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Three Dimensional Microstructural Characterization of Cathode Degradation in SOFCs Using Focused Ion Beam and SEM

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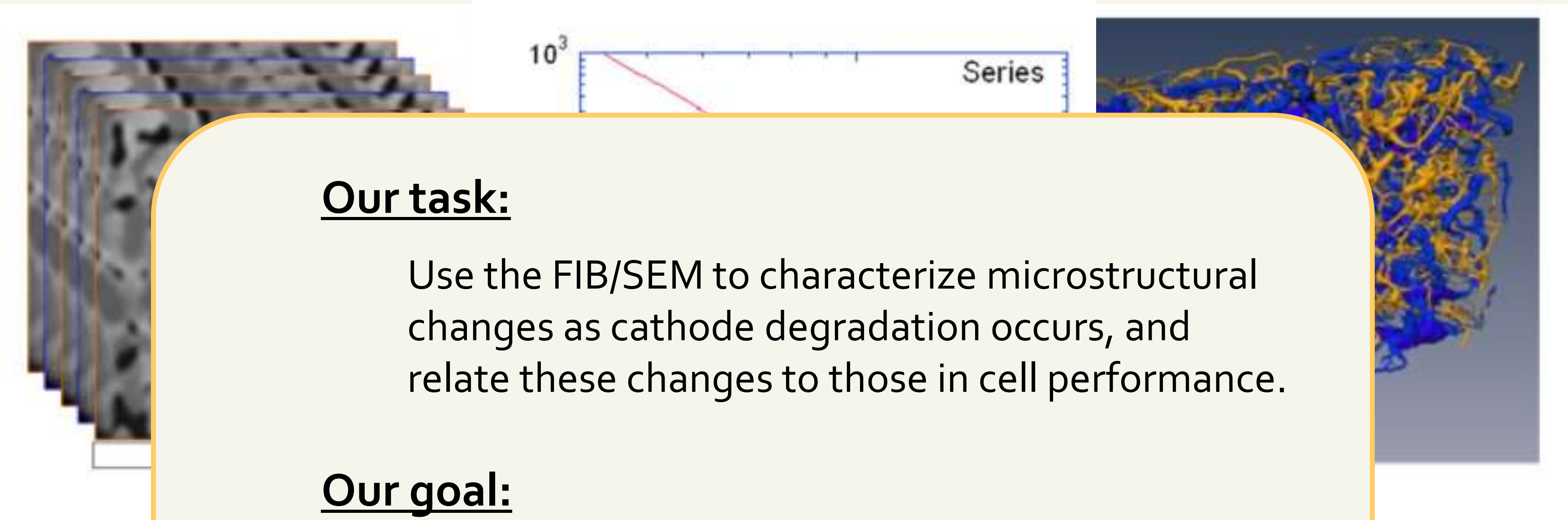
THE DEPARTMENT *of* MATERIALS SCIENCE AND ENGINEERING

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:

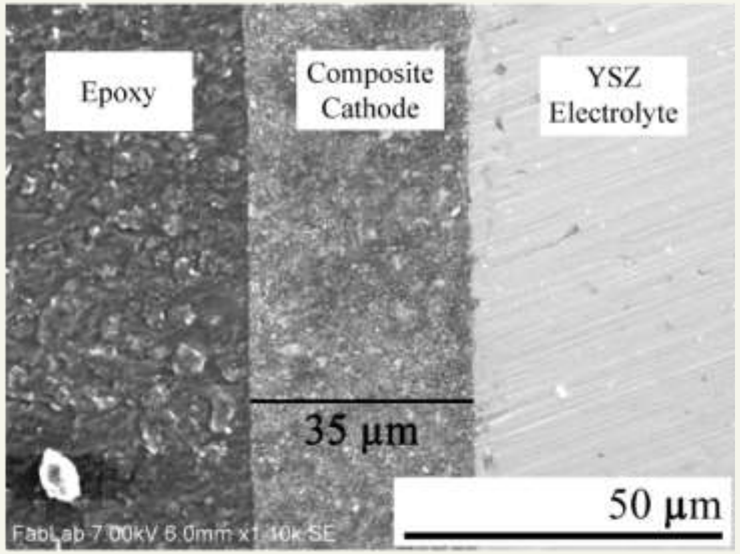
Use the FIB/SEM to characterize microstructural changes as cathode degradation occurs, and relate these changes to those in cell performance.

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
- Aged for 250hr at 800°C
  - Polarization was constant 60mA/cm²

- 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

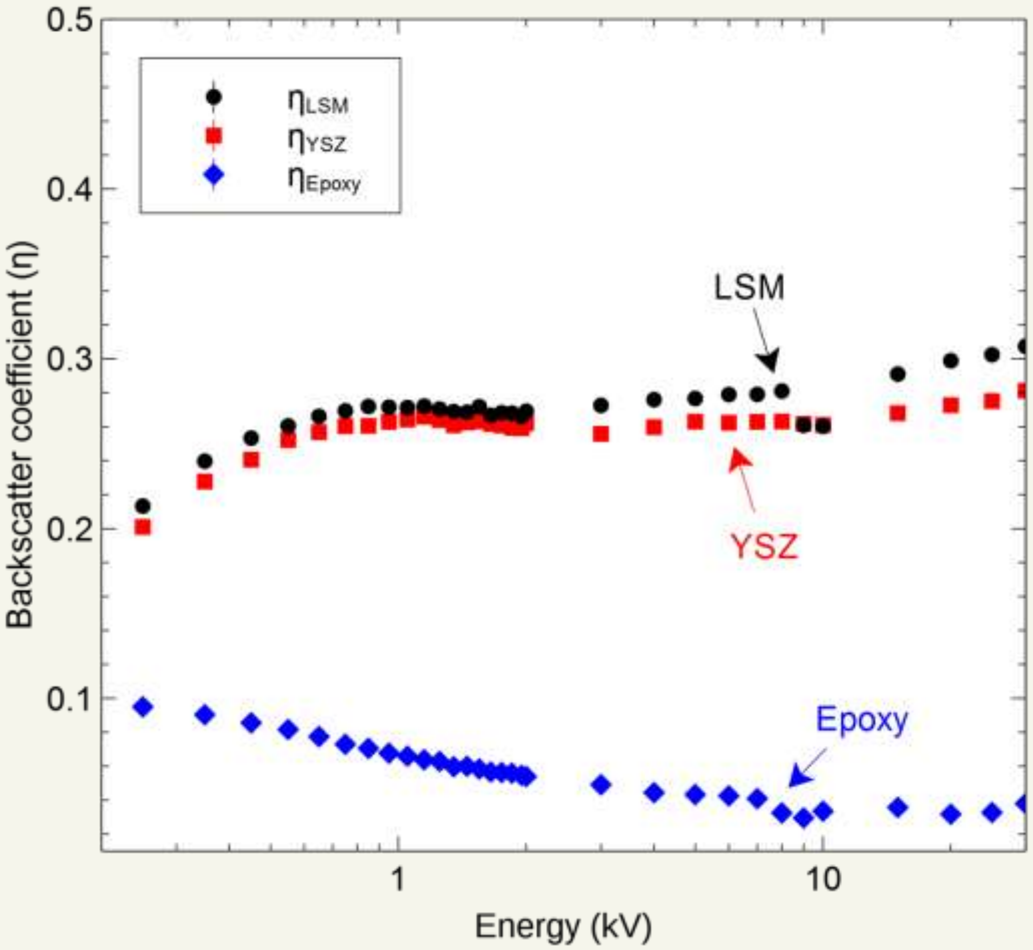
- FEI Helios 650
  - Part of the Center for Nanoscale Science and Technology (CNST) user facility at NIST
  - Multichem, iFast Developer Kit, etc.
- Auto Slice and View version 1.2
- Avizo Fire

