NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL-RUA
Regional University Alliance

NETL Carnegie Mellon PENNSTATE University of Pittsburgh VirginiaTech WestVirginiaUniversity URS

SOFC Cathode Infiltration: Performance Enhancements and Processes of Degradation

Kirk Gerdes

U.S. Dept of Energy

National Energy Technology Laboratory

Research Group Leader – Fuel Cells

U.S. DEPARTMENT OF ENERGY

Outline

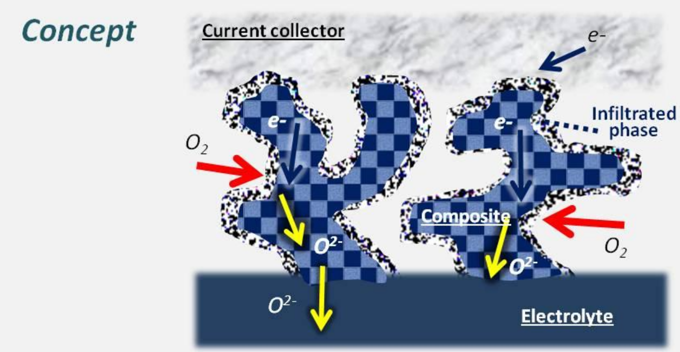
- **NETL RUA Fuel Cell Team**
- **Infiltration methods**
  - Performance metrics
  - Technologies
- **Degradation**
  - Techniques
  - Future approach
- **Summary**

NETL RUA - 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.

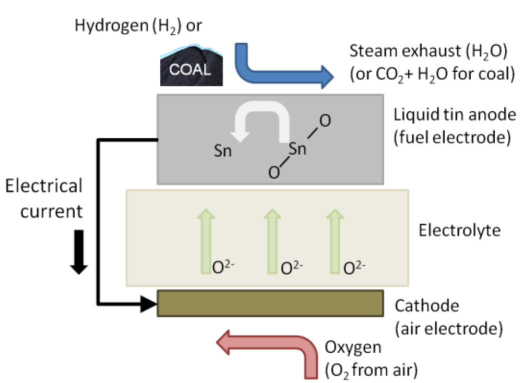


- ***Utilization of composite cathode (MIEC and ionic conductor) Backbone (Type IV) to optimize activity and stability of cathode***

Cathode infiltration technology is being developed to enhance the SOFC operating performance. Initial results have demonstrated > 50% performance improvement and acceptable material stability.

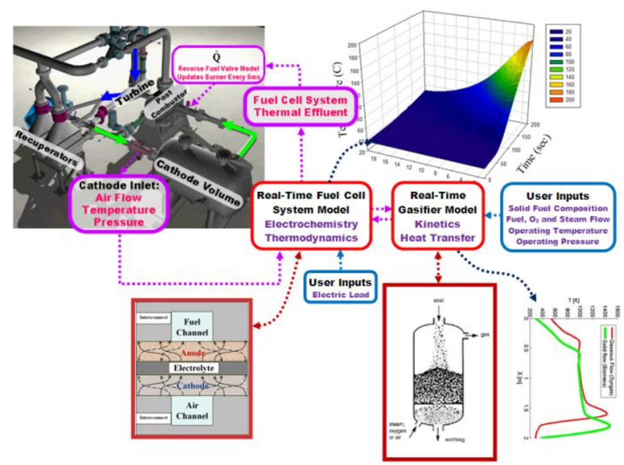
Innovate Technology

Evaluate Advanced Concepts



Liquid tin anode SOFC (at left) is an advanced direct coal to electricity concept. NETL evaluates critical transport and thermodynamic data.

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.



Cathode Engineering: Metrics of performance

- **Materials/processing cost**
  – \$175/kW stack cost, cathode estimated at 5-10%;
- **Cathode performance improvement**
  – Overpotential ~80mV at 500 mA/cm^2, 425 mW/cm2 at 0.85V;
- **Durability**
  – 0.1-1.0% loss in voltage or power / 1000 hours for full cell; and
- **Thermo-mechanical/chemical stability**
  – verified through relevant analytical tests (XRD, SEM/ESD, TEM).

- Initial performance testing completed under common conditions with standard commercial cell
  - MSRI anode supported LSM or LSCF cathode
  - Operated at 800ºC (LSM) or 750º (LSCF) in hydrogen / air
  - Operated at 0.500 A/cm^2 (typically results in 0.90 V operating potential)

Cathode Infiltration (General)

- **Application of discrete active materials into the cathode pore to enhance the electrochemical activity**
  - Electrocatalytic enhancement
  - Surface area enhancement

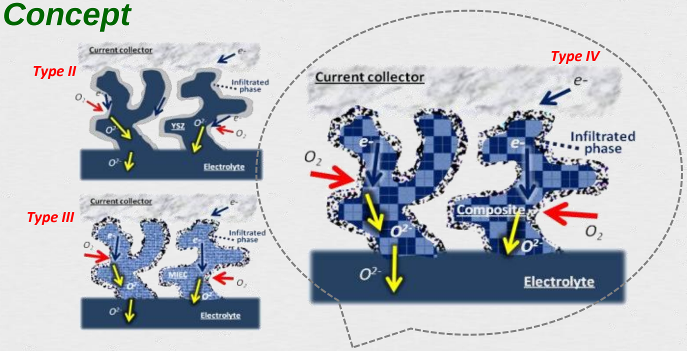
- **Diverse infiltration methods reported**
  - Colloidal suspension infiltration
  - Aqueous solution infiltration
    - Citrate, glycine, and Pechini methods
  - Modified versions of these methods
    - Control pH, viscosity, hydrophilicity, pre-cursor solubility

