Investigating SOFC Electrode Microstructures and Performance Degradation: A High Throughput Integrated Model

William K. Epting,[1,2] Jerry H. Mason,[1,2] Yinkai Lei,[1,2] Paul R. Ohodnicki,[1] Harry Abernathy,[1,2] Gregory Hackett[1]

[1] National Energy Technology Laboratory, 626 Cochrans Mill Road, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA
[2] Leidos Research Support Team, 626 Cochrans Mill Road, P.O. Box 10940, Pittsburgh, PA 15236-0940, USA
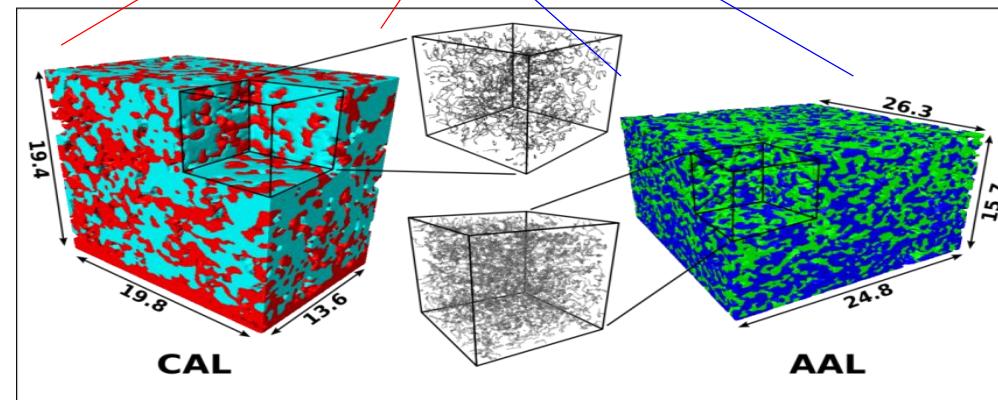
Month 31, 2016

Solutions for Today | Options for Tomorrow

U.S. DEPARTMENT OF ENERGY

Solid Oxide Fuel Cells

- **Electrochemical energy conversion**
  - Highly efficient (no Carnot limit)
  - CO_2 readily captured (no N_2)
  - Scaleable
- **Fuel-flexible – hydrogen, methane, syngas**
- **Main problem – degradation shortens cell lifetime, increasing cost**
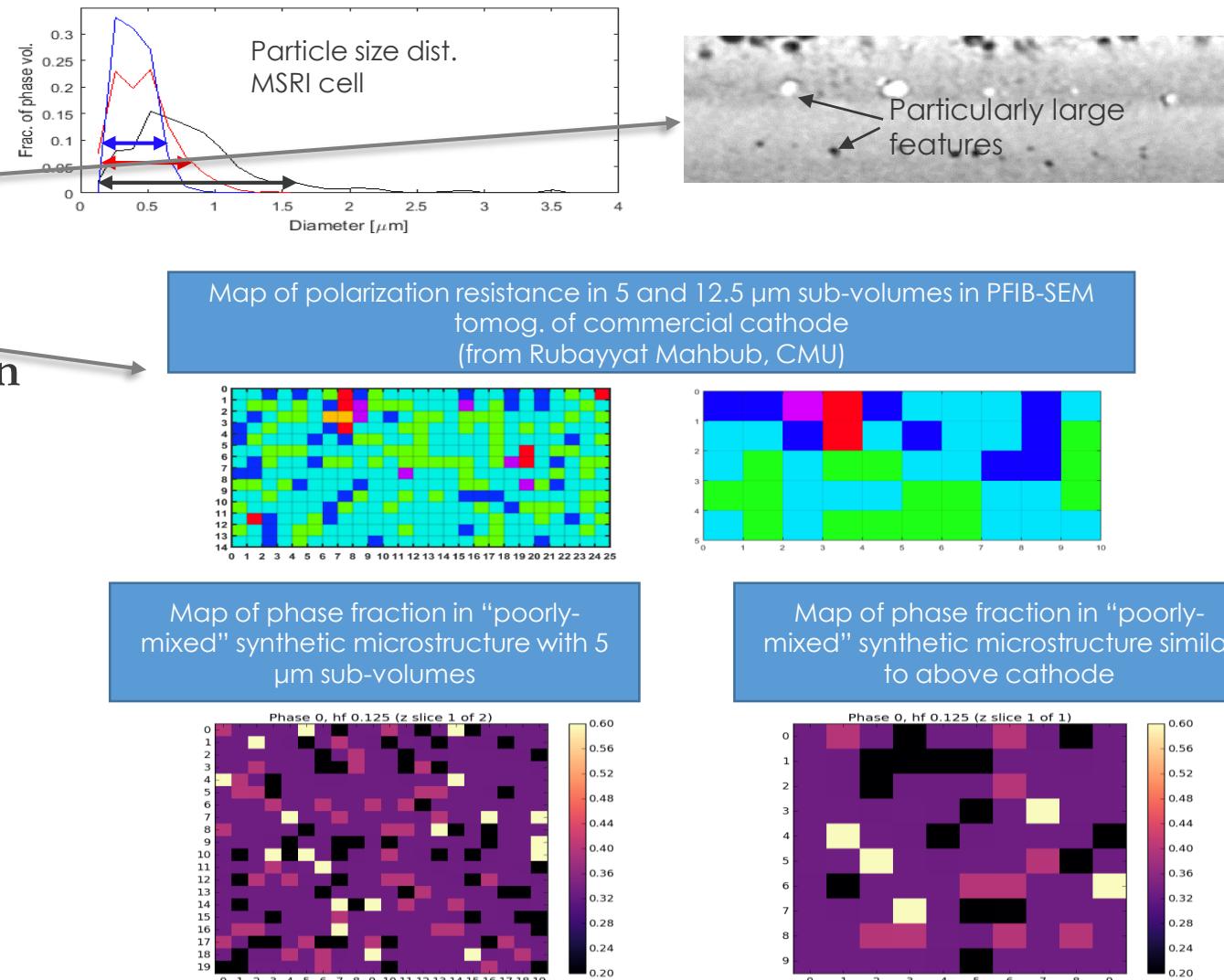- **Degradation strongly linked to microstructural changes, and probably to initial microstructure**
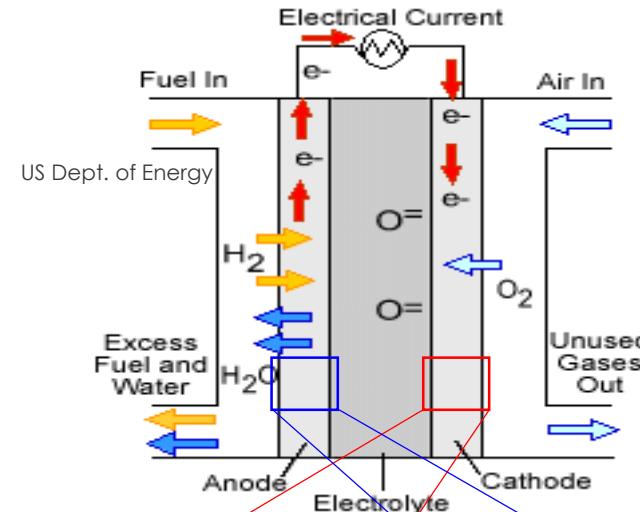
Each electrode's active layer is a **porous cermet composite (3 phases)** where different phases facilitate ion, electron, and gas transport.

The intersection of the 3 phases – **T**riple **P**hase **B**oundaries - is important for facilitating the reaction

Epting et al., JACerS v100 no. 5 (2017)

Microstructural Heterogeneity

- **Fuel cells can have highly heterogeneous microstructures**
  - Wide particle size distributions
  - Outlier particles/pores
  - Poor mixing

- **Heterogeneity itself may impact electrochemical performance and degradation rate**
  - Dead spots / hot spots
  - High local gradients or overpotentials

- **If we quantify this impact, it would be valuable advice to manufacturers**
  - "Sloppy" microstructure is fine if it's cheaper and delivers similar performance
  - But if it leads to unanticipated faster degradation, not so fine
  - Which corners can be safely cut?

Particle size dist. MSRI cell

Particularly large features

Map of polarization resistance in 5 and 12.5 μm sub-volumes in PFIB-SEM tomog. of commercial cathode (from Rubayyat Mahbub, CMU)

Map of phase fraction in "poorly-mixed" synthetic microstructure with 5 μm sub-volumes

Map of phase fraction in "poorly-mixed" synthetic microstructure similar to above cathode

- Six synthetic microstructures of various mixedness modeled using microstructurally resolved Fortran multiphysics model

- Other than good/poor mixing, all other properties globally identical

- Preliminary results show significantly different performance vs. extent of poor mixing, despite identical global average microstructural values

Total cathode overpotential for cathode-comparable synthetic microstructures with poor mixing, L_{block}=12.5 μm, σ=0.6
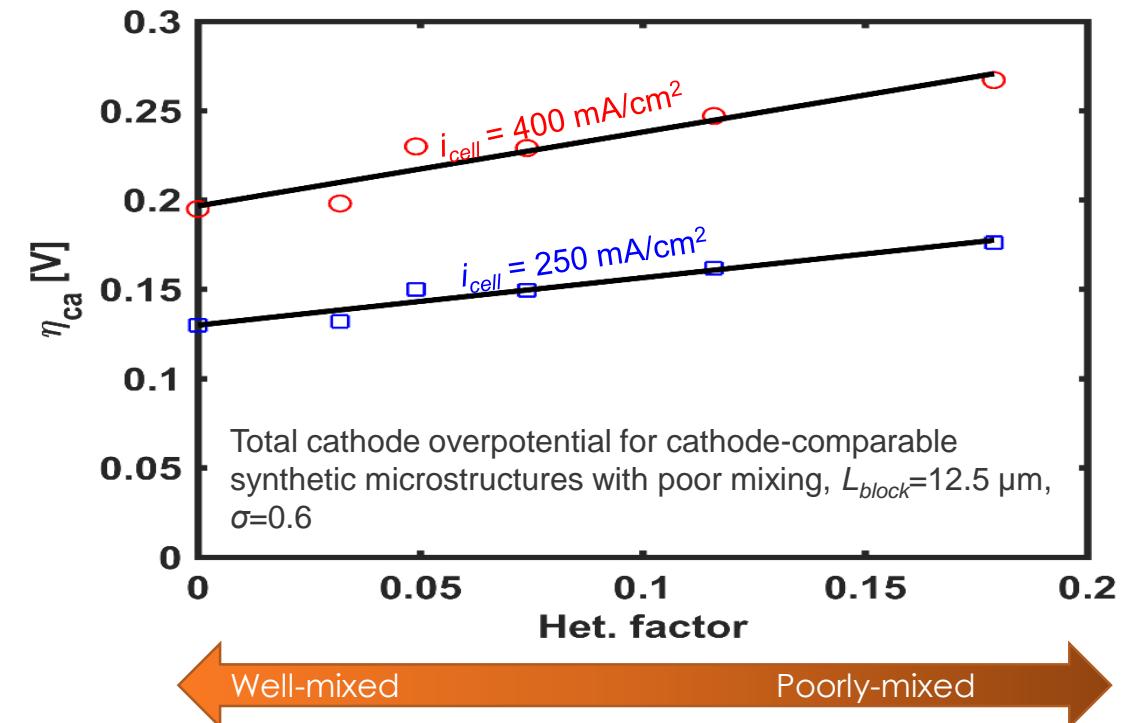
Multiphys. modelling by Dr. Hunter Mason

Degradation vs Initial Microstructure

- **Phase field model from Dr. Yinkai Lei simulates Ni/LSM particle growth***

- **Rate of Ni/LSM coarsening depends on initial microstructure**
  - Volume fractions, initial particle sizes have largest impact
  - Particle size distribution width has weaker impact

