July 15, 2015

NETL Office of Research & Development

Solid Oxide Fuel Cell Team

the **ENERGY** lab

Kirk Gerdes

Lead Engineer – Thermal Sciences Division

Research Group Leader – Fuel Cells

U.S. DEPARTMENT OF ENERGY

Outline

- **NETL ORD research in context of SECA program**
- **Domain of expertise; Broad overview / approach**
- **Developments**
  - Interfacial cation diffusion
  - Electrocatalysts to mitigate degradation
- **Applications / Impacts**
  - Cathode infiltration
- **FY16 Research Portfolio / Conclusions**

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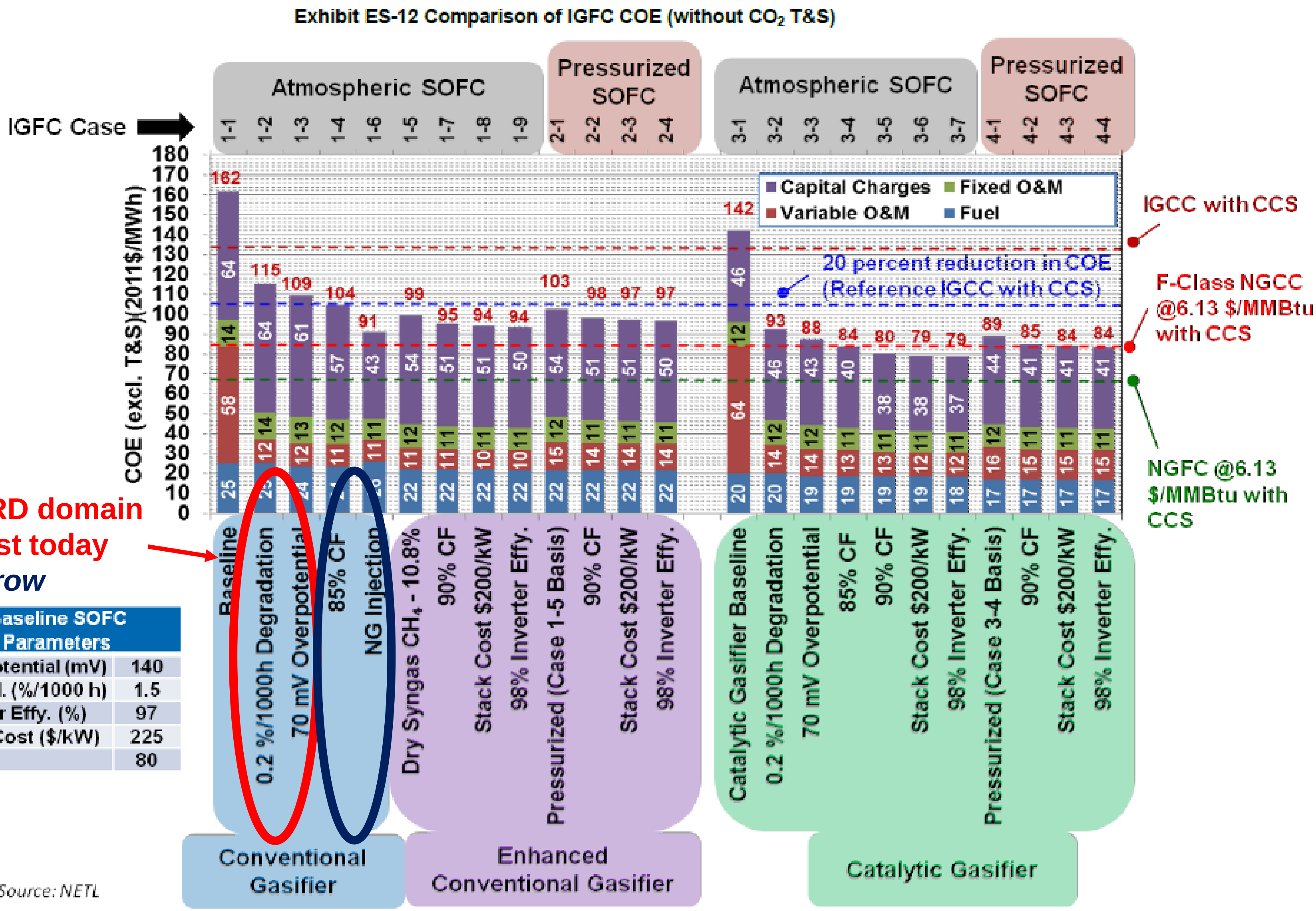
Techno-Economic Analysis



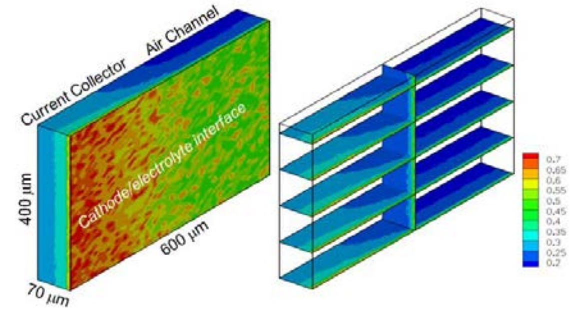
NETL ORD domain of interest today *& tomorrow*

Baseline SOFC Parameters	
Overpotential (mV)	140
Degrad. (%/1000 h)	1.5
Inverter Effy. (%)	97
Stack Cost ($/kW)	225
CF (%)	80

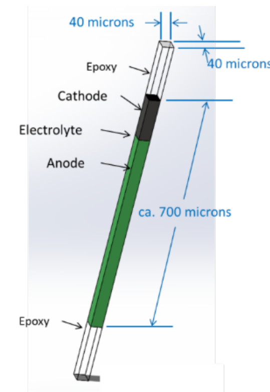
Arun Iyengar, Richard Newby, and Dale Keairns – Booz Allen Hamilton; "Techno-economic analysis of integrated gasification fuel cell systems created by ESPA for SEAP and OPPB" Nov 24, 2014, http://www.netl.doe.gov/research/energy-analysis/publications/listing?progcat=fuelcells

