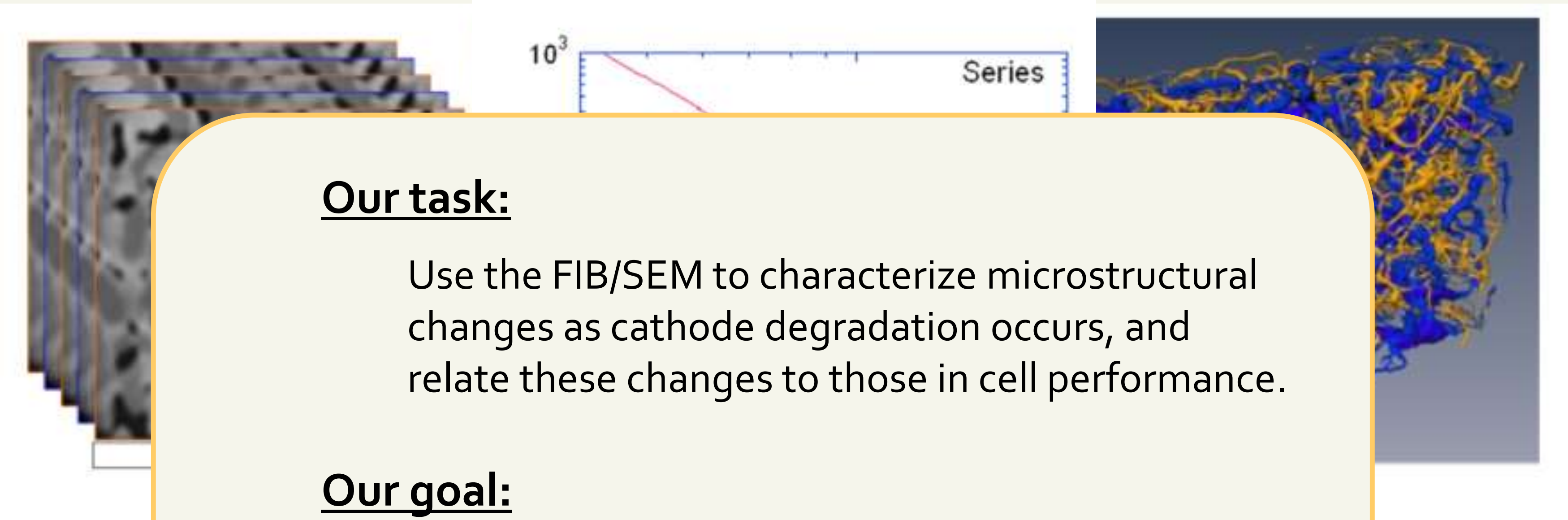
THREE DIMENSIONAL MICROSTRUCTURAL CHARACTERIZATION OF CATHODE DEGRADATION IN SOFCS USING FOCUSED ION BEAM AND SEM

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.

October 2, 2014 , 8:30 AM

Introduction to Solid oxide fuel cells



- Solid oxide fu
  - Low cost, fle
- Problems?
  - High operati
    - Cathode
    - 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).
      - Relationship to cell performance:
        - J. Smith, E. Wachsman, *et al.*, *Solid State Ionics*, **180**(1), 90 (2009).

Our task:

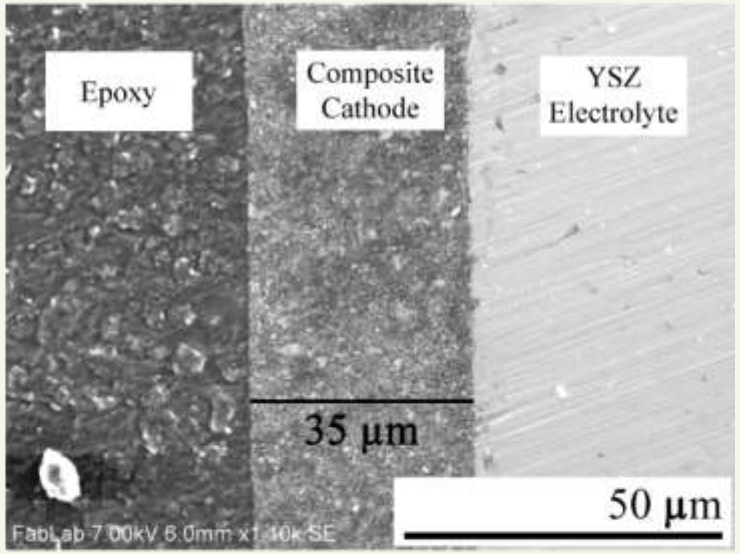
Use the FIB/SEM to characterize microstructural changes as cathode degradation occurs, and relate these changes to those in cell performance.

Our goal:

Better understanding of the fundamental mechanisms behind cathode degradation.

Experimental - Button cell testing

Button cell



Cross-section view

- Symmetric cathode cells
- 8-YSZ electrolyte
- 50 wt. % LSM/YSZ cathode paste
- Sintered at 1000°C for 1hr

- Three conditions compared:
  - Baseline ("*Unaged*")
  - Aged at 800°C for ~400 hr under ambient ("*Aged - dry*")
  - Aged at 800°C for ~400 hrs under 3% H_2O ("*Aged - H_2O*")

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?

Data acquisition – pre-FIB preparation

1) Vacuum epoxy impregnation:

2) Polishing (to 1200 grit):

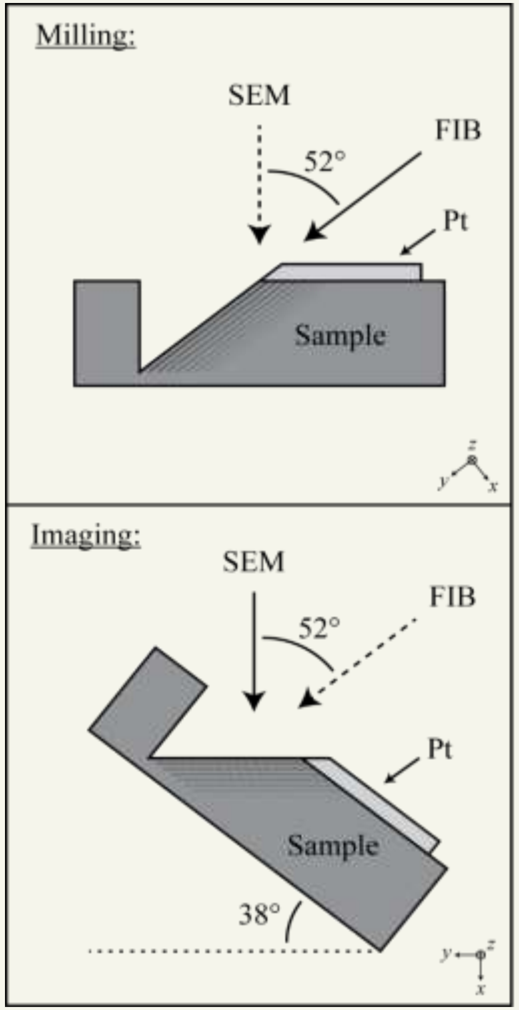
3) Mounting for FIB/SEM:

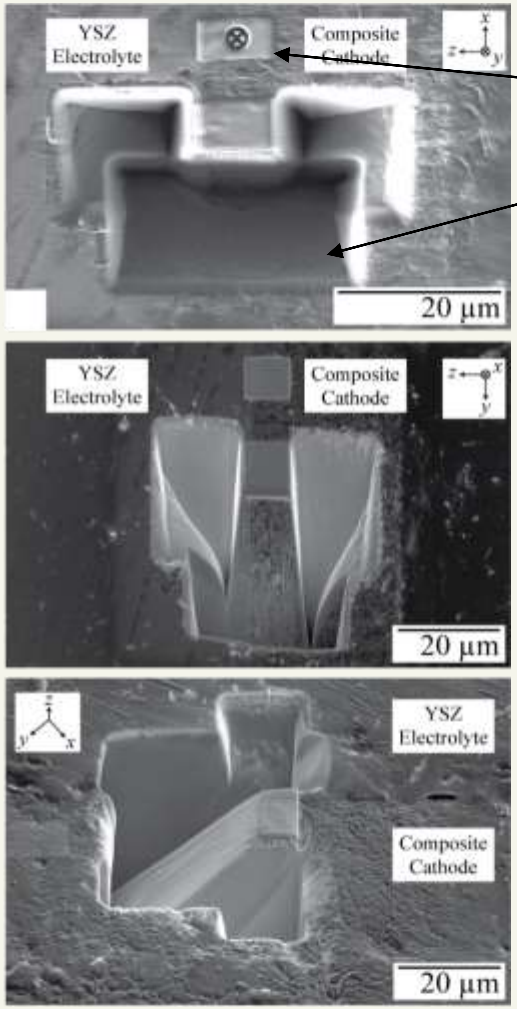
Equipment/Software

- 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

FEI Helios 650 at NIST (CNST)

