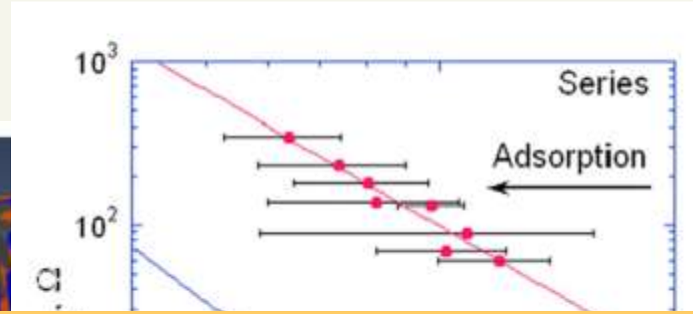
Three Dimensional Microstructural Characterization of Cathode Degradation in SOFCs Using Focused Ion Beam and SEM

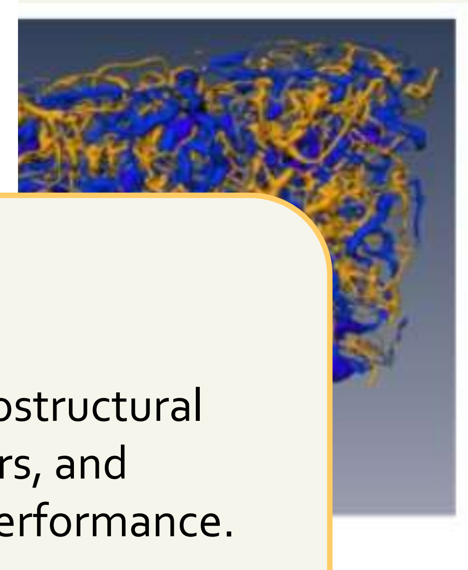
Joshua Taillon, Christopher Pellegrinelli, Yilin Huang,
Eric Wachsman, and **Lourdes Salamanca-Riba**
University of Maryland, College Park

*Supported by DOE-SECA under contract no. DEFE0009084.

Abstract #724
May 13, 2014 , 5:00 PM
Symposium F4: Ionic and Mixed Conducting Ceramics

Introduction





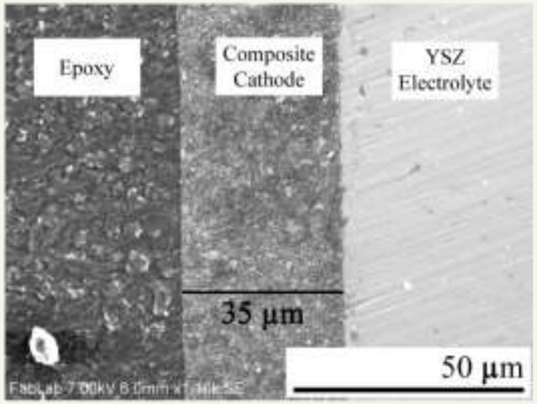
Our goal:

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

- **Micr**
  - 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).

Experimental - Button cell testing

Button cell

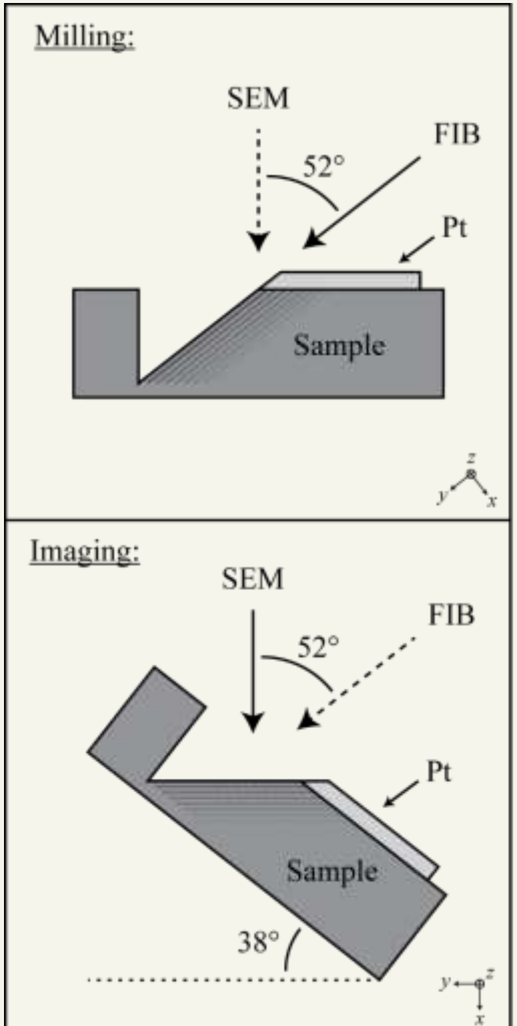


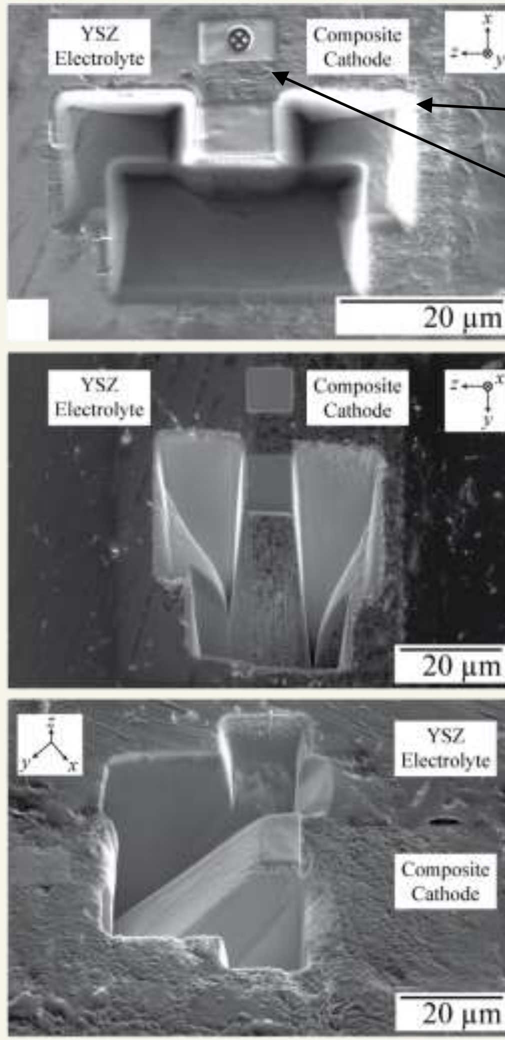
Cross-section view

- 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*")