- **More combinations of materials, test conditions, and microstructures than can be reasonably tested**
    - Functional processes exist, but innovation is suppressed

MIEC Cathode Infiltration Project
Lee/Manivannan (NETL)

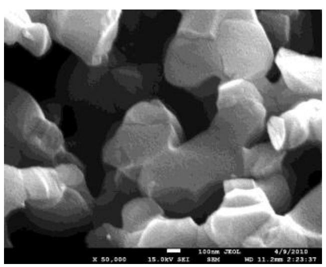
High Performance SOFC with active and stable cathode by application of controlled *infiltration* process

Concept

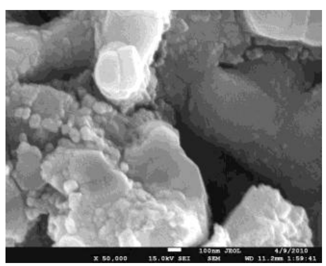


➢ ***Utilization of composite cathode (MIEC and ionic conductor) backbone (Type IV) to optimize activity and stability of cathode.***

Infiltration Microstructure

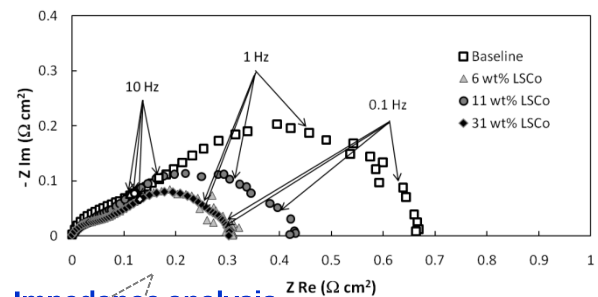


Baseline composite cathode (SDC+LSCF)



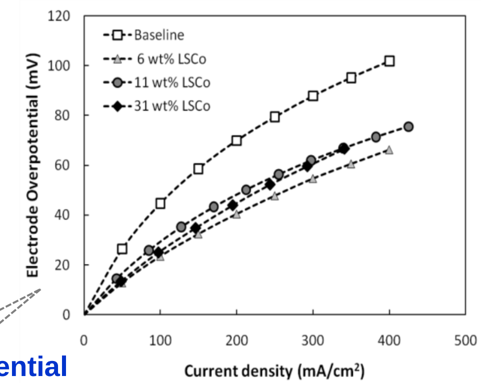
LSCo Infiltrated Cathode (LSCo: $La_{0.6}Sr_{0.4}CoO_3$)

Infiltration Performance



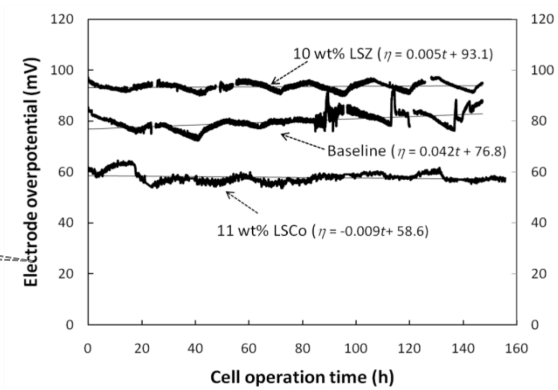
Impedance analysis

Polarization resistance decreased by 38-60%



Electrode overpotential

Overpotential reduced to 58% of that of baseline cell



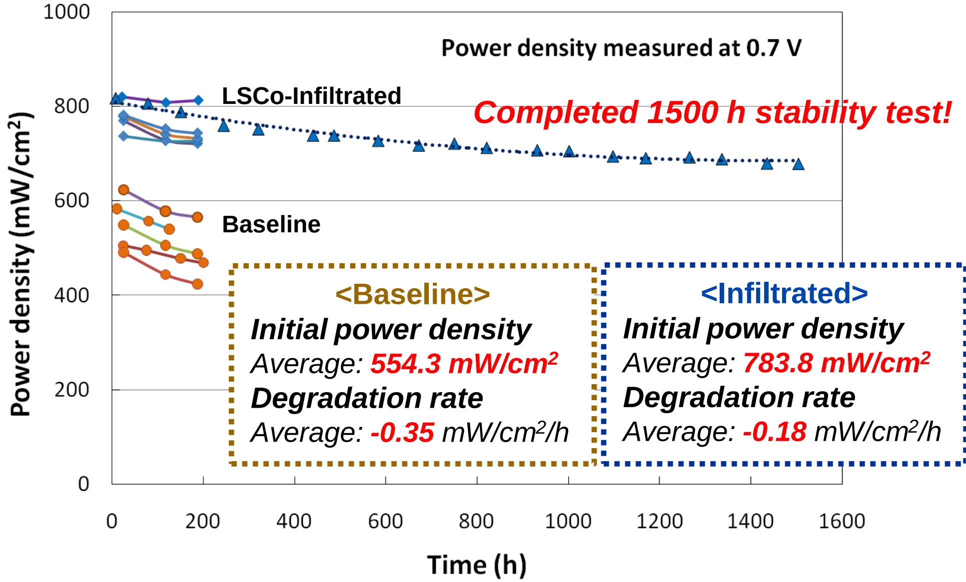
Stability

No degradation in cell voltage for >150 hrs

✓ ***A composite cathode of a commercial cell was successfully modified with LSCo infiltration.***
✓ ***Infiltration methodology correlating dosage to structure was developed.***
✓ ***Effects of electrocatalytic activity of infiltrated materials on cathode performance were demonstrated.***