Data acquisition – Initial procedures

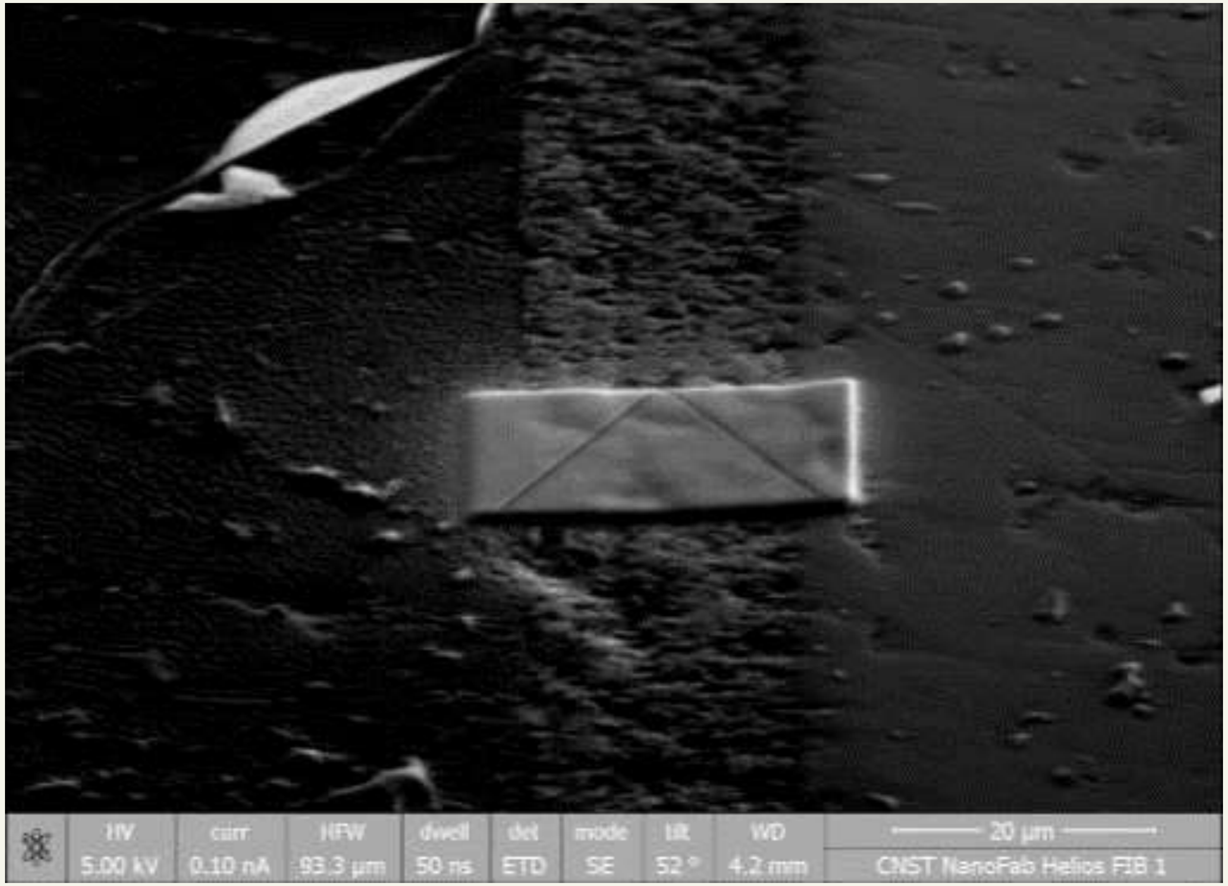




- Protective Pt and fiducial marks
- "C-trench" to prevent shadowing
- Mill at 0° stage tilt
- Image at 38° stage tilt

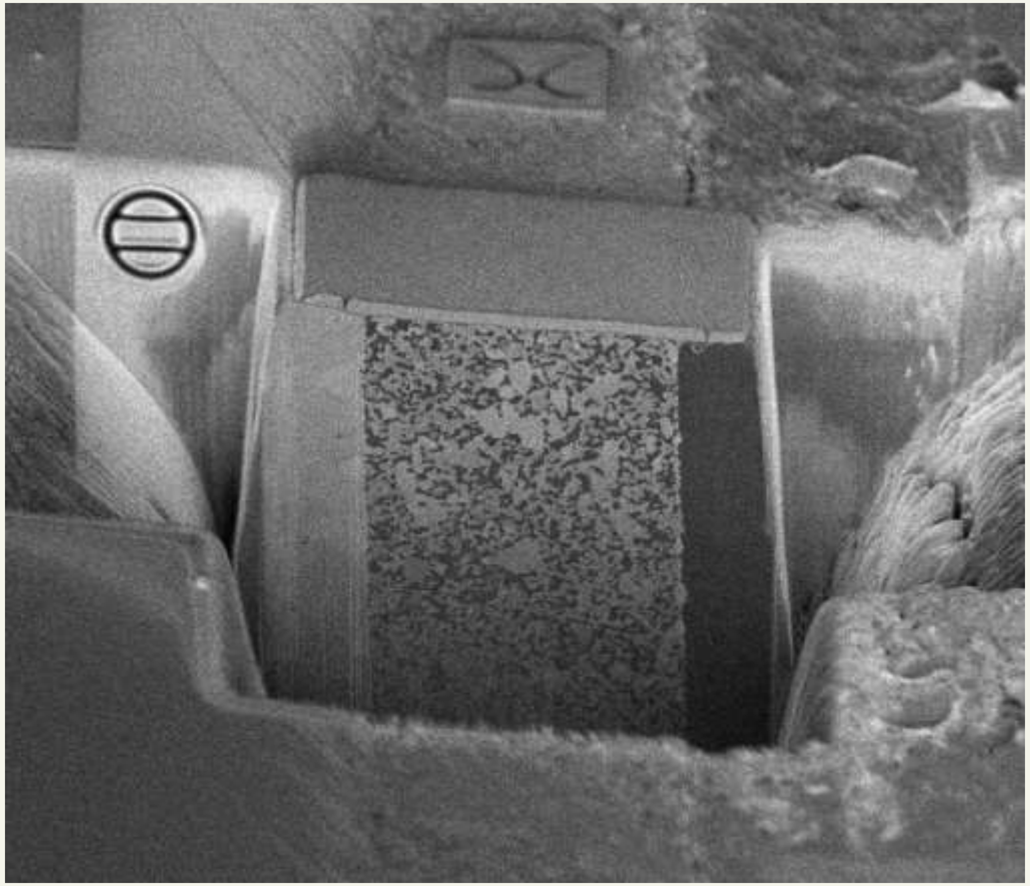
- Unique FIB/SEM geometry means:
  - Improved contrast between LSM and YSZ
  - Perpendicular imaging
  - Limited detector shadowing effect
  - **Increased acquisition time (significant!)**
    - **5 min 40 sec, per slice**
    - 30 nm slice thickness, 20 μm slice width

Data acquisition – Optimized procedures



- Similar trenching, but in usual orientation
- iFast recipe developed to fully automate (takes about 1 hour to complete)
    - Pt deposition
    - Thickness tracking mills
    - C deposition (x2 for fiducial)
    - Fiducial mill
    - Bulk trenches (65 nA)
- Manually mill imaging fiducial and clean up face before beginning acquisition

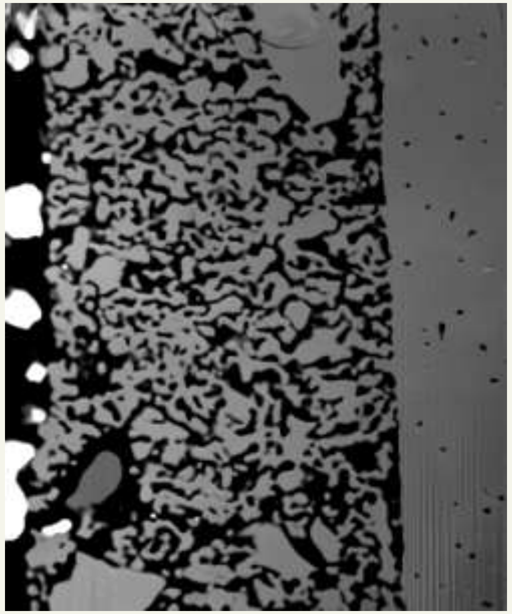
Data acquisition – Optimized procedures



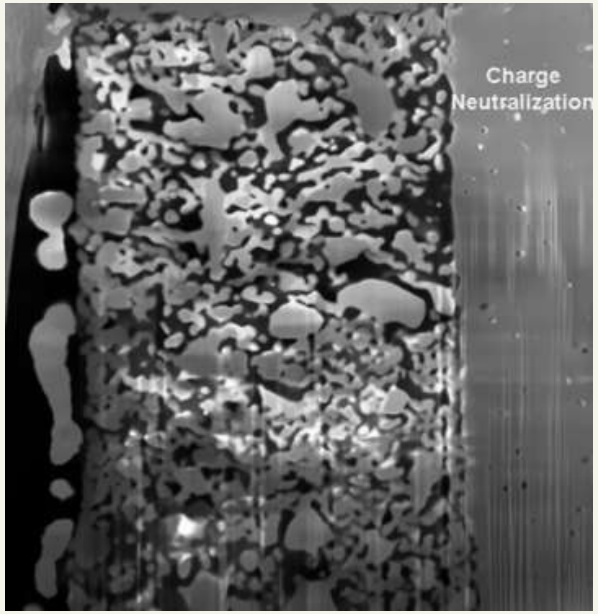
- Setup and ready to mill in about 1.5 hrs
  - Mostly automated
- Electron image fiducial for precise image placement
- Tracking marks for post-run measurement of slice thickness
- Some shadowing deeper into trench, but much faster acquisition
  - **2 min 30 sec, per slice**
  - 20 nm slice thickness, ~ 30 μm slice width
  - Overnight run acquires about 7 μm of depth

