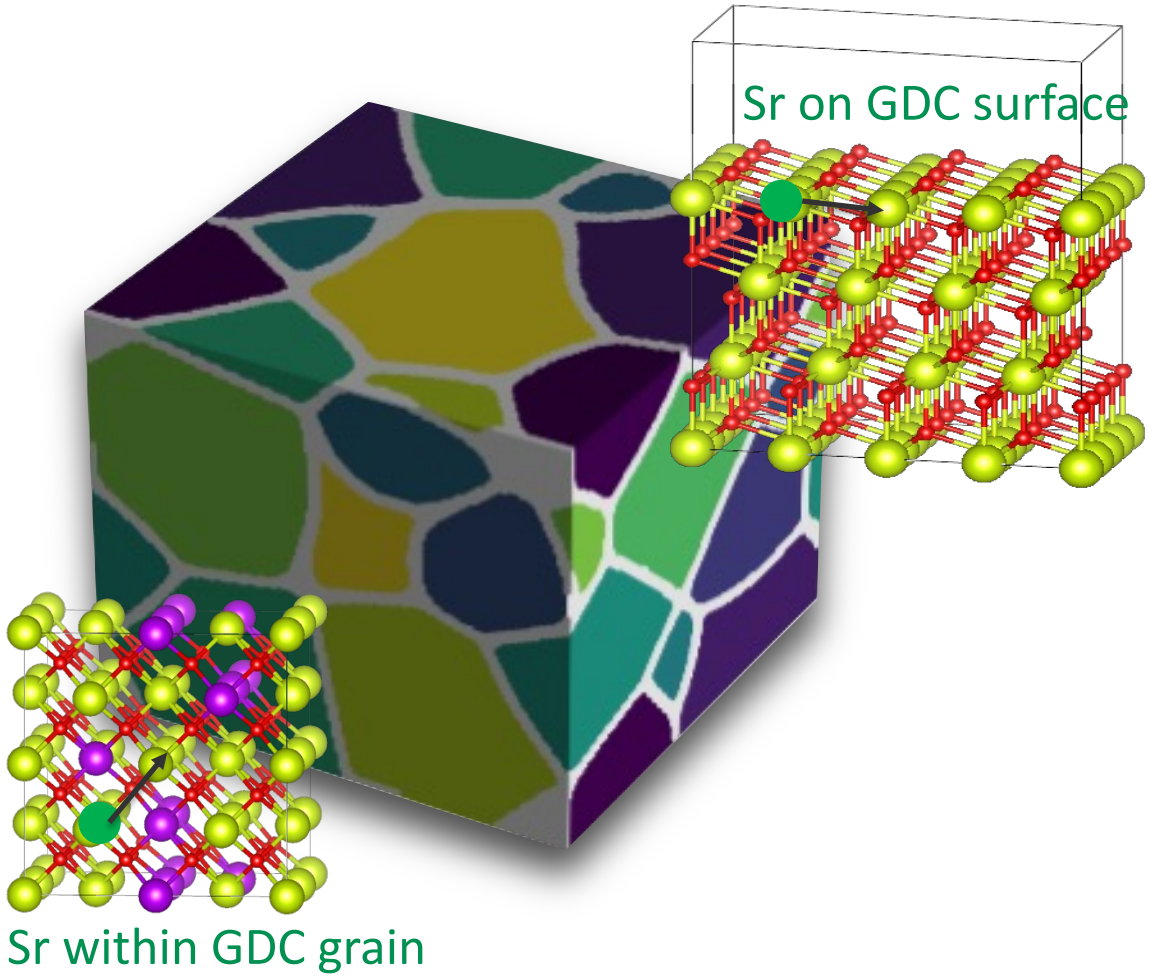
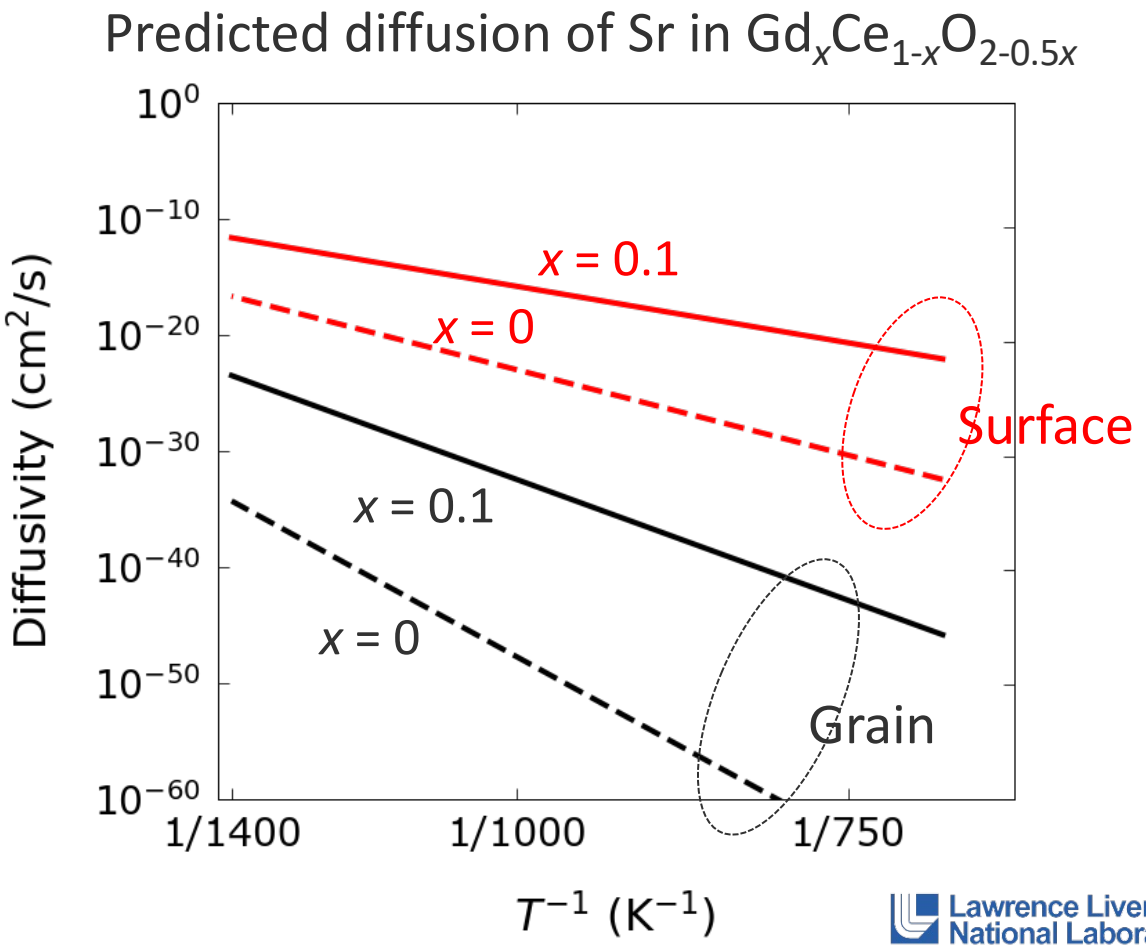
Ab initio calculations parameterize multiscale model and show that Sr diffusion is enhanced by local O vacancy concentration and presence of surfaces





