THREE DIMENSIONAL MICROSTRUCTURAL CHARACTERIZATION OF CATHODE DEGRADATION IN SOFCS USING FOCUSED ION BEAM AND SEM

Joshua Taillon, Christopher Pellegrinelli, Yilin Huang, **Eric Wachsman**, and **Lourdes Salamanca-Riba**

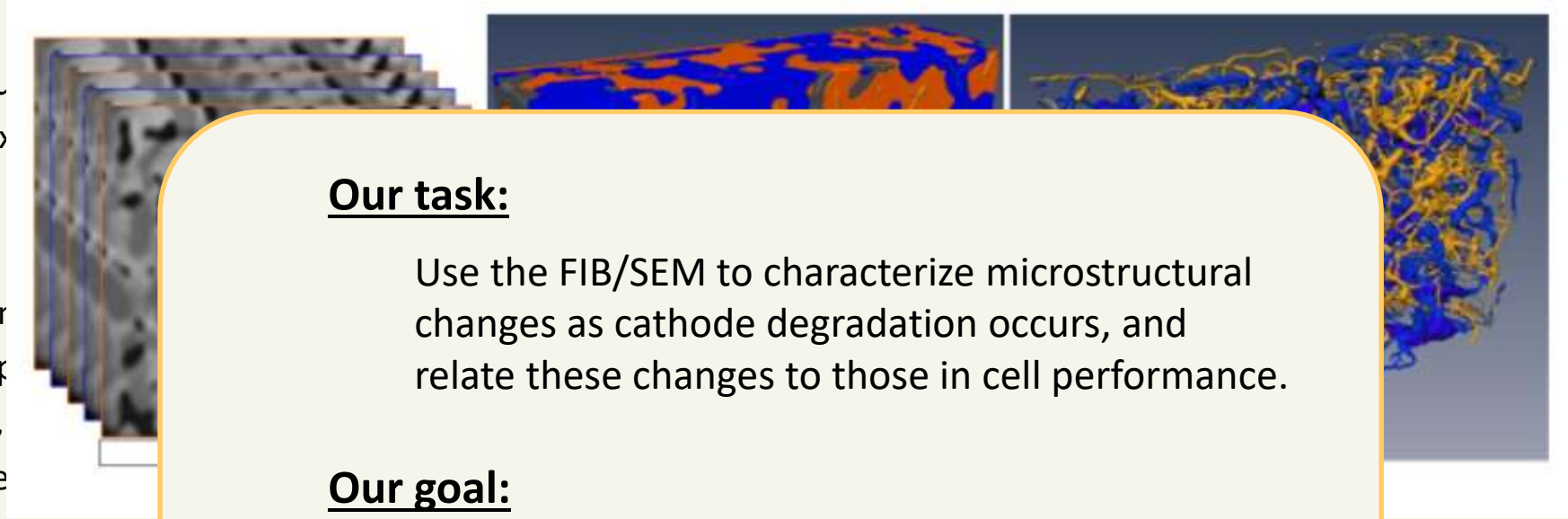
University of Maryland, College Park

*Supported by DOE-SECA under contract no. DEFE0009084
and NSF GRFP grant no. DGE 1322106.

2015 Microscopy and Microanalysis Meeting
Thursday, August 6, 2015 – 2:30 PM
Session A04.3, Room B117

Introduction to Solid oxide fuel cells

- Solid oxide fu
  - Low cost, flex
- Problems?
  - High operatir
    - Cathode p
    - H_2O, CO_2,
    - Adverse e
- What is primary cause
  - **Microstructure!**
    - Previous work:
      - Quantification in the FIB/SEM:
        - J. Wilson, S. Barnett, *Electrochem. Commun.*, **11**(5), 1052 (2009).
        - D. Gostovic, E. Wachsman, *et al.*, *J. Am. Ceram. Soc.*, **94**(2), 620 (2011).



Our task:

Use the FIB/SEM to characterize microstructural changes as cathode degradation occurs, and relate these changes to those in cell performance.

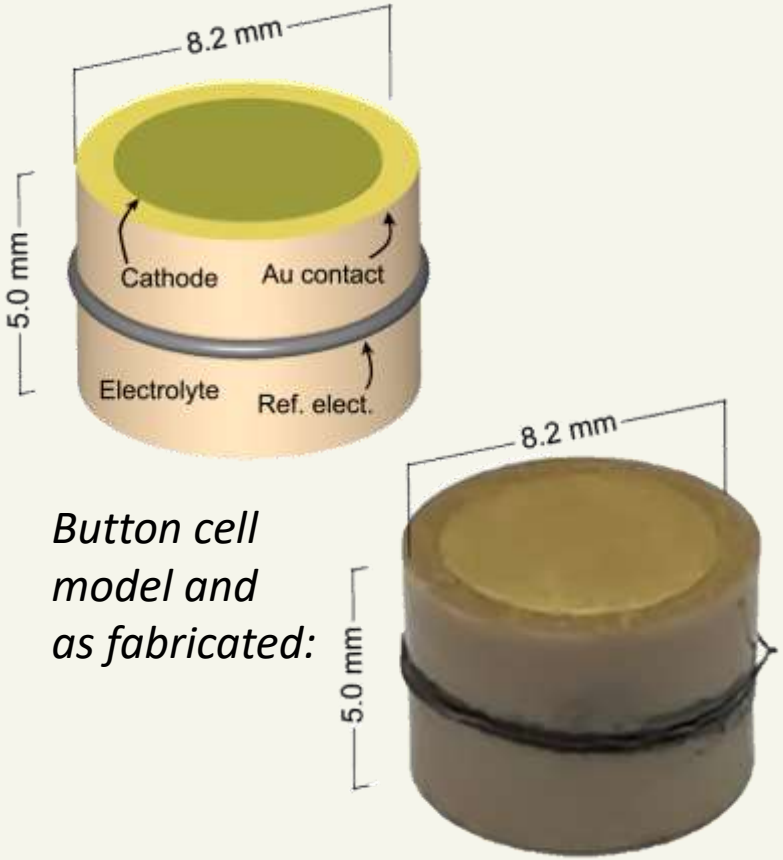
Our goal:

Better understanding of the fundamental mechanisms behind cathode degradation.