Experimental – Electron imaging challenges

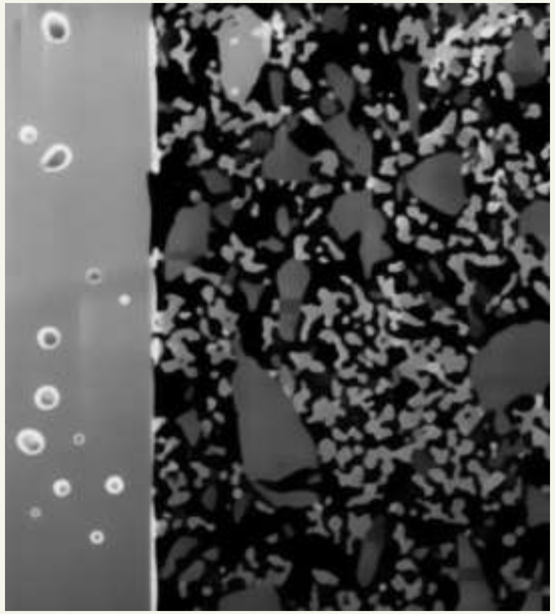
- Challenging system to image due to:
  - Poor RT conductivity
  - Similar electron yields from each phase
- Careful control of imaging parameters allows for charge contrast imaging
  - Not always completely reliable due to local effects



In-lens BSE

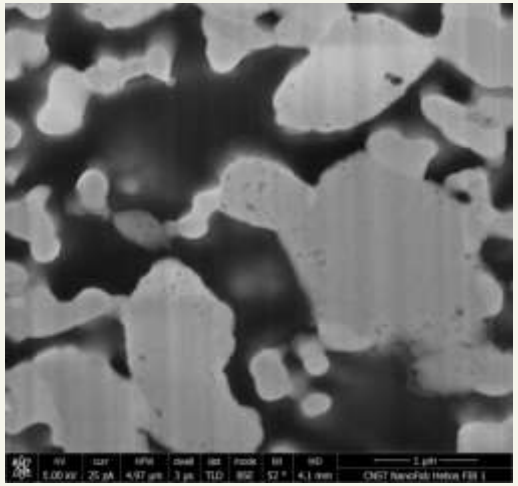


In-lens SE (Charge neutralization setting)



Long-dwell charging contrast (SE)

Experimental – Electron imaging (effect of V_{acc})

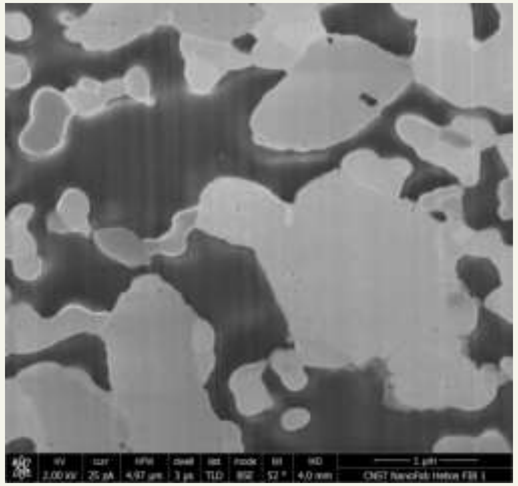


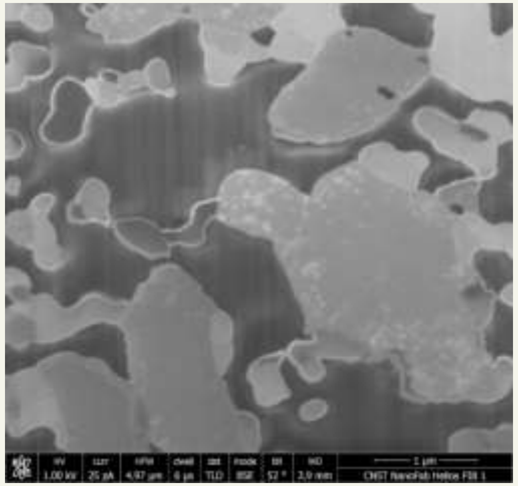
5kV – 25 pA

What contrast is really important?

Need to facilitate segmentation!

2kV – 25 pA



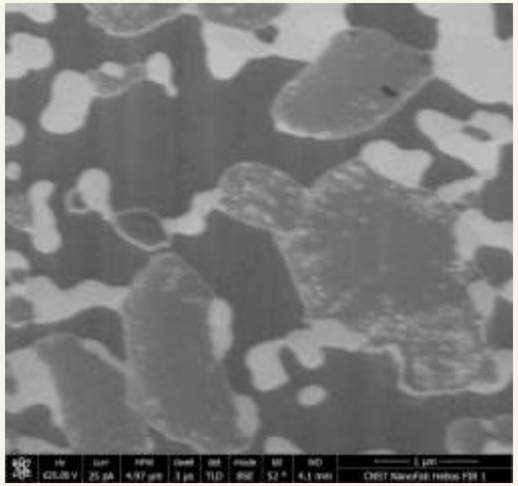


1kV – 25 pA

Image frame integration and longer dwell (6 μs) improve contrast between phases

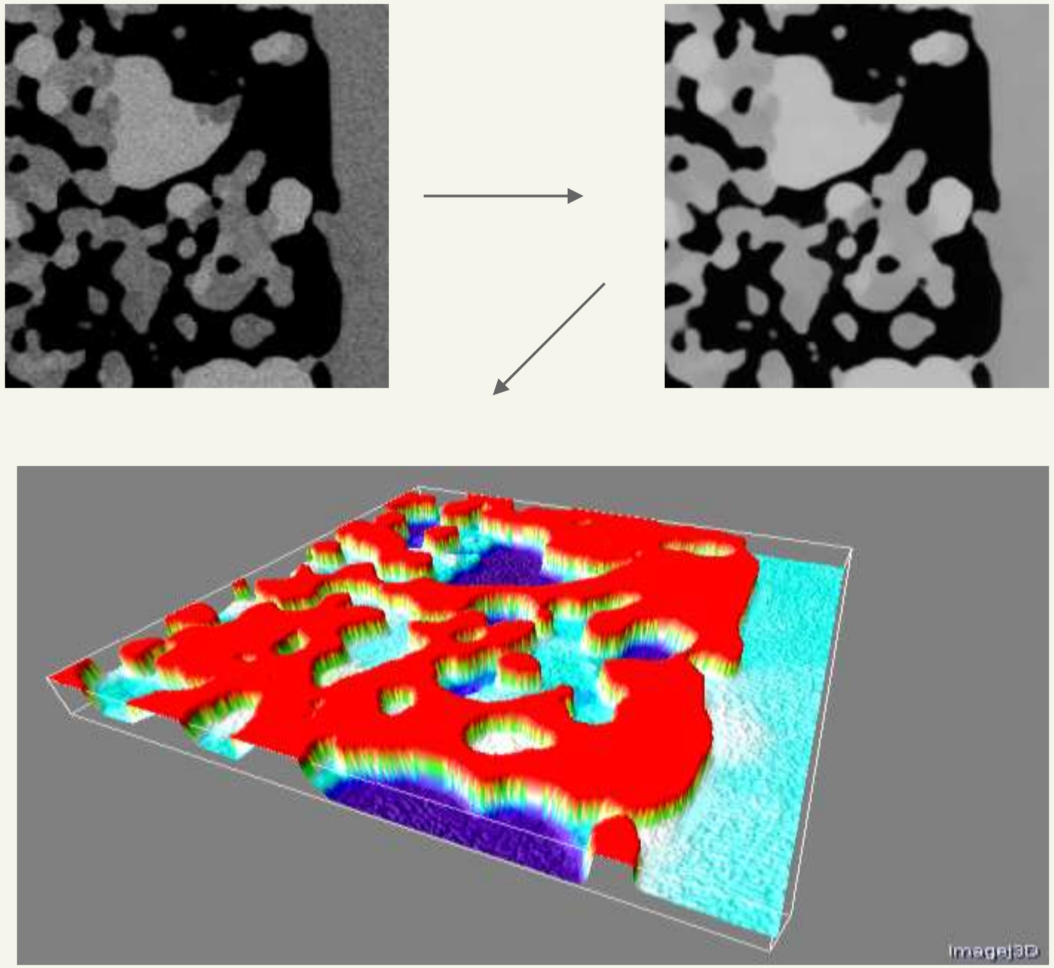
TLD
(through the lens detector)
in backscatter electron mode