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Accomplishment: Demonstrated multiscale framework for predicting Sr penetration into packed GDC as a possible failure mode

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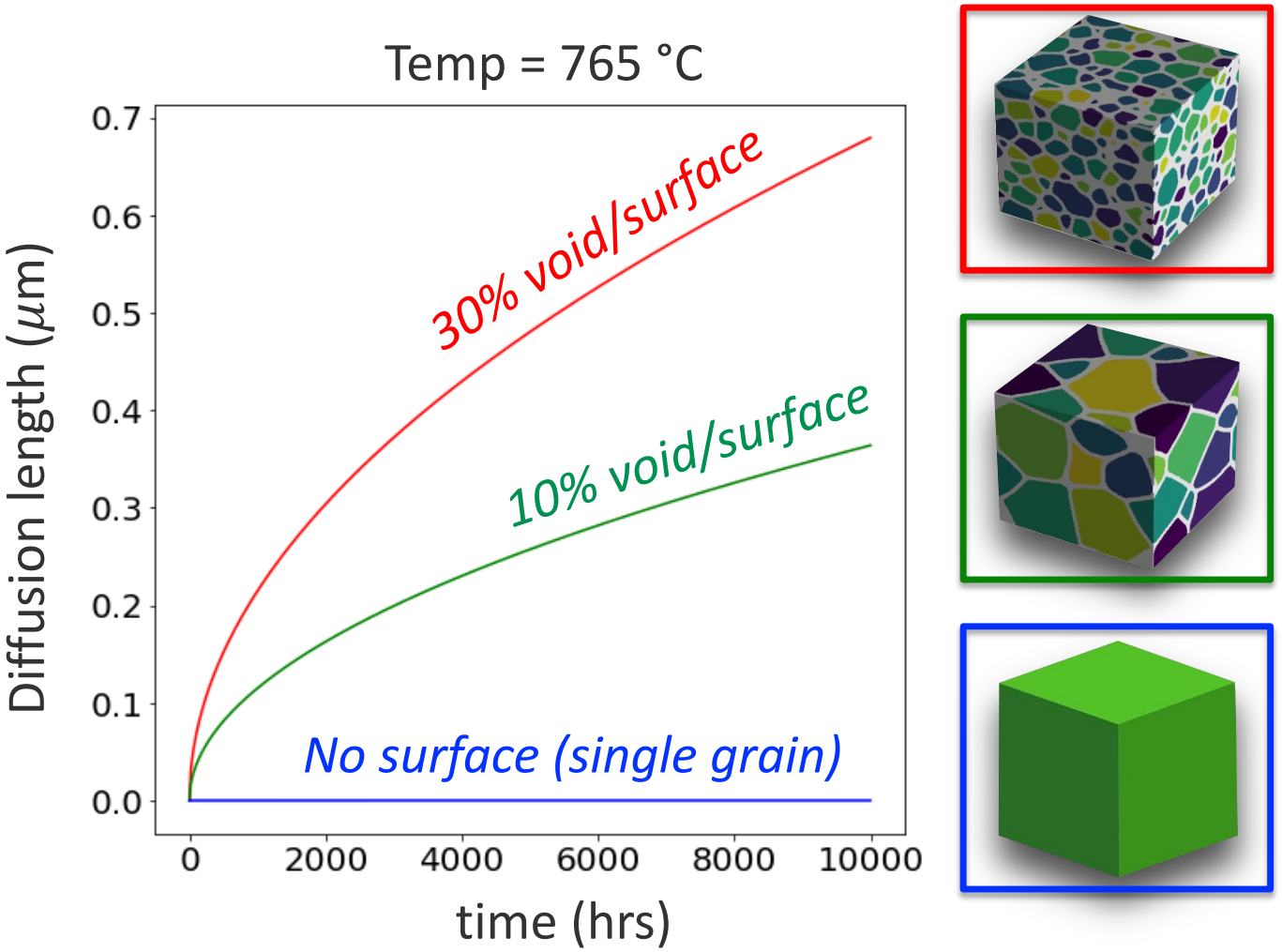