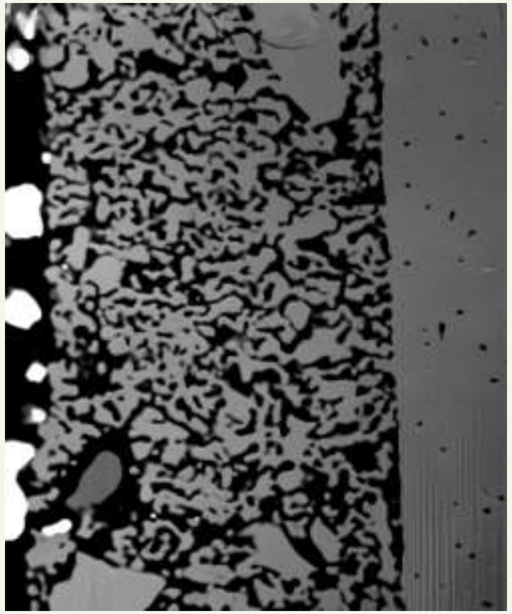
FEI Helios 650 at NIST (CNST)

Experimental – Electron imaging challenges

- BSE coefficients between LSM and YSZ are very similar
  - Very difficult to image using backscatter electrons
  - YSZ and LSM are insulating at RT, causing significant charging artefacts

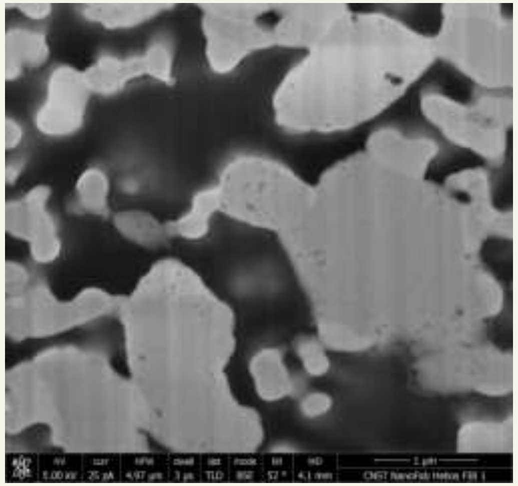
- CASINO (v2.48) simulations:
  - 10nm spot size
  - Normal incidence
  - 100k – 500k electrons
  - LSM, YSZ and epoxy





In-lens BSE (5kV)

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

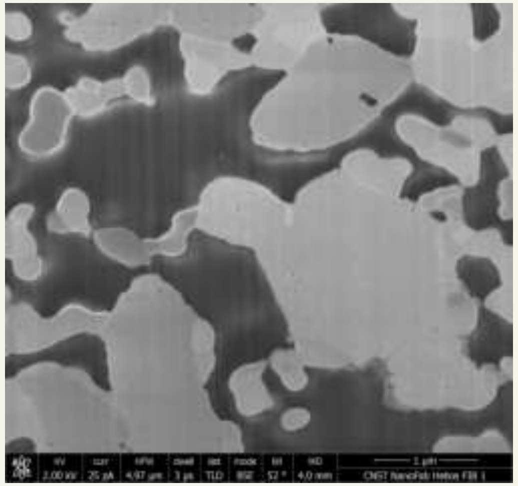


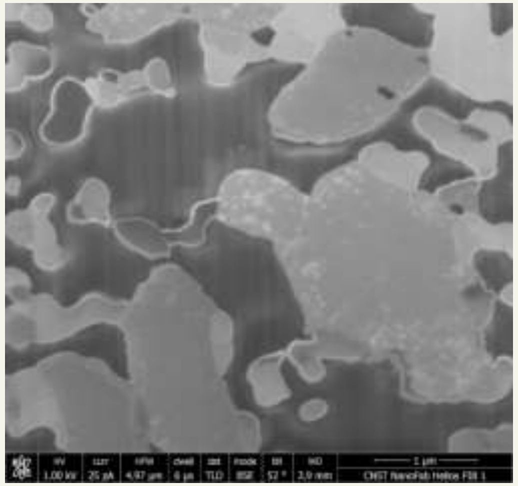
5kV – 25 pA

What type of contrast is really important?

Need to facilitate segmentation!