625 V – 25 pA



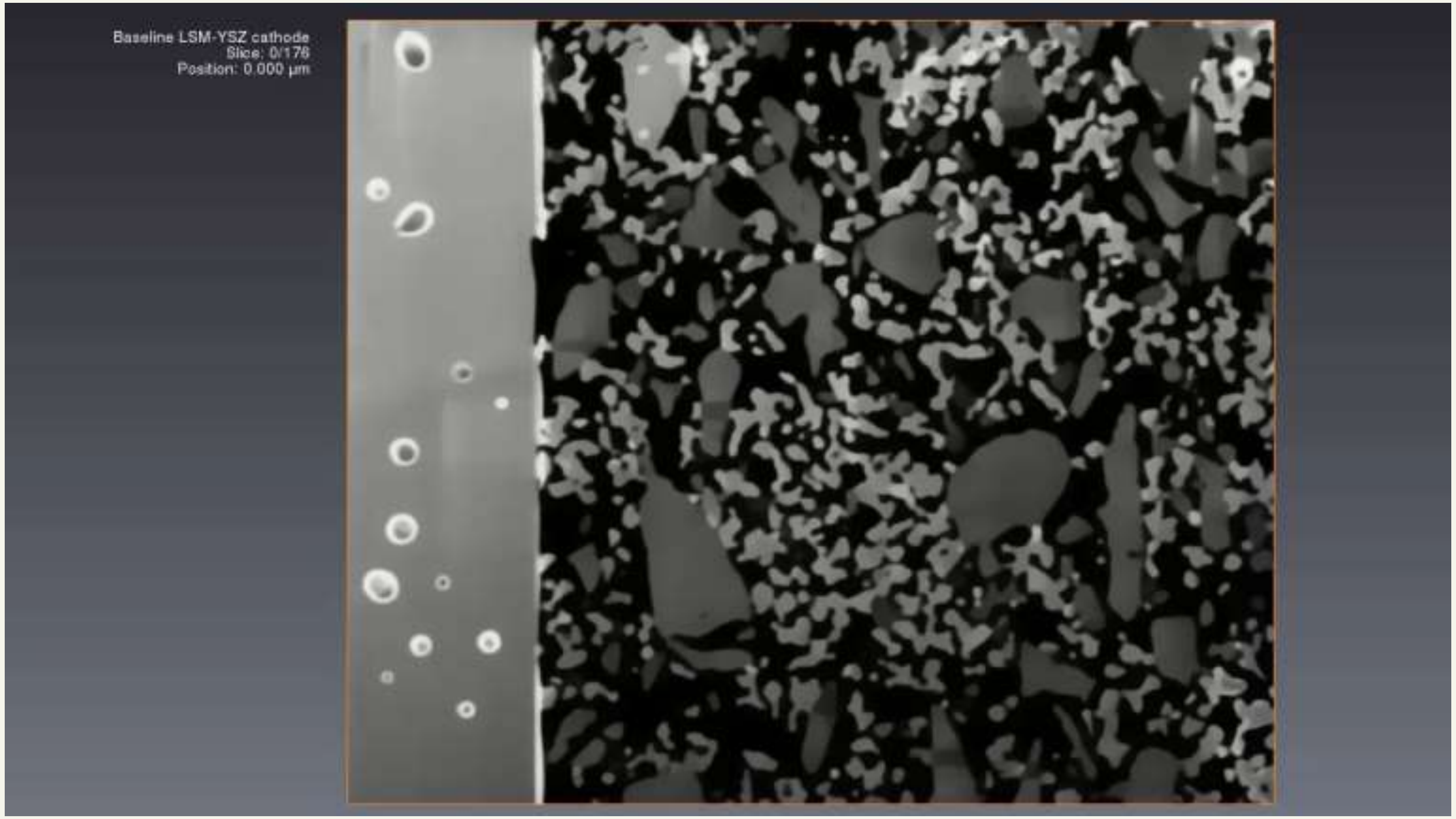
Experimental – post processing of data

- Post-processing done with Avizo Fire:
  - Non-local means filtering of data[1]:
  - Watershed segmentation algorithm[2]:



[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 – *Unaged* SOFC

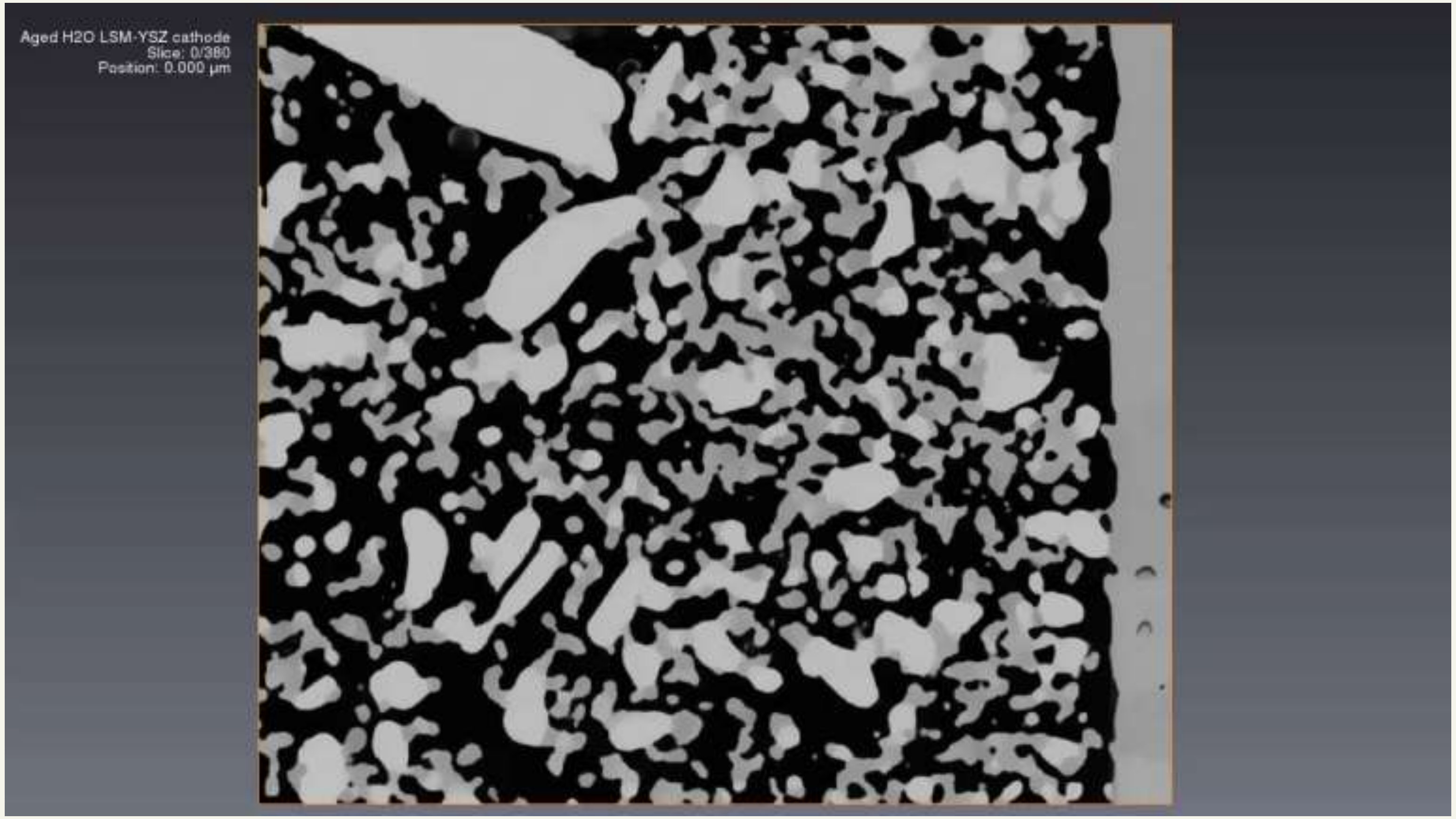


Voxel size: 12 x 12 x 30 nm, SE signal collected on FEI Helios 650, NIST
HFW: 9.5 µm; Depth: 5.25 µm; Total reconstructed cathode volume (excluding electrolyte): 276.84 μm^3

Results – *Aged, Dry* SOFC

Voxel size: 10 x 10 x 10 nm, EsB signal collected on Zeiss Crossbeam 540, courtesy of Carl Zeiss and Fibics, Inc.
HFW: 9.9 µm; Depth: 8.12 µm; Total reconstructed cathode volume (excluding electrolyte): 643.11 μm^3