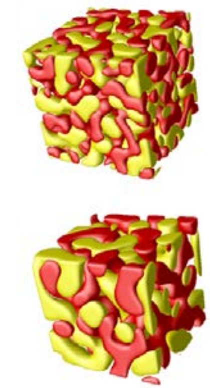
Enhance Fuel Cell Performance for the Fossil Energy Fuel Cell Program

- **NETL ORD Fuel Cell Team supports SECA program**
  - ***Reduce*** *cell production / operation costs*
  - ***Enhance*** *cell activity / efficiency*
  - ***Improve*** *cell lifetime (40+ khr)*

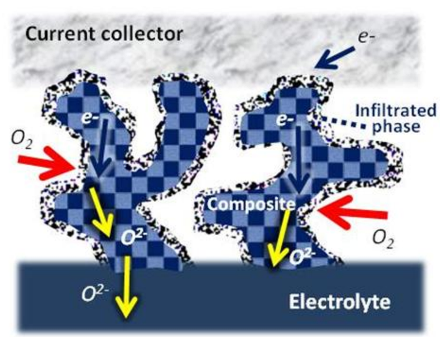


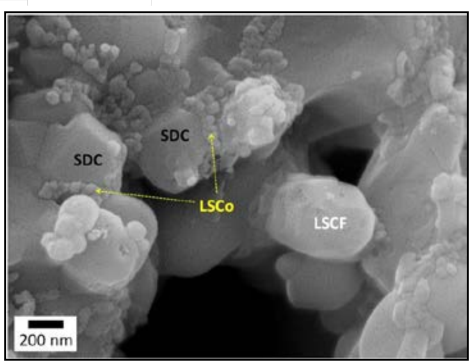
- **Major research tasks**
  - **Cell performance and degradation**
    - Complete 3D multi-physics informed with actual electrode microstructures
    - Evolution of grains and appearance of secondary phases





  - **Electrode engineering**
    - <u>Cathode infiltration</u>
      Efficient oxygen reduction
    - <u>Anode infiltration</u>
      Enhanced fuel reforming





Program requests → ORD deliverables

Development → **SOFC Hurricane Model Components**

Pre-FY16
1) LSM + LSCF ORR
2) Nano-CT (AEC)
3) 3D multi-physics
4) Phase-field model
5) Cathode infiltration
6) Anode infiltration
7) ECR + Ionic Cond + Aging + UQ

FY16
1) Infiltrate ORR
2) Structural analysis
3) On-cell CH4
4) PF + ab initio
5) CI for H2O + CO2
6) AI commercial
7) ECR + Ionic Cond + Aging + UQ

Post-FY16
1) Scale-bridging
2) In-situ methods
3) MP Cell → System
4) PF Atoms → Cells
5) 2nd Gen CI, AI
6) Fundamental examinations
7) UQ

Application → **Lifetime operational performance tool**

Pre-FY16:
1) ORR tool deployed to high power computing env
2) Impedance tool and diagnostic methodologies
3) Cathode infiltration @ TRL 6

FY16:
1) Microstructural evolution tool deployed to SBEUC
2) Structural analysis tools on SBEUC + visualization
3) Anode infiltration @ TRL 5

Post-FY16:
1) Integrated tool coupling domains (atoms to systems)
2) Complete physics and structural visualization tools
3) CI,AI Gen 2 @ TRL 6

Lifetime operational performance tool, variable materials, structure, operating conditions → 40 khr performance analysis and predictions

Impact → **Lower cost of electricity Improved durability Accelerate innovation**

Pre-FY16: Cathode infiltration adopted by industry, 5% improved power density, 30% improved lifetime

FY16: Anode infiltration adopted by industry. Impedance tools accel diagnostics. Vis tool accessed by more than 100 users.

Post-FY16: NETL FC Team: Decr system cost 10% Improve power 30% Increase lifetime 50% Accel innovation

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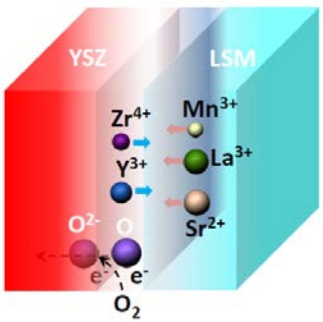
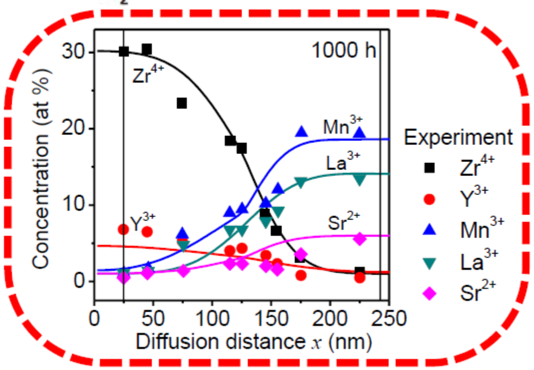
Interfacial Cation Diffusion

Modeled and experimentally validated descriptions of Interfacial cation diffusion via Phase Field Model