Electrocatalytic Cathode Infiltration
Lee/Manivannan (NETL)

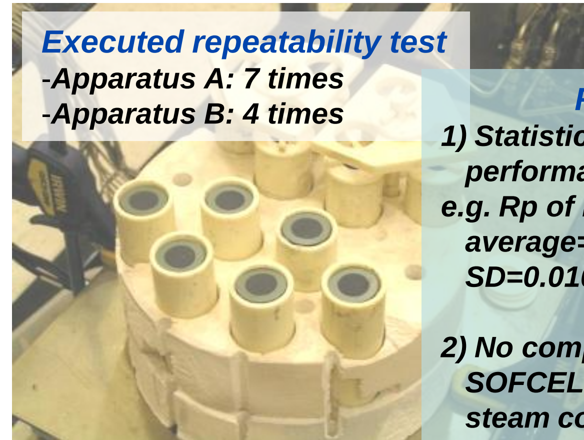
Stability of infiltrated cathode



<Baseline>
Initial power density
*Average: **554.3 mW/cm²***
Degradation rate
*Average: **-0.35** mW/cm²/h*

<Infiltrated>
Initial power density
*Average: **783.8 mW/cm²***
Degradation rate
*Average: **-0.18** mW/cm²/h*

Repeatability test of MCA (Multi-cell array)



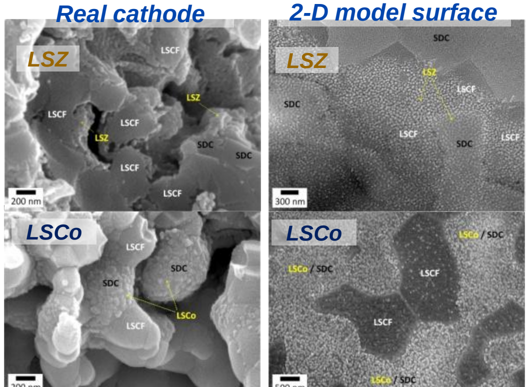
Executed repeatability test
-Apparatus A: 7 times
-Apparatus B: 4 times

Results
1) Statistically reliable in performance comparison
e.g. Rp of LSCF-MSRI (8ea) average=0.202 (Ωcm²), SD=0.010, %SD < 5%.

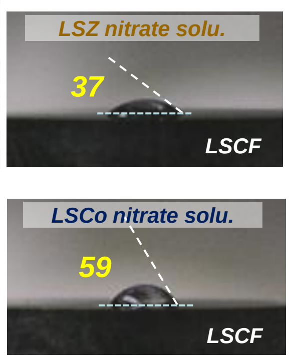
2) No comparability with SOFCEL under different steam content / current collection method.

Cathode microstructure control: Wettability

Real cathode | *2-D model surface*



Sessile drop test



Approach

1) Set up model experiments.

2) Variables: *surface tension of solution & hydrophobicity of backbone.*

Publications

1. R. Chao, J. R. Kitchin, K. Gerdes, E. M. Sabolsky, and P. A. Salvador, "**Preparation of Mesoporous $La_{0.8}Sr_{0.2}MnO_3$ Infiltrated Coatings in Porous SOFC Cathodes Using Evaporation-Induced Self-Assembly Methods**" ECS Transactions, 35 (1) 2387-2399 (2011)

2. Shiwoo Lee, Nicholas Miller, Harry Abernathy, Kirk Gerdes, and Ayyakkannu Manivannan "**Effect of Sr-doped $LaCoO_3$ and $LaZrO_3$ Infiltration on the Performance of SDC-LSCF Cathode.**" J. Electrochem. Soc., Volume 158, Issue 6, pp. B735-B742 (2011)

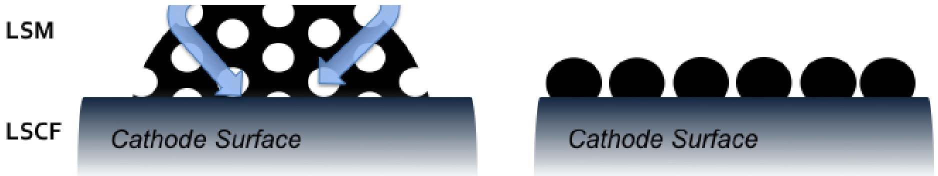
3. Shiwoo Lee, Nicholas Miller and A. Manivannan "**Microstructural Control of Composite Cathode by Wetting Nature of Infiltrated Solution.**" ECS Trans., 35 (1) 2401-2407 (2011)

Presentations

1. Shiwoo Lee, Nicholas Miller, Harry Abernathy, Kirk Gerdes, and Ayyakkannu Manivannan "**Modification of SDC-LSCF cathode functional layer by solution infiltration.**" CACC-S3-030-2011, 35th ICACC, Daytona beach (2011)

Mesoporous Electrocatalysts Coating
Salvador / Chao (CMU)

