NATIONAL ENERGY TECHNOLOGY LABORATORY

NETL-RUA

Regional University Alliance

NETL Carnegie Mellon PENNSTATE University of Pittsburgh VirginiaTech WestVirginiaUniversity URS

Engineering Innovations and Degradation Modeling in SOFC Cathodes

Kirk Gerdes

DOE-NETL, Research Group Leader – Fuel Cells

U.S. DEPARTMENT OF ENERGY

Outline

- **NETL-RUA**
  - Description
  - Engagement
- **Cathode Engineering**
  - Infiltration
  - Microstructural Engineering
- **Cathode Degradation**
  - Degradation framework
  - Constitutive (ORR, Microstructure, *ab initio*)
  - Core (3D multi-physics, Cathode evolution)
  - Additive (Aging effects, Secondary phases / breakdown)
- **Summary**

NETL RUA

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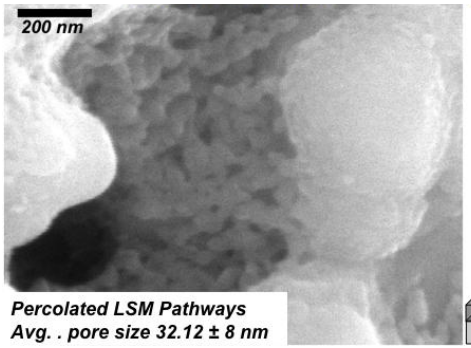
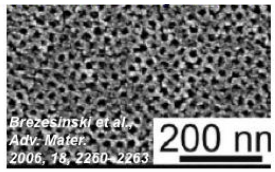
NETL RUA - Solid Oxide Fuel Cells

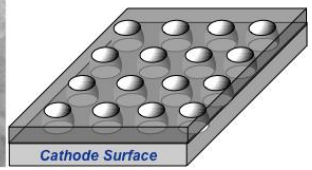
Support Industrial Development

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.

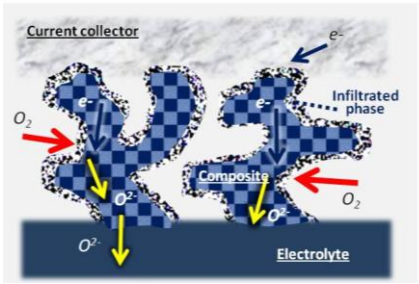
Collected 4,000 + cell-hours of data to support development of gas cleanup systems sufficient for gasifier / fuel cell integration.





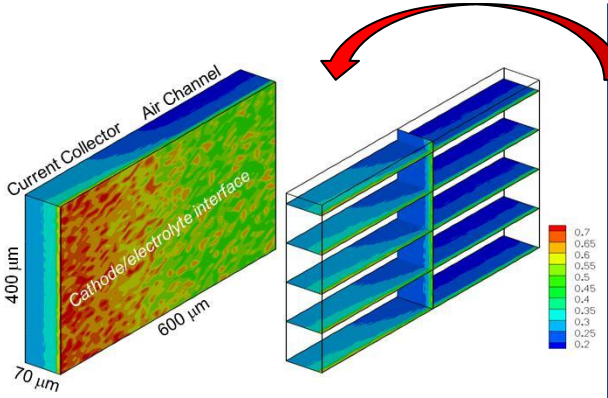


Innovate Technology



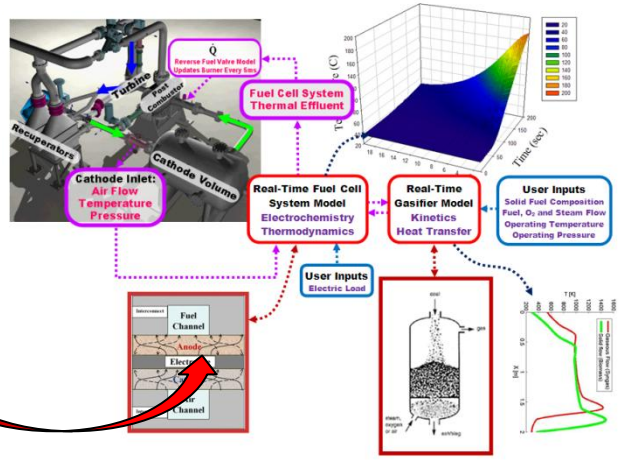
Cathode infiltration technology is being developed to enhance the SOFC operating performance. Initial results have demonstrated > 40% performance improvement and acceptable material stability.

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.



NETL RUA FY12

Harry Abernathy
Kirk Gerdes
Greg Hackett
Shiwoo Lee
Yves Mantz
Rich Pineault
Nick Siefert

Ismail Celik
Harry Finklea
Xingbo Liu
Ed Sabolsky
Xueyan Song

Paul Salvador

LongQing Chen

Tom Kalapos

SECA core + SECA industrial teams

Cathode Engineering

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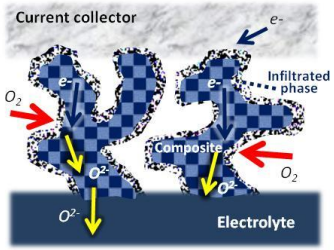
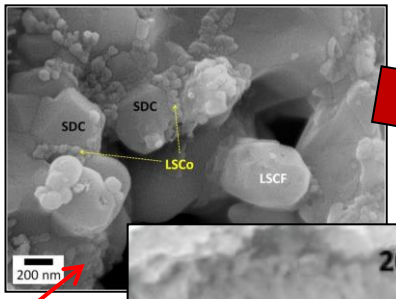
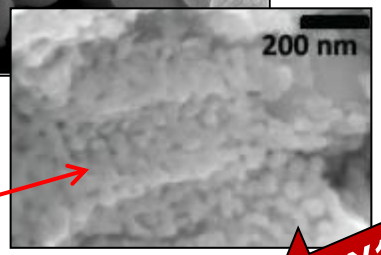
NETL RUA – Cathode Engineering