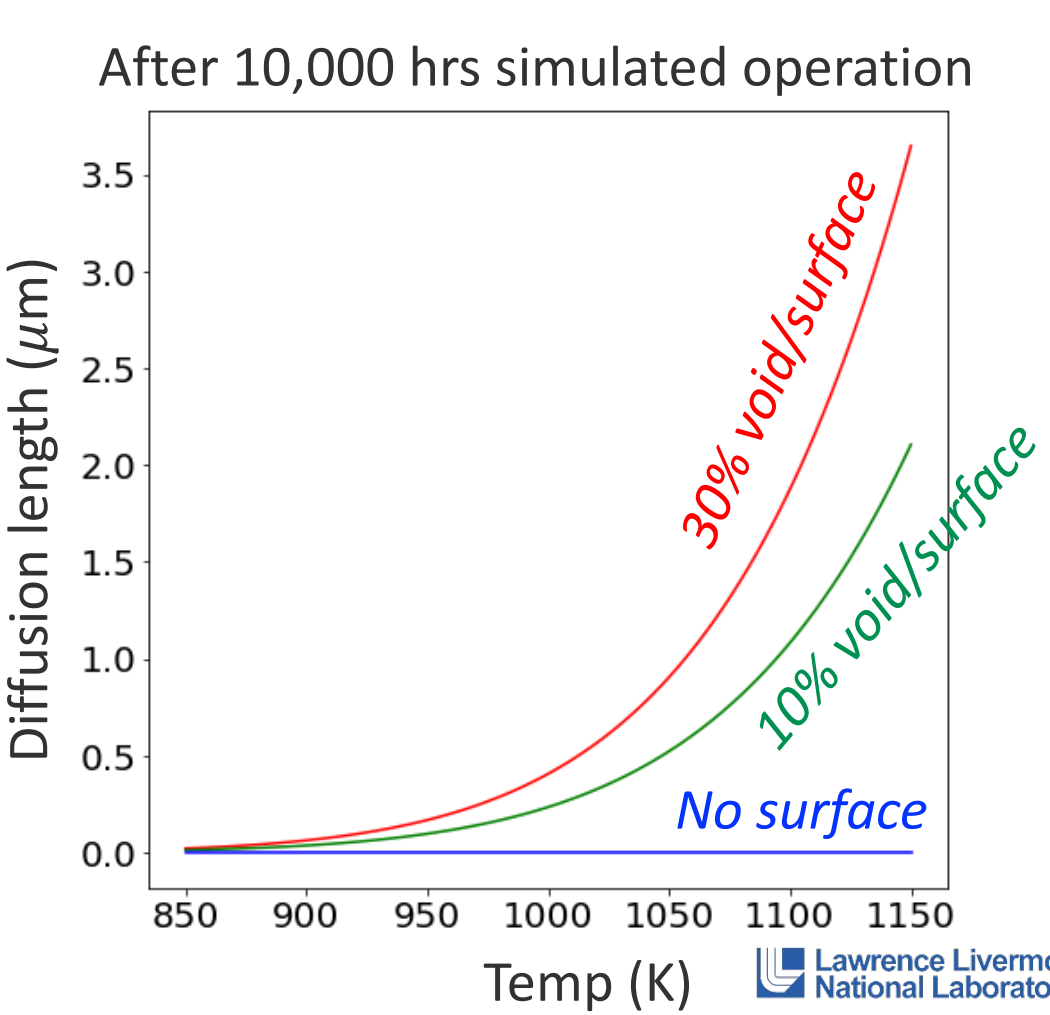
Porosity and loose particle packing create surface-dominated diffusion pathway for Sr and other cation impurities, with full permeation of GDC interlayer predicted as possible under operation