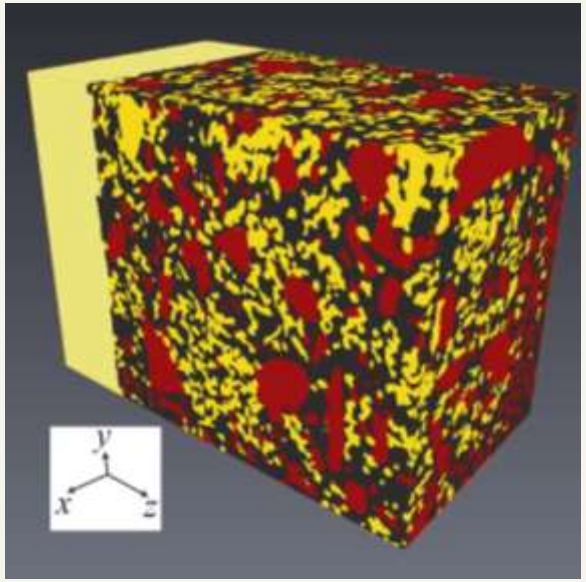
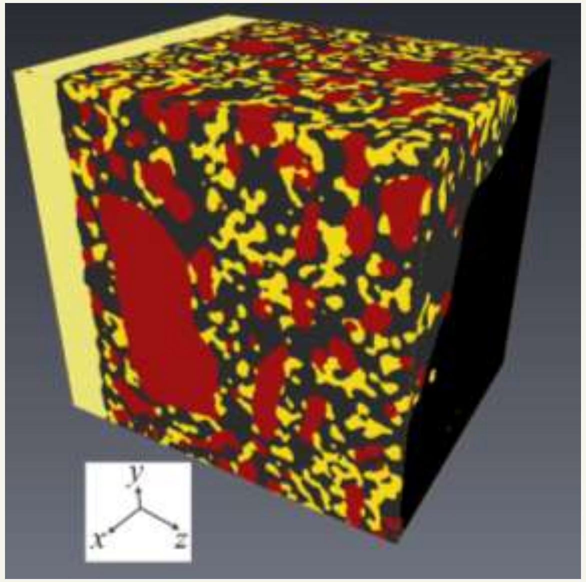
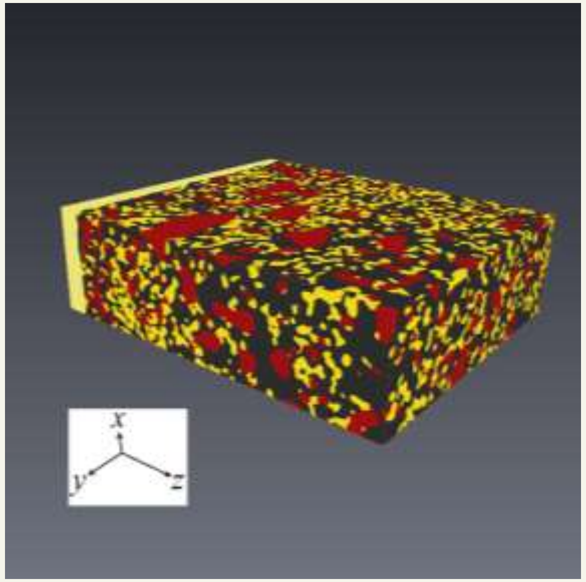
Results – *Aged, H_2O* SOFC



Voxel size: 10 x 10 x 10 nm, EsB signal collected on Zeiss Crossbeam 540, courtesy of Carl Zeiss and Fibics, Inc.
HFW: 13.96 µm; Depth: 3.8 µm; Total reconstructed cathode volume (excluding electrolyte): 627.35 μm^3

Results – Surface generation

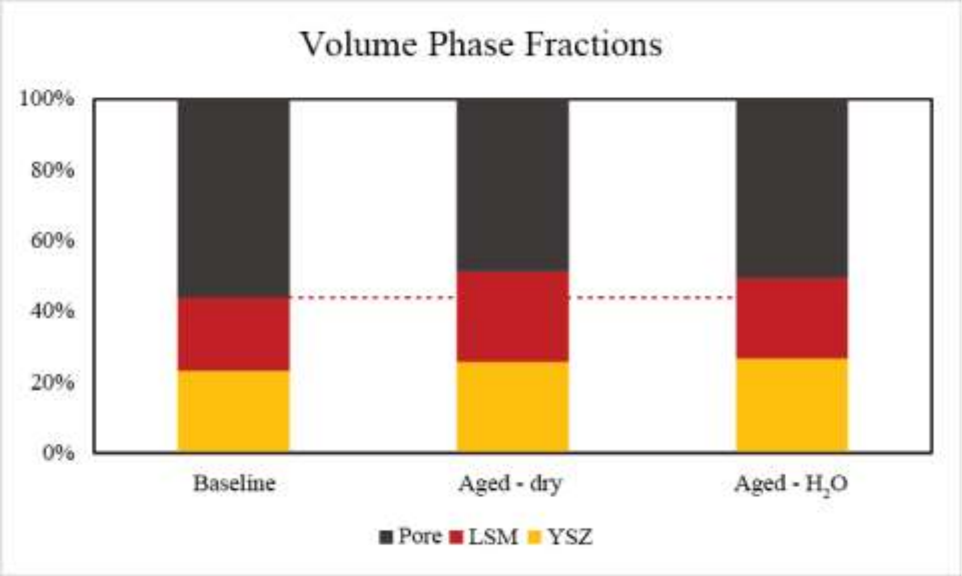
YSZ | LSM | Pore

Baseline	Aged-dry	Aged-H_2O
		
350.8 µm³	761.1 µm³	667.2 µm³

Bounding box dimensions (µm):

	Baseline			Aged-dry			Aged-H_2O	
5.250	7.031	9.504	8.121	9.380	9.991	4.003	11.940	13.960
X	Y	Z	X	Y	Z	X	Y	Z

Results – Surface quantification



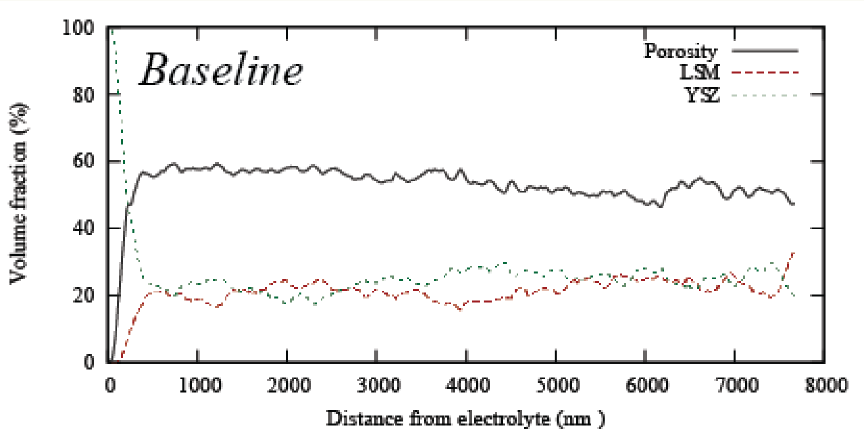
- Porosity is decreased in both aged samples
  - Additional sintering occurring during aging process

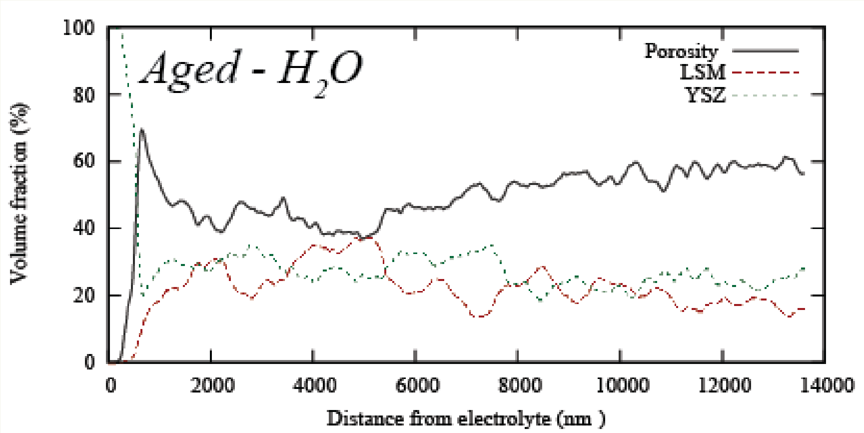
- Phase solid fractions remain similar to expected values (from source materials)

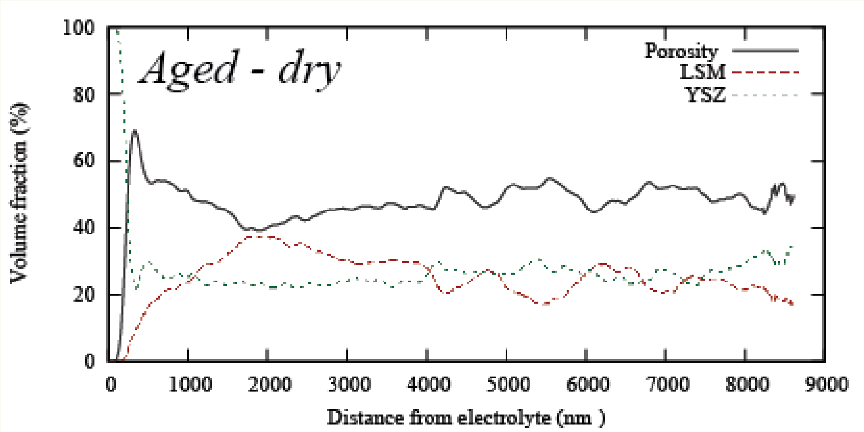
	Exp. YSZ	Exp. LSM	Obs. YSZ	Obs. LSM
Baseline	0.52	0.48	0.527	0.473
Aged-dry			0.503	0.497
Aged-H2O			0.542	0.458

