Visualizing Computed Local Electrochemistry in Solid Oxide Fuel Cell Electrode Microstructures

Tim Hsu[1,2], Rubayyat Mahbub[1,2], William K. Epting[1,3], Harry Abernathy[1,4], Gregory A. Hackett[1], Anthony D. Rollett[1,2], Shawn Litster[1,2], Paul A. Salvador[1,2]
[1]US Department of Energy, National Energy Technology Laboratory, Pittsburgh PA /Morgantown WV; [2]Carnegie Mellon University, Pittsburgh PA; [3]ORISE, Oak Ridge TN; [4]AECOM Corporation, Morgantown WV

Research & Innovation Center

NATIONAL ENERGY TECHNOLOGY LABORATORY

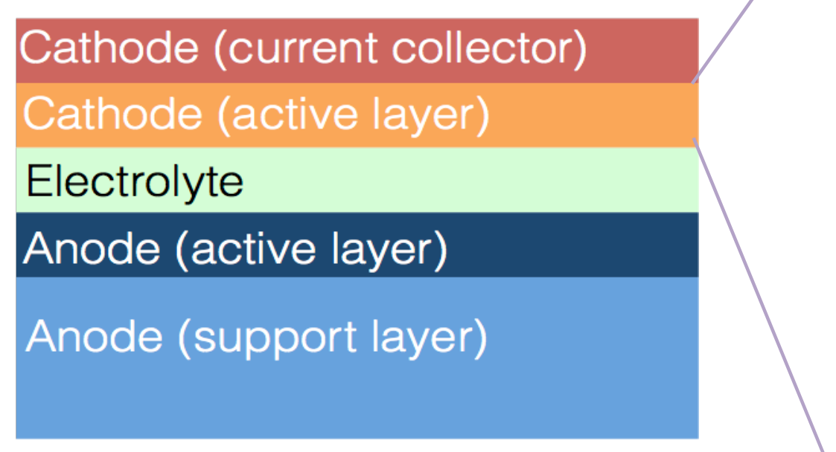
Motivation

3D Microstructure Reconstructions

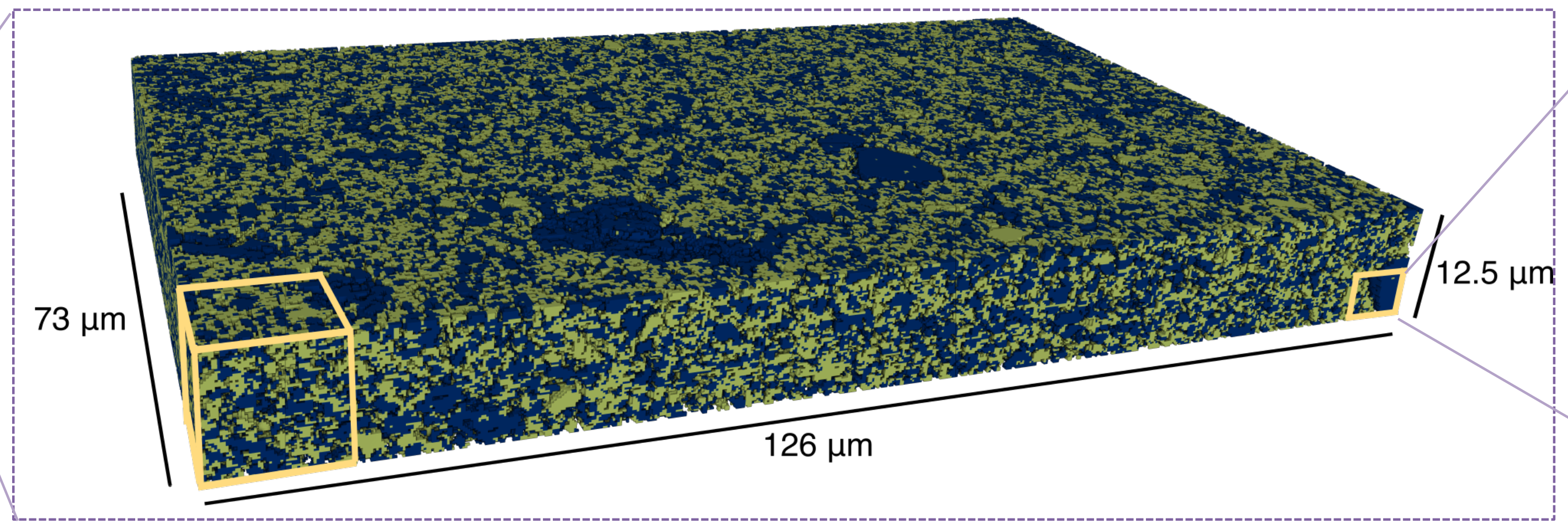
- 3D microstructure characterization has become a standard technique for SOFC electrode studies
- Key microstructural features, including two-phase and three-phase boundaries, are only clearly manifested in 3D
- A 3D PFIB-SEM reconstruction of an active cathode of a commercial SOFC is shown below
- Average performance is thought to be modeled reasonably using 3D data with effective medium theory (EMT)

Microstructure-based Simulations

- Effective medium theories only output an average value and assume relatively high homogeneity within a volume
- Degradation can be linked to local electrochemistry, which can be studied with microstructure-based simulations
- Commercial fuel cells exhibit various types of inhomogeneities that may not conform to EMT assumptions
- Microstructure-based simulations of heterogeneous electrodes require advances in:
  - ❖ large-volume, high-resolution 3D reconstructions (see PFIB-SEM poster)
  - ❖ 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



Schematic of the SOFC electrode-electrolyte assembly used in this work



Reconstructed, segmented 3D microstructure of a commercial SOFC cathode (pores are transparent). The yellow boxes indicate volumes of (left) 12.5^3 µm³ and (right) 5^3 µm³.

