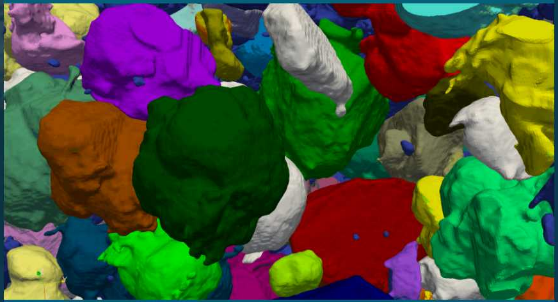
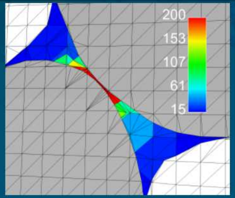
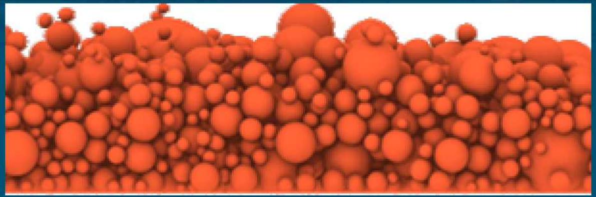
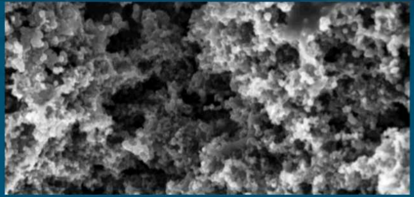
SAND2019-8209C

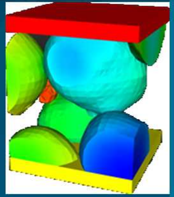
Impact of Mesoscale Morphology on Electrode Performance through Multi-Physics Simulations











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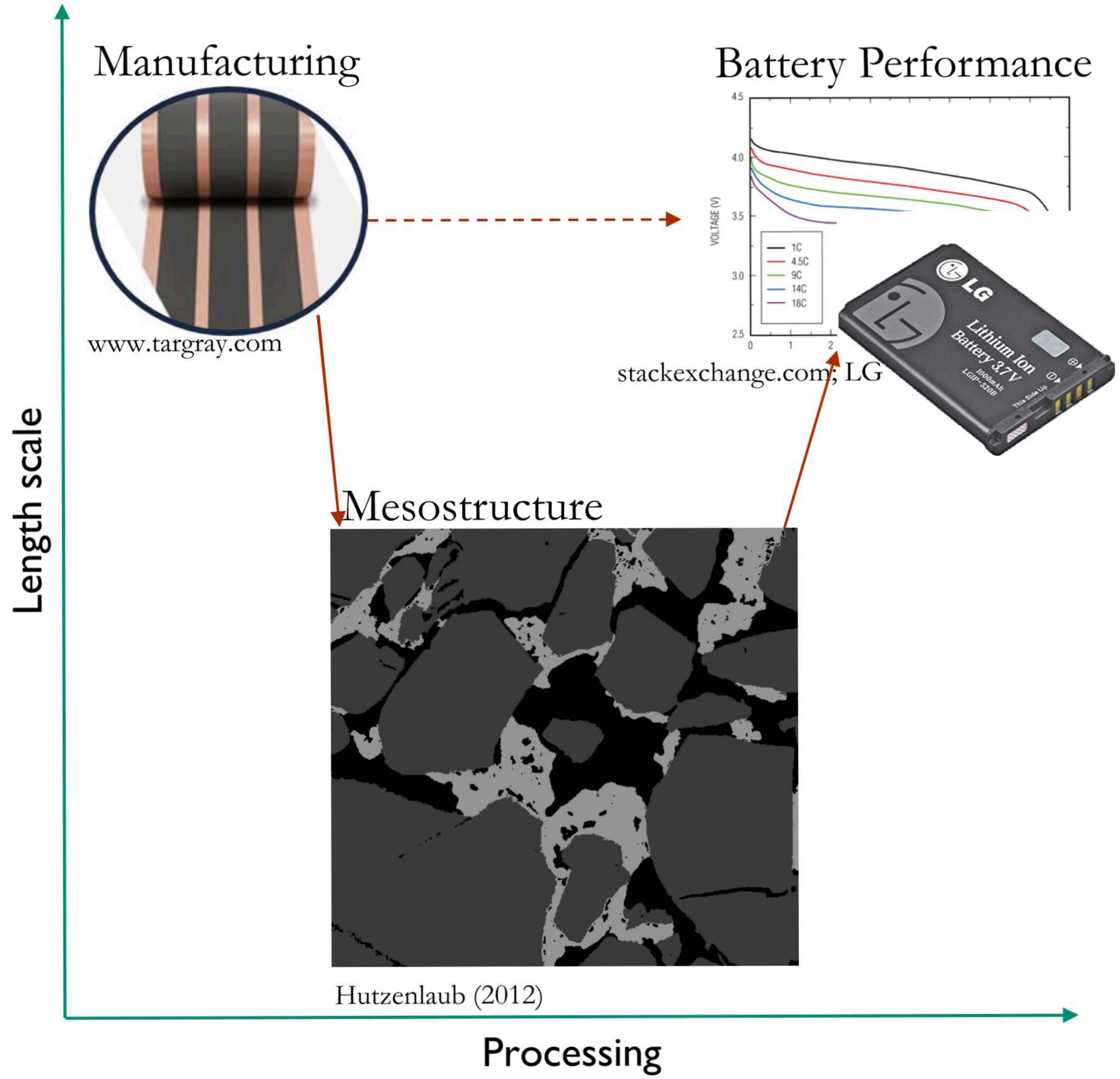
PRESENTED BY

Scott A. Roberts, Ph.D.

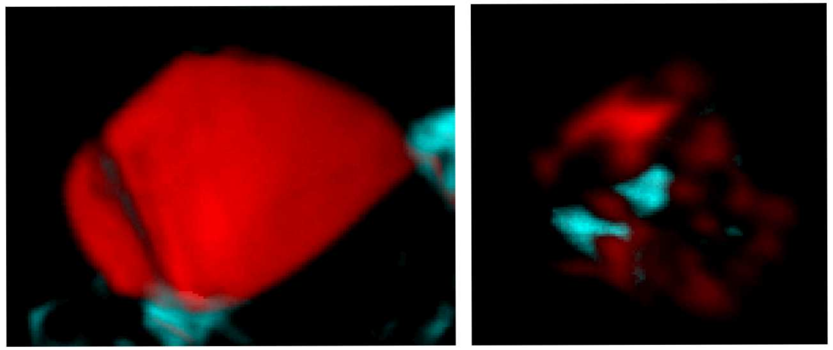
Electrochemical Conference on Energy and the Environment

July 23, 2019

Motivation

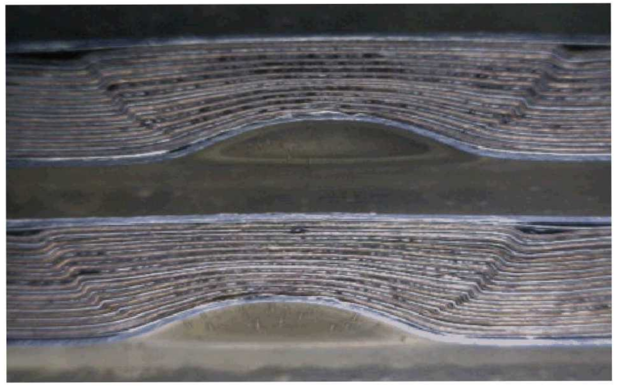


Lithiation-Induced Fracture

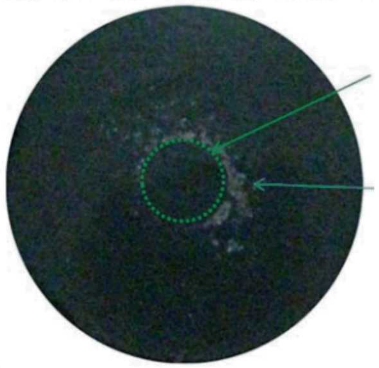


LiCoO2 STXM, Farid El Gabaly Marquez (Sandia)

Mechanical Abuse → Electrochemistry / Mesostructure



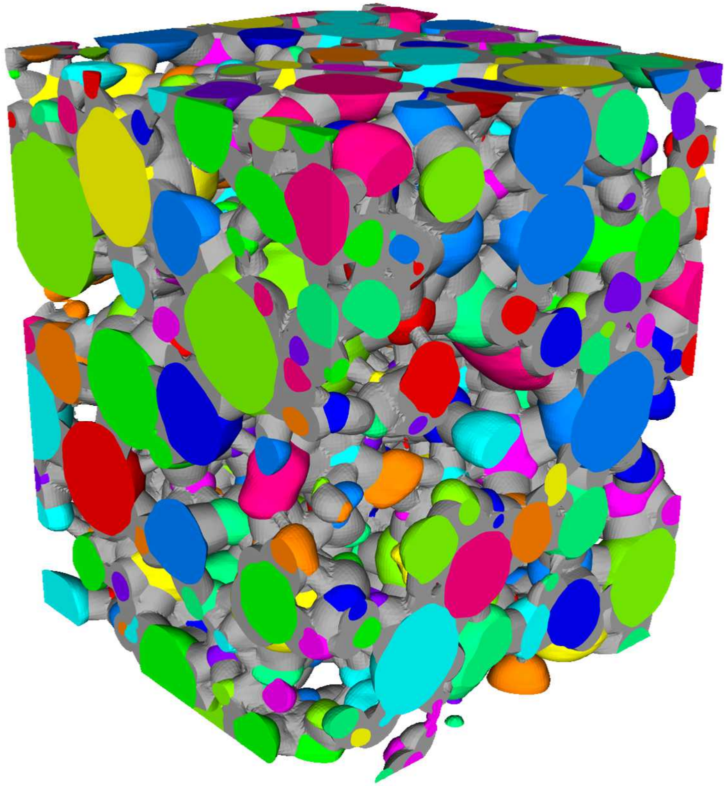
NMC/graphite pouch, H. Wang (ORNL)



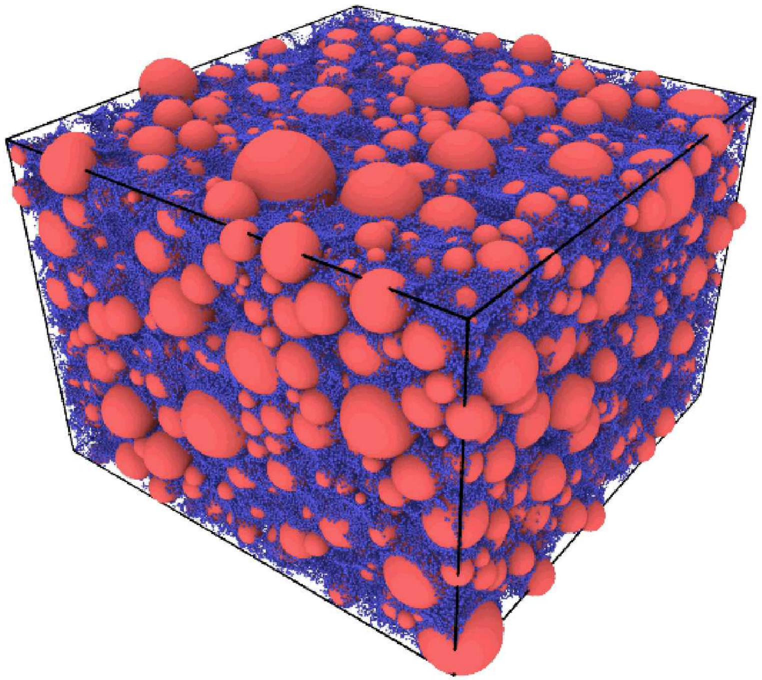
Cannarella/Arnold (2015)

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

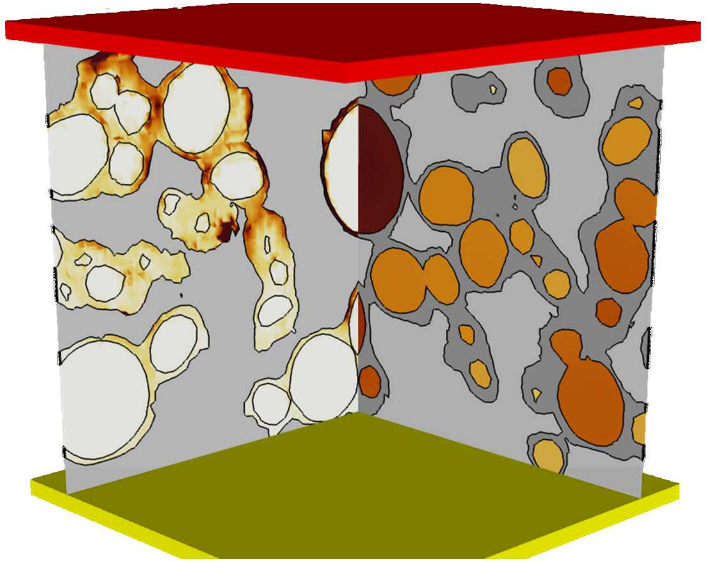
Outline



Computational representation of imaged electrode mesostructures with conductive binder addition

