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SOFC Operational Degradation: Models and Diagnostic Tools

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DOE-NETL

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the **ENERGY** lab

Acknowledgements

- **NETL RUA Fuel Cell Team**
  - Researchers at NETL, CMU, PSU, WVU, and URS
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  - Briggs White, Joe Stoffa, Rin Burke, Travis Shultz
  - Shailesh Vora

- **SECA Industry Teams**
  - Delphi – Rick Kerr, Joe Bonadies, Stephanie Surface, Ken Rahmoeller
  - LGFCS – Rich Goettler, Ted Ohrn, Zhien Liu
  - FC Energy – Hossein Ghezel-Ayagh, Eric Tang, Stephen Jolly

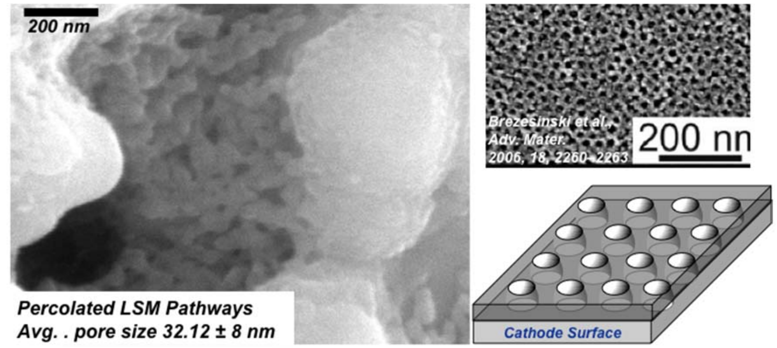
- **SECA Core Teams**
  - PNNL – Jeff Stevenson, Brian Koeppel, John Hardy
  - Core University PIs

NETL ORD - Solid Oxide Fuel Cells

Support Industrial Development

Operation of NETL Solid Oxide Fuel Cell Multi-Cell Array on direct, coal-derived synthesis gas at the National Carbon Capture Center at Wilsonville, AL in August/Sept 2009.

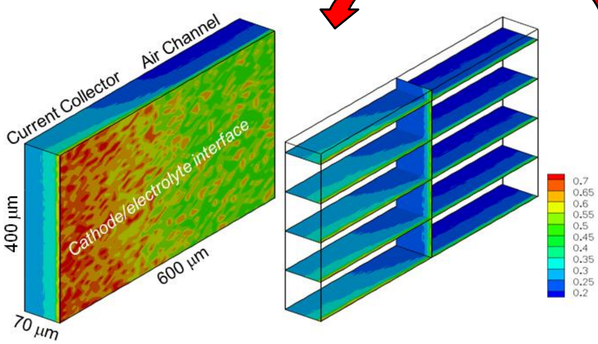
Collected 4,000 + cell-hours of data to support development of gas cleanup systems sufficient for gasifier / fuel cell integration.



Innovate Technology

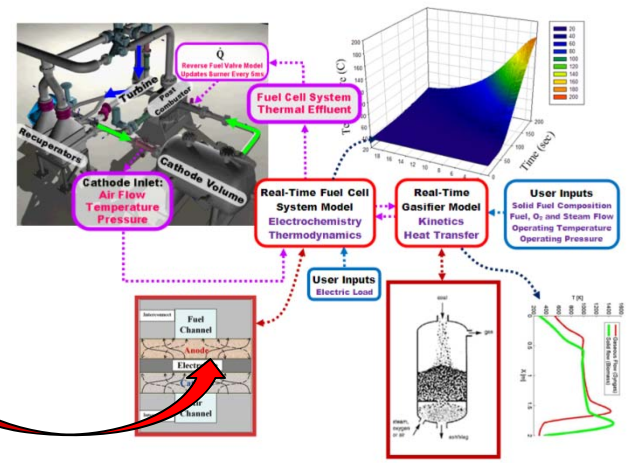
Cathode infiltration technology is being developed to enhance the SOFC operating performance. Initial results have demonstrated > 40% performance improvement and acceptable material stability.

Evaluate Advanced Concepts



Fundamental computations (3D multi-physics model, at left) inform modeling of advanced degradation, performance, and microstructural evolution at the cell and stack level.

Integrated gasifier / fuel cell / turbine systems (IGFT, at right) support advanced fuel cell demonstrations efforts (2013+). NETL operates a system hardware evaluation and controls development platform.



Multi-year research: SOFC Hurricane Model

SOFC lifetime operational modeling

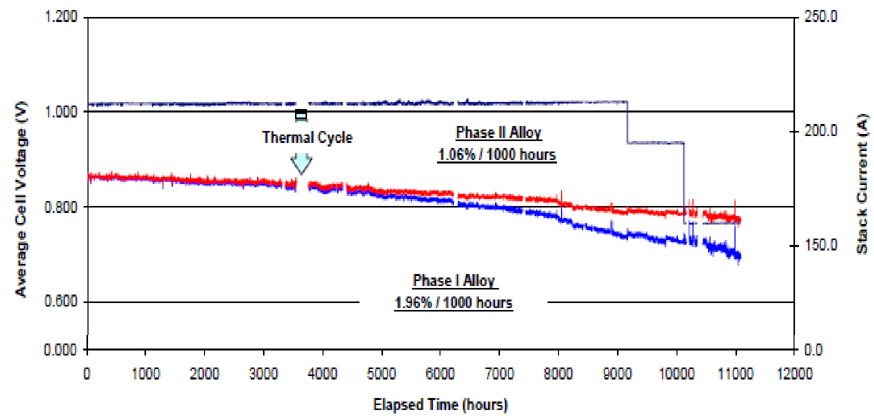
Critical thrust (broad): Computationally guided materials development

Specific: SOFC "Hurricane Model"

Eventual landfall near New Orleans, LA

http://www.katrina.noaa.gov/forecast

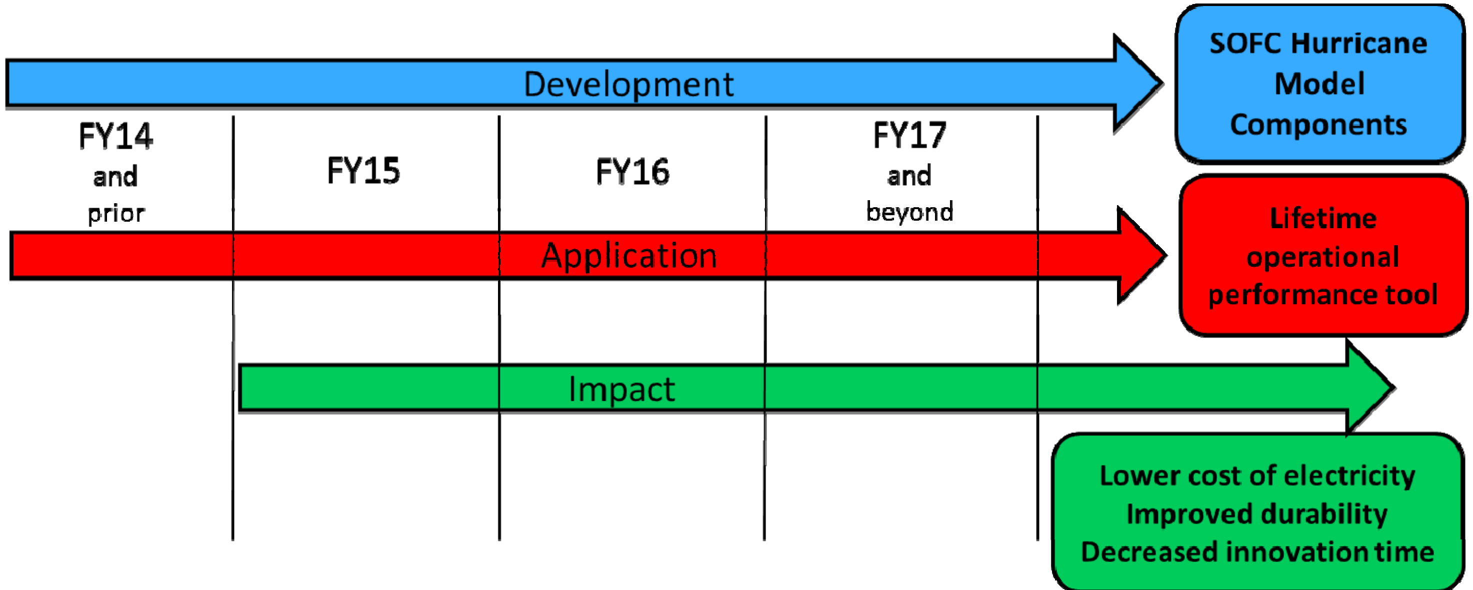
Hossein Ghezel-Ayagh, "Progress in SECA Coal-Based Program"
12th Annual SECA Workshop, Pittsburgh, PA, July 26-28, 2011