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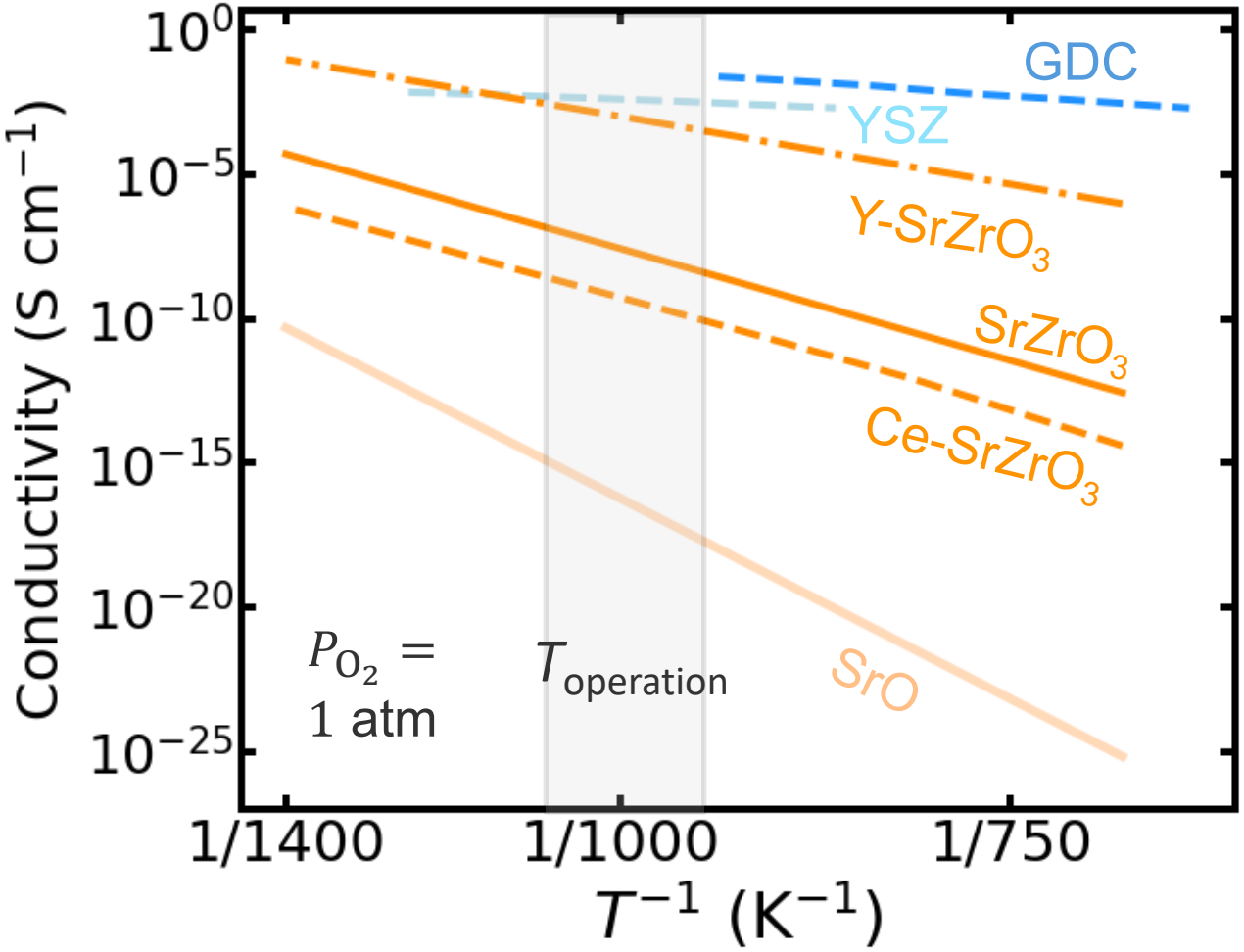
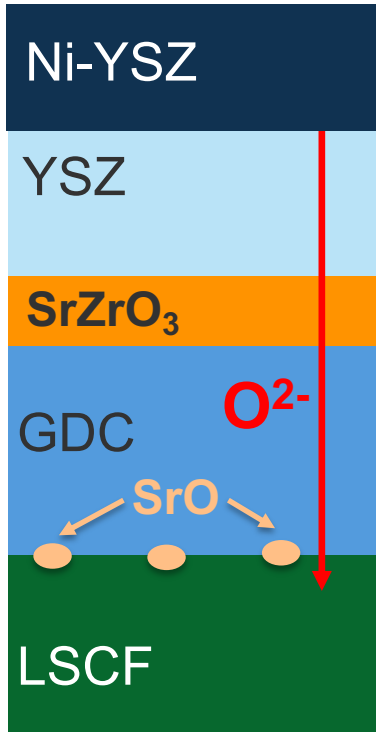
Accomplishment: Predicted effects of secondary phase formation on desired oxide ion transport across electrolyte & barrier layer

Atomistic simulations show that accumulation of SrO at interfaces would significantly impact oxide ion conductivity. Sufficiently thick films of $SrZrO_3$ could also be problematic.