- **Some of this also suggested by experiment****
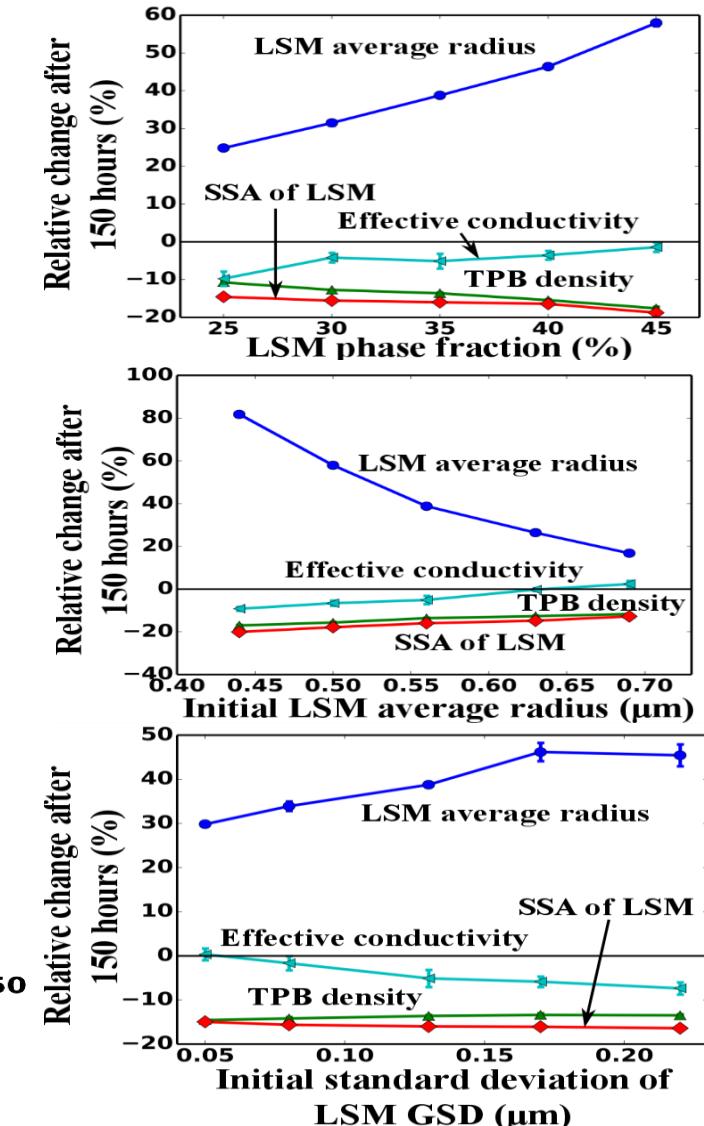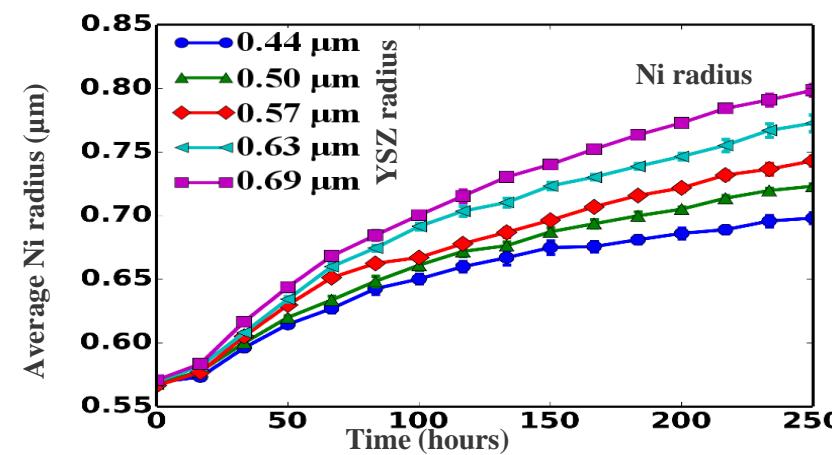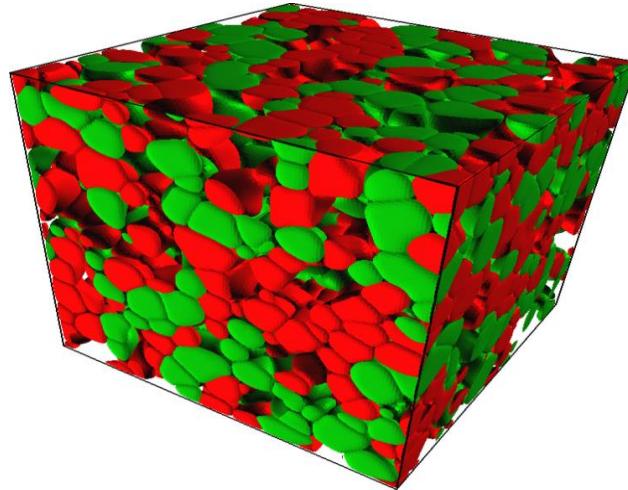
* Yinkai Lei *et al.*, J. Power Sources, 345 (2017) 275-289
**Chen-Wiegart *et al*, J. Power Sources, 307 (2016) 604-612
   Abdeljawad *et al*, J. Power Sources, 250 (2014) 319-331
   Lei *et al*, J. Electrochem. Soc., 164 (2017) F3073-F3082

Coarsening, Microstructure, and Multiphysics

Goal: model coarsening, microstructure, and cell performance over lifetime of a cell in a linked, unattended model

Why?
To predict performance degradation for a large parameter space of initial microstructures as well as real, measured cells

Microstructural analysis extracts performance-relevant properties

Multiphysics model predicts cell performance from microstructural properties

Coarsening model predicts microstructure after operation
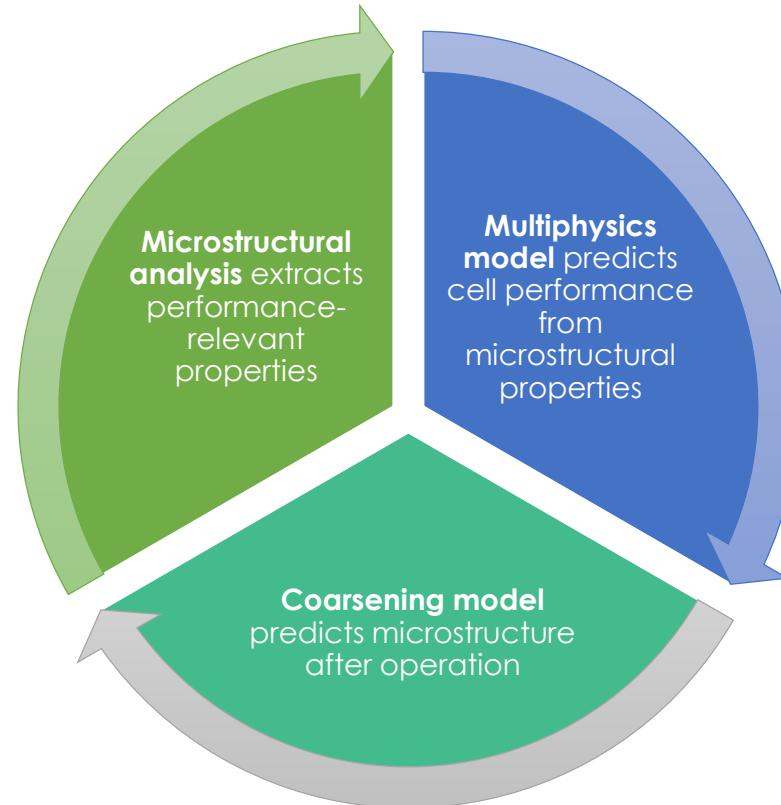
Some degradation methods are impacted by local overpotential, local temperature, etc

Integrated Degradation Model
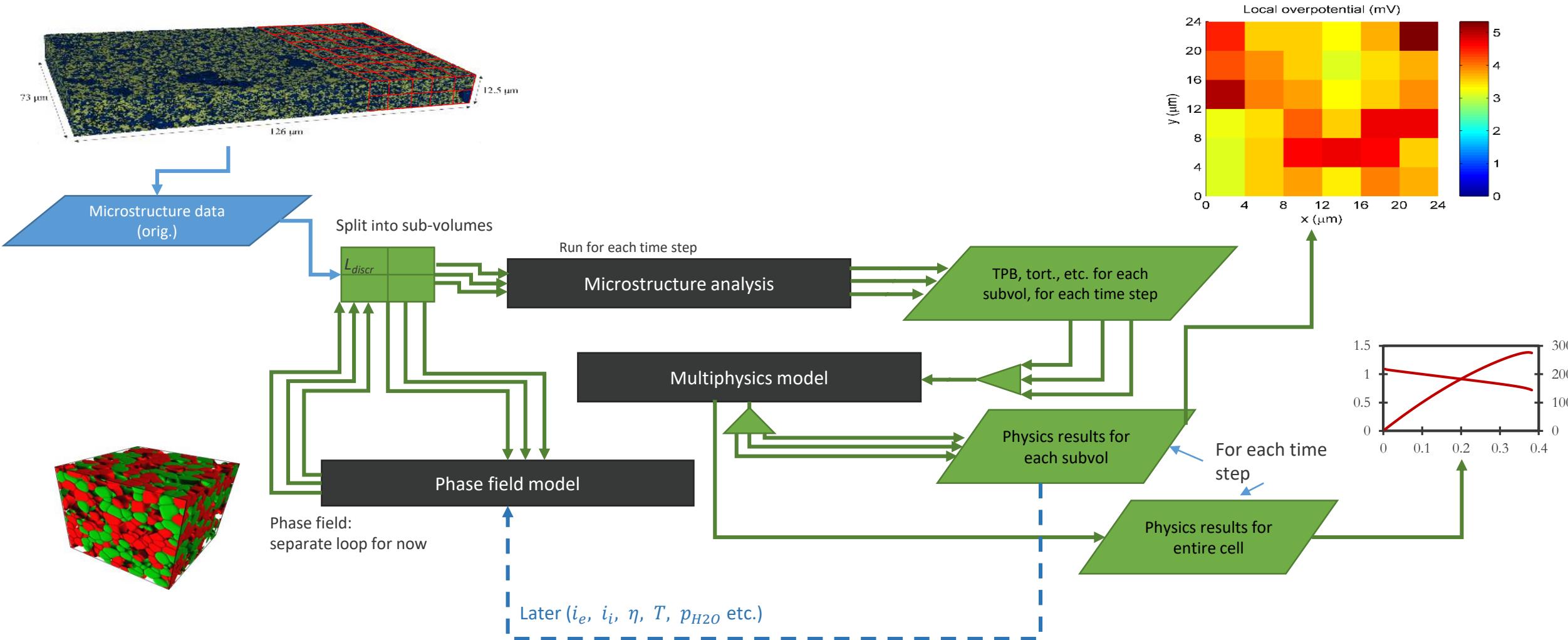
Overview of Microstructural Analysis
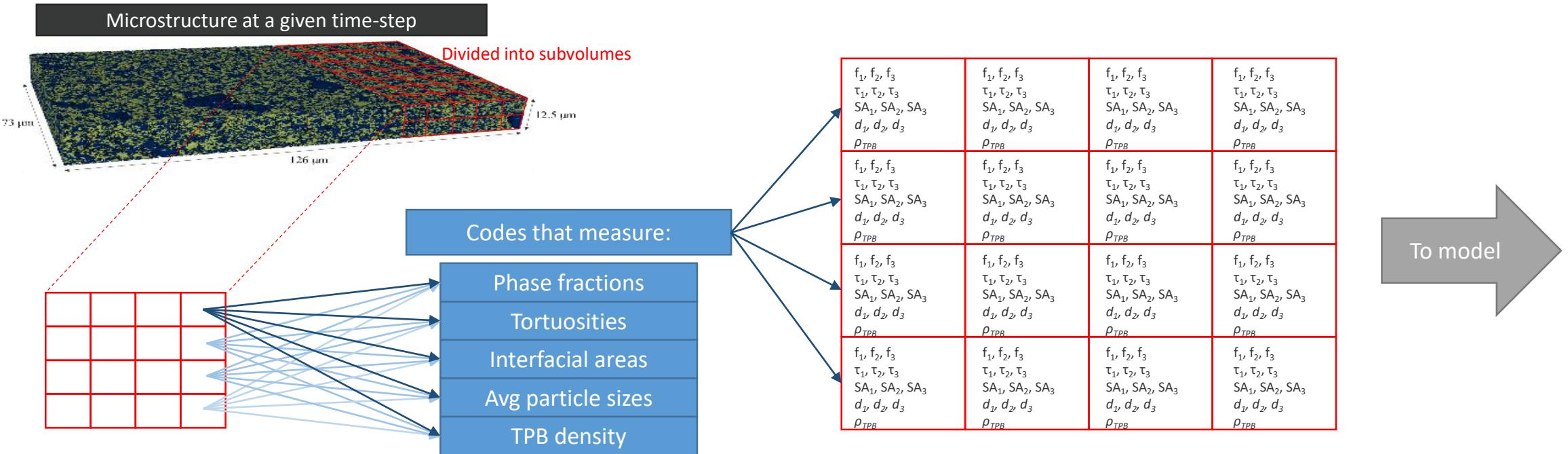
Components of Microstructural Analysis