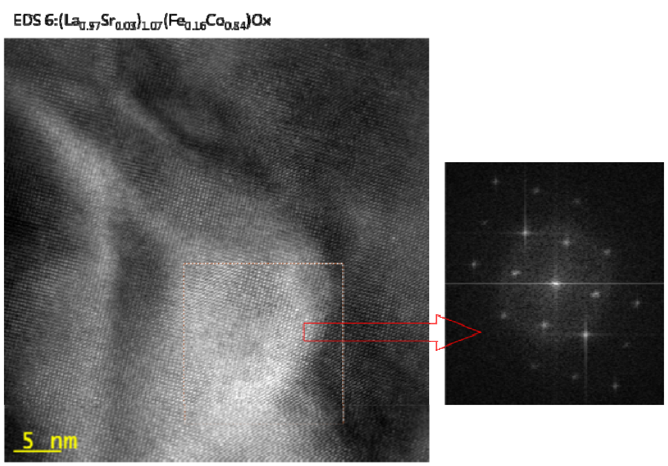
Current Focus of "Hurricane Model" Task:

- Integrate existing models – ORR, 3D multi-physics, Evolution, UQ
- Generate high fidelity simulations and visualizations
- Initiate computationally guided materials/system development

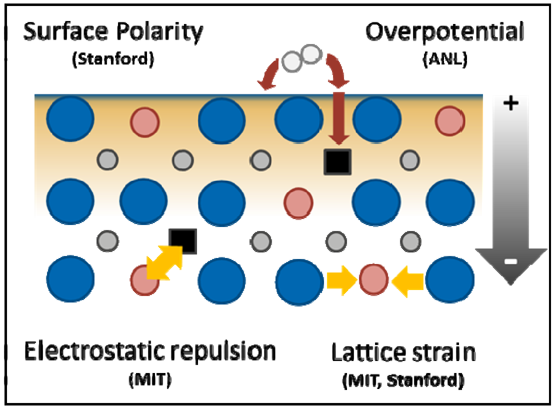
NETL ORD research execution



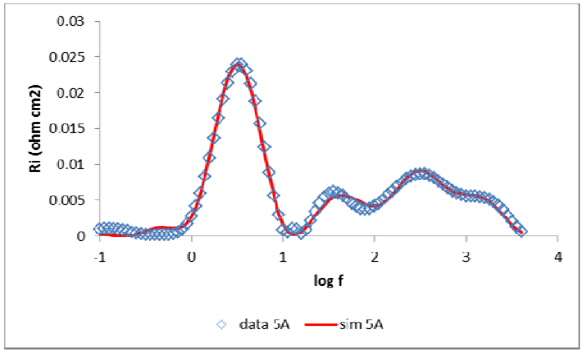
TEM analysis of industry-provided source material (LSCF analysis)



Cation diffusion in cathode materials



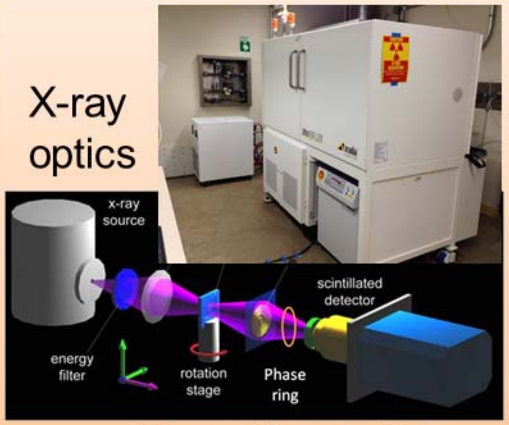
Impedance modeling and advanced analytical tool development



SOFC Development

Please review our team's posters during the exhibition

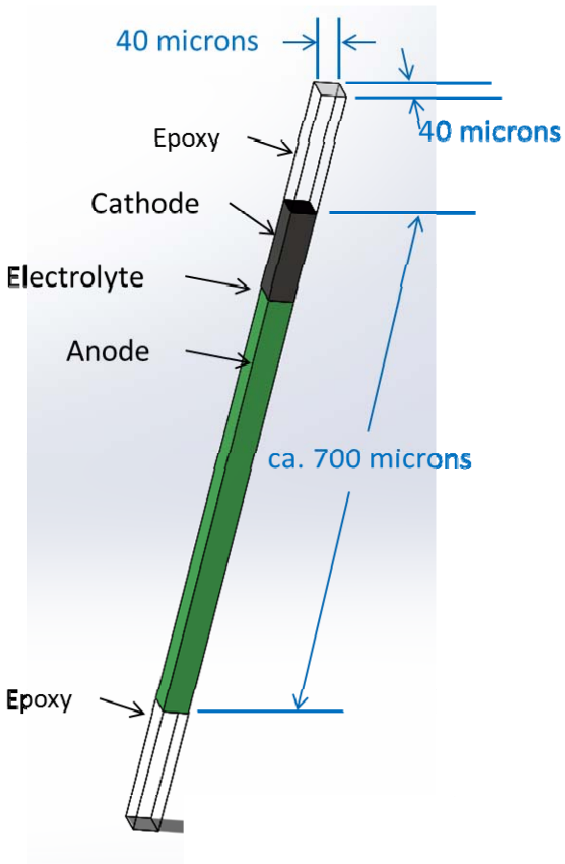
Development: 3D rendering via nano-CT

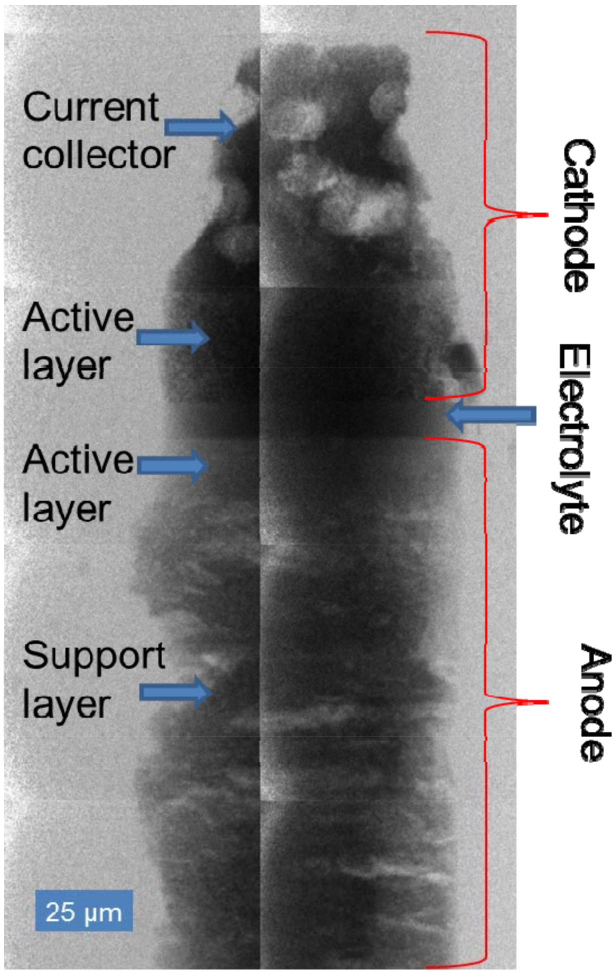


Nano X-ray CT

X-ray optics
50 nm resolution

Sample needs to fit *within* the nano-CT's 65 µm field of view for proper 3D reconstruction