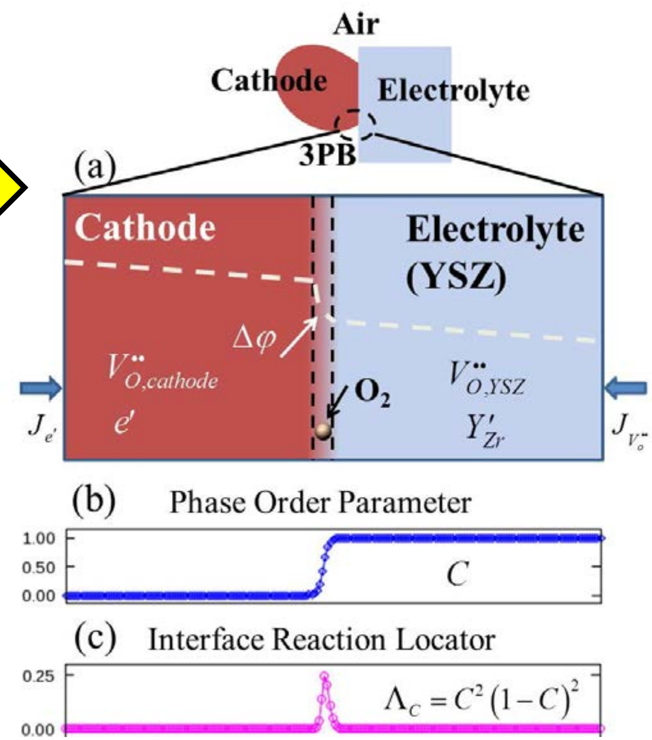
Model system describes cation diffusion across YSZ/LSM interface at 1000°C held for 1000 hours



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

Original model:
Cation Chemical Diffusion only

Updated model:
Vacancies Included with Electrostatic Potential

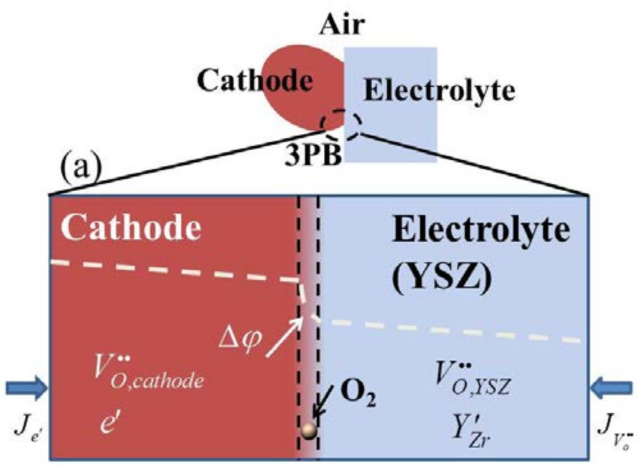


Jia-Mian Hu, Linyun Liang, Yanzhou Ji, Liang Hong, Kirk Gerdes, Long-Qing Chen. "Interdiffusion across solid electrolyte-electrode interface" Applied Physics Letters 104 (2014) 213907

Liang Hong, Jia-Mian Hu, Kirk Gerdes, Long-Qing Chen. "Oxygen Vacancy Diffusion across Cathode/Electrolyte Interface in Solid Oxide Fuel Cells: An Electrochemical Phase-Field Model" J. Power Sources 287 (2015) p396

Interfacial cation diffusion

Model created to represent diffusion immediately at 3PB

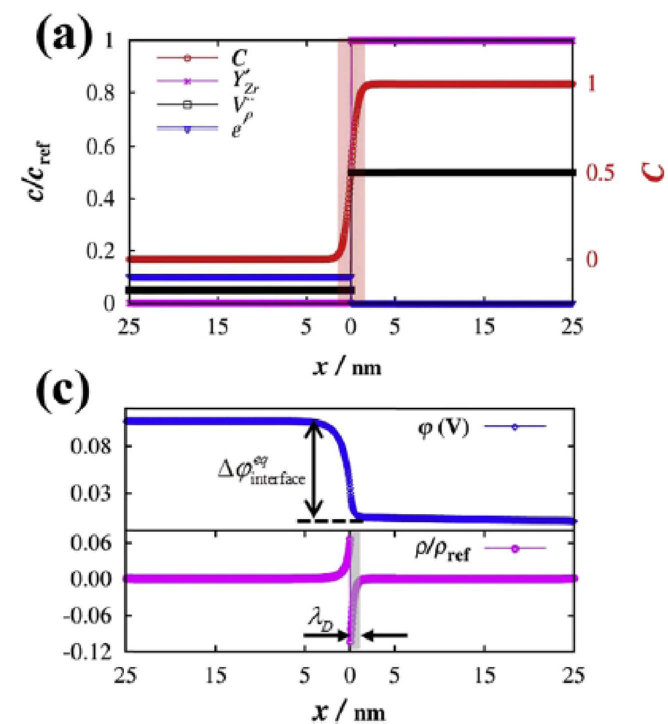


Interfacial Oxygen Exchange

$\frac{1}{2} O_2 + 2e' + V_{\ddot{O},\,YSZ} \rightarrow O^{\times}_{O,\,LSM}$

Electrolyte Vacancy Formation (Extrinsic Defect)

$Y_2O_3 + 2Zr^{\times}_{Zr,\,LSM} + O^{\times}_{O} \rightarrow 2Y'_{Zr} + V_{\ddot{O}} + 2ZrO_2$



The electrochemical potential of a species i is expressed as,

$$\overline{\mu}_i = \mu_i^0 + k_B T \ln a_i + z_i e \varphi, \quad i \in \{V_O^{\cdot\cdot}, e', Y'_{Zr}\} \qquad (2)$$

$$\frac{\partial c_i(x,t)}{\partial t} = -\nabla \cdot J_i - R_i^{3PB} K \Lambda_C = \nabla \cdot \frac{D_i c_i}{k_B T} \nabla \mu_i^0 + \nabla \cdot D_i \nabla c_i(x,t) + \nabla \cdot \frac{D_i z_i e c_i}{k_B T} \nabla \varphi - R_i^{3PB} K \Lambda_C, \qquad (4)$$

Liang Hong, Jia-Mian Hu, Kirk Gerdes, Long-Qing Chen. "Oxygen Vacancy Diffusion across Cathode/Electrolyte Interface in Solid Oxide Fuel Cells: An Electrochemical Phase-Field Model" J. Power Sources 287 (2015) p396

