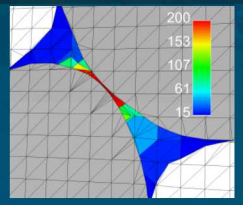
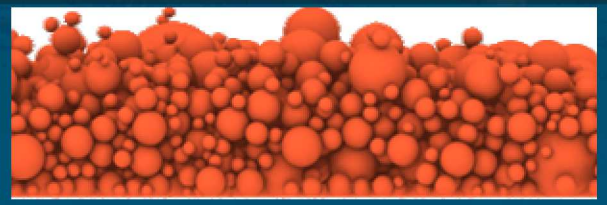
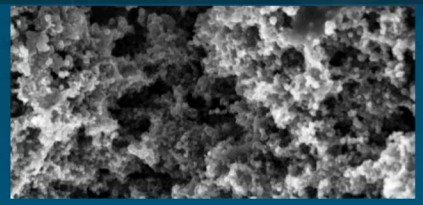
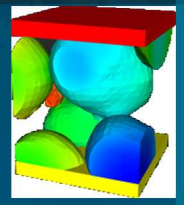
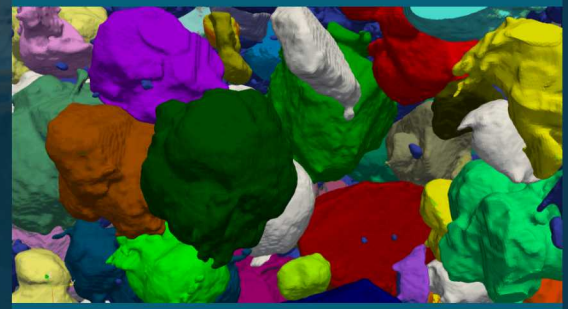
SAND2019-2508PE

Interplay Between Electrode Morphology and Mechanical Stress in Battery Performance and Safety



PRESENTED BY

Scott A. Roberts, Ph.D.

March 6, 2019

Contributors:

- Srikanth Allu (ORNL)
- Victor E. Brunini
- Mark E. Ferraro
- Aashutosh Mistry (Purdue)
- Partha Mukherjee (Purdue)
- David R. Noble
- Bradley L. Trembacki

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Motivation

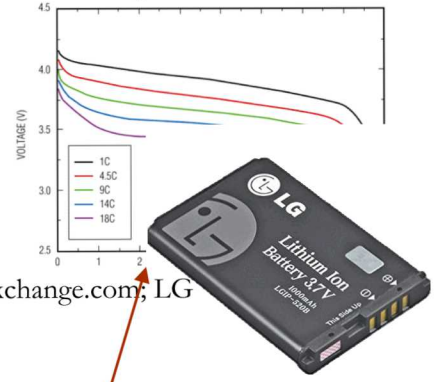
Length scale

Processing

Manufacturing

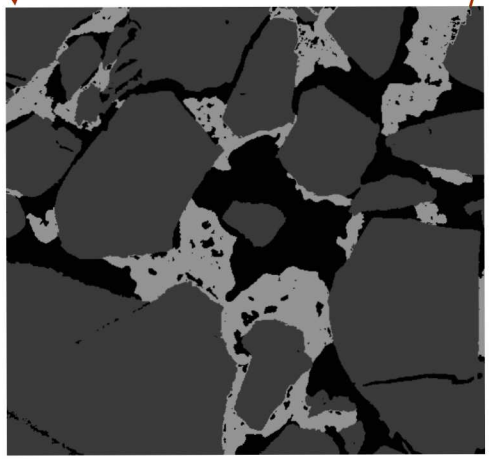
www.targray.com

Battery Performance



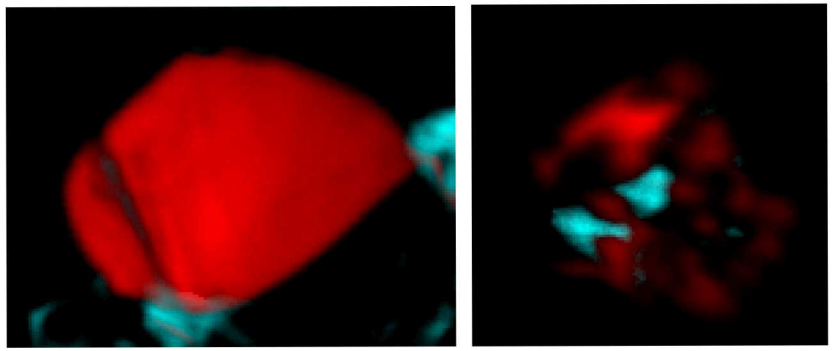
stackexchange.com; LG

Mesostructure



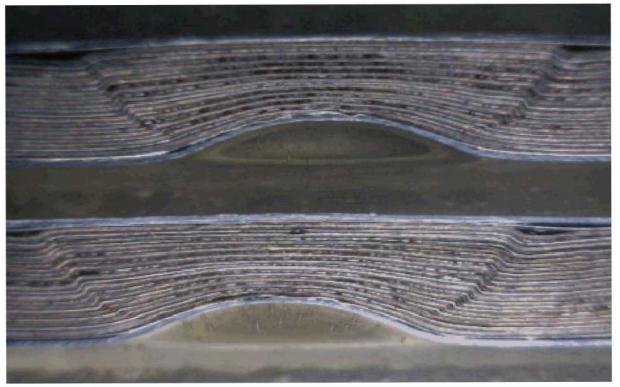
Hutzenlaub (2012)

Lithiation-Induced Fracture

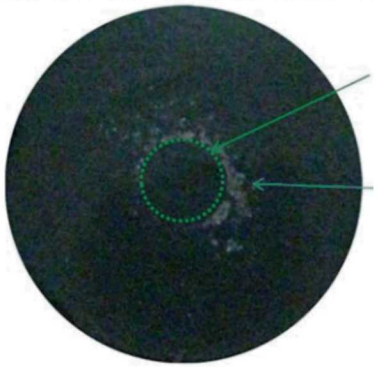


LiCoO2 STXM, Farid El Gabaly Marquez (Sandia)

Mechanical Abuse → Electrochemistry / Mesostructure



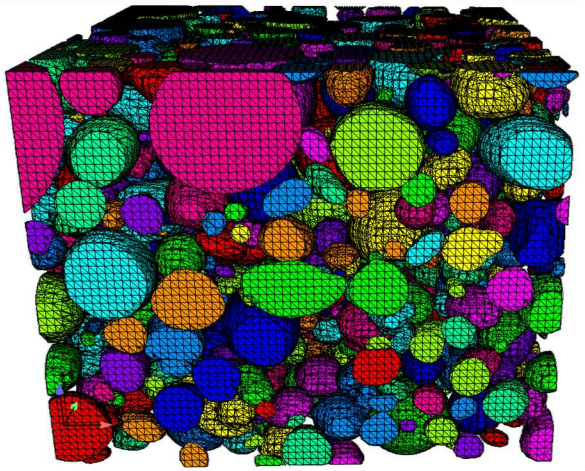
NMC/graphite pouch, H. Wang (ORNL)



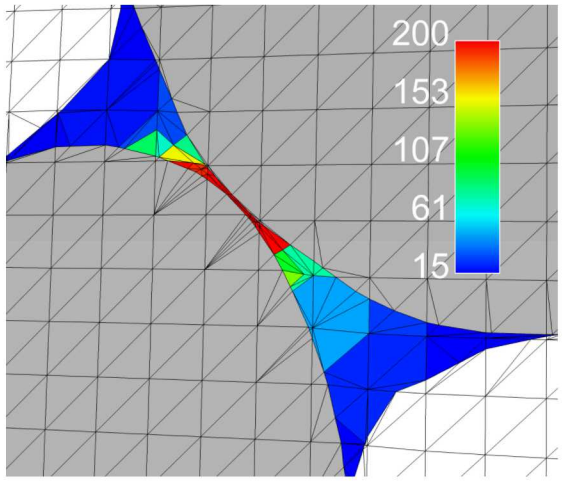
Cannarella/Arnold (2015)

Coupled electrochemical-mechanical effects at mesoscale connect battery manufacturing and performance

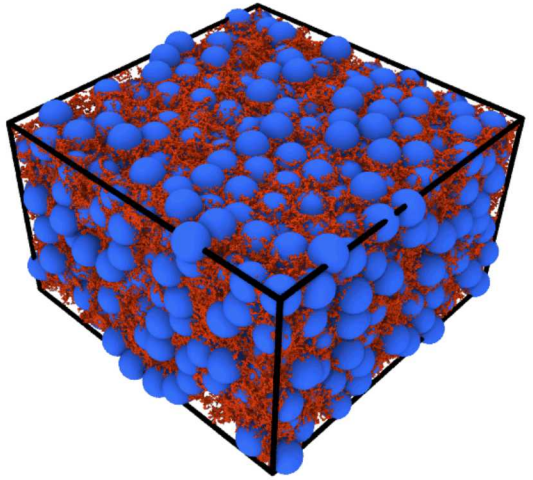
Outline



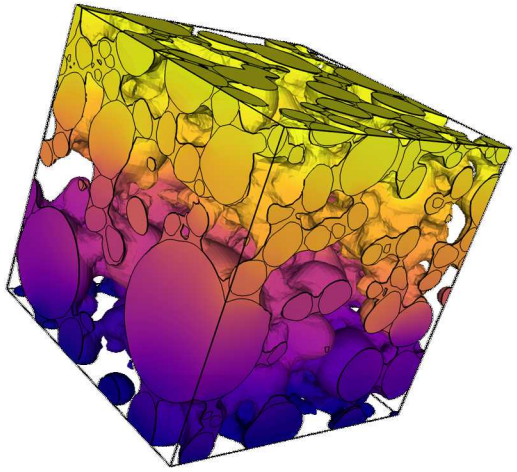
Computational representation of imaged electrode mesostructures



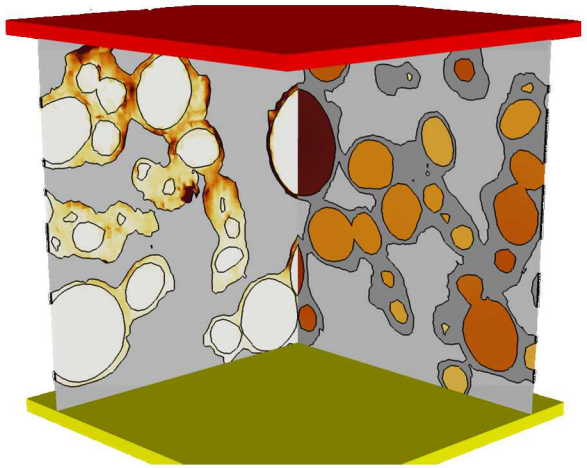
Representation and role of conductive binder morphology