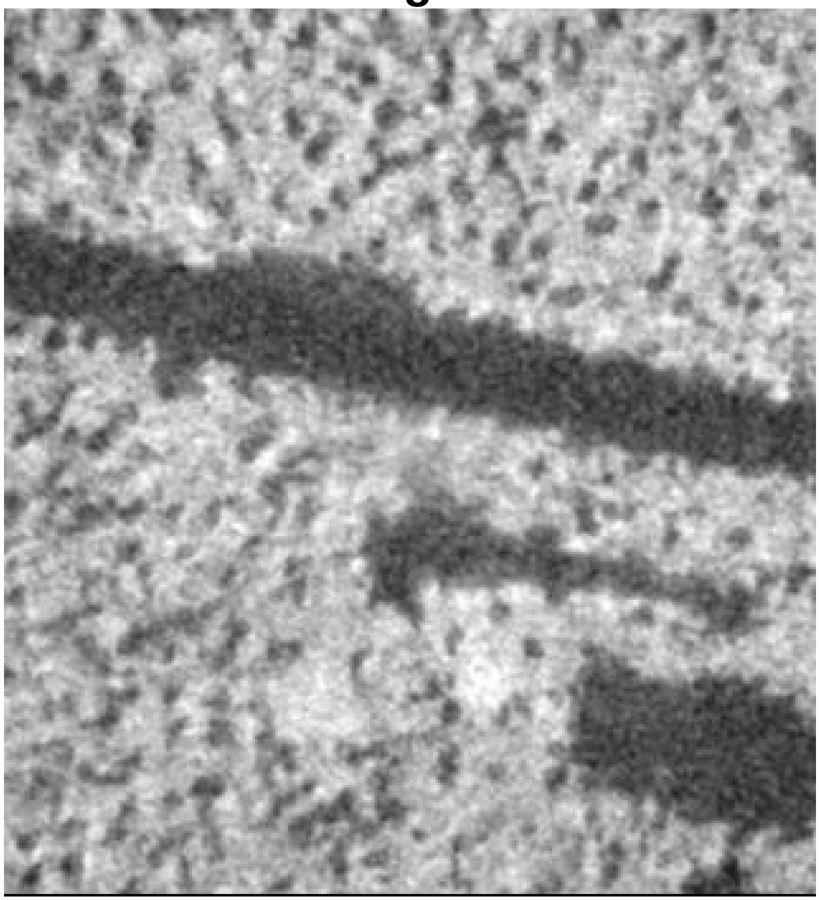




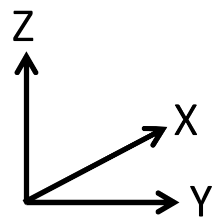
Development: 3D rendering via nano-CT

➢ **Ni-YSZ Anode**

Scanned images 2D Slices

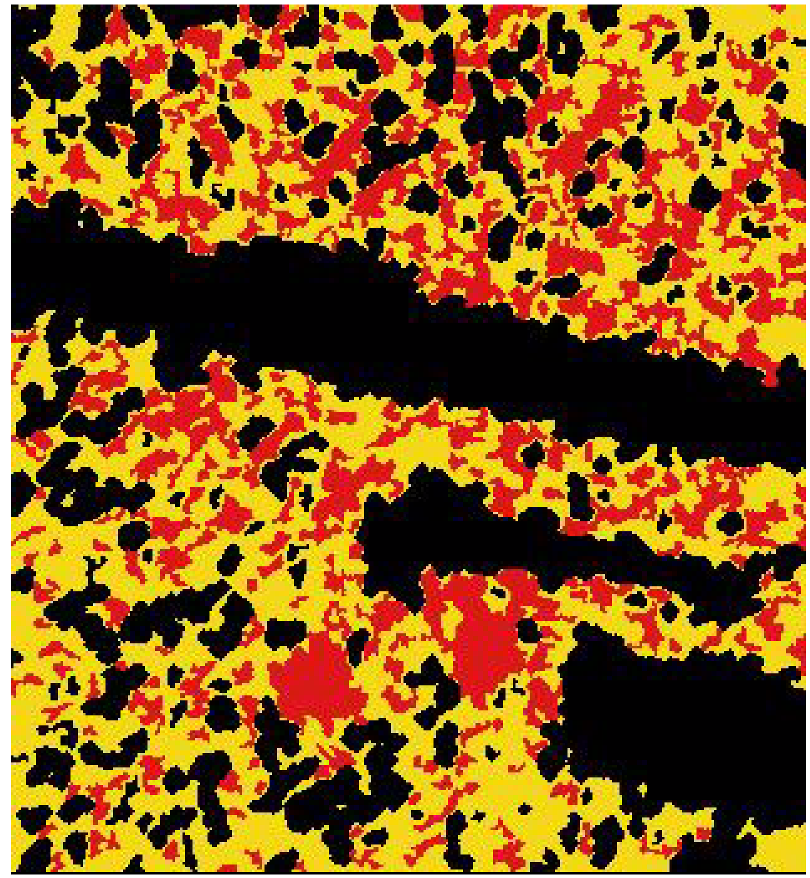


10um



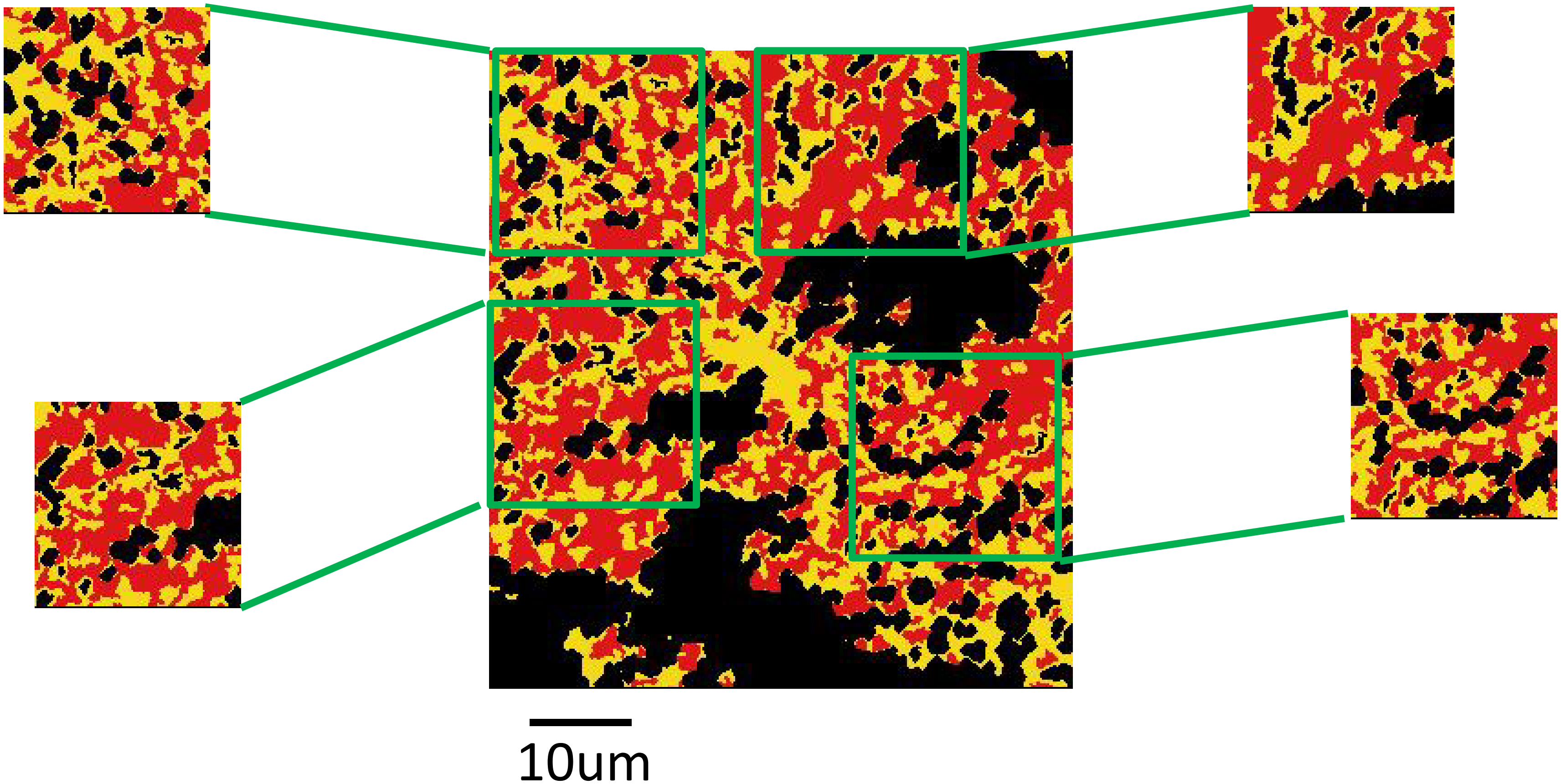
Black: Pore
Yellow: YSZ
Red: Ni

Segmented images 2D Slices



Development: 3D rendering via nano-CT

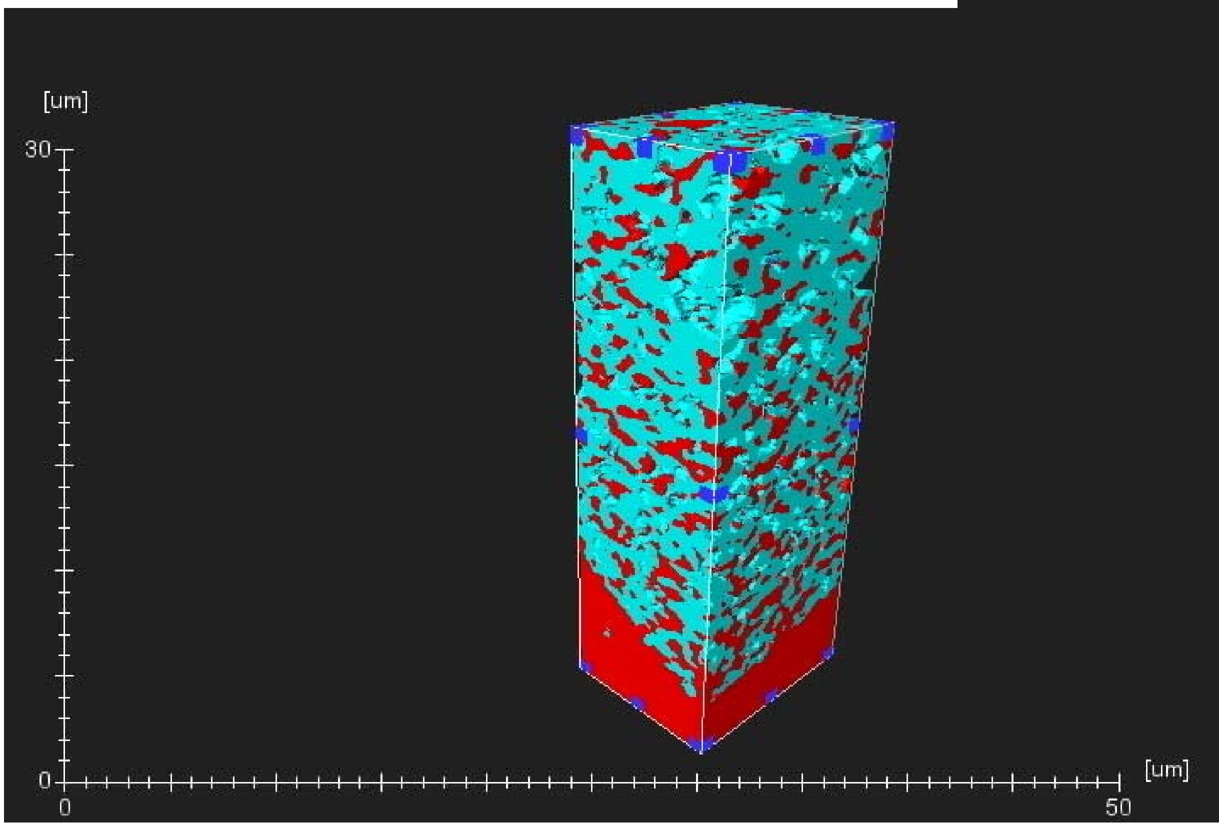
- Ni-YSZ Anode

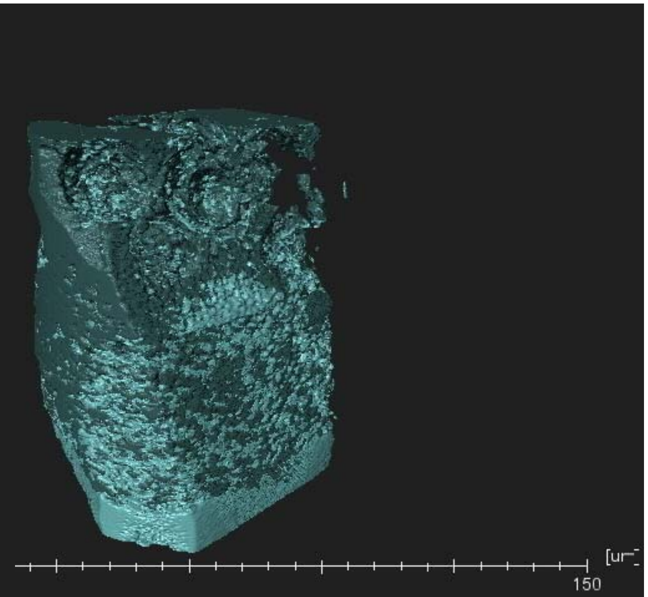