2kV – 25 pA



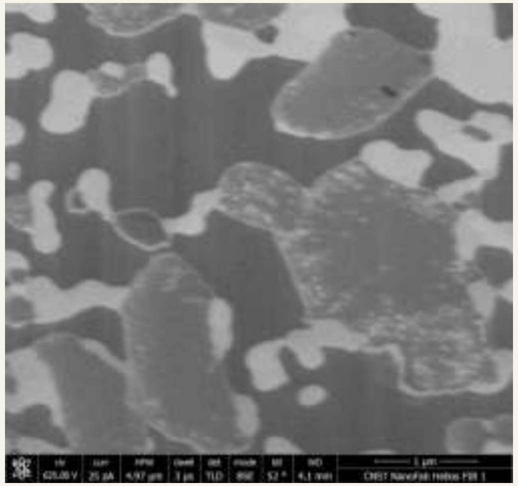


1kV – 25 pA

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



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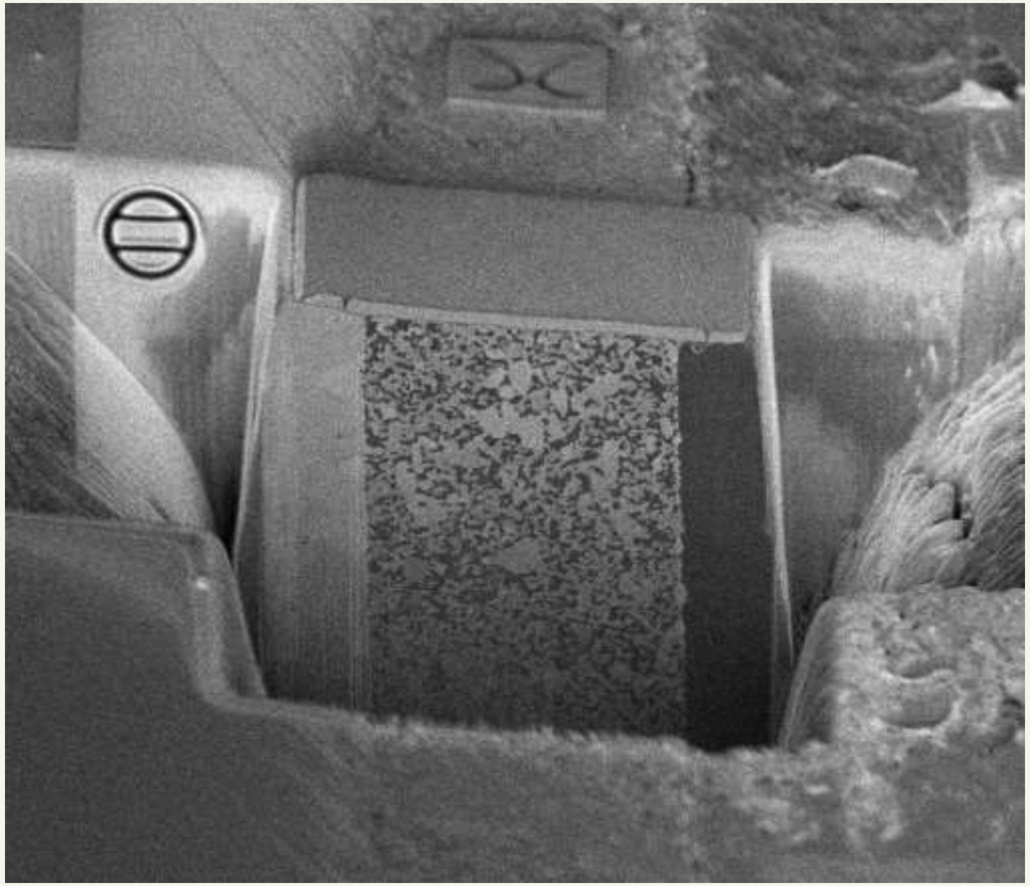
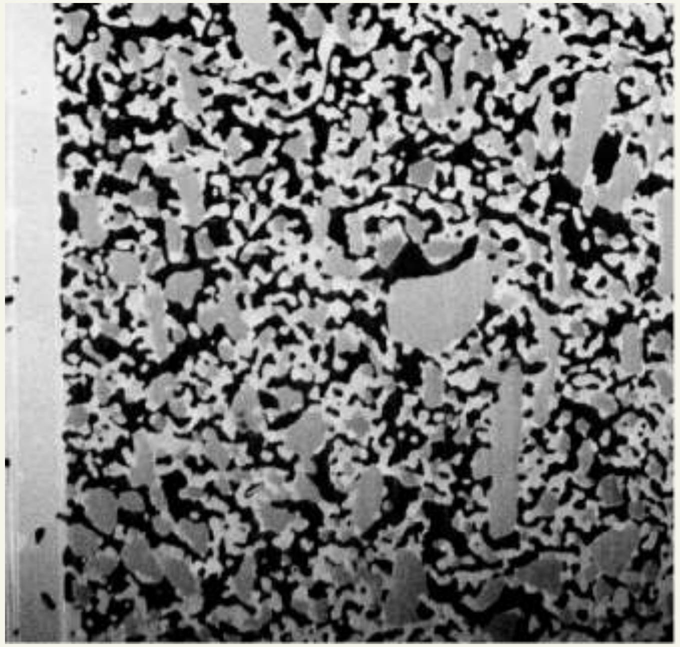
Data acquisition – Optimized procedures



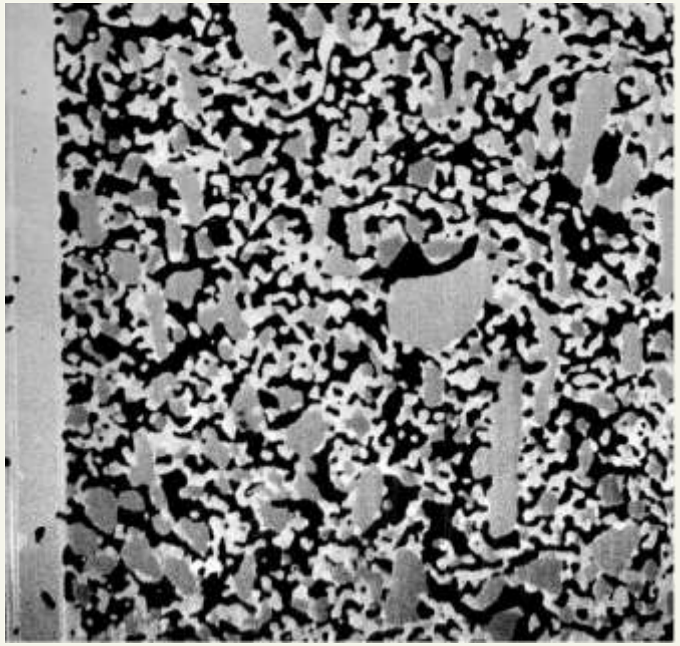
- Bulk trenching, ion beam normal to sample
- Automated recipe developed to fully automate (takes about 1 hour to complete)
  - Pt dep, slice thickness mills
  - C deposition, Fiducial mill
  - Bulk trenches (65 nA)
- Setup and ready to mill in about 1.5 hrs
  - Mostly automated, besides electron fiducial
- Some shadowing deeper into trench, but 20 nm slice thickness, ~ 30 μm slice width
  - Overnight run acquires about 5-6 μm of depth; stable enough to run longer

Experimental – post processing of data

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



Shading correction implemented with ImageJ



[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).