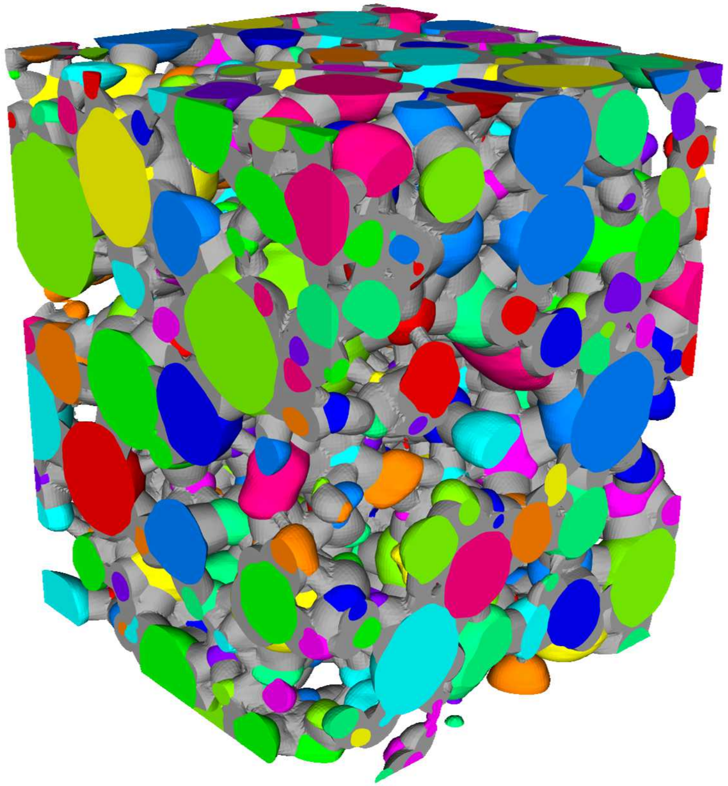


Discrete element method mesostructure generation including conductive binder



Electrochemical-mechanical discharge of NMC half-cells

Outline



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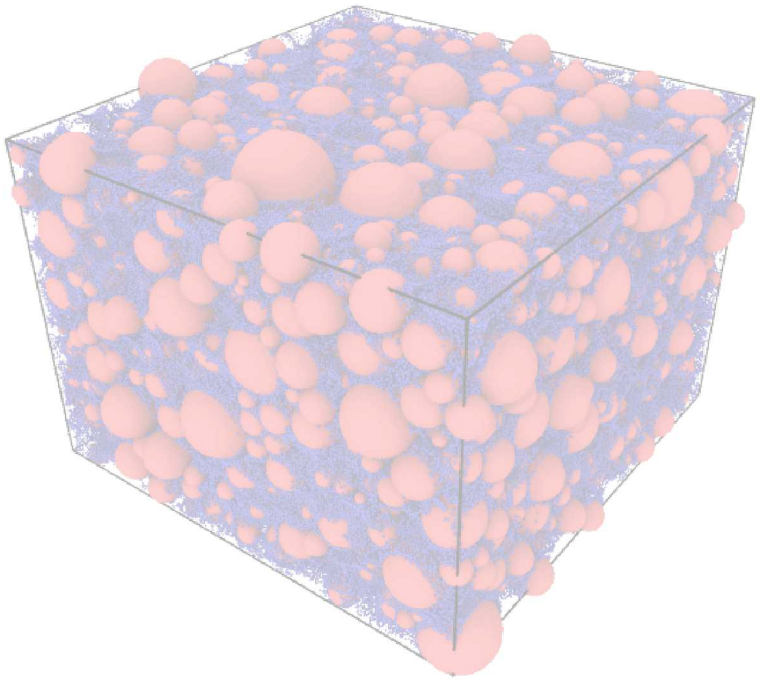
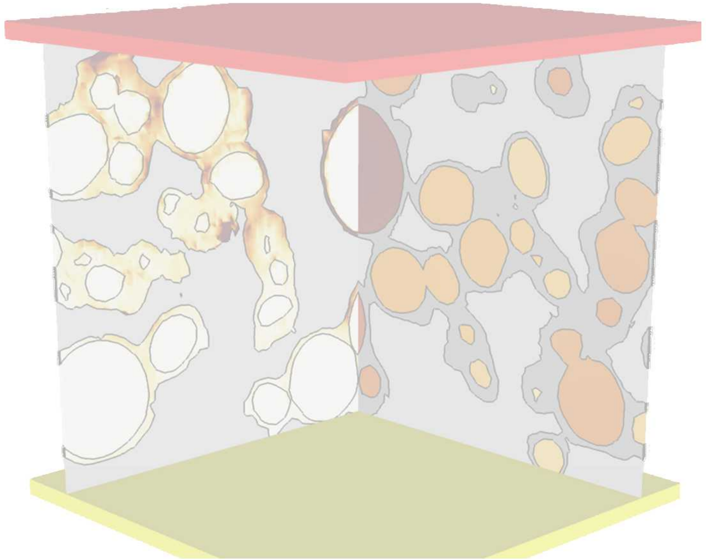
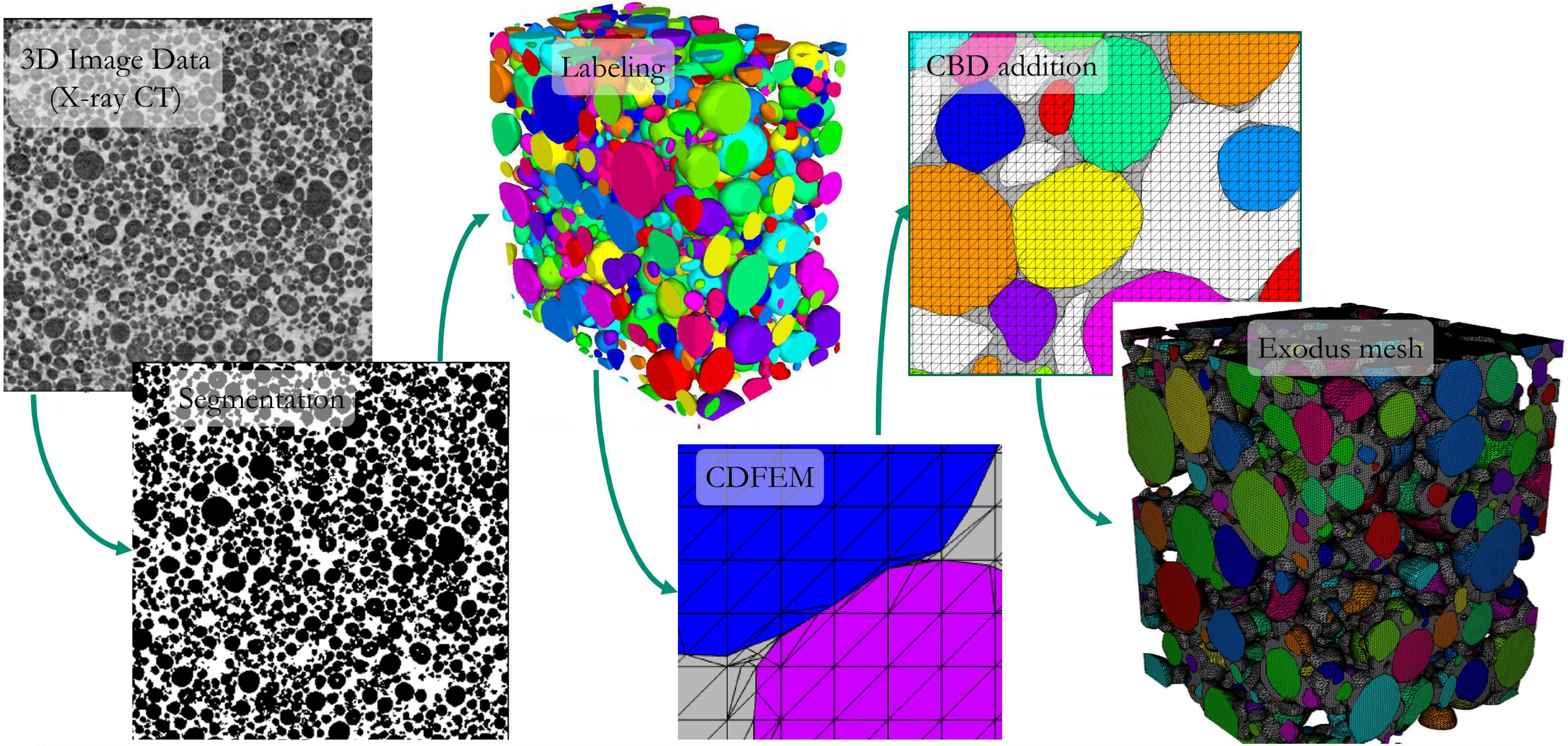


Discrete element method mesostructure generation including conductive binder



Electrochemical-mechanical discharge of NMC half-cells

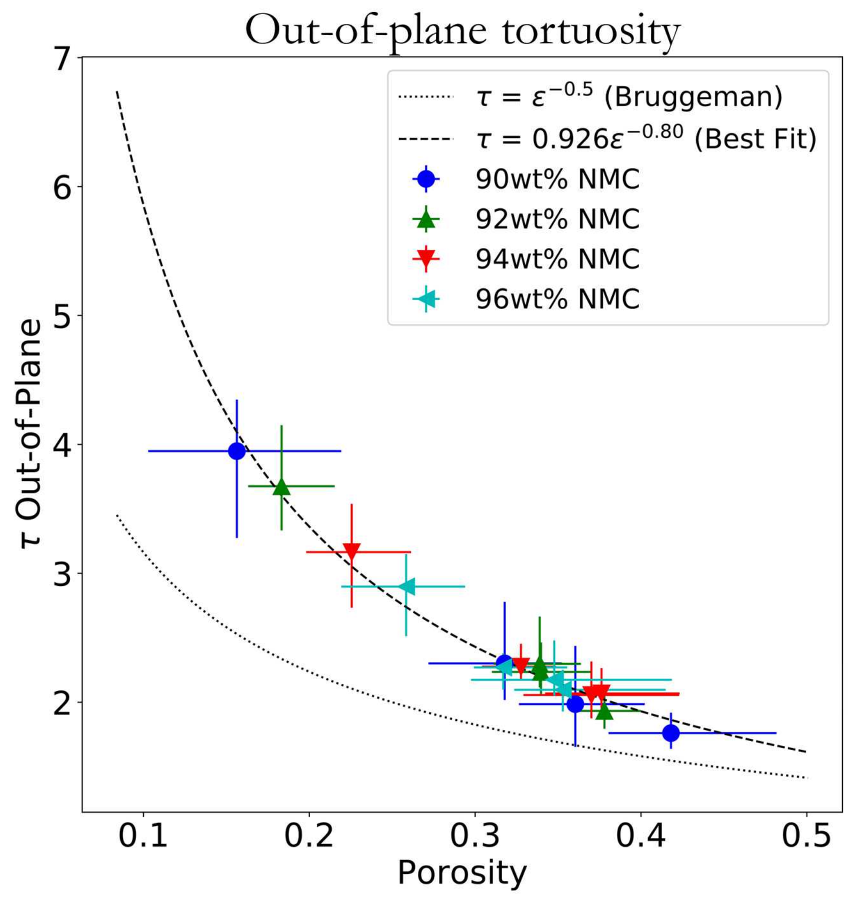
Mesoscale geometry from CT data using CDFEM

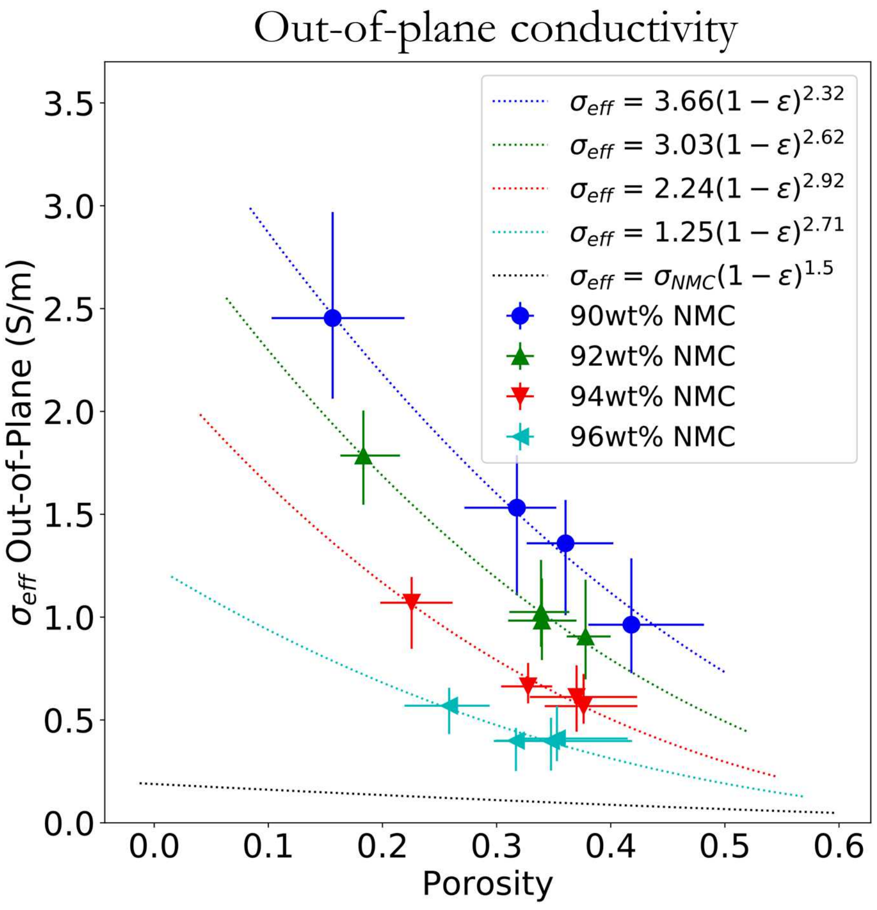


Detailed 3D reconstruction and image processing necessary to get usable mesostructure data