Interfacial cation diffusion

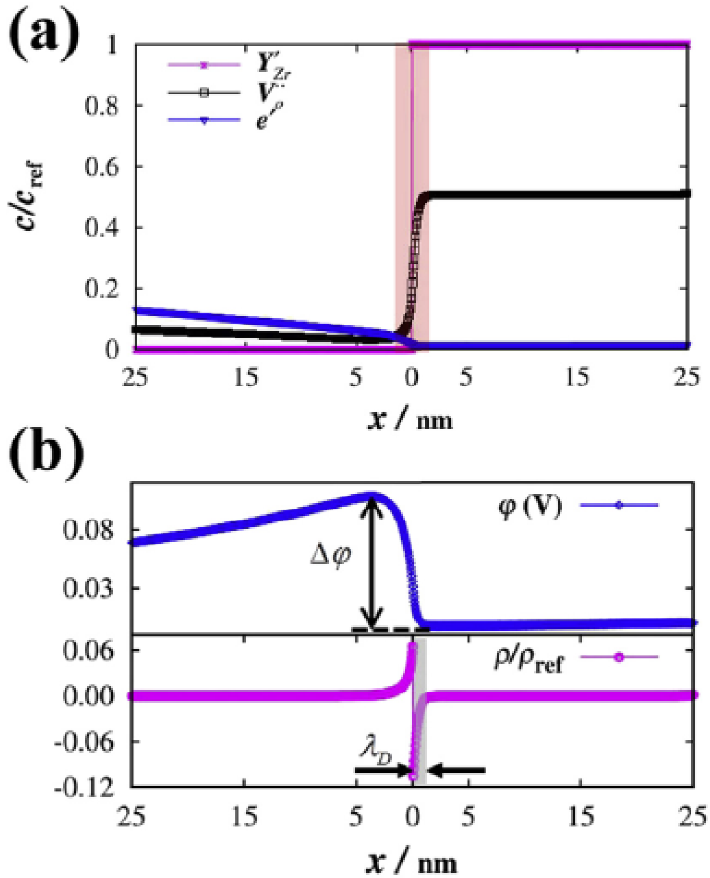


Fig. 3. (a) Equilibrium distributions of $c_{Y'_{Zr}}$, $c_{V^{\cdot\cdot}_O}$ and $c_{e'}$, and (b) φ and ρ with $i_a = -8 \times 10^6$ A m^{-2}. The central light red region represents the interface defined by order parameter C. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

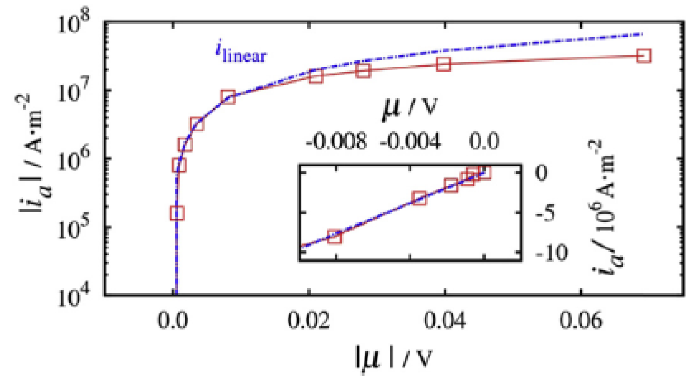


Fig. 4. Magnitude of the current i_a as a function of the overpotential μ, plotted on log-linear and linear (inset figure) scales. The dash-dot line is a plot of the linear current–overpotential relation $i_a = i_0 \frac{F}{RT} \mu$ for $i_0 = 1.15 \times 10^8$ A m^{-2}.

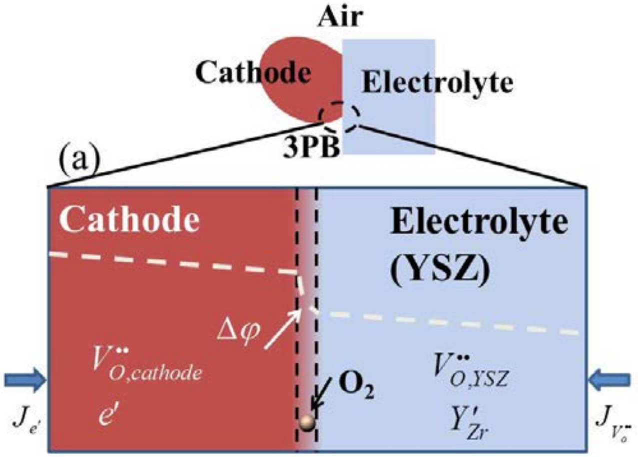
- **Oxygen vacancies and electrons equilibrate rapidly**
- **Oxygen vacancy profile minimum at 3PB results from model assumptions**
- **I/V relationship well-matched to linear (pure resistor) model at low voltages**

Liang Hong, Jia-Mian Hu, Kirk Gerdes, Long-Qing Chen. "Oxygen Vacancy Diffusion across Cathode/Electrolyte Interface in Solid Oxide Fuel Cells: An Electrochemical Phase-Field Model" J. Power Sources 287 (2015) p396

Interfacial cation diffusion

Next Steps (FY16)

- Replace simple vacancy exchange reaction model with real 3PB ORR model
- Add vacancy and lattice oxygen transport across 2PB
- Update interface (e.g. D_v) according to interface function or actual compositional variations and compare results to static property case



Tool

- Accurately describe cation evolution in critical interfaces of cathode and anode
- Establish composition predictions to be used as basis for comp chem
- Predict and measure evolved interface properties

Impact: Approach provides fundamental basis for performance evolution predictions that address reliability

Liang Hong, Jia-Mian Hu, Kirk Gerdes, Long-Qing Chen. "Oxygen Vacancy Diffusion across Cathode/Electrolyte Interface in Solid Oxide Fuel Cells: An Electrochemical Phase-Field Model" J. Power Sources 287 (2015) p396