15µm x 15 um x 15 um cubes for high resolution analysis

Development: 3D rendering via nano-CT

- **LSM cathode**

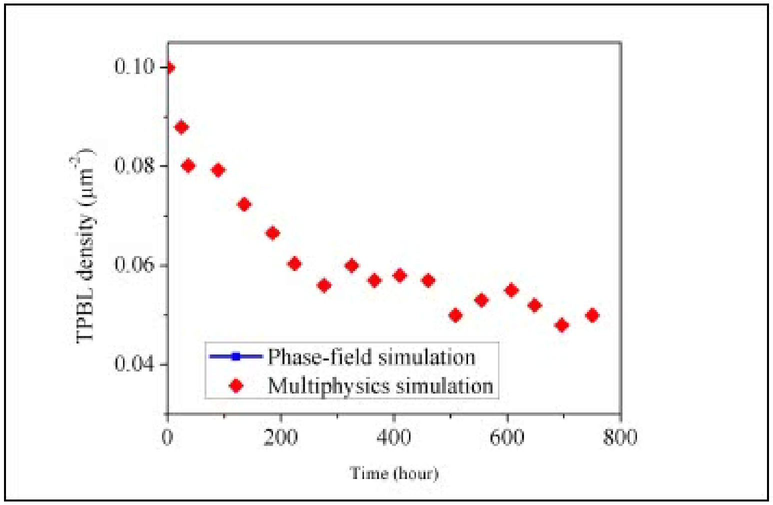


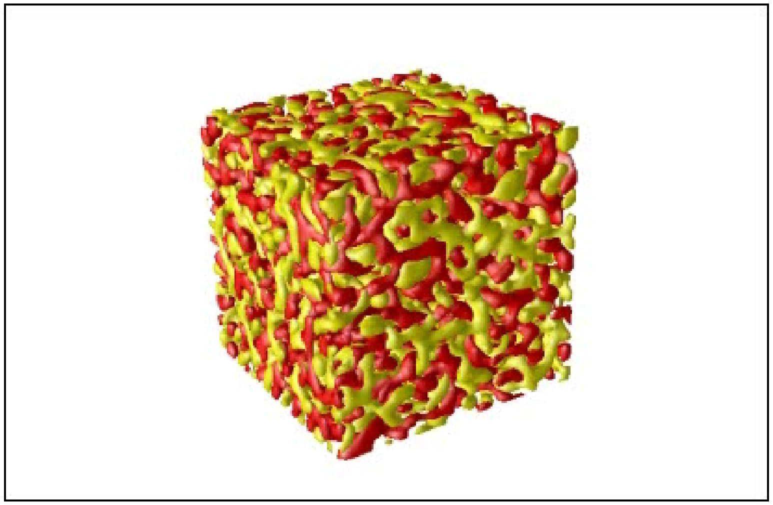


- NEXT: `Reconstruction of a complete commercial → data to inform computations
- Time-dependent examinations will proceed in next project period

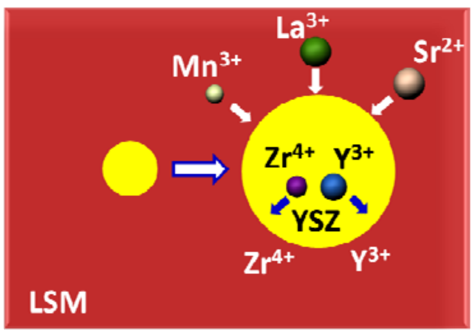
Development: Diffuse Interface Model

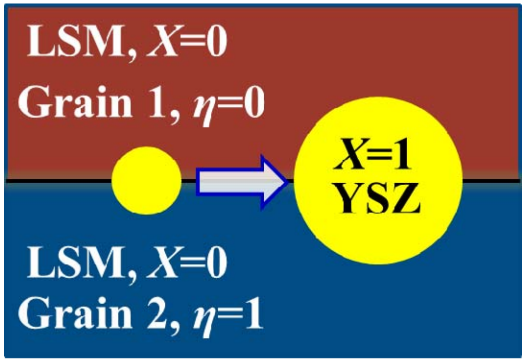
- **FY13 demonstration of phase field coarsening model**