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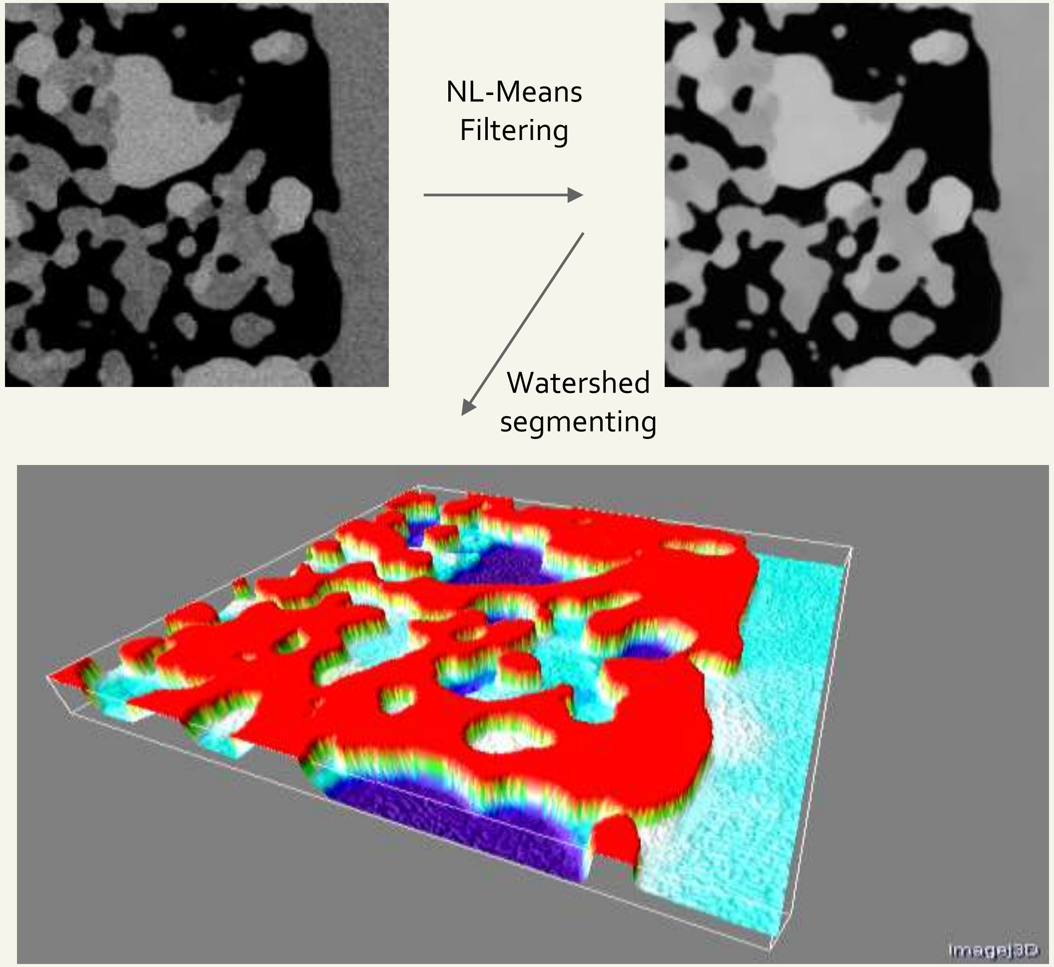

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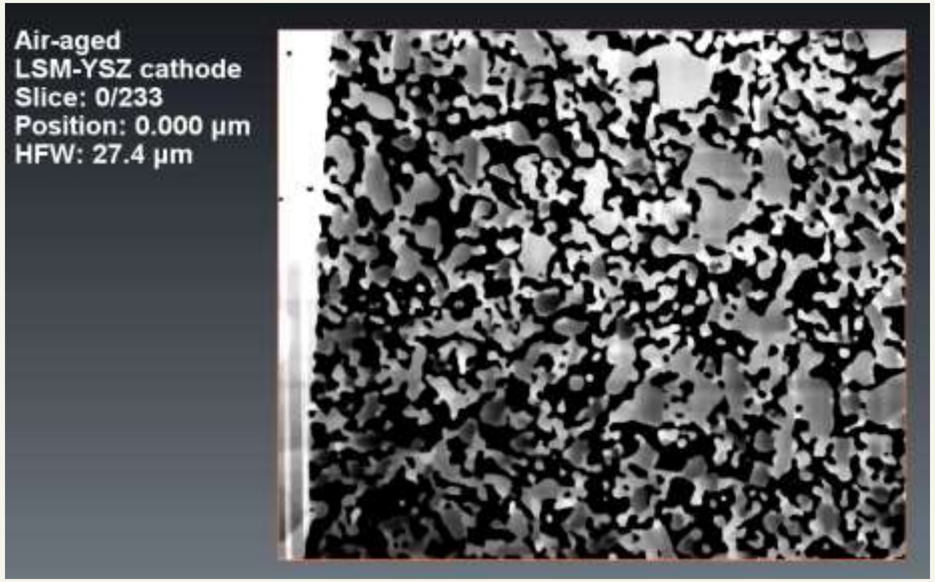
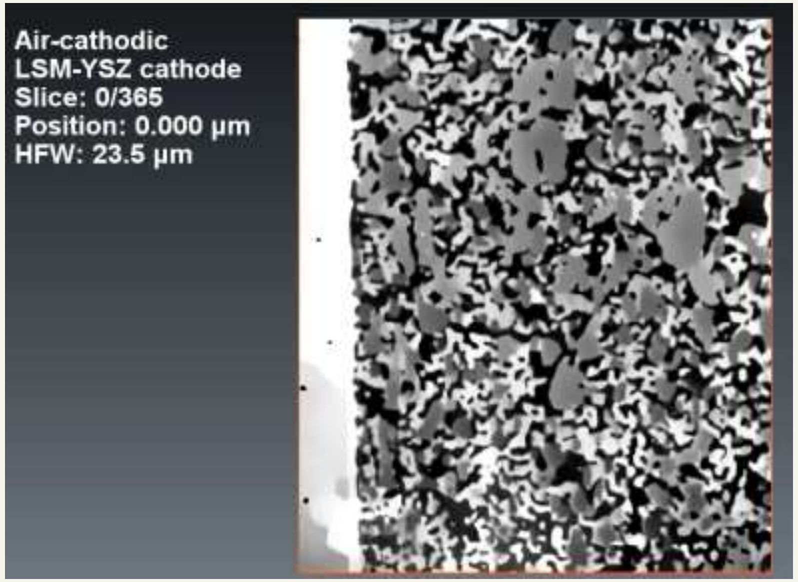
Acquired Data