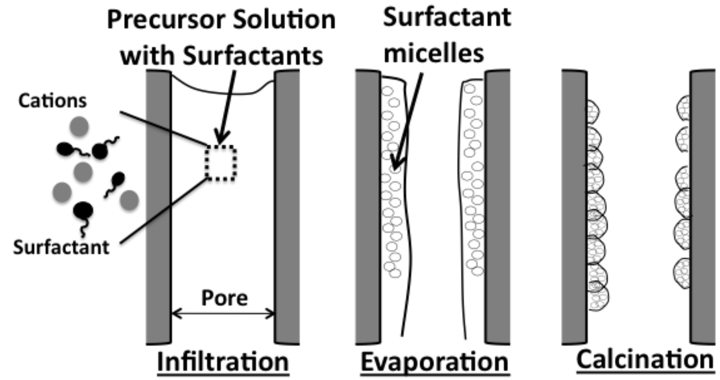
Mesoporous Infiltration: Inverse Nanoparticles — ***Typical Infiltration: Nanoparticles***



Improvements for Mesoporous Infiltrations

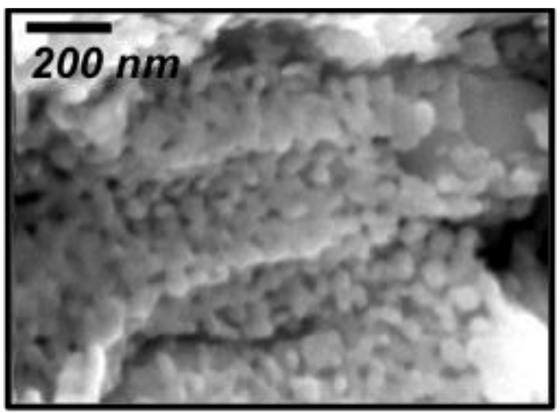
1. *Higher surface areas for O_2 adsorption*
2. *Contiguous solid and pore networks of infiltrates*
3. *Thermal Stability Demonstrated (wall thickness /pore diameters)*
4. *Surfactant controls the microstructure*
5. *Large catalyst loading possible and demonstrated*

Evaporation-induced Self-assembly

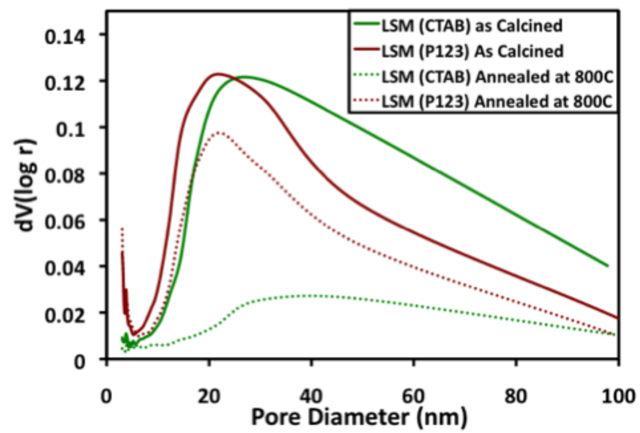


High catalyst loading (10 wt%) can be achieved in single infiltration step

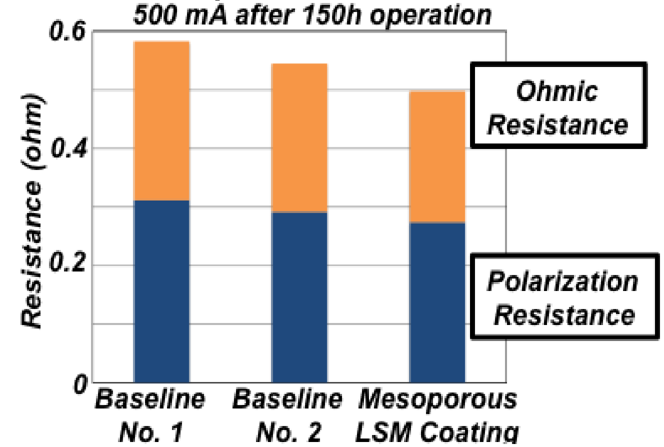
Inverse LSM Nanoparticles
2 mol/L Infiltrated with CTAB in 1 step



Stability of Mesoporous Powders
P123 has thicker pore walls

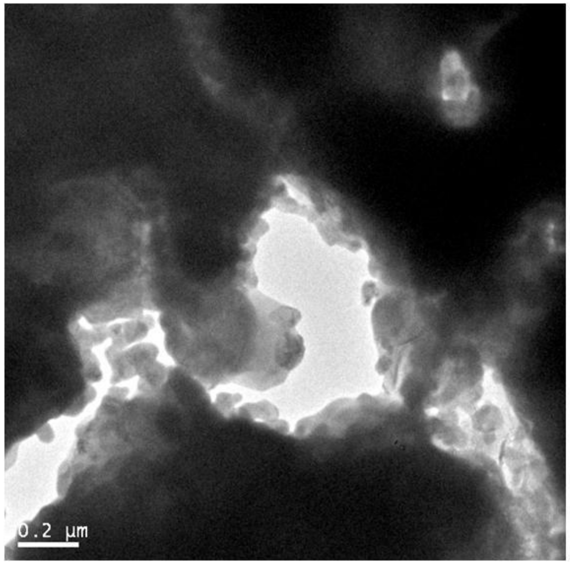


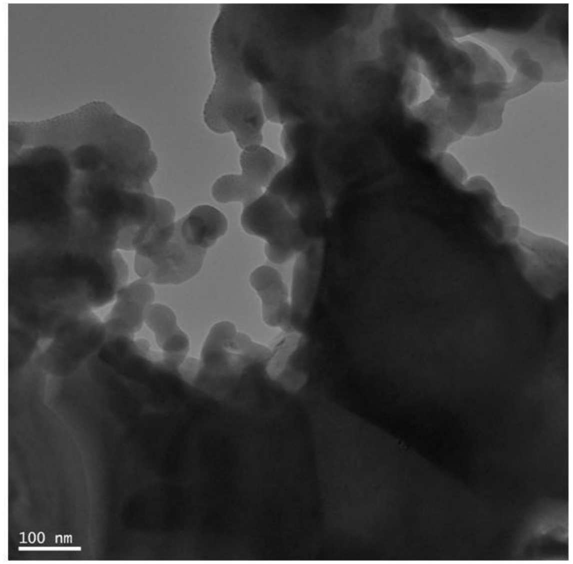
12 % Improvement in Resistance with Mesoporous Infiltration
500 mA after 150h operation