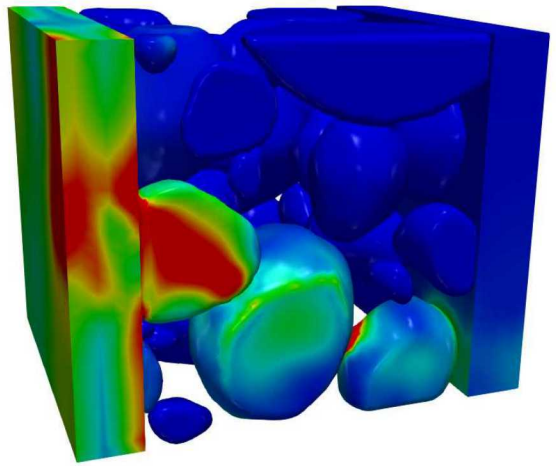
Discrete element method mesostructure generation



NMC cathode effective property prediction and upscaling

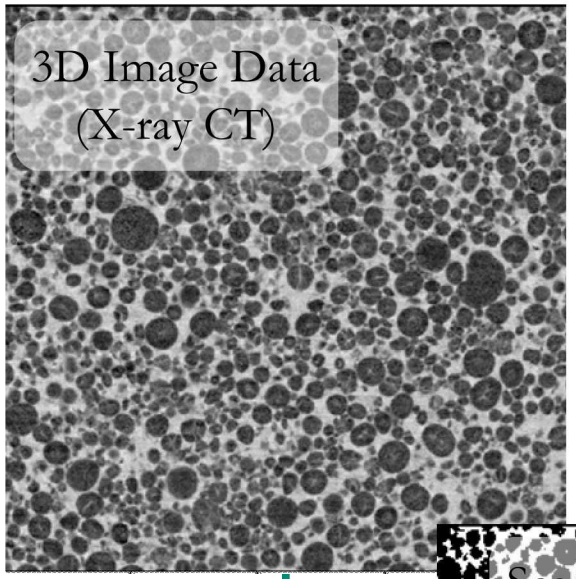


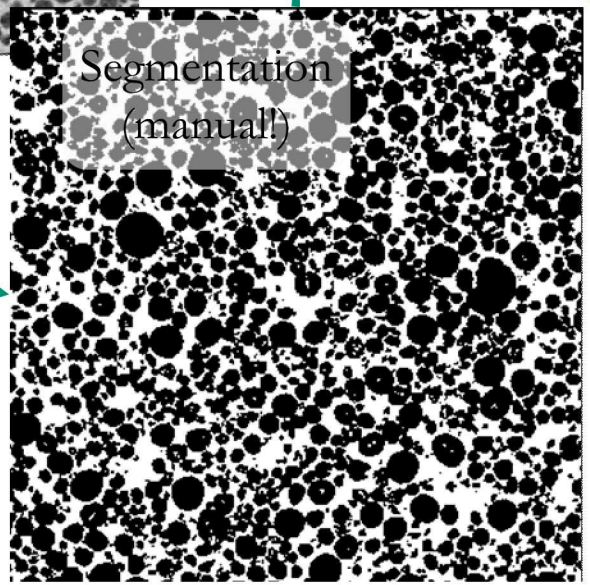
Electrochemical-mechanical discharge sims. of NMC half-cells

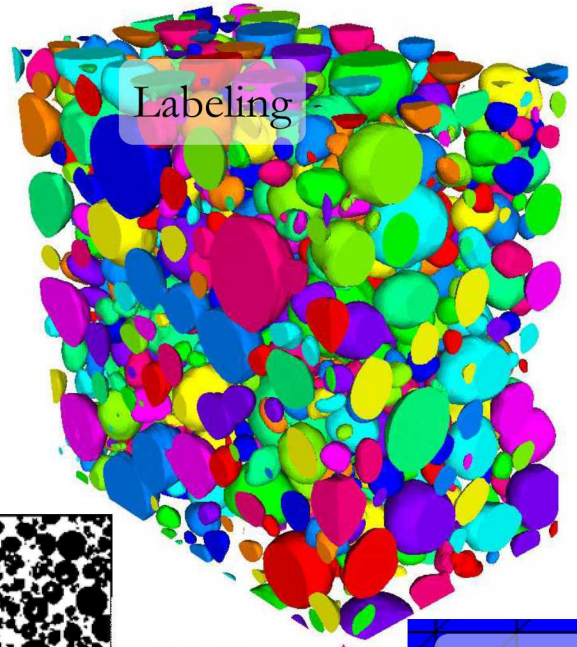


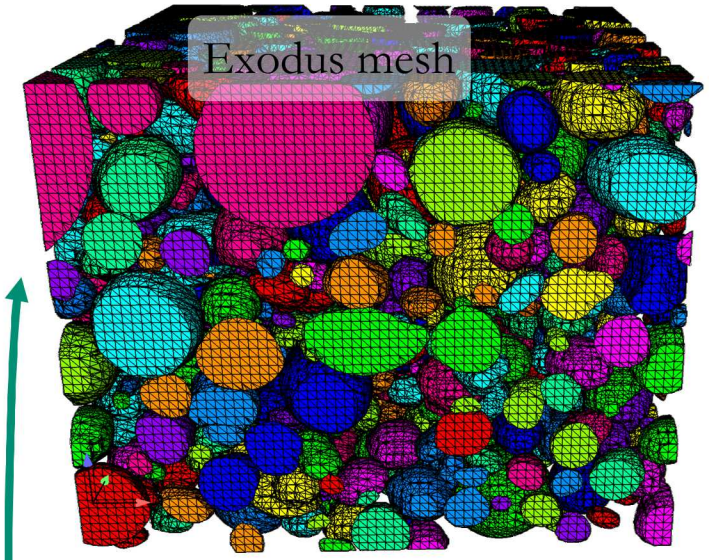
Future directions in electrode mesoscale modeling

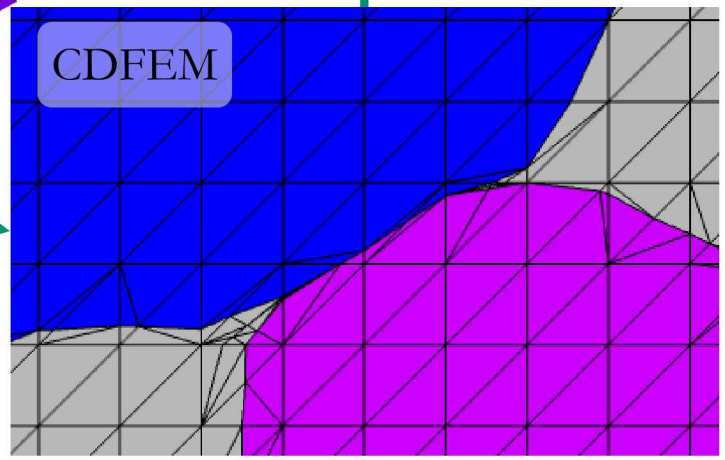
Mesoscale geometry from CT data using CDFEM











Detailed 3D reconstruction and image processing necessary to get usable mesostructure data

Roberts et al JES 2014, Roberts et al JEECS 2016

What about the conductive binder?

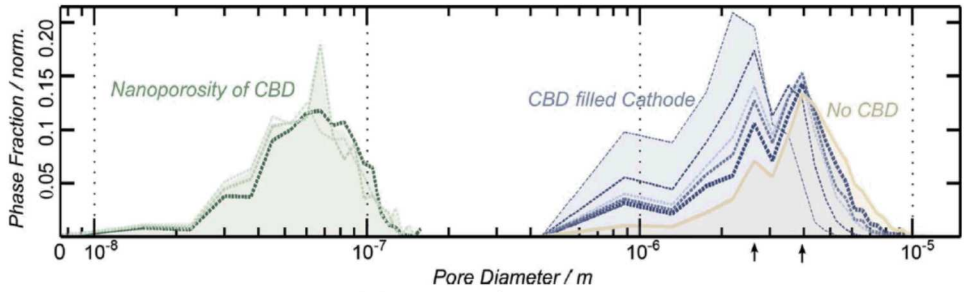
Resolving conductive binder in 3D imaging difficult

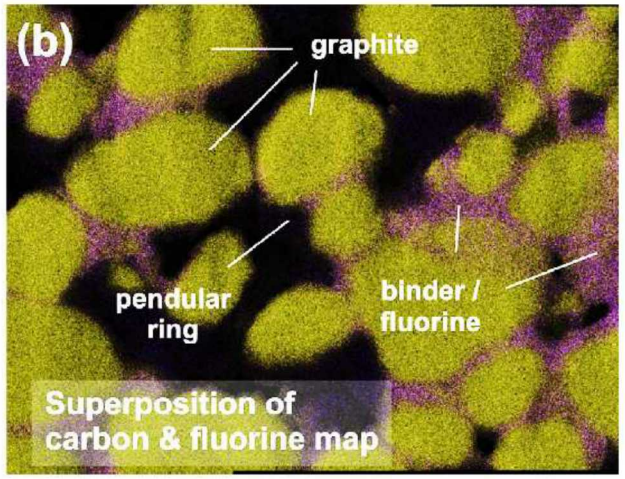
- Binder often neglected, assuming non-active void space is electrolyte
- Limited imaging results can hint at binder location

Amorphous binder is significantly nanoporous

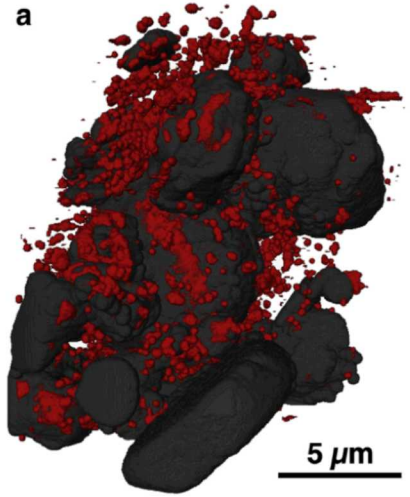
- 47% Zielke (2015); 45% Grillet (2016)
- 5% ionic conductivity of pure electrolyte

Binder weight fraction	Dense volume binder:particle	Porous volume binder:particle
0.04	0.10	0.15
0.06	0.16	0.23
0.08	0.22	0.31
0.10	0.28	0.40