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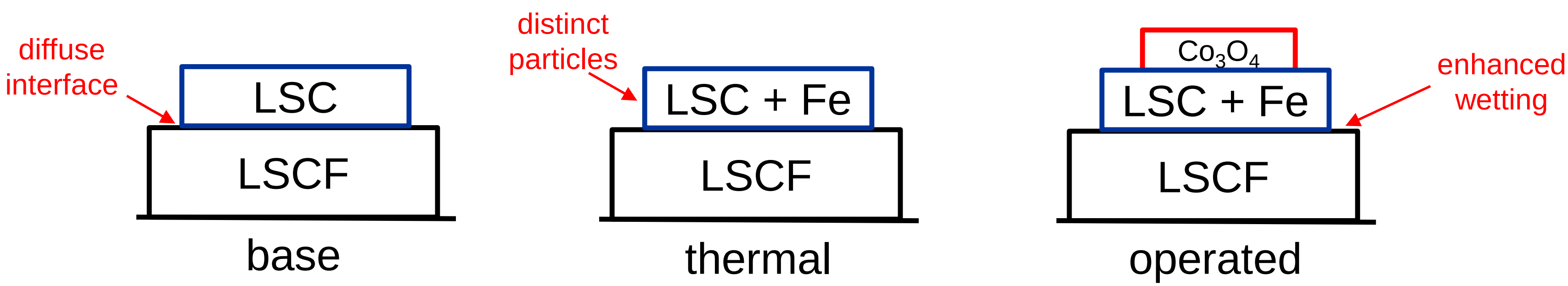
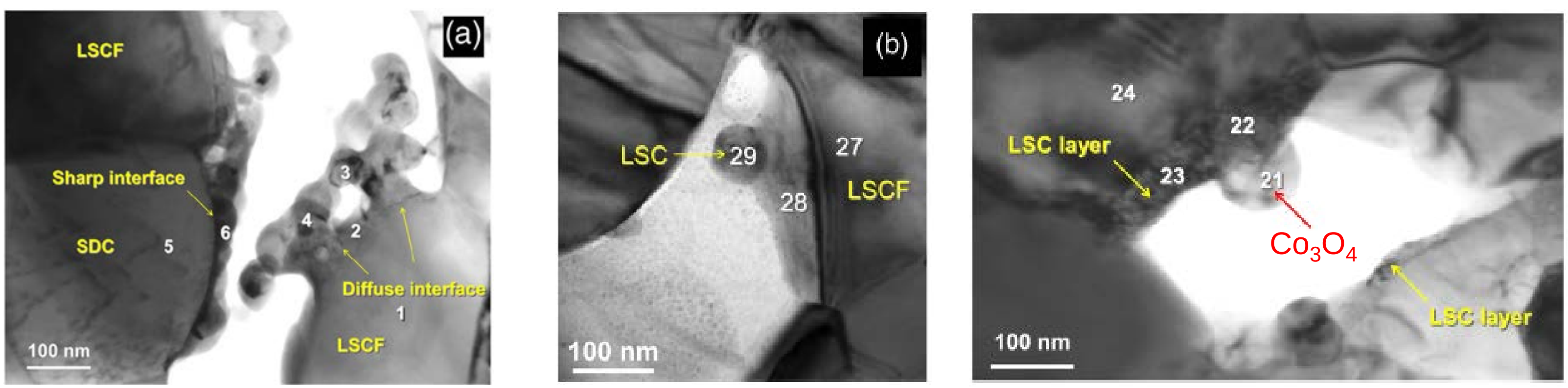
Electrocatalysts to mitigate degradation

Examine infiltrate stability in SDC/LSCF cathode backbone

- **Controlled Systems**
  - Base SDC/LSCF backbone with LSC infiltration (as fabricated)
  - Same system thermally aged 1500 hours in air
  - Same system operated 1500 hours in conventional state
- **TEM analysis revealed significant structural differences**



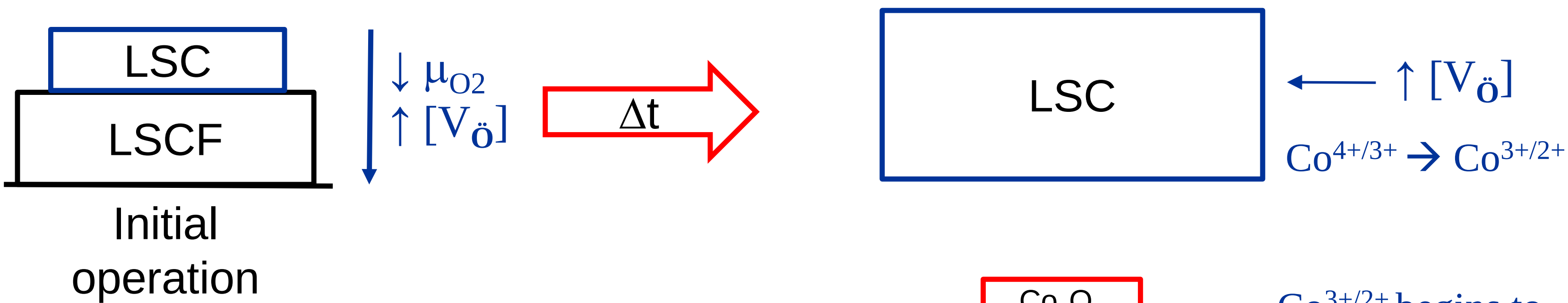


Xueyan Song, Shiwoo Lee, Yun Chen, Kirk Gerdes. "Electrochemically influenced cation interdiffusion and Co_3O_4 formation on $La_{0.6}Sr_{0.4}CoO_3$ infiltrated into SOFC cathodes" Solid State Ionics 278 (2015) p91.