Experimental – FIB/SEM nanotomography





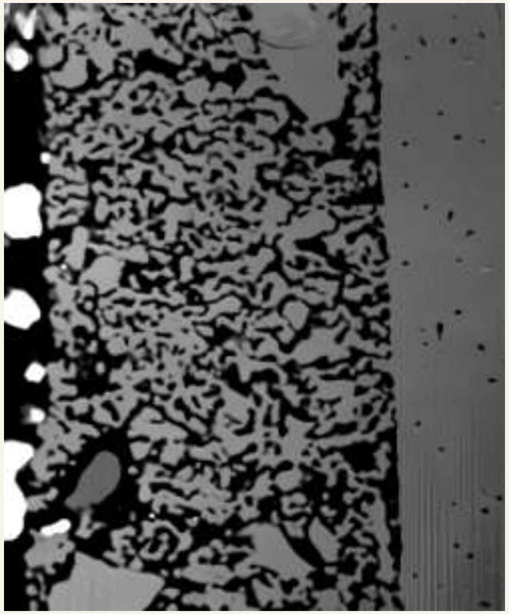
- "C-trench" to prevent shadowing
- Protective Pt and fiducial marks
- Mill at 0º stage tilt
- Image at 38º tilt

- Unique FIB/SEM geometry means:
  - Improved contrast between LSM and YSZ
  - Limited detector shadowing effect
  - Increased acquisition time

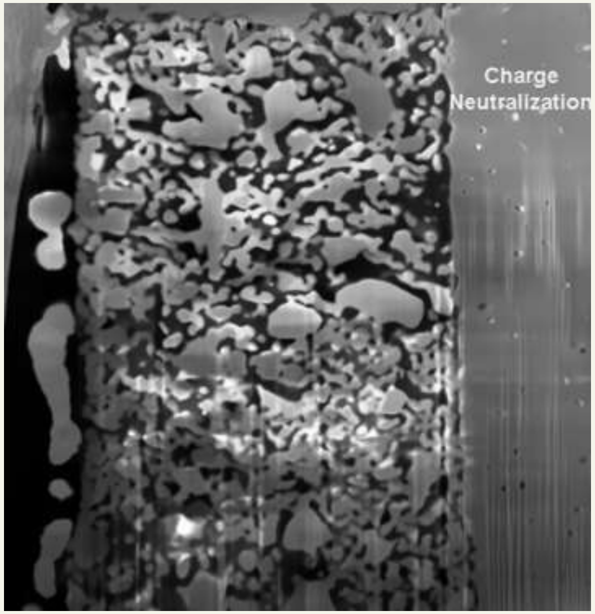
Experimental – Imaging challenges

- Challenging system to image due to:
  - Poor RT conductivity
  - Similar electron yields from each phase

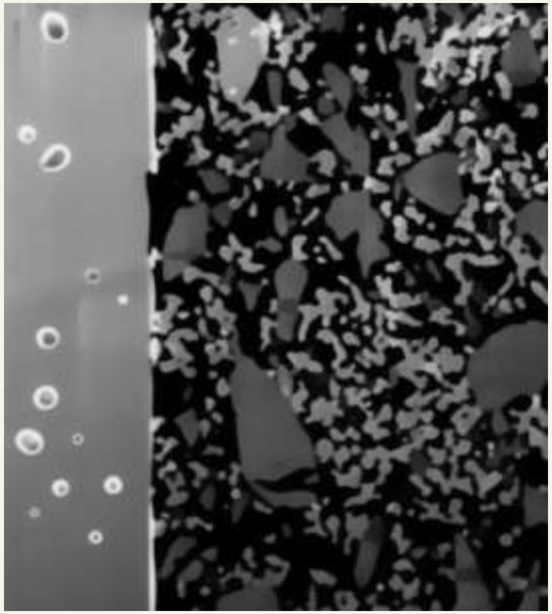
- Careful control of imaging parameters allows for charge contrast imaging
  - Low kV, long dwell, moderately high current (~few nA), perpendicular face



In-lens BSE



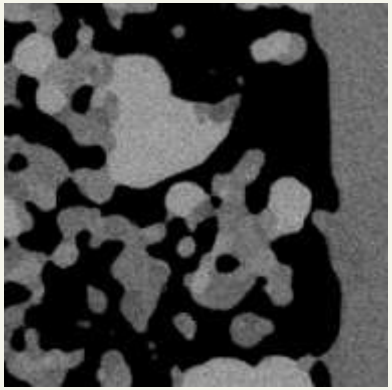
In-lens SE (Charge neutralization setting)

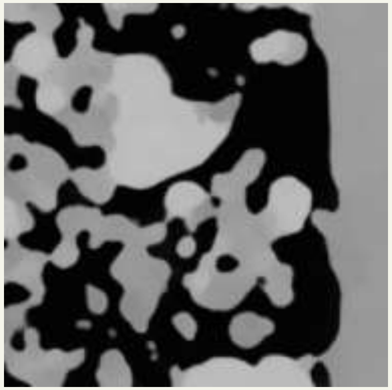


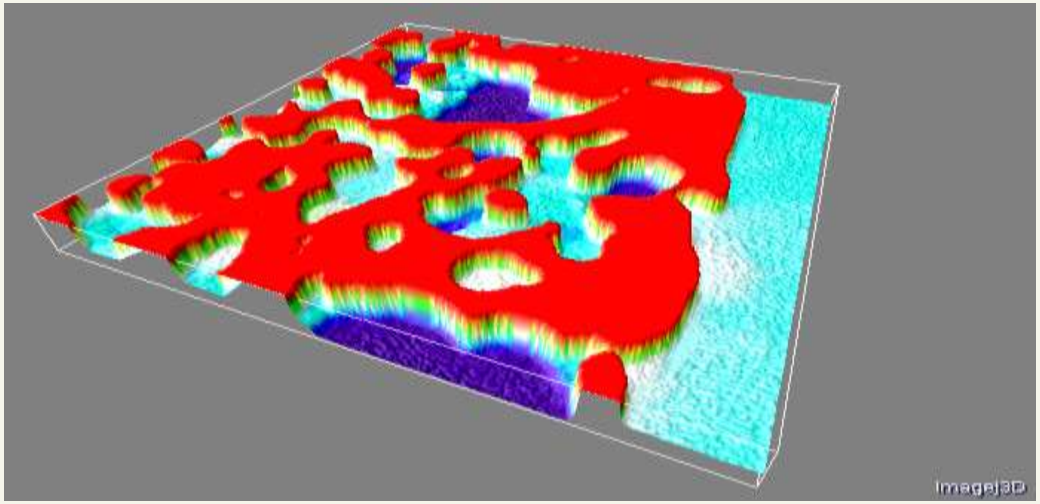
Long-dwell charging contrast (SE)