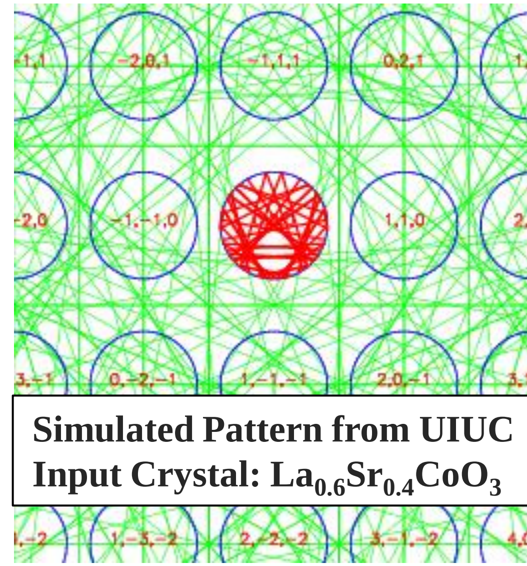


Coating morphology is currently being optimized to enhance the infiltrated cathode performance

Mesoporous Electrocatalysts Coating
Salvador / Chao (CMU)



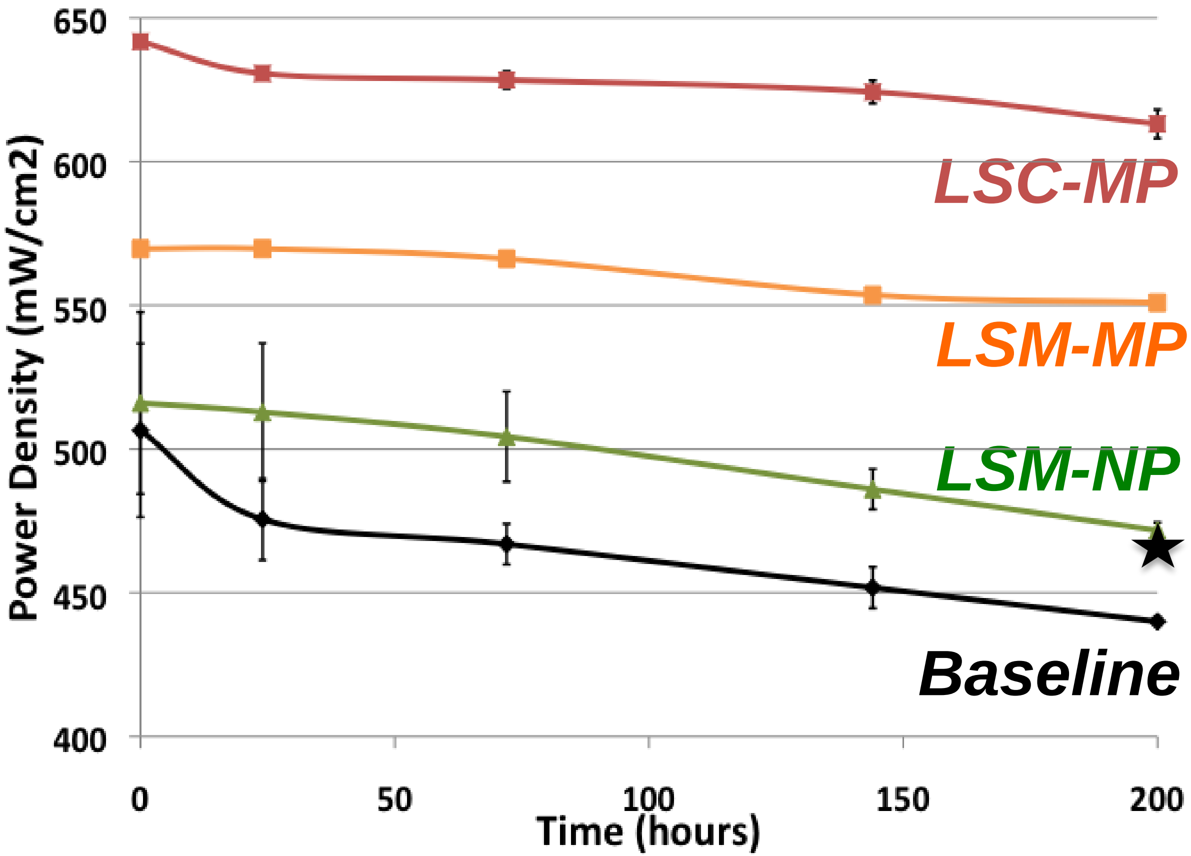




Simulated Pattern from UIUC
Input Crystal: $La_{0.6}Sr_{0.4}CoO_3$

- The coatings were uniformly applied to the functional layer pore walls
- The infiltrated coatings have nanostructured porous structure with pore size about 30-50 nm (measured using ImageJ)
- Consistent with cubic perovskite with lattice parameter of 3.854

