TOMOGRAPHIC AND HYPERSPECTRAL ANALYSIS OF POROUS THREE-DIMENSIONAL SOLID OXIDE FUEL CELL CATHODES AT MULTIPLE LENGTH SCALES

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University of Maryland, College Park

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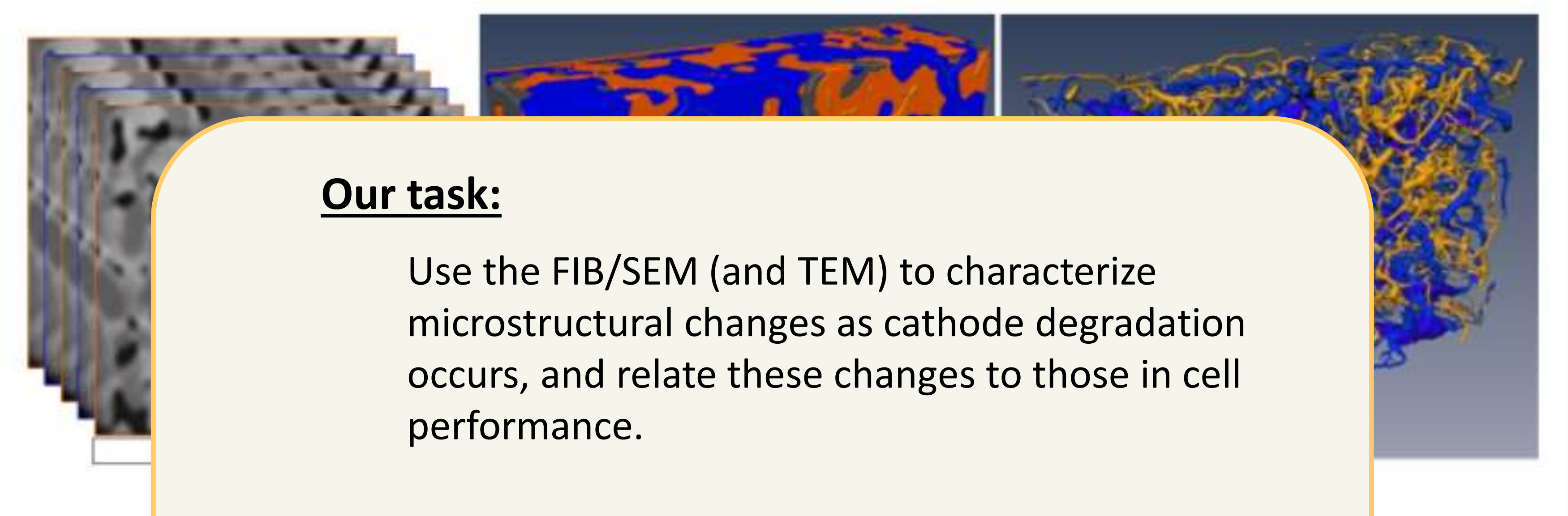
2015 Fall MRS – AAA1.02
Monday, November 30, 2015 – 9:00 AM
Hampton Room, Sheraton Hotel

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 (and TEM) to characterize microstructural changes as cathode degradation occurs, and relate these changes to those in cell performance.

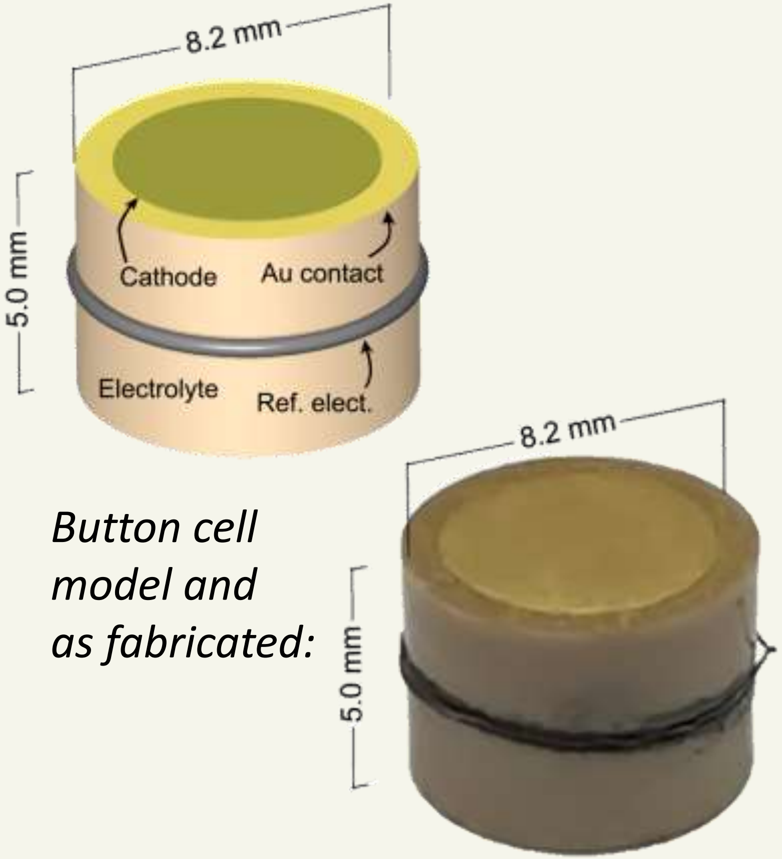
Our goal:

Better understanding of the fundamental mechanisms behind cathode degradation.

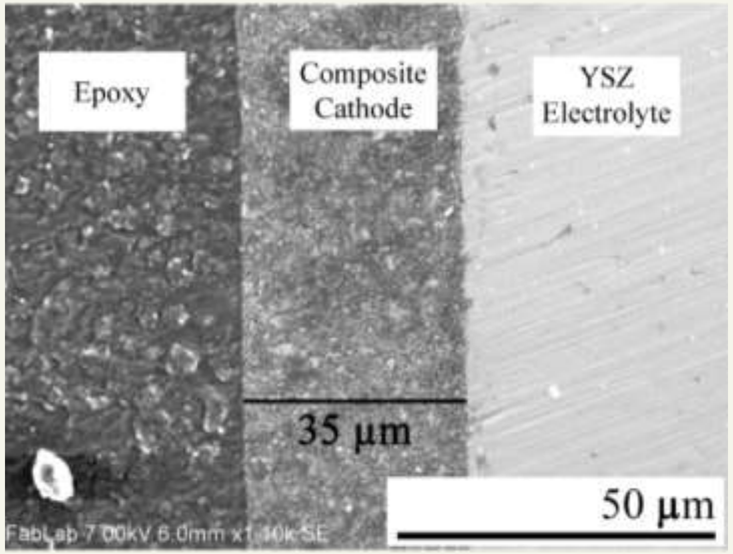
Outline

- Data acquisition
  - Sample prep and imaging conditions
- FIB/SEM Data processing and quantification
  - Filters, artefact correction, and segmentation
  - Microstructural quantification
- STEM-EELS Hyperspectral imaging
  - Machine learning signal decomposition

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

FIB/SEM DATA ACQUISITION

FIB/SEM 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?

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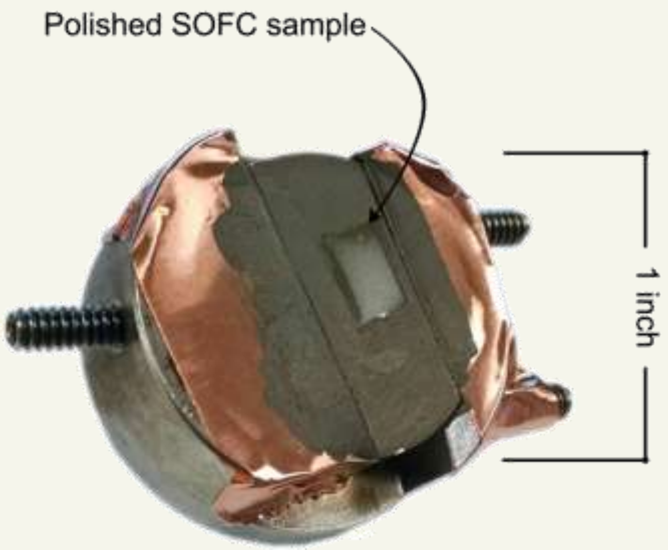
Pre-FIB sample prep

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
  - Process development underway