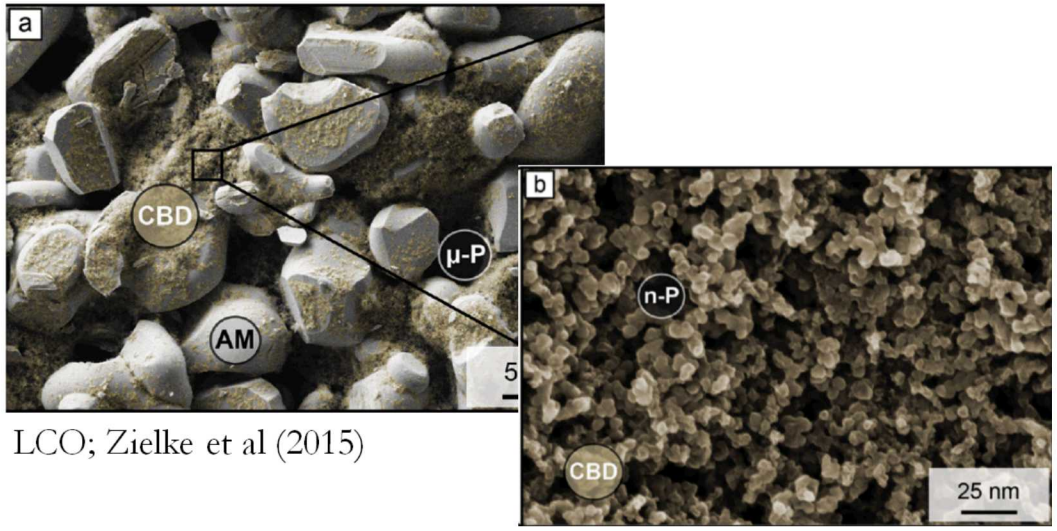




Graphite; Jaiser et al. (2017)



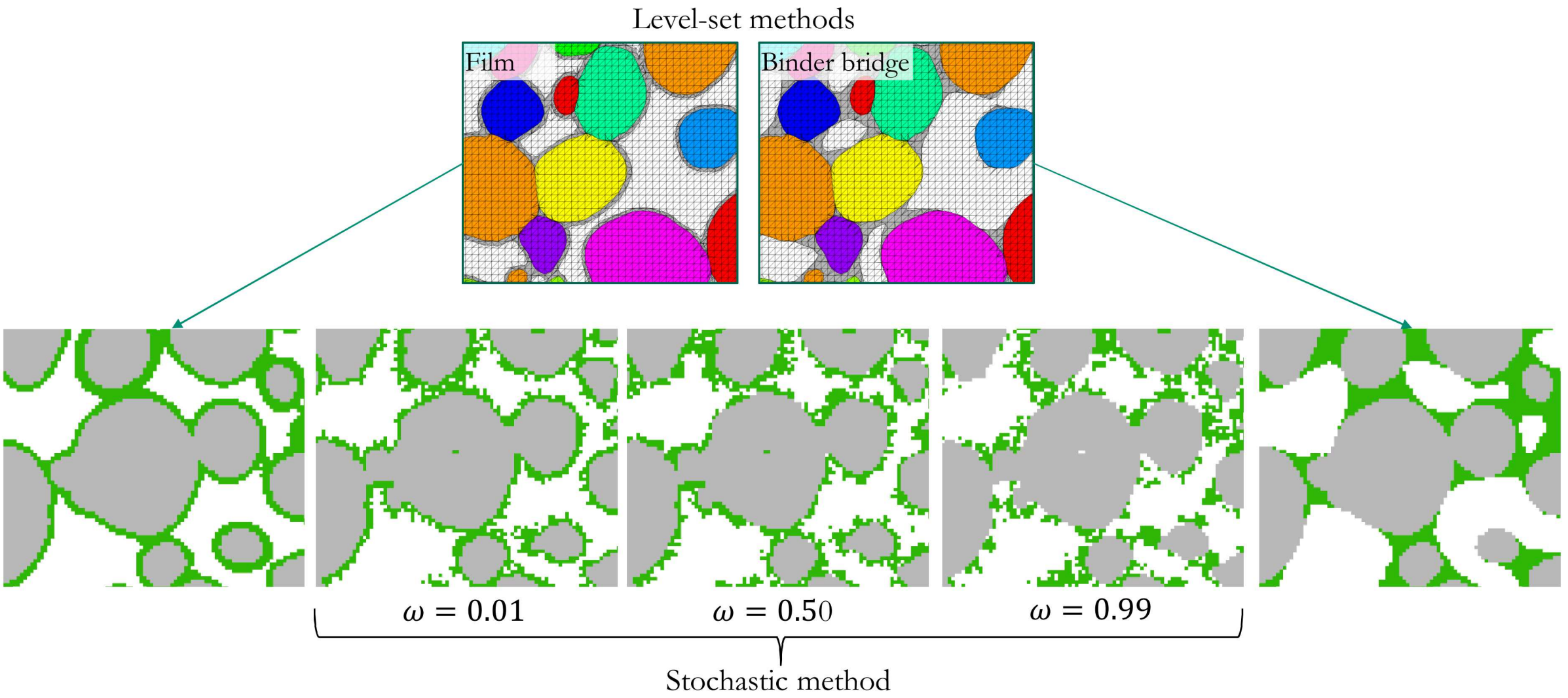
LCO; Komini Babu et al (2015)



LCO; Zielke et al (2015)

How are electrode-scale properties affected by the inclusion of binder? How does the morphology matter?

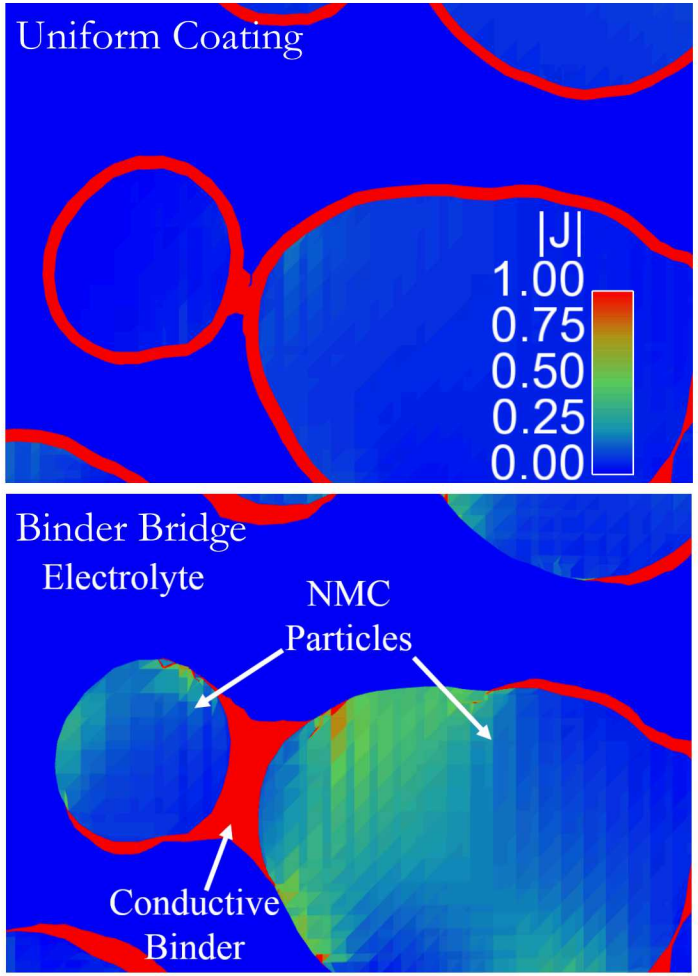
Binder bridge morphology approaches

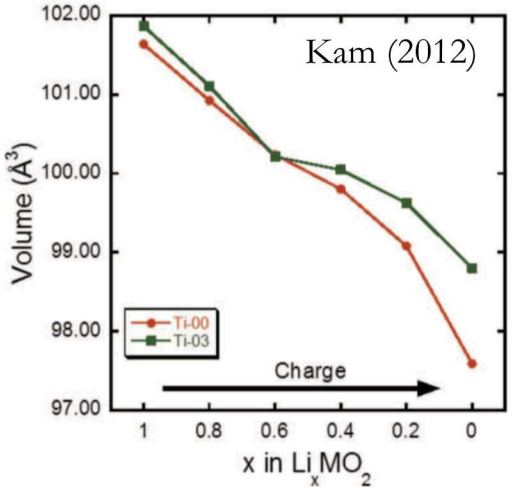


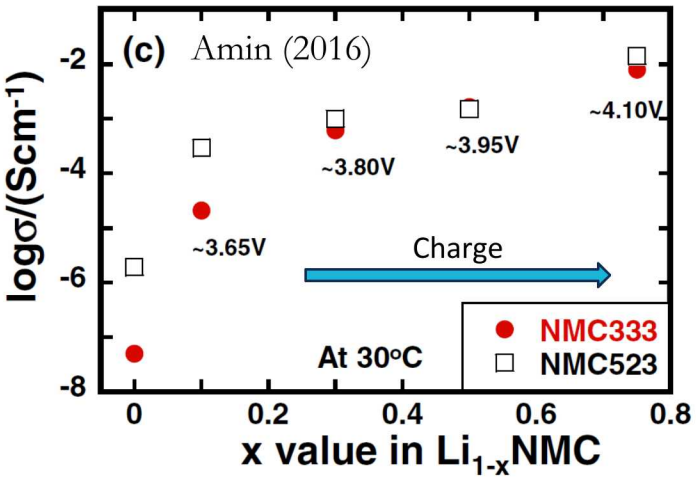
Two level-set morphologies visually bracket the range of stochastic morphologies

Trembacki (2017), Mistry (2018)

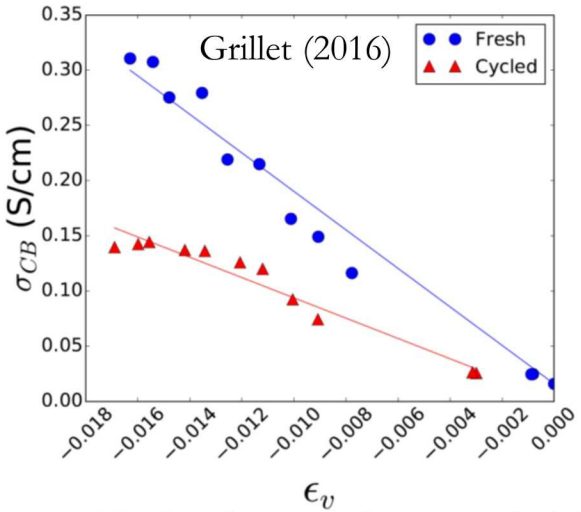
Why does the morphology matter?