Experimental – post processing of data

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

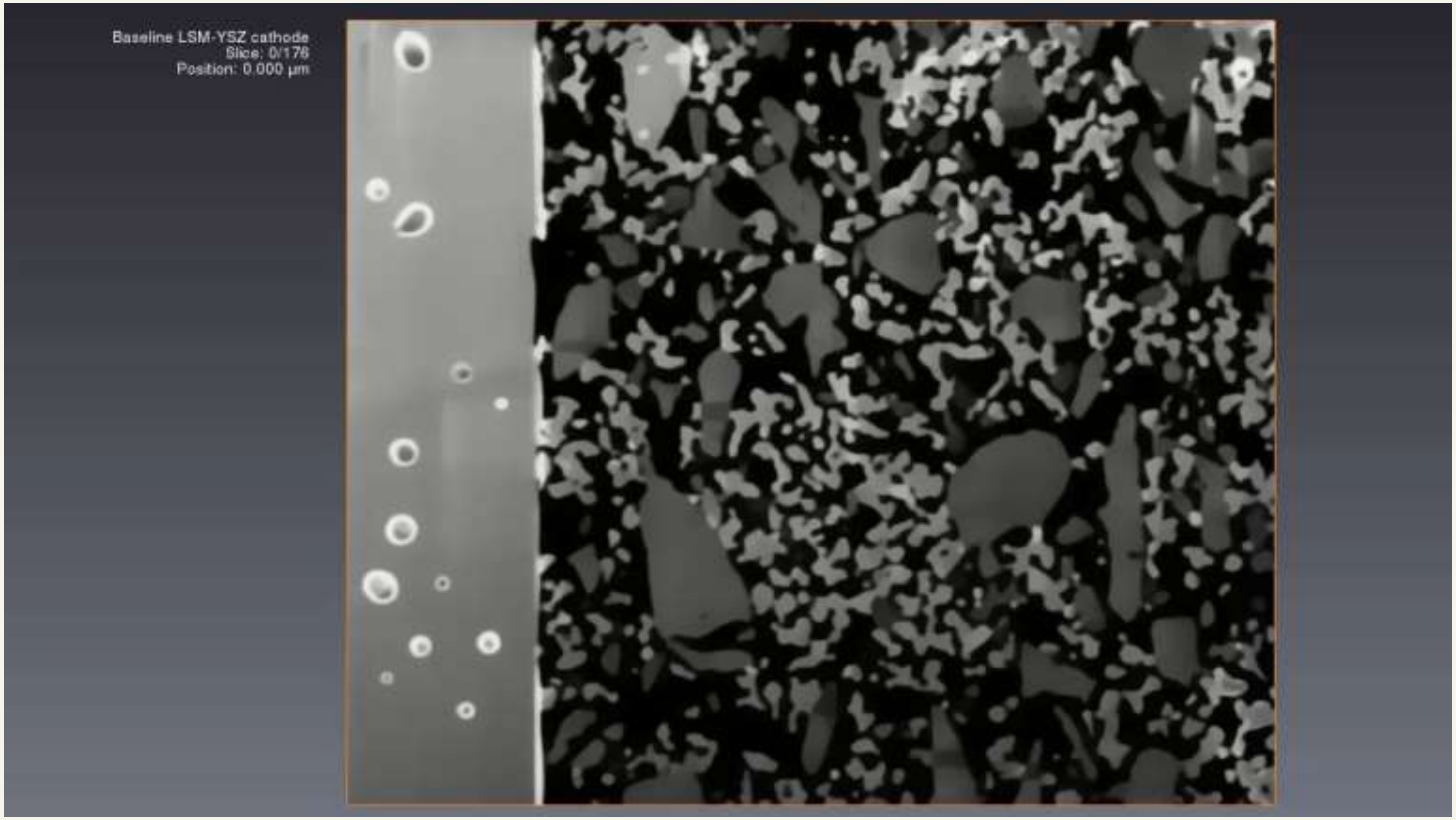






[1] Based on A. Buades *et al*. in *2005 IEEE Comput. Soc. Conf. Comput. Vis. Pattern Recognit.*, Vol. 2, p. 60. IEEE.
[2] L. Vincent and P. Soille, IEEE Trans. Pattern Anal. Mach. Intell., 13(6), 583 (1991).