Average Power Density vs. Time
Salvador/Chao (CMU/NETL)



Averaged from 2 cells tested

★*: Baseline avg. from 10 cells: 464 mW/cm^2*

Overall Degradation Rate (mW/hr)

Baseline #1	0.41
Baseline #2	0.16
LSM-MP-2M #1	0.11
LSM-MP-2M #2	0.12
LSC-MP-2M #1	0.12
LSC-MP-2M #2	0.11
LSM-NP #1	0.39
LSM-NP #2	0.06

- All infiltrated cells showed improved performance
- Mesoporous LSM coatings generate higher power density than nanoparticle LSM infiltrates
- Cells infiltrated with LSC showed higher power density than those with LSM coatings
- Mesoporous coating infiltrated cells showed consistent degradation rate reduction

Power Density Improvement (compared to the baseline)

	At 0 hour	At 200 hour
LSM-NP	2%	7%
LSM-MP-2M	12%	25%
LSC-MP-2M	27%	39%

Possible Causes of Infiltrated Cathode Degradation with Time

Lee (NETL)

1. Particle Coarsening (sintering)

- Loss of active electrochemical reaction area

2. Decomposition (Phase segregation) of infiltrated material

- e.g. Sr exsolution leading to reduced acceptor dopant concentration

3. Interdiffusion at Interfaces

-Chemical reaction with electrolyte (Perovskite-YSZ)

-Ni diffusion cause LSM coarsening and densification

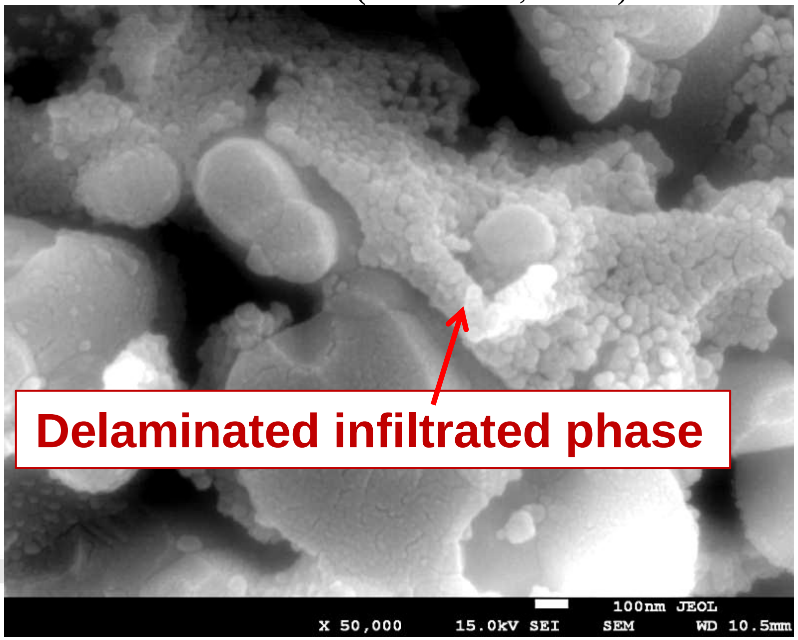
4. Delamination (Spallation)

-Reduction in contact area

5. Formation of resistive phases

- Gaseous impurities

Infiltrated MSRI cathode (Shiwoo Lee, NETL)



Possible Causes of Infiltrated Cathode Degradation with Time

Lee (NETL)

1. Particle Coarsening (sintering)
- Loss of active electrochemical reaction area

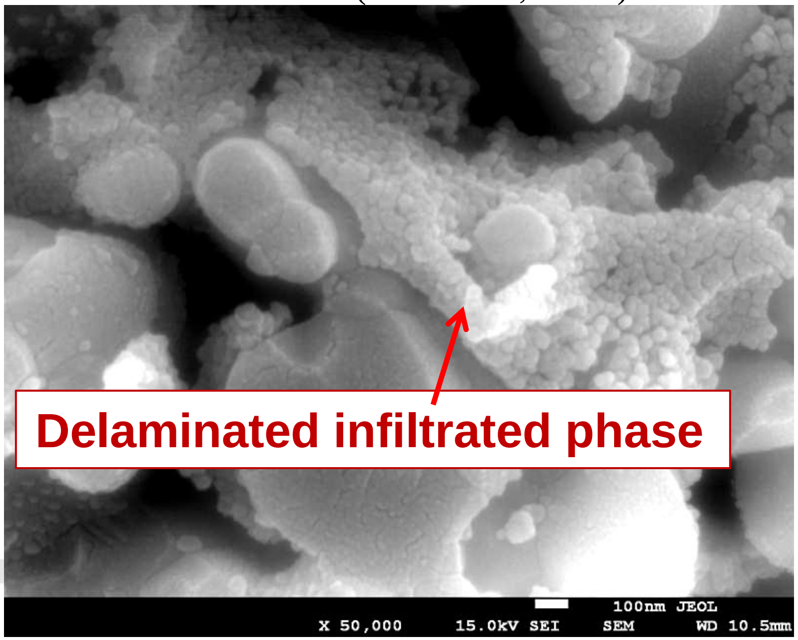
2. Decomposition (Phase segregation) of infiltrated material
- e.g. Sr exsolution leading to reduced acceptor dopant concentration