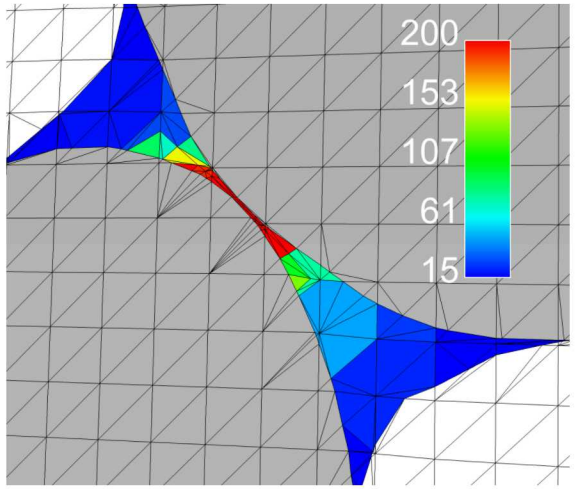






NMC swells on lithiation, compressing binder





Binder has strain- (e.g. lithiation-) dependent properties

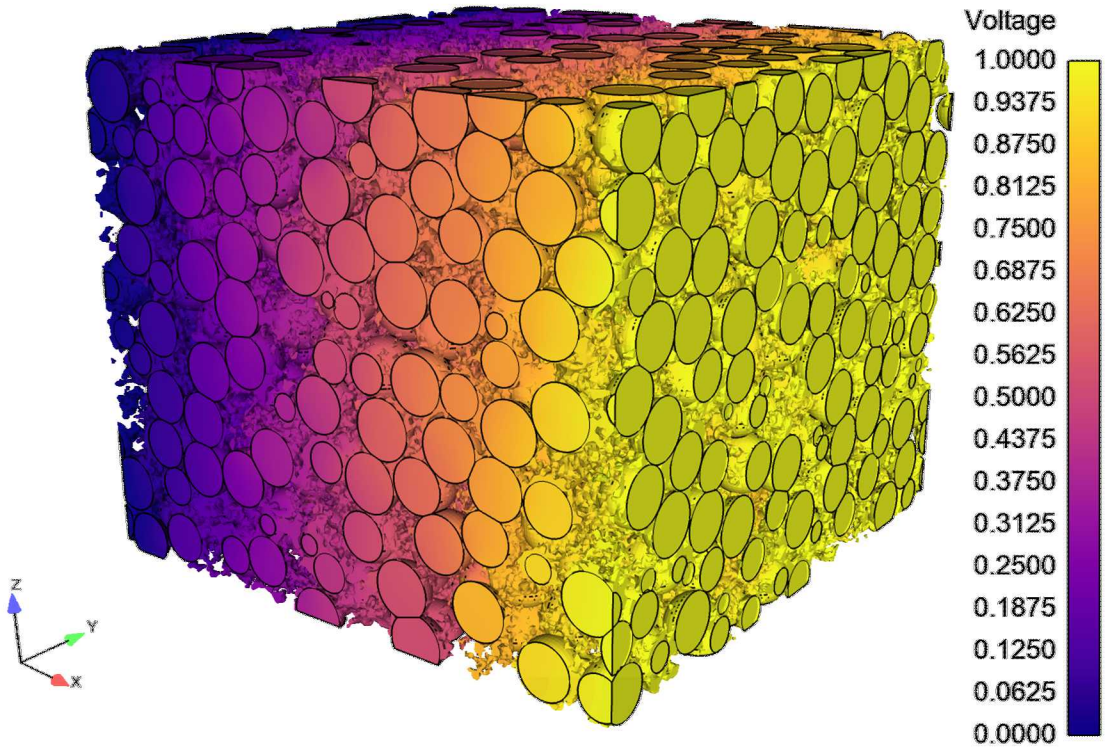
Effective electrode property calculations

Calculate effective transport properties for upscaling

- Particle specific surface area
- Electrical conductivity
- Tortuosity

NMC image data from Ebner (2013)

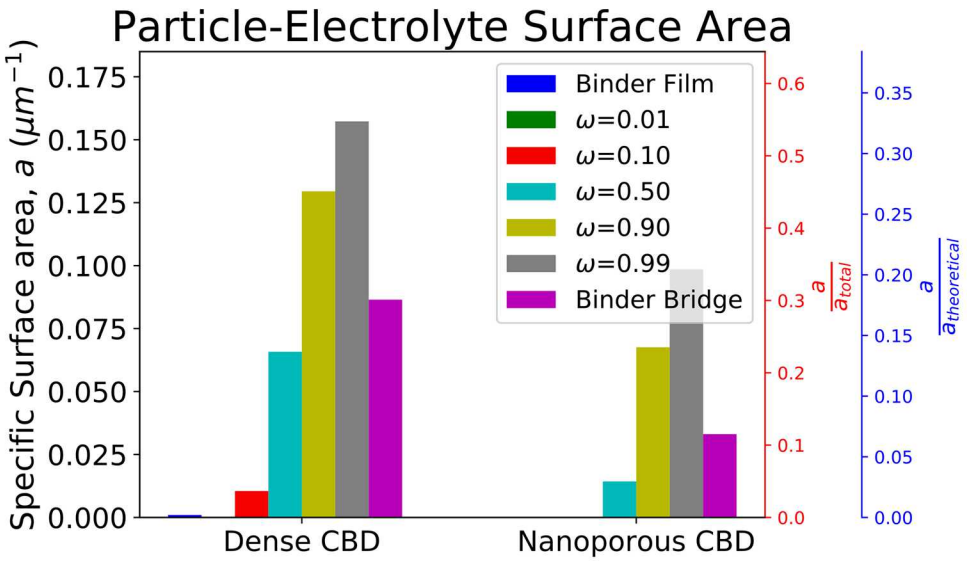
- 90, 92, 94, 96 wt% NMC (remainder 1:1 CB:PVDF)
- 0, 300, 600 & 2000 bar calendering
- 100 µm x 100 µm x 60 µm domain (20 realizations eac
- Binder bridge (porous) morphology approach



Effective properties are an important first step for upscaling mesoscale data

Trembacki, in preparation

Porous binder and morphology considerations



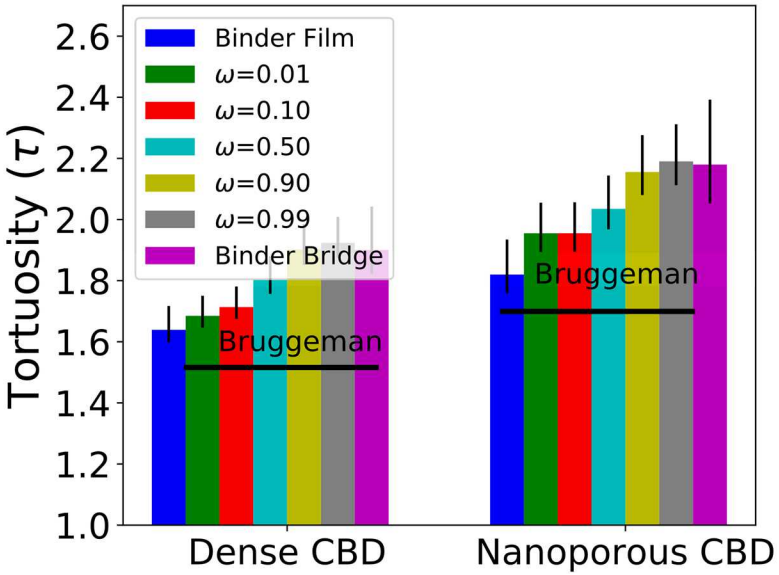
- More particle surface area available with non-uniform morphologies
- Nanoporous binder decreases bare particle surface area, but binder area is porous
- Surface are much less than theoretical

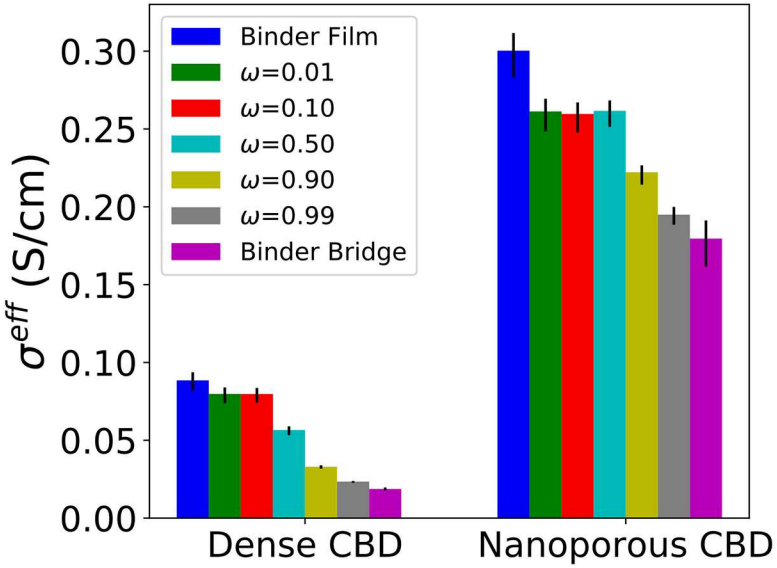
Non-uniform binder:

- Increases tortuosity
- Decreases conductivity

Nanoporosity:

- Increases tortuosity
- Increases conductivity

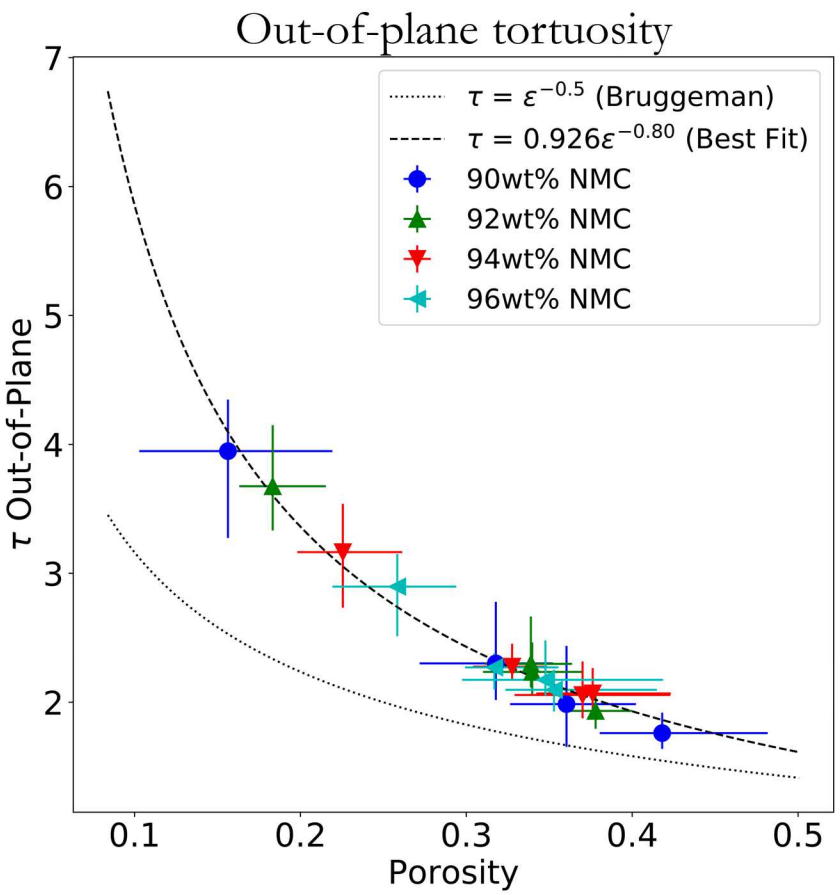


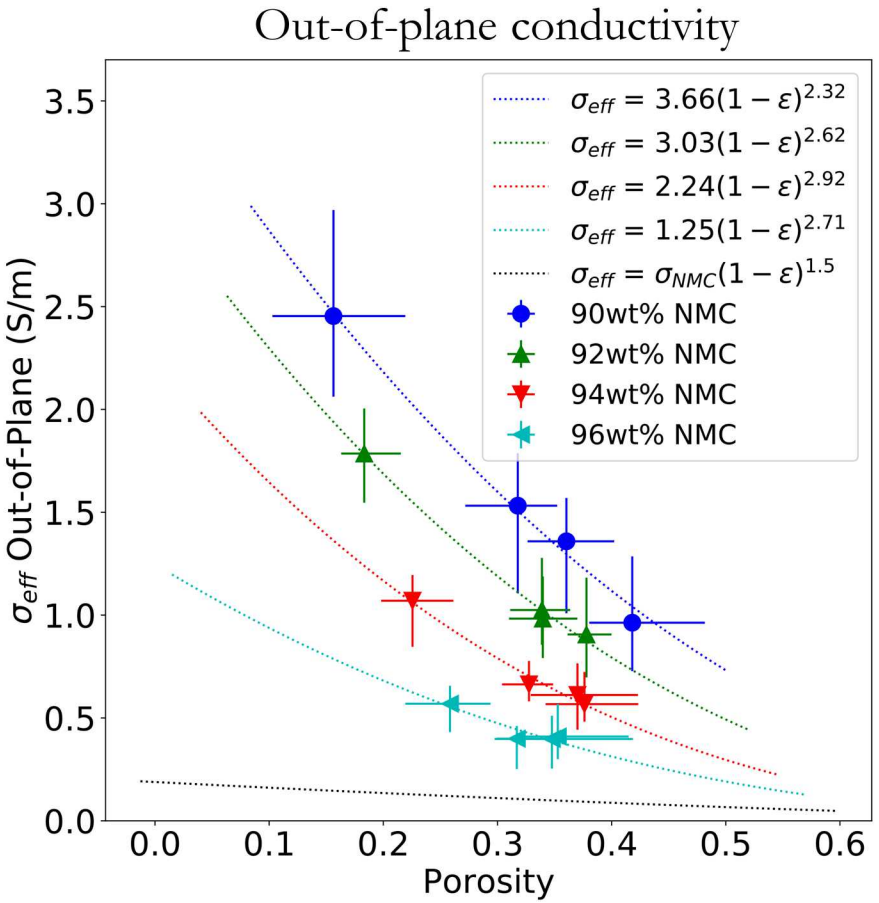


Limiting cases of both morphology methods show similar (but not identical) behavior; nanoporosity is important!

Trembacki JES (2018)

Effective electrode property calculation results – Transport

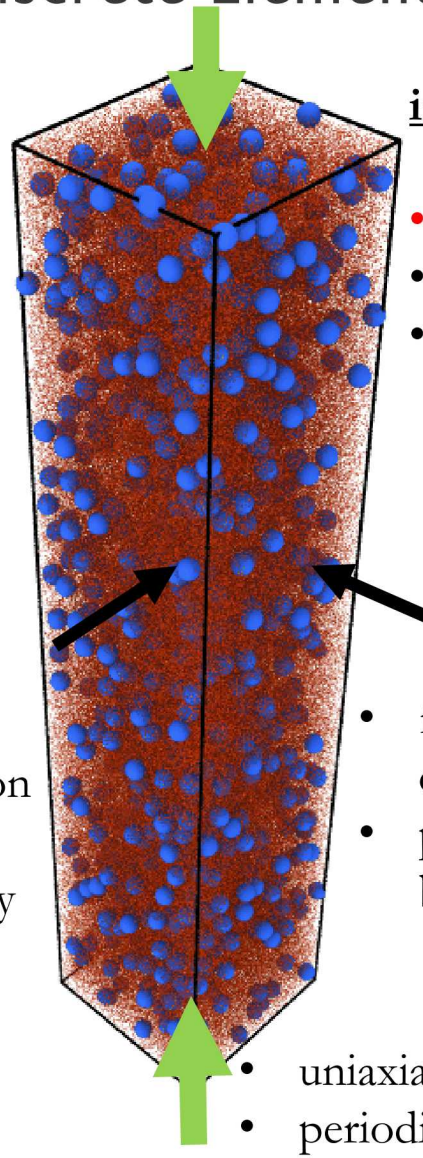




Bruggeman relationships must be re-calibrated to fit simulated data

Trembacki, in preparation

Discrete Element Method (DEM) mesostructure g



initial microstructure

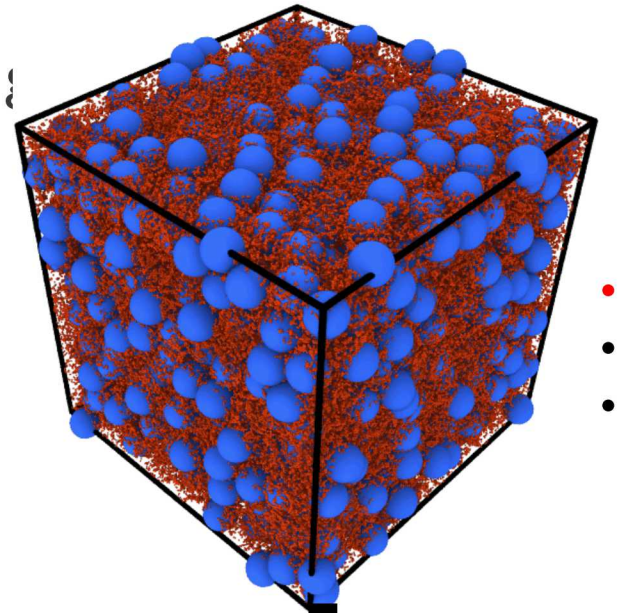
- **porosity: 90%**
- height: 525 um
- width: 100 um

- fixed dimension
- periodic boundary

- fixed dimension
- periodic boundary

- uniaxial compression
- periodic boundary

compression (drying)



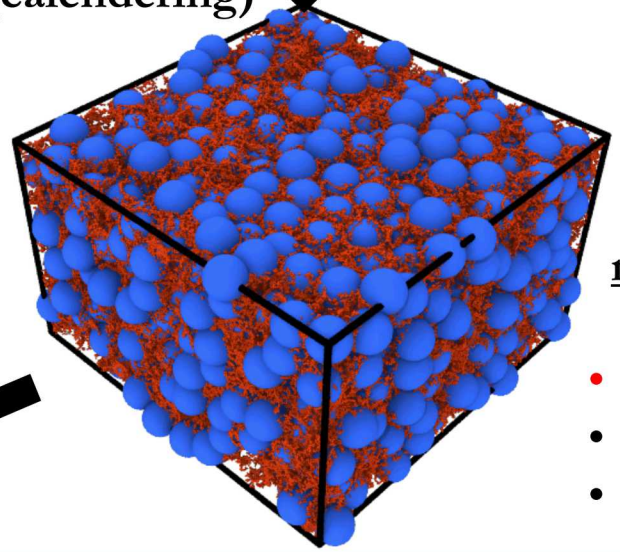
intermediate microstructure

- **porosity: 50%**
- height: 100 um
- width: 100 um

compression (calendering)

94% AM electrode

- ~1k AM particles (10 μm)
- ~1M CBD coarse grained particles (0.5 μm)



compressed microstructure

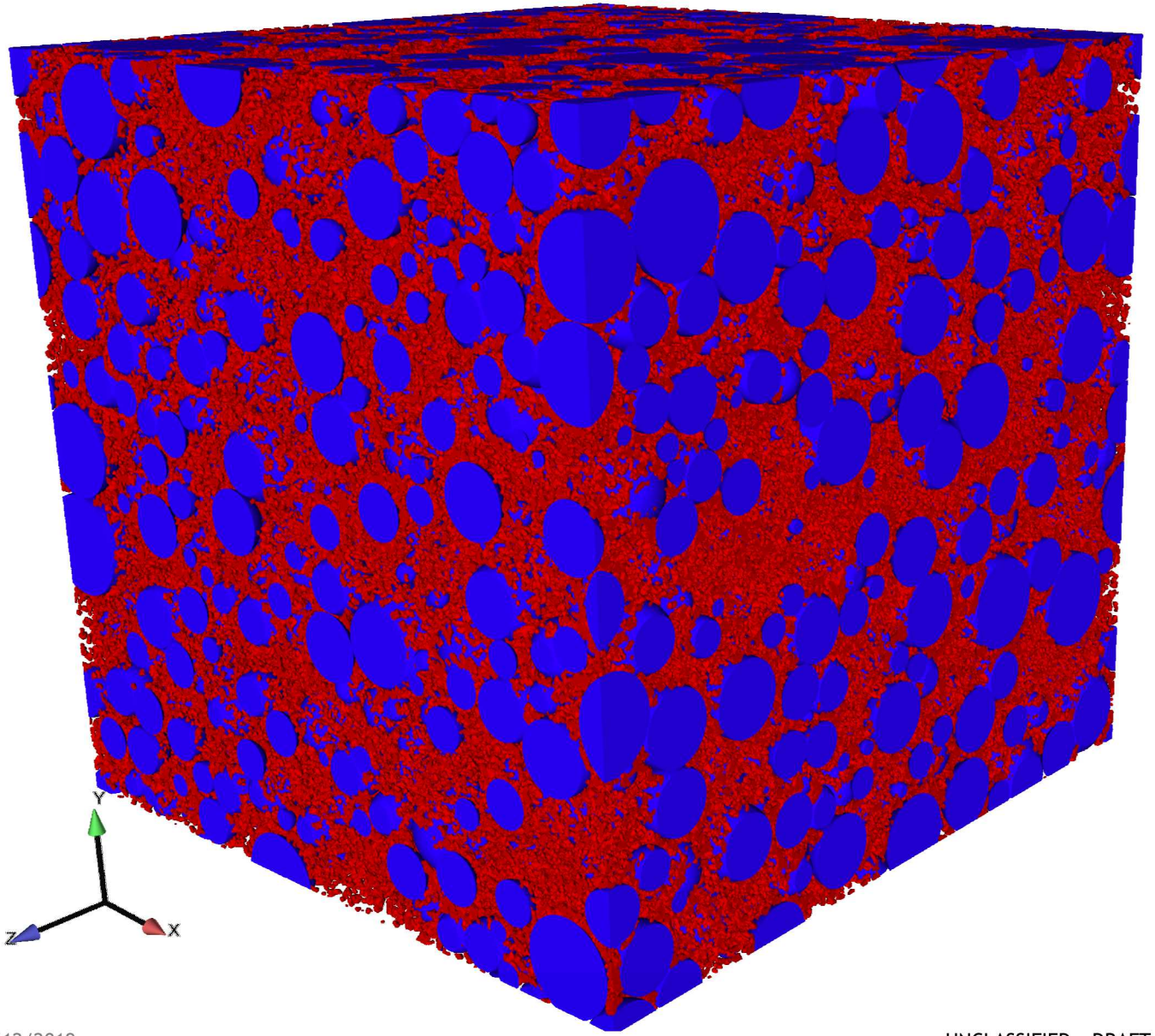
- **porosity: 30%**
- height: 66 um
- width: 100 um