Electrocatalysts to mitigate degradation

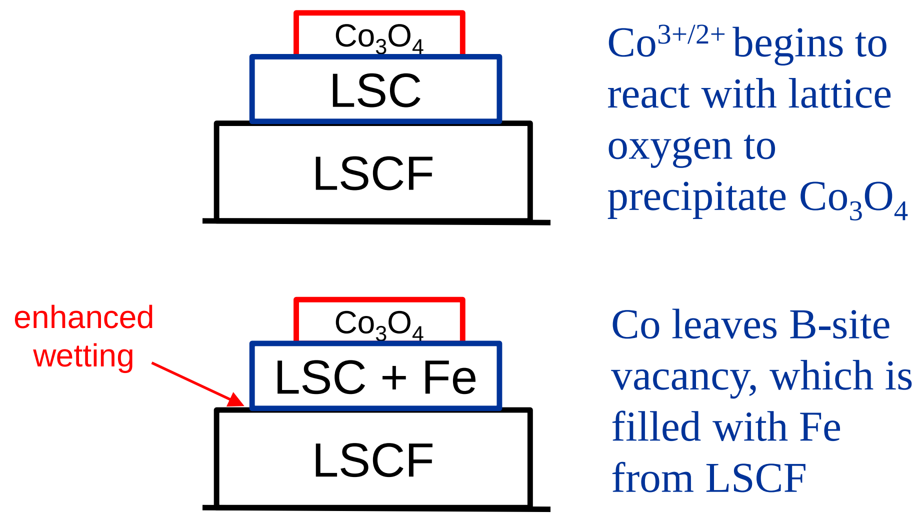
Hypothesis: Operation forces Co_3O_4 formation owing to local charge balancing

- **Cartoon illustrates driving forces for degradation**



Conclusions

- **LSC decomposition is not detrimental to infiltrated cell performance**
- **Hypothesis is testable with computational chemistry methods**
- **LSC infiltration could be used as a chemical marker for cathode activity**



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Electrocatalysts to mitigate degradation

Examine mitigation of water-induced degradation via electrocatalyst

- **Prior analysis of LSM system indicated accelerated degradation when exposed to water at high current density**

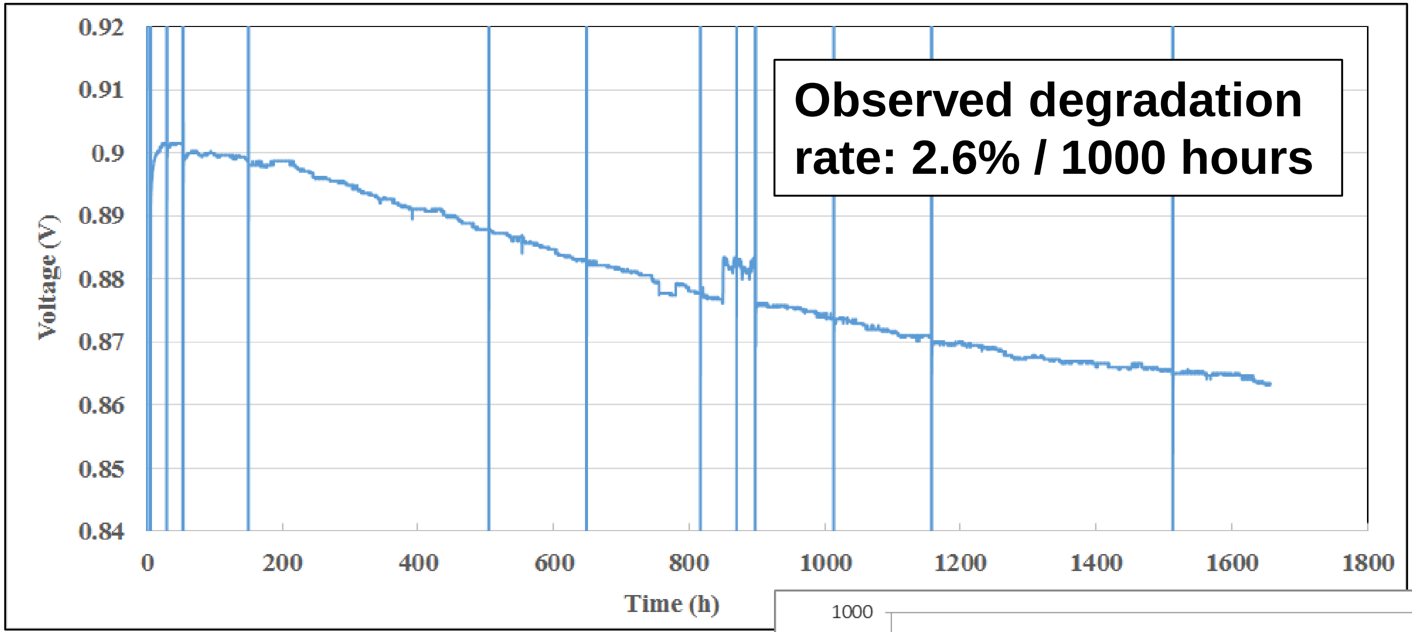
Test	Degradation rate at 100 h [per 1000 h]	Degradation rate at 1000 h [per 1000 h]	R_P at t=0 [Ω×cm²]	R_P at t_F [Ω×cm²]	Current [A/cm²]
0% Steam 500 h	1.8%	1.8%	0.22	0.15	0.75
10% Steam 200 h	0.1%	0.1%	0.32	0.32	0.25
10% Steam 500 h (1)	9.6%	9.6%	0.17	0.19	0.75
10% Steam 500 h (2)	9.9%	9.9%	0.22	0.20	0.75
10% Steam 500 h (3)	11.7%	11.7%	0.22	0.20	0.75
20% Steam 100 h	20.2%	20.2%*	0.21	0.23	0.75
20% Steam 500 h	25.0%	4.6%	0.34	0.50	0.25

Operating conditions:
hydrogen on anode;
air + 10% steam on cathode;
elevated current density;
750C;

Results:
Degradation rates exceeding 9% / 1000 hours were measured in repeat testing

Gregory Hackett "Progress Report on Degradation Associated with Elevated Steam Content in SOFC Cathode Oxidant" May 2, 2014 (NETL ORD internal report).