A. JAMES CLARK SCHOOL OF ENGINEERING

Results – Graded phase fractions





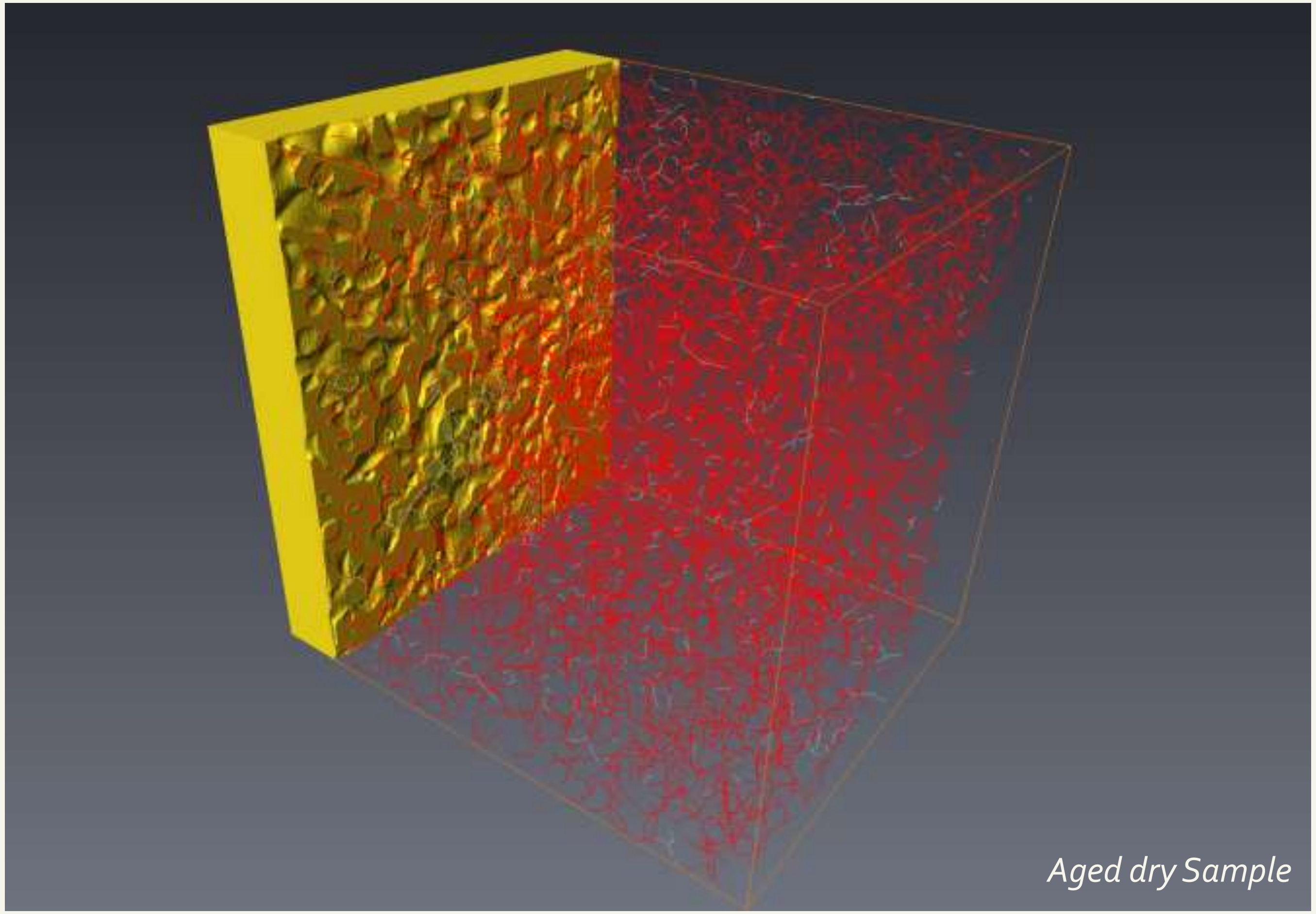


- Plotting phase volume fraction as a function of distance from cathode/electrolyte interface
  - Influence of aging on phase distribution

- Greater variability in aged samples:

σ of phase fraction	Pore	LSM	YSZ
Unaged	2.51	2.24	2.83
Aged-dry	3.75	5.45	2.61
Aged-H2O	6.73	5.92	3.92