Results – *Unaged* SOFC

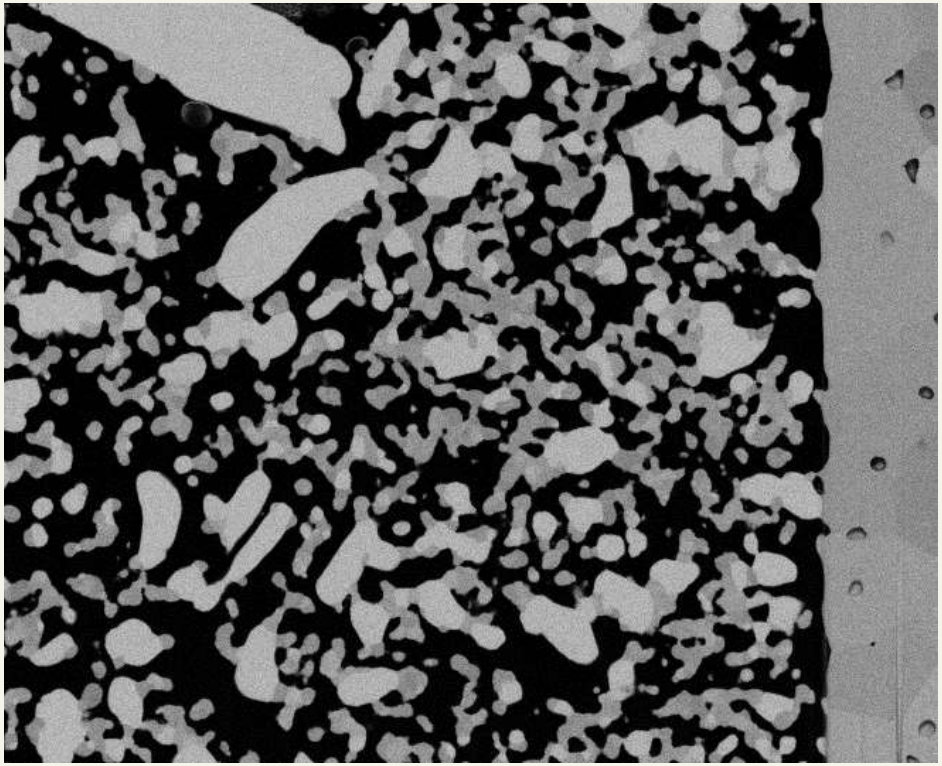


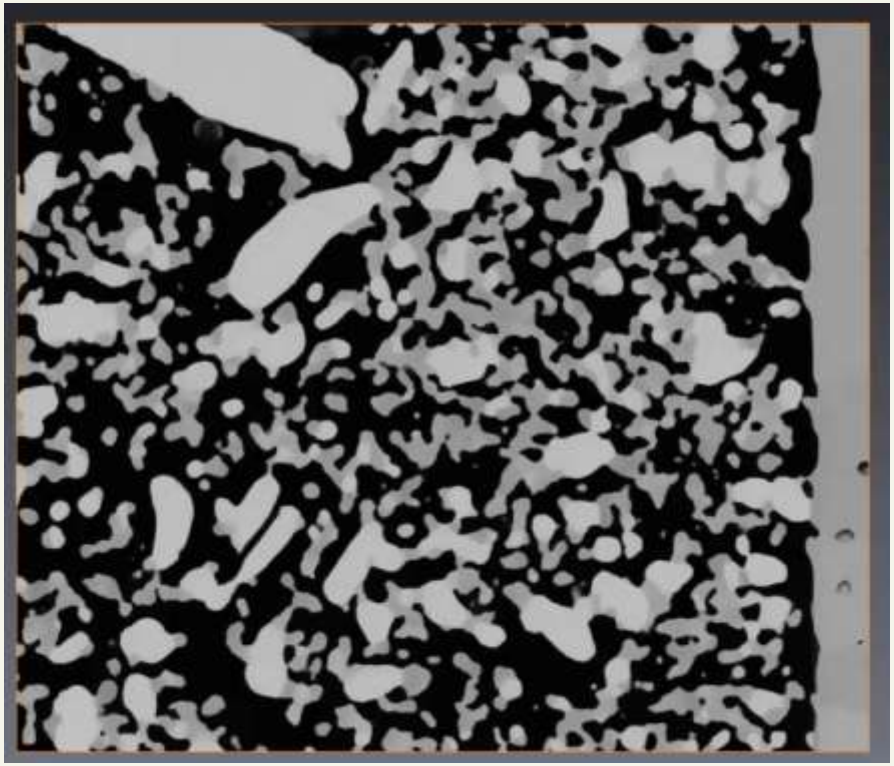
Voxel size: 12 x 12 x 30 nm, SE signal collected on FEI Helios 650, NIST
HFW: 9.5 µm; Depth: 5.25 µm; Total reconstructed cathode volume (excluding electrolyte): 276.84 μm^3

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

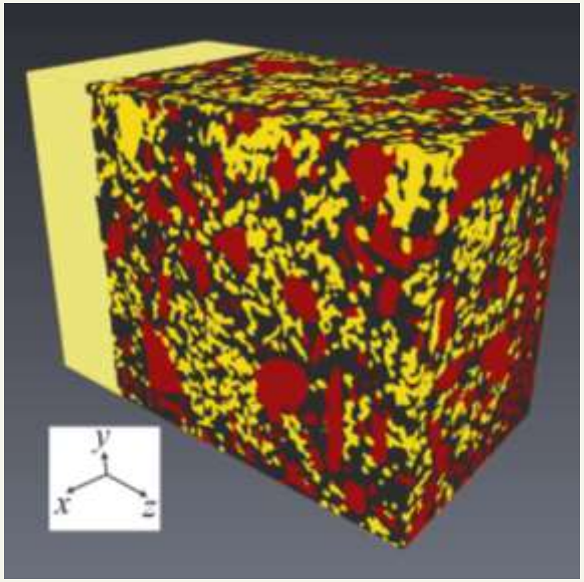
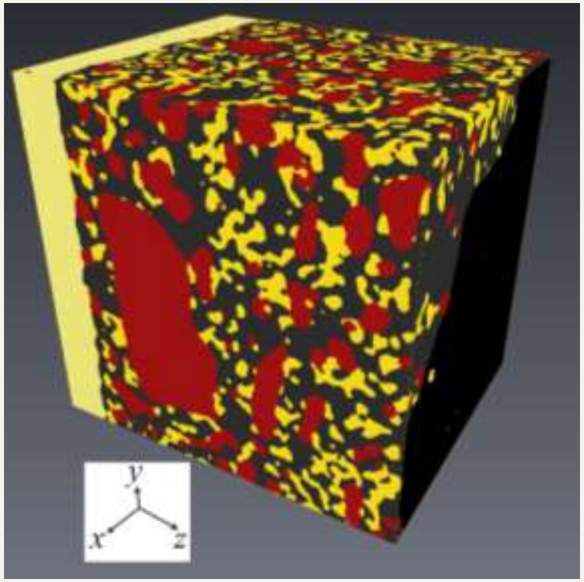
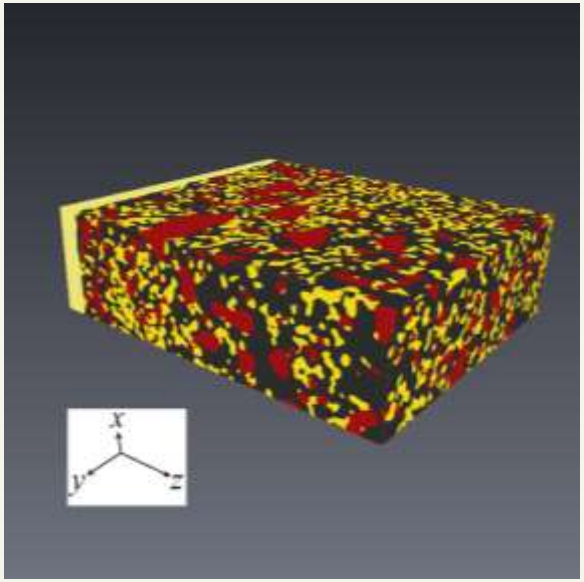