Roberts JES 2014, Roberts JEECS 2016, Trembacki JES 2017, Roberts JCP 2018, Trembacki JES 2018

Effective electrode property calculation results – Transport





Bruggeman relationships must be re-calibrated to fit simulated data

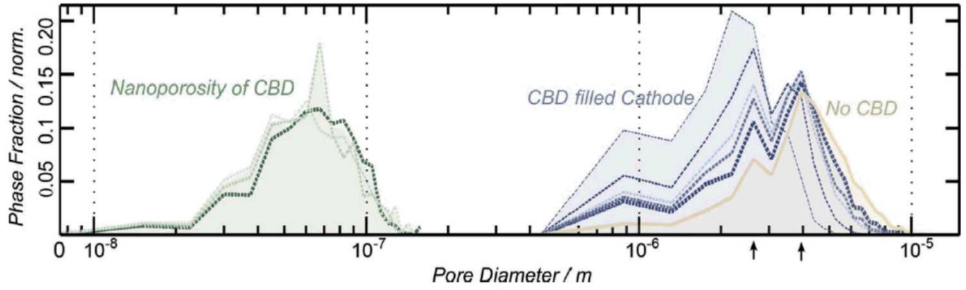
Trembacki, in preparation

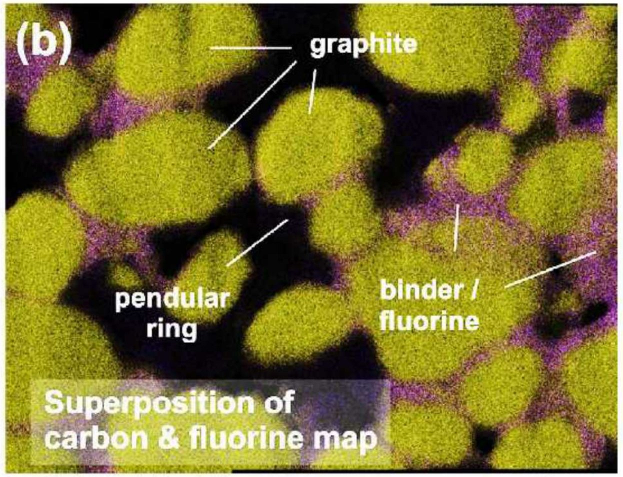
What about the conductive binder?

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

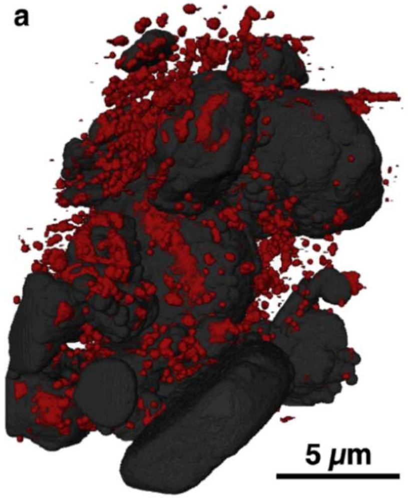
Amorphous binder is significantly nanoporous
- 47% Zielke (2015); 45% Grillet (2016)
- 5% ionic conductivity of pure electrolyte

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

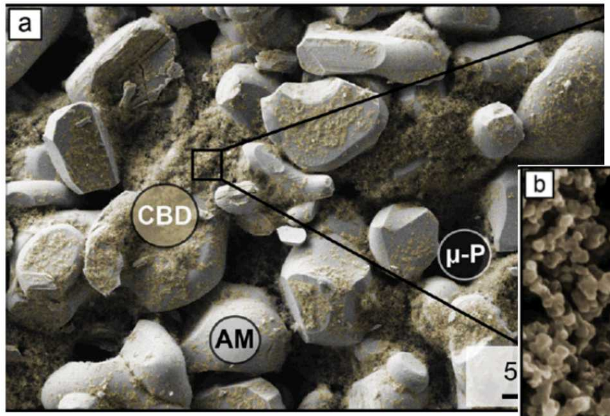


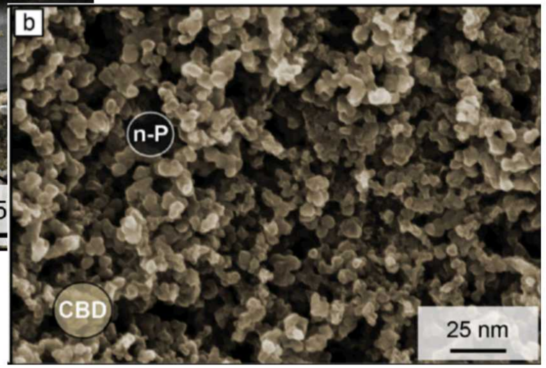


Graphite; Jaiser et al. (2017)



LCO; Komini Babu et al (2015)

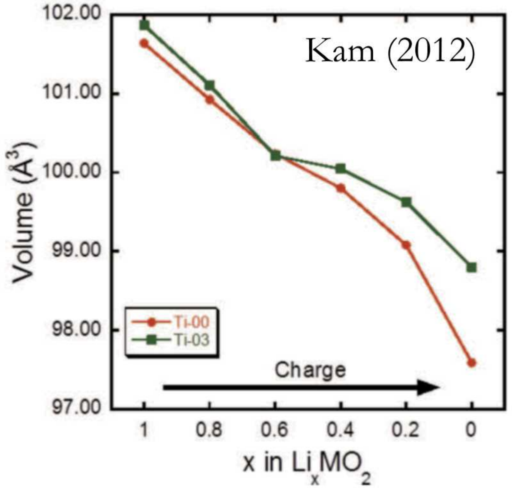


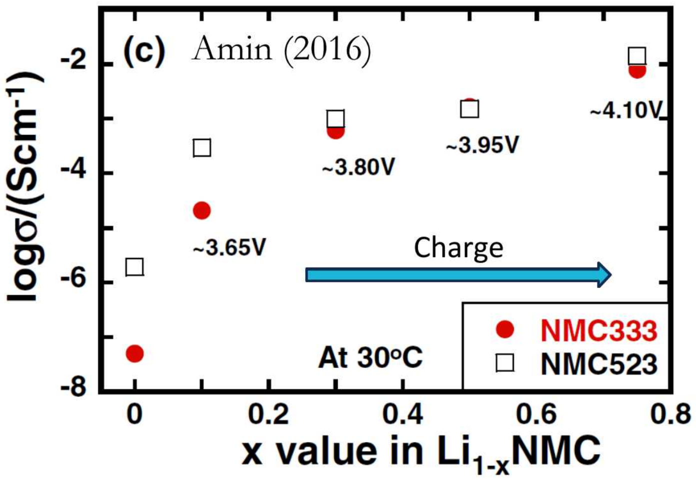


LCO; Zielke et al (2015)

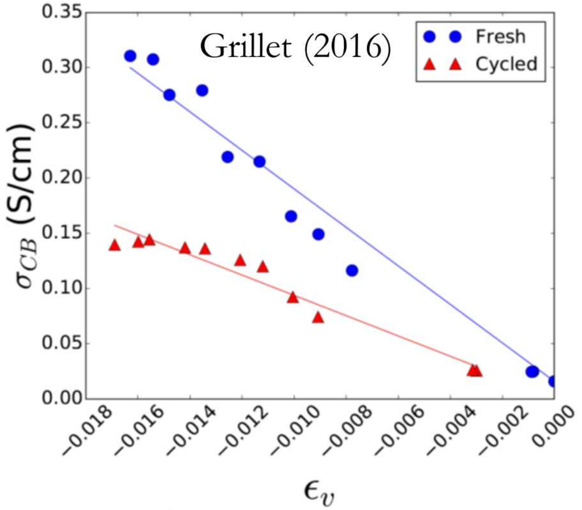
How are electrode-scale properties affected by the inclusion of binder? How does the morphology matter?

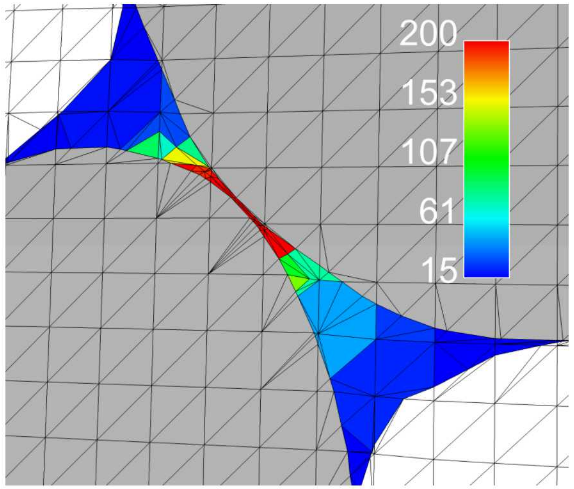
Why does the conductive binder domain (CBD) morphology matter?