3. Interdiffusion at Interfaces
-Chemical reaction with electrolyte (Perovskite-YSZ)
-Ni diffusion cause LSM coarsening and densification

4. Delamination (Spallation)
-Reduction in contact area

5. Formation of resistive phases
- Gaseous impurities

Infiltrated MSRI cathode (Shiwoo Lee, NETL)

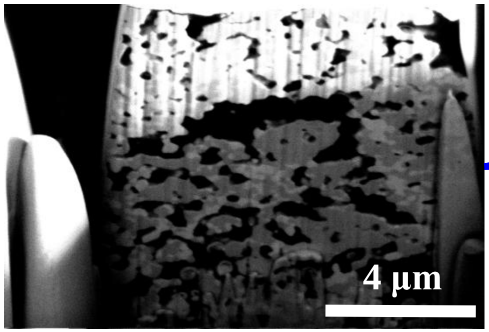


Approach to Degradation Modeling

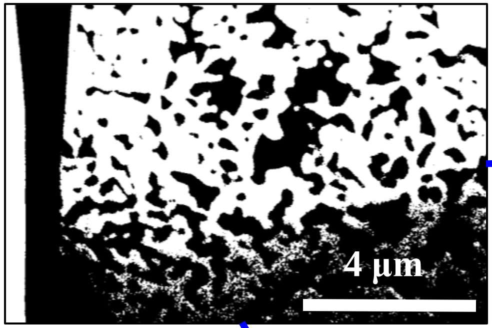
1. **Characterize the initial microstructure (backbone plus infiltrate)**
2. **Describe the microstructural evolution**
3. **Inform the evolution model's kinetic and thermodynamic relationships with targeted experiments**
4. **Compare computational predictions to final microstructure**

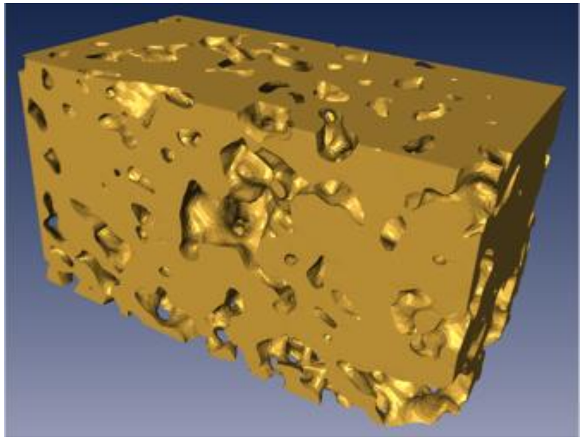
3D microstructural reconstruction
Salvador / Miller / Ohodnicki (CMU/NETL)

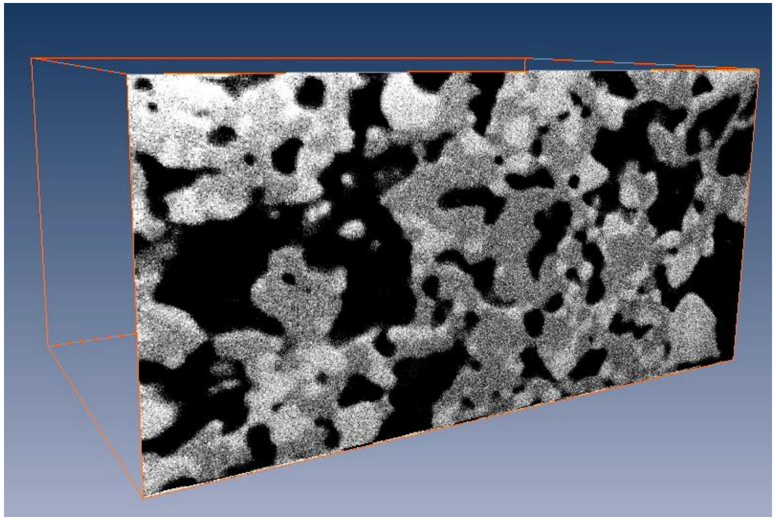
Cathode Reconstruction:
FIB-SEM: ***TLD***
Active Region

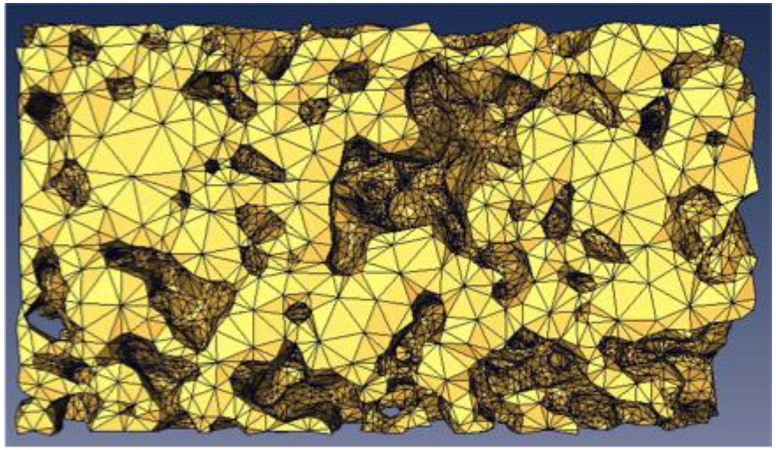


Current Collector Region:
binary thresholded image









Reconstructed volume = 54 µm^3
5.65 µm^3 x 3.15 µm^3 x 3 µm^3 (60-50 nm slices)