Voxel size: 10 x 10 x 10 nm, EsB signal collected on Zeiss Crossbeam 540, courtesy of Carl Zeiss and Fibics, Inc.
HFW: 13.96 µm; Depth: 3.8 µm; Total reconstructed cathode volume (excluding electrolyte): 627.35 $µm^3$

Results – Surface generation

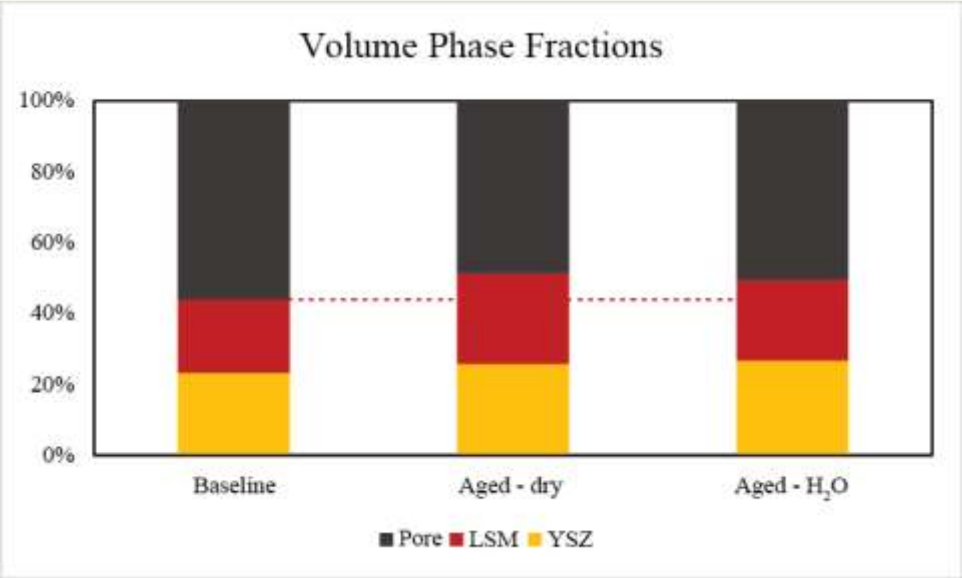
YSZ	LSM / Pore

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

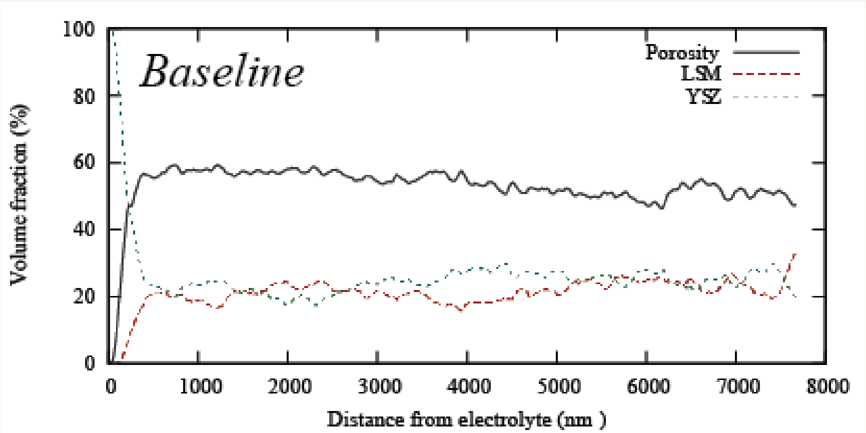


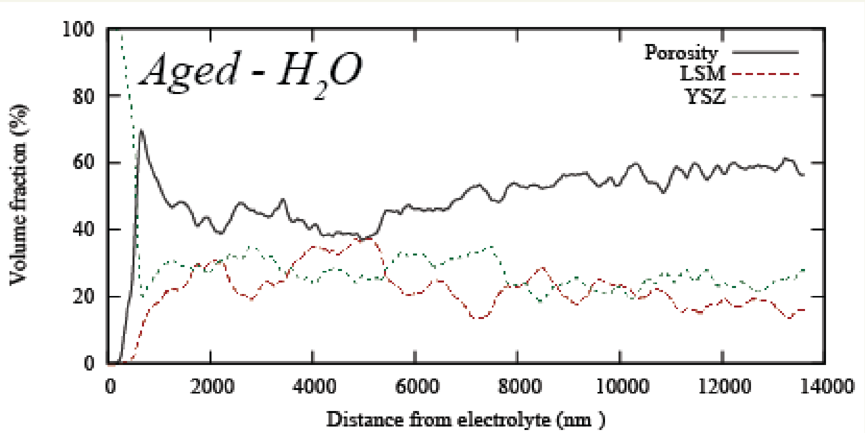
- Porosity is decreased in both aged samples
  - Additional sintering occurring during aging process

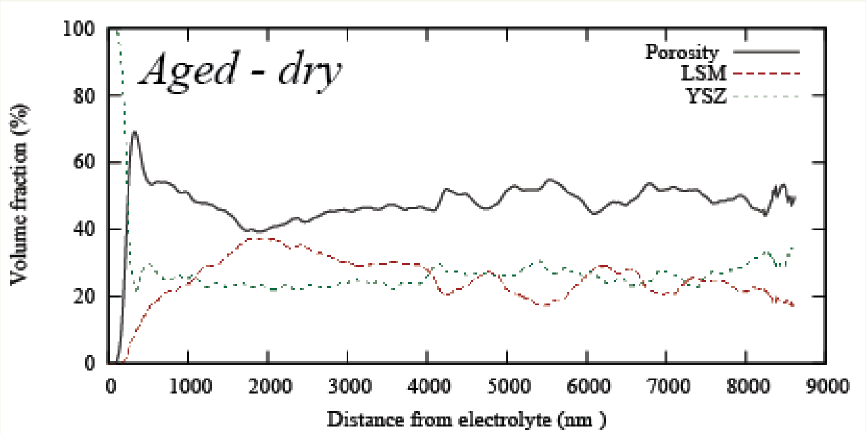
	Exp. YSZ	Exp. LSM	Obs. YSZ	Obs. LSM
Baseline	0.52	0.48	0.527	0.473
Aged-dry			0.503	0.497
Aged-H2O			0.542	0.458