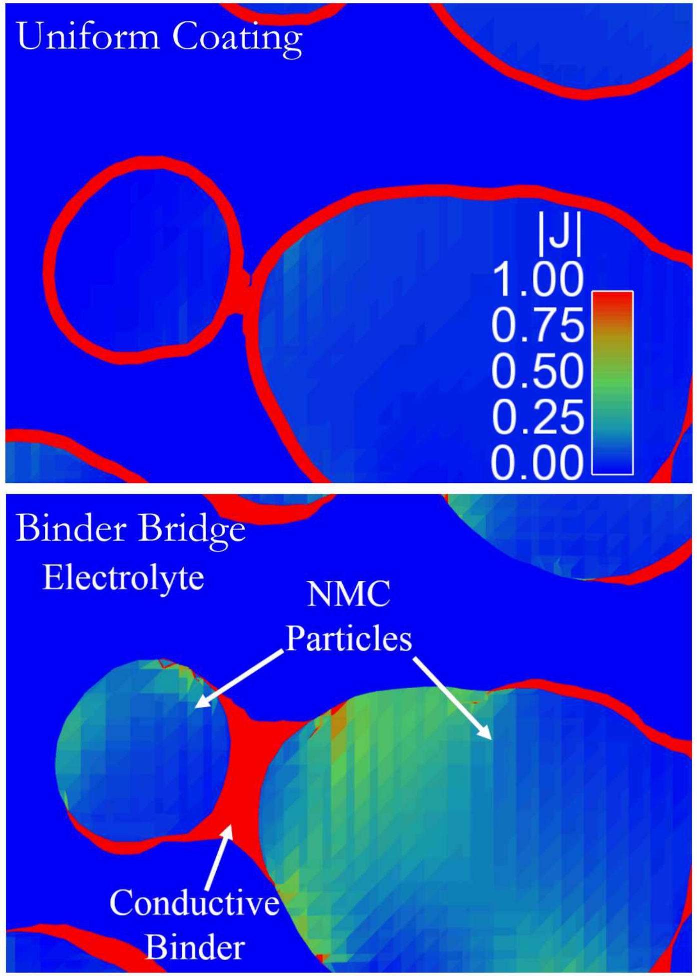


NMC swells on discharge, compressing binder





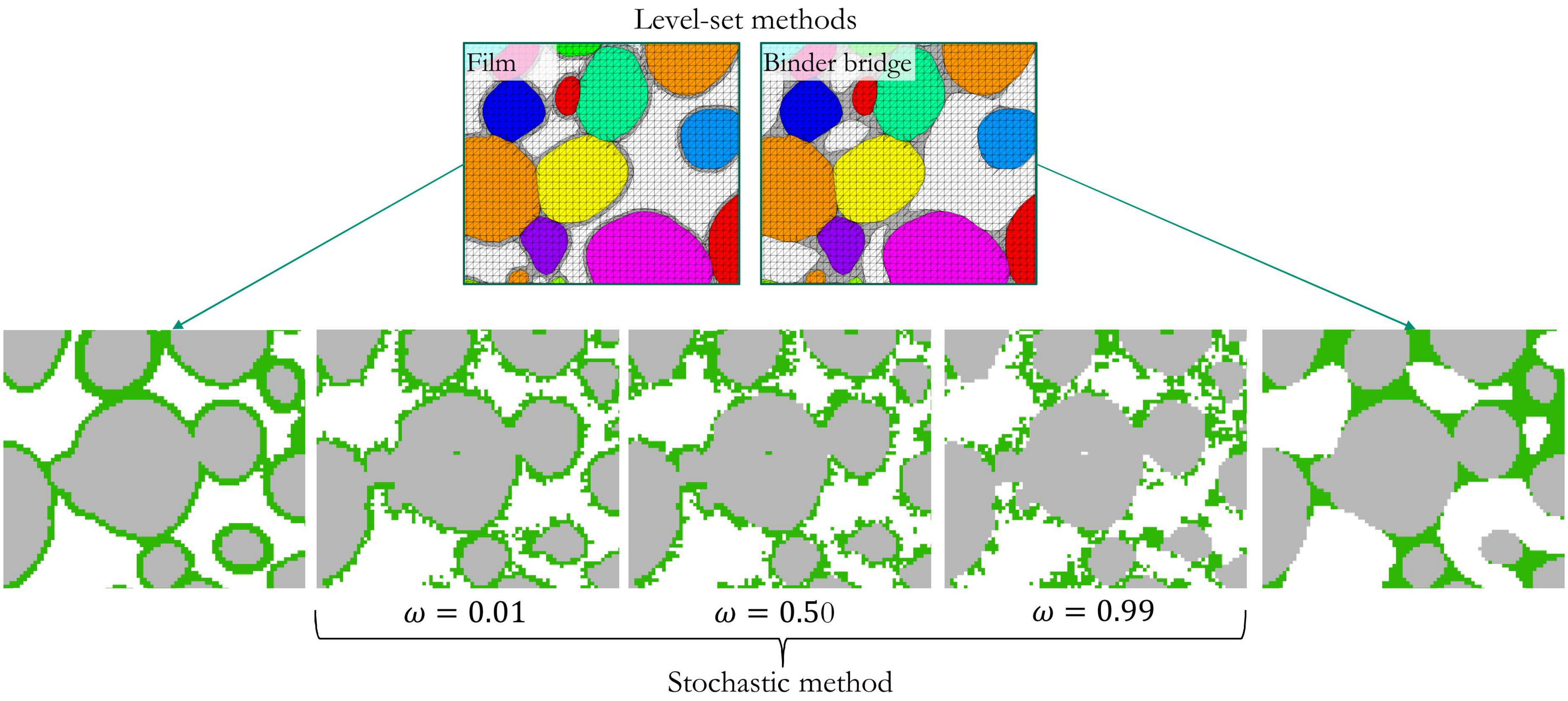
Binder has strain- (e.g. lithiation-) dependent properties



Binder morphology controls electrical transport pathways

CBD morphology is critical for determining transport and can fill up to 40% of pore space

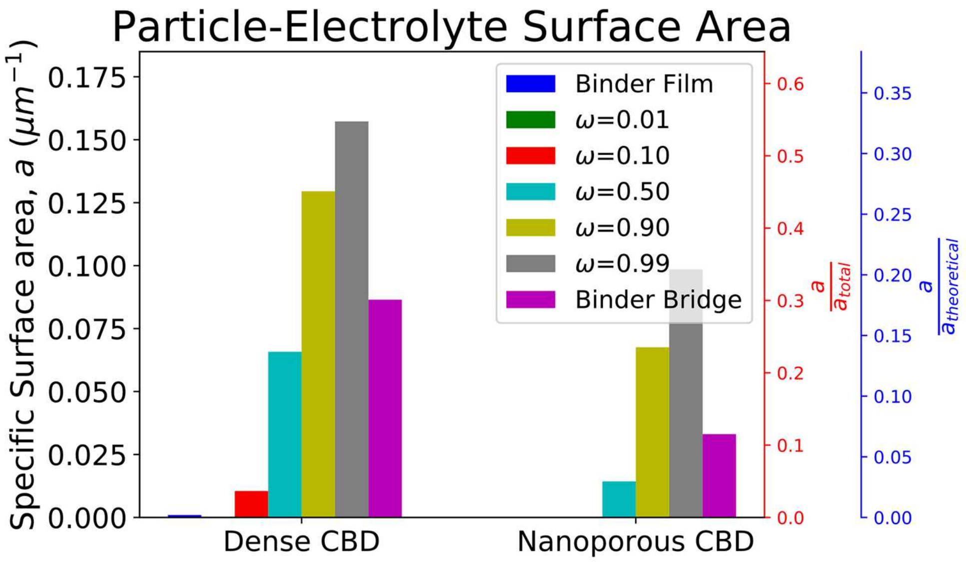
Binder bridge morphology approaches



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

Trembacki JES 2018

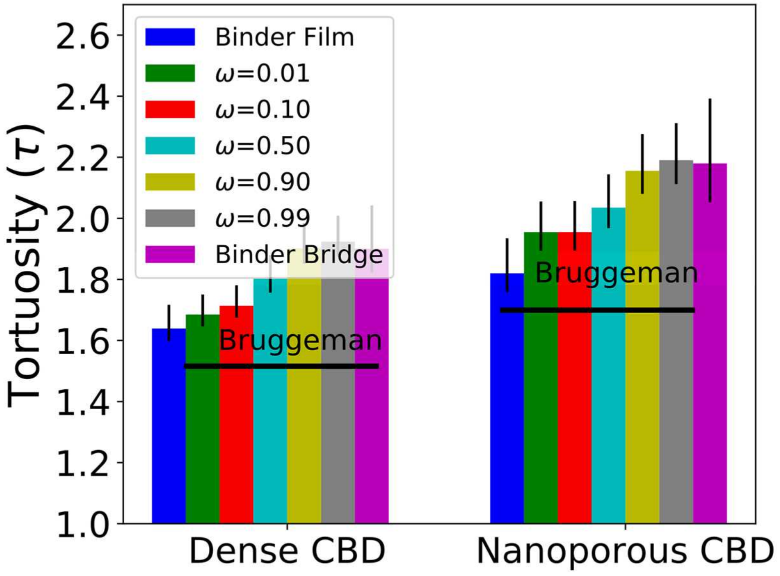
Porous binder and morphology considerations

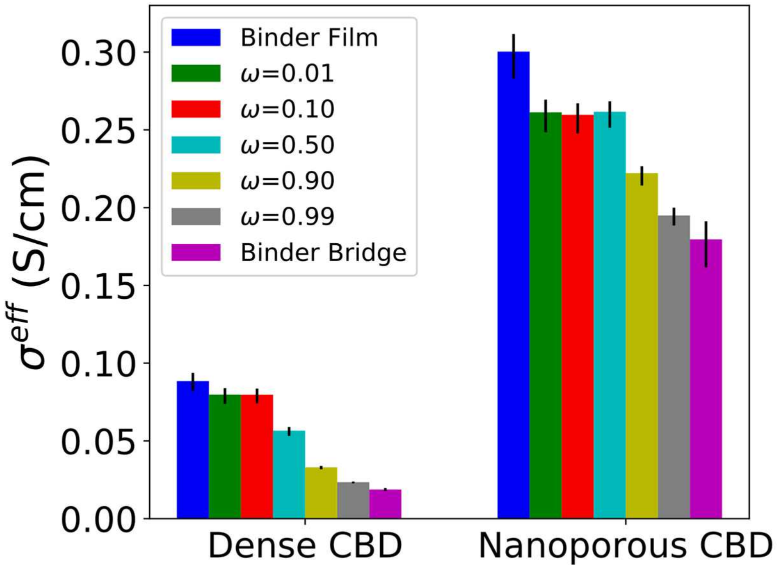


- More particle surface area available with non-uniform morphologies
- Nanoporous binder decreases bare particle surface area, but binder area is porous
- Surface are much less than theoretical

Non-uniform binder:
- Increases tortuosity
- Decreases conductivity

Nanoporosity:
- Increases tortuosity
- Increases conductivity

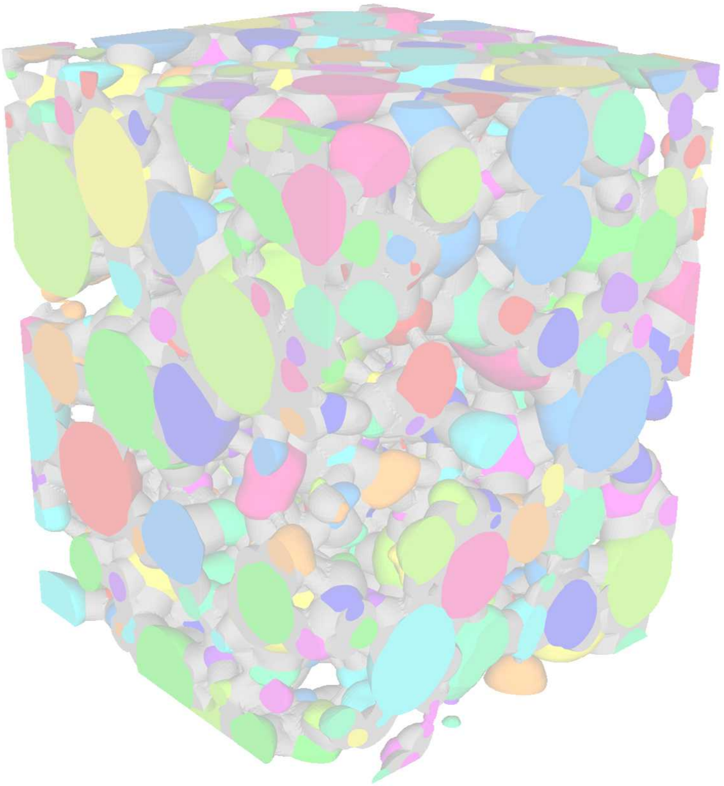




Limiting cases of both morphology methods show similar (but not identical) behavior; nanoporosity is important!

Trembacki JES 2018

Outline



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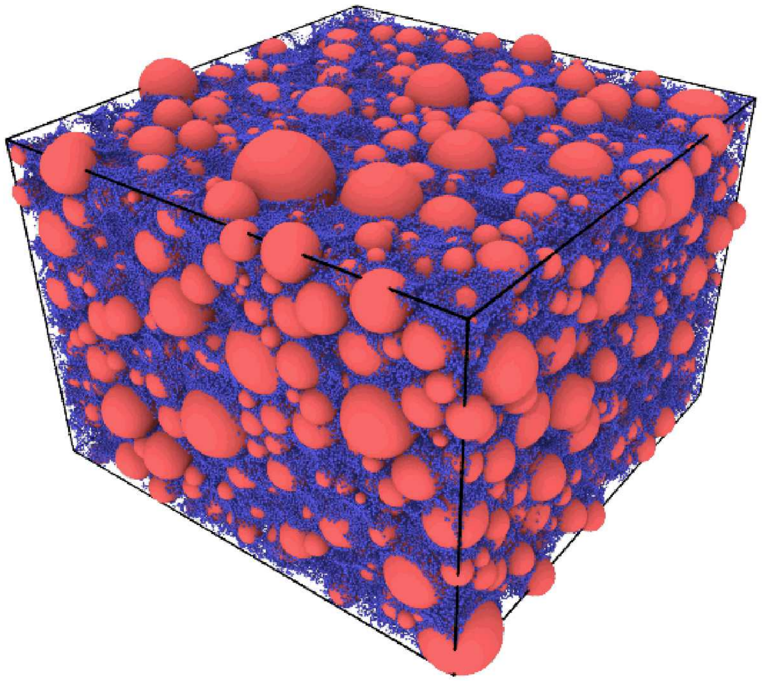
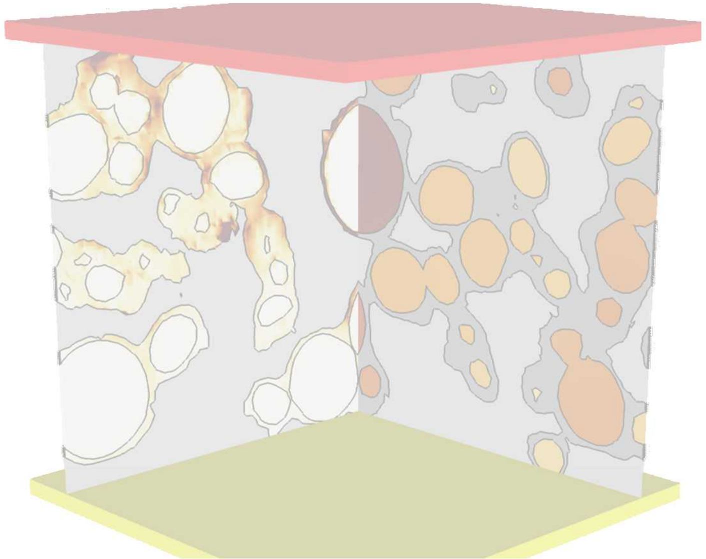
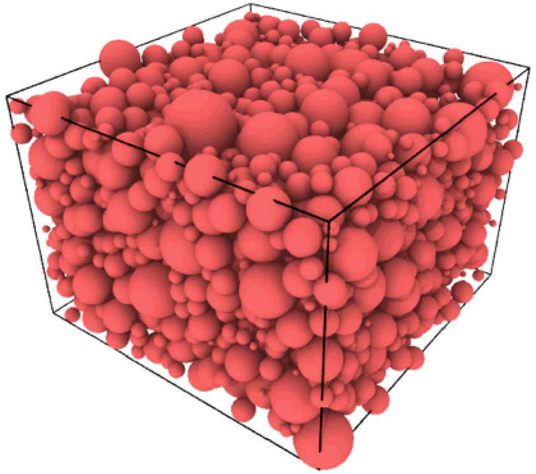