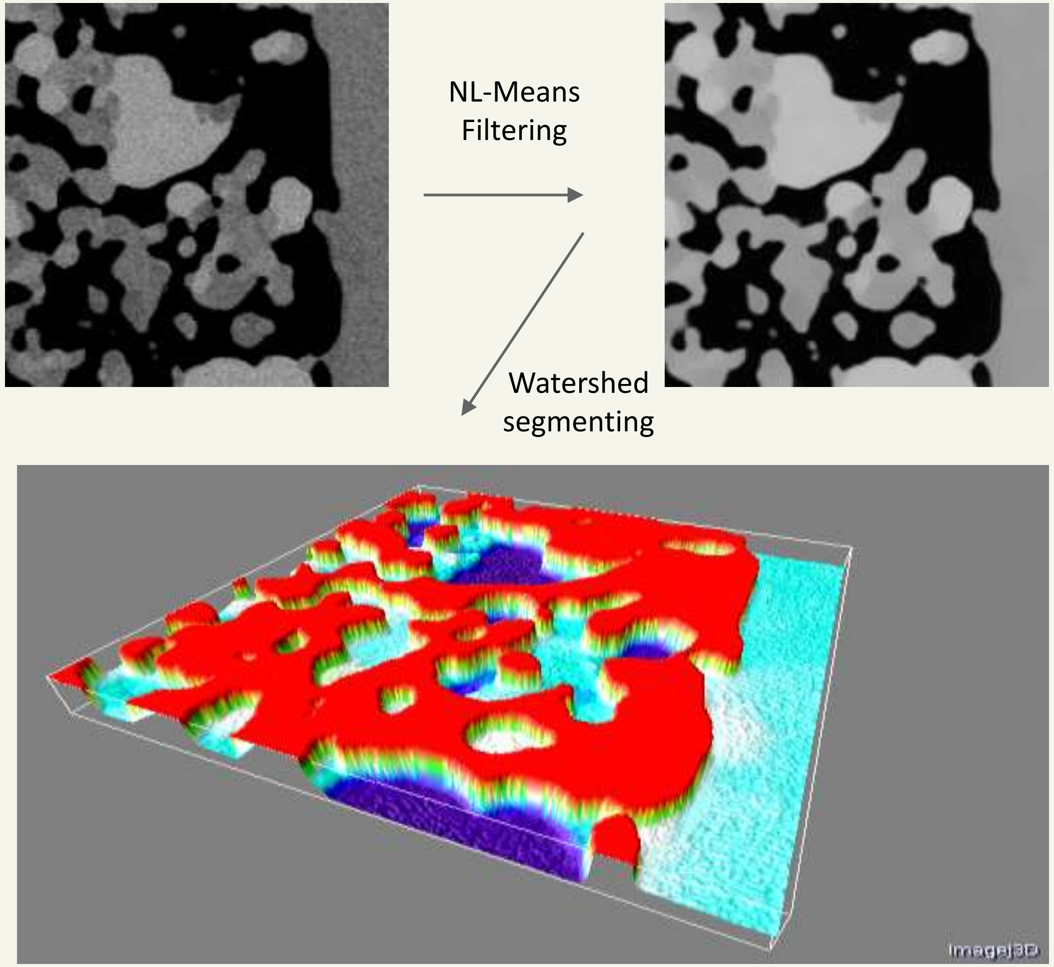
FEI Helios 650 at NIST (CNST)

Tescan Gaia at UMD AIMLab

FIB/SEM DATA PROCESSING

Experimental – post processing of data

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

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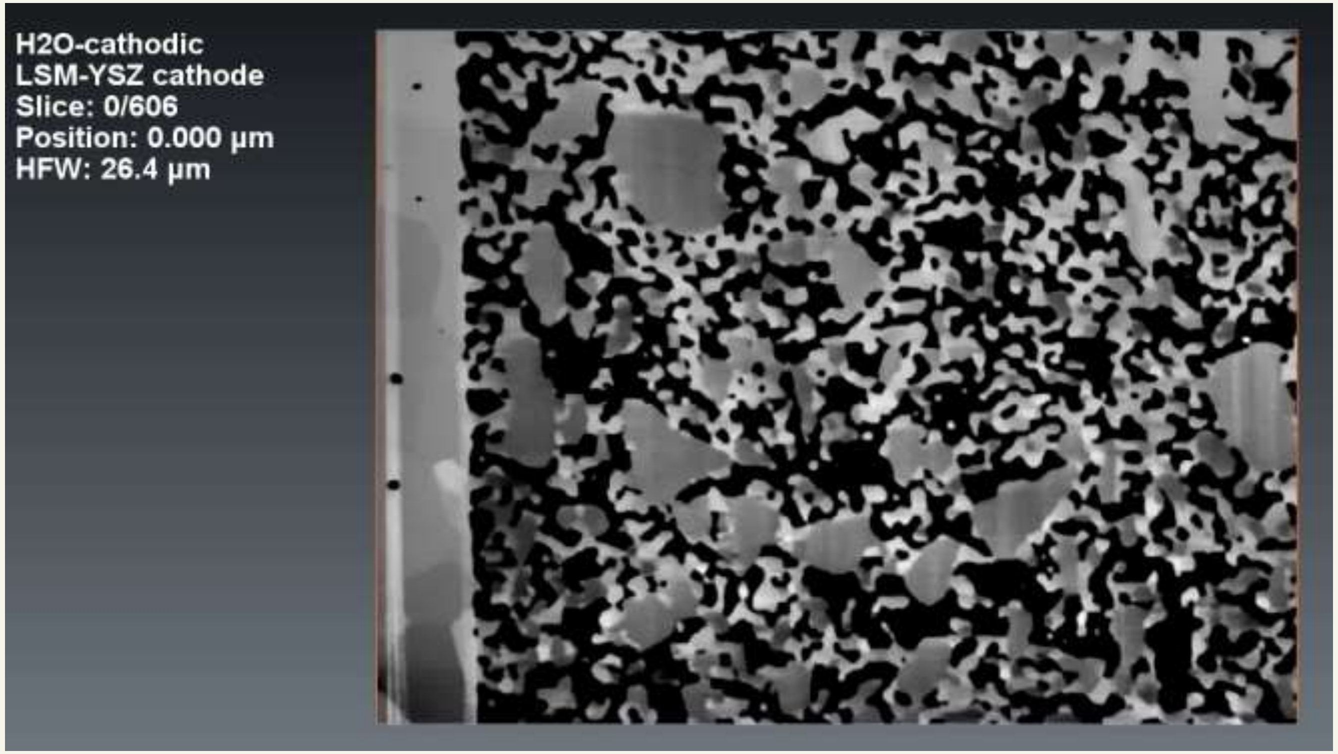
Visualizations of LSM/YSZ Fuel Cell reconstruction



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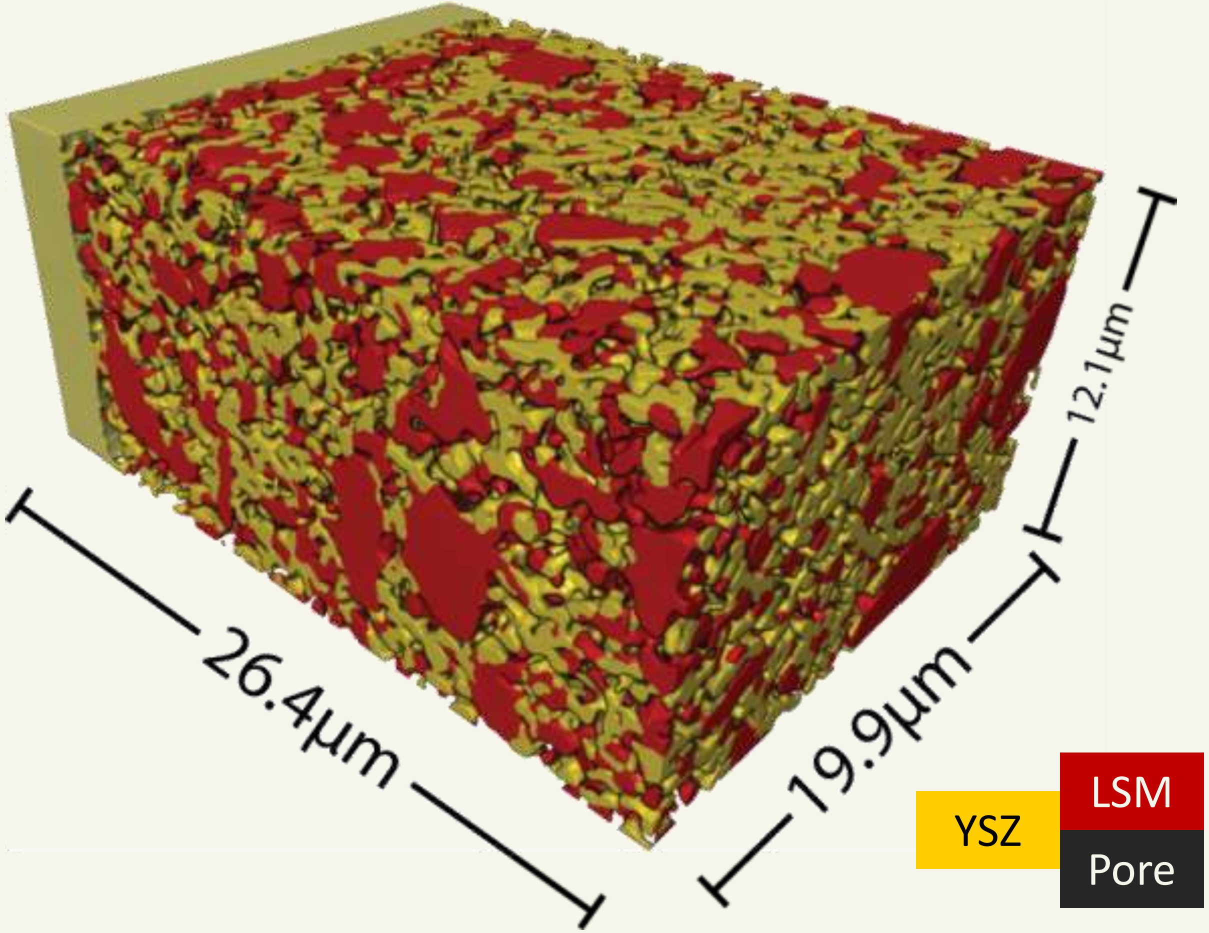
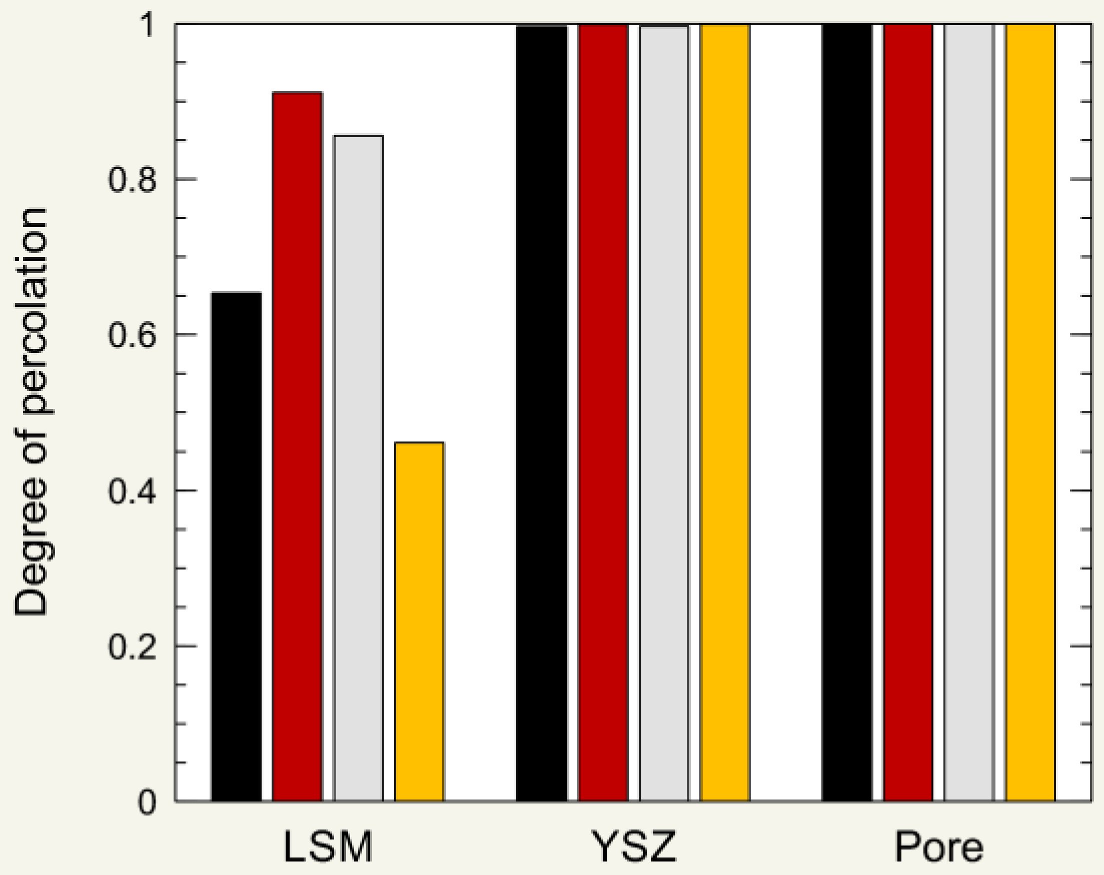


