Quantifying the Nature and Impact of Mesoscale Heterogeneities in SOFC Electrodes

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Motivation

- Key factors limiting the commercialization of SOFCs:
  - I. High cost of manufacture
  - II. Poor reliability
  - III. Low durability
- A tradeoff exists between cost of manufacture and reliability / durability of electrodes:

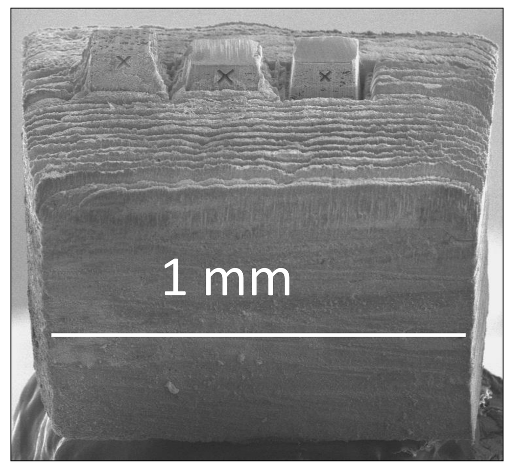
Research-grade SOFC Samples	Commercial SOFC Samples
I. Higher-cost synthesis II. Ideal feedstock materials III. Produced in low quantities IV. Highly homogeneous microstructures	I. Lower-cost synthesis II. Less perfect feedstock materials III. Mass Production IV. Heterogeneous microstructures

- In commercial SOFCs, microstructural variations over mesoscale (≈ hundreds of microns) and over even longer length scales are expected.
- How can we quantify the impact of microstructural variations to processing / performance:

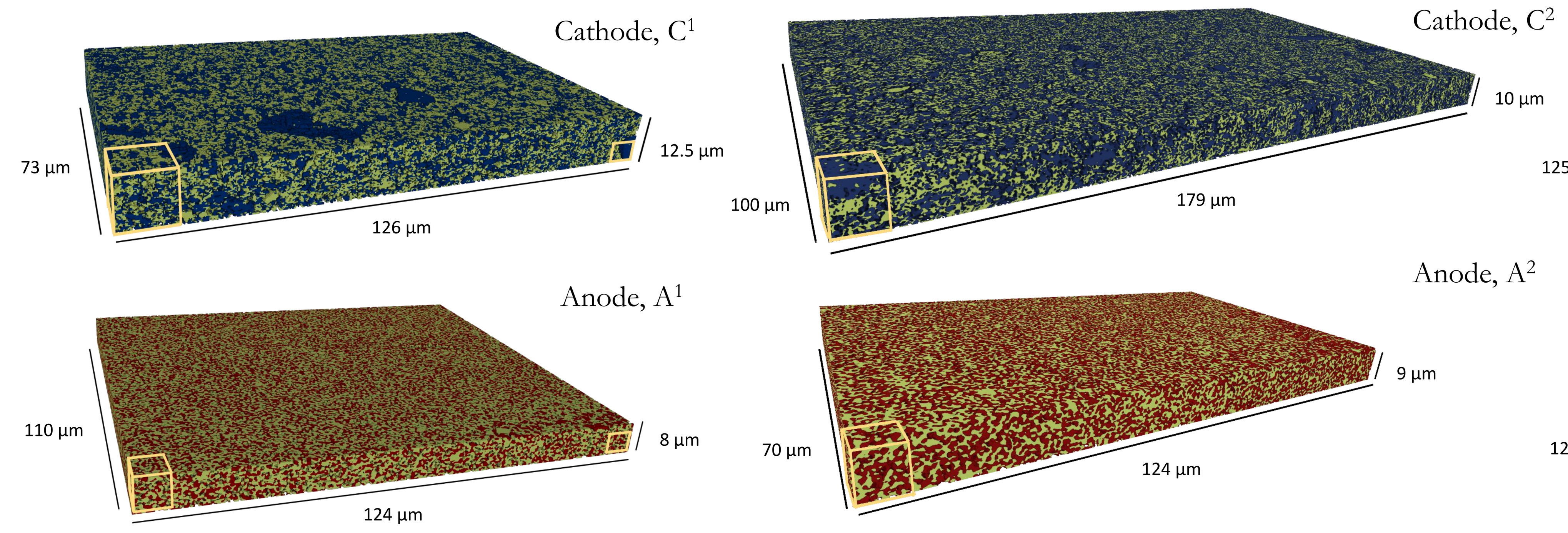
Quantify Heterogeneities in Electrode Microstructures ⇒ Quantify Impact on Local Electrochemical Activity ⇒ Quantitatively Rationalize Origin of Heterogeneities ⇒ Feedback Loop to Improve Reliability / Durability