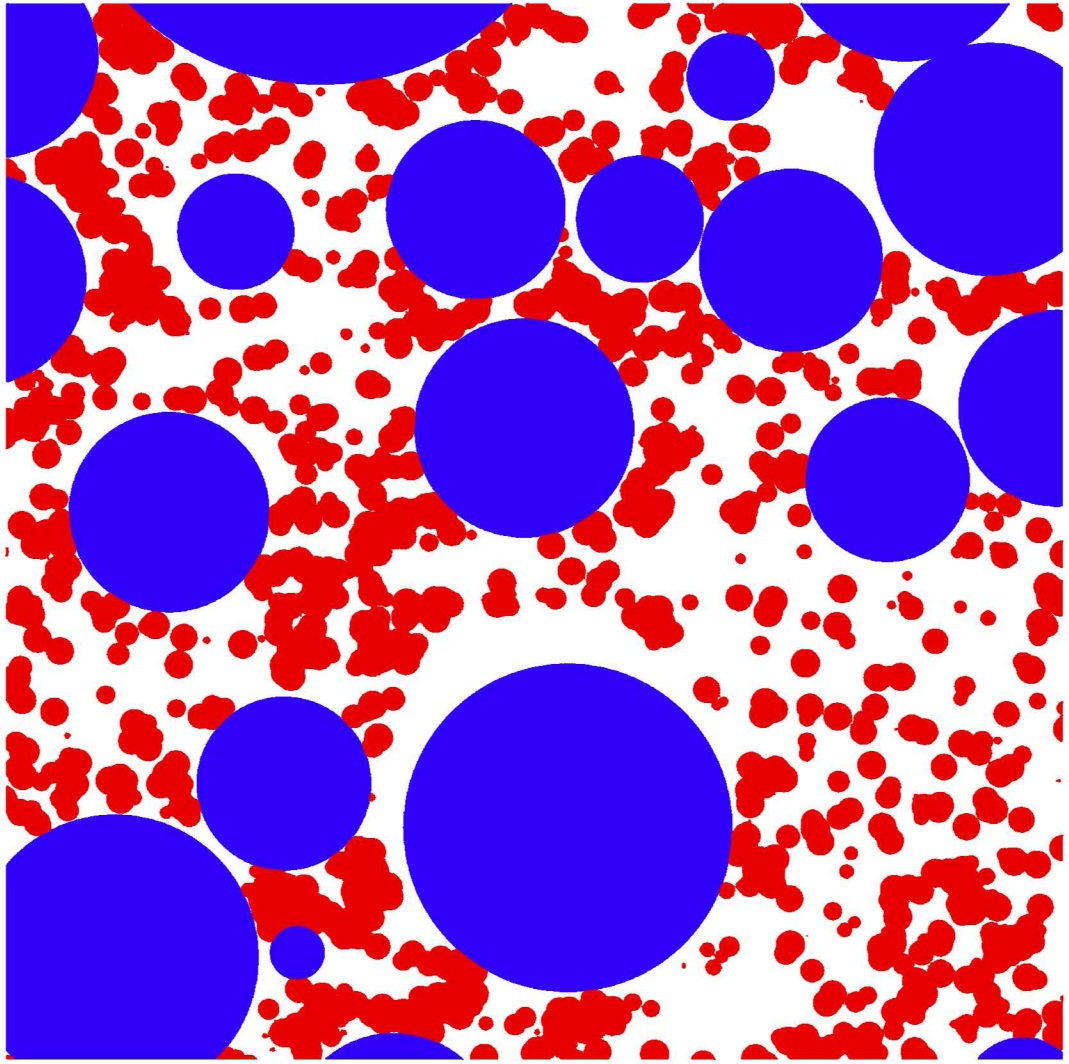
final

- expand CBD 2x
- create FEM mesh

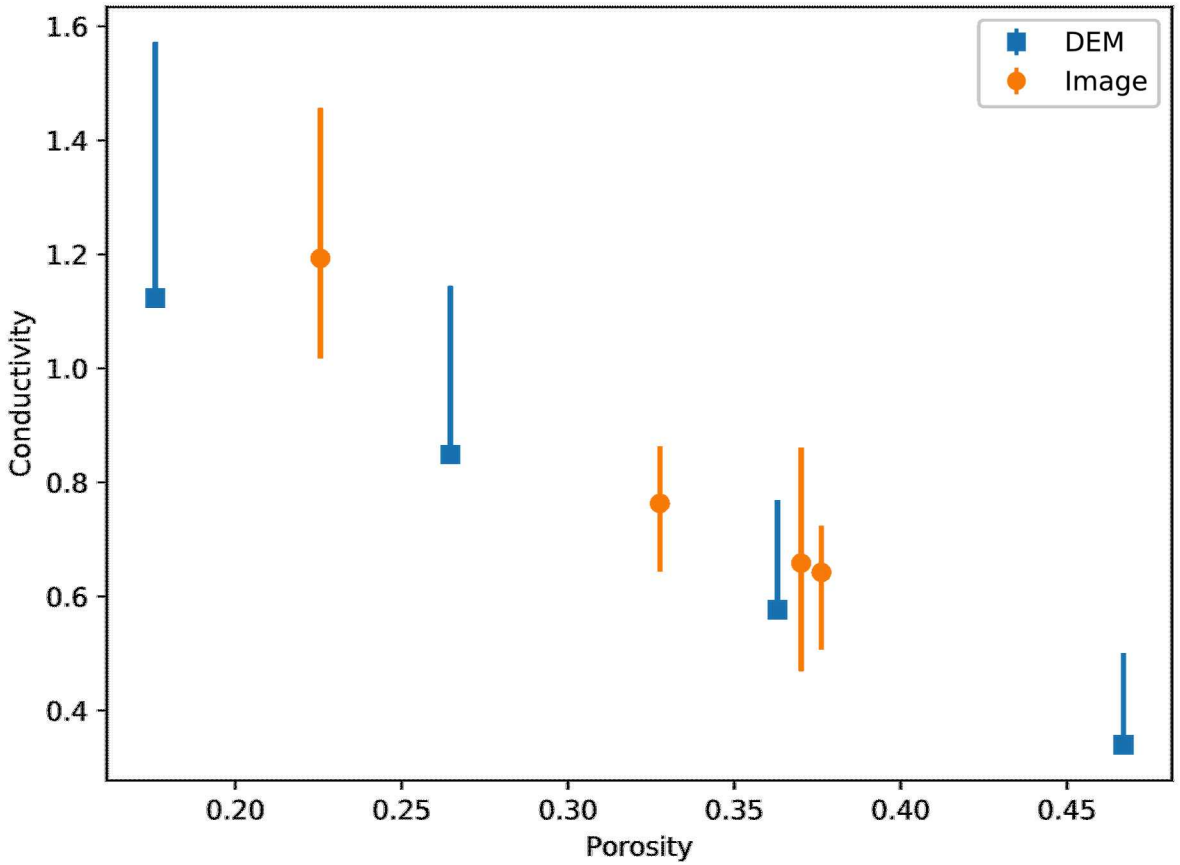
Uniaxial compression with granular and Brownian forces enable study of AM consolidation and CBD aggregation

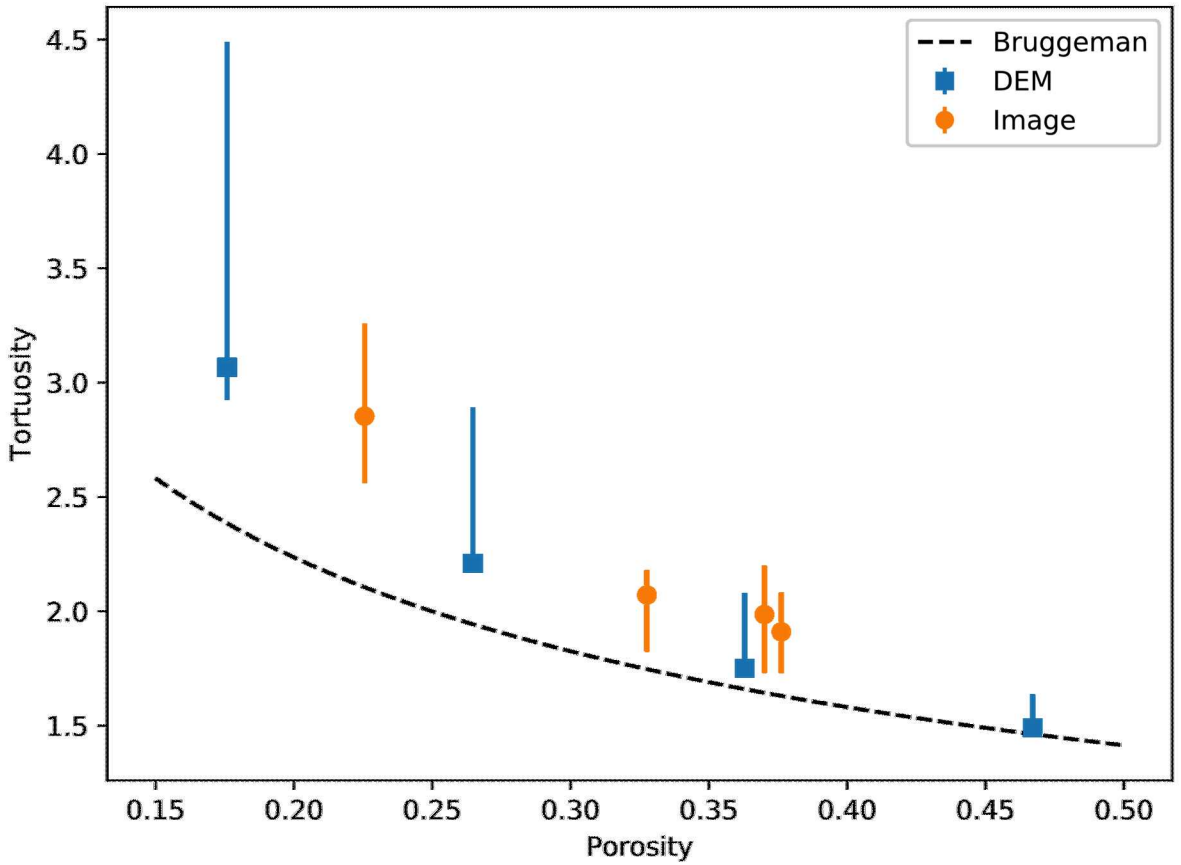
CDFEM mesh of DEM-generated mesostructures