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

Results – Graded phase fractions





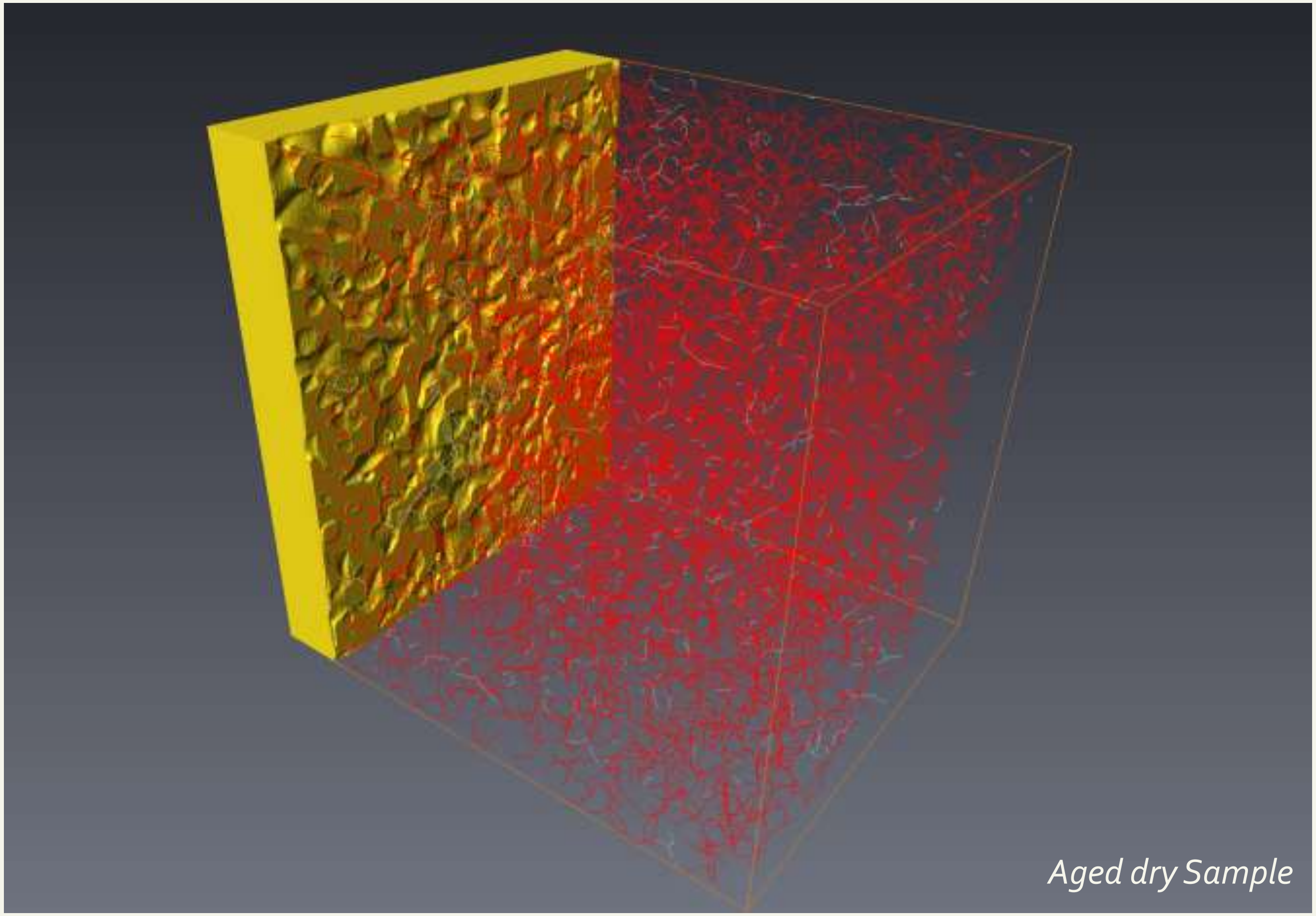


- Plotting phase volume fraction as a function of distance from cathode/electrolyte interface
  - Influence of aging on phase distribution