- Y and Ce impurities vary O^{2-} diffusion in $SrZrO_3$, which could induce unwanted concentration gradients
- Results draw attention to SrO as an especially problematic phase
- Multiscale models will further assess effect of secondary phase morphology on performance

Accomplishment: Computational assessment of propensity for mechanical degradation and fracture of LSCF

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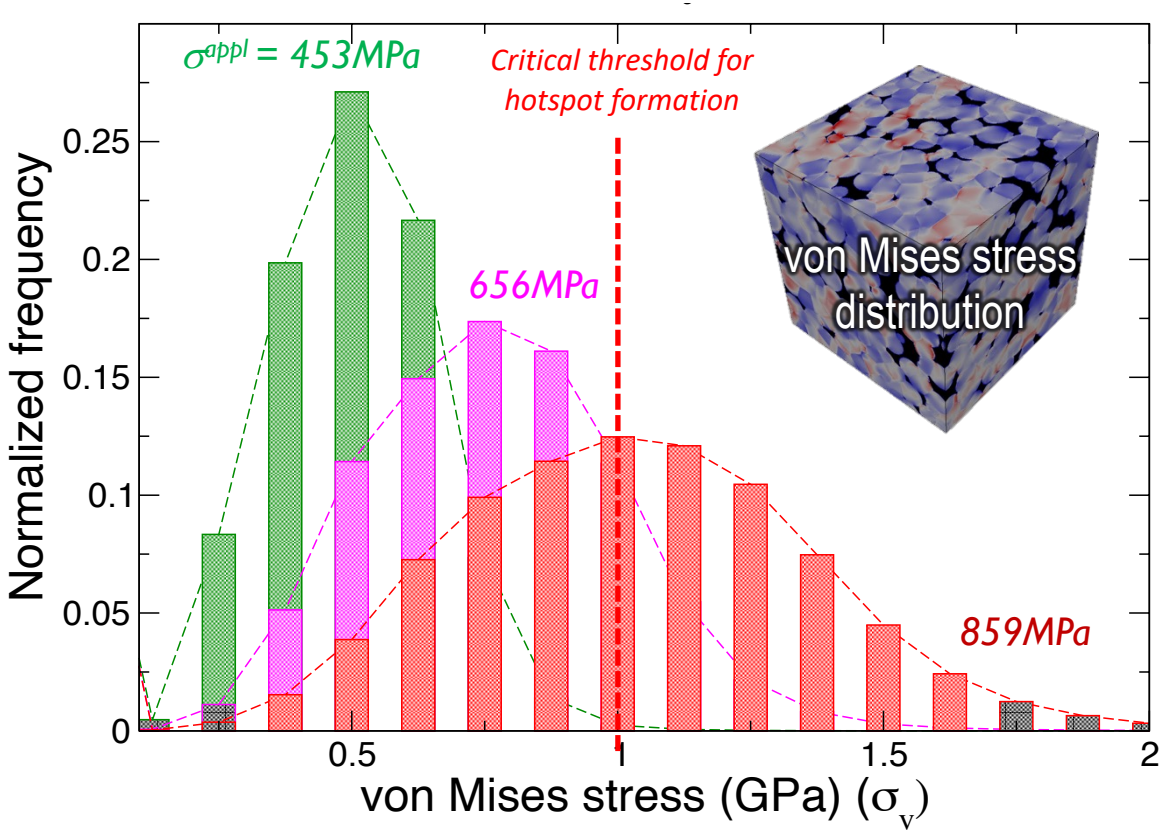
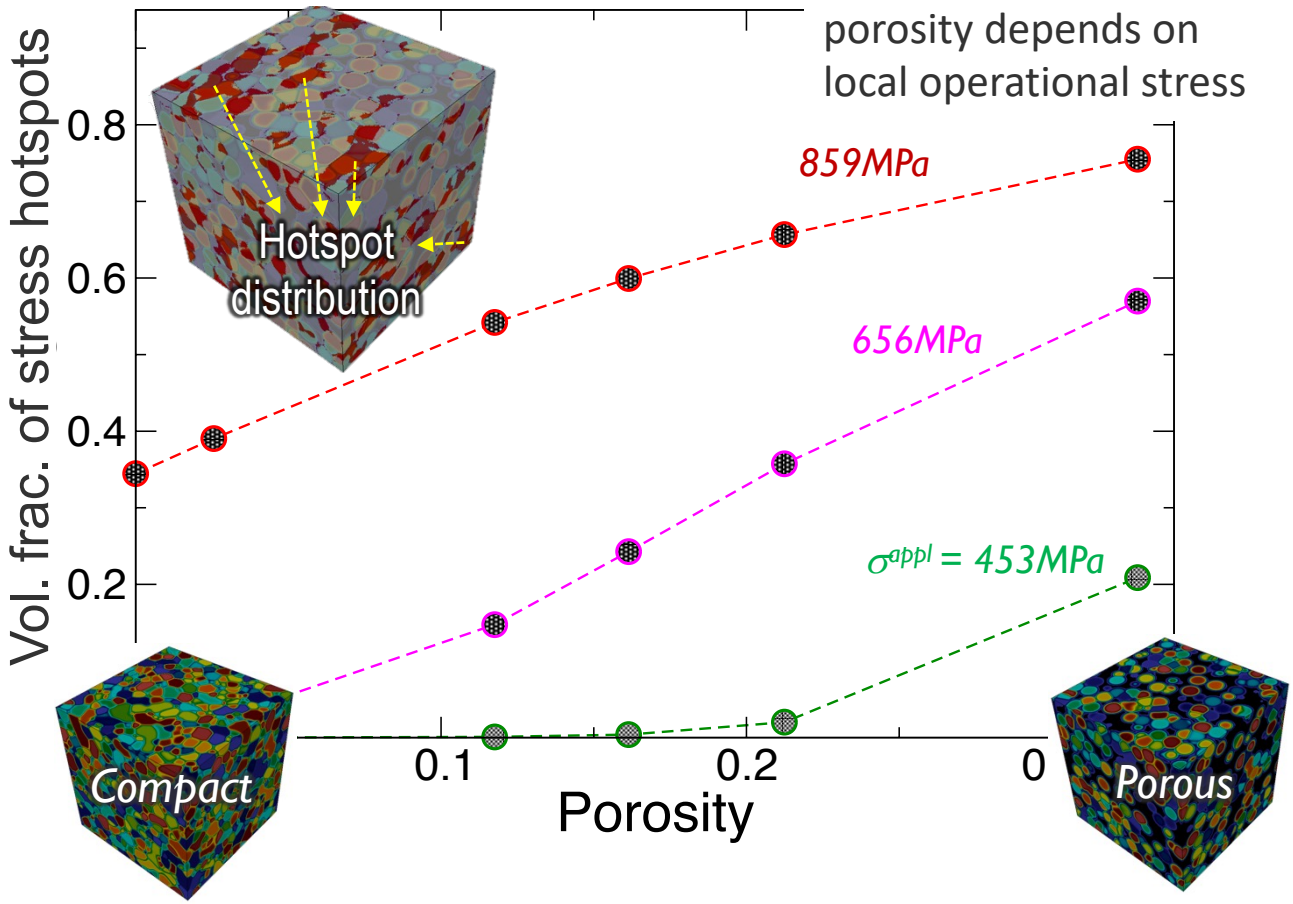
Preliminary micromechanics simulations under thermochemically induced stress predict conditions for evolution of mechanical hotspots that could induce fracture