Infiltration concept



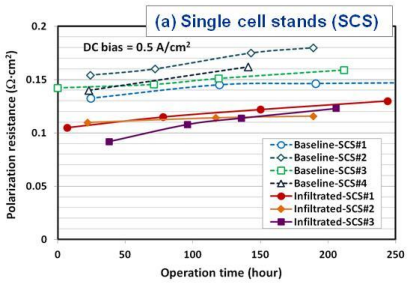


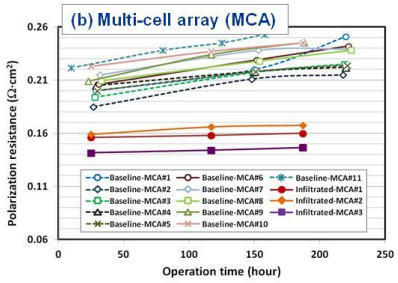


Cathode infiltrates
- **Nano-scale electrocatalysts**
- **High-surface area (EISA)**

FY10

➢ Polarization resistance vs. time of baseline cells and infiltrated cells





(a) Average Rp after 24 h operation (SCS)
Baseline cells: 0.14 ± 0.009 Ωcm²
Infiltrated cells: 0.10 ± 0.012 Ωcm²

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

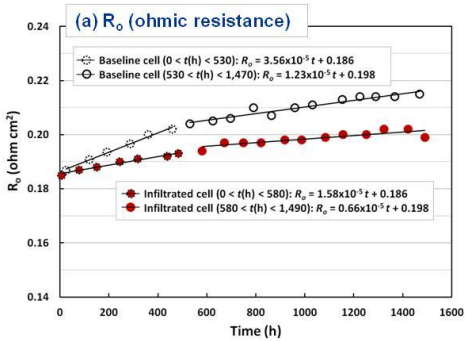
Short-term performance validation

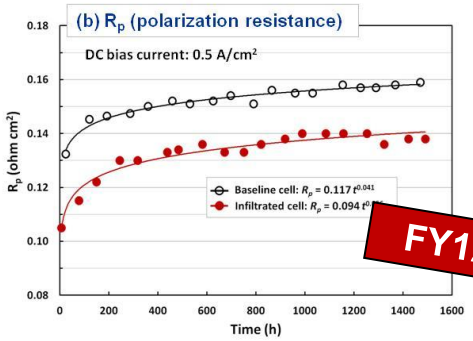
FY11

Demonstrated <u>statistically significant</u> performance improvement for infiltrated cathodes in <u>200 hour tests</u>
> 30% peak power density increase (average) observed

Long-term stability verification

➢ Variation of R_o and R_p of selected baseline cell and infiltrated cell for 1,500 h



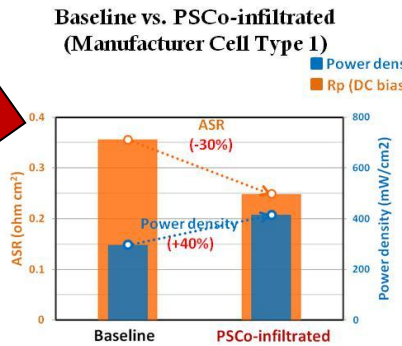


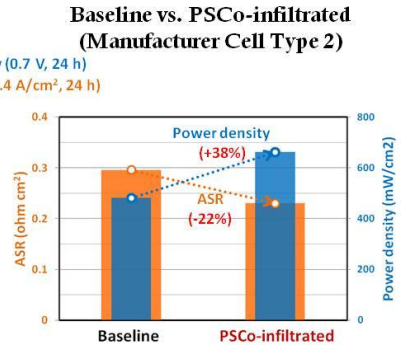
Verified stability of electrochemical performance in <u>1500 hour test</u>, cell *degradation not accelerated* above baseline

FY12

Industry Engagement

Unaltered industry cells + unmodified infiltrate: <u>200 hour tests</u> > 38% power density increase @ 0.7 V (average)





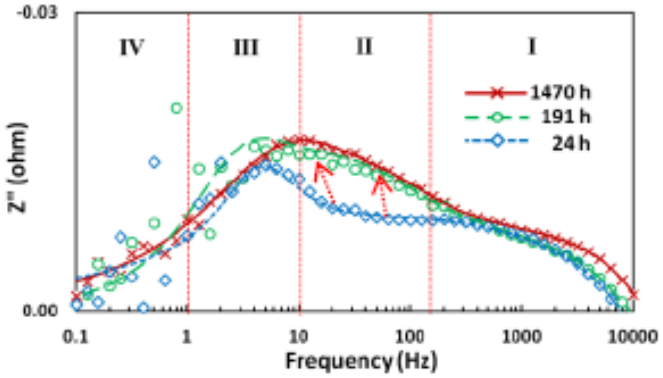
Images and data: Shiwoo Lee, National Energy Technology Laboratory
Paul Salvador, Carnegie Mellon University

Electrocatalytic Infiltration

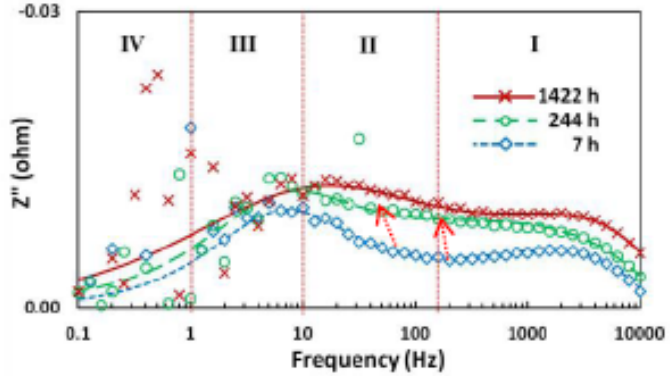
- **Focus on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$**
- **Activity enhancement**
  > 30% power output @ 0.7 V
- **Stability**
  No phase breakdown or interphase reaction
- **Durability**
  Equal or better than baseline @1500 hours
- **Cost / Scalability**
  Requires 6 wt% infiltrate (or less)
  Formula compatible w/ commercial cathode structures/materials