Model Description

Oxygen Reduction Reaction Pathways

The reaction-and-transport model simulates oxygen reduction reactions (ORRs) via 2 parallel pathways:

- TPB pathway – diffusion (pore) / **TPB reaction** / drift (YSZ)
- MIEC pathway – diffusion (pore) / **surface exchange** / diffusion (LSM) / **charge transfer** / drift (YSZ)

Model Operation

The model overpotential is applied across the overall domain to drive transport and reaction

$$\eta_{model} = E_{model} - (\phi_{LSM} - \phi_{CE})$$

The simulation solves for local values of pO_2 , $V_{O,L}^{\cdot\cdot}$, ϕ_{YSZ} given specific material parameters

Post-processors and visualization tools output current density, spatial distributions, …

TPB (Triple Phase Boundary) Pathway

With relatively fast kinetics, oxygen is reduced by the TPB reaction

$$O_{2(g),p} + 2V_{O,Y}^{\cdot\cdot} + 4e_{vb,L}^{*} \overset{O_{P\to Y}, e_{L\to Y}}{\Longleftrightarrow} 2O_{O,Y}^{*} + 4h_{vb,L}^{\cdot}$$

The reaction rate follows the Butler-Volmer form

$$s_{tpb} = 2s_{0,tpb} \sinh\left(\frac{0.5zF}{RT}\eta_{tpb}\right)$$

MIEC (Mixed Ionic and Electronic Conductor) Pathway

This pathway is more dominant when an MIEC is the cathode material. Oxygen incorporates into LSM (a poor MIEC) by Surface Exchange:

$$\frac{1}{2}O_{2(g),p} + V_{O,L}^{\cdot\cdot} + 2e_{vb,L}^{*} \overset{O_{P\to L}}{\Longleftrightarrow} O_{O,L}^{*} + 2h_{vb,L}^{\cdot}$$

The SE reaction rate is linearly proportional to exchange coefficient (*k*)