Comparison of image- and DEM-based mesostructures





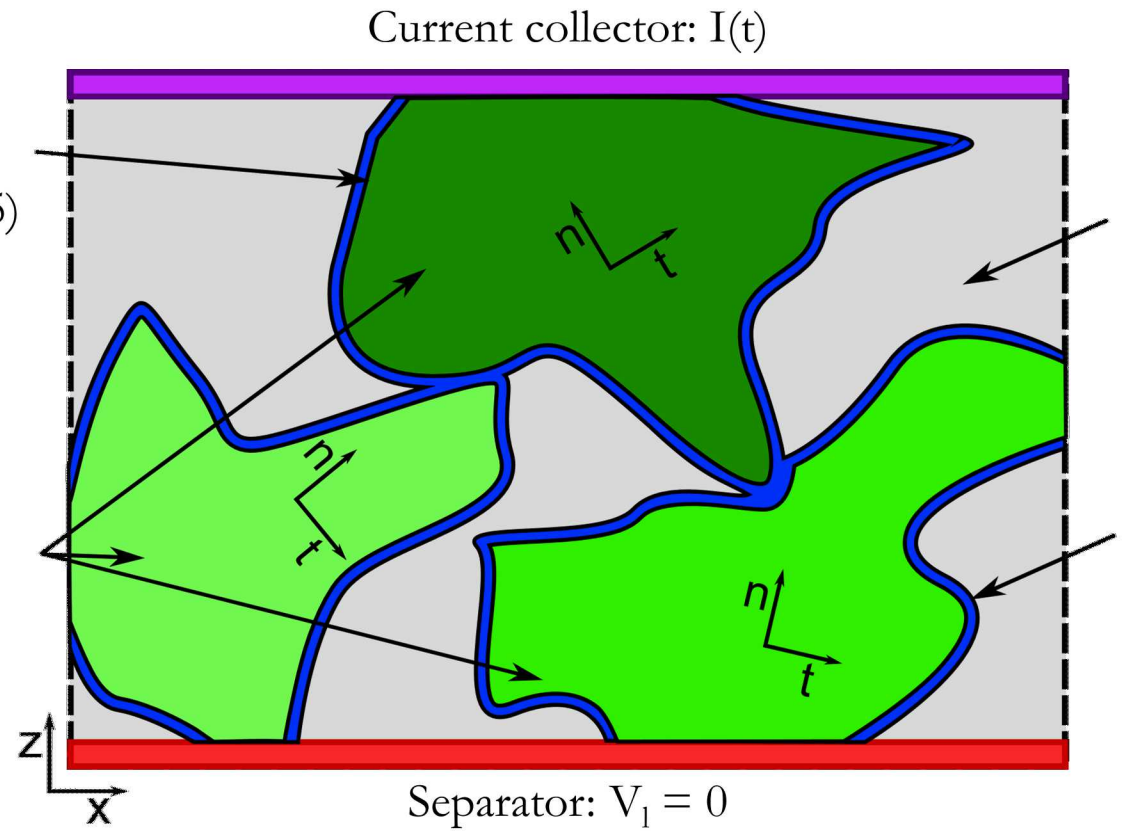
All simulations for T=600, $\gamma=10^{-5}$, AM=94 wt%, 0 bar calendaring

Calendaring → lower porosity → more CBD connectivity → higher conductivity and tortuosity

Coupled electrochemical-mechanical half-cell discharge simulations

Particle Interface:
- Butler-Volmer reaction
- OCV from Smekens (2015)

Particles:
- Species – Li tr
  - Chemica
  - Stress pc
- Electrical – O
- Mechanics - E
  - Li-induc



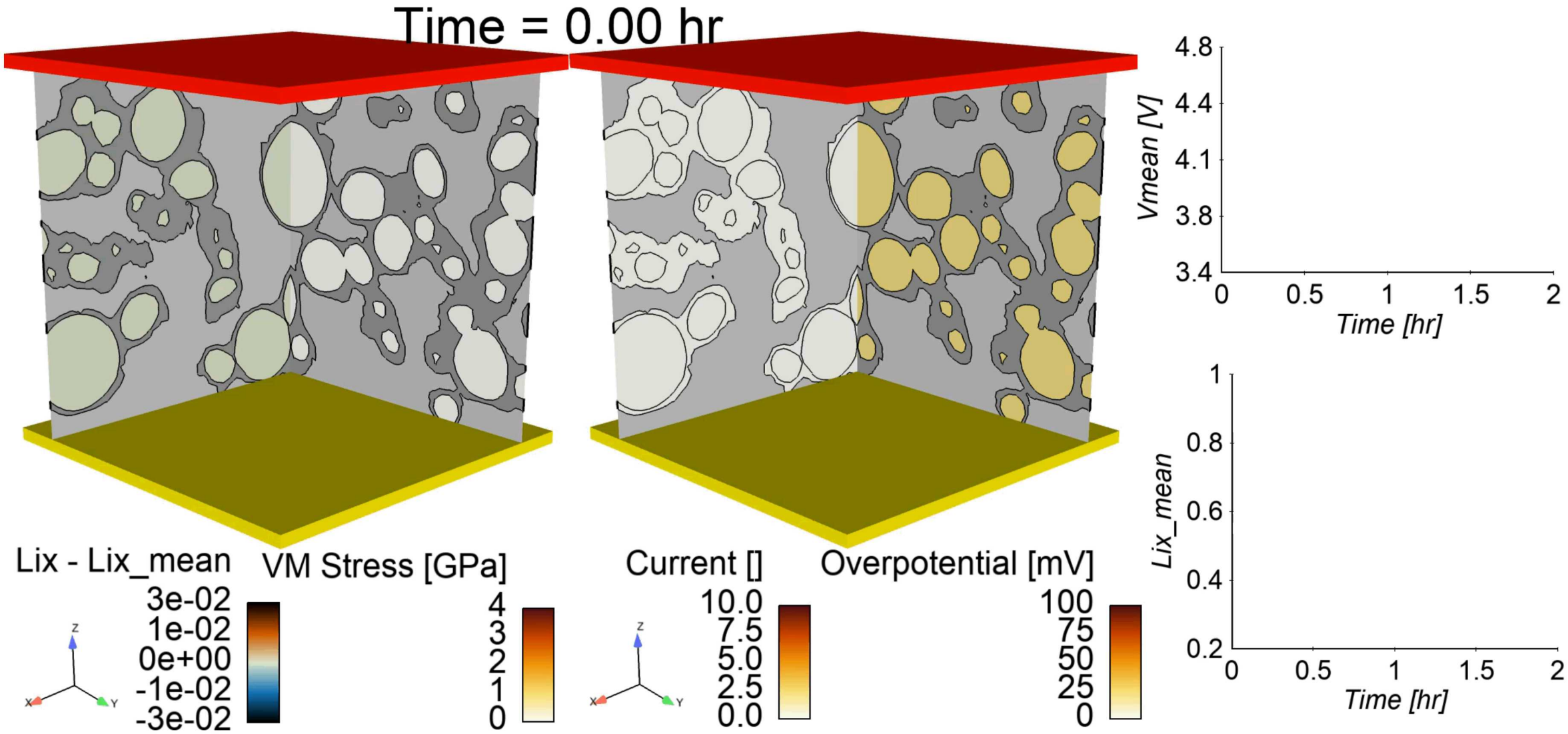
Electrolyte:
- Species – Li^+ transport
  - Nernst-Planck fluxes
  - Electroneutrality for PF_6^-
- Current conservation

Conductive binder:
- Species – Porous Li^+ transport
- Electrical
  - Solid: Porous Ohm's law
    - Strain-dependent electrical conductivity
  - Liquid: Ionic conservation & electroneutrality
- Mechanics – Elastic

Mathematical formulation builds off of Mendoza (2016) LCO studies

Predictions of discharge curves, effects of mechanics, rate effects, and spatial variations in performance

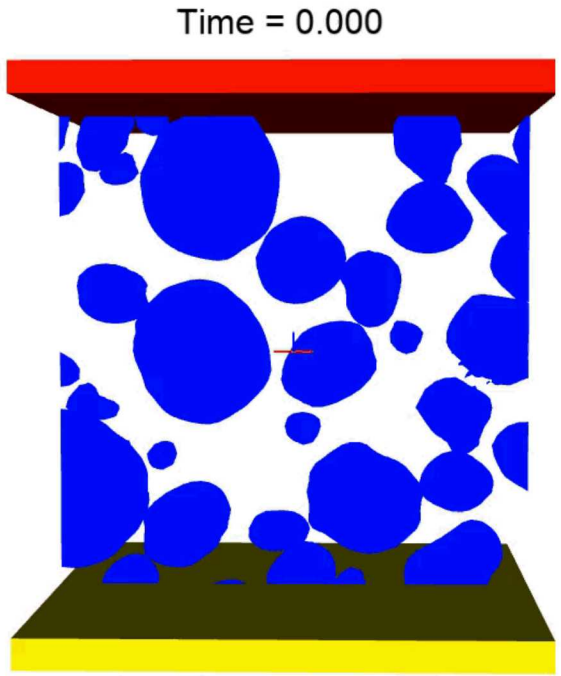
Demonstration of NMC half-cell discharge simulation at C/2

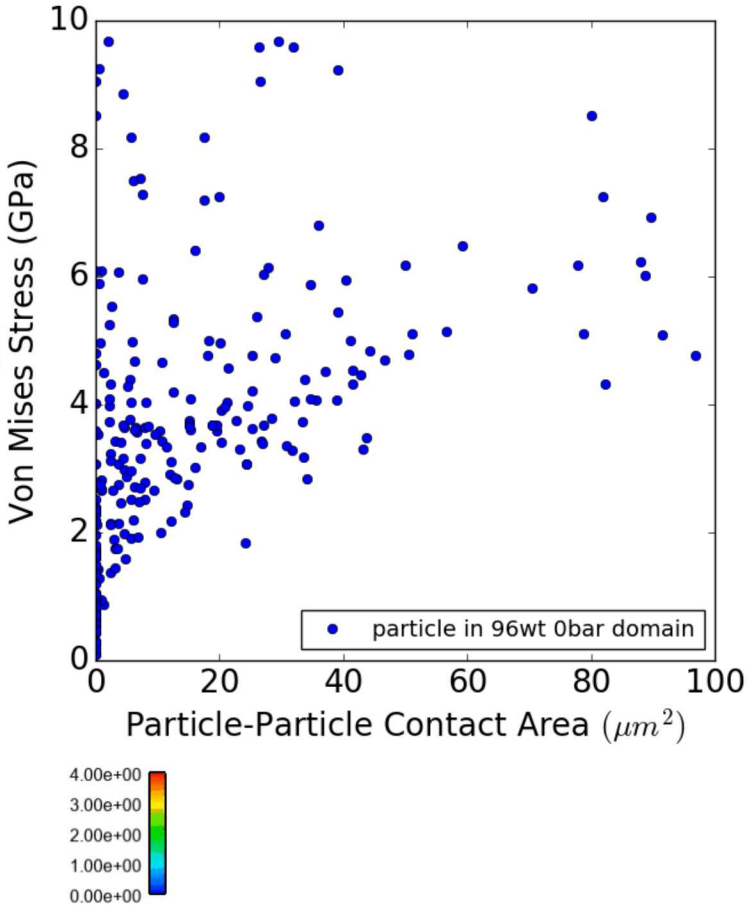


Coupled electrochemical-mechanical simulation yields detailed insight, predicts electrode-scale response