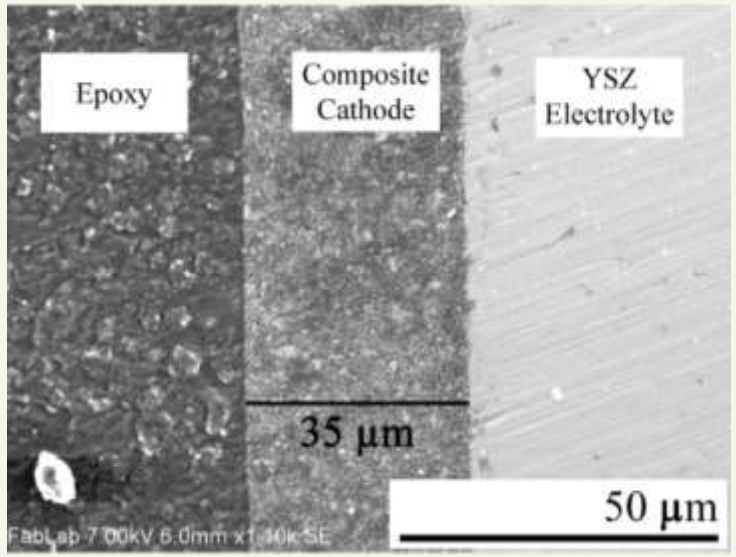
Outline

- Data acquisition
  - Sample prep and imaging conditions
- Data processing
  - Filters, artefact correction, and segmentation
- Quantification strategies
  - Tortuosity
  - Triple phase boundary
  - Electrochemical activity determination

Experimental - Button cell testing



Button cell model and as fabricated:



Cross-section view

- Symmetric cathode cells
  - 8-YSZ electrolyte
  - 50 wt. % LSM/YSZ cathode paste
- Sintered at 1000ºC for 1hr
- Aged for 250hr at 800°C
  - Polarization was constant 60mA/cm^2

- Four conditions compared:
  - Aged – dry air
  - Aged – dry air – cathodic polarization
  - Aged – 3% H_2O – anodic polarization
  - Aged – 3% H_2O – cathodic polarization

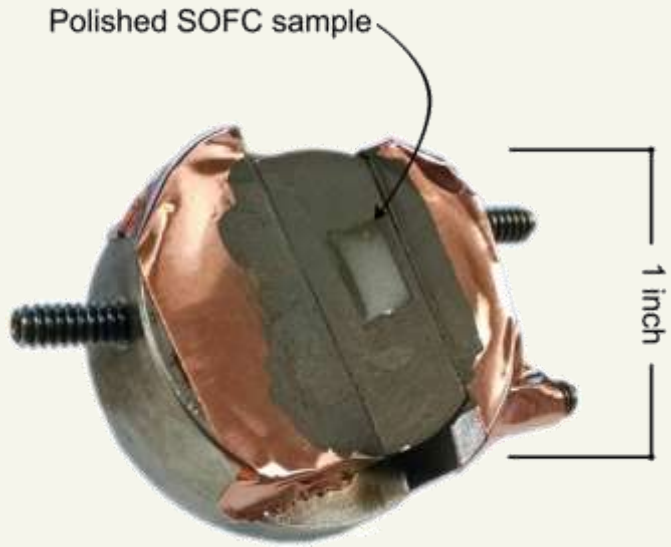
Data acquisition

- Our results (and conclusions) can only be so good as our inputs
  - We need good inputs! (GIGO)

- Important considerations:
  - Initial sample preparation (pre-FIB)
  - Sample preparation within the FIB/SEM
  - Slicing resolution (for fidelity of reconstruction)
  - Electron beam parameters - image noise and resolution vs. data acquisition time
  - What is it we need to accentuate?

Pre-FIB sample prep

1. Vacuum impregnation of porous structure
2. Grinding/polishing to 1200 grit
3. Carbon coating and sample mounting



Instrumentation

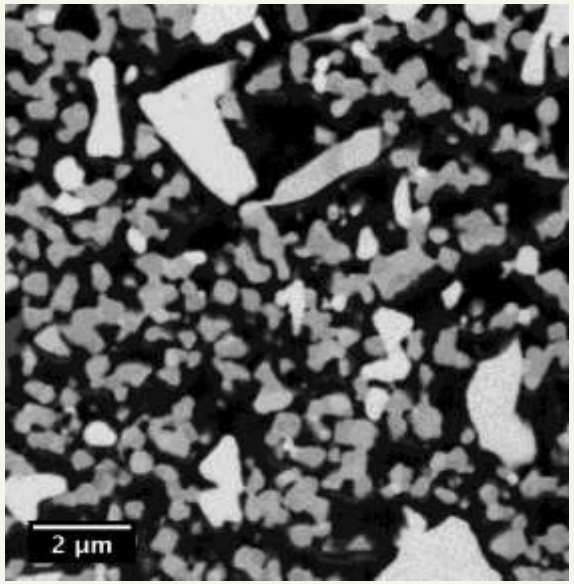
- FEI Helios 650
  - Part of the Center for Nanoscale Science and Technology (CNST) user facility at NIST
  - Multichem, iFast Developer Kit, etc.
- Auto Slice and View version 1.2
- Avizo Fire + personal Python code
- Tescan Gaia (+ Xeia) at UMD
  - Soon!

FEI Helios 650 at NIST (CNST)

Tescan Gaia at UMD AIMLab

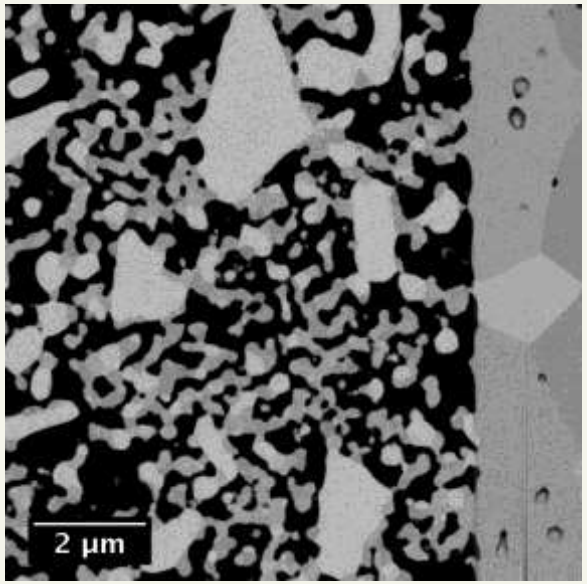
Experimental – Electron imaging (detector positioning)

FEI Helios 660 "In-column" detector (3 kV)



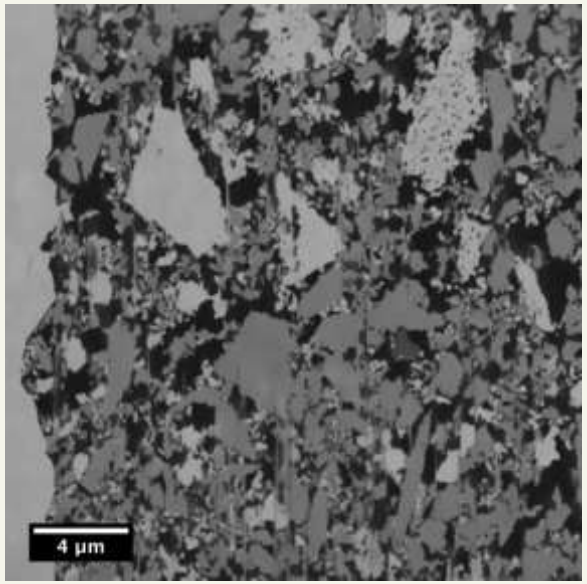
LSM/YSZ

Zeiss Crossbeam 540 "EsB" detector (1.5kV)