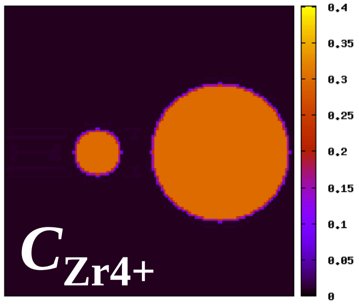




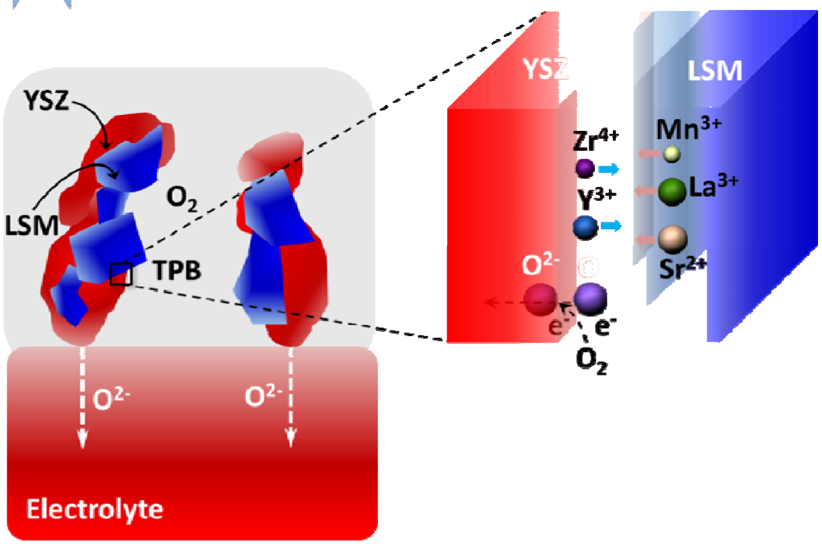
Original model considers interfacial energies and surface mobility
More detailed fundamental parameter assignment → interfacial cation diffusion







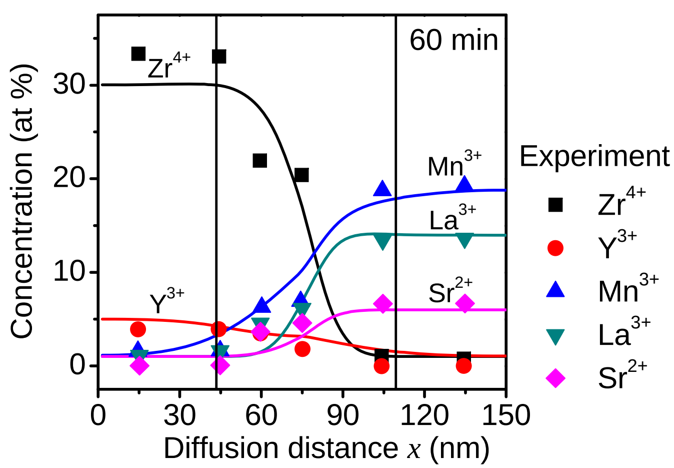
Development: Diffuse Interface Model



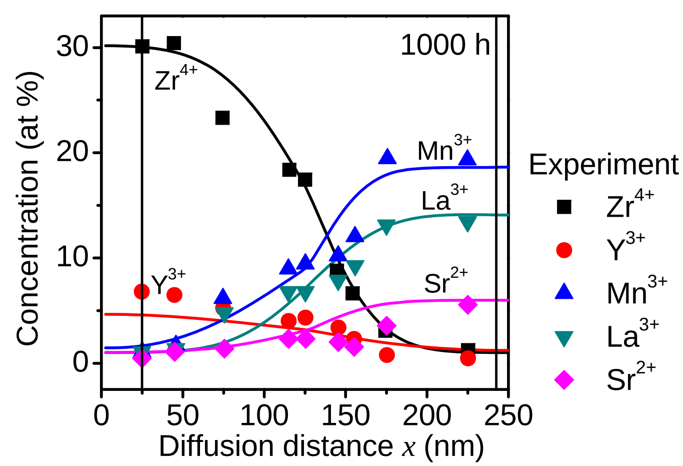
Original Model: Coarsening is driven by the differences in curvature, described by Cahn-Hilliard equation.