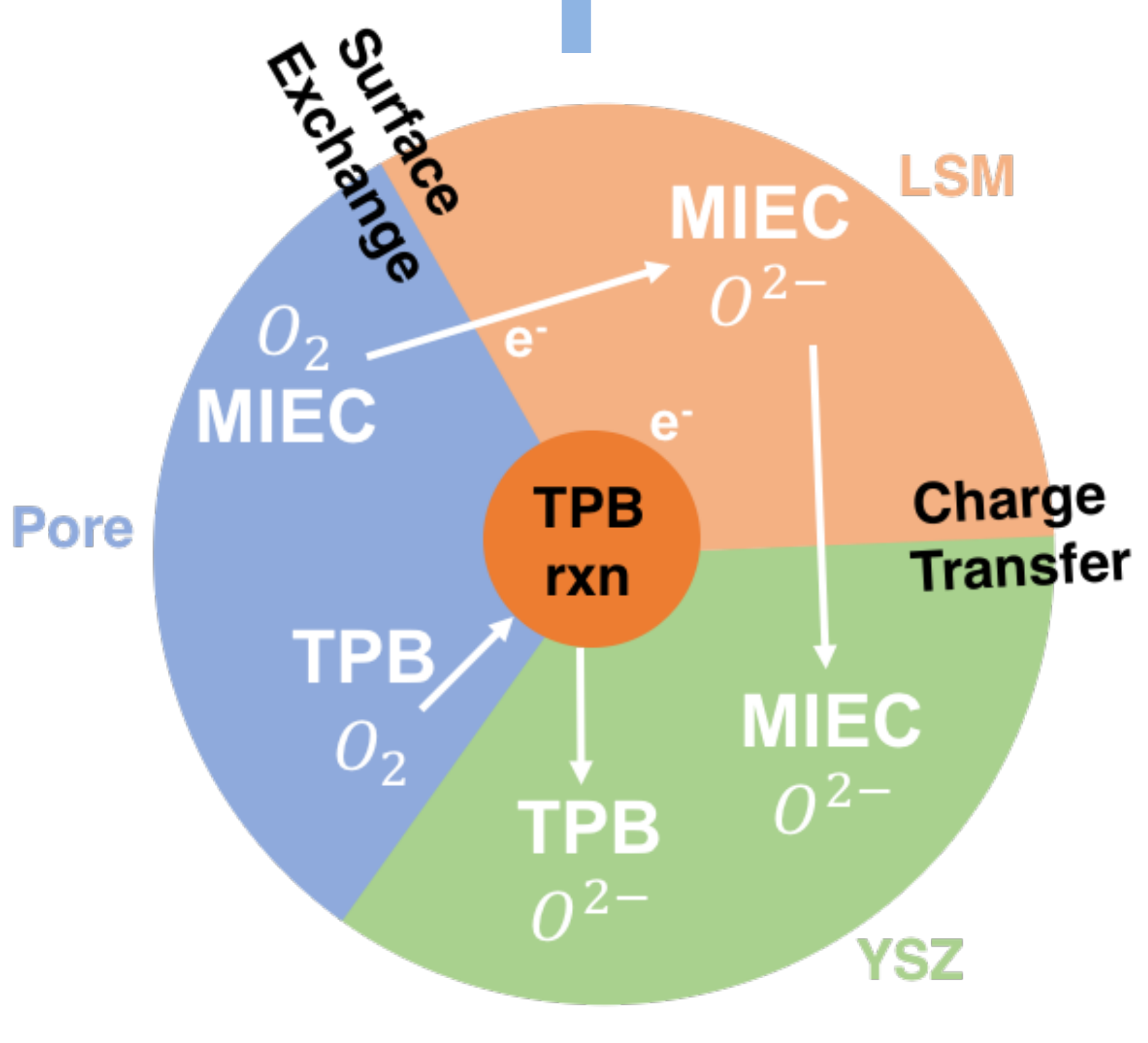
$$J_{se} = -k(c_{O,eq} - c_{O})$$

Oxygen is transferred to YSZ by Charge Transfer:

$$V_{O,Y}^{\cdot\cdot} + O_{O,L}^{*} \overset{O_{L\to Y}}{\Longleftrightarrow} V_{O,L}^{\cdot\cdot} + O_{O,Y}^{*}$$

The CT reaction rate follows the Butler-Volmer form

$$j_{ct} = 2j_{0,ct} \sinh\left(\frac{0.5zF}{RT}\eta_{ct}\right)$$



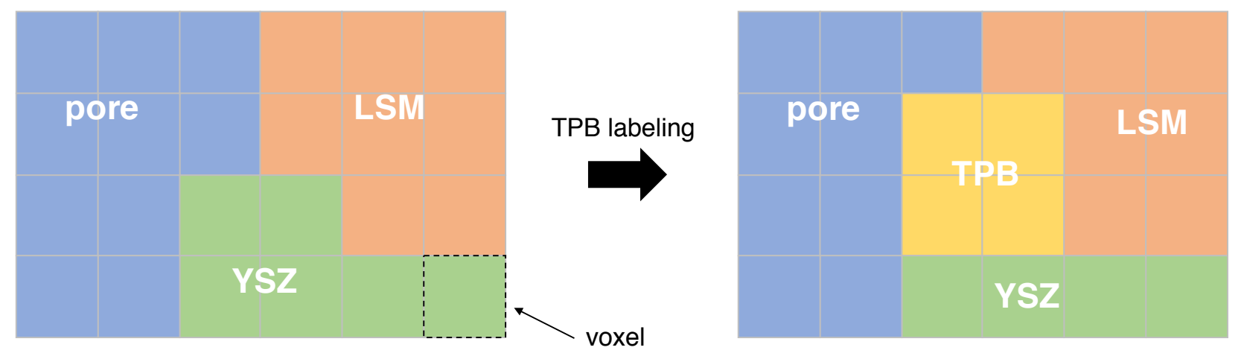
Schematic of the two ORR pathways through the 3-phase cathode microstructure