Discrete element method mesostructure generation including conductive binder



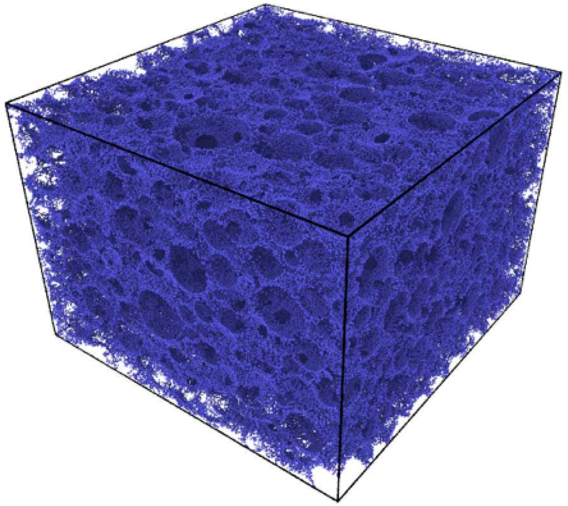
Electrochemical-mechanical discharge of NMC half-cells

Discrete Element Method



Active Material:
- Elastic
- Frictional
- Cohesive
- Polydisperse (2-20 microns) from experiments[1]

[1]Ebner et al., Adv. En. Mat., 3 (2013)



Coarse-grained CBD gel:
- Brownian
- Frictional
- Cohesive
- Monodisperse (500 nm)

Inter-particle interactions

$$F_{\text{total}} = F_{\text{JKR}} + F_{\text{visc}} + F_{\text{brown}}$$

$$F_{\text{JKR}} = \left(\frac{4E\delta^3}{3a} - 2\pi\delta^2 \sqrt{\frac{4\gamma_c E}{\pi\delta}} \right)$$

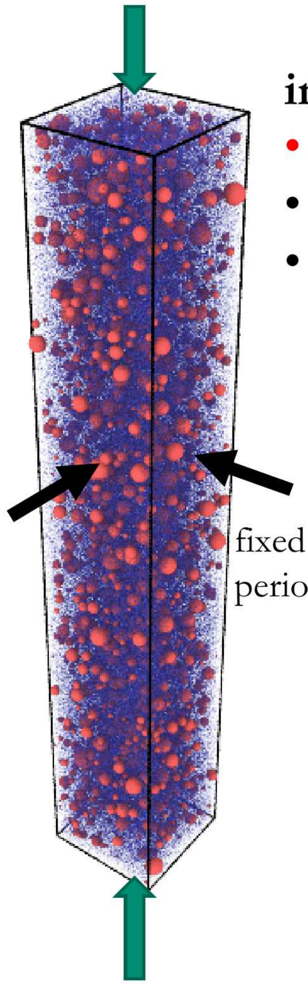
$$F_{\text{visc}} = 6\pi\eta a v$$

$$F_{\text{brown}} = \sqrt{2mk_B T\eta\delta(t)}$$

Combined Granular and Brownian Dynamics are simulated in LAMMPS

Srivastava, in preparation

Drying and calendaring



initial microstructure:

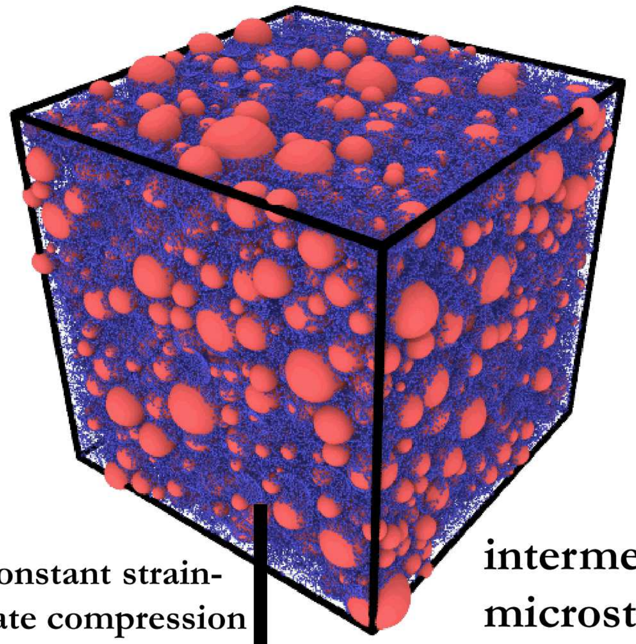
- **porosity: 90%**
- height: 700 um
- width: 100 um

fixed dimension
periodic boundary

uniaxial compression
periodic boundary

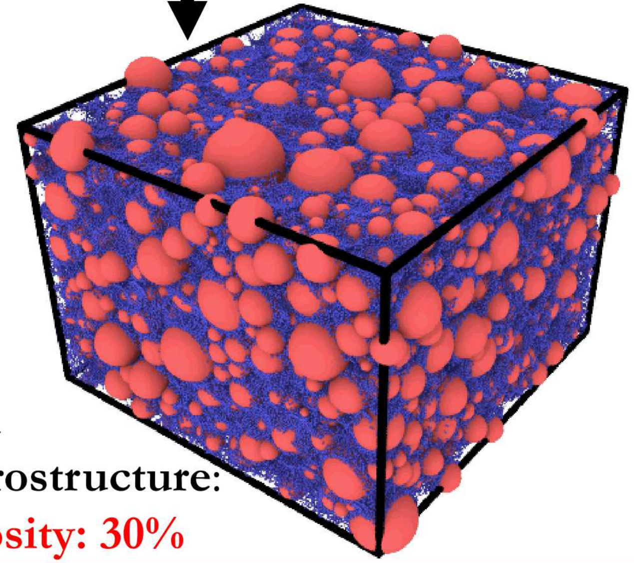
rapid initial compression

slurry deposition + drying



intermediate microstructure:
porosity: 50%

constant strain-rate compression (calendaring)



final microstructure:
porosity: 30%

Design Space (960 sims, 50M core-hrs)

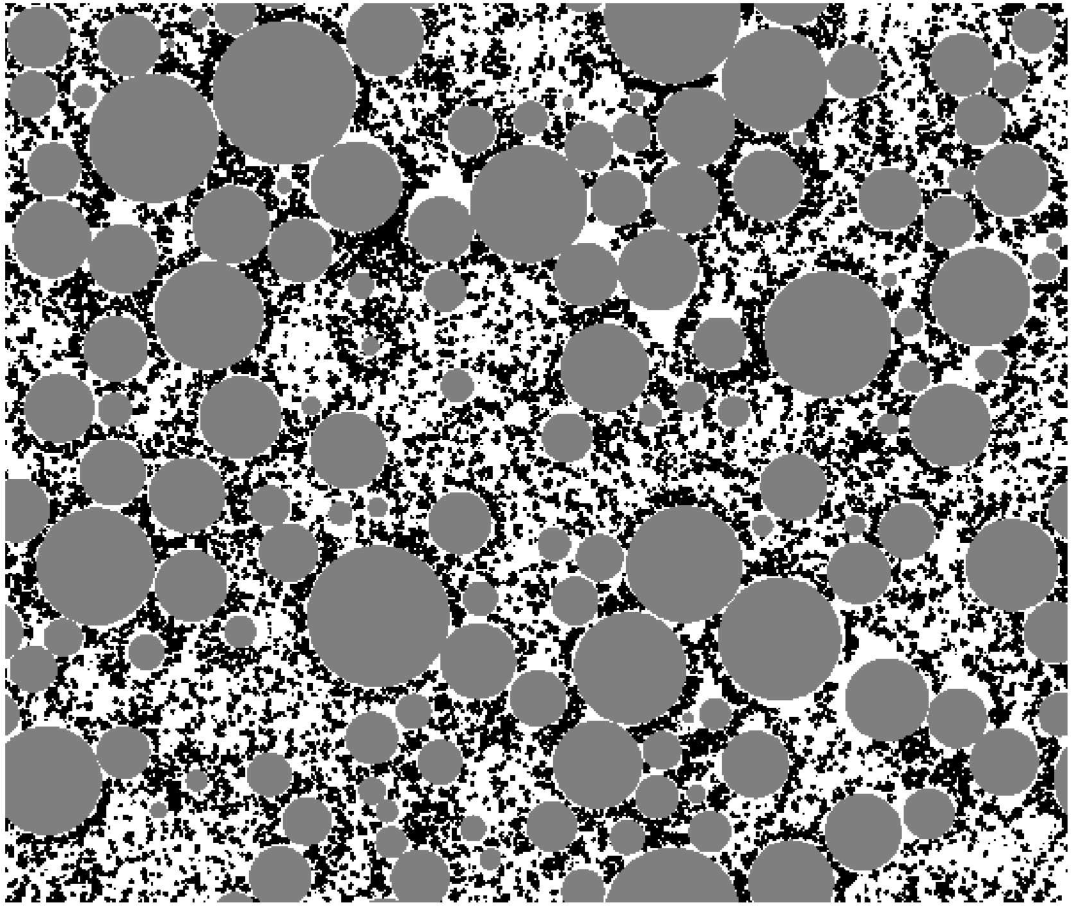
Property	Parameters
AM weight percentage [%]	90 – 96
CBD-CBD cohesion ratio	10^{-1} – 10^{2}
AM-CBD adhesion ratio	10^{-1} - 10^{2}
Porosity	0.5 – 0.3
Stochastic realizations	3