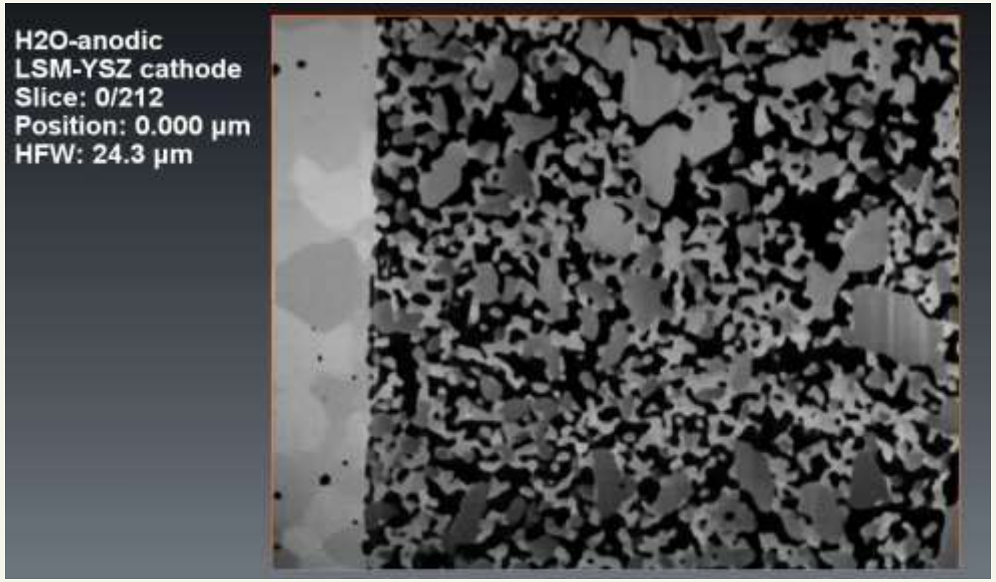
Average voxel size:
X – 20.8 nm
Y – 26.5 nm
Z – 20.2 nm

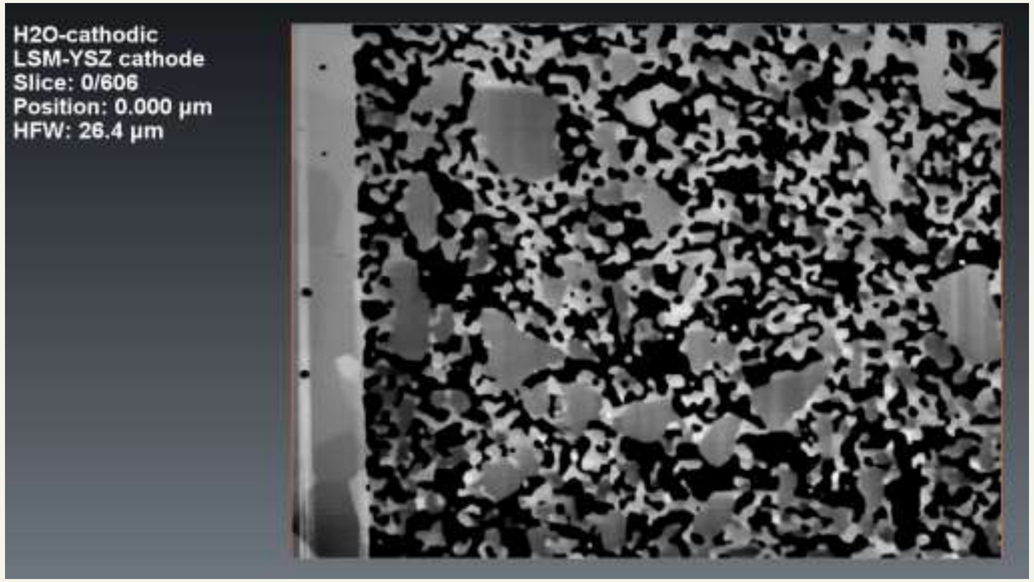
Average acquisition time per sample:
15 hrs

Data shown has been processed to facilitate segmentation





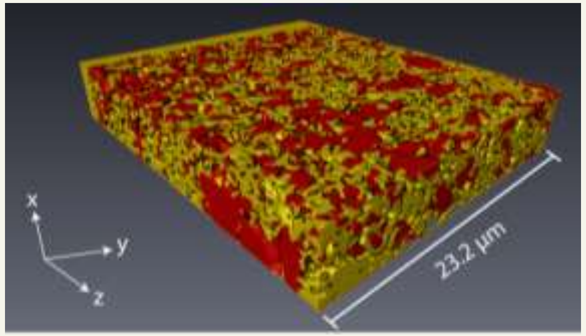




Results – Surface generation

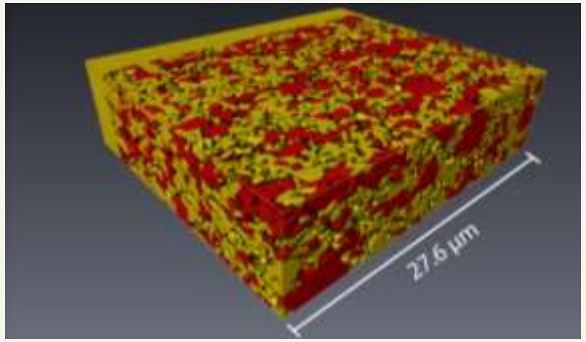
YSZ | LSM | Pore

Air-aged



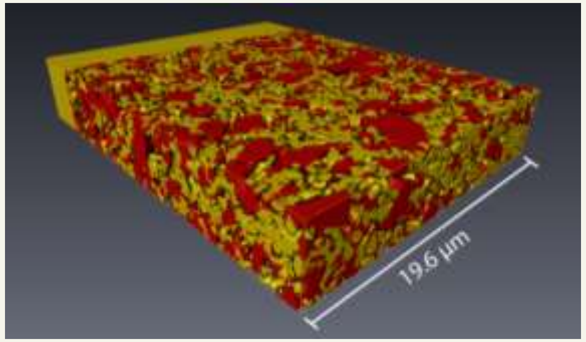
2,948.26 μm^3

Air-cathodic



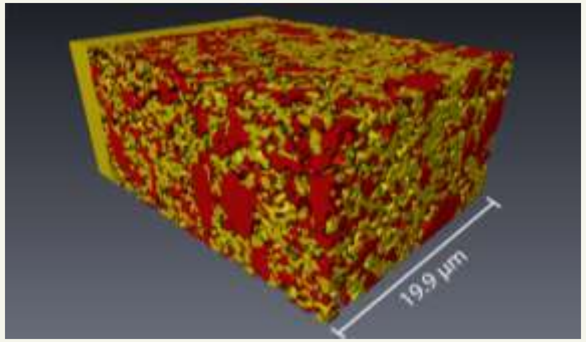
4,723.65 μm^3

H_2O-anodic



2,009.16 μm^3

H_2O-cathodic



6,354.65 μm^3

Bounding box dimensions (µm):