Numerical Model

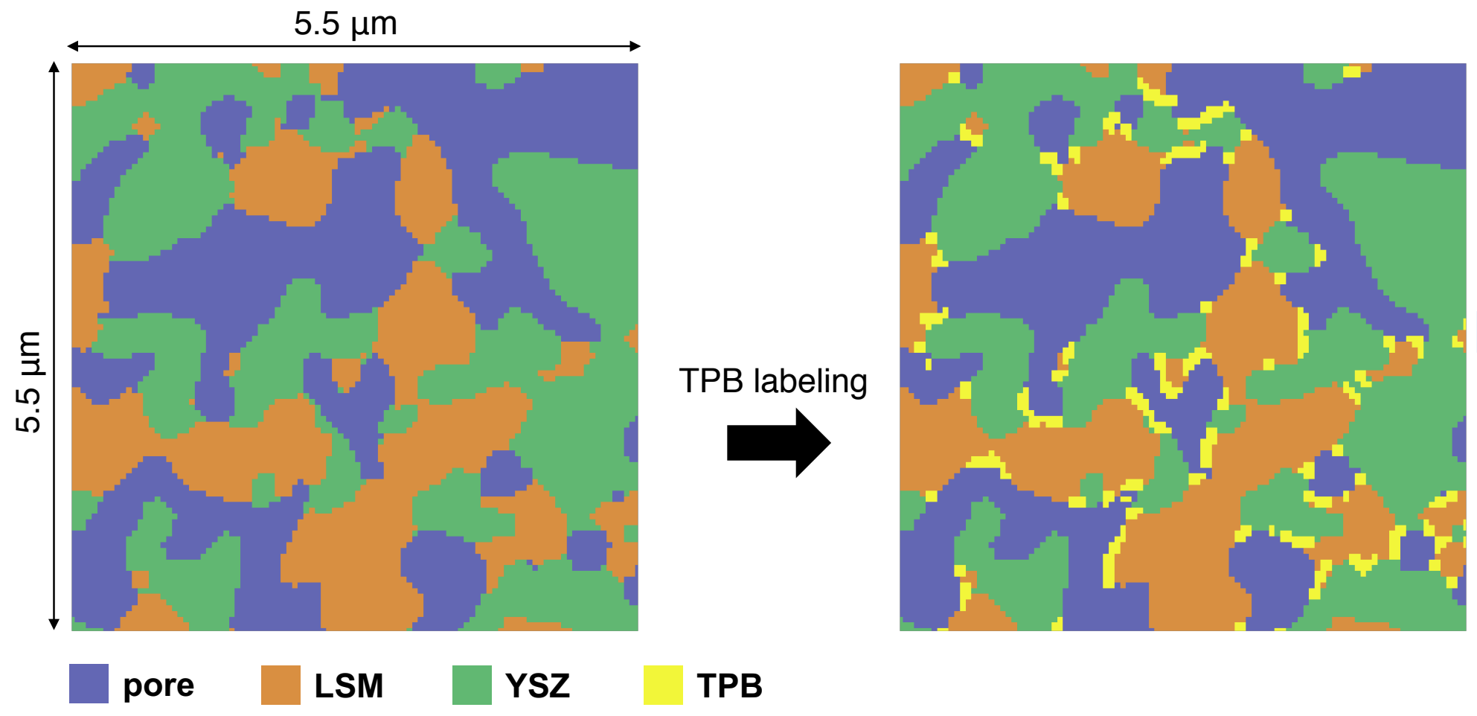
Morphology-preserving Meshing

TPB Labeling Algorithm

- TPBs are the important reaction sites
- TPBs are 1D lines in 3D space
- Modeling 1D features is an issue in 3D FEM
- Instead, we assign TPBs as volumes in which the reaction rate is readily simulated as source
- TPB volumes are created by relabeling segmented image voxels (Matlab)
- TPB are then meshed simply as a fourth phase

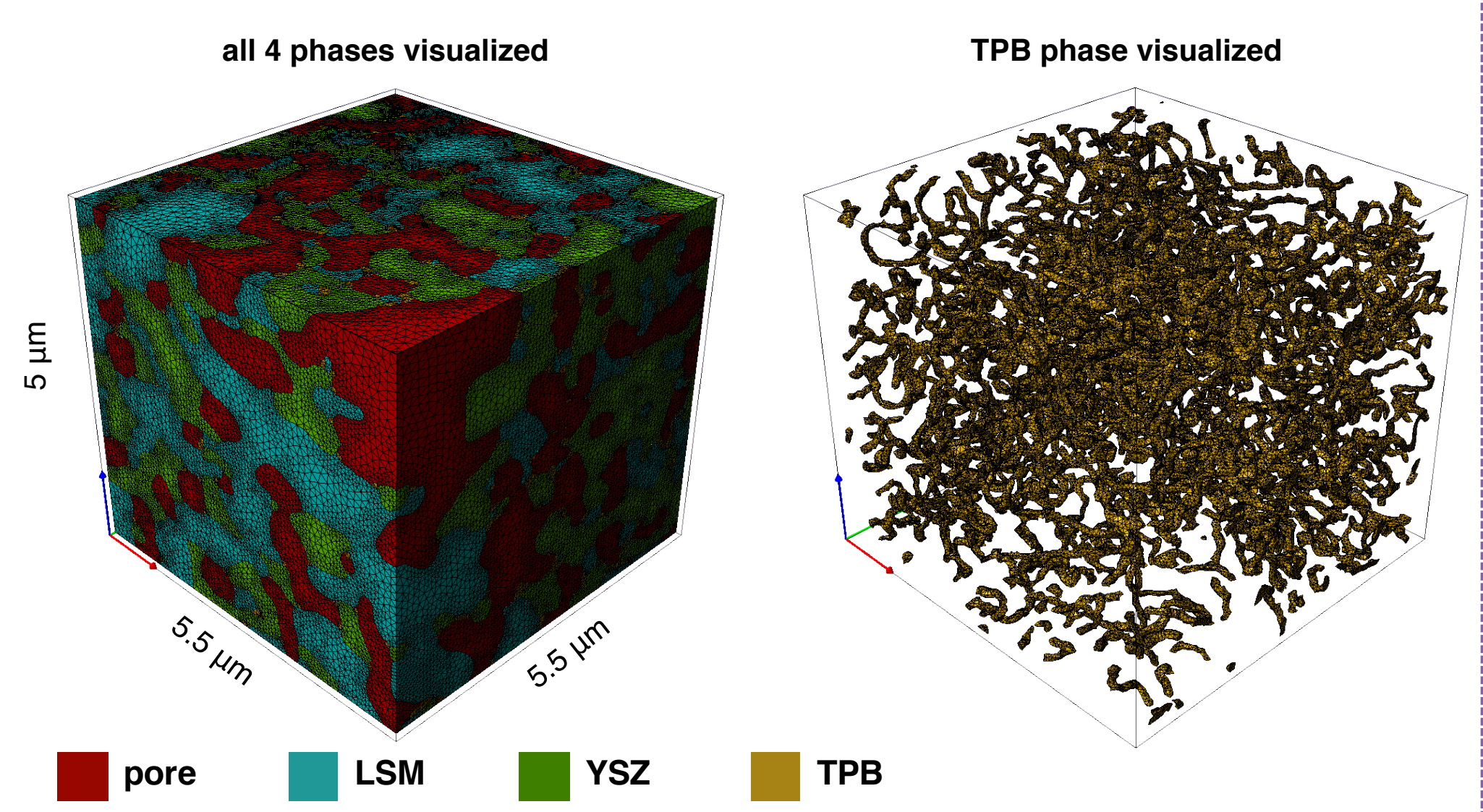


Schematic of TPB labeling algorithm example.
The algorithm operates on voxel-based image data.
All voxels at the TPBs are re-labeled as the TPB voxels.