Electrocatalysts to mitigate degradation

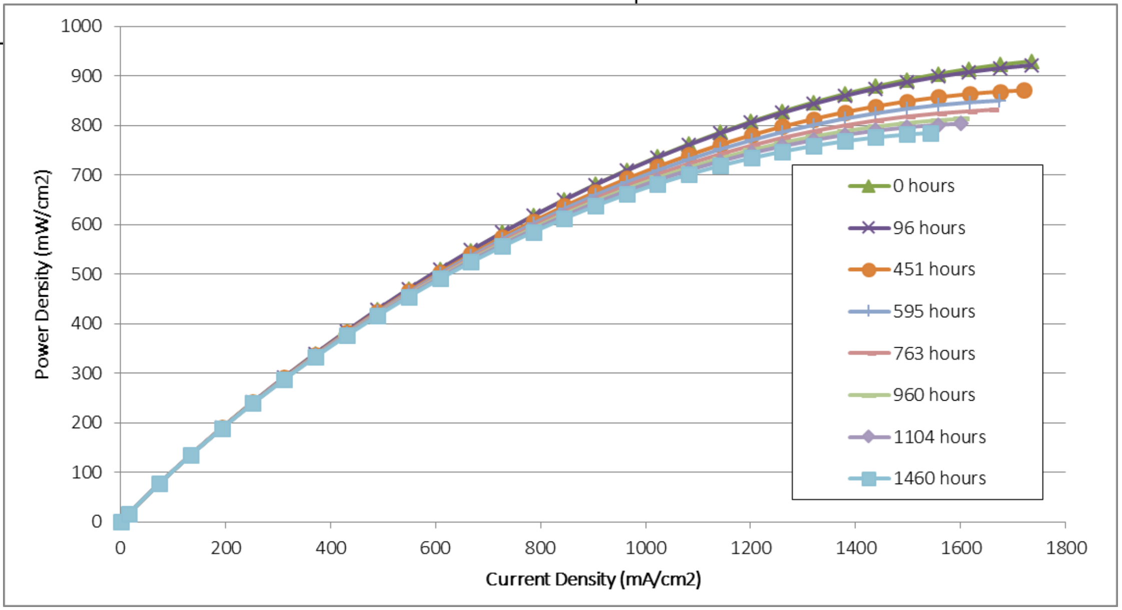


Simple electrocatalyst is deposited using conventional methods.

Degradation rate drops from greater than 9% / khr to less than 3% / khr

Analyses are preliminary and must tests must be repeated for validation

Will examine for overall stabilization of cathode structure and enhanced stability owing to decreased electric overpotential



Lynn Fan, April-July 2015 (NETL ORD internal communications)

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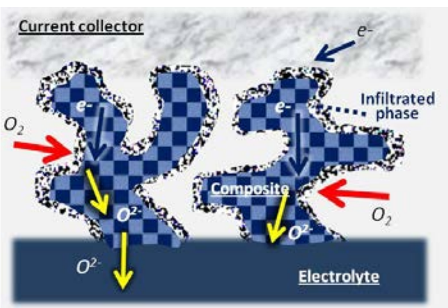
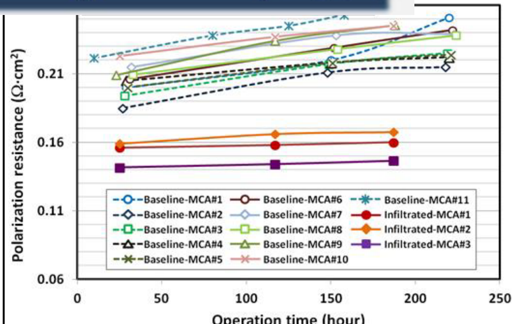
Cathode Infiltration

Concept to commercial

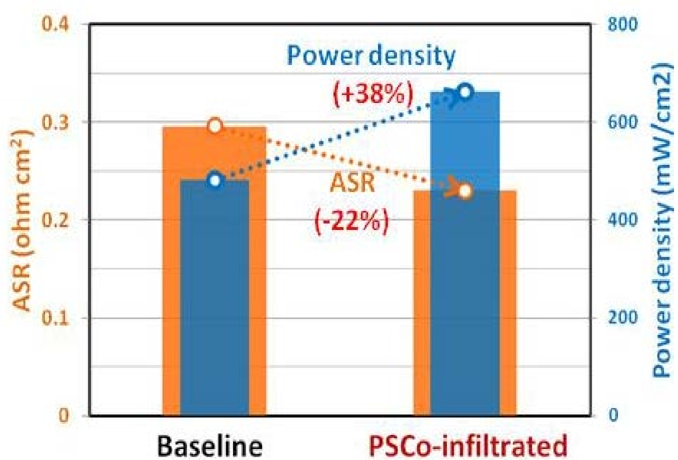
(Pre-) 2010	2012	2014
Laboratory activity, button cells TRL 2-3	Manf. component in simulated environment TRL 3-4	Prototype, manf. env. (short-stack test) TRL 5





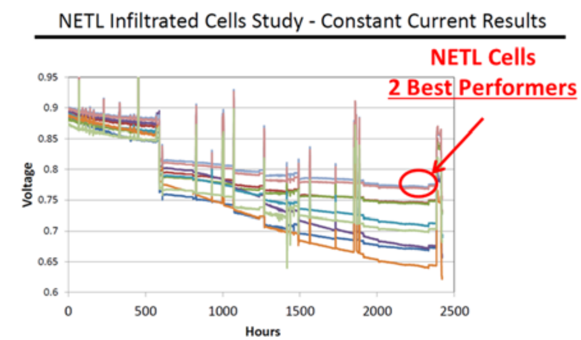
(b) Average Rp after 24 h opeation (MCA)
Baseline cell = 0.21 ± 0.014 Ωcm²
Infiltrated cell = 0.15 ± 0.010 Ωcm²