Cell degradation with operation time

(a) Baseline cell



(b) Infiltrated cell



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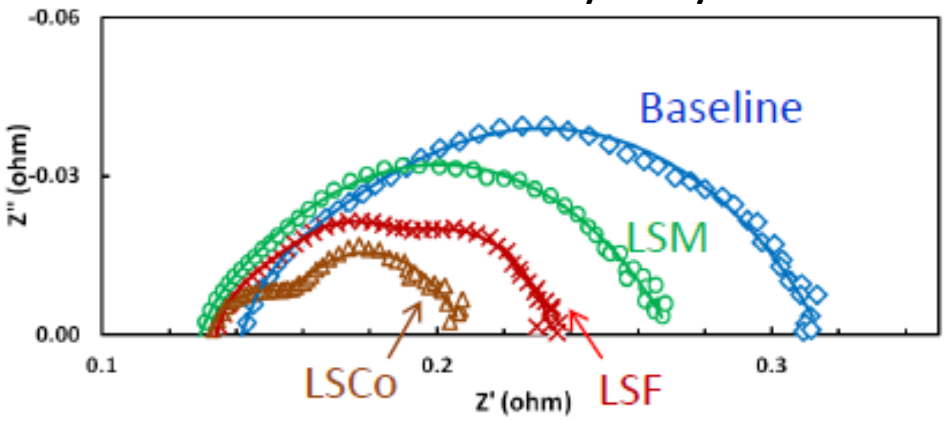
Images and data: Shiwoo Lee, National Energy Technology Laboratory

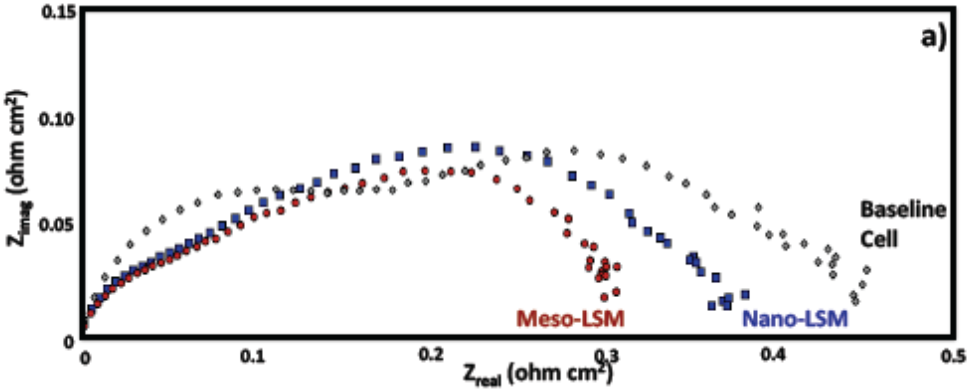
Cathode Infiltration

- **Improved infiltration process to minimize total number of infiltration steps**
- **Developed EISA process to increase infiltrate surface area (mesopores) and enhance thermal stability**
- **Evidence for role of structural relationships between infiltrate and backbone**
  - LSM infiltrated by LSM (top)
  - LSCF infiltrated by two morphologies of LSM (bottom)

Infiltration of LSM cathode by survey of infiltrates



Infiltration of LSCF cathode by two infiltrate morphologies



NETL-RUA

Images and data: Shiwoo Lee, National Energy Technology Laboratory
Paul Salvador & Robin Chao, Carnegie Mellon University

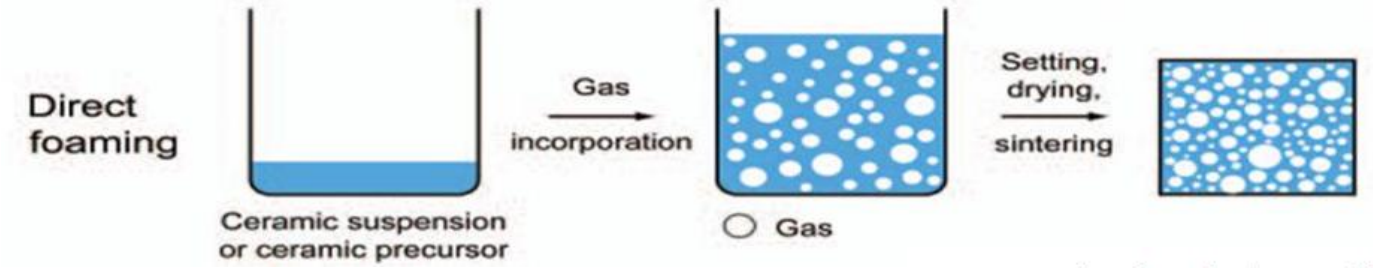
Cathode Infiltration

- **Prior accomplishments**
  - Developed and demonstrated a functional infiltrate (LSC)
- **Recent progress**
  - Generated evidence of structure-dependent performance enhancements
  - Examined the role of infiltrate wetting in fabrication and infiltrate function
- **Continued research**
  - Examination of stability and improvements from infiltrates composed of doped and/or non-standard materials