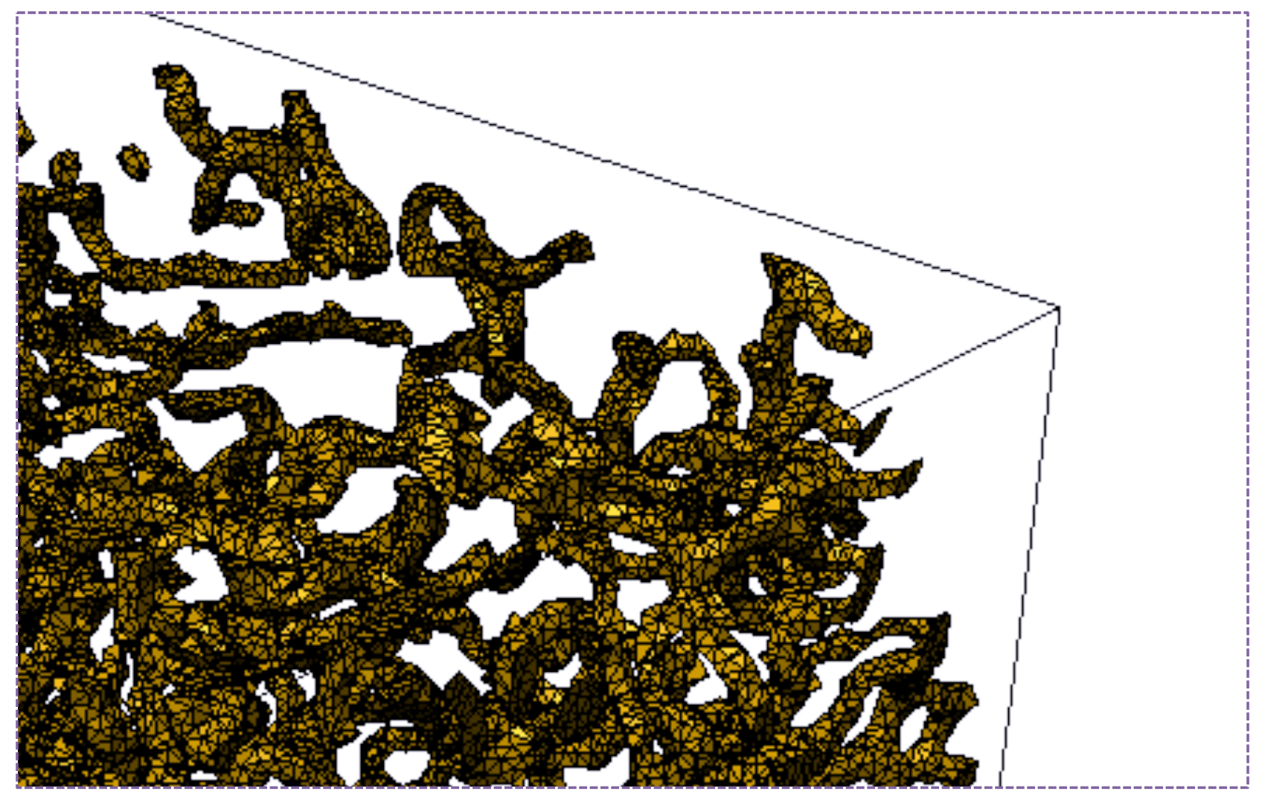


2D slice of a 3D cathode microstructure before (left) and after (right) volumetric TPB labeling is applied.

Mesh File



Meshed microstructure of the commercial cathode.
All phases are shown on the left. Only the TPB phase is shown on the right.



TPBs as Thin Volumetric Strings

TPB voxels are volumetrically meshed and volumetric reaction rates are solved in the numerical model.

Simpleware Meshing

- Simpleware ScanIP+FE 7.0 was used to mesh the the four-phase microstructure.
- Simpleware is a commercial package with proprietary algorithms capable of high-throughput scripting for many volumes.
- We used an unstructured mesh consisting of tetrahedral elements.
- The numbers of millions of tetrahedral elements for the 5^3 µm³ volume to the left :