Results – Phase percolation

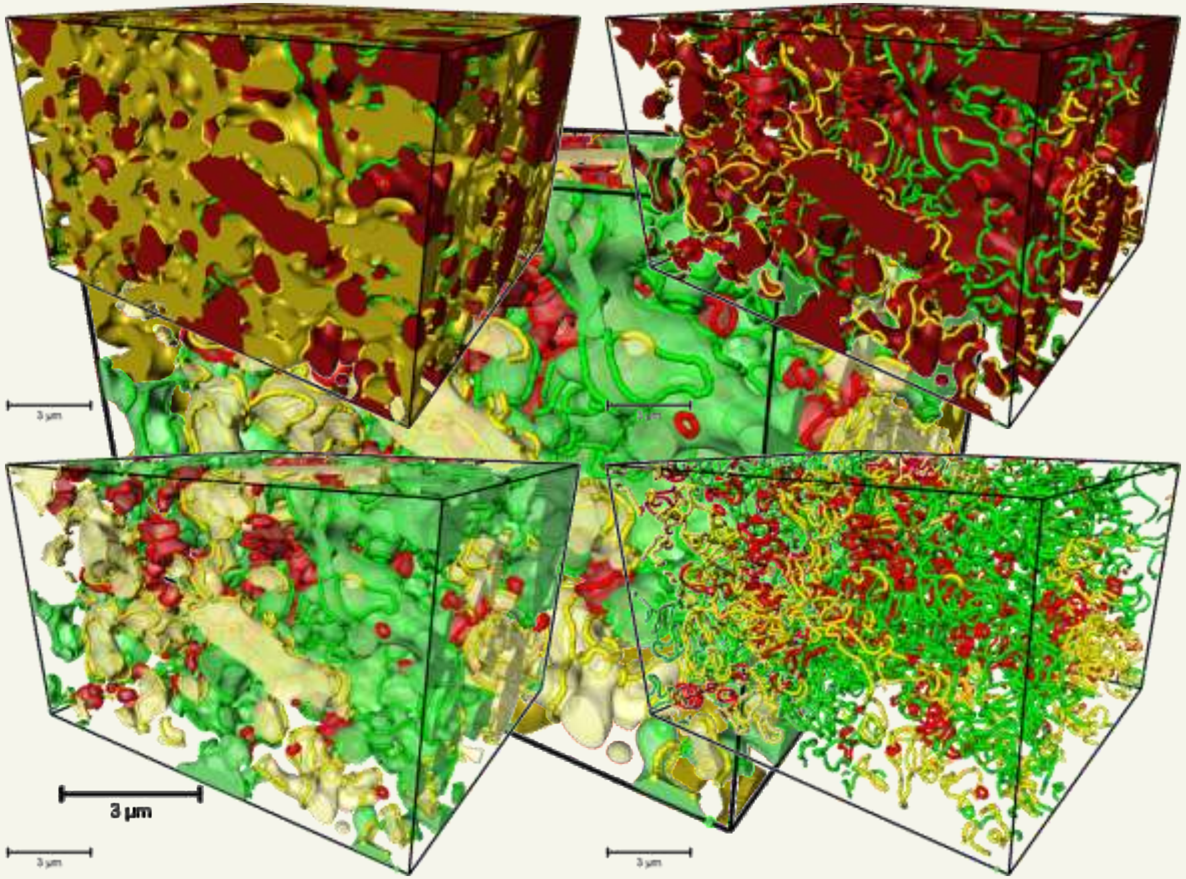
- Comparison of longest section of each phase to overall network
  - Used 5 longest components