Quantitative Analysis of Heterogeneities in Electrode Microstructures

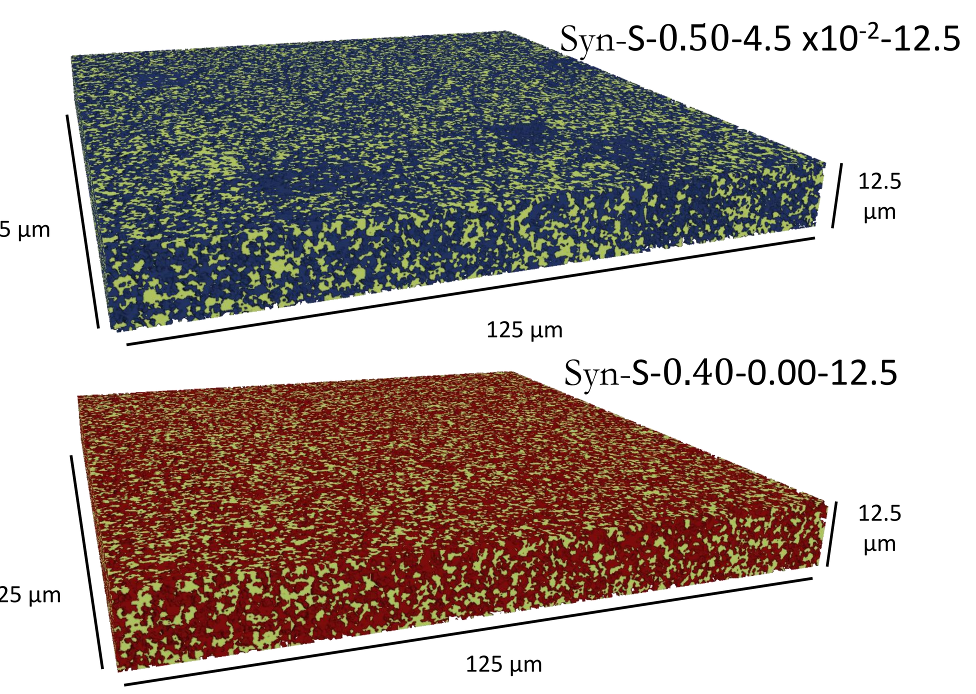
Pillars for PFIB-SEM



Experimental Microstructures



Synthetic Microstructures



Semi-empirical Model for Quantitatively Rationalizing Origin of Heterogeneities

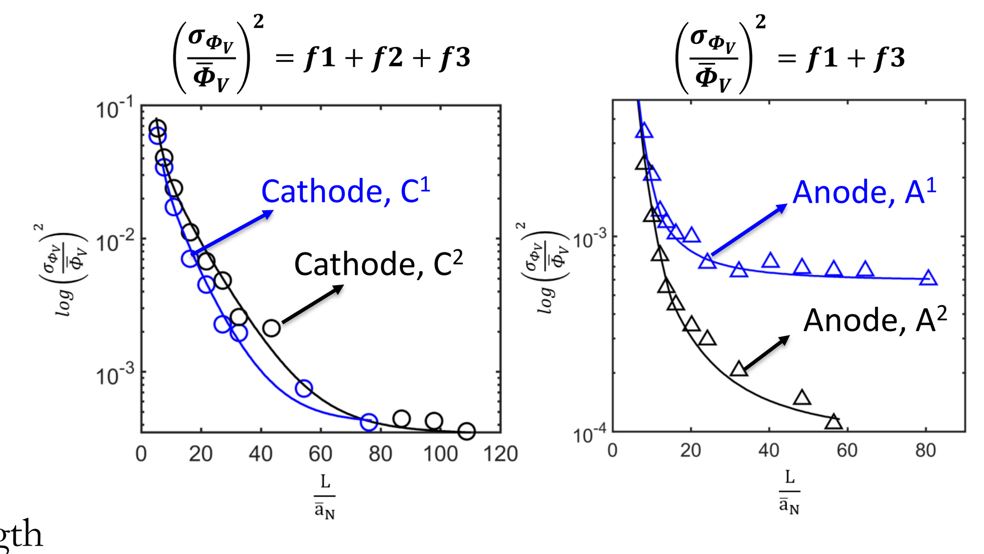
$$\left(\frac{\sigma_{\Phi_V}}{\bar{\Phi}_V}\right)^2 = \begin{cases} A_{PSD}\left(\frac{L}{\bar{a}_N}\right)^{-3} + A_{VFD}\, e^{-B_{VFD}\frac{L}{\bar{a}_N}} + C_{L_m}, & L < t \\ A_{PSD}\left(\frac{t}{\bar{a}_N}\right)^{-1}\left(\frac{L}{\bar{a}_N}\right)^{-2} + A_{VFD}\, e^{-B_{VFD}\frac{L}{\bar{a}_N}} + C_{L_m}, & L \geq t \end{cases}$$