- 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



Aged dry Sample

Skeletonization of individual phases reveals connectivity

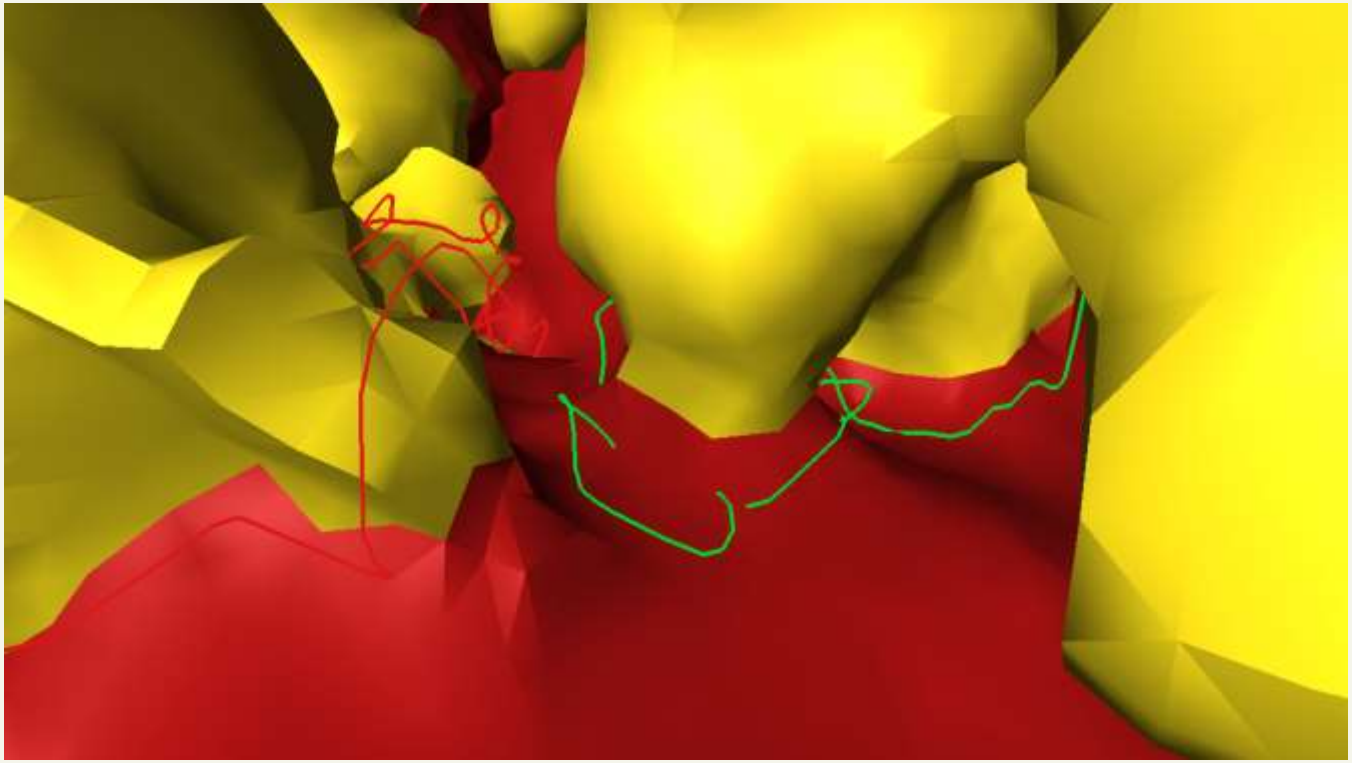
Isolated LSM networks within volume

Contiguous YSZ and pore networks

Results – Triple phase boundaries

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

Results – Triple phase boundaries

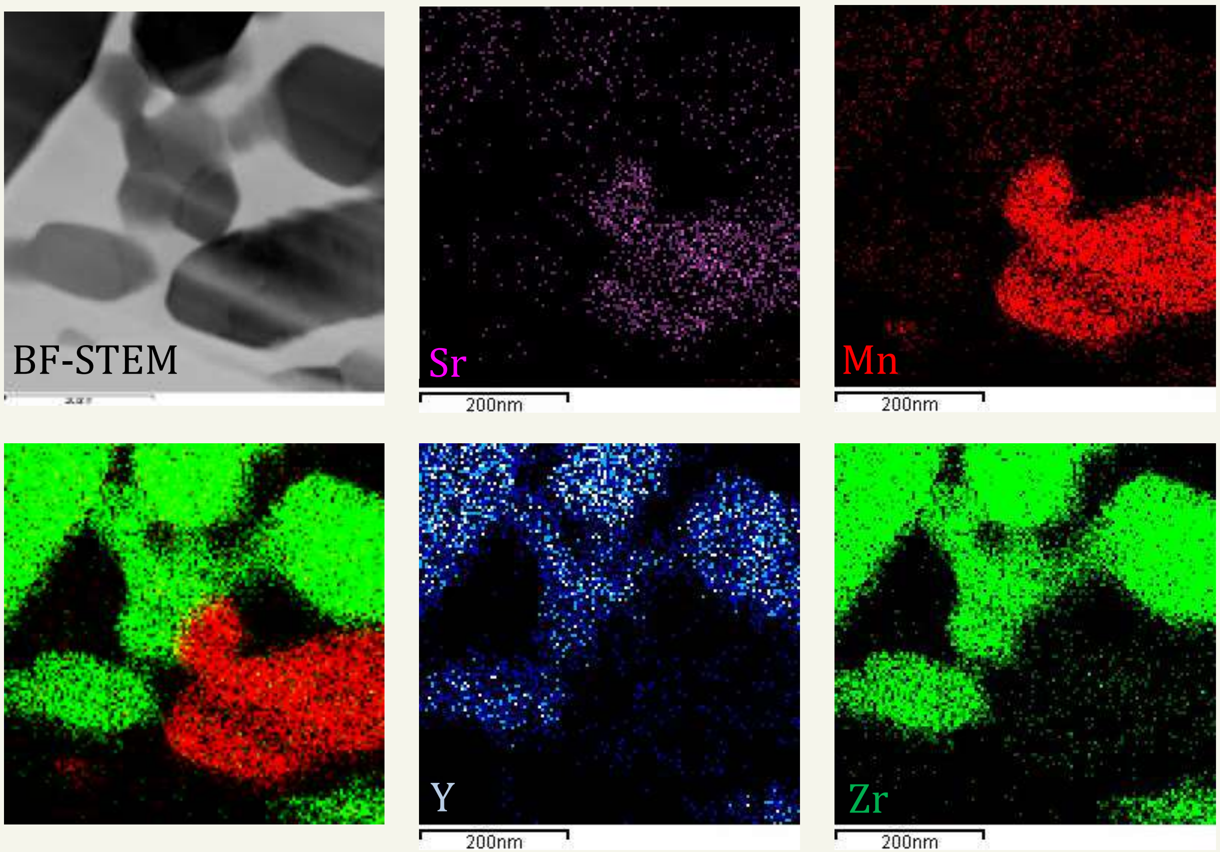


Results – Triple phase boundaries

**Relative to baseline*	**Baseline**	**Aged-dry**	**H2O**
Active TPB [norm]	100%	32.5% *	27.5% *
Total ρ_{TPB} [µm/µm^3]	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