LSM/YSZ

Tescan Xeia "In-beam BE" detector (5kV)

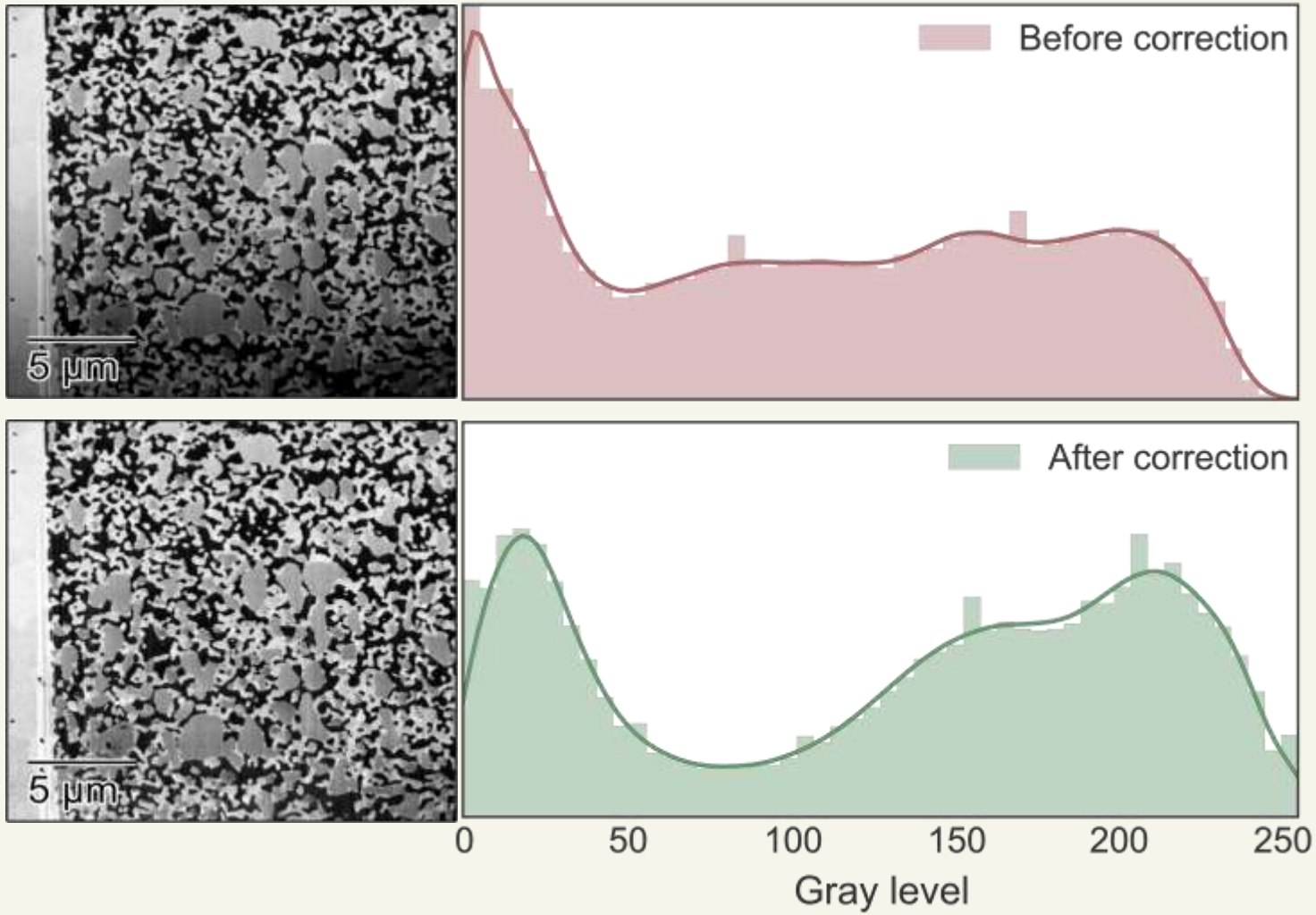


LSCF/GDC

- Positioning of detector and/or energy filtering
  - Careful selection of contrast mechanism
- For SOFC ceramics:
  - Low voltage, elastically scattered BSE provide best contrast between phases

Experimental – post processing of data

- Post-processing done with mix of software:
  - Avizo Fire:
    - Non-local means filtering of data[1] (also Perona–Malik diffusion filter)
    - Watershed segmentation algorithm[2]
  - ImageJ/Python
    - Intensity gradient correction
    - Fiducial tracking/slice thickness measurement



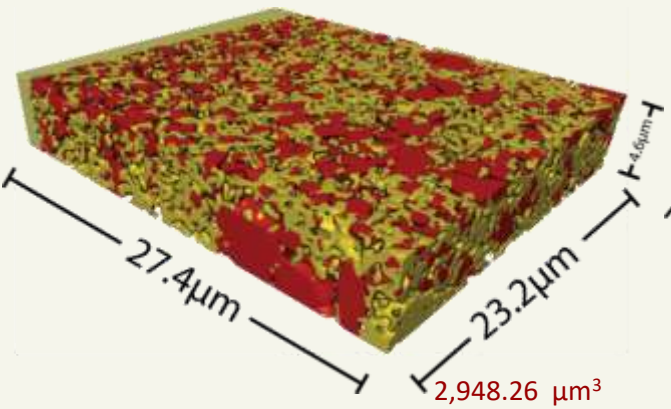
[1] Based on A. Buades *et al*. in *2005 IEEE Comput. Soc. Conf. Comput. Vis. Pattern Recognit.*, Vol. 2, p. 60. IEEE.

[2] L. Vincent and P. Soille, IEEE Trans. Pattern Anal. Mach. Intell., 13(6), 583 (1991).