Simulate electrode fabrication using physical models

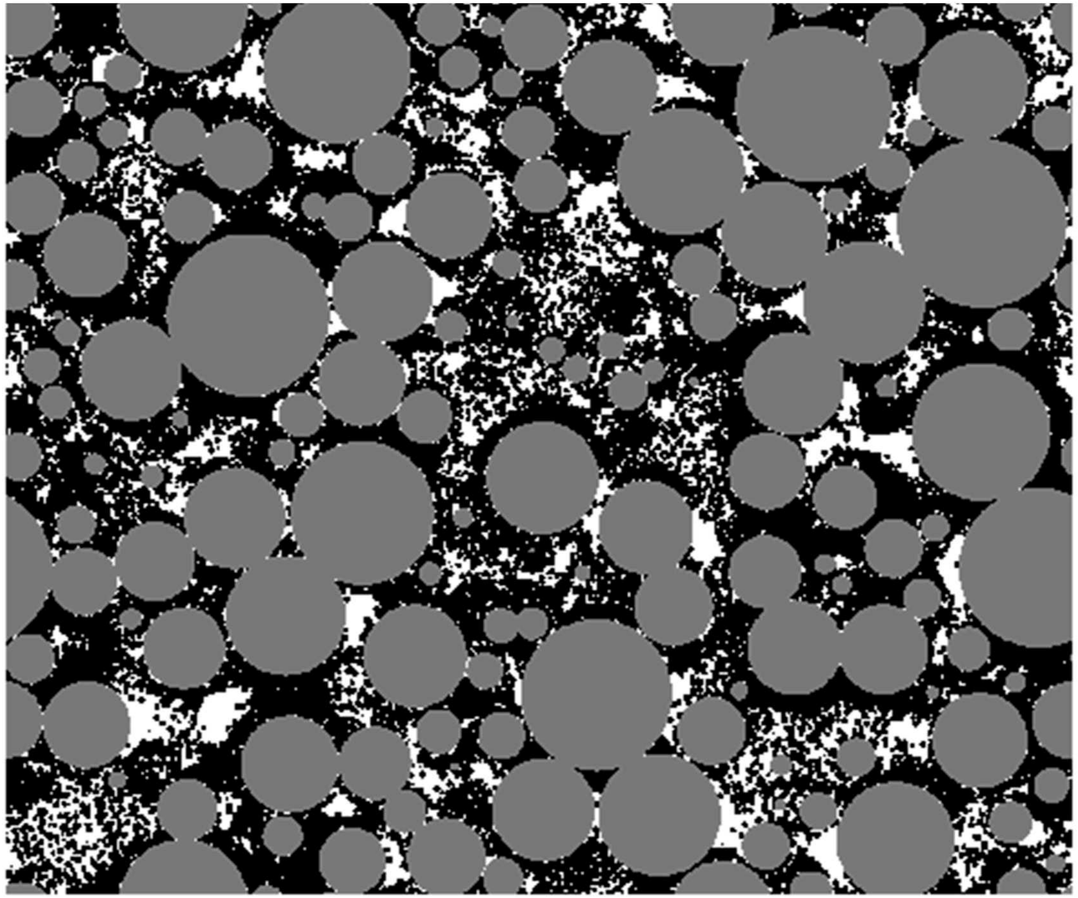
Srivastava, in preparation

Mesostructure phase distribution

Low AM-CBD adhesion; High CBD-CBD cohesion; High 50% porosity



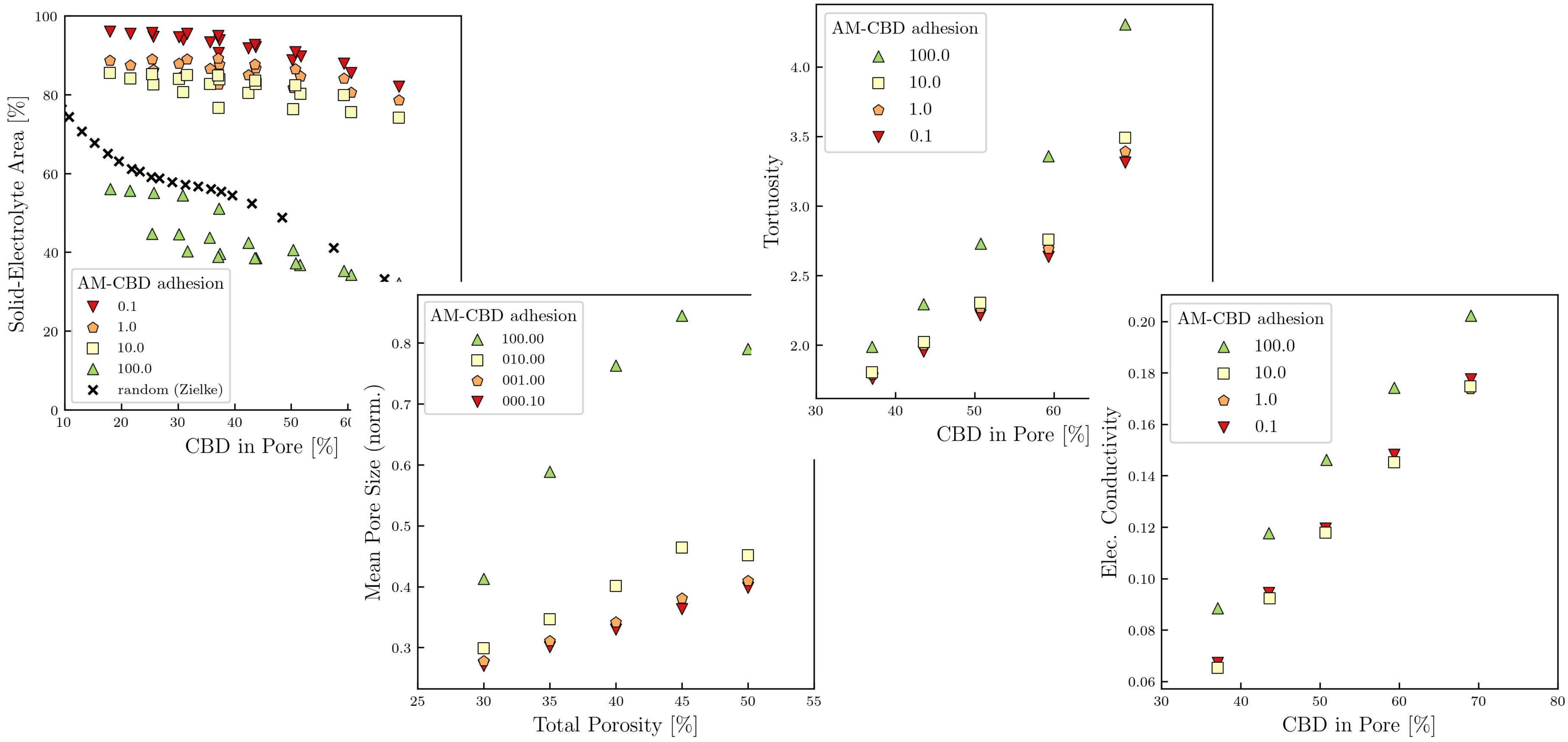
High AM-CBD adhesion; Low CBD-CBD cohesion; Low 30% porosity



Adhesion and cohesion between CBD and AM significantly changes electrode morphology

Srivastava, in preparation

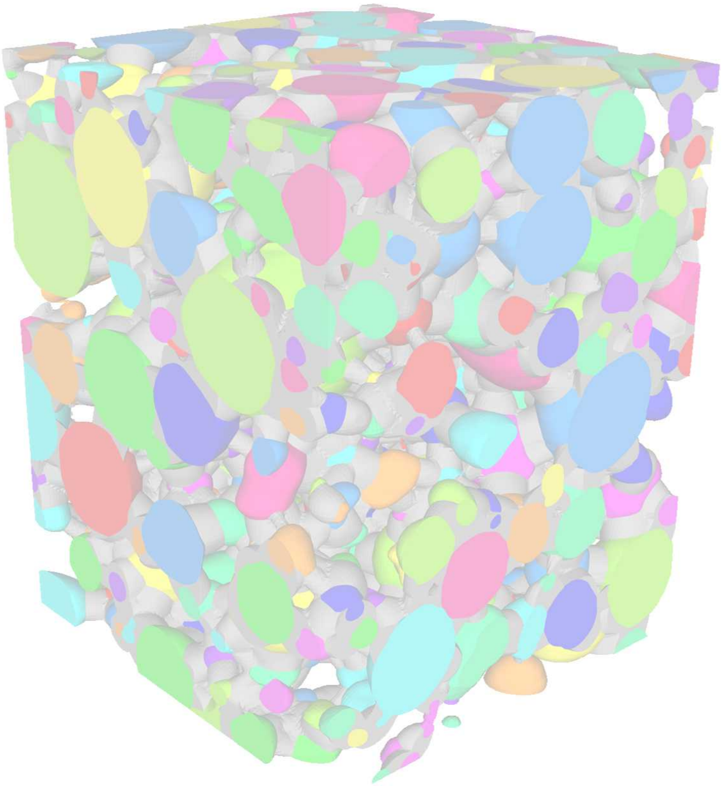
Electrode properties from DEM



CBD chemistry strongly influences electrode effective properties

Srivastava, in preparation

Outline



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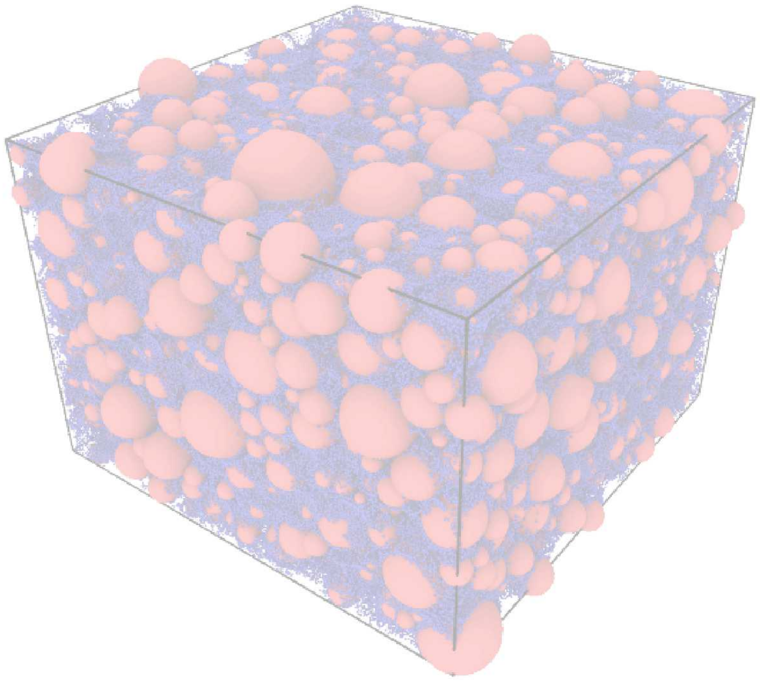
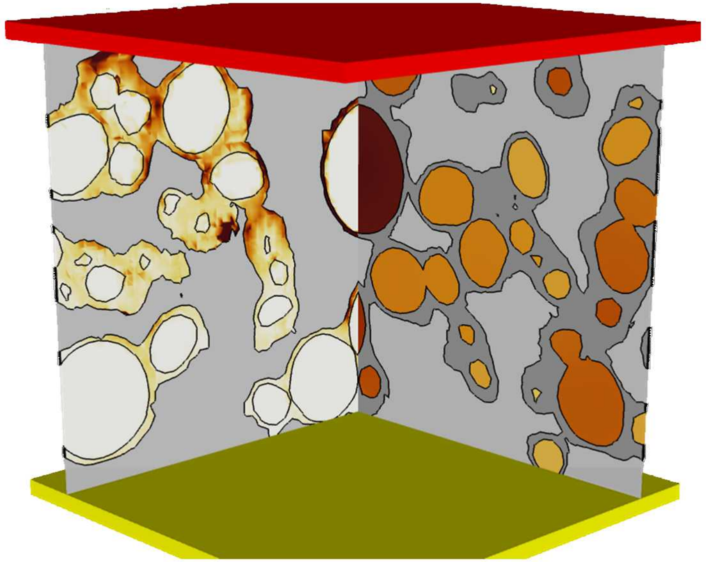


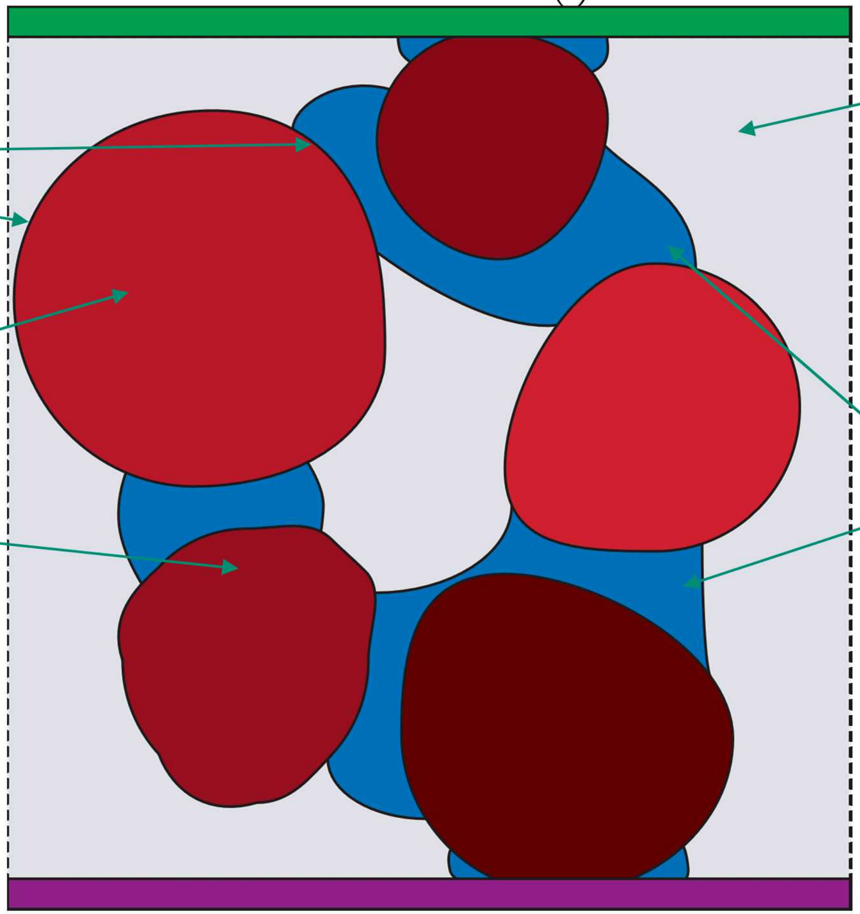
Discrete element method mesostructure generation including conductive binder



Electrochemical-mechanical discharge of NMC half-cells

Coupled electrochemical-mechanical half-cell discharge simulations

Current collector: I(t)



Separator: $V_l = 0$

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

Particles:
- Species – Li transport
  - Chemical potential
  - Stress potential
- Electrical – Ohm's law
- Mechanics - Elastic
  - Li-induced swelling