Pore :	1.22	LSM :	0.99
YSZ :	0.87	TPB :	0.9

Mesh File

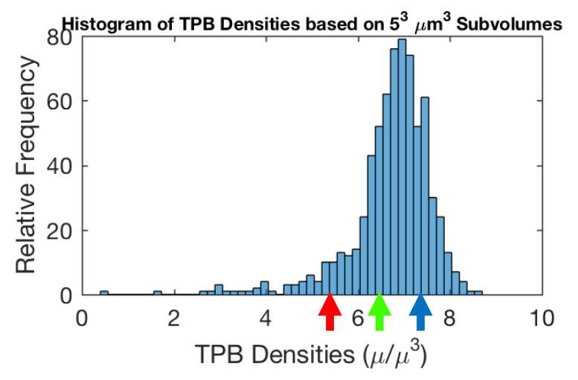
Result Visualization and Data Analysis

MOOSE Framework and Parallel Computation

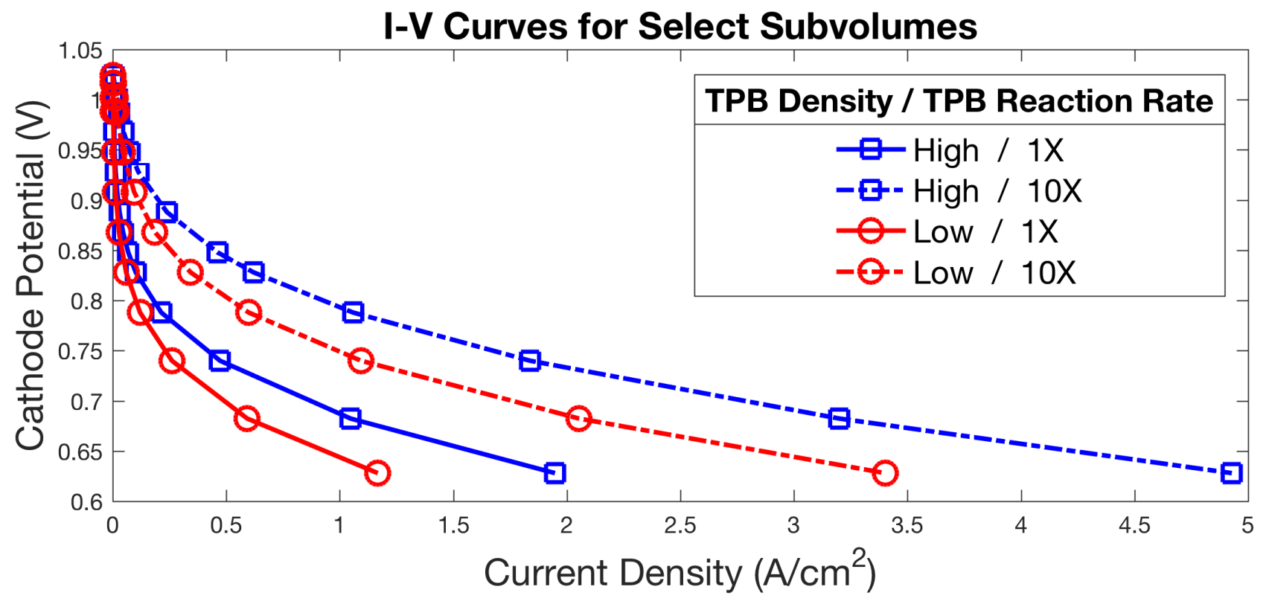
- Developed by Idaho National Laboratory
- An open-source C++ Finite Element framework
- Readily accepts the user defined mesh described above
- User-defined physics and large user network
- Modular nature allows specification on solver type, number of parallel cores, preconditioning type, etc…
- Built upon the libMesh and PETSc libraries that enable automatic parallel computation through Message Passing Interface (MPI) and multithreading
- Implemented and run on the Joule supercomputer at NETL