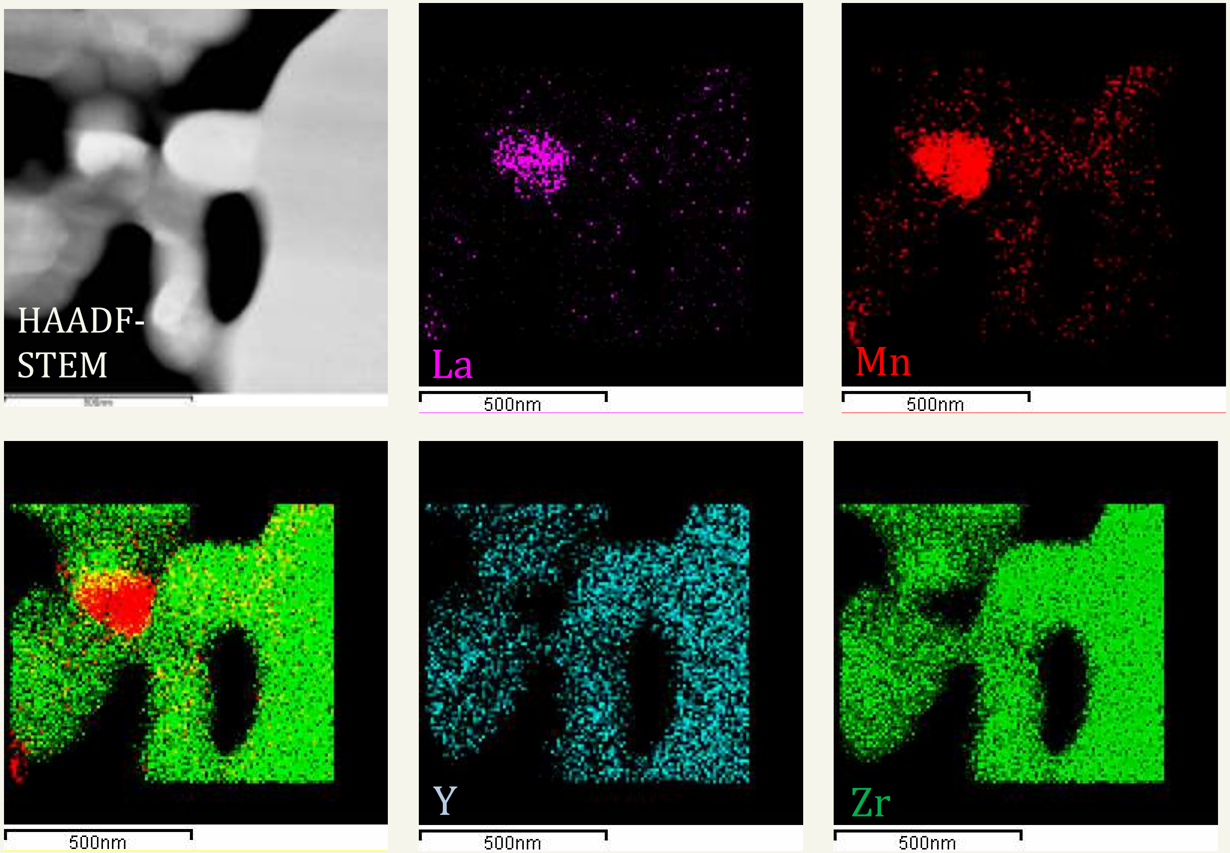
Results – Preliminary TEM/EDS work



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

- Distinct particles of LSM and YSZ

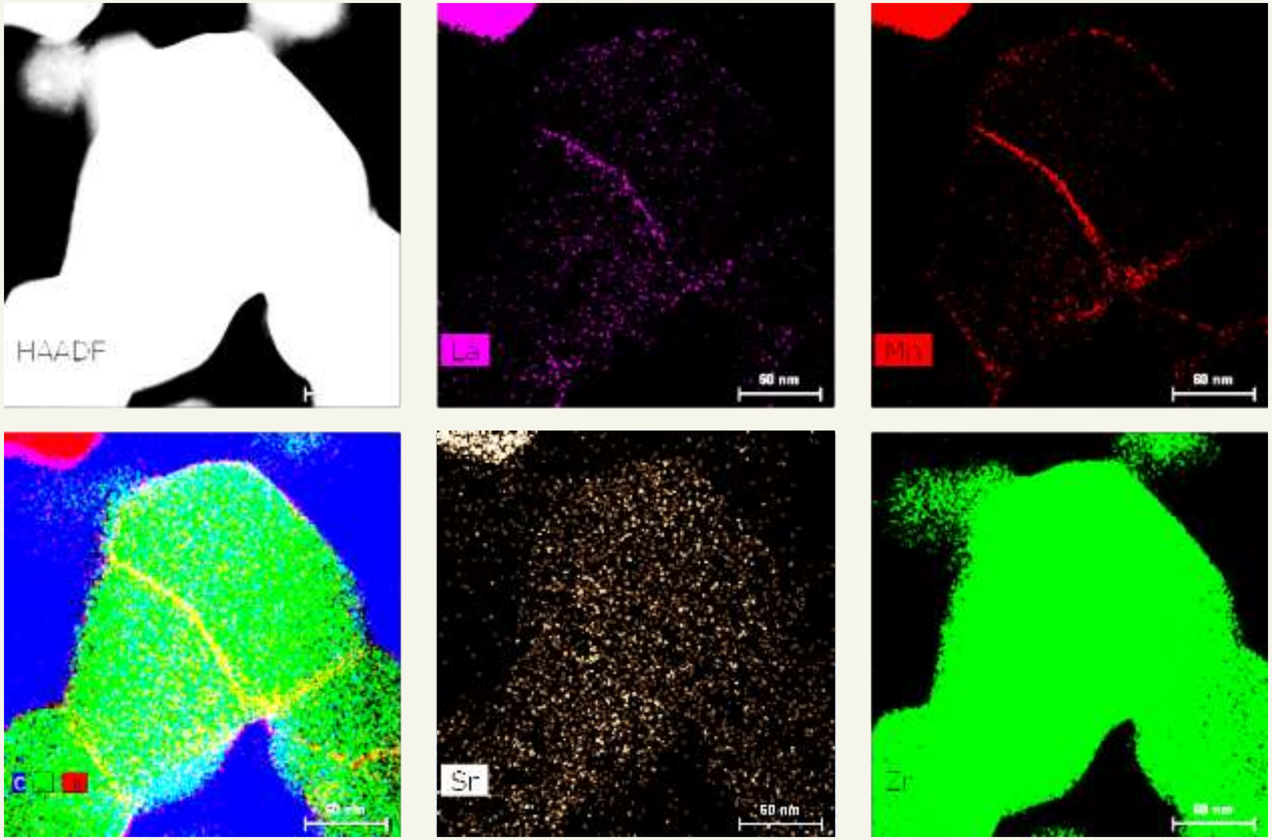
Results – Preliminary TEM/EDS work



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



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

- At these conditions, 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

MARYLAND NANOCENTER NISPLAB NANOSCALE IMAGING, SPECTROSCOPY AND PROPERTIES LABORATORY

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

THANK YOU

Questions and comments?