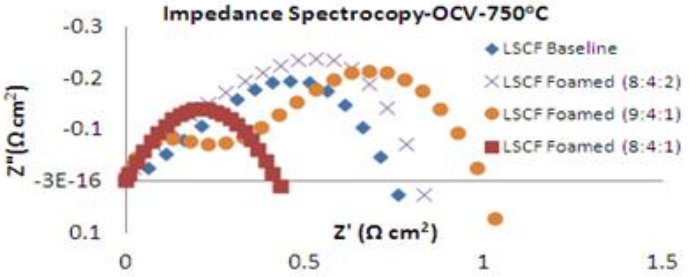
Infiltration Publications

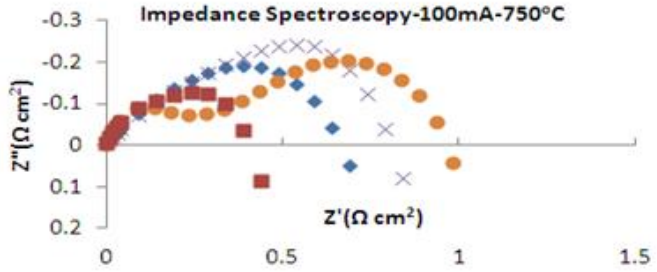
1. S. Lee, N. Miller, and K. Gerdes, **J Electrochem Soc, Volume 159, Issue 7, pp. F301-F308 (2012)**
2. R. Chao, R. Munprom, R. Petrova K. Gerdes, J.R. Kitchin, and P. A. Salvador, **J Am Ceram Soc 96 (7) 2339-2346 (2012)**
3. S. Lee, N. Miller, H. Abernathy, K. Gerdes, et al , **J. Electrochem. Soc., Volume 158, Issue 6, pp. B735-B742 (2011)**
4. S. Lee, N. Miller, M. Staruch, K. Gerdes, M. Jain, and A. Manivannan, **Electrochemica Acta 56 (2011) 9904-09**
5. S. Lee, N. Miller and A. Manivannan, **ECS Trans., 35 (1) 2401-2407 (2011)**
6. R. Chao, J. R. Kitchin, K. Gerdes, E. M. Sabolsky, and P. A. Salvador, **ECS Transactions, 35 (1) 2387-2399 (2011)**

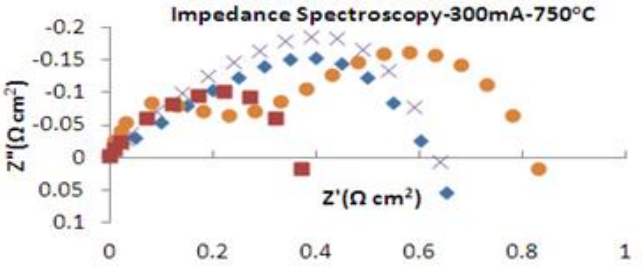
In-situ Foamed Cathode



- **In-situ foaming process**
  - One-step, functionally graded cathode microstructure
  - Enhanced receptiveness to infiltration
- **Electrolyte supported system development → anode supported**
- **Optimized formula decreases cathode polarization by > 50% over traditional microstructure**