Results – Phase connectivity

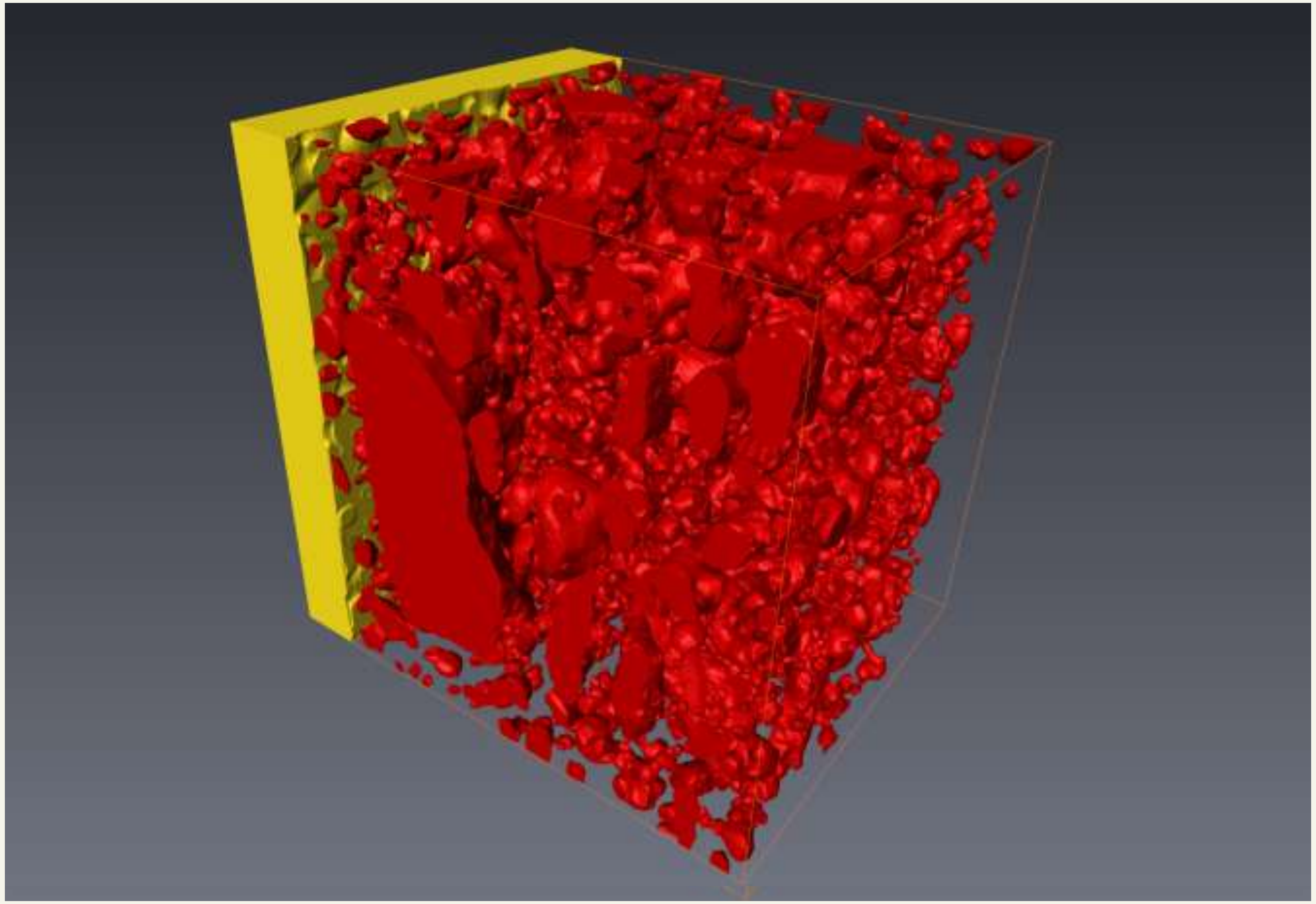


Skeletonization of individual phases reveals connectivity

Isolated LSM networks within volume

Contiguous YSZ and pore networks

Results – Phase connectivity

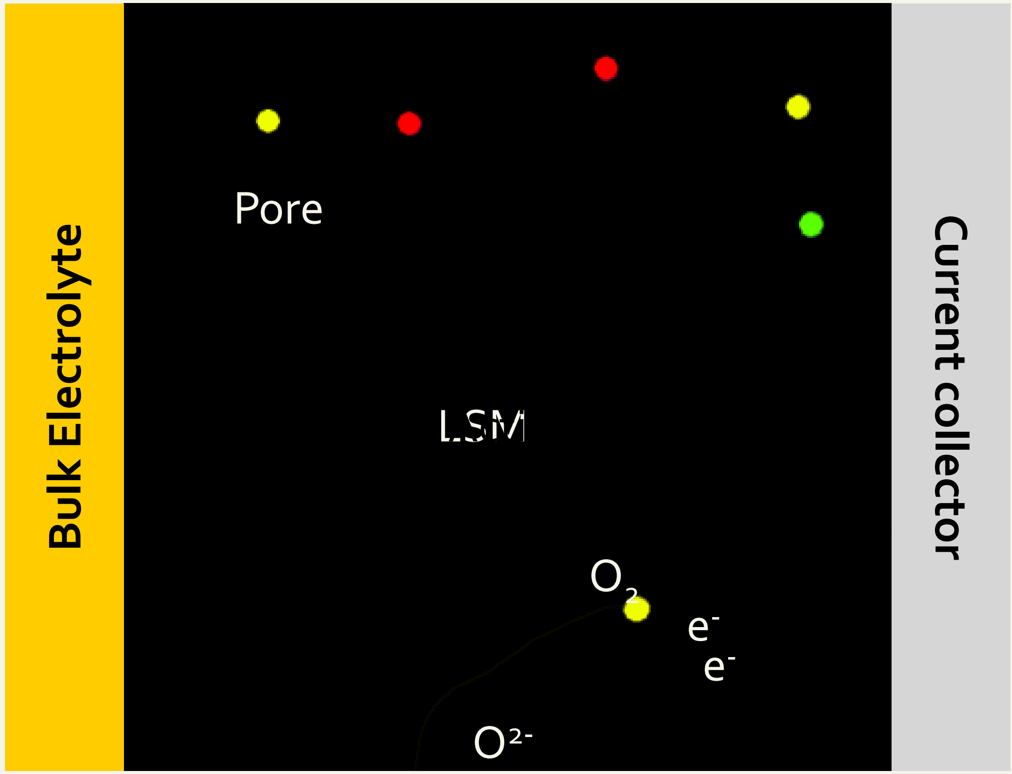


- How to quantify the connectivity?
  - Average degree of connectivity ($< k >$)
  - Max degree of connectivity
  - Percent of length connected to contiguous pathway

- All of these depend on how the skeleton is calculated
  - Two main options within Avizo:
    - Auto skeleton module
    - Centerline tree module
  - Is either really appropriate?

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

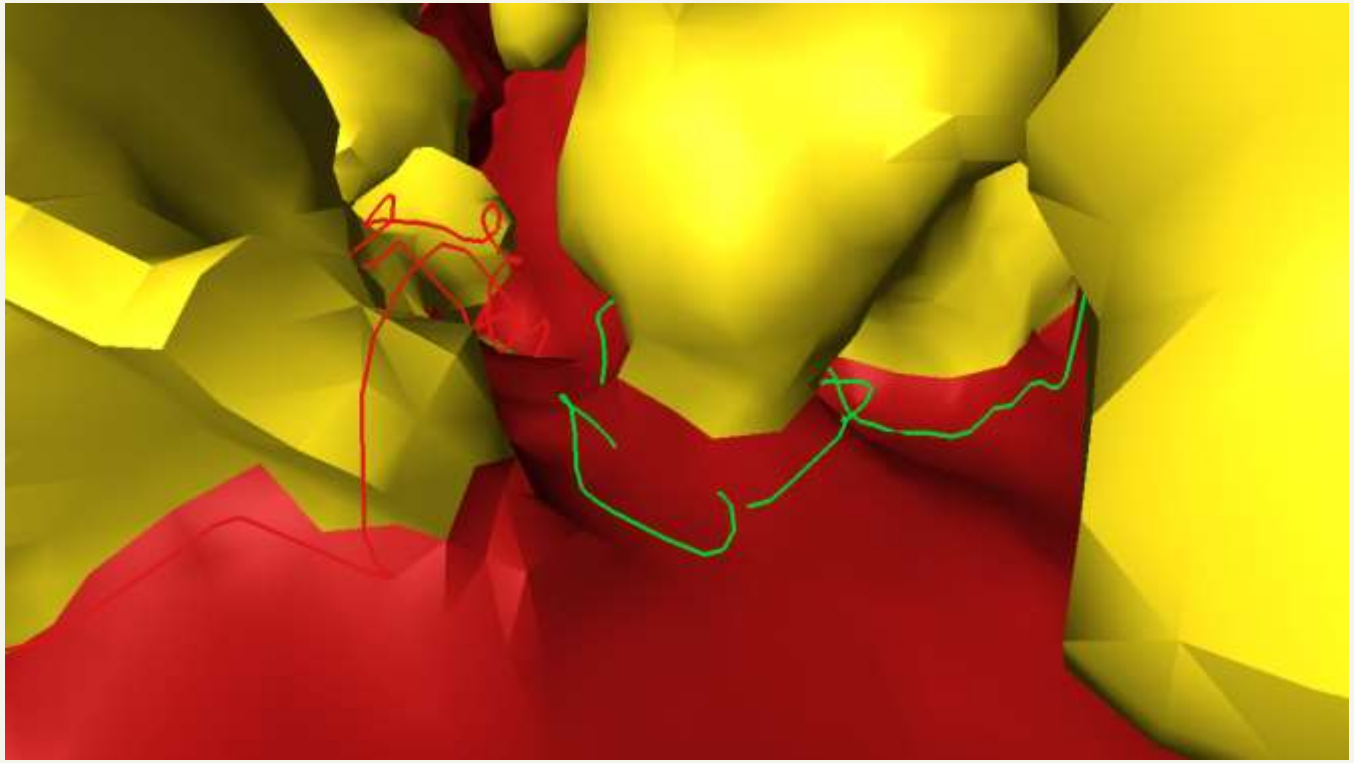


Results – Triple phase boundaries

To be active, all three connected components of the TPB must be contiguous throughout the volume

(which requires a large enough sampling volume to be representative)

Results – Triple phase boundaries

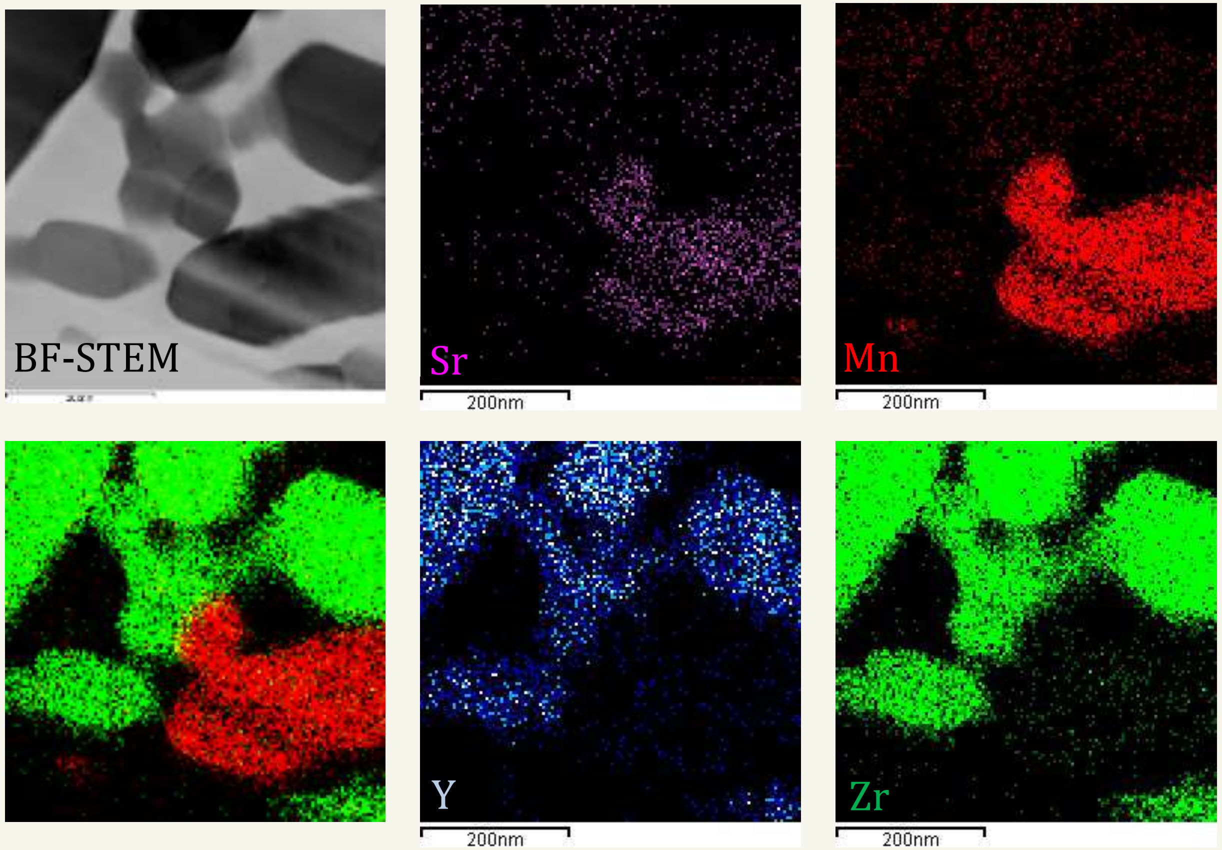


Results – Triple phase boundaries

*Relative to baseline	Baseline	Aged-dry	H_2O
Active TPB [norm]	100%	32.5% *	27.5% *
Total ρ_{TPB} [μm/μm³]	19.2	9.69	8.57