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

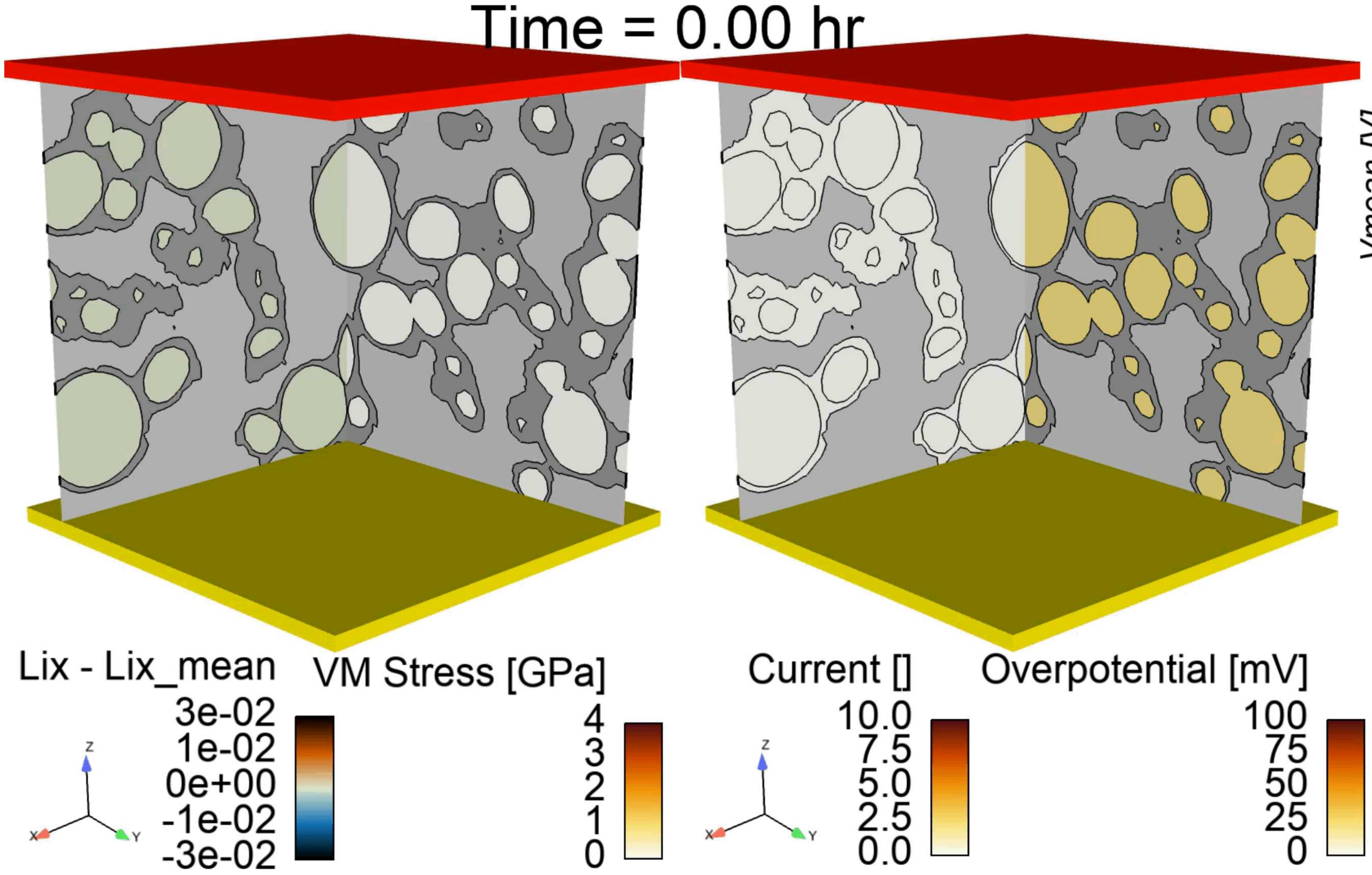
Conductive binder:
- Species – Porous Li^+ transport
- Electrical
  - Solid: Porous Ohm's law
    - Strain-dependent electrical conductivity
  - Liquid: Ionic conservation & electroneutrality
- Mechanics – Elastic

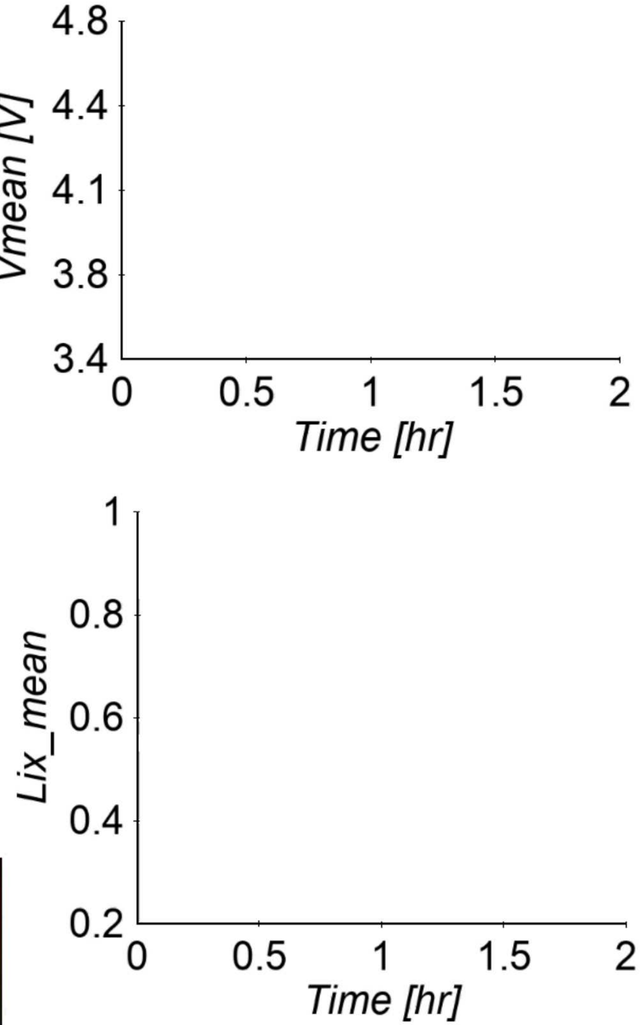
Mathematical formulation builds off of Mendoza (2016) LCO studies

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

Ferraro, in preparation

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

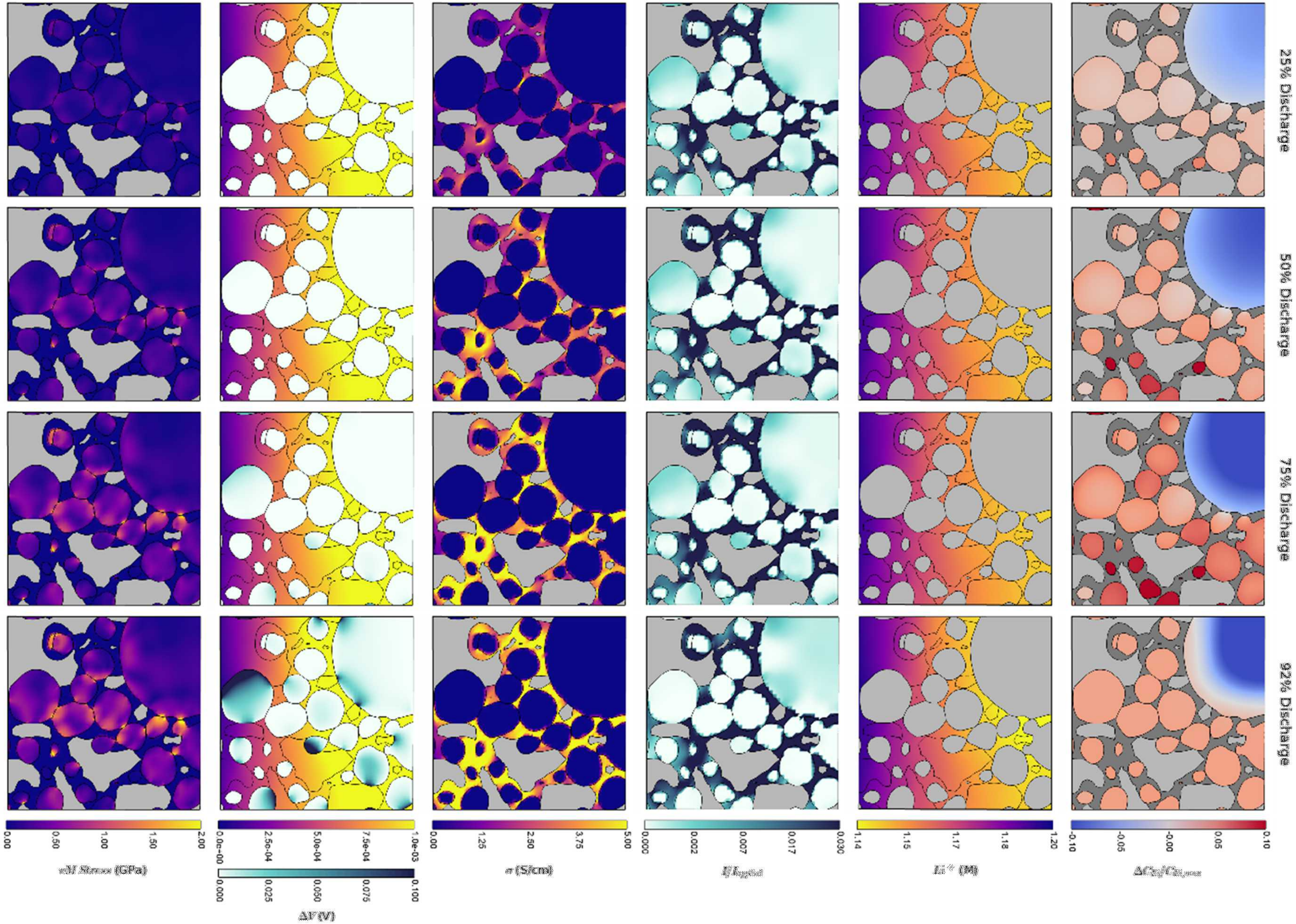




Coupled electrochemical-mechanical simulation yields detailed insight, predicts electrode-scale response

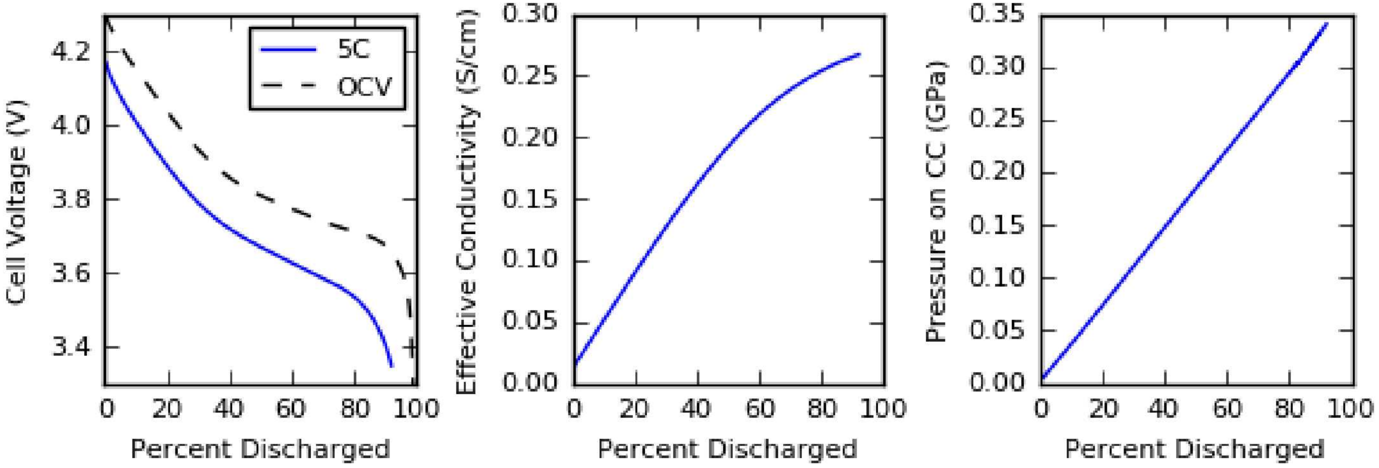
Ferraro, in preparation

Overview of electrochemical-mechanical behaviors

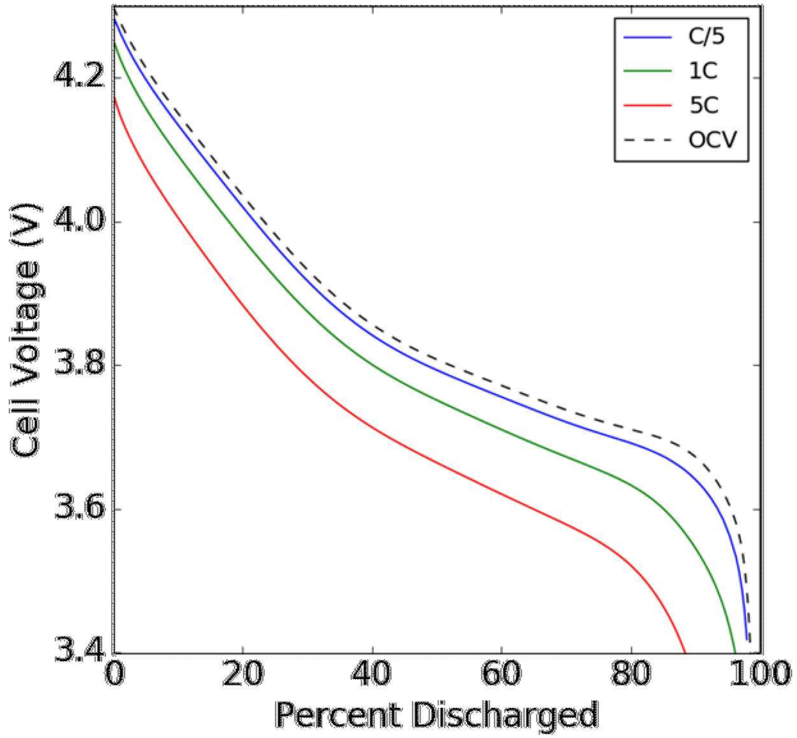


Ferraro, in preparation

Cell-scale behavior



Effective electrical conductivity and mechanical pressures increase during electrochemical discharge