Delphi's button cells



Program → 50% ASR decrease
Research → 22% ASR decrease

Commercial cells, 100% scale

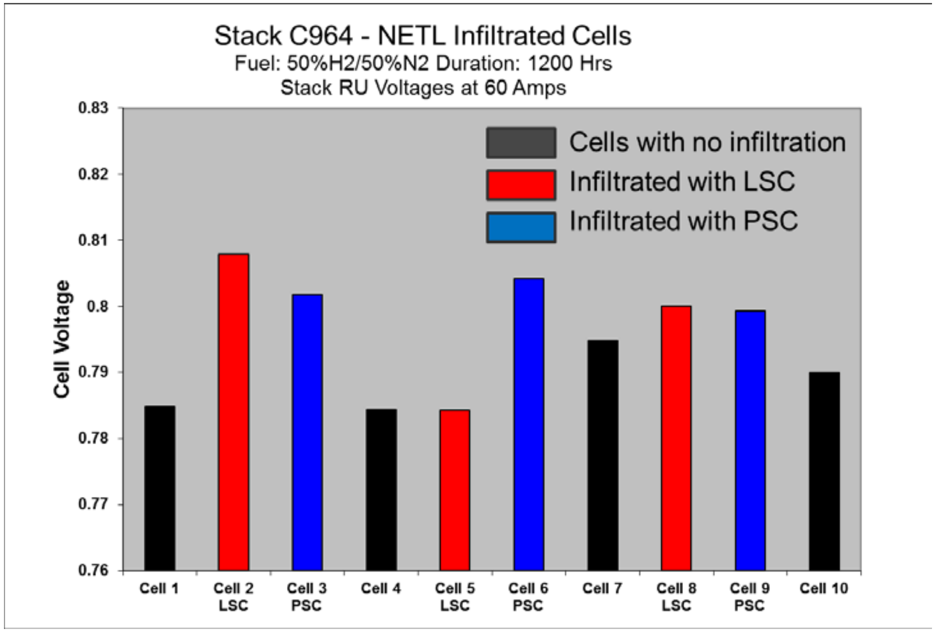


Result: ↑10% peak power, 33% ↓relative degradation, > 200% ↑ lifetime

Cathode Infiltration: Impact

2013 → 2014 → Phase End

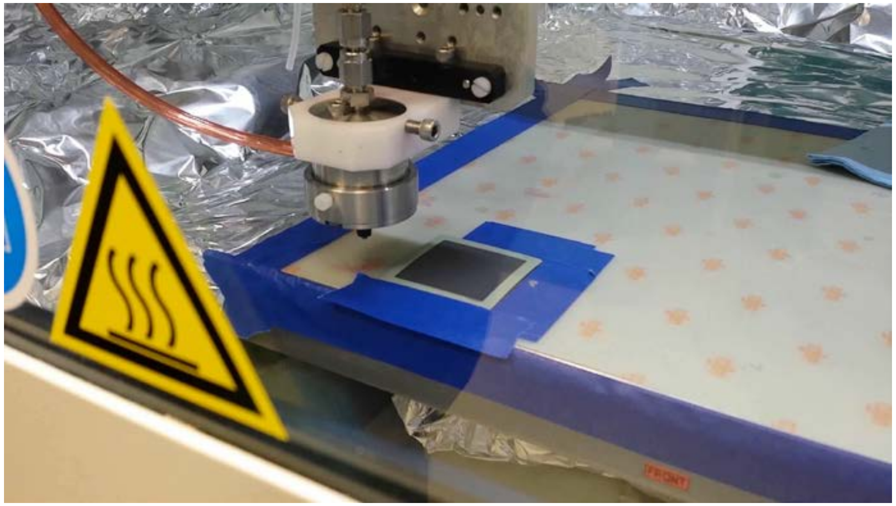
- Complete manufacturer-specific infiltrate development
- Submitted ROI and patent application for graded infiltration concept
- Submitted ROI and provisional patent for scalable manufacturing process
- Continued pursuit of manufacturing scale-up with industrial collaborator(s)



On-going 10-cell stack test
6 infiltrated cells, 4 base cells
1200 hours reported (above)
> 2000 hours operated
“Conventional” operating mode

Mature ORD Program: Impact

Commercially scalable process available



NETL has provided more than 7000 cm^2 of infiltrated cells to industry partners for evaluation at no cost to evaluator

ORD can infiltrate 1000+ cells annually at less than \$0.006/cm^2 via advanced manufacturing

U.S. Provisional Patent Application 62/191,548 filed July 13, 2015 "Method of forming catalyst layer by single step infiltration"

U.S. Provisional Patent Application 62/026,876 filed July 21, 2014 "Functional Grading of Cathode Infiltration for Spatial Control of Activity"

Shiwoo Lee and Kirk Gerdes, "Functional nanostructure engineering of SOFC cathode by solution infiltration," ECS Electrochem. Lett. 2015 volume 4, issue 3, F17-F20.

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FY16 Research Portfolio / Conclusions

Continued research correlating structural features and cell performance

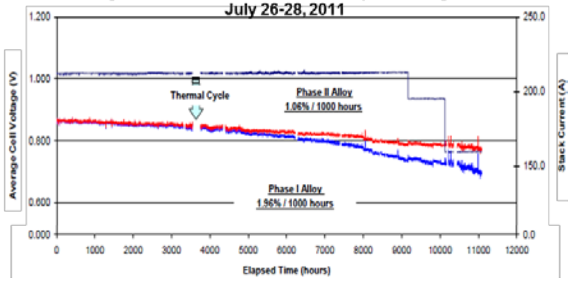
Especial focus on examination of critical interfaces and scale-bridging from atoms to particles to predict performance evolution

Ultimate goal: *High fidelity predictive models* intended for accelerated materials development and operational diagnostics

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



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Thank you for your time and attention.

Contact:

Kirk Gerdes

DOE-NETL

Lead Engineer – Thermal Sciences

Office: (304)285-4342

EM: Kirk.Gerdes@NETL.DOE.GOV

the **ENERGY** lab

U.S. DEPARTMENT OF ENERGY