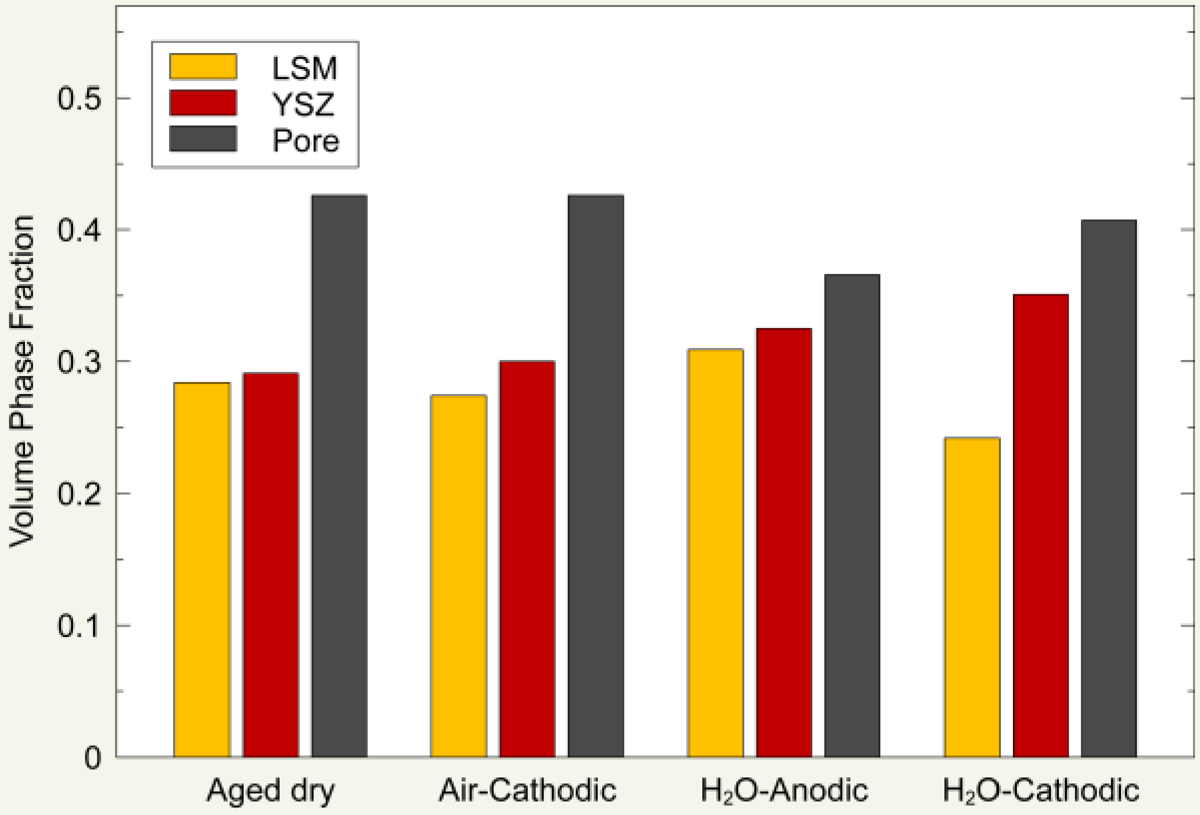
27.42	23.17	4.64
X	Y	Z

23.53	27.58	7.28
X	Y	Z

24.27	27.58	4.22
X	Y	Z

26.39	19.90	12.10
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)
  - Slight deviation for *H_2O-cathodic*

	Exp. YSZ	Exp. LSM	Obs. YSZ	Obs. LSM
Aged air	0.52	0.48	0.506	0.494
Air-cathodic			0.523	0.477
H_2O-anodic			0.512	0.488
H_2O-cathodic			0.591	0.409