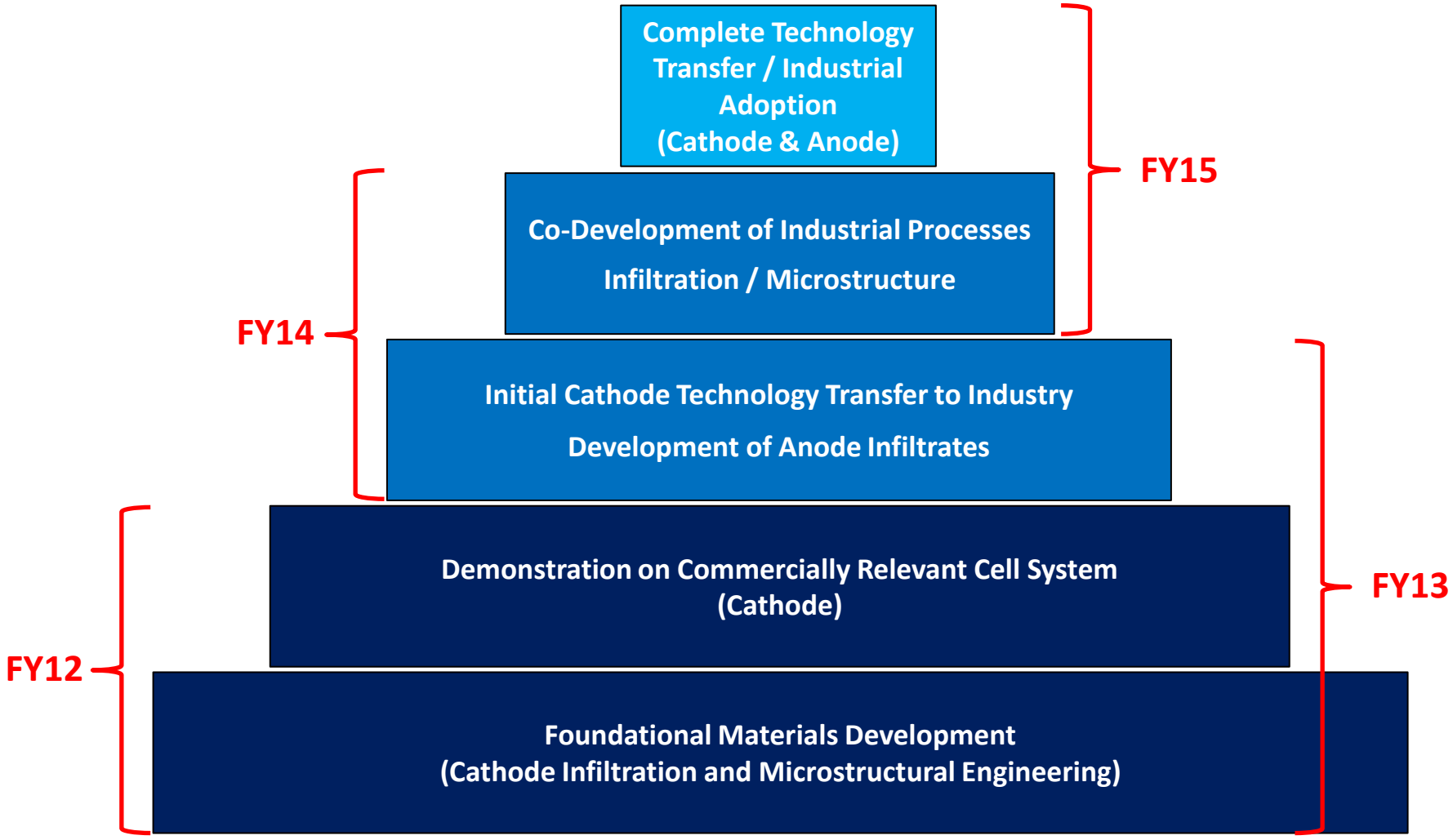
FY12-FY13 Cathode Engineering

- **NETL RUA**
  - Increased engagements with SECA core
    - Argonne National Laboratory - initiated
    - Georgia Institute of Technology – executing
    - Additional partners arising from FY13 starts
  - Increased engagements with industrial teams
    - Primary demonstrations on unmodified MSRI button cells
    - FY12 demonstration with SECA industrial partner cell
  - Finalize cathode and extend effort to include anode
    - Anode – catalytic enhancement, chemical resistance, durability

Cathode Materials Testing

- **MCA Video**

Cathode/Electrode Engineering Beyond FY13



Cathode Degradation

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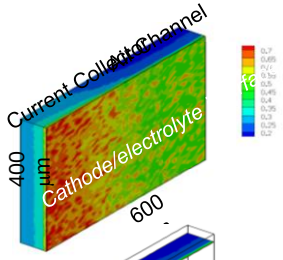
Degradation framework

- **Degradation**
  - Topic too vast to cover in industrial report (as collection of relevant observations or description of applied heuristic approaches)
  - Too many combinations of materials, too many operating states
- **Framework organization**
  - Attempt to generalize/categorize degradation
  - Provide a simple framework based on *degradation source* and *mechanistic complexity*
  - *Intrinsic* v. *extrinsic*; and *primary* v. *secondary*

	Intrinsic	Extrinsic
Primary (direct or single step)	*Best Engineering Practices*	*i) Best Engineering Practices* *ii) Operating Protocols*
Secondary (indirect or multi-step)	*i) Operating Protocols* *ii) Best Engineering Practices*	*Best Engineering Practices*

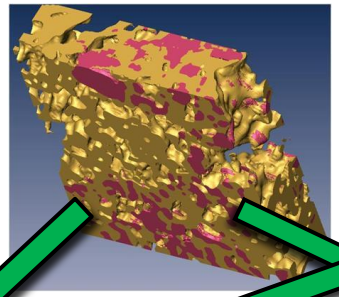
NETL RUA – Degradation Modeling

- *Integrated modeling and experimental* efforts to quantify degradation
- Model validation – ongoing validation using literature and direct experimental sources

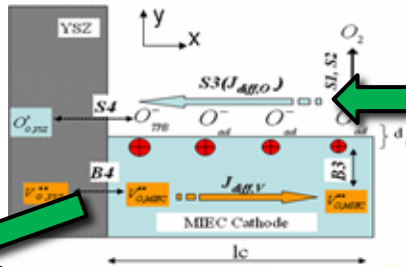


3D multi-physics
(Celik – WVU)

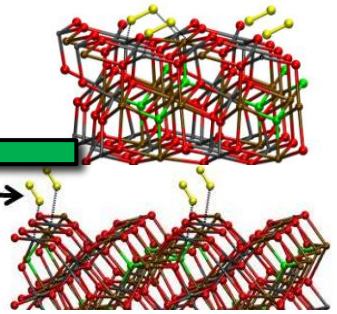
3D reconstructions
(Salvador – CMU)



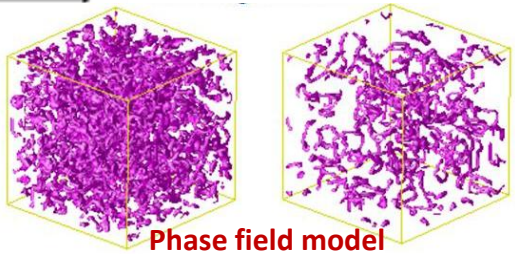
ORR model
(Liu – WVU; Gemmen – NETL)



ab intio model
(Mantz – NETL)

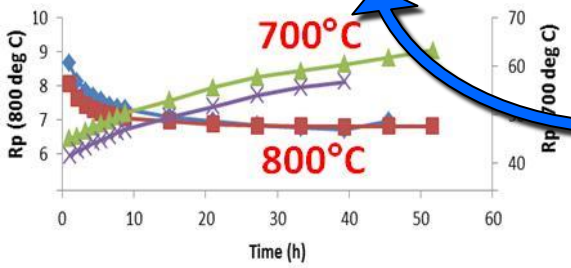


Constitutive
FY10-FY12

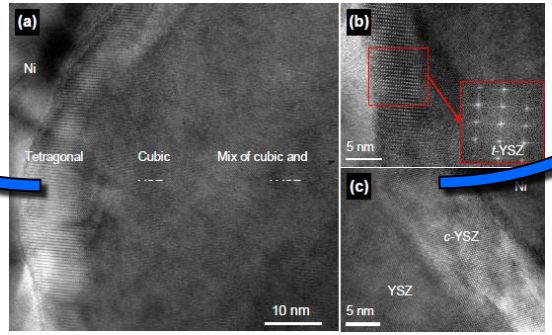


Phase field model
(LQ Chen – PSU)