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

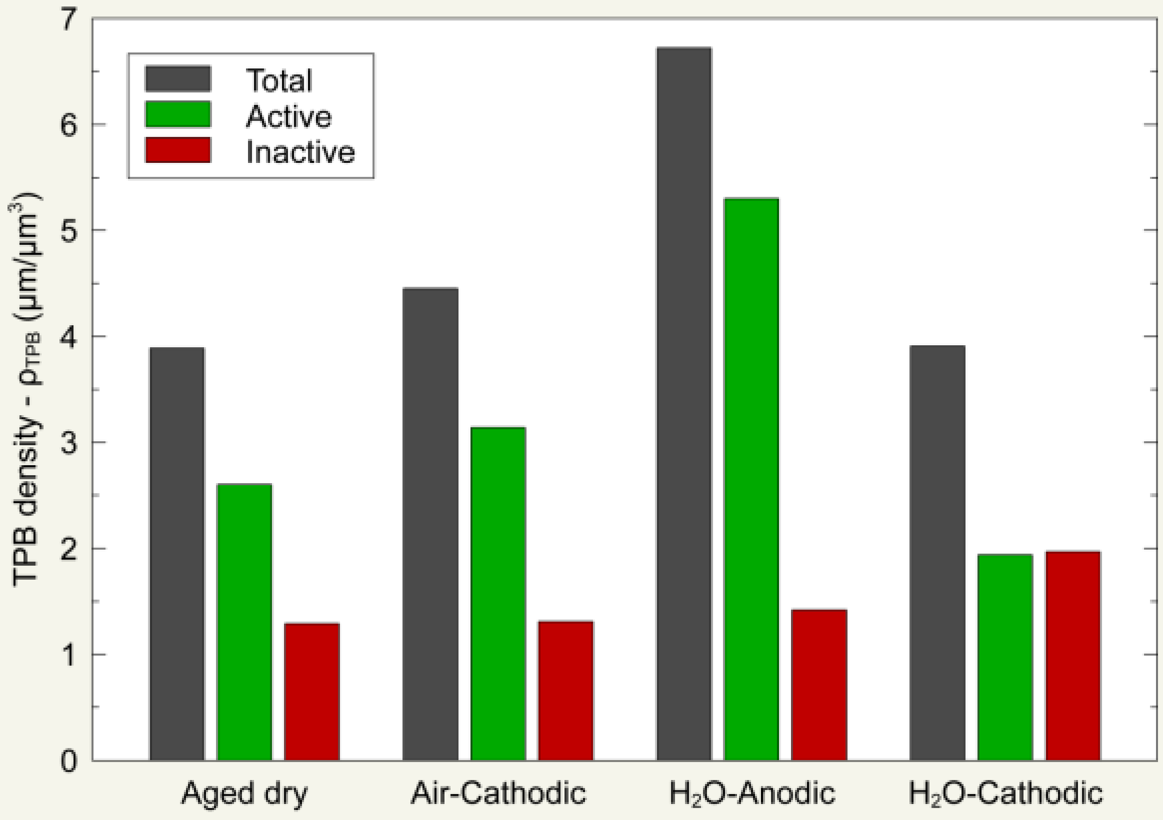


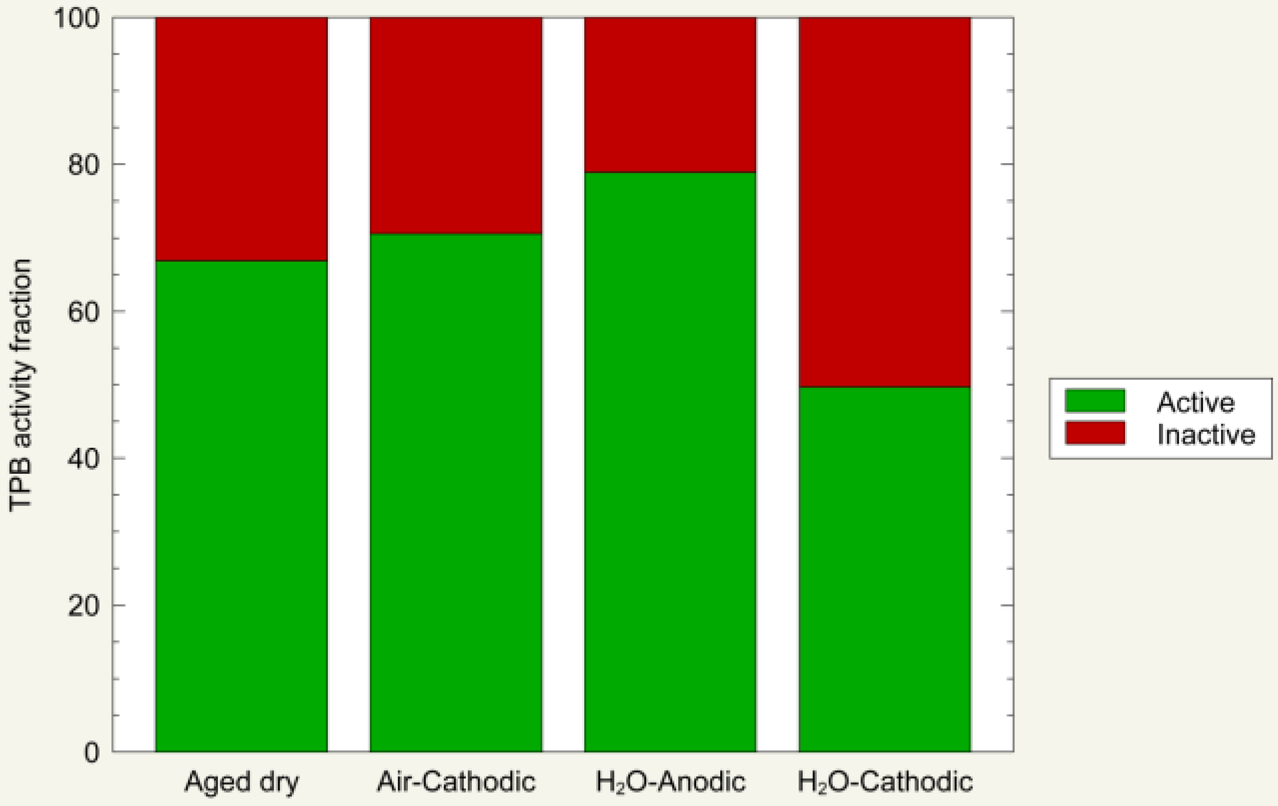
Triple phase boundary (L_{TPB}) determination

- 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

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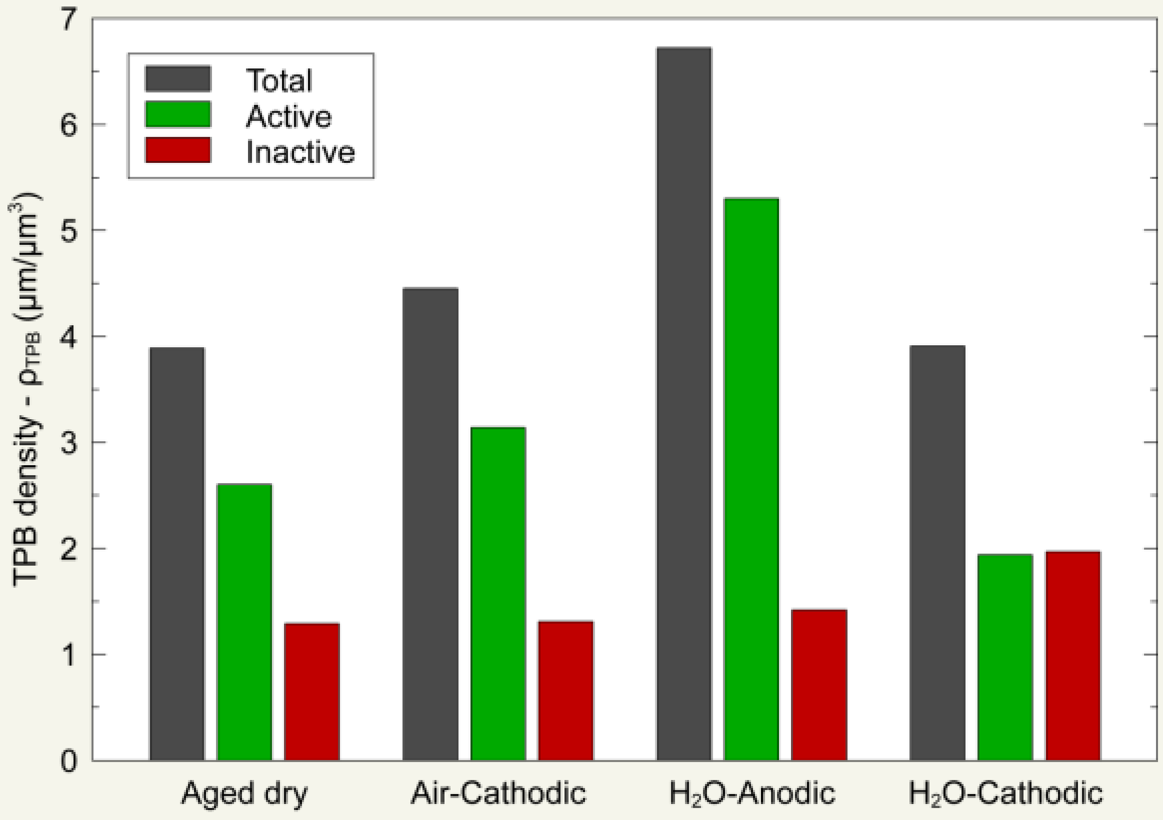