f1: Polydispersity of Particle Size Quantifies Microscale Heterogeneity

f2: Agglomeration of Phases Quantifies Mesoscale Heterogeneity

f3: Quantifies Longer Wavelength Heterogeneity

Model Fit to Experimental Datasets

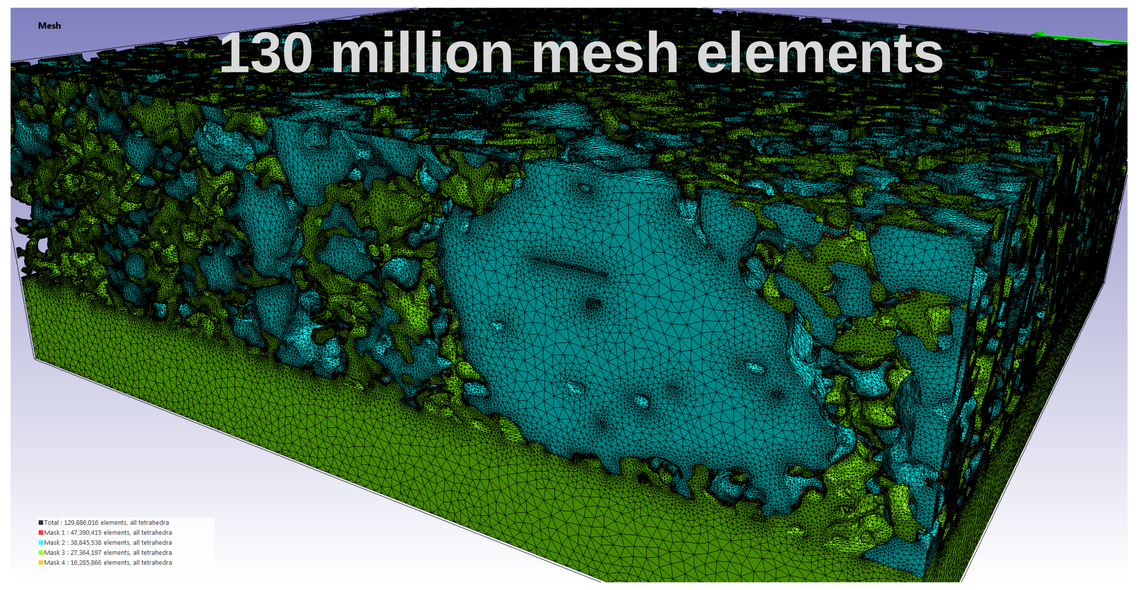


Datasets	$\frac{\sigma_{a_N}}{\bar{a}_N}$	A_{PSD}	A_{VFD}	B_{VFD}	$\frac{1}{B_{VFD}}$	C_{L_m}
Anode-A[1]	0.42	1.3×10^{0}	0.00	-	-	5.9×10^{-4}
Anode-A[2]	0.40	1.3×10^{0}	0.00	-	-	9.0×10^{-5}
Cathode-C[1]	0.50	6.1×10^{0}	4.0×10^{-2}	1.1×10^{-1}	9	3.9×10^{-4}
Cathode-C[2]	0.50	6.1×10^{0}	5.0×10^{-2}	9.0×10^{-2}	11	3.3×10^{-4}

