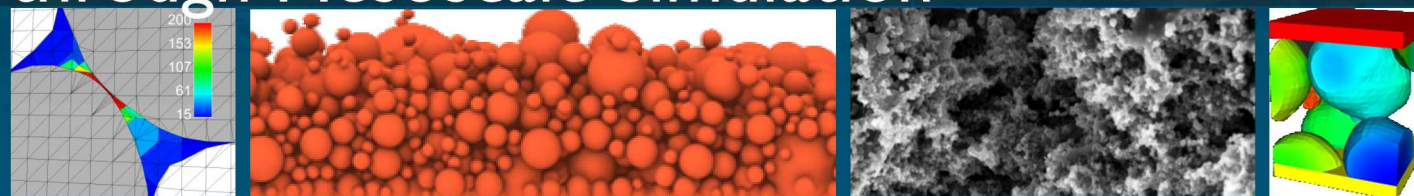
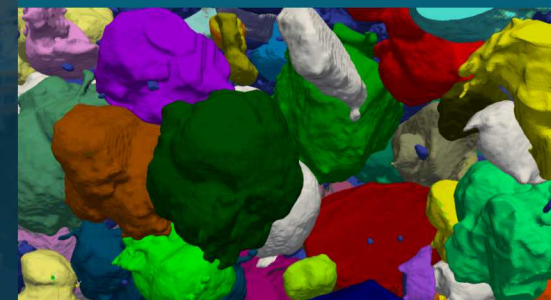


Elucidating the Role of Mesoscale Morphology on Lithium-Ion Battery Mechanical and Electrochemical Performance through Mesoscale Simulation



Contributors:

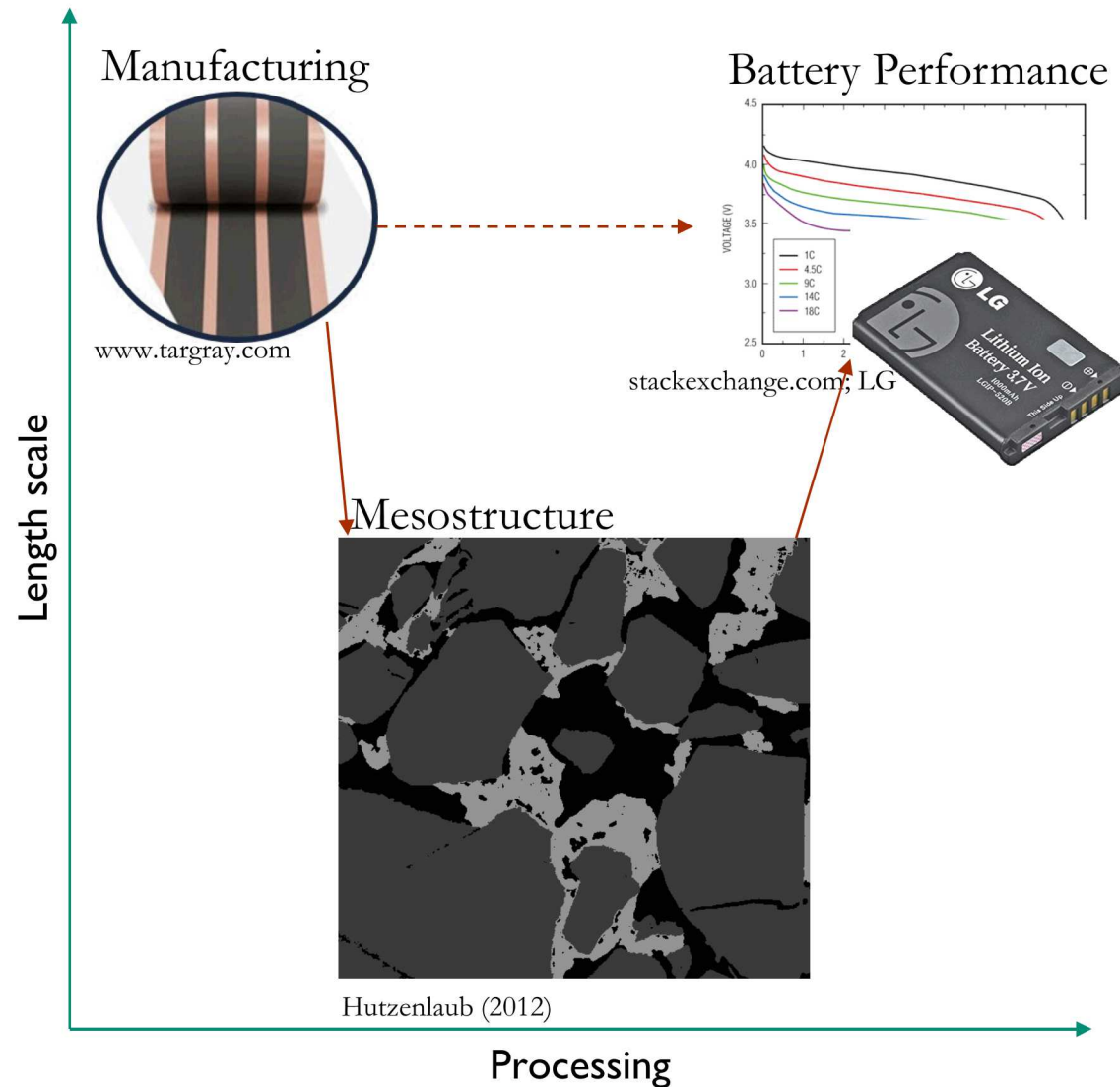
- Dan S. Bolintineanu
- Mark E. Ferraro
- Jeremy B. Lechman
- Aashutosh Mistry (Purdue)
- Partha Mukherjee (Purdue)
- David R. Noble
- Ishan Srivastava
- Bradley L. Trembacki