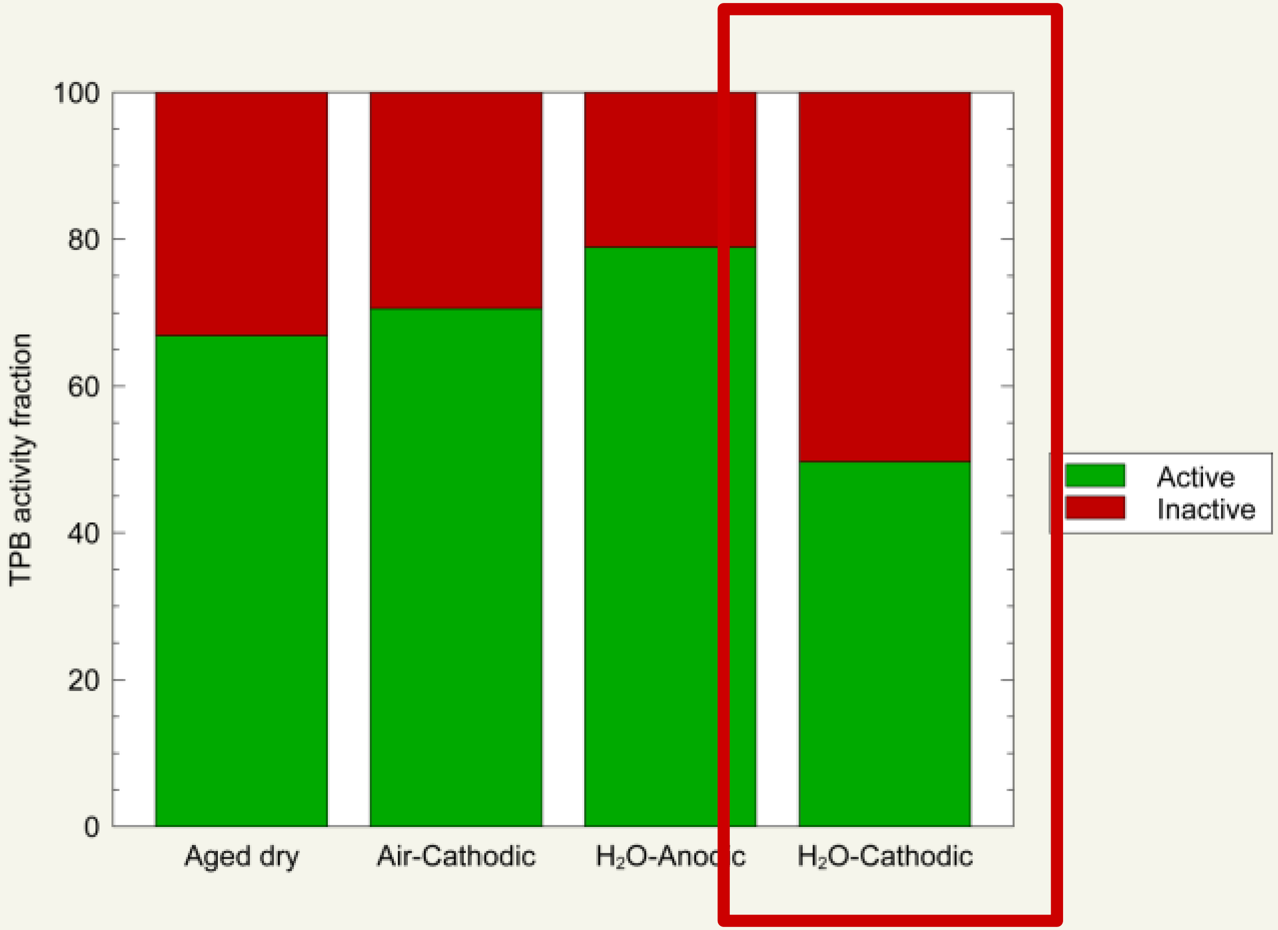

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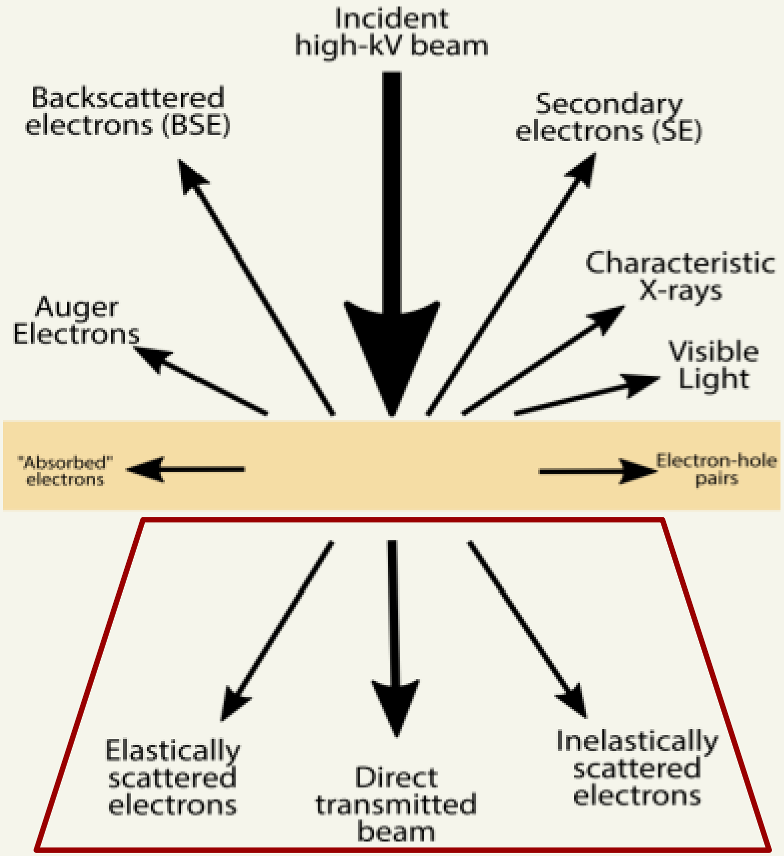
TEM-EELS HYPERSPECTRAL IMAGING

Electron Energy Loss Spectroscopy (EELS)

- E-beam has many interactions with specimen:



Adapted from Williams and Carter, *Transmission Electron Microscopy*, (2009).

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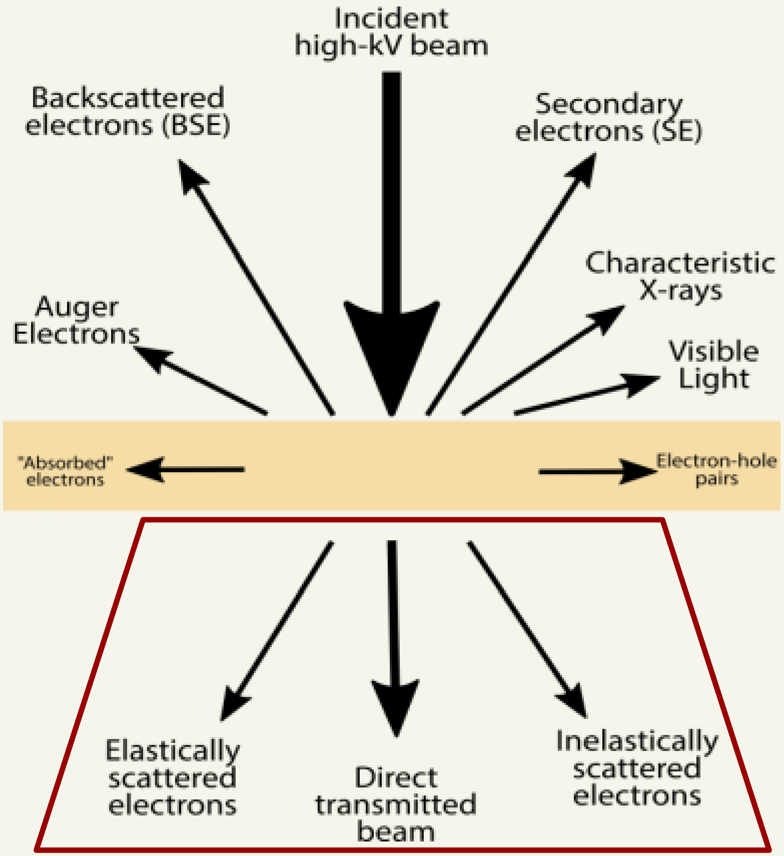

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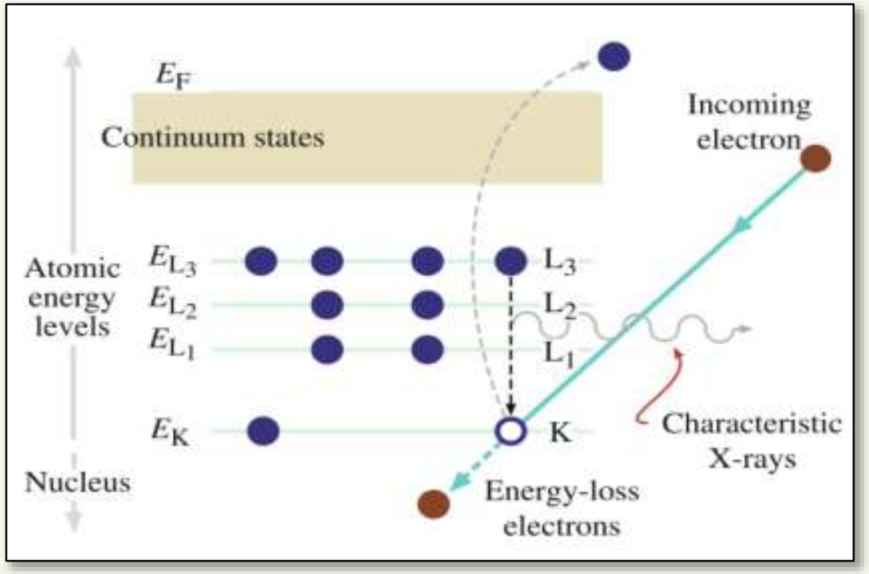
- EELS is measurement of the energy lost when an electron interacts with the sample:

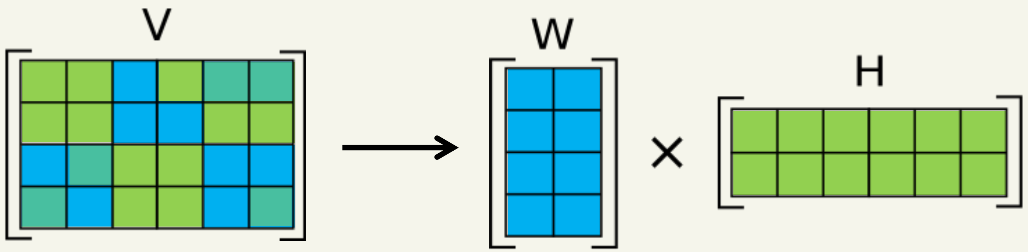


Williams and Carter, *Transmission Electron Microscopy*, (2009).

Decomposition analysis

- Machine learning for hyperspectral decomposition
  - How to tease out convoluted and complex signals
  - Use redundancy of information in spatial dimensions to learn more about differences in the signal dimension(s)
  - Used in EEG, audio processing, fMRI, etc.