Results – Surface generation

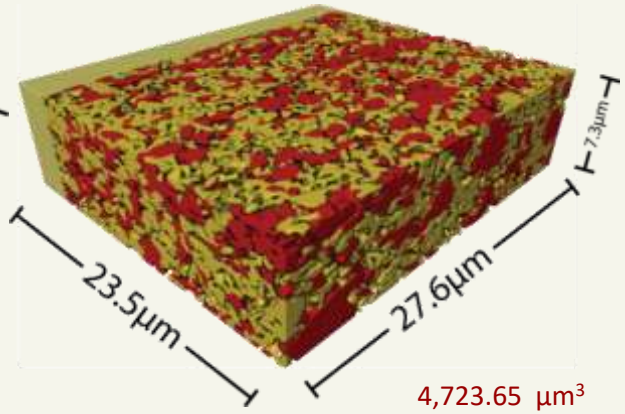
YSZ
LSM
Pore

Air



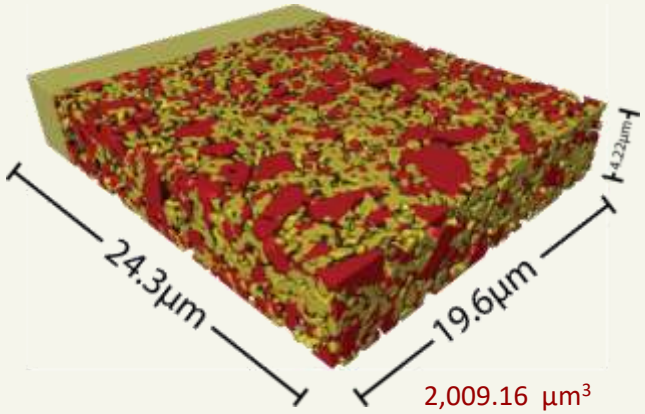
2,948.26 μm³

Air-cathodic



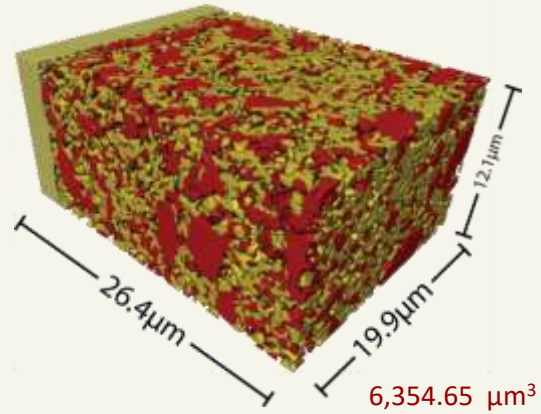
4,723.65 μm³

H_2O-anodic



2,009.16 μm³

H_2O-cathodic

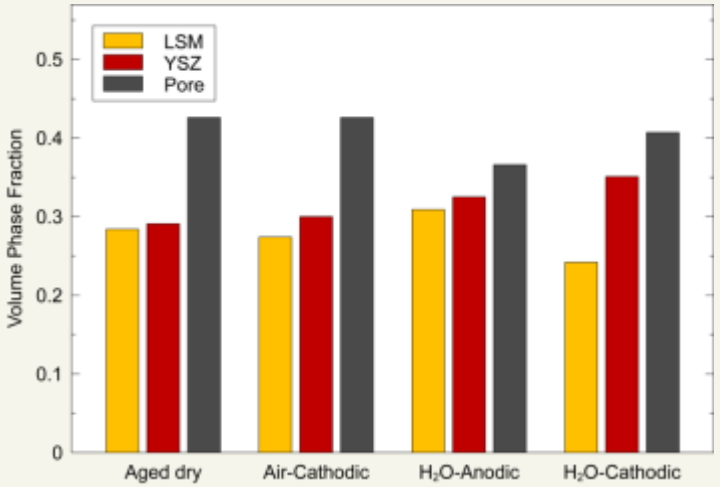


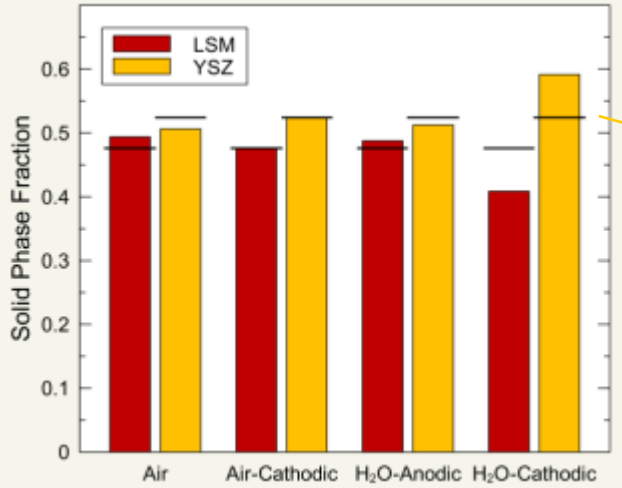
6,354.65 μm³

Bounding box dimensions (μm):

27.42	23.17	4.64	23.53	27.58	7.28	24.27	27.58	4.22	26.39	19.90	12.10
X	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**	**X**	**Y**	**Z**

Results – Phase fraction and surface quantification





- Overall porosity decreases upon exposure to H_2O
- Phase solid fractions remain similar to expected values (from source materials)
  - Except for *H_2O-cathodic*
  - *Will impact diffusivity estimates*

	Exp. YSZ	Exp. LSM	Obs. YSZ	Obs. LSM
Aged air	0.52	0.48	0.51	0.49
Air-cathodic			0.52	0.48
H_2O-anodic			0.51	0.49
H_2O-cathodic			0.59	0.41