TPB Density: 7.45 µm^{-2}

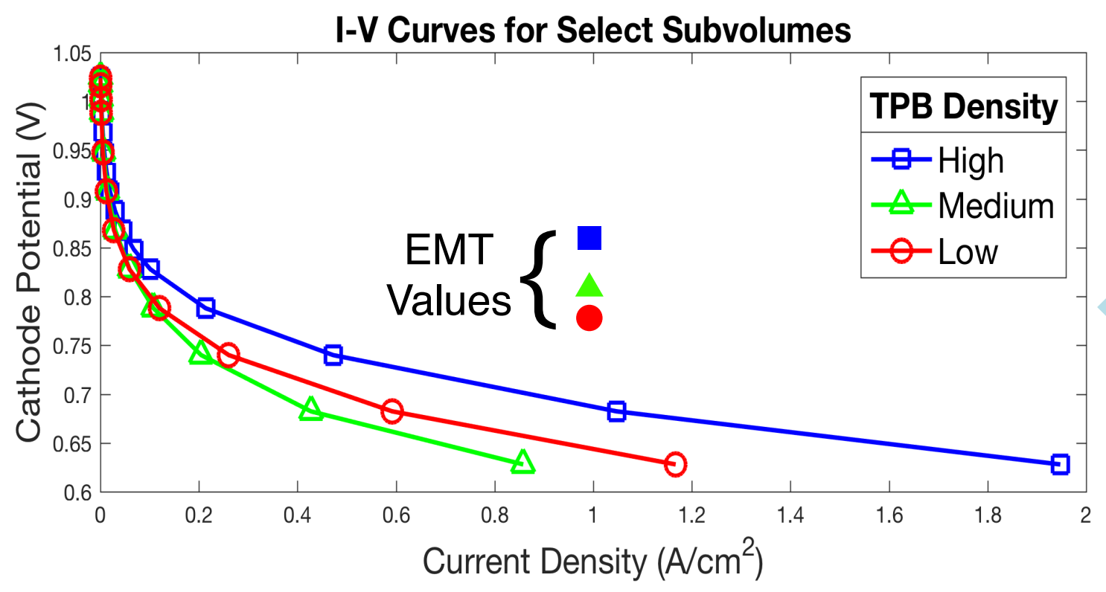
TPB Density: 5.36 µm^{-2}

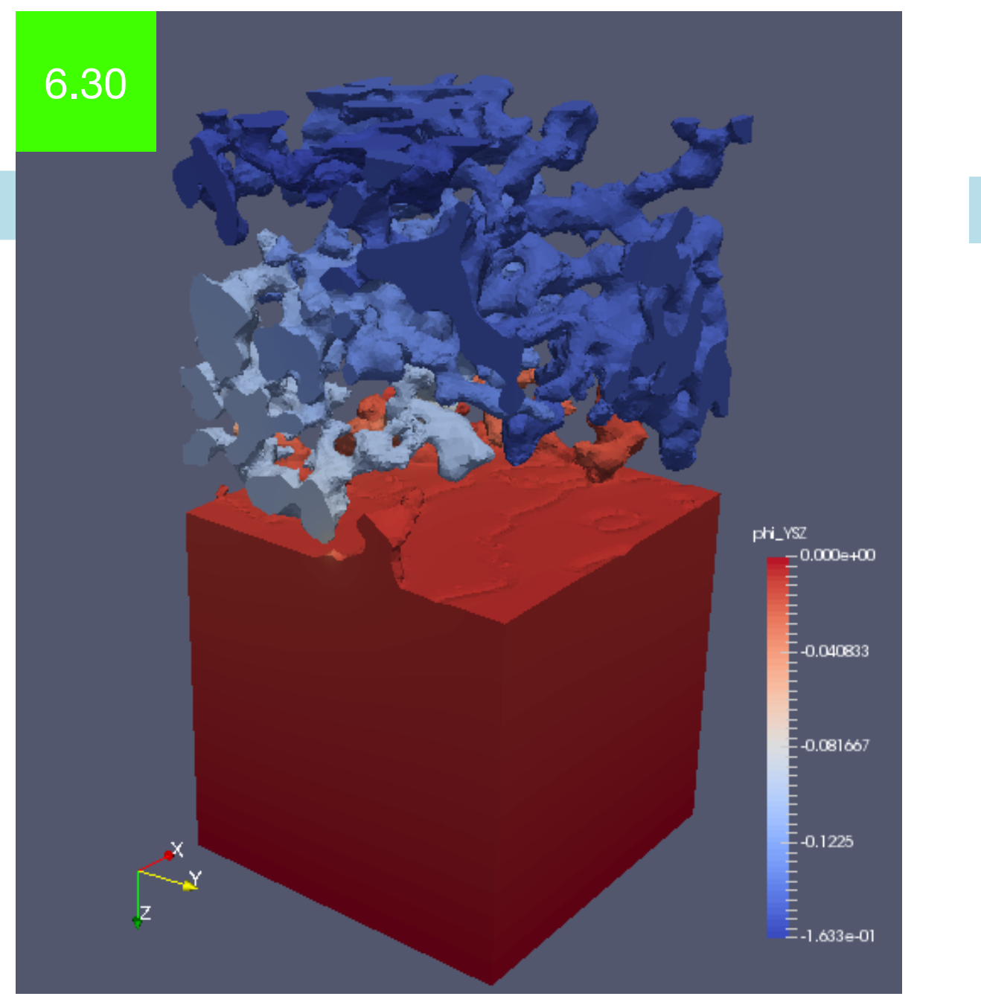


Two subvolumes (5^3 µm³ in size) with drastically different TPB densities based on the histogram (see above) are chosen for simulations.



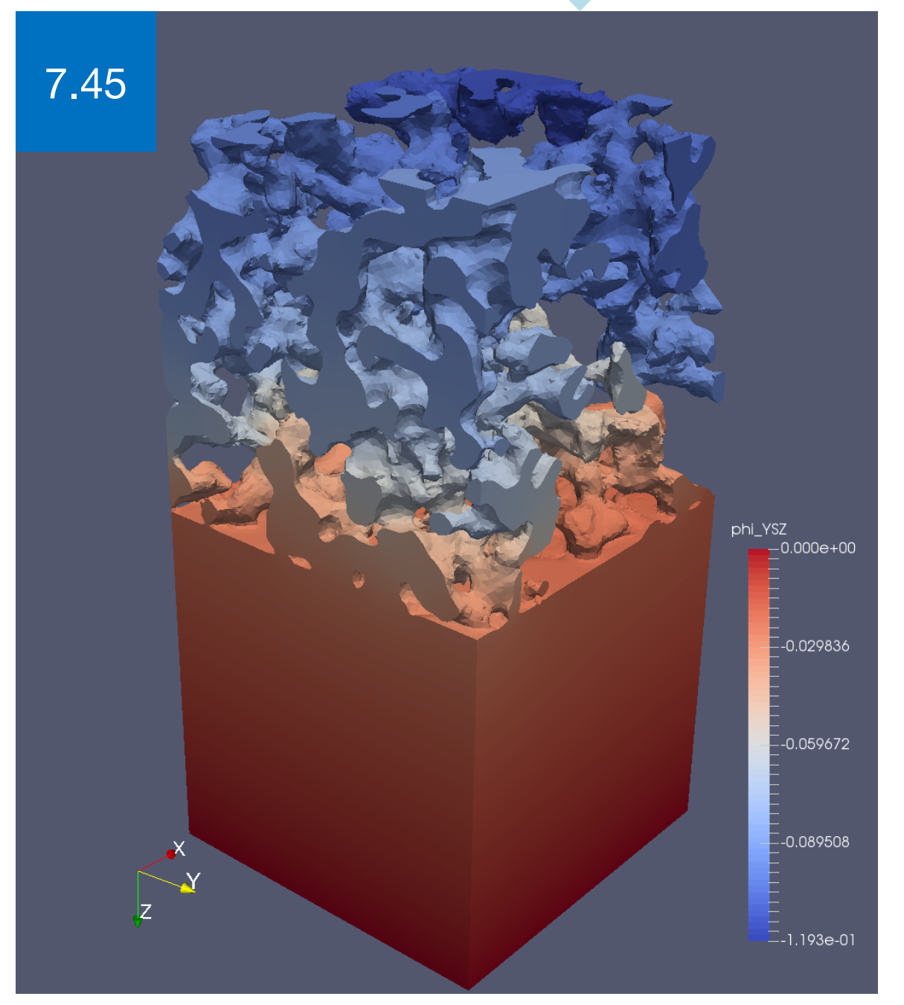
- Current-voltage plots are physical, within appropriate scale
- Higher TPB density leads to increased current density output
- Increasing TPB exchange reaction rate reduces activation overpotential