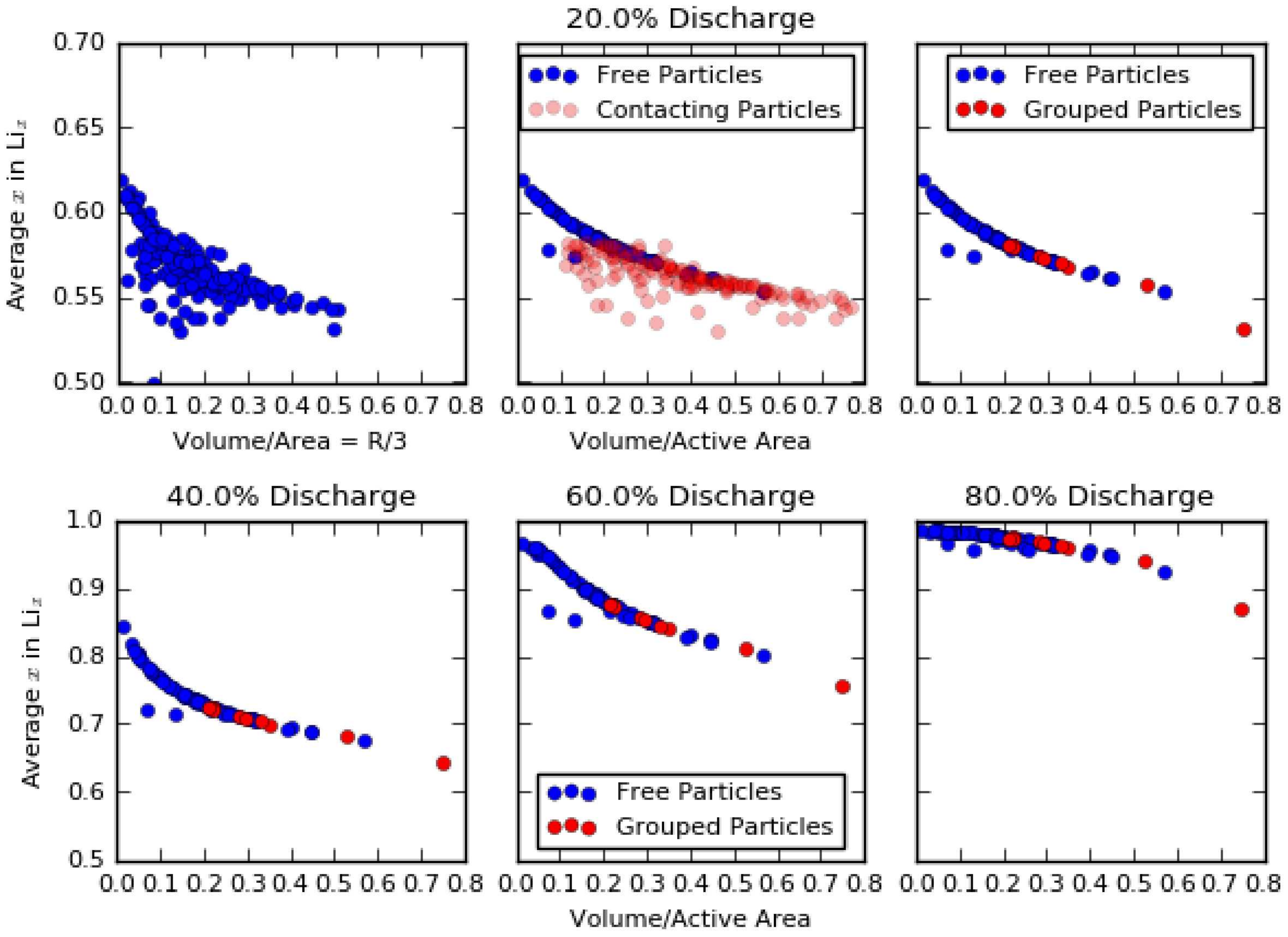


Predicting expected voltage polarization loss at high rates

Mesoscale model predicts cell-scale performance

Ferraro, in preparation

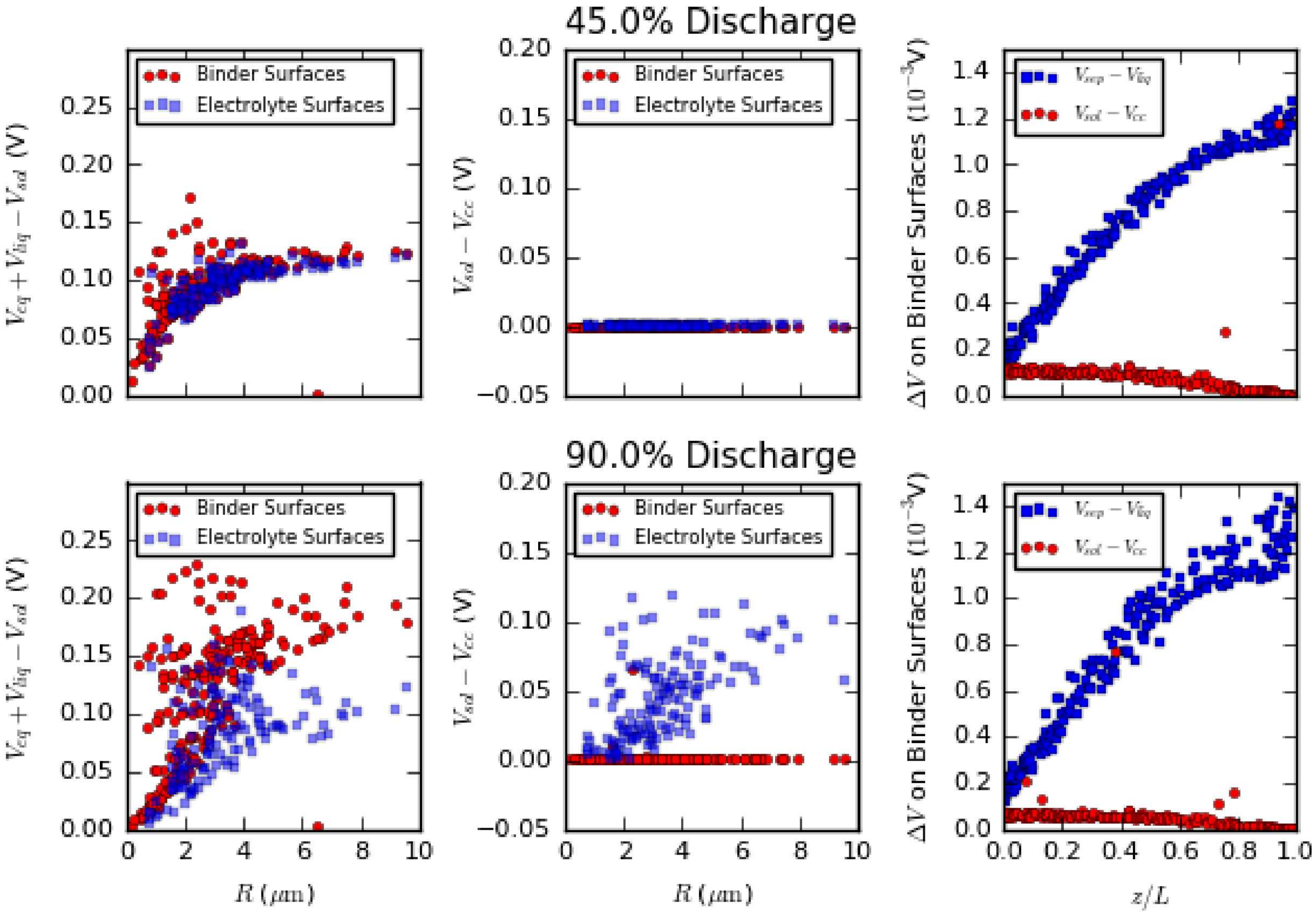
Particle-scale: Connectivity of the mesostructure



Connected particle volume/capacity to surface area governs overall state of charge distribution

Ferraro, in preparation

Particle-scale: Loss mechanisms



When particles become electrically resistive, reactions preferred under the binder

Ferraro, 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

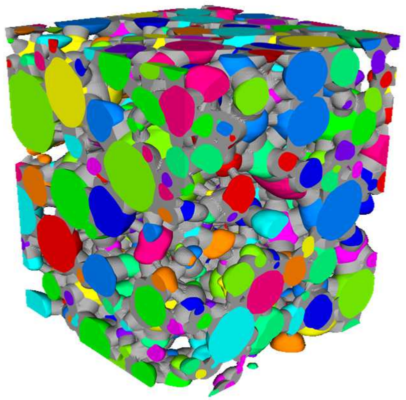
Publications available upon request

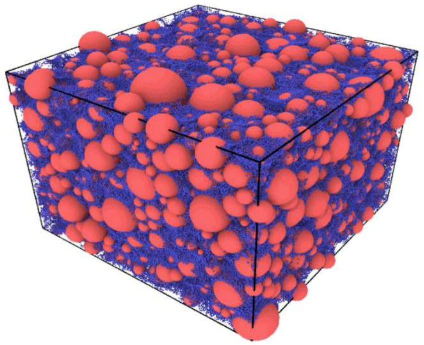
Data

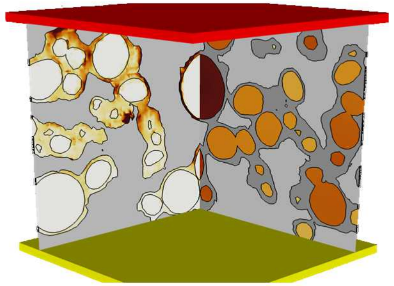
- V. Wood Group – ETH Zurich
- S. Thiele Group – U. Freiburg
- L. Zhu Group – IUPUI

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



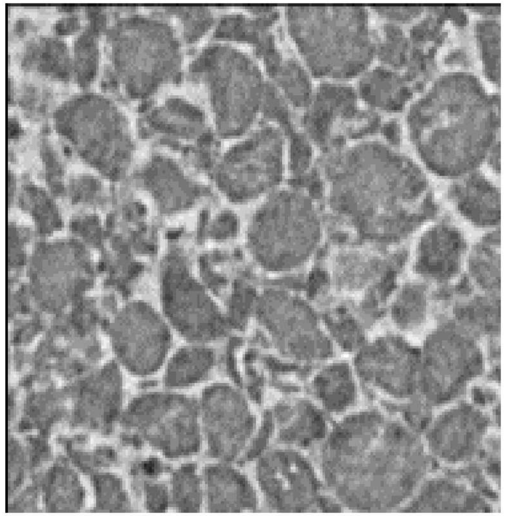




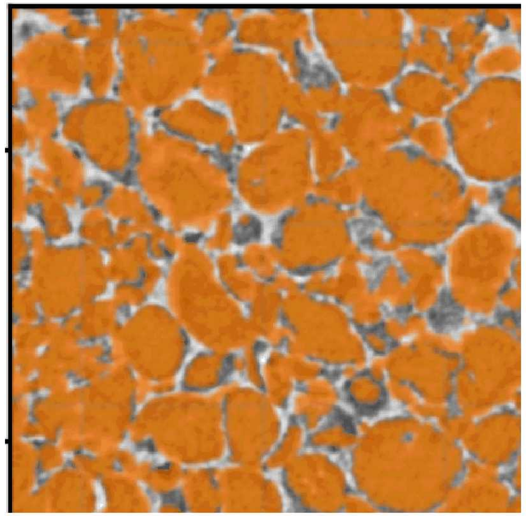
Mesoscale modeling is a powerful tool for predicting electrode behavior under extreme environments

A look forward

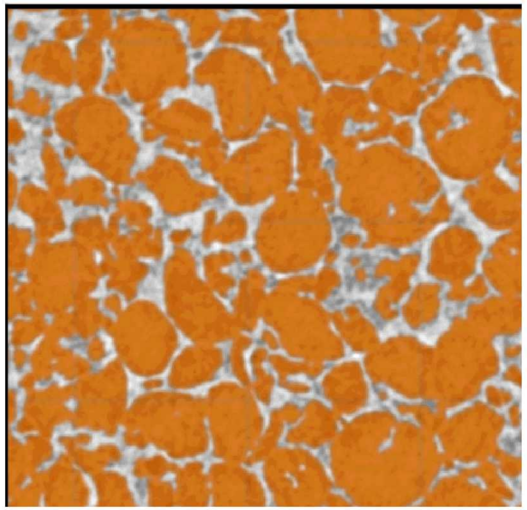
Slice from CT image of graphite electrode



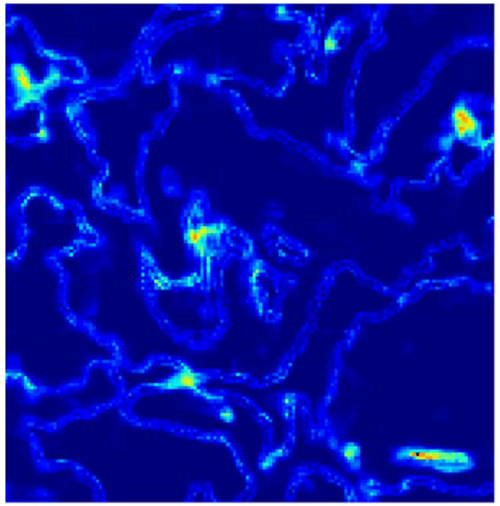
Human label (orange) overlaid on CT scan



Deep learning label (orange) overlaid on CT scan



Deep learning uncertainty estimate



Machine learning for image segmentation improves accuracy and provides in-situ uncertainty estimates

Questions?

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