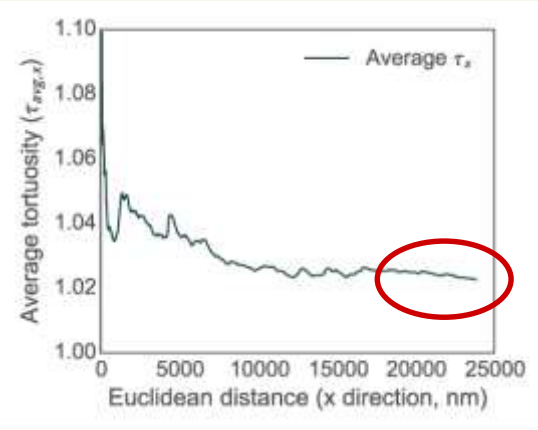
Results – Tortuosity

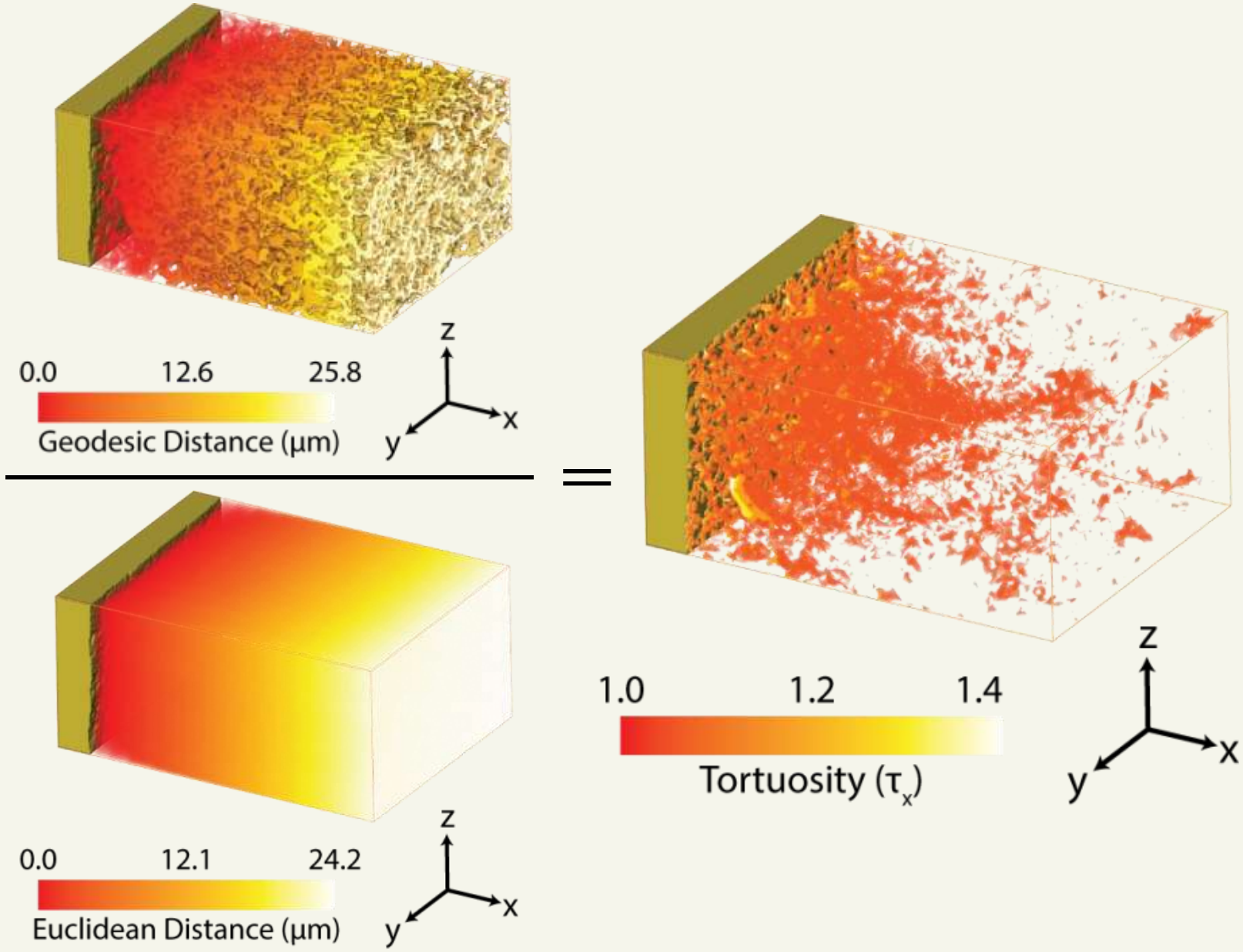
- Tortuosity is comparison of:

$$\tau = \lim_{L_G \to \infty} \left(\frac{Geodesic\ distance}{Euclidean\ distance} \right)$$

Clennell, M. B. Geol. Soc. London. 122, 299–344 (1997).

- Geodesic distance calculated with “fast marching method”
  - scikit-fmm Python library



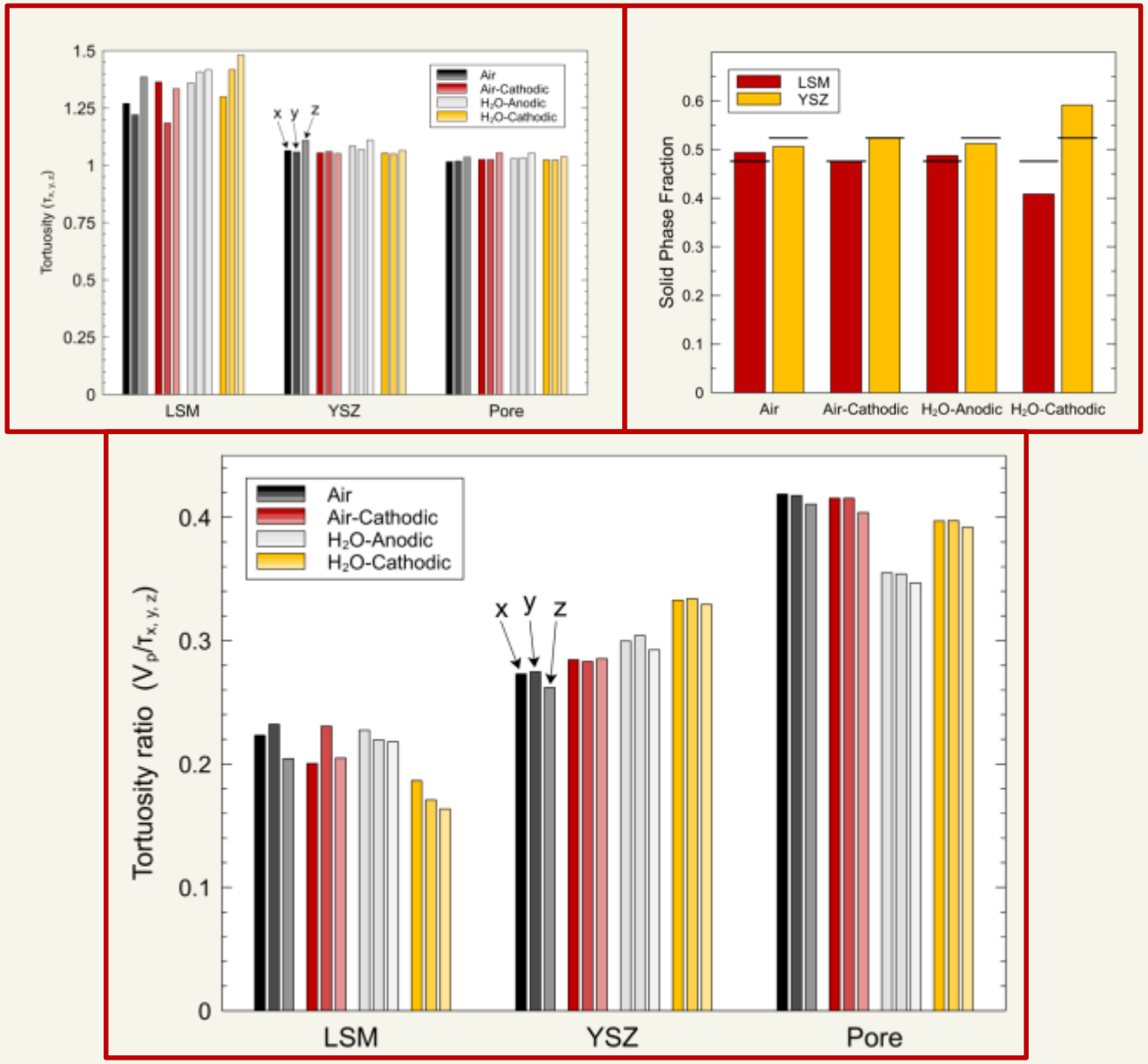


Results – Tortuosity

- Effective diffusion coefficient is dependent on volume fraction and tortuosity*:

$$D_{\text{eff}} = D\left(\frac{V_p}{\tau}\right)$$

- V_p/τ relatively constant, except slightly larger for YSZ in H_2O samples
- Agrees with slight performance enhancement