- Absolute quantifications are forthcoming, but we can analyze differences between the two samples, which show decrease in all L_{TPB} values upon exposure to H_2O contamination

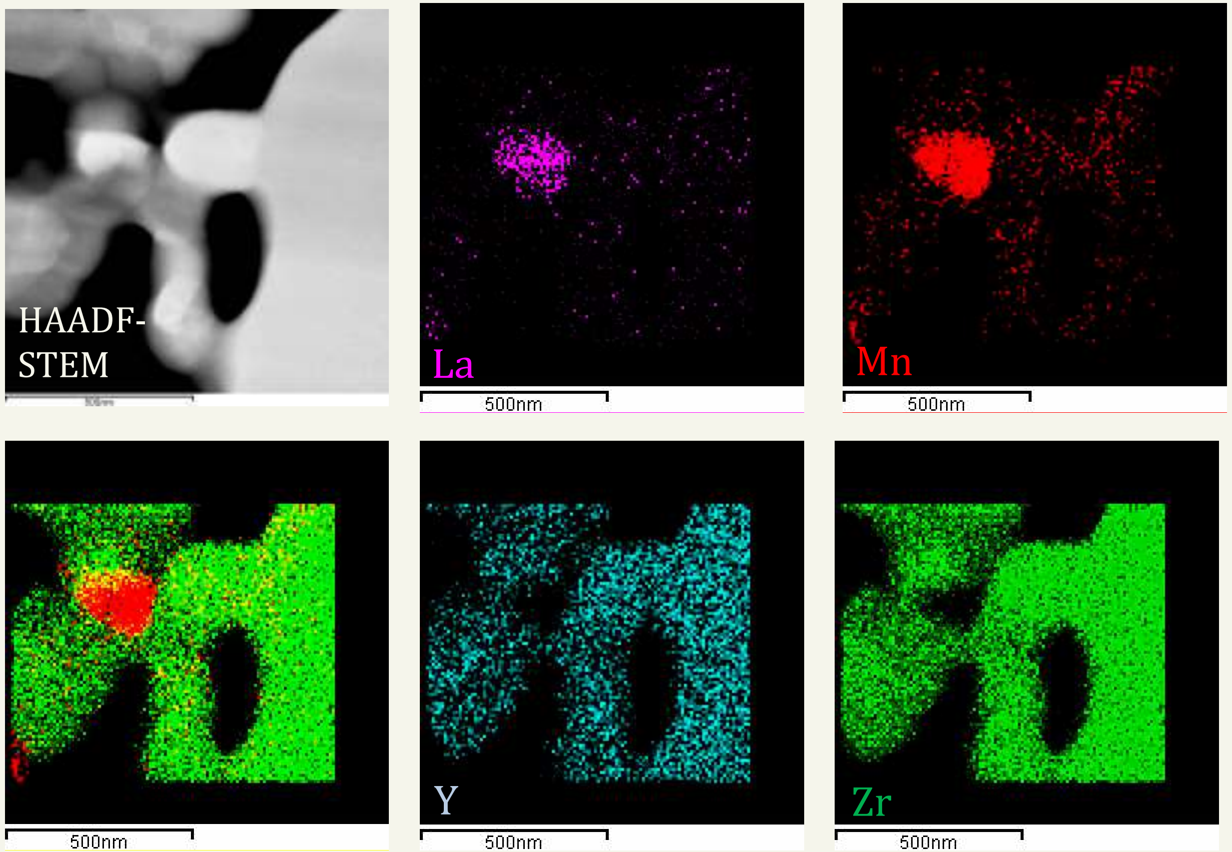
Results – Preliminary TEM/EDS work



STEM-EDS maps of *Baseline* SOFC cathode near electrolyte interface

- Distinct particles of LSM and YSZ

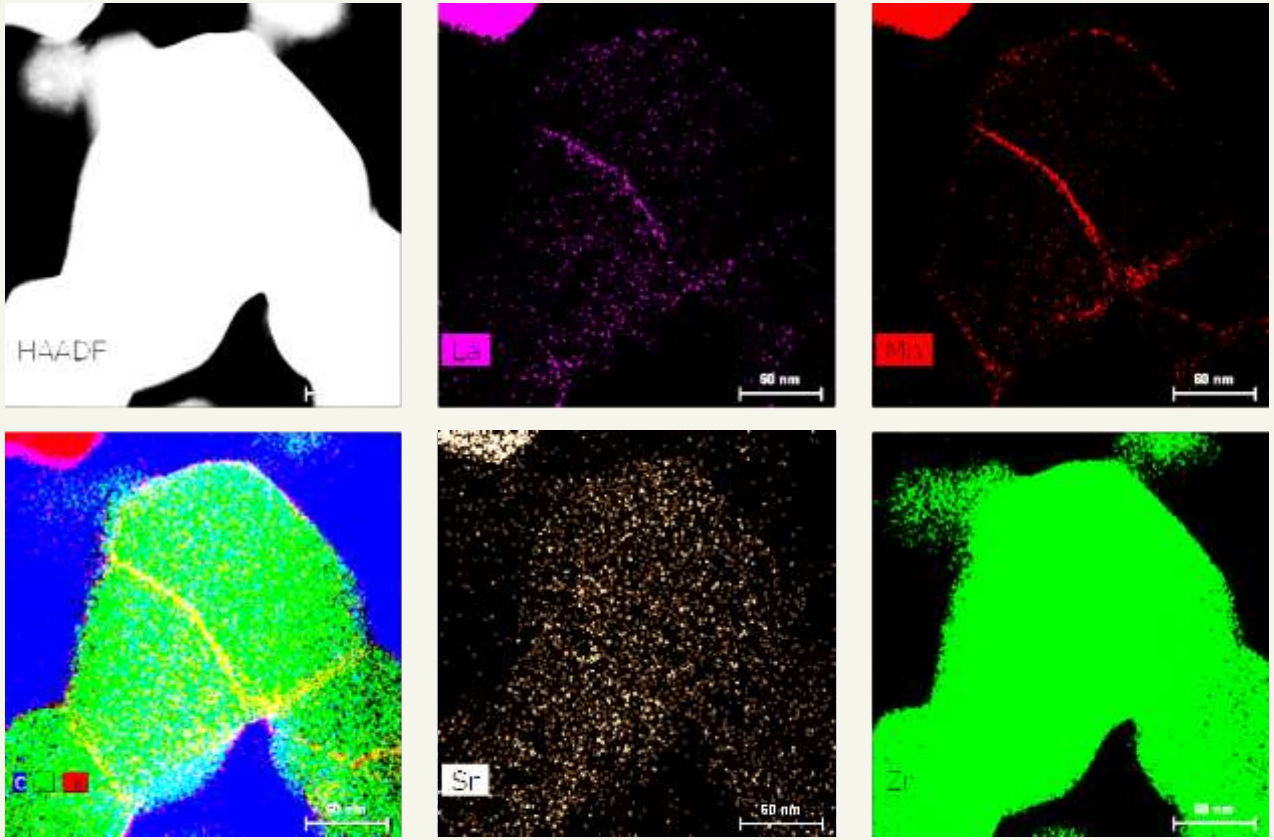
Results – Preliminary TEM/EDS work



STEM-EDS maps of *Aged-dry* SOFC cathode near electrolyte interface

- Still distinct particles of LSM and YSZ
- Perhaps more Mn distributed throughout YSZ

Results – Preliminary TEM/EDS work



Collected on FEI Titan™ G2 80-200 ChemiSTEM, courtesy of FEI Company

STEM-EDS maps
Aged-H2O SOFC cathode

- Distinct particles of LSM and YSZ
- Segregation of La and Mn at YSZ grain boundaries
- Sr is not localized at 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, additional sintering causes changes in phase fractions throughout cathode
- $\rho_{TPB,active}$ decreases when aged under H_2O contamination
- Segregation of La and Mn to YSZ grain boundaries in aged-H_2O (but not Sr)

Upcoming Work

- Observe sample aged in higher H_2O concentrations to confirm effects
- Analyze and quantify composition of segregation products using TEM/EELS
- Correlate with corresponding EIS data

Acknowledgements

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

NIST

CNST Center for Nanoscale Science & Technology — Joshua Schumacher

Scientific Applications & Visualization Group — John Hagedorn, Wesley Griffin, Judith Terrill

UF — Danijel Gostovic, Nicholas Vito

Fibics Incorporated — Ken Lagarec, Mike Phaneuf

FEI — Jessica Riesterer (Hillsboro, OR)

University of Maryland

Maryland NanoCenter NISPLAB — Nanoscale Imaging, Spectroscopy and Properties Laboratory

THANK YOU

Questions and comments?