- Non-negative matrix factorization and Blind source separation
  - Finding simpler descriptive basis vectors of overall data; one component per "source"



Adapted from: https://upload.wikimedia.org/wikipedia/commons/f/f9/NMF.png

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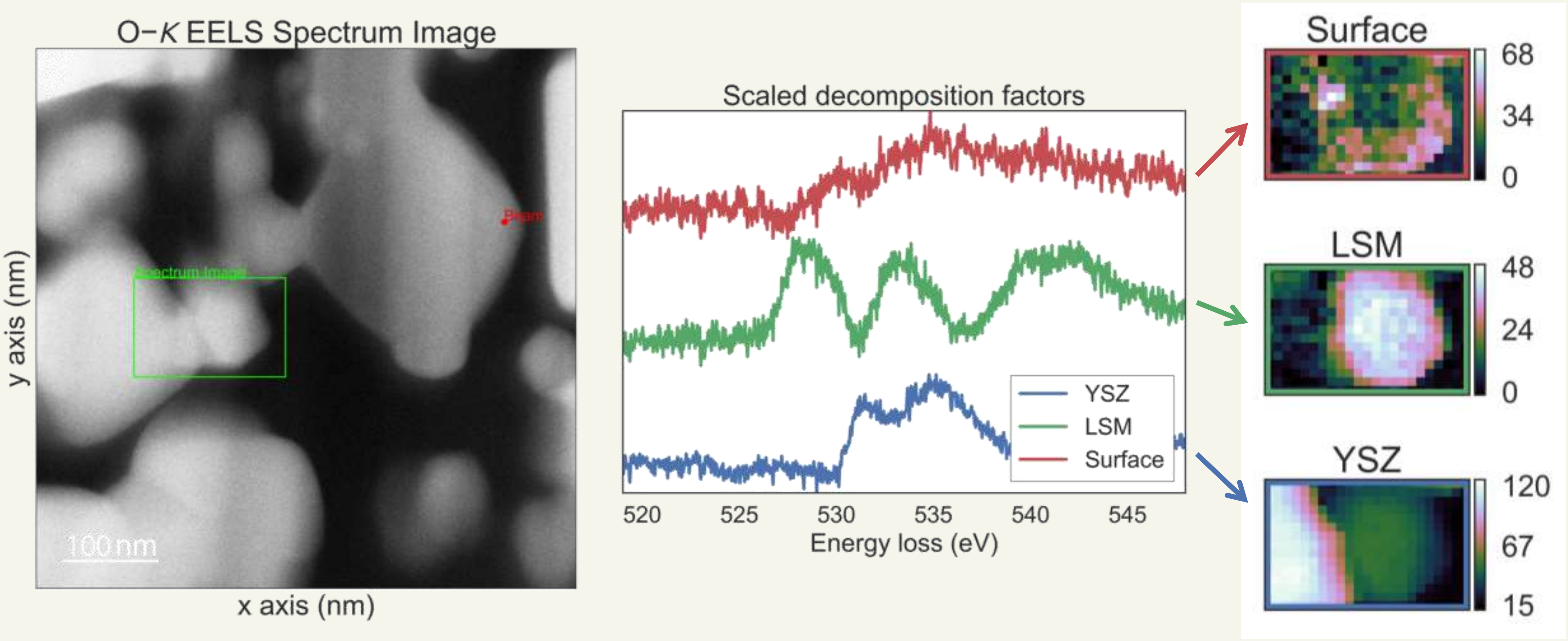
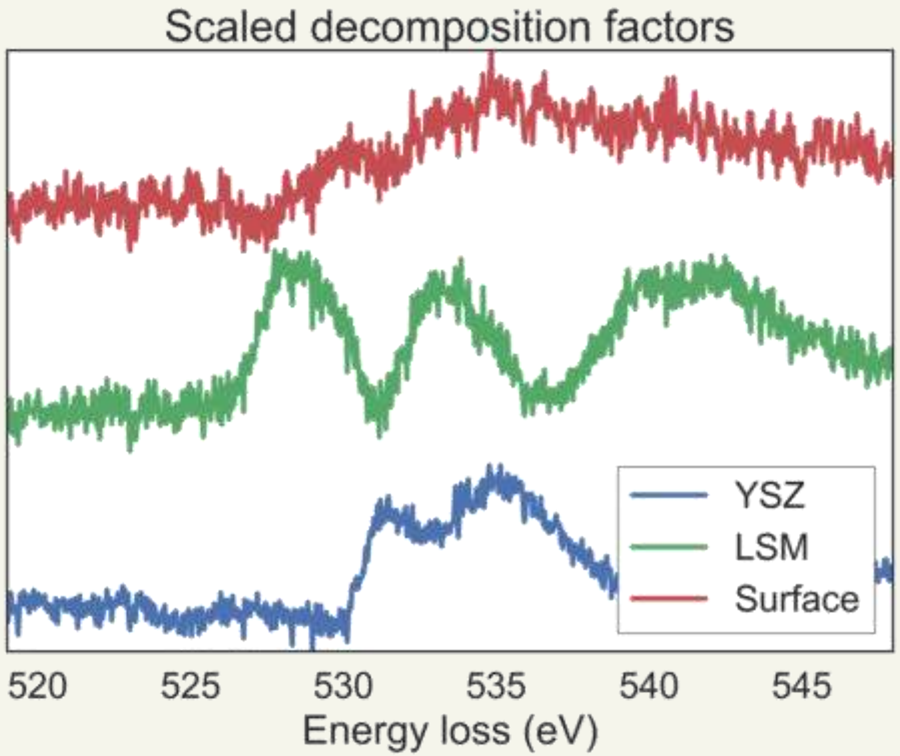
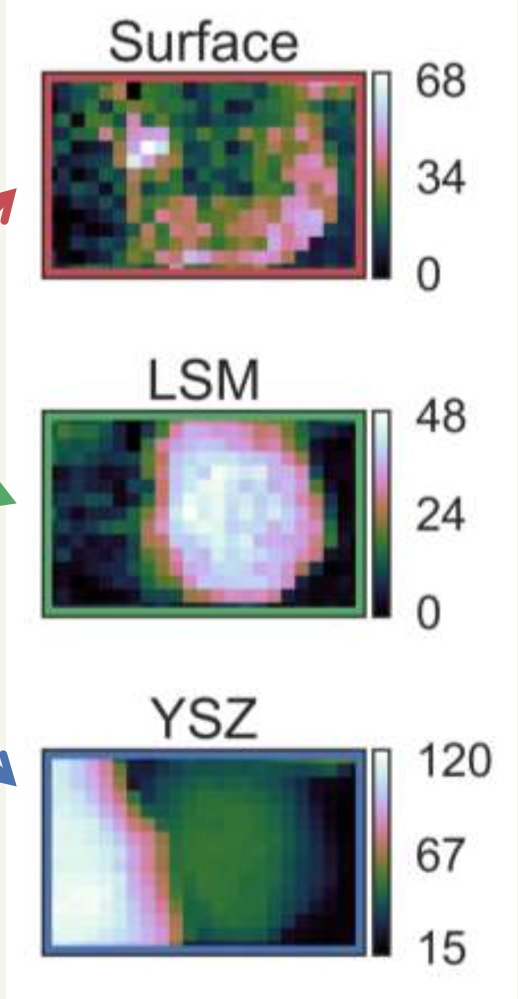
Hyperspectral decomposition of oxygen signal



Hyperspectral decomposition of oxygen signal

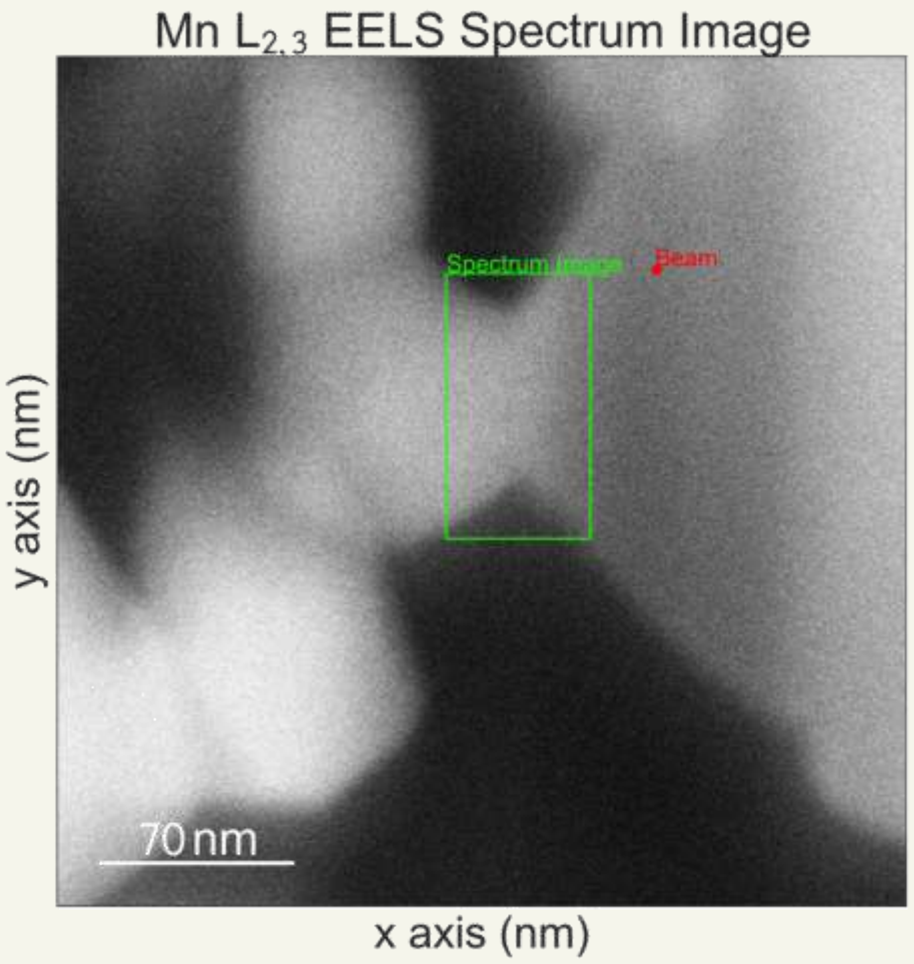
- Discrete surface component
  - Independent from LSM or YSZ
- Lack of peak in O-*K* EELS signal at surface
  - Suggests decrease in oxygen 2nd nearest neighbors
  - More oxygen vacancies
- Increase in edge onset (compared to LSM)
  - Increased bandgap, lower electrical conductivity