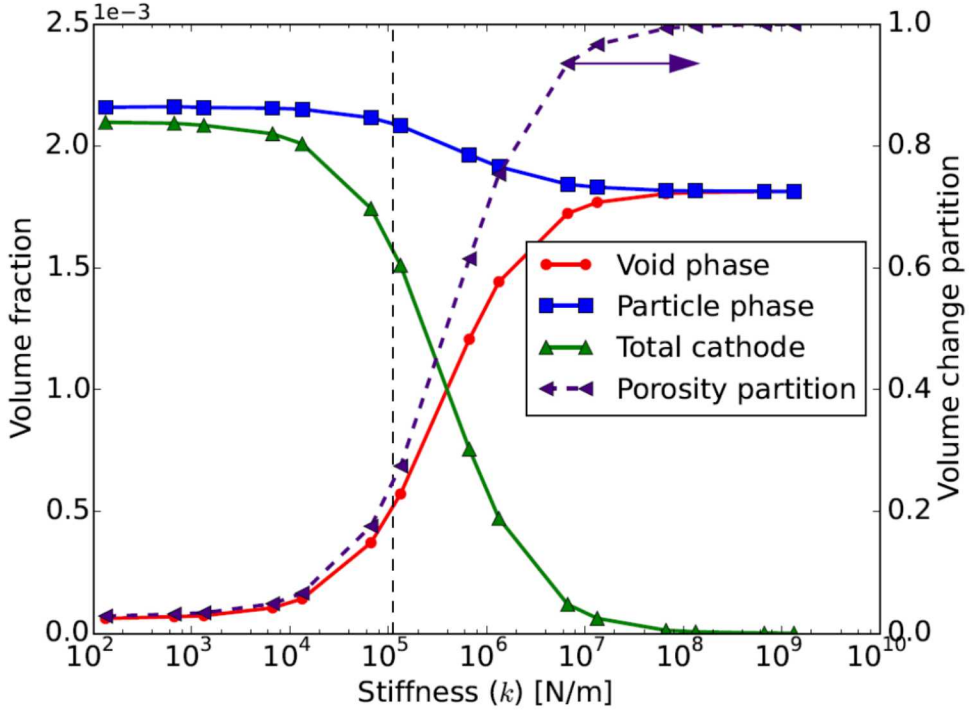
Ferraro, in preparation

What can you learn from coupled half-cell simulations?





LCO is a non-ideal solution, gradients not as dominant as some believe



Separator/collector stiffness/boundary conditions influence electrode mesostructure evolution

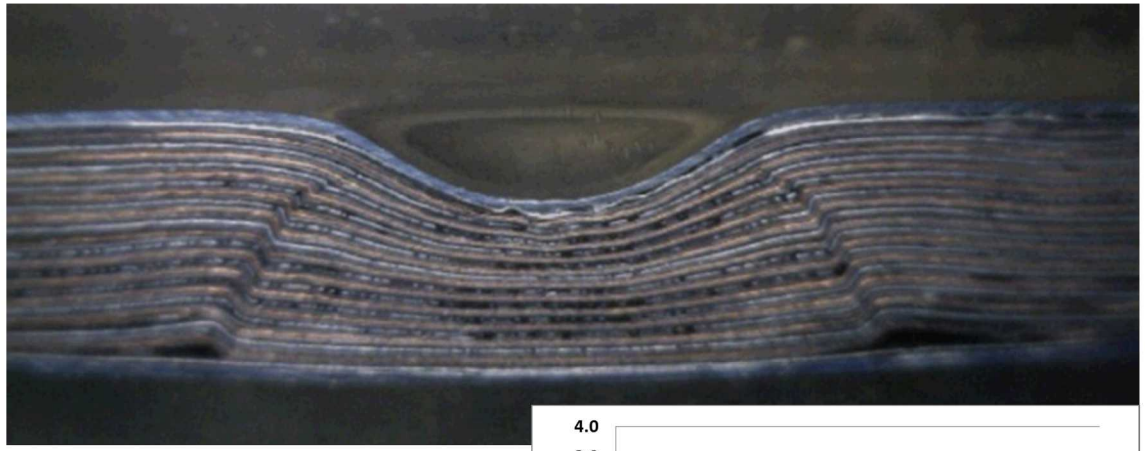
Details at the mesoscale influence cell performance … and vice versa!

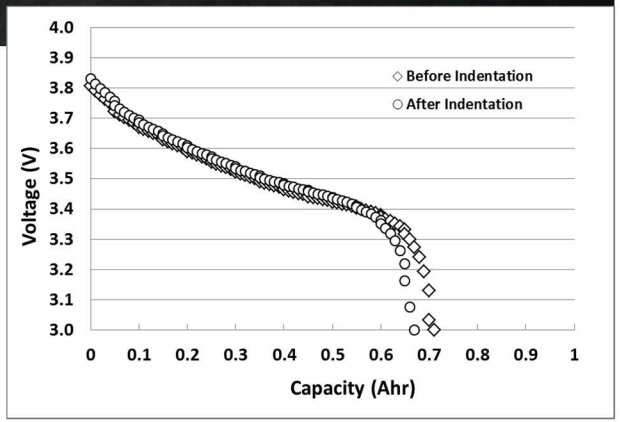
Ferraro, in preparation; Mendoza (2016)

Upscaling effective properties for pouch-level modeling

Functional forms as function of porosity integrated into VIBE/OAS and compared to simulation

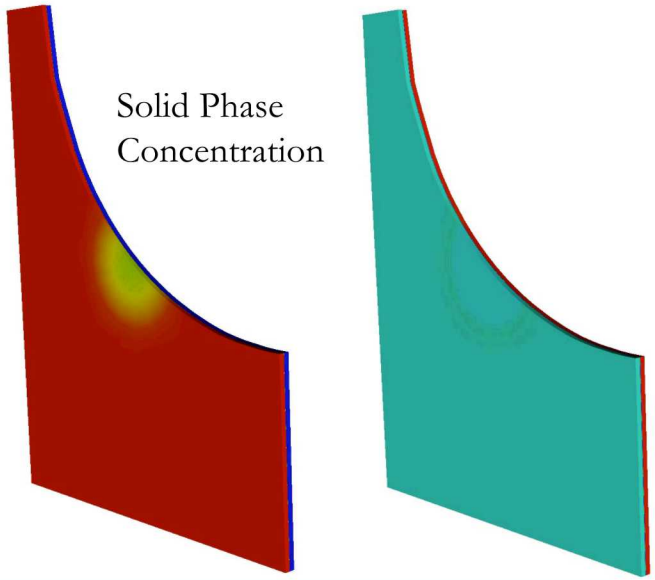
- 10 cell pouch with 80 μm electrodes
- Indented with 13 mm diameter spherical indenter
- Modeled mechanics of indentation (porosity change)
- Simulated 1C discharge

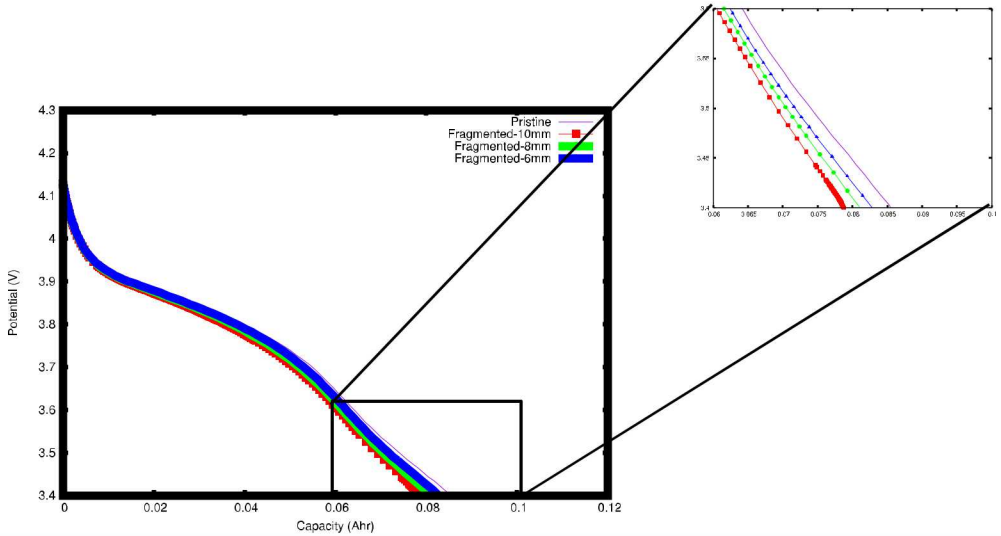




Solid Phase Potential

Solid Phase Concentration





Pouch simulation with effective properties shows similar-scale capacity decrease; demonstrates mesoscale integration

Allu, in preparation

Summary

We have developed a **unique image-to-mesh capability** to enable rapid analysis of as-manufactured parts

We can augment imaging with **physics-based mesostructure generation**

We have applied this technique to **lithium-ion battery cathode** mesostructures and have:

- Created and characterized the impact of conductive binder morphology
- Calculated and correlated effective properties
- Predicted coupled electrochemical-mechanicals effects during charge/discharge

We can **upscale mesoscale predictions** to impact cell/pouch-level simulations

Publications available upon request

Data

- V. Wood Group – ETH Zurich
- S. Thiele Group – U. Freiburg
- L. Zhu Group – IUPUI

Funding

- Sandia's Laboratory Directed Research and Development (LDRD) program – 2013-2016, 2018-2021
- Computer Aided Engineering for Batteries (CAEBAT) program, DOE/EERE/VTO – 2015-2019

Mesoscale modeling is a powerful tool for predicting electrode behavior under extreme environments

Questions?

Scott A. Roberts, Ph.D.
Thermal/Fluid Component Sciences Department
Sandia National Laboratories, Albuquerque, NM
http://www.sandia.gov/~sarober/
sarober@sandia.gov