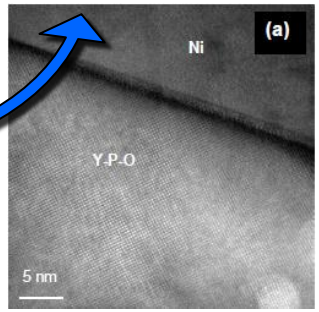
Integrated, Domain scale
FY11-FY12



Aging
(Finklea – WVU; Abernathy – NETL)



Phase breakdown
(X Song – WVU)



Secondary phases
(X Song – WVU; Gerdes/Hackett – NETL)

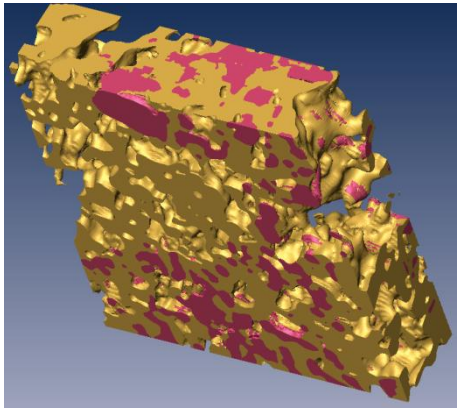
Additive
FY11-FY12

Constitutive Models and Reconstructions

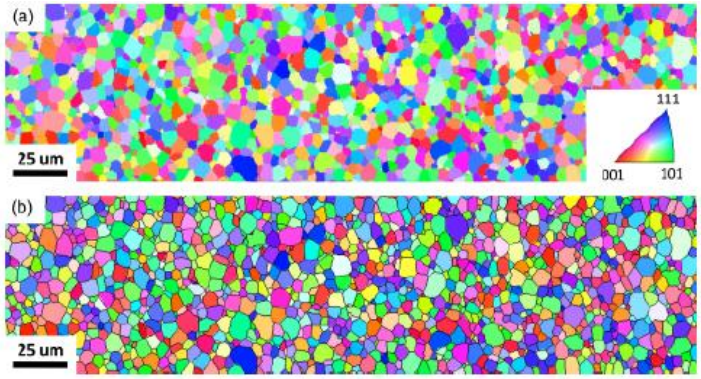
- **Oxygen Reduction Reaction (ORR)**
  - Treats parallel pathway (2PB v. 3PB)
  - Assumes surface potential separation

M.Gong, R. Gemmen, X. Liu, "Modeling of oxygen reduction mechanism for 3PB and 2PB pathways at solid oxide fuel cell cathode from multi-step charge transfer" **Journal of Power Sources 201 (2012) 204– 218**

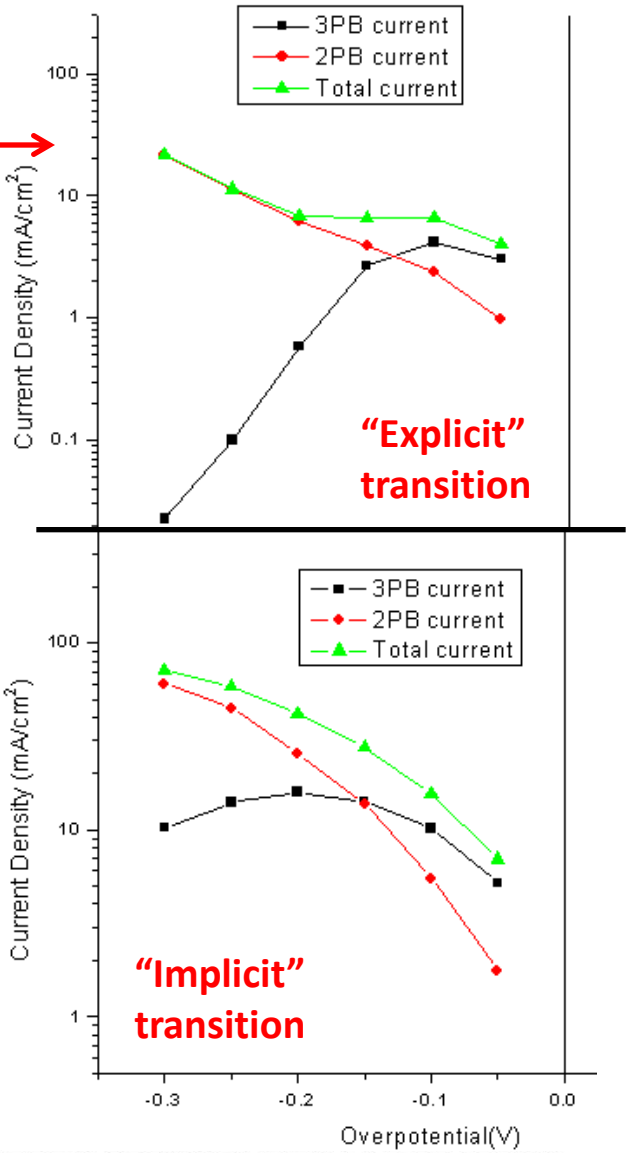
- ***ab initio* simulations – LSZ → LSM**
- **FIB-SEM reconstructions, FIB-OIM**