Tortuosity (each phase) by geometric definition

Interfacial areas (each phase pair) by smoothed mesh
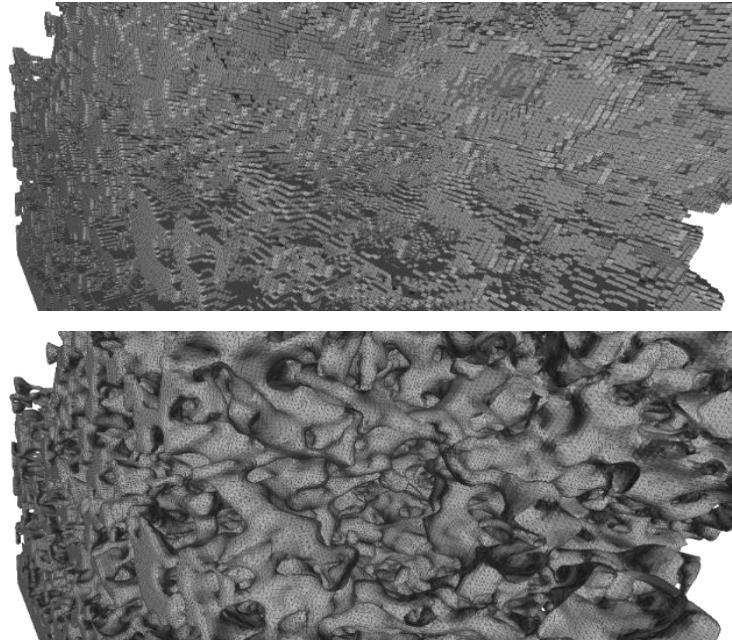
Avg particle/pore size (each phase) by inscribed sphere method

$$\tau_i = \frac{L_{act}}{L_{ideal}} = \frac{4.6}{2.3} = 2$$

$$\tau_{tot} = avg(\tau)$$

Spheres of increasing size are fit within features

R=1

R=2

Local "radius" value overwritten if larger sphere fits
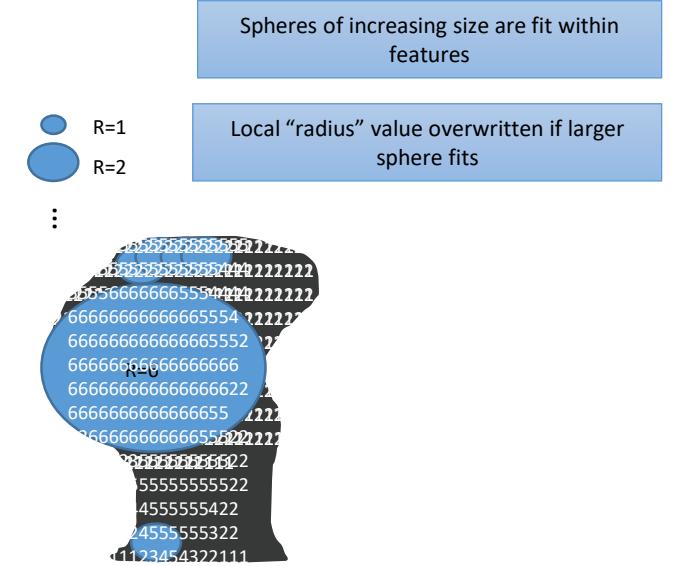
Components of Microstructural Analysis

TPB density

TPB vertices

TPB line segments

Smoothing: Each path is upsampled and smoothed based on a 3D Gaussian kernel with σ = voxel length

Smoothing is necessary to prevent over-estimation due to voxelated (i.e. cubic) nature of data

YSZ

LSM

YSZ

L = 10 (apparent)

L = 7.1 (actual)
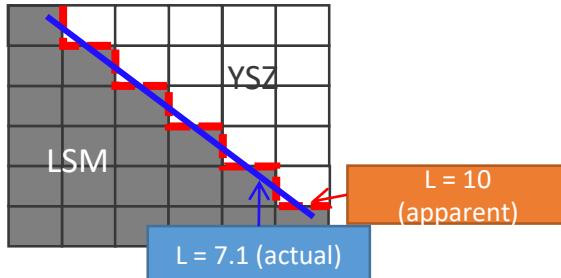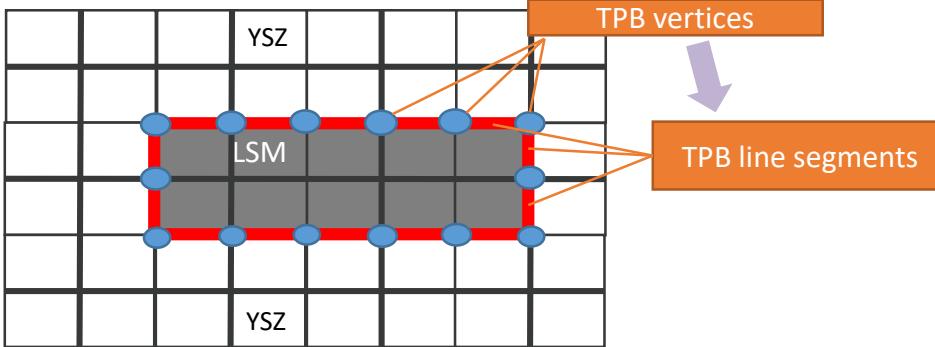
(Suppose there's a large void on the next layer out of the screen, so LSM/YSZ borders are TPBs)
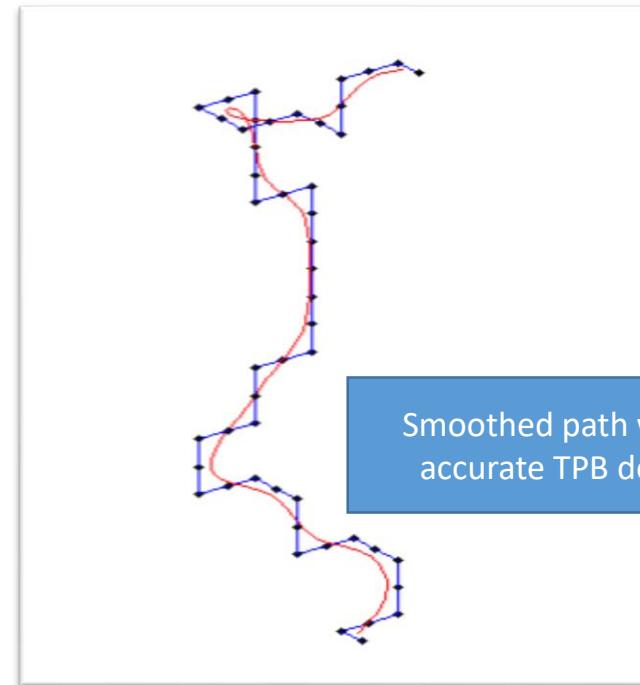
Smoothed path will yield accurate TPB densities

Accuracy validated with model systems
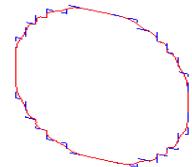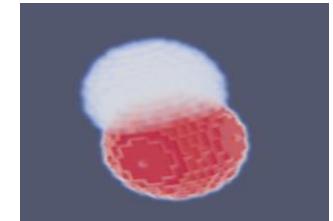
Initial Microstructure Inputs
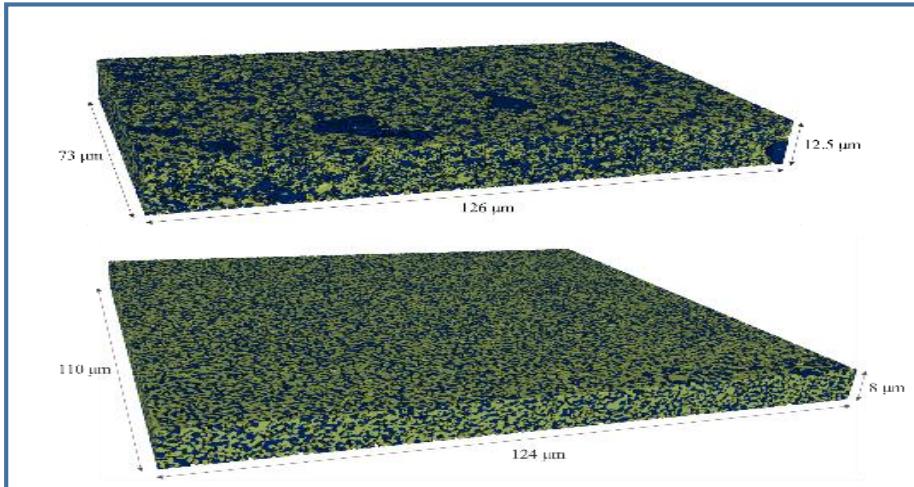
Experimentally imaged microstructures

- Directly relevant to applications
- Compare to experiments
- Predict how a particular cell might degrade, and how it might be improved
  - More useful with baseline for comparison!
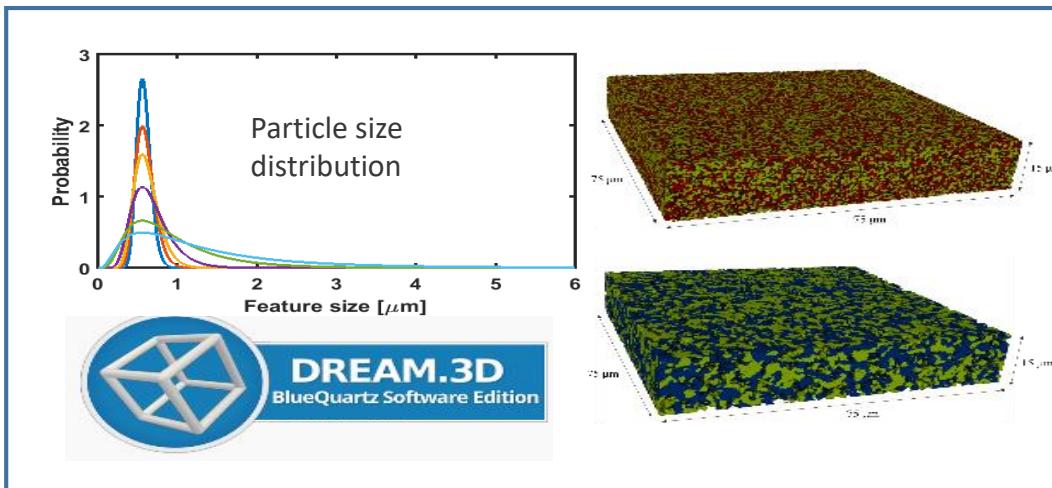
Generate Synthetic Microstructures

- Can deliberately explore a span of nearly any parameter
- Faster/easier than imaging thousands of real cells, which take days to prep & image
- Map out parameter spaces and use as baseline for real systems

Results from Real Microstructures

T. Hsu et al., JPS 386 pg. 1 (2018)
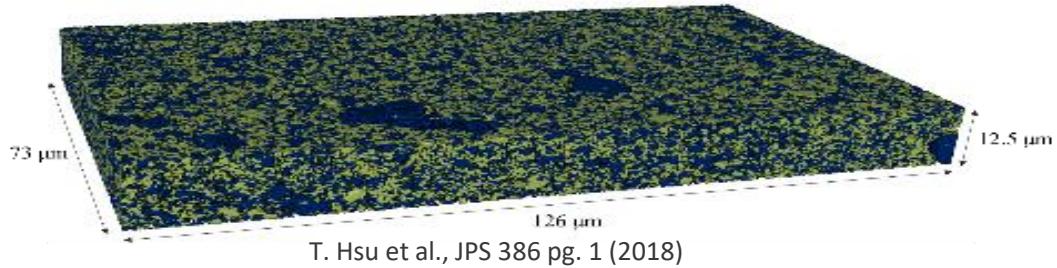
MSRI Cathode (real microstructure)
- Imaged at CMU by PFIB-SEM
- Segmented and run through integrated degradation model

Cell potential at 0.25 A/cm2 (performance at 800°C)