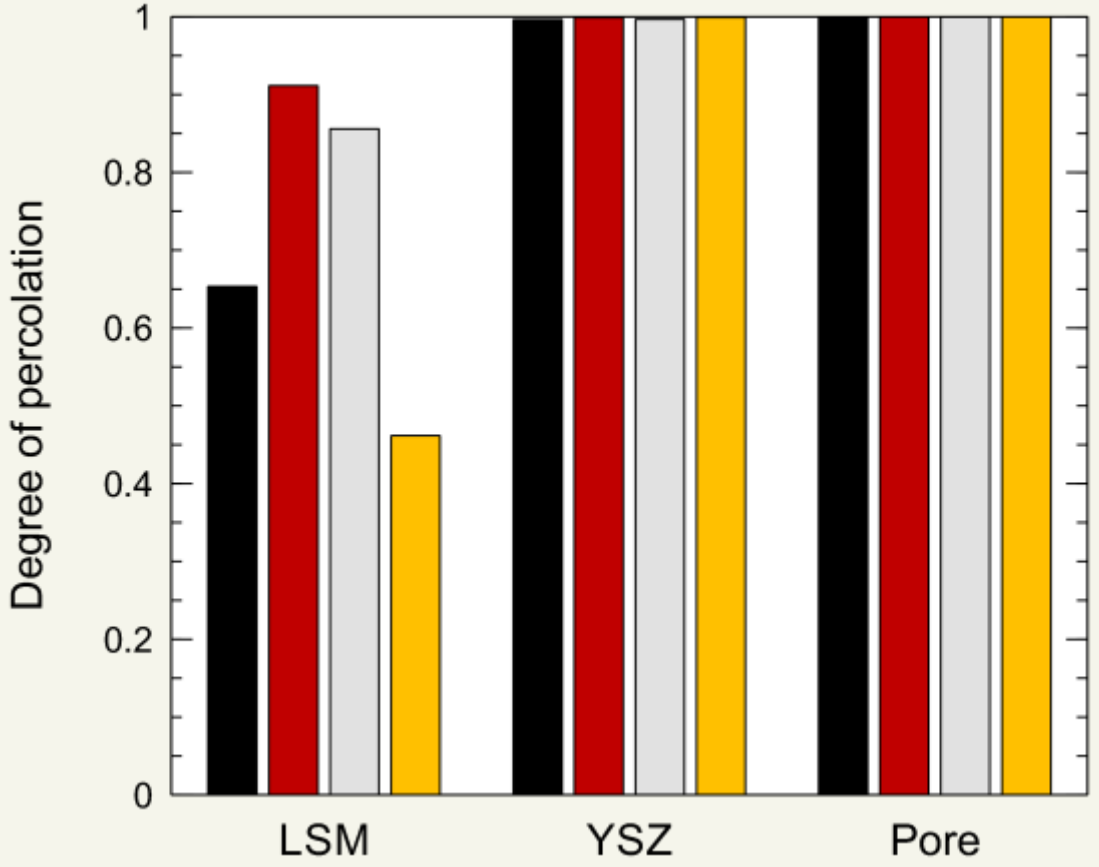


* CJ Gommes *et al*, AIChE Journal **55** (2009) p. 2000.

Results – Phase percolation

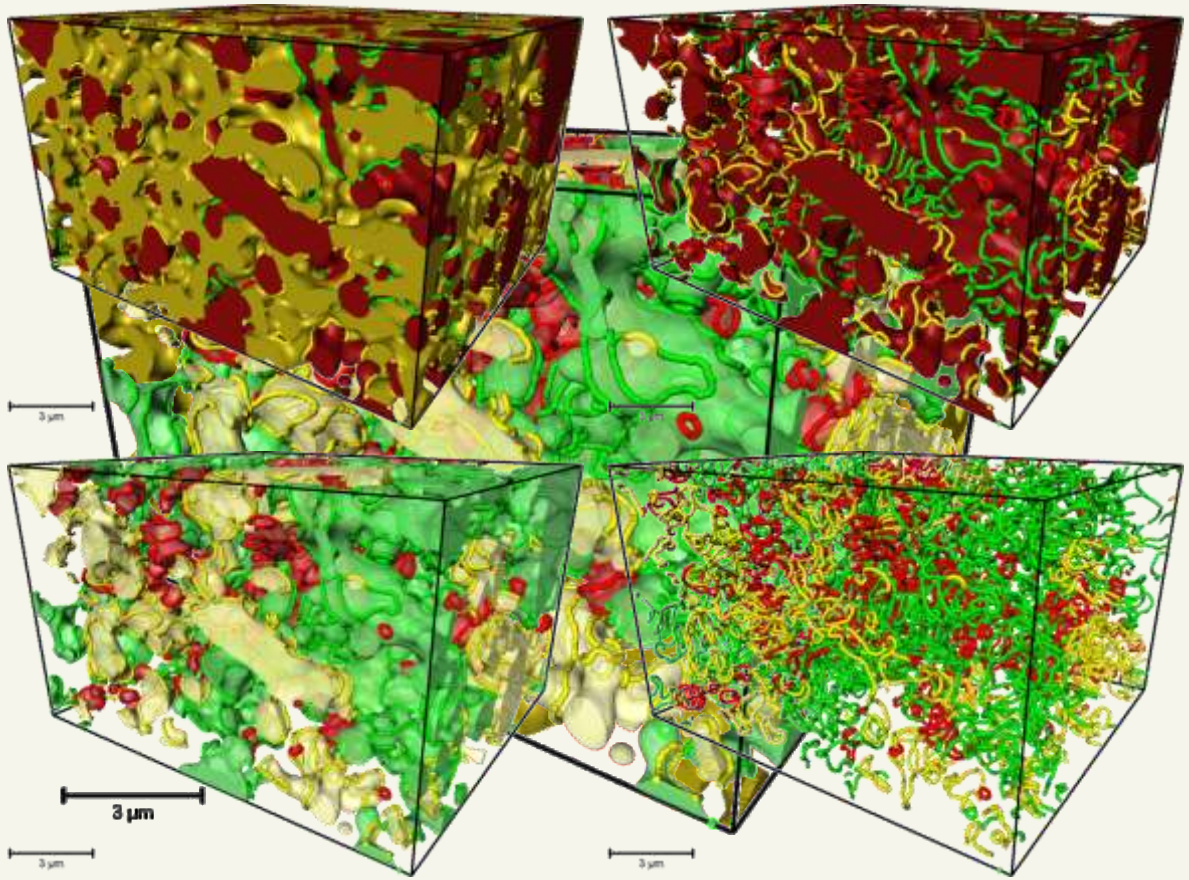
- Comparison of longest section of each phase to overall network
  - Used 5 longest components

- Result:
  - YSZ and pore completely interconnected
  - LSM is limiting transport