Locally-resolved Simulations of Microstructures

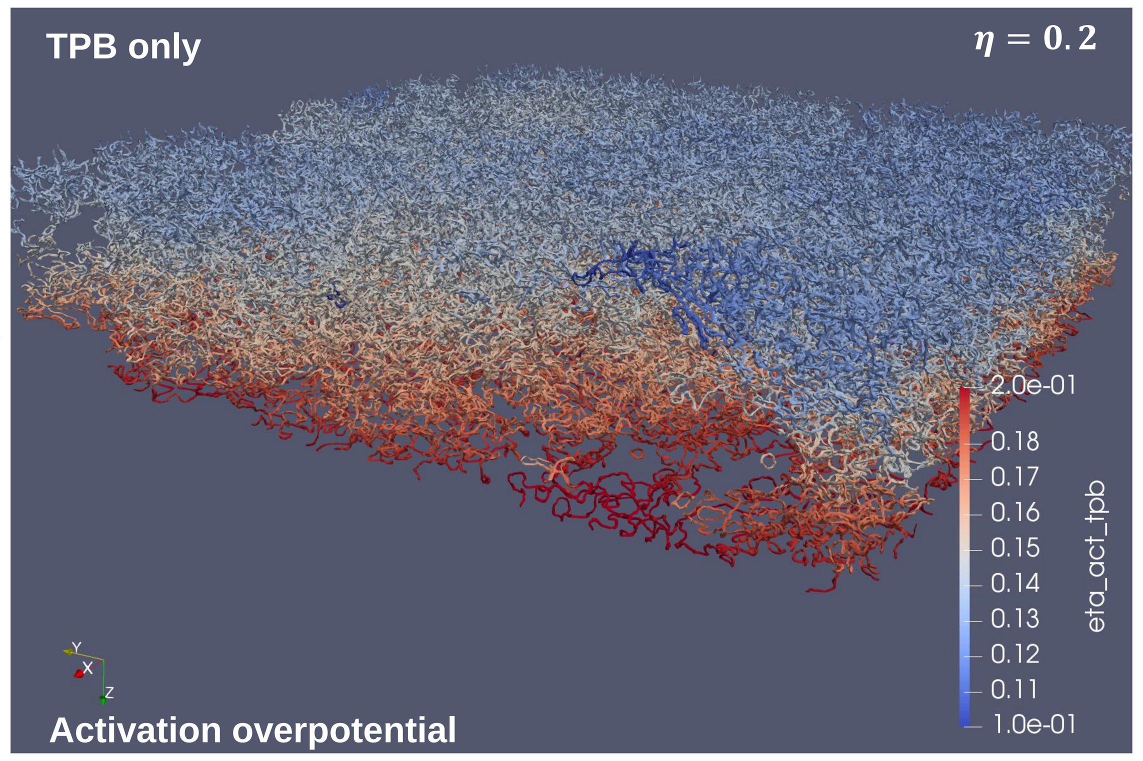
Microstructure-based Simulations

- Effective medium theories only output averaged performance values and assume relatively high homogeneity within a volume
- Degradation is strongly dependent on local electrochemistry, which can be studied with microstructure-based, locally resolved simulations
- Commercial fuel cells exhibit various types of inhomogeneities that do not conform to effective medium theory assumptions
- Microstructure-based simulations of heterogeneous electrodes require advances in:
  - ❖ large-volume, high-resolution 3D reconstructions
  - ❖ morphology preserving meshes that capture 2 and 3 phase boundaries and that can be automated
  - ❖ massively-parallel, multi-physics, finite-element codes implemented on high performance computers



Large-scale meshed microstructure. The size is 30 x 30 x 10 [µm]. The number of mesh elements is 130 millions. The presence of an abnormally large feature is shown in the image.