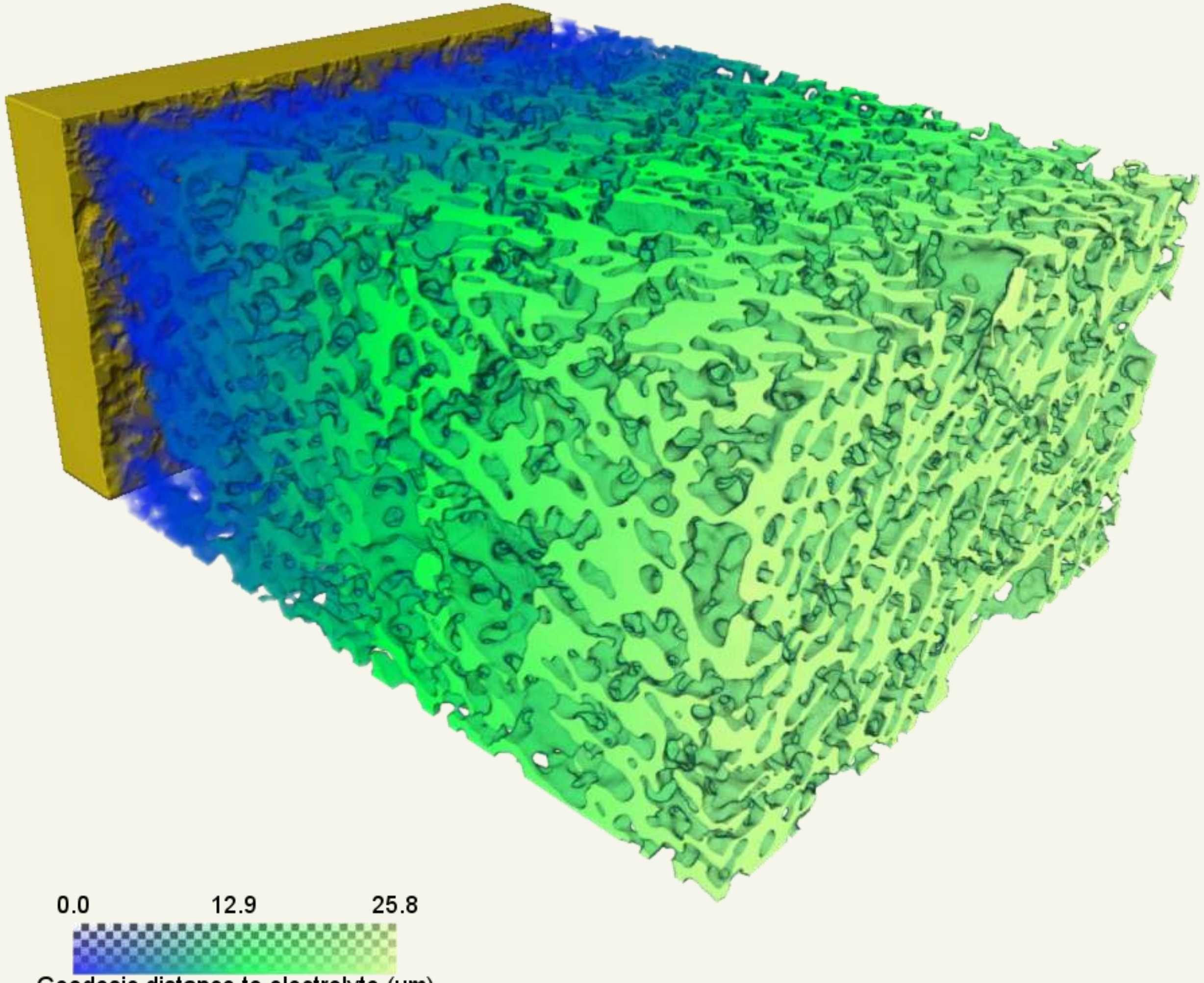
Results – Tortuosity

- Tortuosity is comparison of:

$$\tau = \frac{Geodesic\ distance}{Euclidean\ distance}$$

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

H2O-cathodic

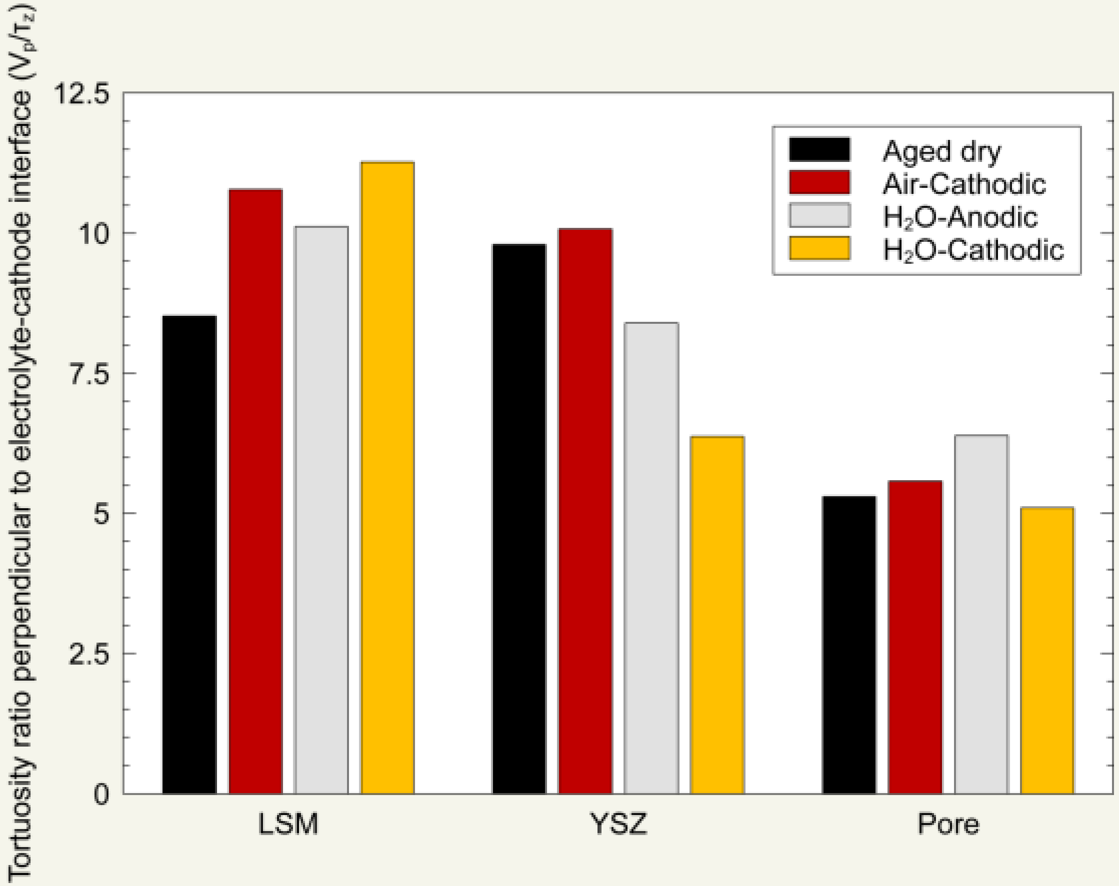


Results – Tortuosity

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

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

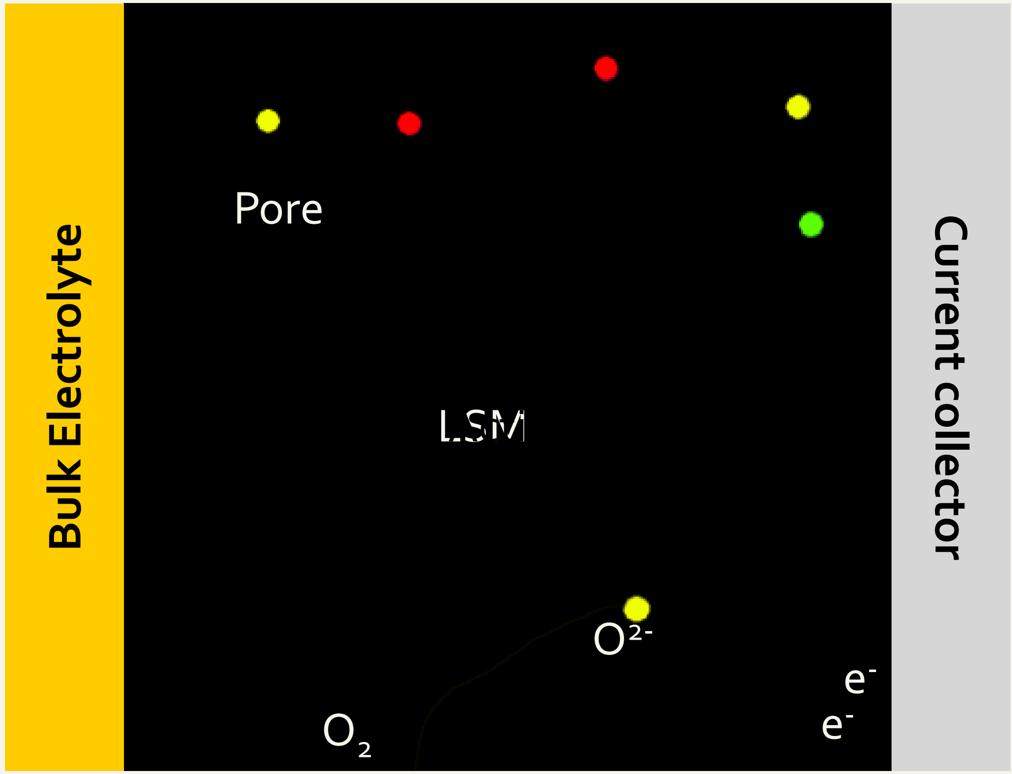
- V_p/τ relatively constant, except for YSZ in H_2O samples
- Lower D_{eff} expected in these samples