Legend: 800°C, 900°C, 1000°C

Y-axis: Cell Potential (V), X-axis: Time (hrs)
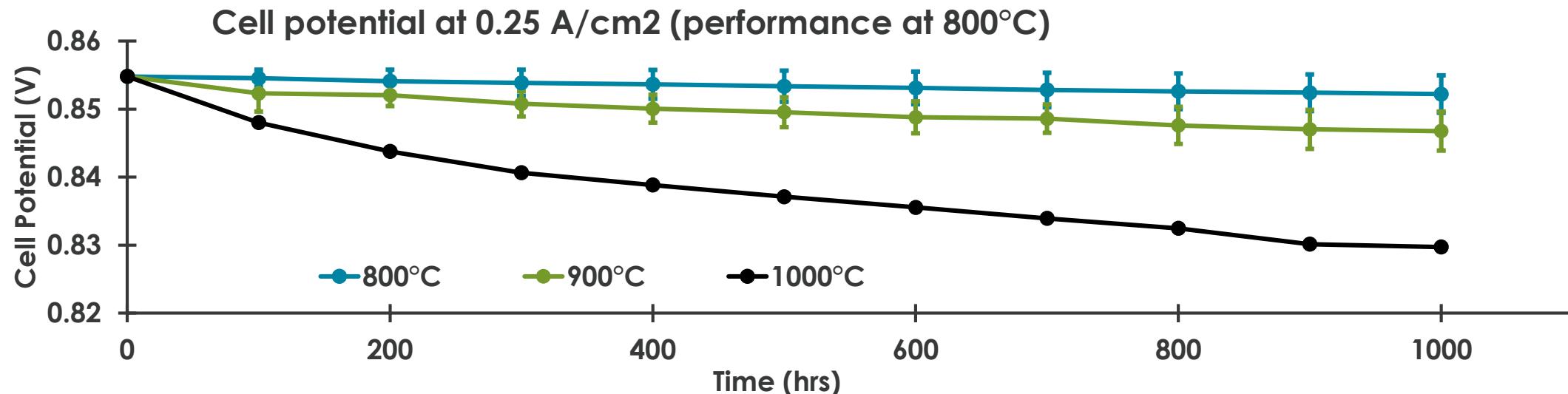
Synthetic Microstructures: Exploring Parameter Space

Phase fraction
- Hold porosity at 0.33 (little effect)
- Vary YSZ/LSM 0.23, 0.28, 0.33, 0.38, 0.45

Avg particle diam
- 300, 400, 500, 600, 700 nm for all 3 phases

Stdev of part. size dist.
- YSZ: 0.15, 0.3, 0.6
- LSM/Ni/Pore: 0.3, 0.6

Mixedness
- Stdev of 0, 0.05, 0.1 among subvolume phase fractions

Total of 45,000 unique microstructures

Largest and broadest bank of fuel cell electrode microstructures ever?

Dream.3D can be made to work on supercomputing systems (command-line only).

A similar automation paradigm was used as shown previously, together with simple parallelization, to quickly generate thousands of microstructures on a cluster

Phase reassignment (swapping phase IDs) can be used to reduce actual number of microstructures to be generated and stored.

These have been generated using *Joule* supercomputer

Input vs Output Comparison

Using high-throughput microstructure analysis code, with correct voxel size

Shown: distributions in input vs. output property in
2,400 (6.25 μm)^3 microstructures
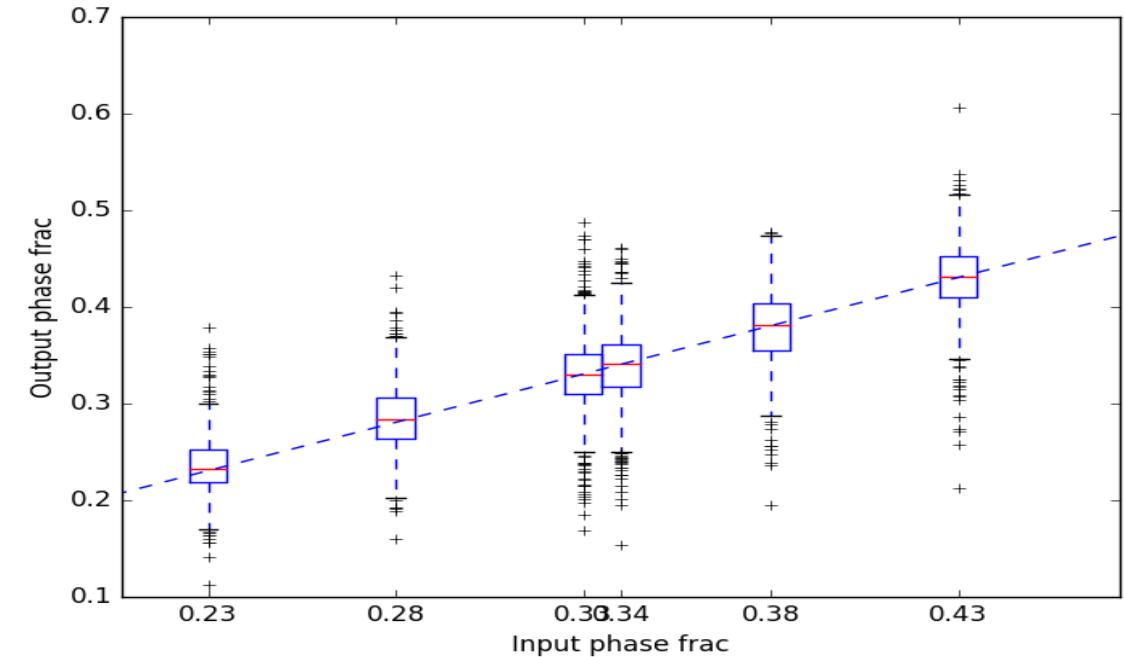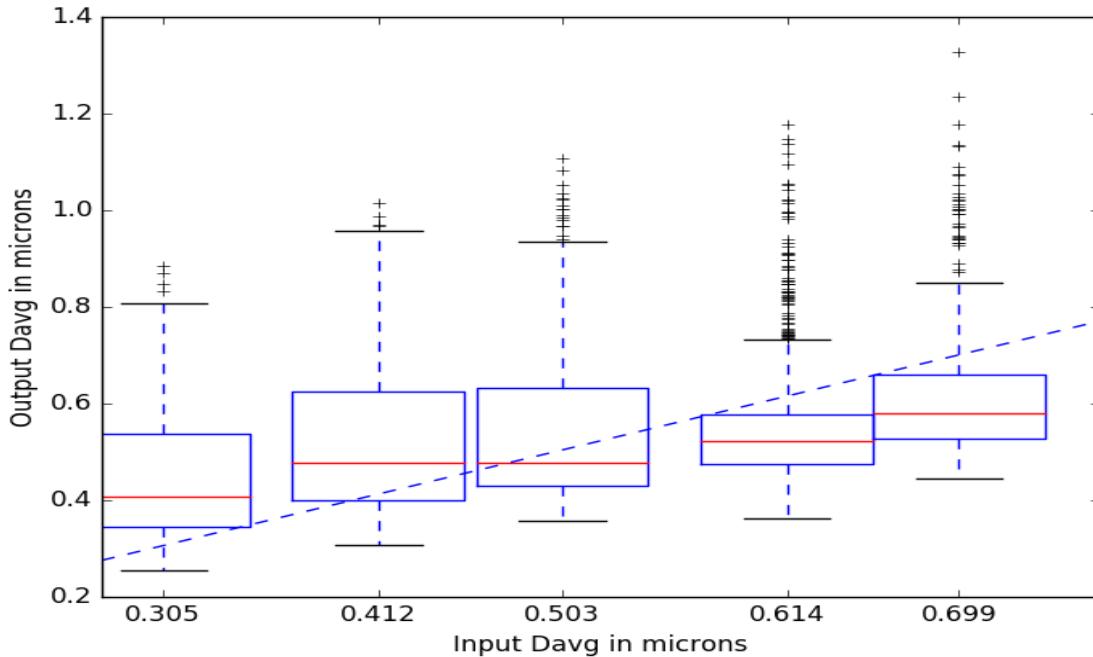
Reduced set of microstructures

Initial testing run on 96 initial cathode microstructures spanning expected high-impact parameters

Phase fraction

- Hold LSM/Ni at 0.33 (little effect)
- Vary YSZ/porosity 0.23, 0.28, 0.33, 0.38, 0.45

Avg particle diam

- LSM only: 400, 500, 600500 nm for all 3 phases
- 500 nm for pore, YSZ

Stdev of part. Size dist.

- Pore: 0.3
- LSM: 0.15, 0.3, 0.6
- YSZ: 0.15, 0.3, 0.6

Mixedness

- Not studied in this initial batch

Evolution of Properties in Time

Example system: MSRI LSM/YSZ cathode, 0 hrs (actual) to 1,000 hrs (simulated)
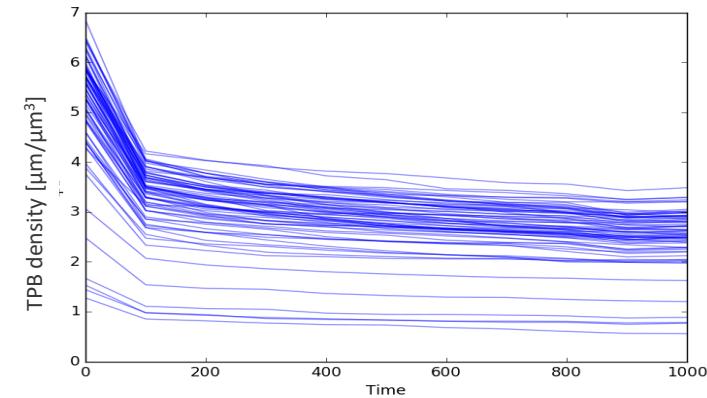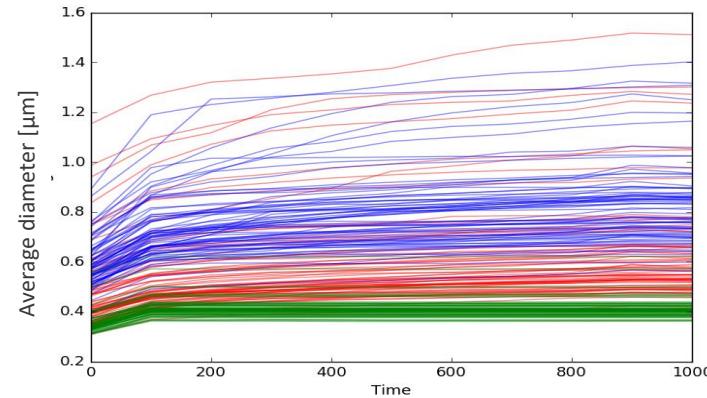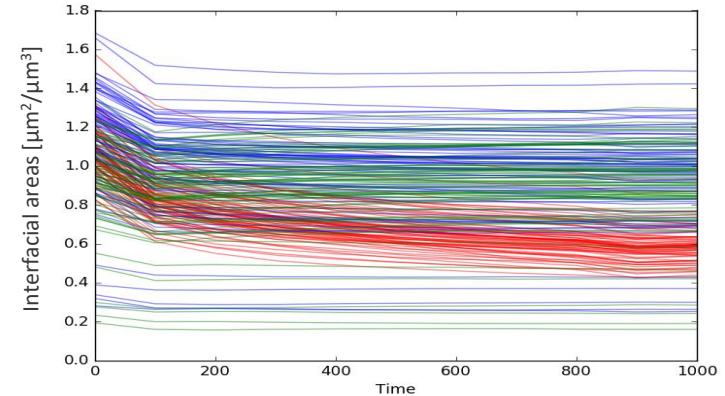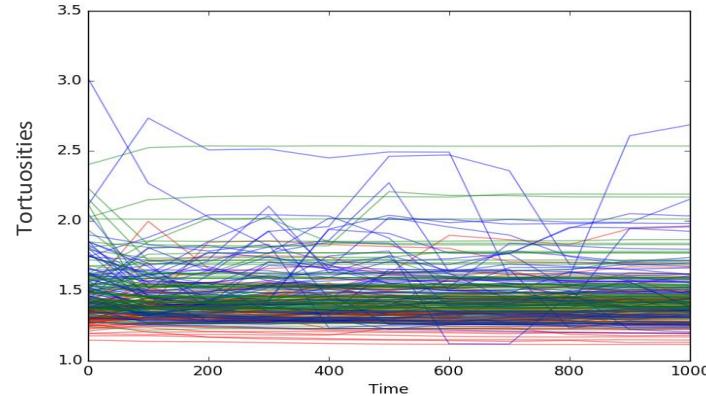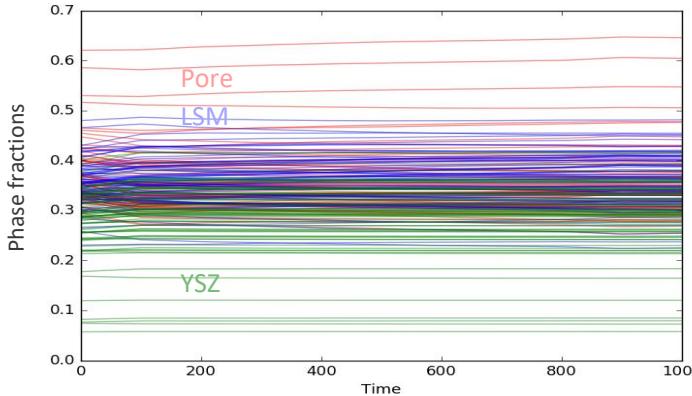
Results: Polarization Curves Over Time