Sensitivity of hotspot formation to LSCF porosity depends on local operational stress



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Accomplishment: Generated initial electrode microstructures with varying properties as step towards larger database

Electrode structures will be used within a complex workflow for sensitivity analysis and statistical analysis of degradation likelihood for microstructural features under different operating conditions

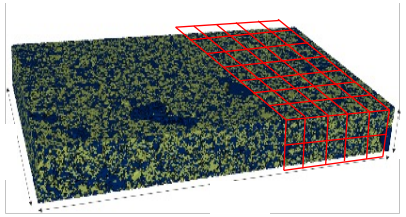
Porosity

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

Varied properties:
Ni-YSZ ratio, Porosity, pore size and pore tortuosity

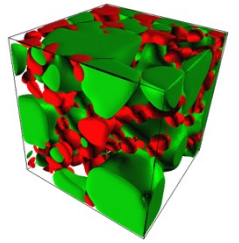


3D electrode microstructures

Synthetic microstructures generated by DREAM.3D

Reconstructed microstructures from PFIB-SEM of commercial electrode

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



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

Multiphysics performance model
- Polarization curves
- Impedance spectra
- T, P Distributions
- Hotspots

Cell lifetime prediction

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

Accomplishment: Computationally assessed impact of Ni/YSZ ratio, operating conditions, and microstructure on Ni redistribution