Update: Cation inter-diffusion is driven by concentration gradients, described by diffusion equation

Experimental data from Yang et al., JaCers 87, 1110 (2004)



Co-firing @1400 °C for 1 h



Annealing @1000 °C for 1000 h

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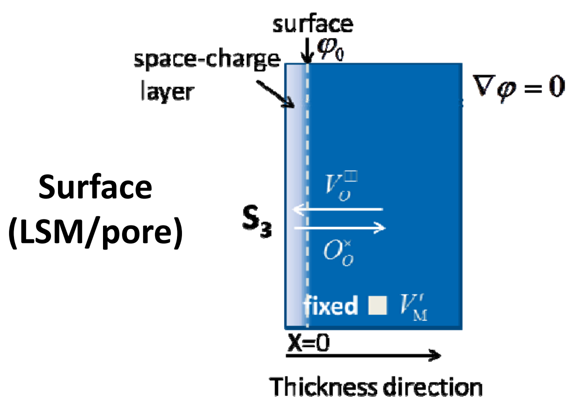
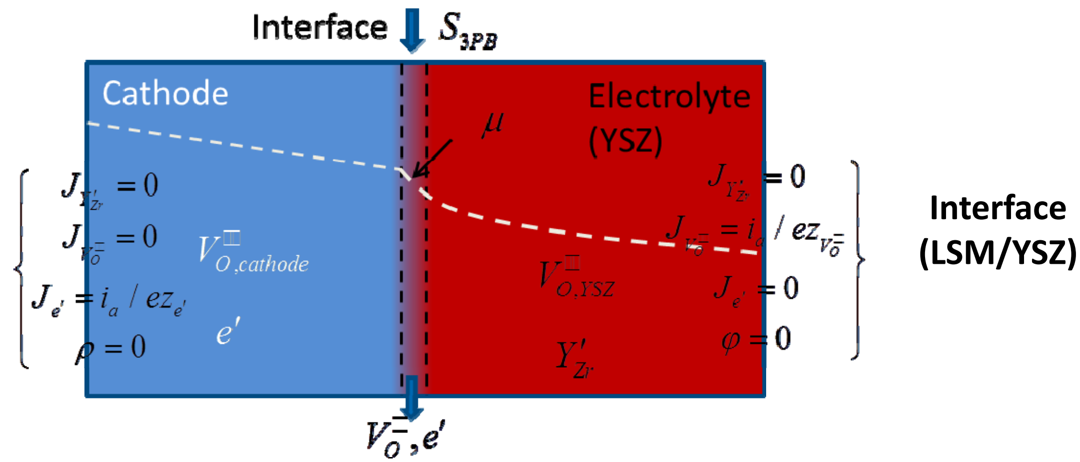
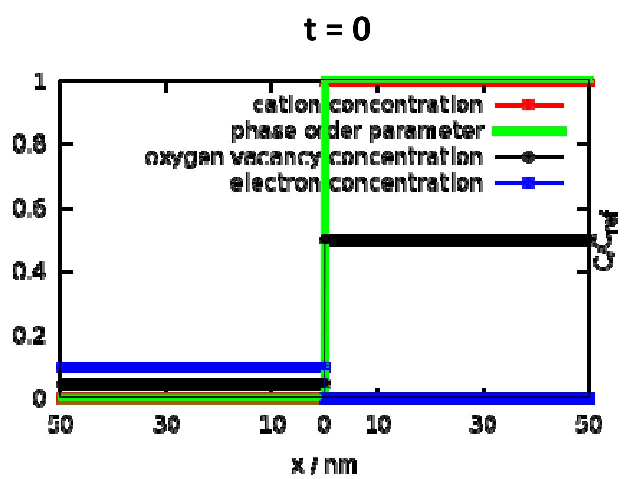
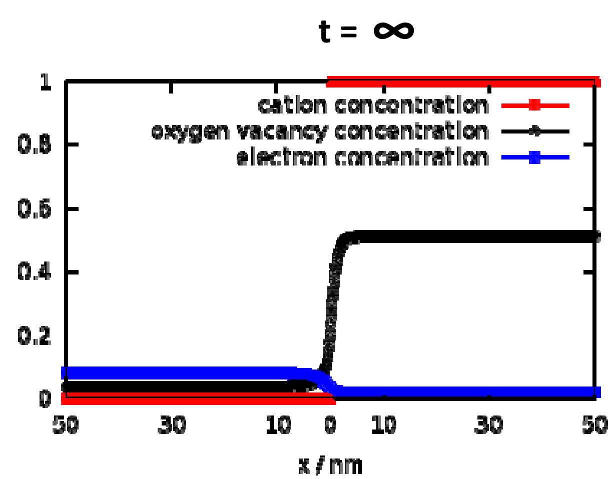
Development: Diffuse Interface Model

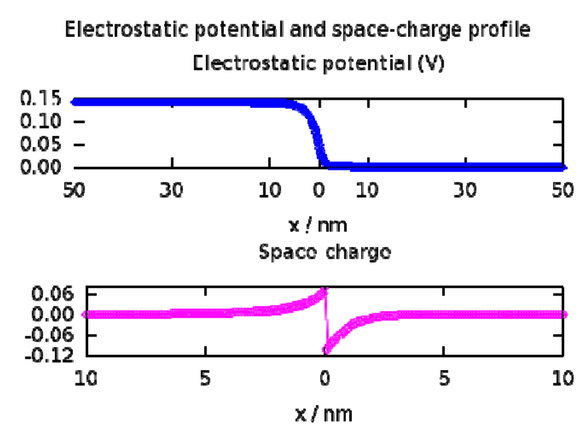
- **Adding local oxygen vacancy concentrations and applied electrostatic fields**











- **Oxygen vacancy equilibrium is rapid compared to cation**

PENNSTATE

Development: Diffuse Interface Model

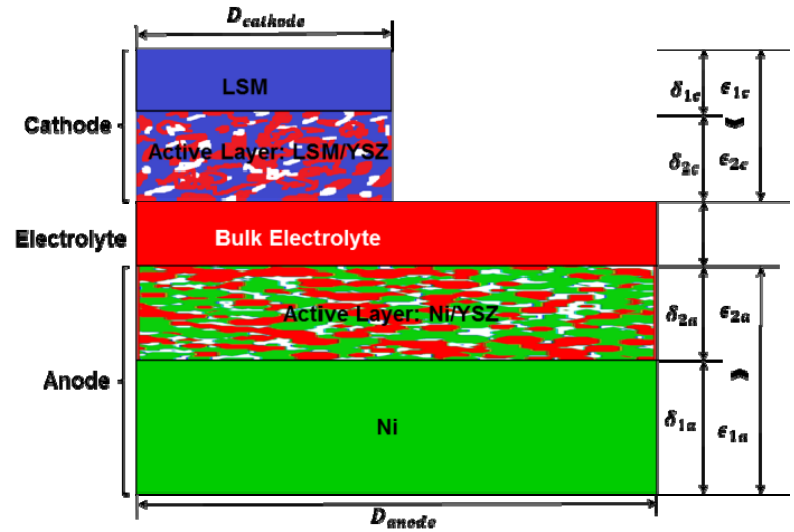
- **Accomplishments**
  - Tunable model describing particle coarsening complete
  - Independently validated descriptions of cation diffusion in LSM/YSZ interfaces complete
  - Oxygen vacancies treated, physically accurate static model
- **In progress**
  - NETL validating experiments for LSM/YSZ, generation of temperature dependent model
  - Validation of dynamic oxygen vacancy model
- **Next project period**
  - Correlate interface evolution with activity changes and altered microstructural evolution kinetics