One random selection of initial microstructure

pf34-38-28_Davg500-500-500_sigma0.3-0.3-0.3_hf0_ca T = 900 C

Legend: 0h, 100h, 200h, 300h, 400h, 500h, 600h, 700h, 800h, 900h, 1000h

η_C [V] vs i [A/cm^2]

Voltage Decay at Given Current

pf34-38-28_Davg500-500-500_sigma0.3-0.3-0.3_hf0_ca : V_cell at i = 0.4 A/cm^2

Voltage Decay at Given Current

pf34-38-28_Davg500-500-500_sigma0.3-0.15-0.6_hf0_ca : V_cell at $i = 0.4\ A/cm^2$
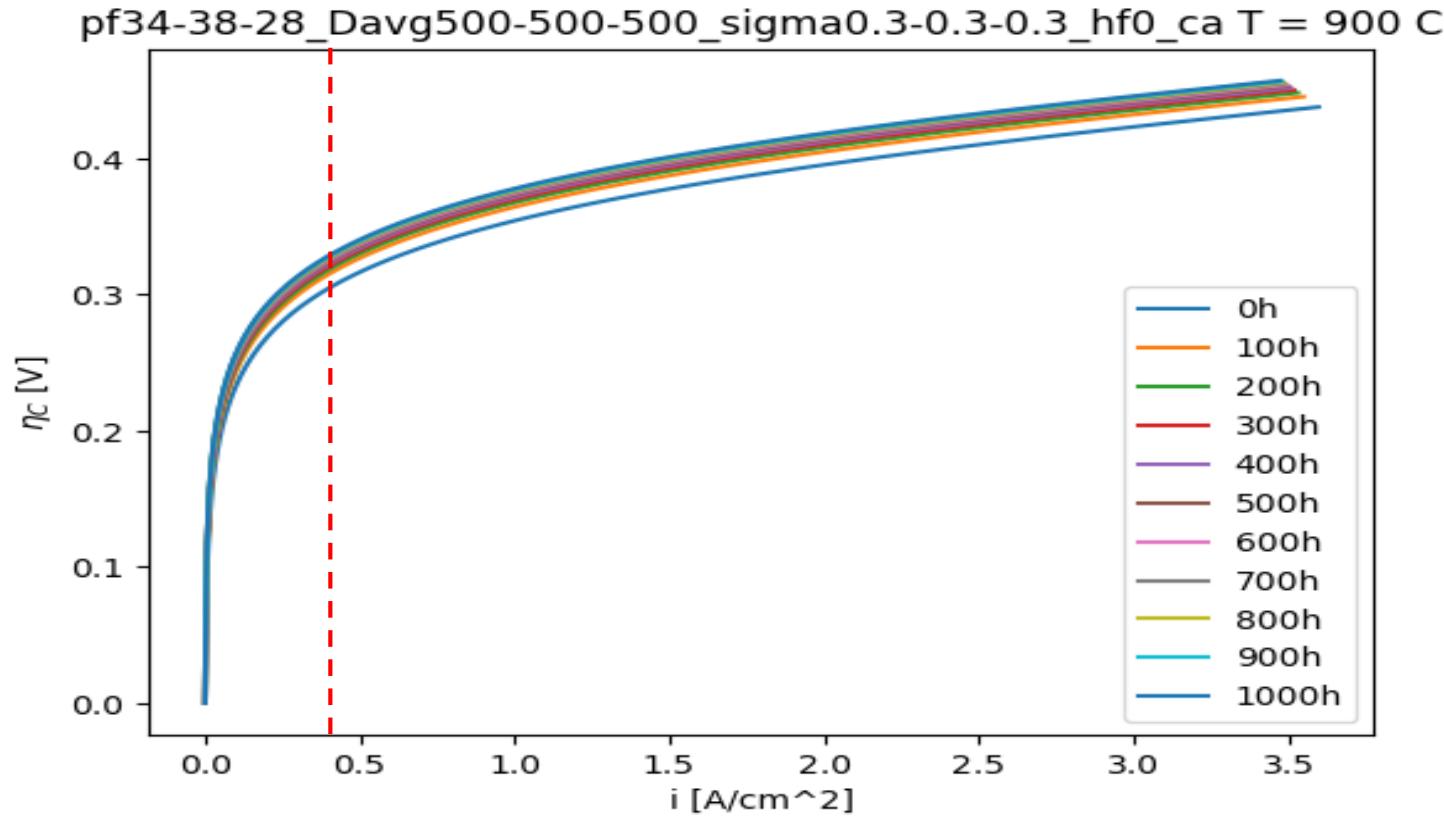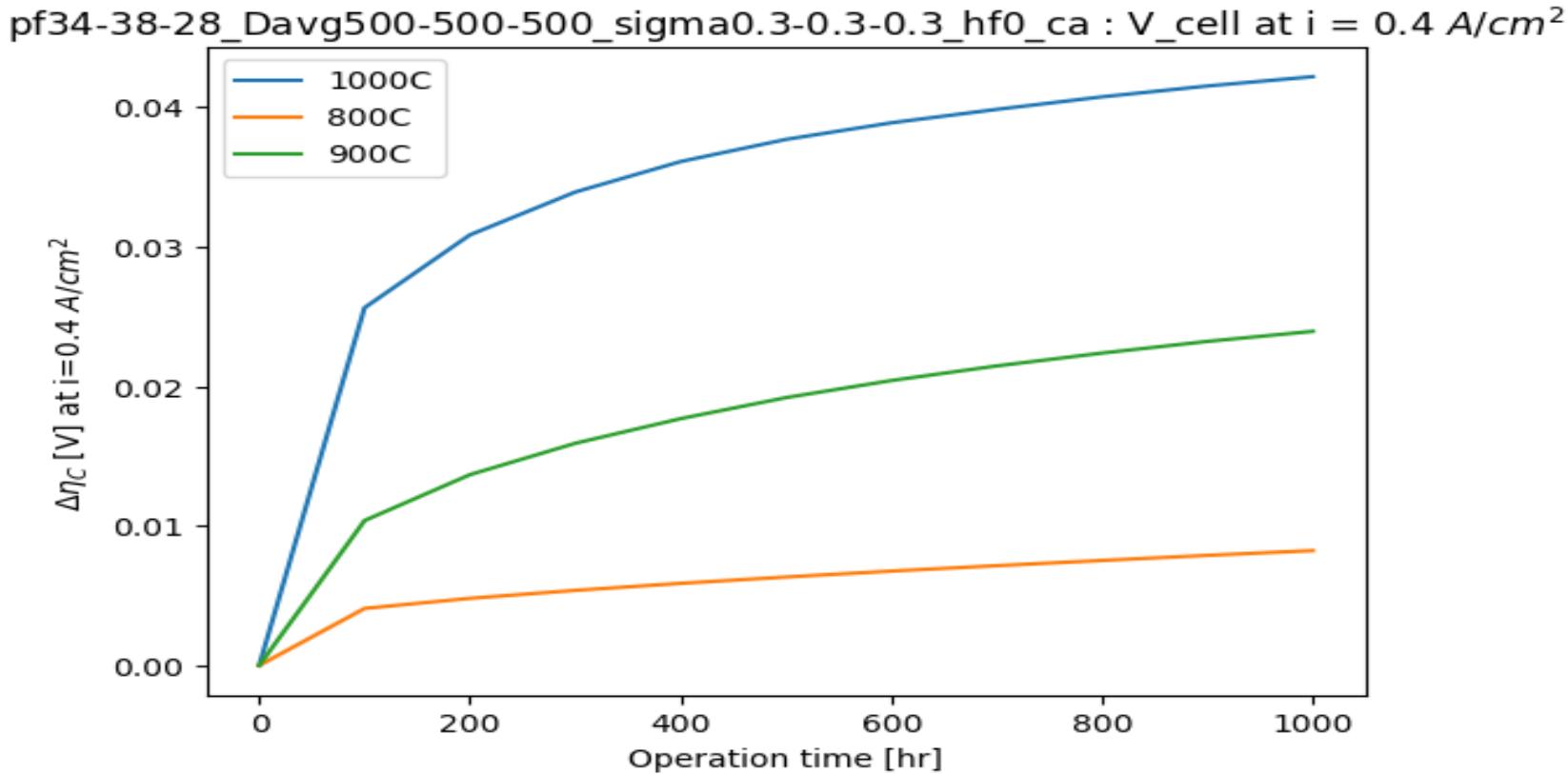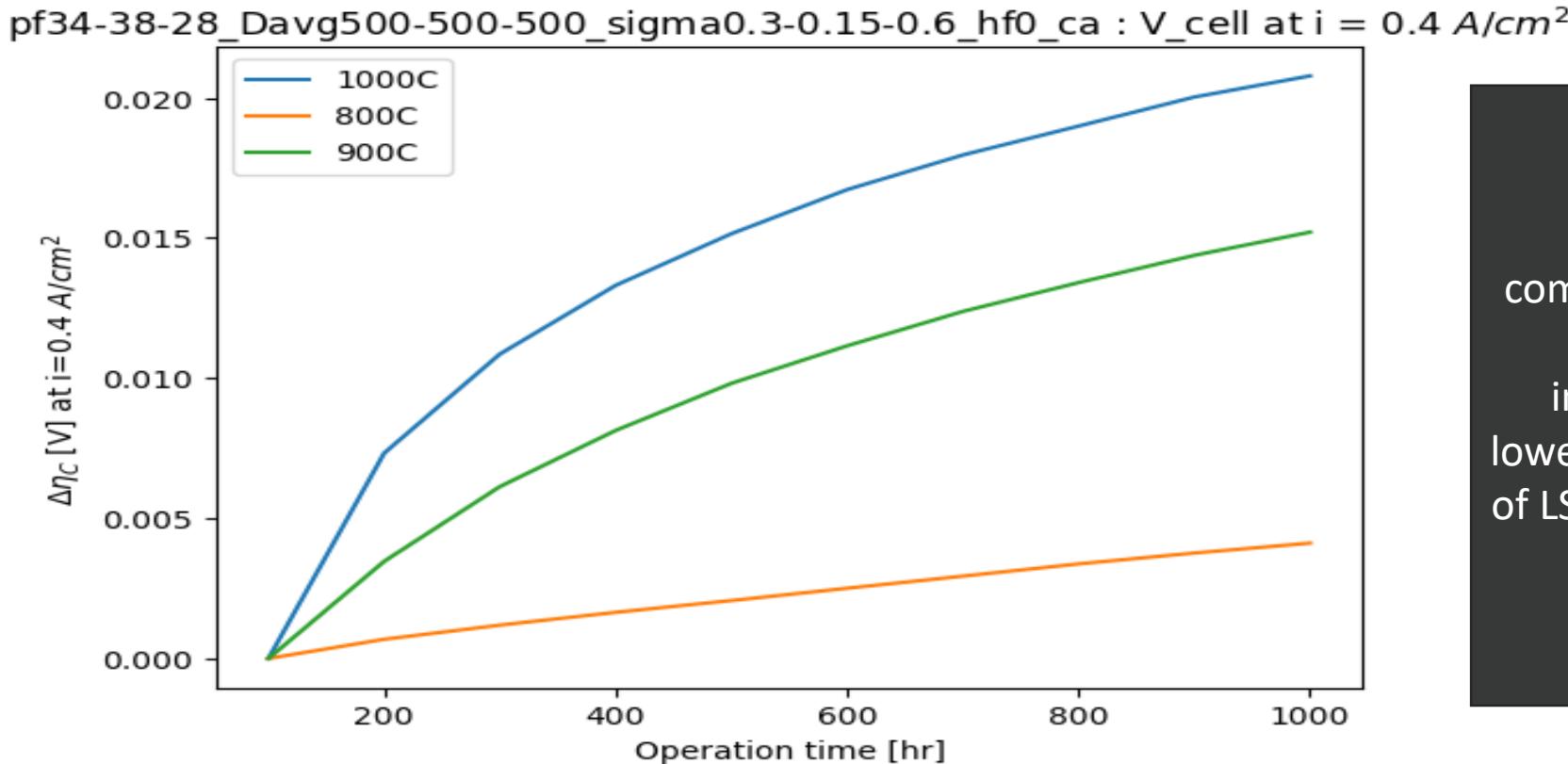
In this 1-to-1 comparison, we see a significant improvement by lowering polydispersity of LSM and raising that of YSZ