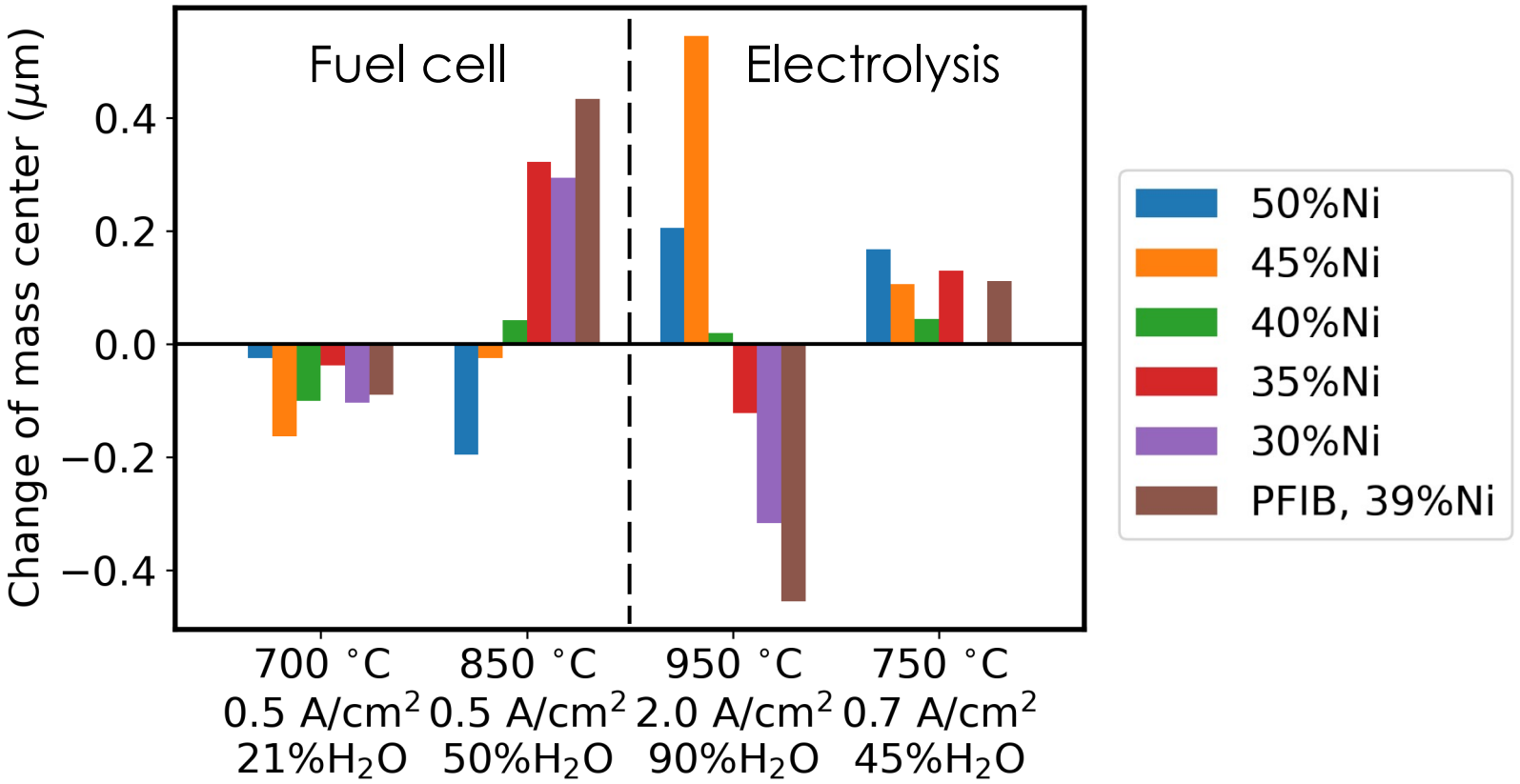
*Models suggest that not just **operating conditions**, but also **microstructural features** and **Ni loading** can impact the direction and magnitude of Ni redistribution*

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%



Additional collaboration and coordination

Carnegie Mellon University – Paul Salvador and Rachel Kurchin (funded)

- Microstructural analysis support
- Machine learning analysis of microstructural and performance data

Northwestern University – Peter Voorheis and Scott Barnett (funded)

- Characterization and electrochemical modeling of performance degradation
- Mechanistic studies of priority degradation modes

Dalhousie University – Penghao Xiao (unfunded)

- Development of nonequilibrium kinetic simulations to examine spinel formation and evolution in air electrode under different conditions

Boston University – James Chapman (unfunded)

- Methods for computing ionic conductivity in atomically disordered oxide regions using machine learning and Kinetic Monte Carlo

Remaining challenges and barriers

- **Timescale incompatibility between experiments and simulations for degradation**

  Degradation within our current predictive simulation framework can only access relatively short timescales, but the testing occurs over longer time periods. Rather than attempting to directly bridge these gaps, our aim is to use the simulations to predict when the necessary conditions for each of the primary proposed degradation modes could theoretically be achieved. One example is the stress hotspot formation simulation, which does not tackle fracture directly (for now), but rather focuses on the initial conditions that could induce fracture.