False color FIB-SEM reconstruction of commercial LSM/YSZ/pore cathode



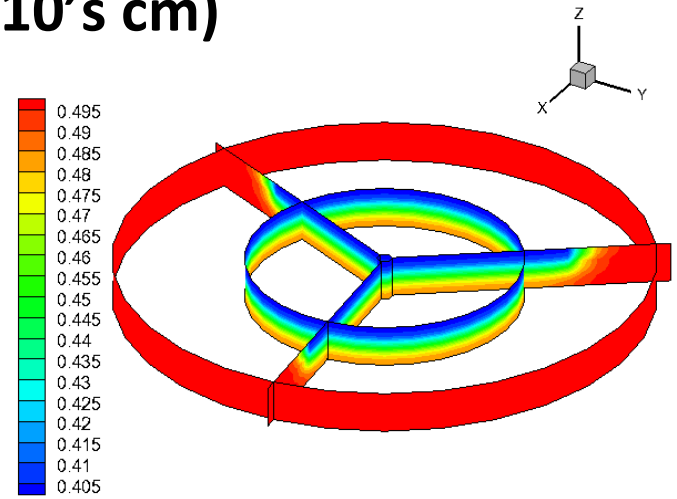
Lam Helmick, et al "Crystallographic Characteristics of Grain Boundaries in Dense Yttria-Stabilized Zirconia" **Int'l J Appl Cer Tech, Volume 8, Issue 5, p 1218–28, Sept/Oct 2011**



Integrated, domain scale models

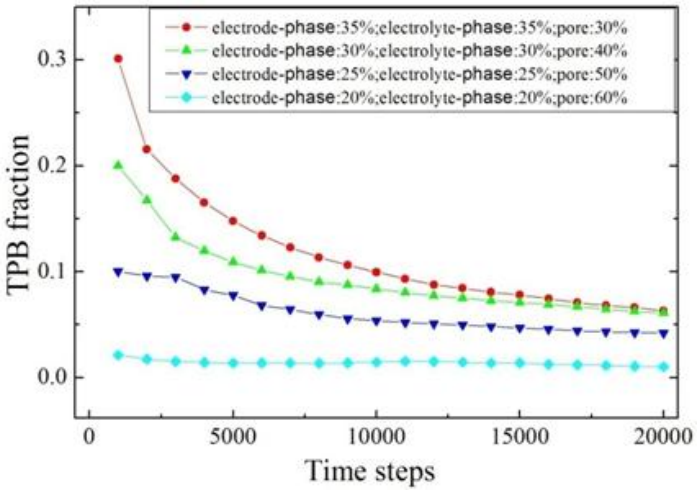
- **3D multi-physics model (space domain, 10's cm)**
  - Powerful dynamic model predicts full 3D multi-physics (e.g. T, species, η, impedance response)
  - Informed by ORR and full 3D reconstructions
  - Validated by parametric analysis and comparison to independently published data

S. Pakalapati, I. Celik, H. Finklea, M. Gong, X. Liu, K. Gerdes, "Micro Scale Dynamic Modeling of LSM/YSZ Composite Cathodes" **submitted to Journal of Power Sources (2012)**



- **Microstructural evolution model (time domain, 1000's hrs)**
  - Describes evolution of 3-phase microstructure subject to thermodynamic and kinetic drivers
  - Predicts geometric and topological parameters relevant to fuel cell reaction and transport

Q. Li, L. Liang, K. Gerdes, and L-Q Chen "Phase-field modeling of three-phase electrode microstructures in solid oxide fuel cells" **Appl. Phys. Lett. 101, 033909 (2012); http://dx.doi.org/10.1063/1.4738230**



Additive degradation phenomena

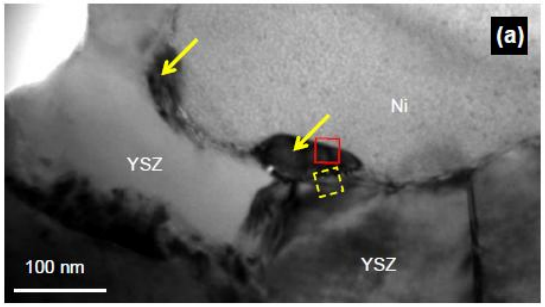
- **Cathode – Aging**
  - R_p of LSM symmetric cell held at OCV and cycled between 700°C and 800°C changes between two steady states requiring 10's hrs to acquire
  - Believed attributable to cation diffusion

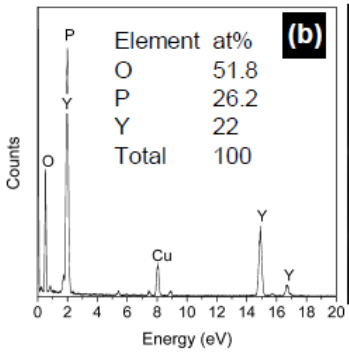
H. Abernathy, H.O. Finklea, D.S. Mebane, X. Chen, K. Gerdes, M.D. Salazar-Villalpando, "Reversible aging behavior of $La_{0.8}Sr_{0.2}MnO_3$ electrodes at open circuit" **Journal of Power Sources 216 (2012) p11-14**

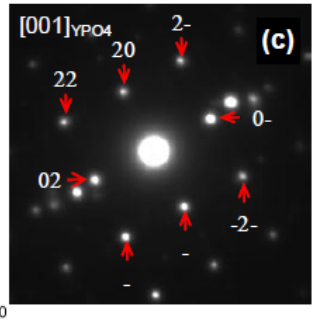
- **Anode - Direct syngas exposure**
  - Direct syngas produces only minor secondary phases
  - Degradation of seal and mechanical obstruction of pores

G. Hackett, K. Gerdes, X. Song, Y. Chen, V. Shutthanandan, M. Engelhard, Z. Zhu, S. Thevuthasan, R. Gemmen, "Performance of solid oxide fuel cells operated with coal syngas provided directly from a gasification process" **Journal of Power Sources 214 (2012) p142-52**