Spatial Variation During Degradation
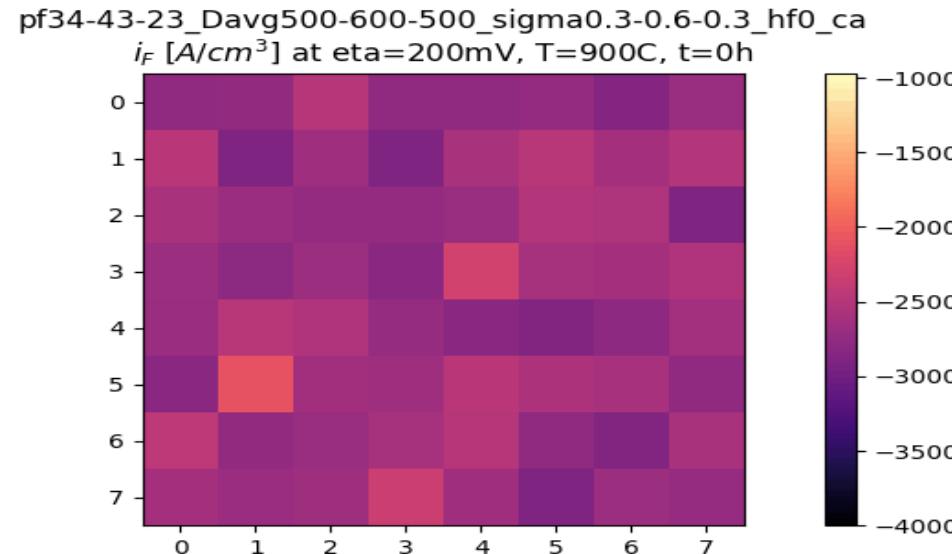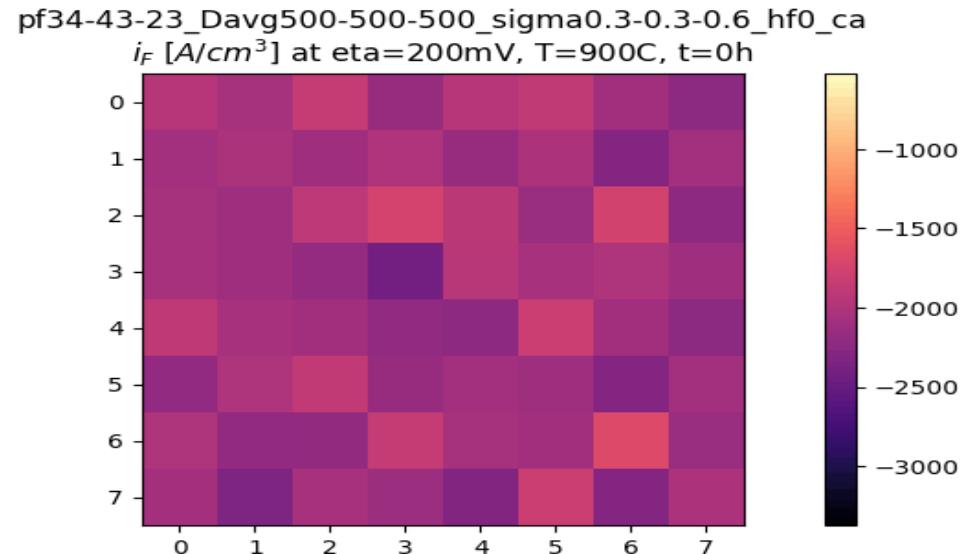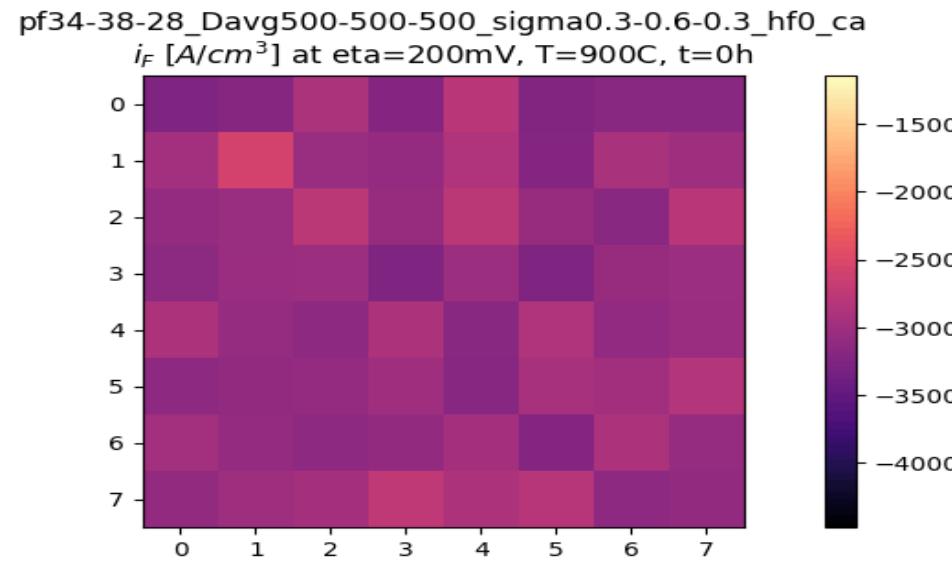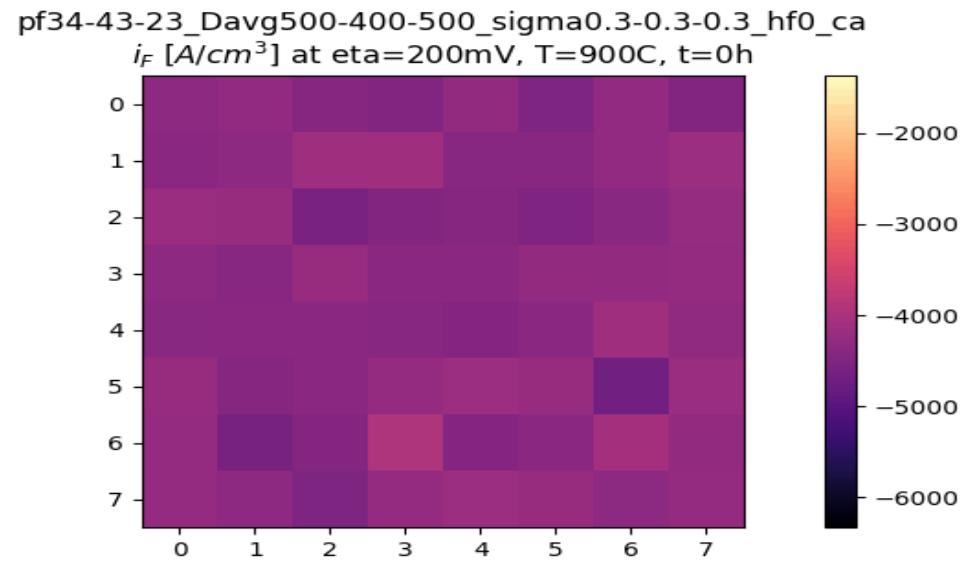
Final Decay Ranked by Initial Electrode
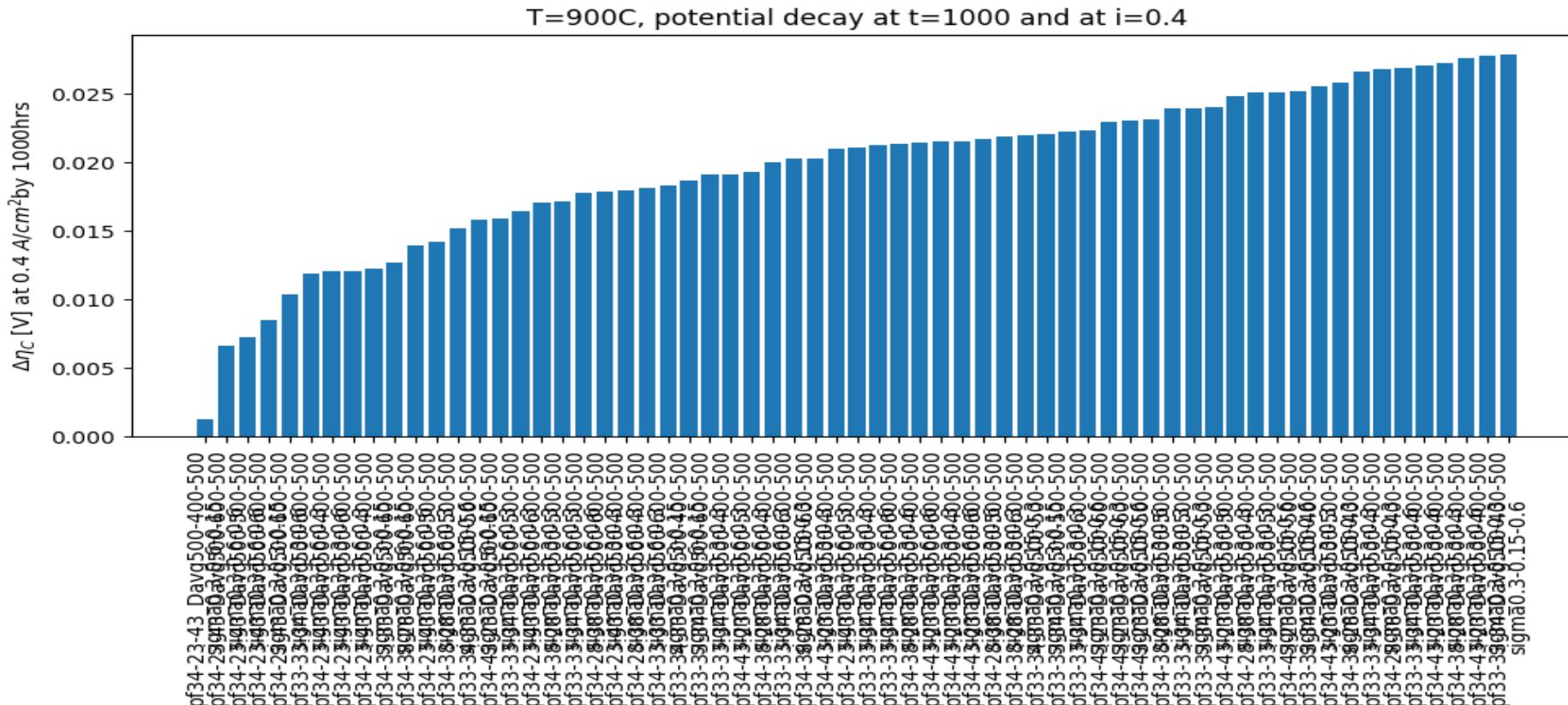
Note that on y-axis, lower is better
However, these plots do not capture whether *initial* performance was good or bad