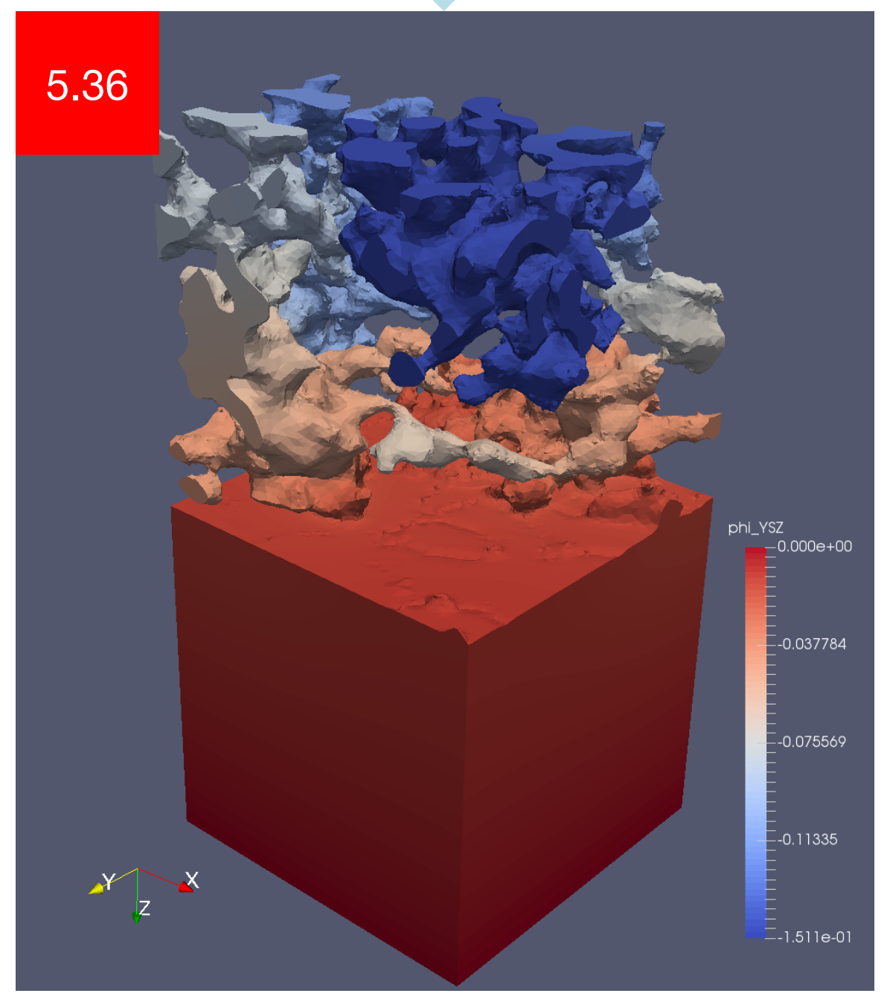


Bad YSZ Connectivity to Electrolyte

- This third subvolume has a medium TPB density.
- The current output for the medium TPB density is lower than for the low-TPB density, in contrast to EMT (see IV curve).
- 3D visualization indicates that this subvolume has the worst YSZ connectivity between cathode and electrolyte.



Uniform Microstructure



Heterogeneous Microstructure

3D visualization of the simulation results. Only the YSZ phase is shown. Color indicates electric potential. The visualization supports the I-V curve plot:

- It is revealed that the subvolume with the higher TPB density also appears to be more uniform
- The heterogeneous microstructure has less YSZ connectivity to the electrolyte

Conclusions

- **A microstructural-based electrochemical model simulates local TPB and MIEC pathways in experimental microstructures captured with morphology-preserving mesh**
- **TPB reactions is modeled as a source term in thin, string-like meshed volumes**
- **Implemented using parallel computation on Joule supercomputer**
- **Outputs physically appropriate results**
- **Model outputs vary from EMT values, indicating local heterogeneities (YSZ connectivity) are very important**

U.S. DEPARTMENT OF ENERGY

Science & Engineering To Power Our Future