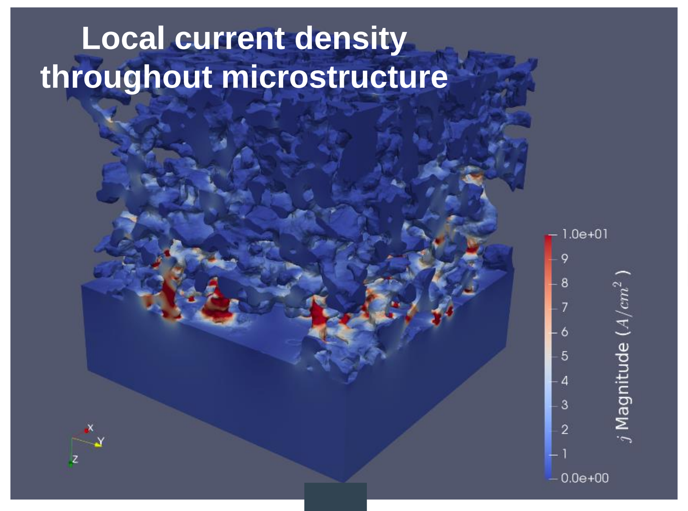
MOOSE framework ~500 cores < 2 days

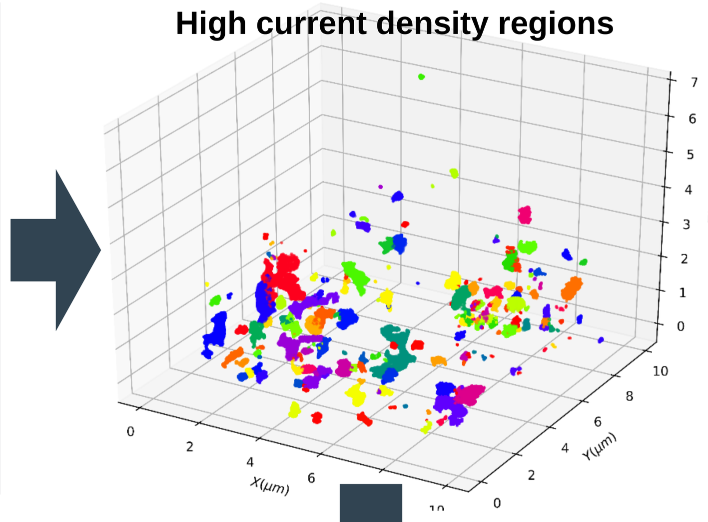


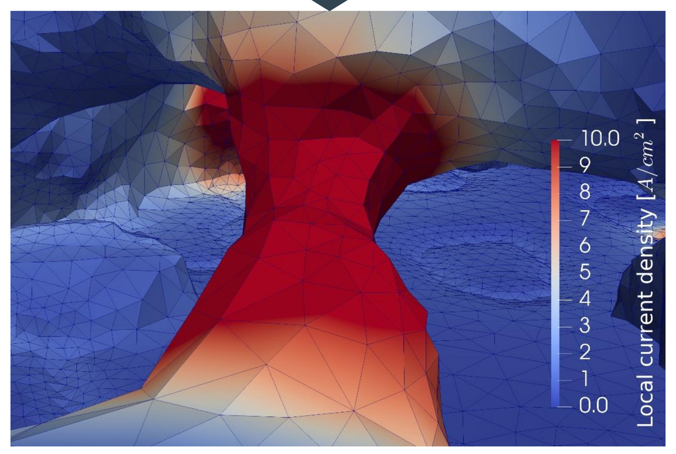
Visualization of a computed variable solution field. In this instance the activation overpotential at the TPBs is visualized in 3D space. Notice that the large boulder affects the surrounding local electrochemistry, located at the top of the boulder.

Extract and separate local hotspots

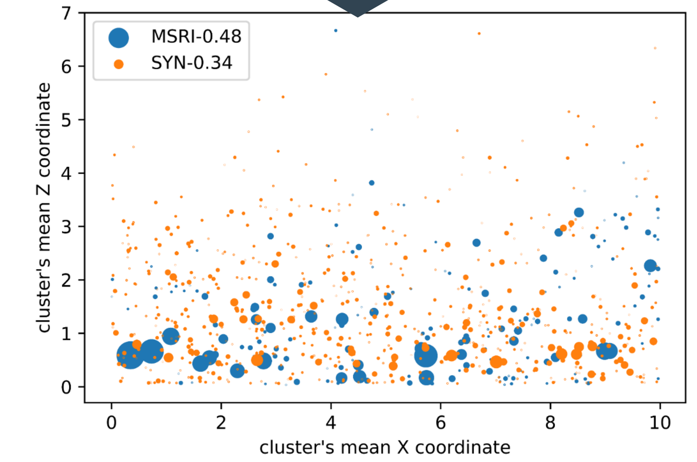
An example analysis is to threshold and separate high current density regions, which are considered local hotspots. Analysis of these hotspots may help inform local degradation phenomena.







Constriction effect of local current density leads to extremely high magnitudes (i.e., hotspots)



Hotspots spatial distributions in two different microstructures – one is heterogeneous (MSRI), the other is homogeneous (SYN). Marker size denotes relative hotspot volume. MSRI exhibits more clustered/aggregated hotspots.

Conclusions

- Reconstructions of commercial grade SOFC electrode microstructures using PFIB-SEM confirmed heterogeneity exists over multiple length in these electrodes.
- Combining experimental microstructures with a large number of synthetic ones a semi-empirical model is presented that quantifies microstructural variations present in the electrode microstructures.
- A high-throughput microstructure base finite element approach is developed to study the impact of heterogeneities on the statistical variation in local property.
- The model confirms that the heterogeneous commercial electrodes exhibit more performance hotspots than the less heterogeneous synthetic ones.

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