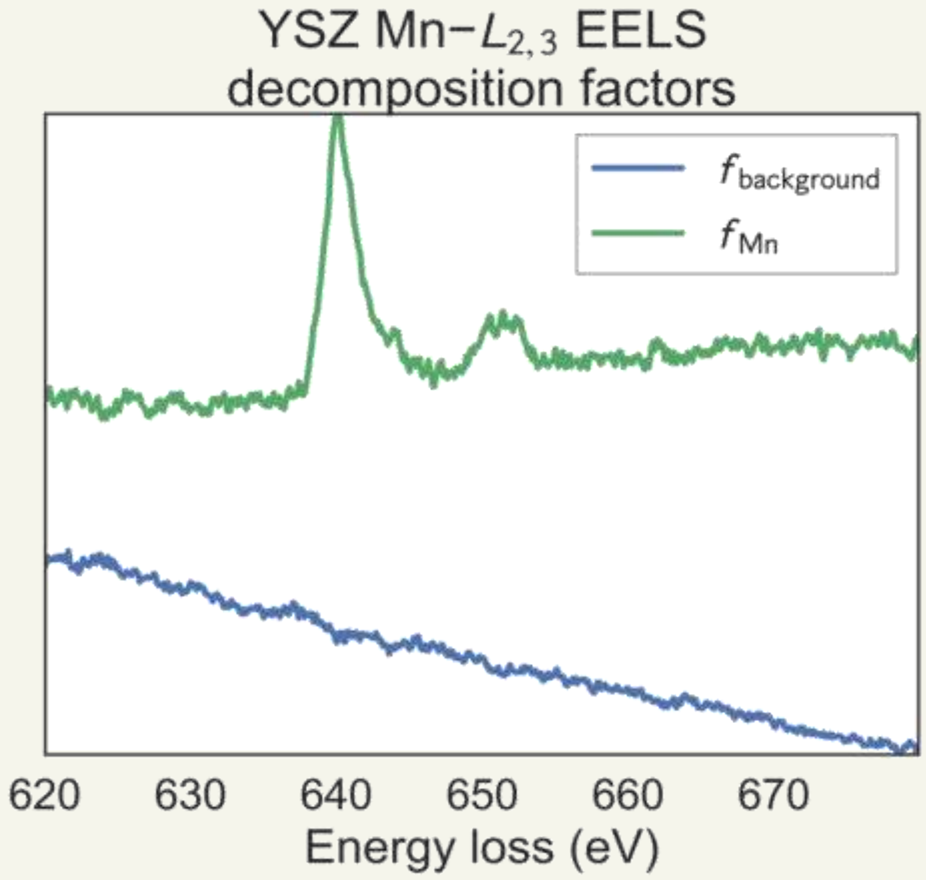


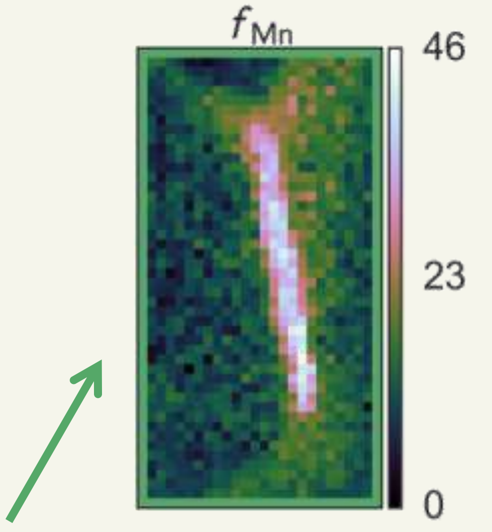


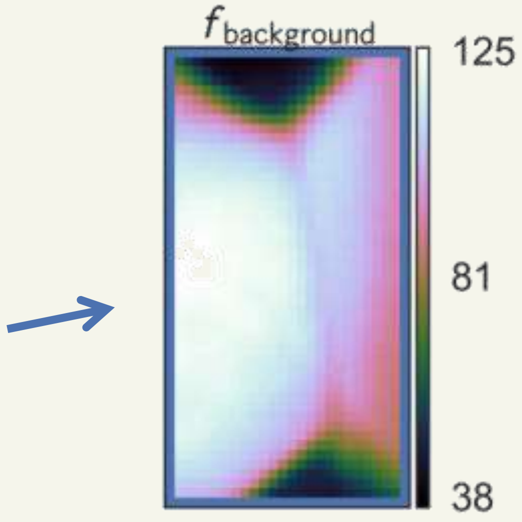
D. Muller, et al., *Nature.*, **399**, 758 (1999).