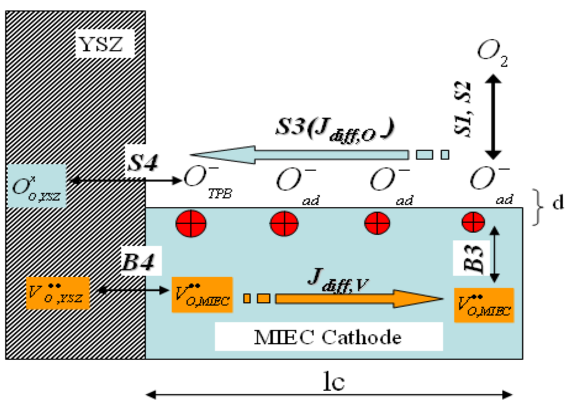
Application

Applications: EIS Simulation Tool

Fundamental development → Application

- **Reaction and transport model**
  - Ismail Celik (poster)
  - **Pakalapati et al. Solid State Ionics 258 (2014) p 45**
- **Oxygen reduction reaction model**
  - Xingbo Liu (poster)
  - **Gong et al. J Electrochem Soc 161 (3) F344 (2014)**
- **VI and EIS experiments**
  - Harry Finklea (poster)
  - **Finklea et al. J Electrochem Soc 160 (3) F1055 (2013)**



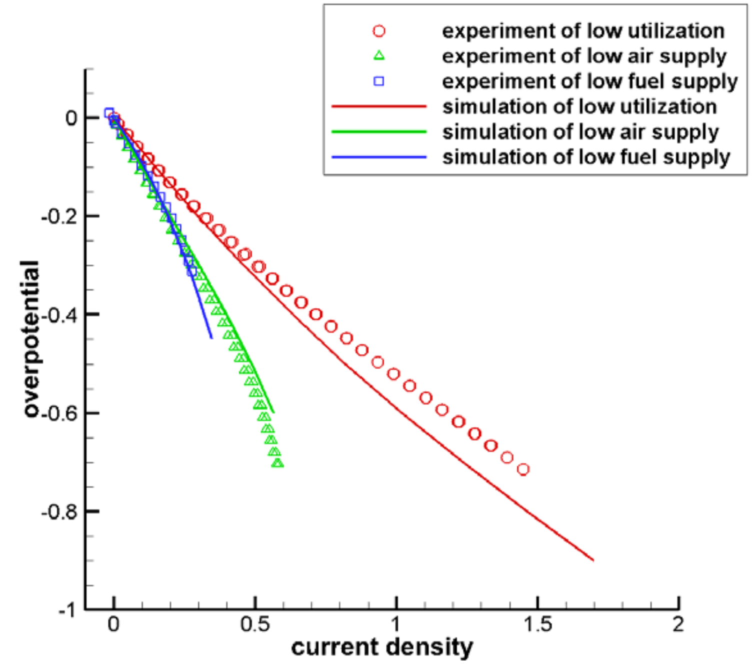


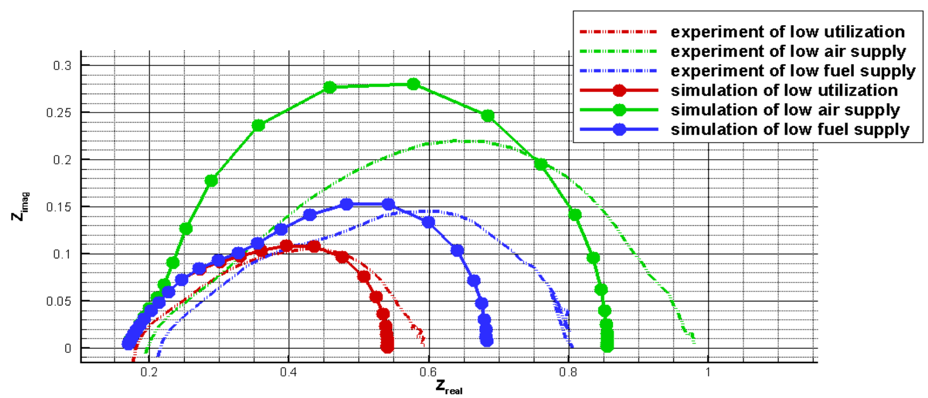
Application: *Impedance simulation to analyze cell performance*

Tool Deployment: *Modules to examine ORR and visualize cell structures*

Applications: EIS Simulation Tool

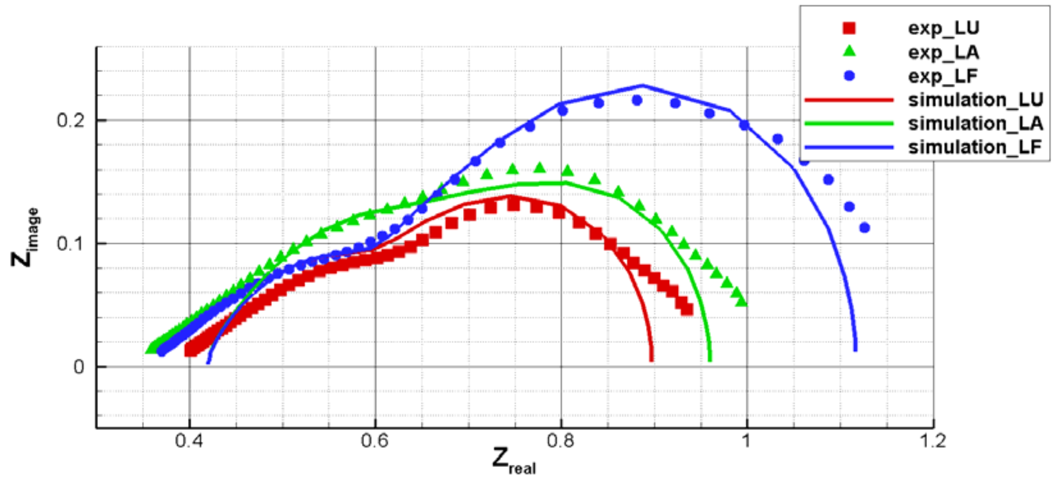
- Simulation uses **physically relevant reaction and transport processes to model VI and Impedance behavior**
- Electrode reaction mechanisms / equations defined by user
- Butler-Volmer reactions used for results at right
- Experimental data are collected for several operational configurations on the same cell
- VI simulations are generated using parameters accurate within a known range
- Dynamic modeling allows simulation of impedance