- pores = 29 % volume
- pore/LSM surface area per volume = 4.57 $\boldsymbol{l}^{-1}$

- Continuing to explore 3d x-ray tomography technique – promising first dataset; calibration problems with 3D reconstruction

***Reconstruct 3D sections of SOFCS ---- Generate statistical metrics** --- input to models --- correlate to performance*

Phase Field Method
Chen / Li (PSU)

Description of Project

1. Develop a phase-field model for temporally evolving three-phase SOFC cathode microstructures.
2. Couple gas, electronic, and ionic transport equations with phase-field model of microstructure evolution to study the effect of local electrochemical conditions on microstructure degradation.
3. Compare simulation results with experimental microstructures obtained under different thermal/electric conditions such as temperature and average overpotential for validation

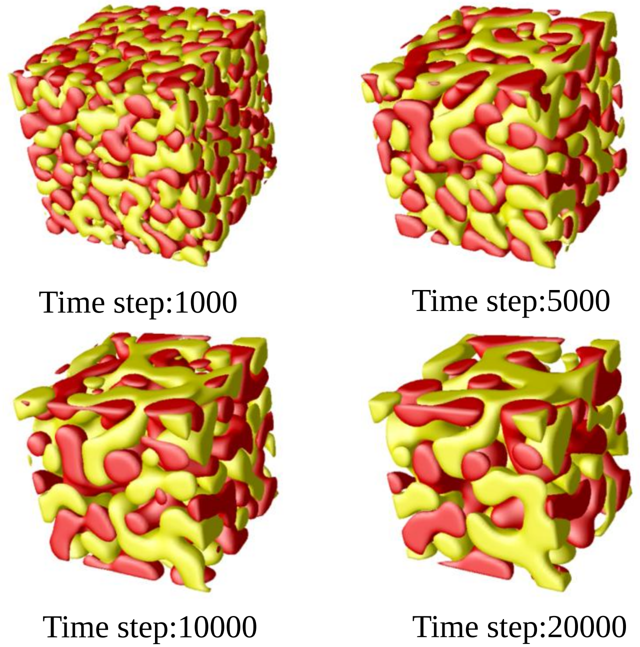
A preliminary Phase Field model of 3D 3-phase cathode microstructure is developed

YSZ	LSM
$C(r)=C_\beta \quad \eta_1=1$	$C(r)=C_\alpha \quad \eta_i=0$
$C'(r)=C_\alpha \quad \eta_i'=0$	$C'(r)=C_\beta \quad \eta_1'=1$

Pore $C(r)=C'(r)=C_\alpha \quad \eta_i=\eta_i'=0$

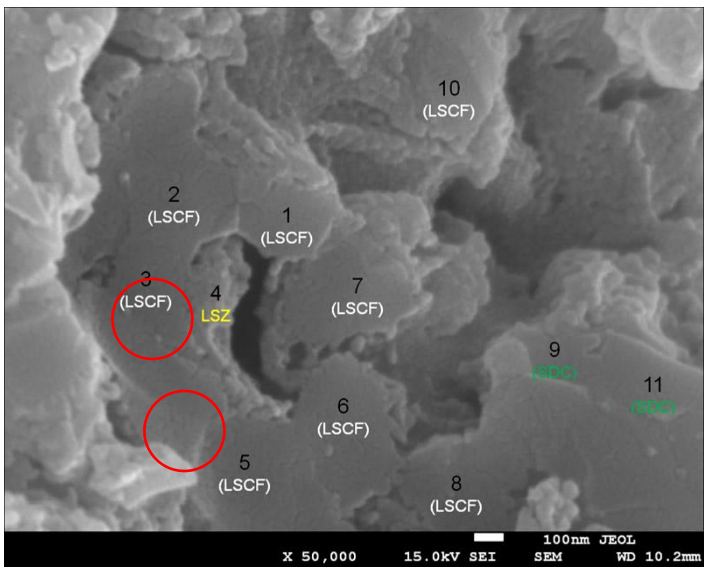
Two concentration fields *C* and *C'* are used to define compositions of LSM and YSZ. The temporal evolution of the field variables is described by Cahn-Hilliard Equations

$$\frac{\partial C_i(\mathbf{r},t)}{\partial t}=\nabla\left(M_i\nabla\frac{\partial F}{\partial C_i(\mathbf{r},t)}\right)$$



Creep Microbeam Bending
Messing/Kupp/H.Lee (PSU)

- **Creep microbeam bending measurement**
  - Model stress evolution of infiltrated system during processing and operation
  - Multilayer structures used to approximate thickness and density variations of the infiltrated system
  - Data used to calculate stress evolution in the infiltrated system



LSCF/SDC cathode infiltrated with LSZ material (Shiwoo Lee, NETL)

➔ *Thickness dependence*

➔ *Density dependence*

Summary

- **Cathode infiltration is possible and performance has been demonstrated for single chemistry**
- **Degradation issues have been initially investigated but more thorough characterization (1+ khr) is required**
- **Degradation can be simulated through a computational framework supported with direct experiments**
- **Computational/modeling framework has been formulated and initial results generated for each framework component**

Acknowledgements

- **NETL RUA**
  - Shiwoo Lee, A. Manivannan (NETL)
  - Paul Salvador, Robin Chao (CMU)
  - Gary Messing, Libby Kupp, Haijoon Lee (PSU)
  - LongQing Chen, Qun Li, Liangjun Li (PSU)
  - Nicholas Miller (URS)