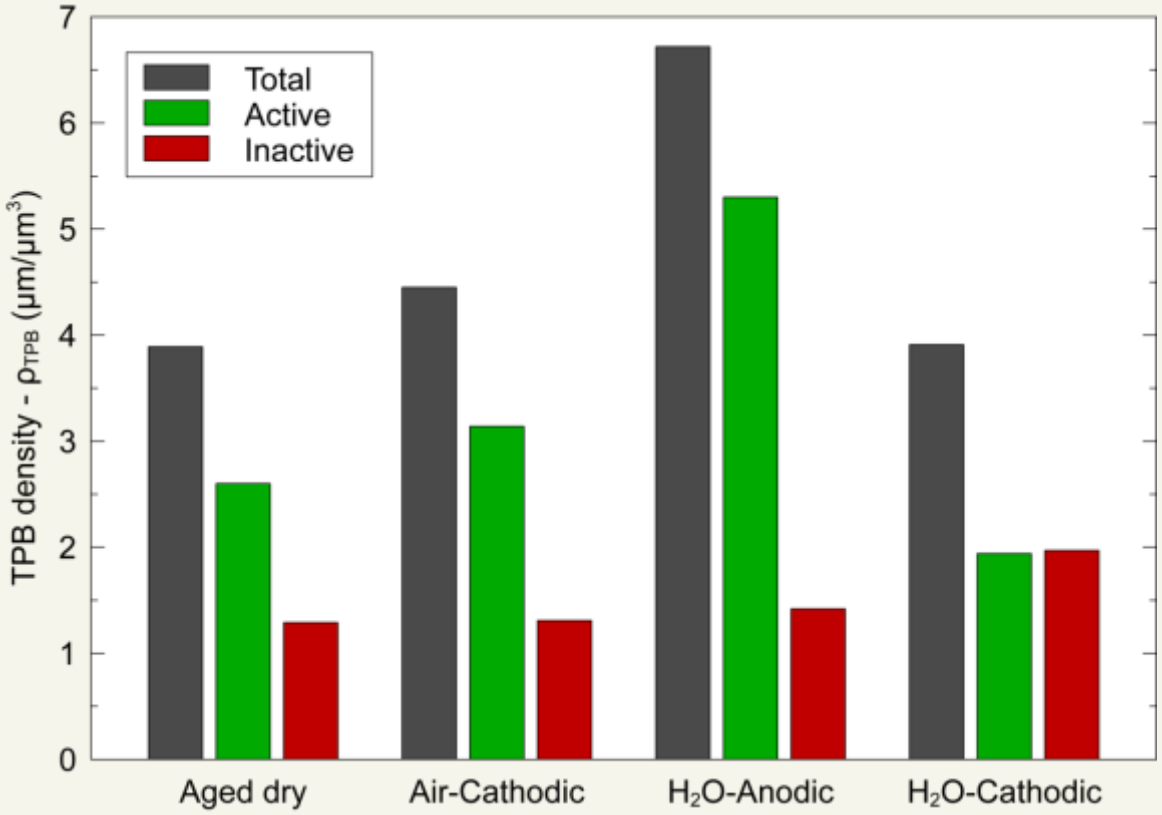


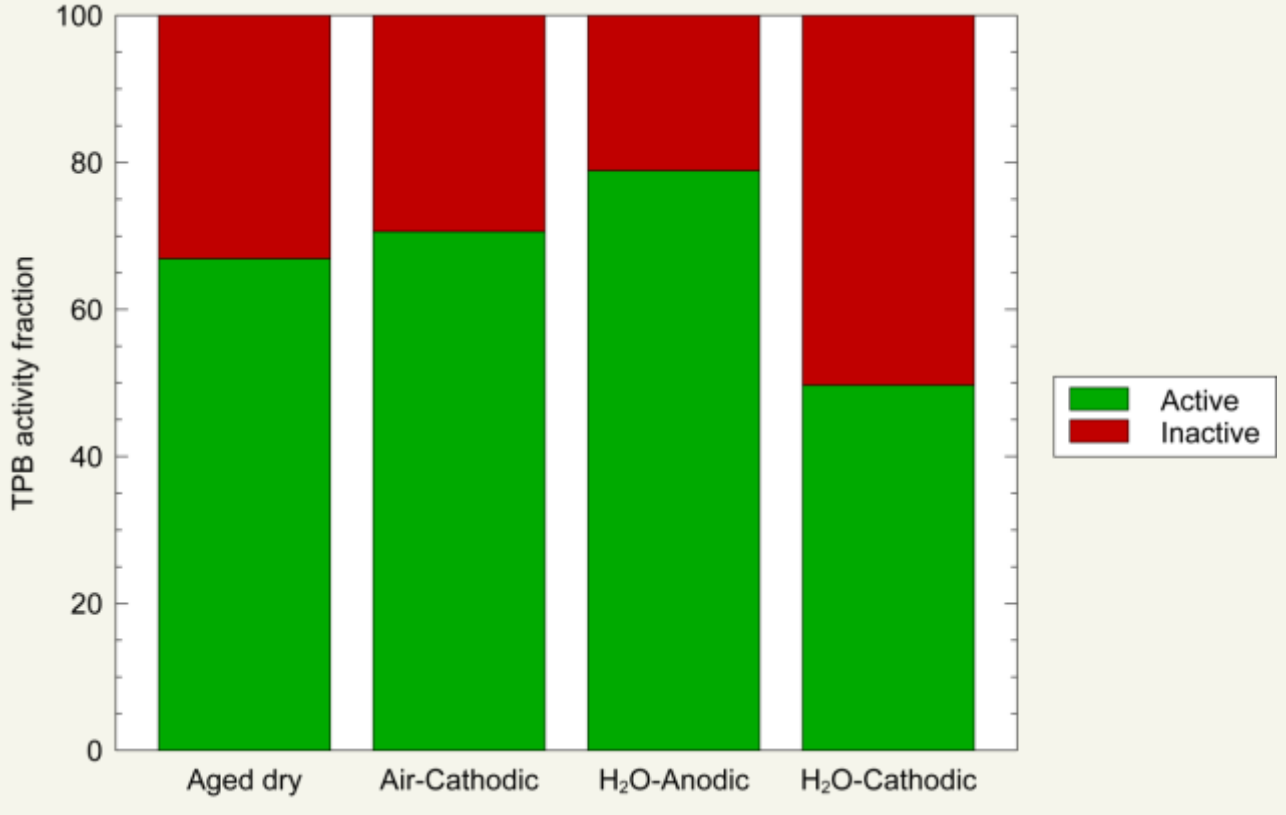
Triple phase boundary (L_{TPB}) determination

- Intersection of three phases is necessary for the oxygen reduction reaction to occur:
  - ORR: $\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$
  - This quantity can be directly related to cell performance
- Within analysis volume, a phase and boundary site can be described as **active**, **inactive**, or **unknown**
- Labels depend on connection to edges
  - Unknown have at least 1 border with edges (dead-end)
  - Active have two borders across a dimension (transverse)
  - Inactive networks have no intersection with an edge (isolated)
- Collaboration with Scientific Applications and Visualization Group at NIST
  - Implemented edge-counting more accurate than morphological expansion (current trend in literature)