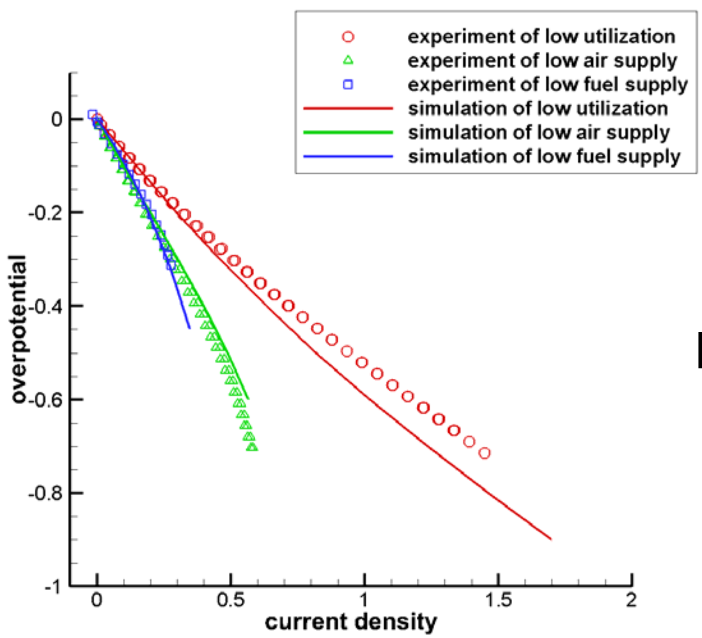


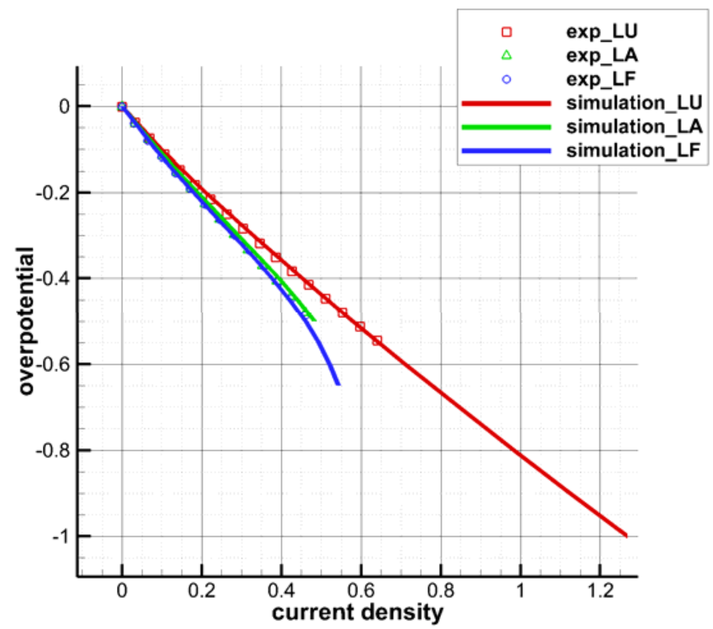


Applications: EIS Simulation Tool

- Simulation is refined to produce an accurate fit to experimental data
- Optimized parameters are re-compared to experimental results to assure physical plausibility







Applications: EIS Simulation Tool

- **In progress: Time dependent association of EIS features to model parameters (LSM system)**
- **Tool will be refined to make it accessible to R&D teams**
  - User supplies impedance data as input
  - Tool allows alteration of model and model parameters
- **Supports computationally guided electrode optimization and lifetime analysis**

- **Next project period: Validation of LSCF model**
- **Short term degradation assignments (500 hours) → Impedance v. Parameters**
  - Including analytical verification
- **Seeking: Validating data from industry teams**

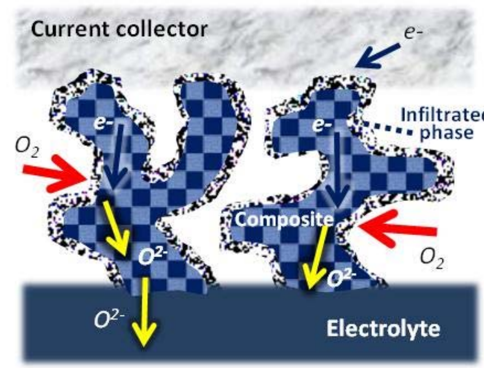
Impact: *Directly associate impedance features with a unique and definable physical process*

→ detailed understanding of manufacturer-specific degradation mechanisms

Impact

Impact: Cathode Infiltration

- **FY13 testing with commercial partner**
  - Partner 1: No discernable improvement (post operational analysis identified problem)
  - Partner 2: > 10 % power density improvement at 700°C



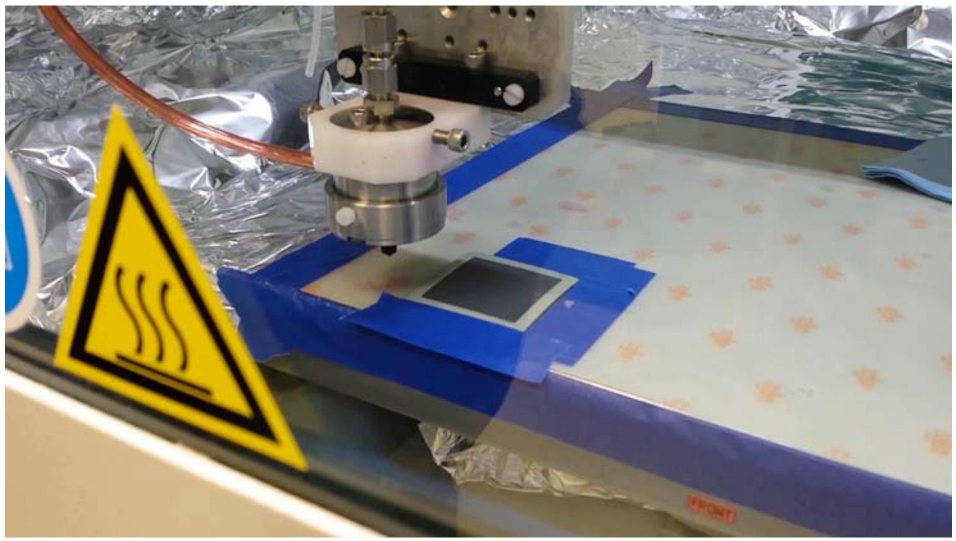
- **FY14: Repeat test with commercial partner**
  - Short stack (9 cells)
  - Cell area > 100 cm^2 manually infiltrated
  - 'Conventional' operation for 500 hours, high current density for next 2000 + hours. Air utilization raised to 50% at 1000 hours, 65% at ~1800 hours

Impact: Cathode Infiltration

- **2 cells with 'conventional' infiltrate**
  - Initially superior performance degrades over 2700+ hour test very small distinguishable improvement
- **2 cells with 'advanced' infiltrate**
  - Cells are #1 and #2 performers in 9-cell stack
  - After 2700 hours, both infiltrated cells are
    - 3% higher power than best baseline (un-infiltrated) cell
    - 20% higher power than lowest baseline cell
    - 11% higher power than avg baseline cell
  - Degradation (@ 2700 hrs)
    - 38% relative improvement over baseline cells (8% absolute)
    - Direct improvement in cell lifetime

Impact: Cathode Infiltration

- **TRL 6 complete in November 2014 –scalable manufacturing process for reliably generating 1000’s of cells**



- **Infiltrate cost today (manual process, small batches):**
  - ‘Conventional’ → $\$0.0038/cm^2$; ‘Advanced’ → $\$0.0054/cm^2$
- **Final steps: Cut cost by 50%, scale ‘1-step’ infiltration**

Impact: Cathode Infiltration

- **NETL Fuel Cell Team - Infiltration**
  - Will provide standard and advanced infiltration to SECA-associated teams for short and full stack testing
    - Strong interest in kW+ test
    - NETL team can support operational monitoring and post-operational analysis
  - Will provide complete technical details of 'standard' infiltrate
    - Detailed data from more than 4 years of testing are available
    - Provisional patent filed on advanced infiltration techniques

July 22, 2014

Thank you for your time and attention.

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the **ENERGY** lab