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

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

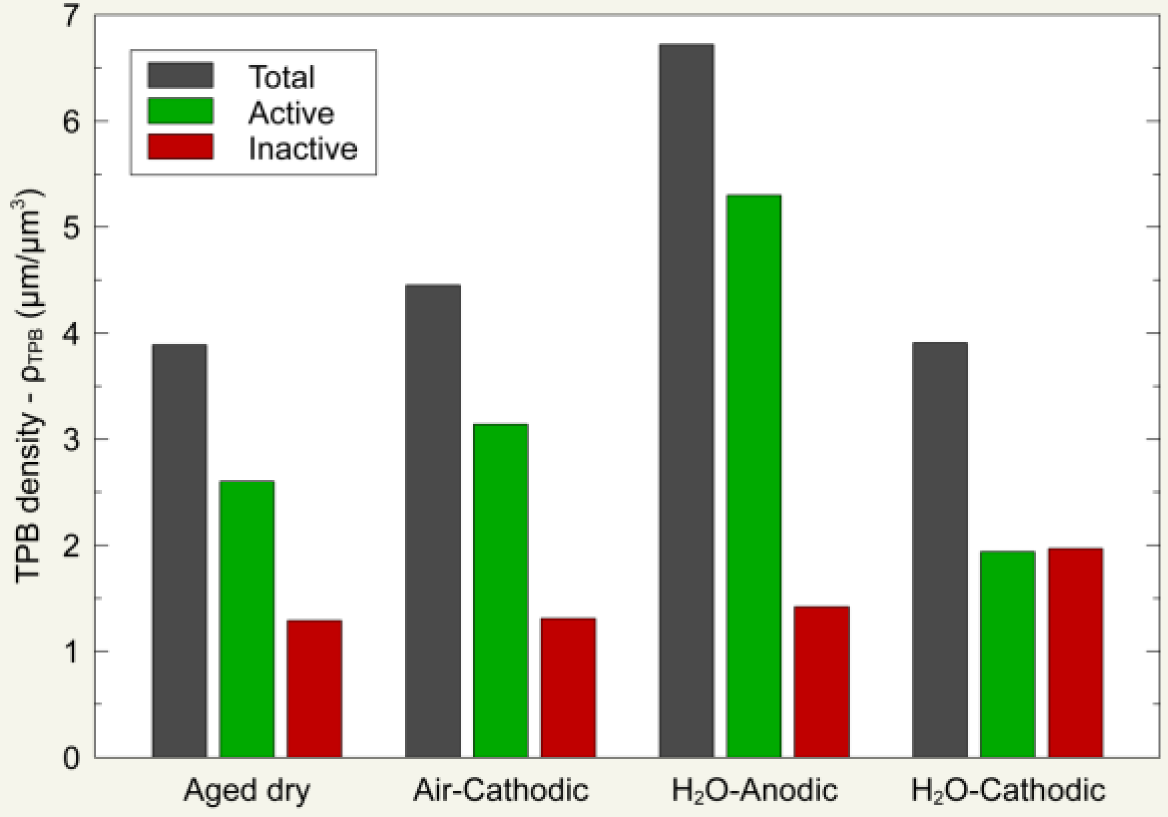


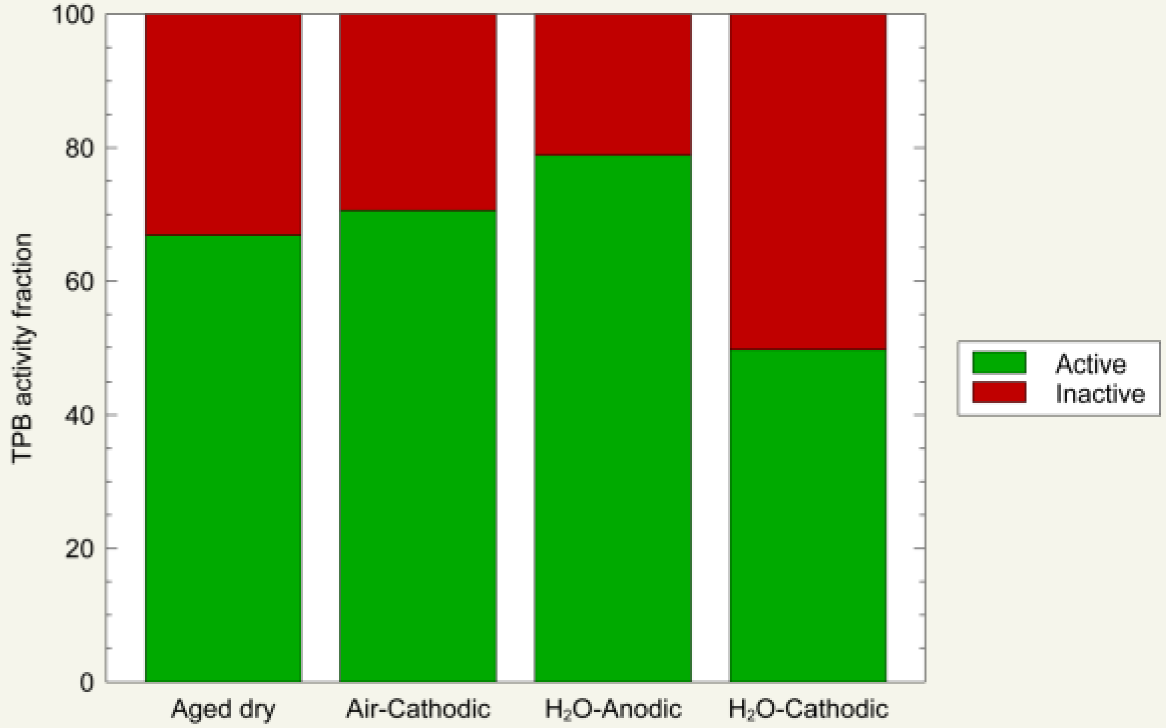
Results – Triple phase boundaries

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





- 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

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

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Ken Lagarec,
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MARYLAND NANOCENTER NISPLAB NANOSCALE IMAGING, SPECTROSCOPY AND PROPERTIES LABORATORY

Open source projects:
Scikit-fmm
Hyperspy
OpenCV

THANK YOU

Questions and comments?