Results – Triple phase boundaries

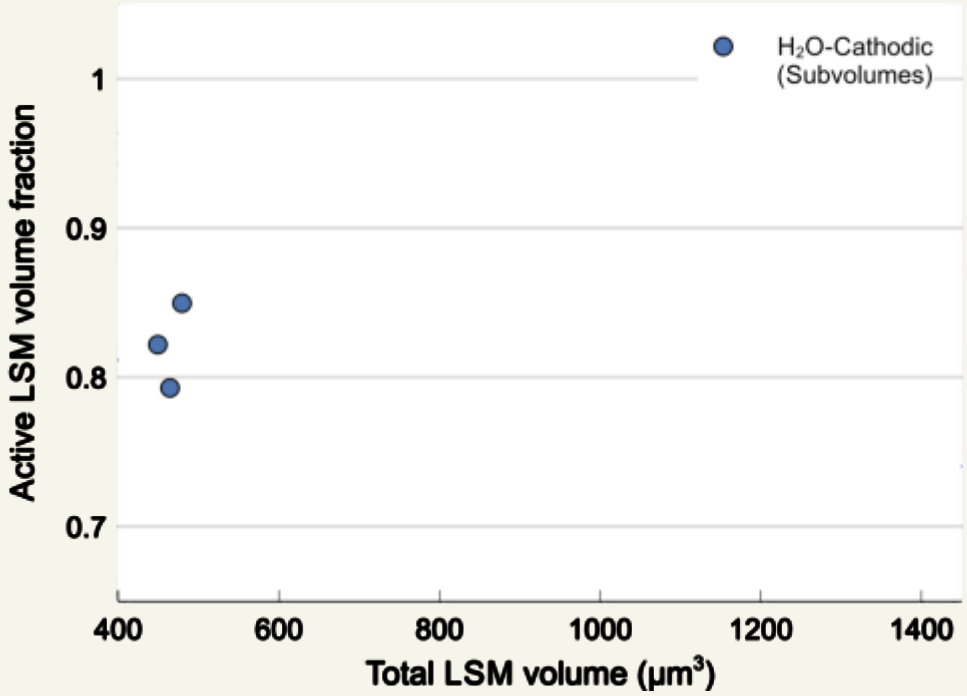


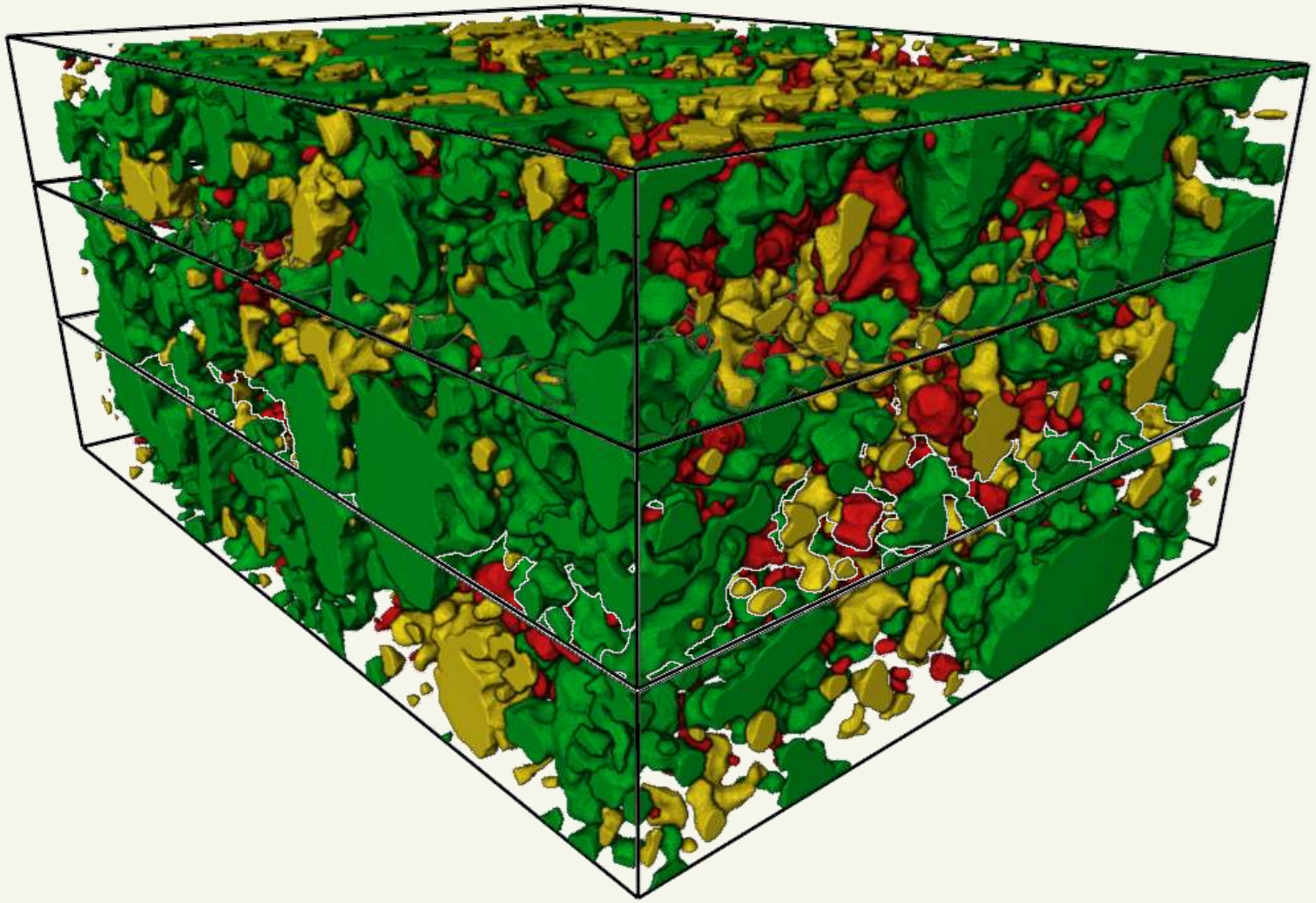


- Total ρ_{TPB} relatively constant (except H_2O-anodic, which has low sampling volume)
- H_2O-cathodic has significant decrease in active TPB density, suggesting drop in active sites for ORR

Results – Impact of aspect ratio?

- H_2O Cathodic has less active TPB
  - Real result, or artefact of measurement?
  - Our classification depends on analysis of volume boundaries





Summary

Conclusions

- We have developed and refined methods using both Avizo Fire and external calculations to quantify 3D microstructure of solid oxide fuel cell cathodes
- At the conditions tested, subtle changes in microstructure occur; which agree with subtle changes in cell performance
- $\rho_{TPB,active}$ decreases when aged under H_2O contamination and cathodic polarization
- Segregation of La and Mn to YSZ grain boundaries in H_2O-cathodic (but not Sr)

Upcoming Work

- Analyze and quantify composition of segregation products using TEM/EELS
- Further correlation with EIS data from same samples
- Investigation of LSCF/GDC composite cathode degradation

Acknowledgements

SECA, Contract No. DEFE0009084
NSF GRFP, Grant No. DGE 1322106

Joshua Schumacher

John Hagedorn
Wesley Griffin
Judith Terrill

Danijel Gostovic,
Nicholas Vito

Ken Lagarec,
Mike Phaneuf

Open source projects:
Scikit-fmm
HyperSpy
OpenCV
ImageJ/Fiji

THANK YOU

Questions and comments?

Email:
jtaillon@umd.edu
and/or
riba@umd.edu