Decay vs Average LSM Particle Size

Nominal diameter

T=900C, potential decay at t=1000 and at i=0.4
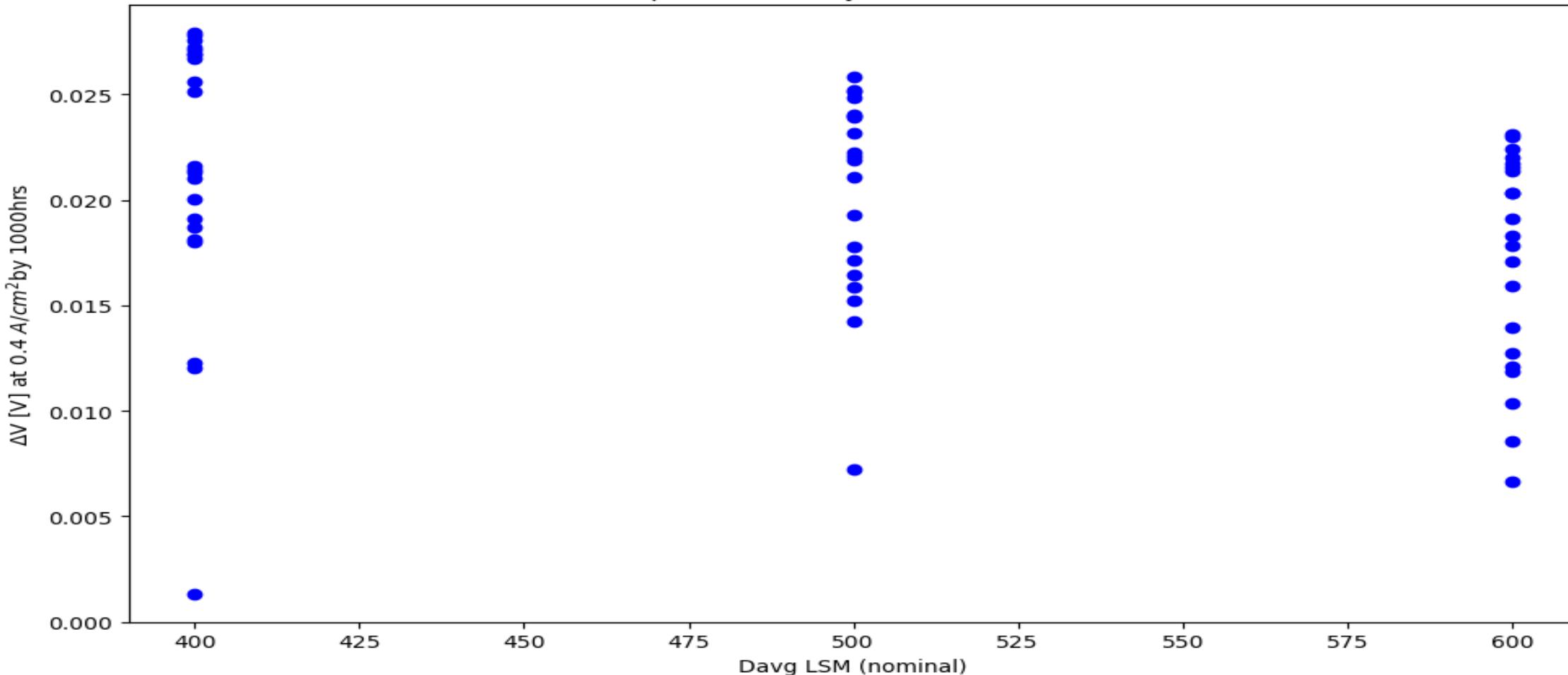
Nominal diameter, grouped by constant other parameters

T=900C, potential decay at t=1000 and at i=0.4

Decay vs Average LSM Particle Size

Nominal diameter, grouped by constant other parameters
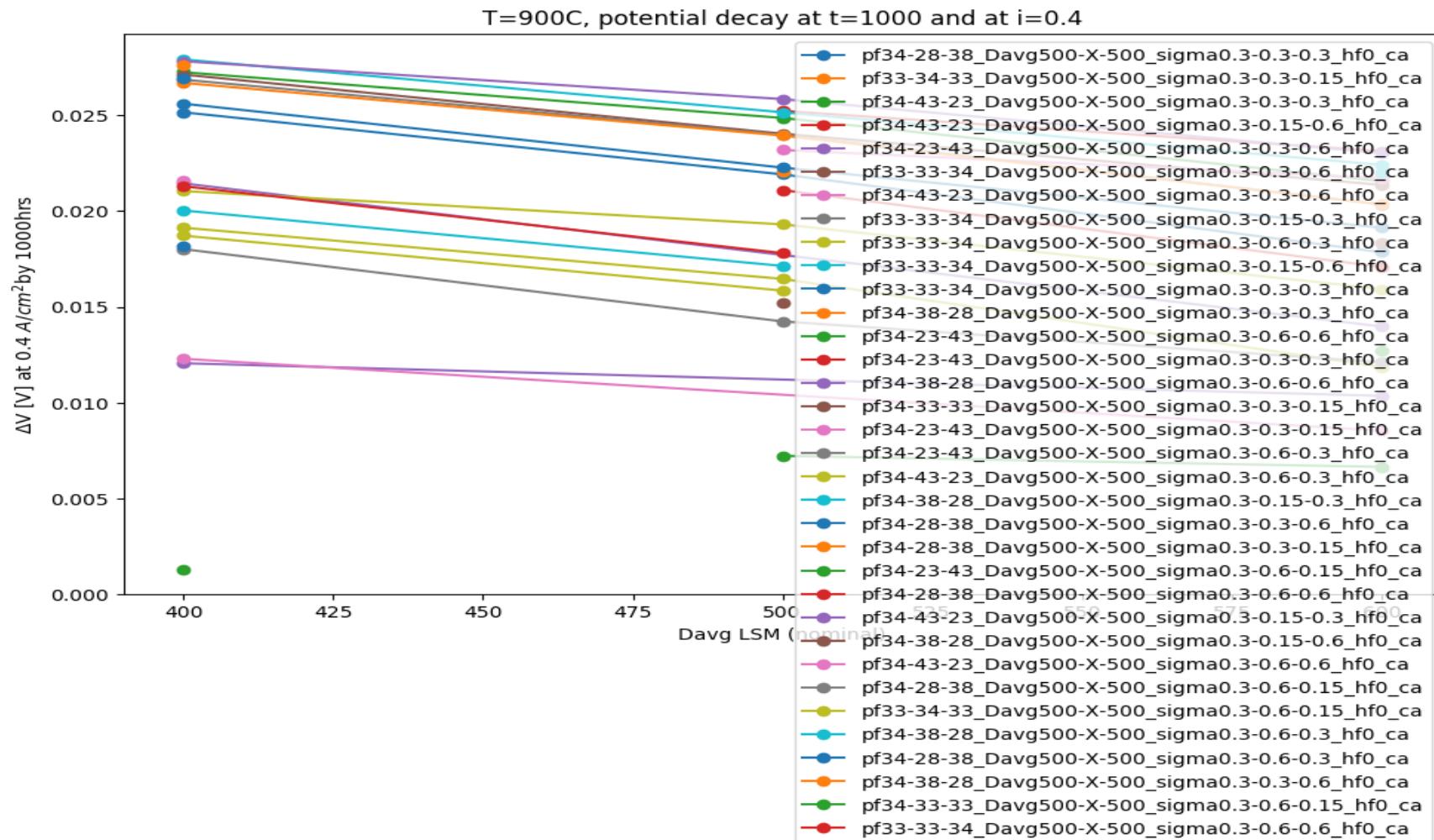
T=900C, potential decay at t=1000 and at i=0.4

Decay vs Average LSM Particle Size

Actual diameter, grouped by nominally constant other parameters

T=900C, potential decay at t=1000 and at i=0.4
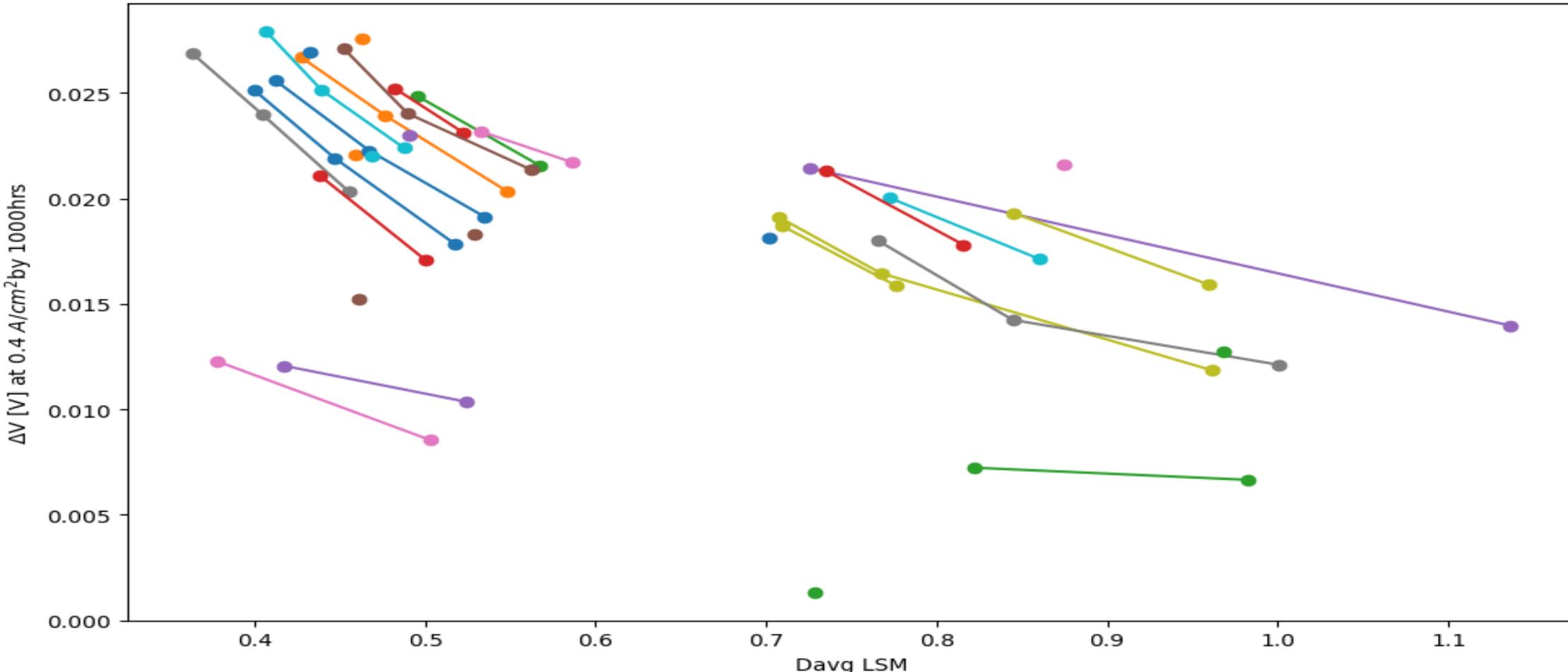
Decay vs LSM/YSZ Ratio

T=900C, potential decay at t=1000 and at i=0.4

Porosity constant (33%)
*YSZ fraction is remaining balance*

T=900C, potential decay at t=1000 and at i=0.4
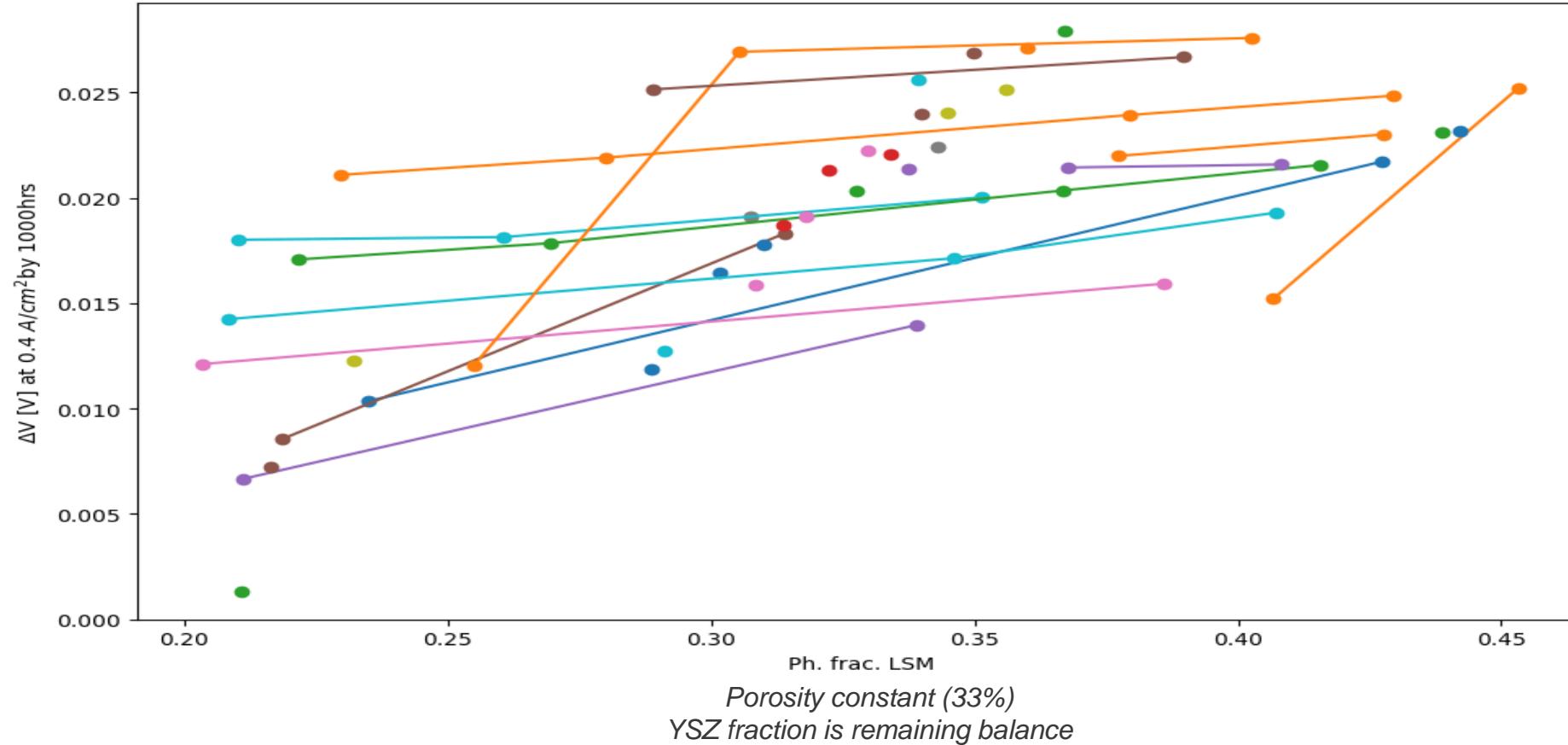
Decay vs YSZ Polydispersity