Hyperspectral decomposition – Mn segregation

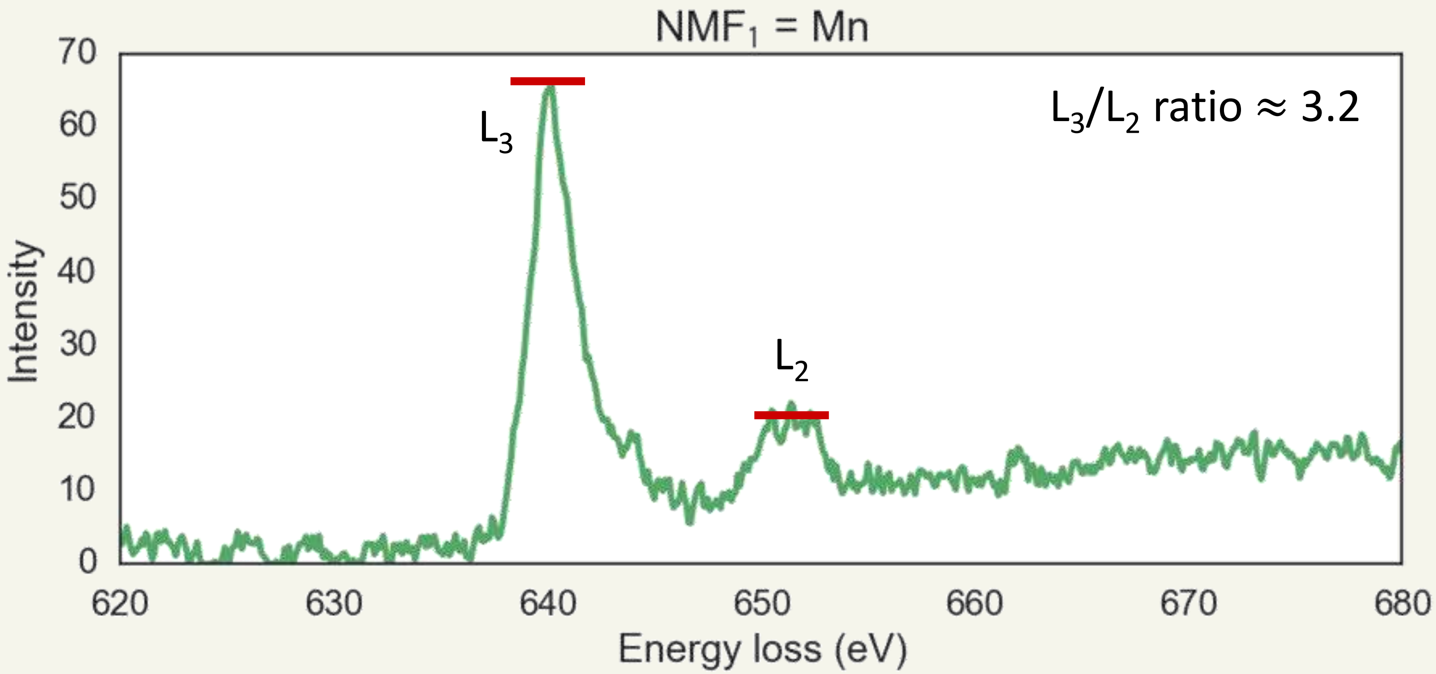








Mn-segregation valence analysis



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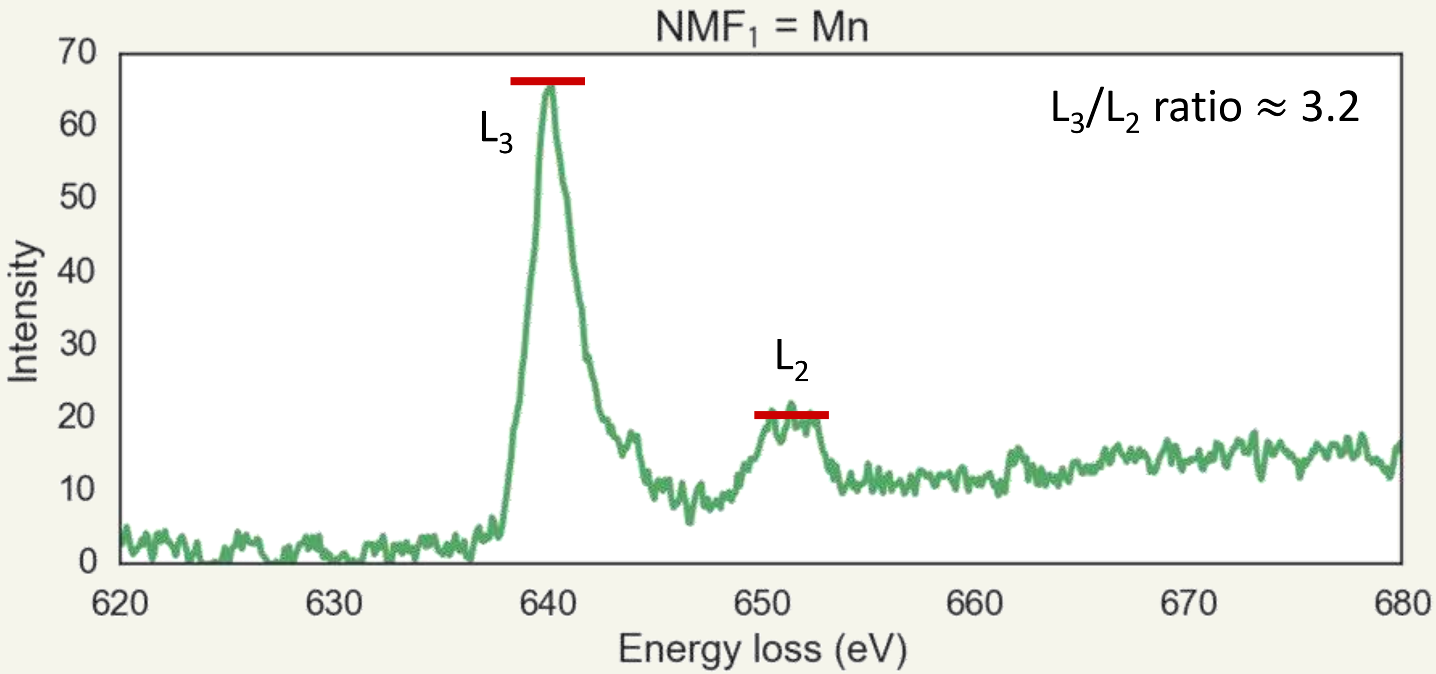

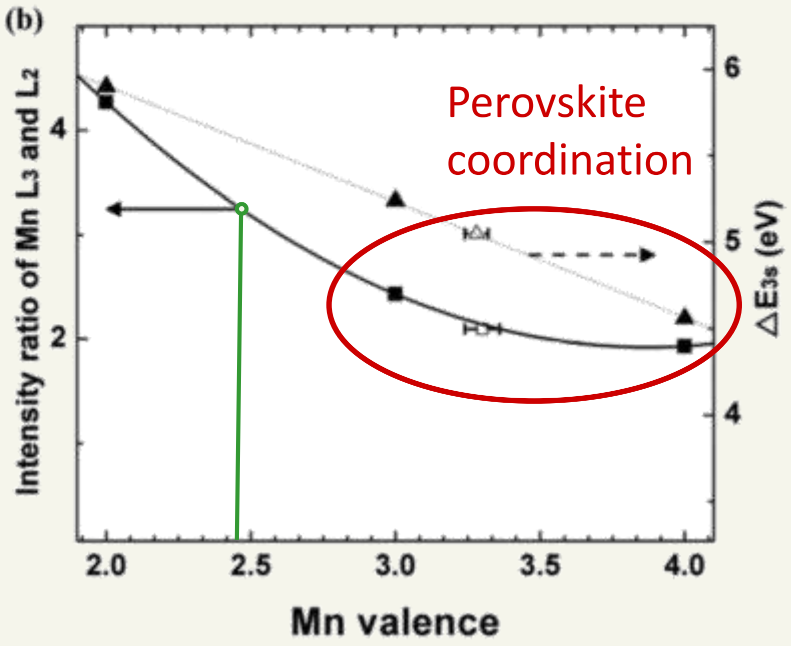

S.J. Shih, et al., *J. Electrochem. Soc.*, **158**(10), B1276, (2011).

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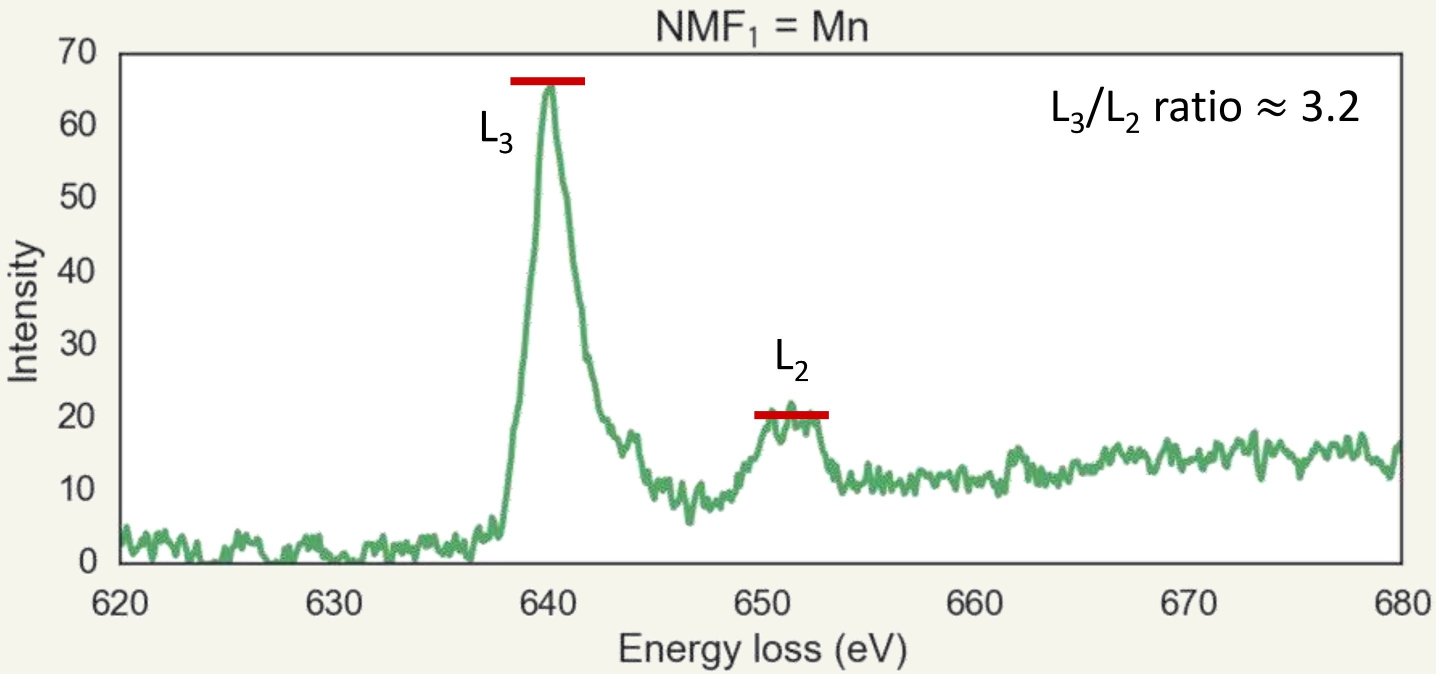

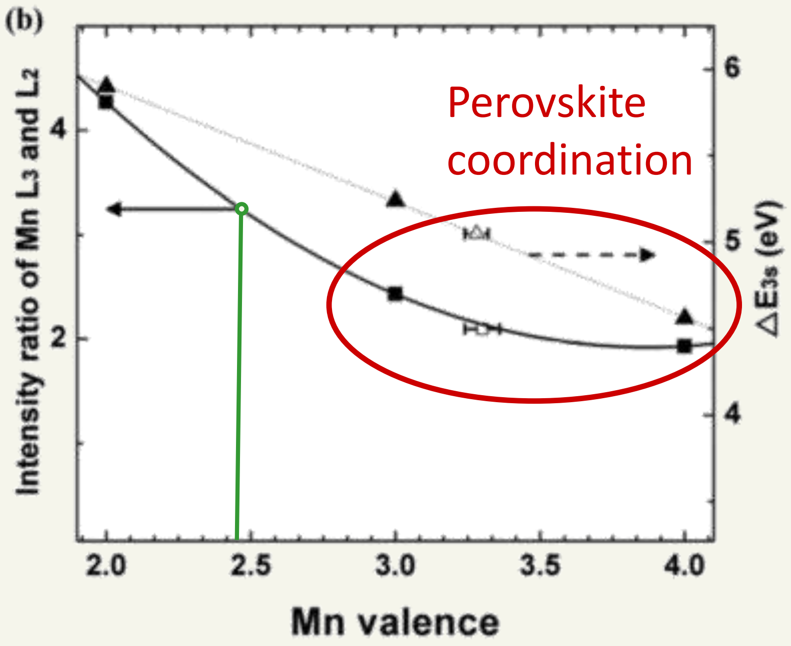

S.J. Shih, et al., *J. Electrochem. Soc.*, **158**(10), B1276, (2011).

- EELS reveals mobile Mn ions with valence of ≈2.5 at the interface of YSZ particles
    - Suggests not a full perovskite coordination

Summary

Conclusions

- Developed methods to quantify 3D microstructure of solid oxide fuel cell cathodes
- Subtle changes in LSM/YSZ 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 Mn and La to YSZ grain boundaries in H_2O-cathodic (but not Sr); change in LSM Mn valence

Ongoing 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

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HyperSpy hyperspectral data analysis

UNIVERSITY OF MARYLAND

MARYLAND NANOCENTER AIMLAB ADVANCED IMAGING & MICROSCOPY LABORATORY

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

THANK YOU

Questions and comments?

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