- **Electrolyte - YSZ attack by phosphine**
  - Stable Y-P-O phase is generated at electrolyte in PH_3-exposed anode







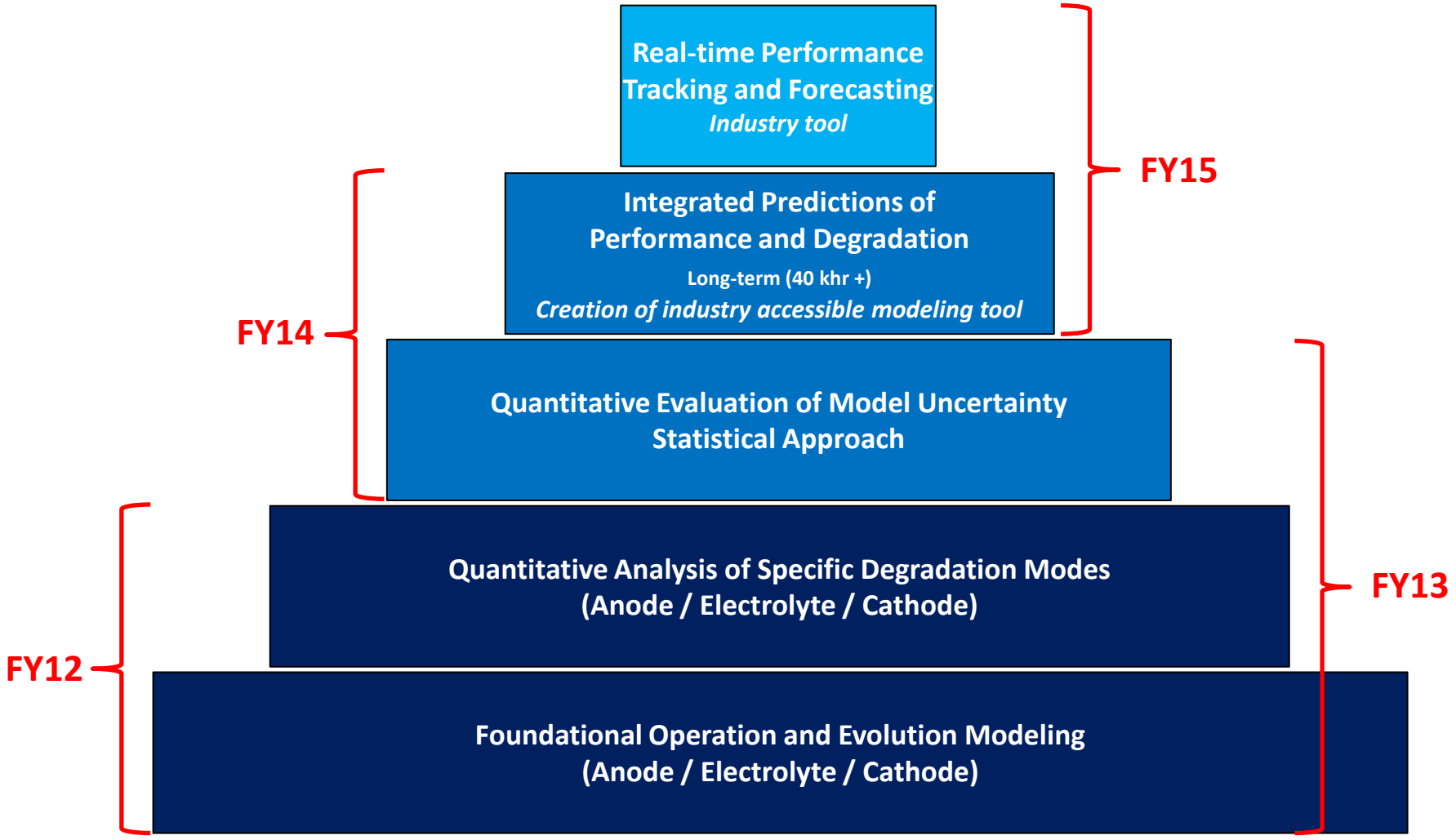
Pattern from Y-P-O and YSZ

Y. Chen, S. Chen, G. Hackett, H. Finklea, J. Zondlo, I. Celik, X. Song, K. Gerdes, "Microstructure origin of electrochemical degradation of SOFC anodes operated in phosphine-containing fuels" **submitted to Journal of Power Sources**

FY12-FY13 Degradation Modeling

- **NETL RUA**
  - Increased engagements with SECA core
    - Argonne National Laboratory - initiated
    - Boston University - discussions
    - Additional partners arising from FY13 starts
  - Initiate engagements with SECA industry teams
    - Information sharing and stack analysis
  - Continue cathode and extend effort to include anode
    - Principal modes of degradation must be considered

Degradation Modeling Beyond FY13



Cathode Degradation

- **NETL-RUA**
  - Description
  - Engagement
- **Cathode Engineering**
  - Infiltration
  - Microstructural Engineering
- **Cathode Degradation**
  - Degradation framework
  - Constitutive (ORR, Microstructure, *ab initio*)
  - Core (3D multi-physics, Cathode evolution)
  - Additive (Aging effects, Secondary phases / breakdown)
- **Summary**

Summary

- **NETL RUA has developed significant expertise and demonstrated maturity in two principal areas**
  - Materials development, infiltration, and testing
  - Cell degradation modeling and testing
- **NETL RUA supports industrial development**
  - Direct R&D engagements with SECA industry teams
  - Analytical support and diagnostics
- **NETL RUA collaborates with SECA core**
  - Intensification of depth of understanding
  - Facilitate transfer of fundamental knowledge to applied cell development

Questions

- **DISCLAIMER:** Part of this report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.