T=900C, potential decay at t=1000 and at i=0.4
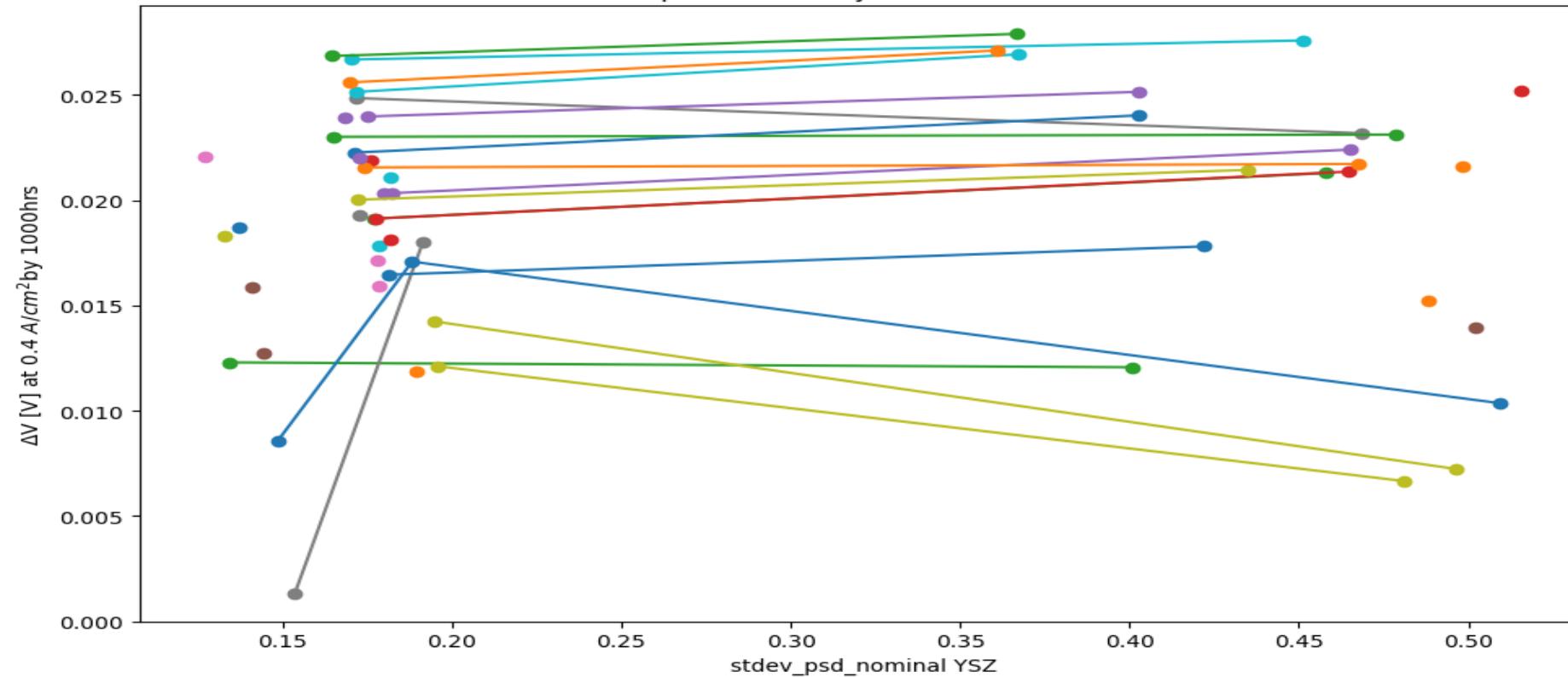
Summary

- **Performance and degradation depend on initial microstructure**

- **We have successfully generated a large library of synthetic microstructures that represent, to our knowledge, the largest variety of microstructural parameters covered in the fuel cell world**

- **NETL's integrated model framework has been successfully tested on a large pilot batch**

- **Basic analysis of results already shows effects of several parameters**
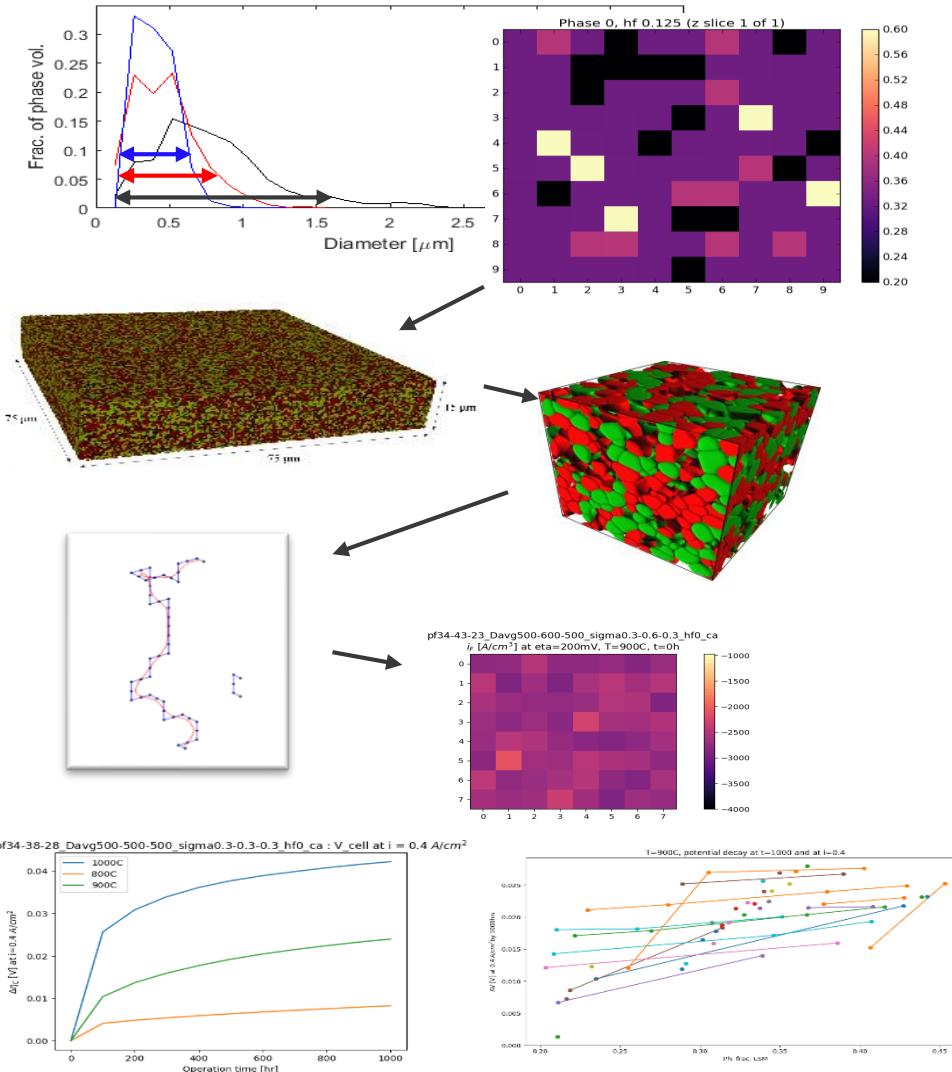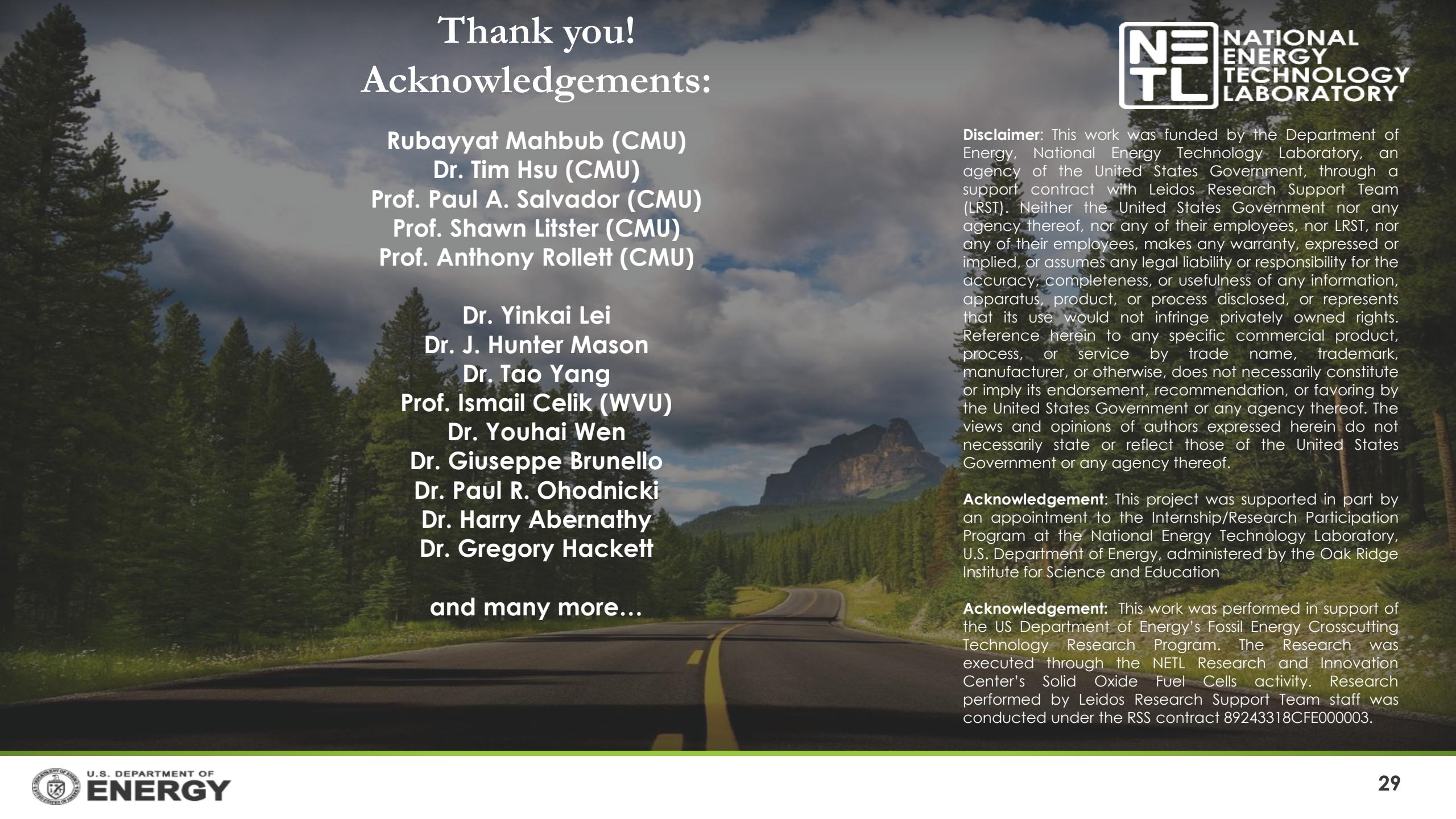
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Dr. Paul R. Ohodnicki
Dr. Harry Abernathy
Dr. Gregory Hackett

and many more…