- **Results from parallel testing are difficult to connect to predictive degradation models**

  This prompts the need for a dual approach that merges data-driven analysis of the parallel test data with the predictive approach. The predictive simulations will reveal the key factors (materials, components, and operating conditions) that ought to impact performance for each of the proposed degradation modes. These results will be used to suggest additional test conditions, which can diagnose whether those degradation modes could indeed be active.

- **Key unknowns in models (e.g., local defect concentration) can significantly impact predictions**

  Certain atomistic quantities like local defect concentrations depend strongly on the stoichiometry, microstructure, and electric field, with implications for degradation predictions. These quantities are difficult to obtain experimentally, and predictive ab initio simulations have large uncertainties in what they can deliver on this front. We are now defining avenues for using the simulation values to predict indirect macroscopic quantities that can be probed experimentally, which can in turn bound the values we should consider.

Proposed Future Work

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LSCF degradation

- Continue evaluating thermodynamics of degradation pathways as a function of local electrochemical potential, oxygen partial pressure, and stoichiometry.
- Begin computing kinetic pathways for decomposition, including interdiffusion of cations that can induce formation of spinels and other secondary phases.
- Predict fractions and distributions of secondary phases and integrate into device performance model.
- Investigate mechanical hotspot formation under a broader range of local conditions.

Electrolyte and barrier layer degradation

- Refine permeation models to include more complex microstructures and packing geometries, and predict impacts on effective cation and oxide ion diffusion in YSZ, GDC, and Sr-containing degradation layers.
- Integrate microstructure-dependent diffusion models into device performance model to assess performance losses.

Ni coarsening and intermetallic formation

- Continue development phase field models for Ni coarsening and NiZr(M) intermetallic formation.

Interconnect corrosion

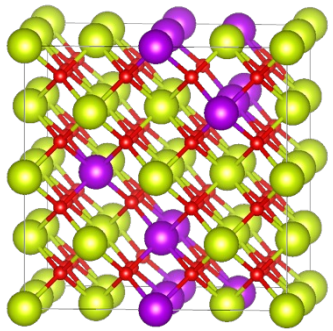
- Begin model formulation for simulating interconnect corrosion under harsh electrochemical conditions.

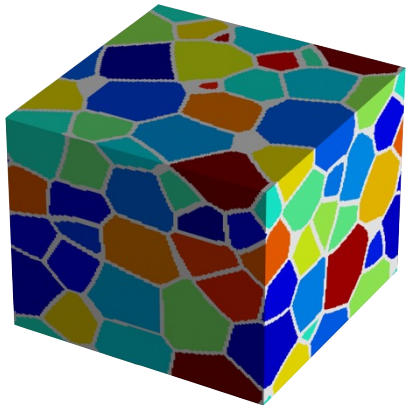
Note: Any proposed future work is subject to change based on funding levels

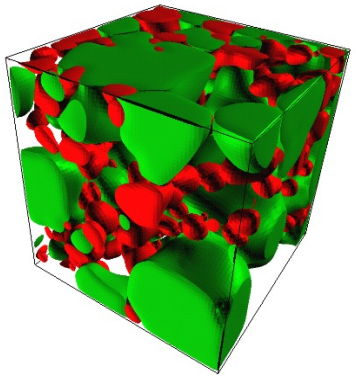
Summary

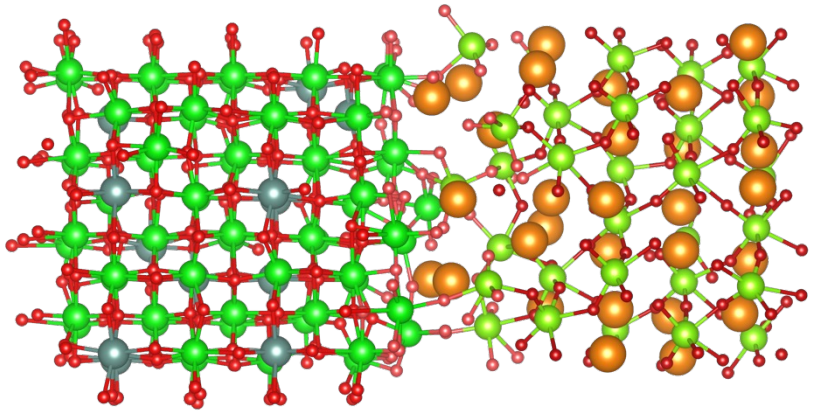
Multiscale degradation simulations can inform development of testing protocols by diagnosing conditions and implications of different proposed HTE degradation modes

- Ab initio thermodynamics of component decomposition under local thermal and oxygen partial pressure conditions
- Multiscale prediction of porosity/packing on permeation of electrolyte and interlayer, with implications for processing
- Identification of secondary phases that are most problematic for blocking desired oxide ion conductivity
- Ability to predict hotspots that can lead to (thermo)mechanical failure
- Generation of “digital twin” electrode microstructure models to examine variations in Ni redistribution









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