PRESENTED BY

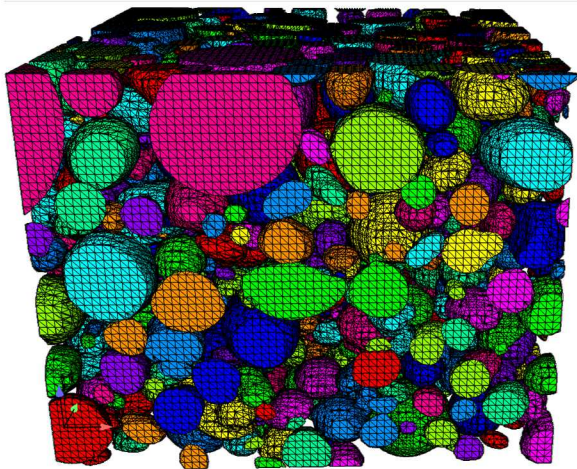
Scott A. Roberts, Ph.D.

TMS 148th Annual Meeting & Exhibition

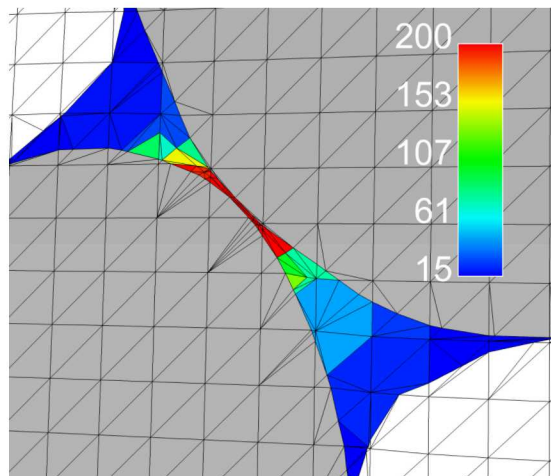
March 12, 2019



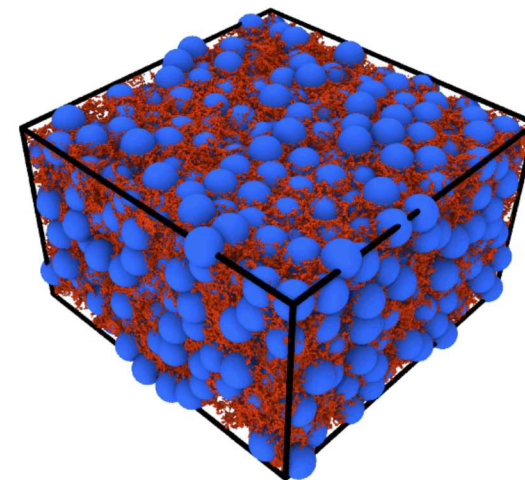
Coupled electrochemical-mechanical effects at mesoscale connect battery manufacturing and performance



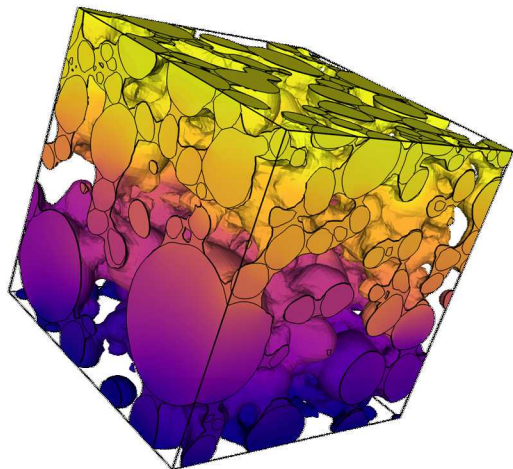
Computational representation of imaged electrode mesostructures



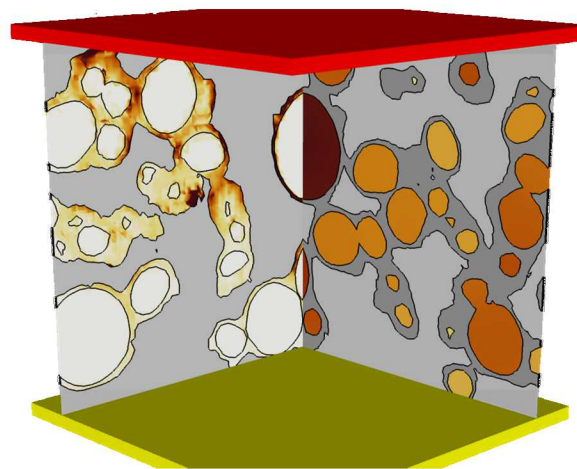
Representation and role of conductive binder morphology



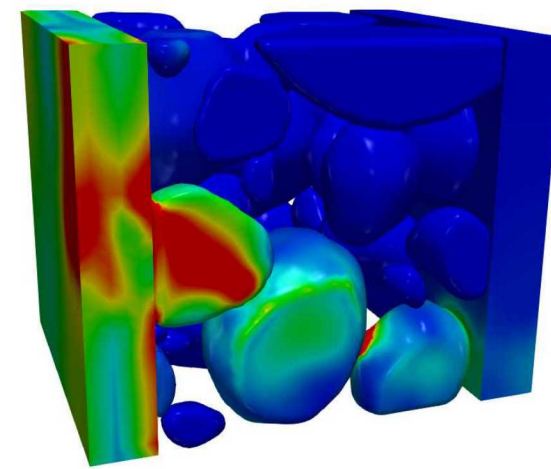
Discrete element method mesostructure generation



NMC cathode effective property prediction and upscaling

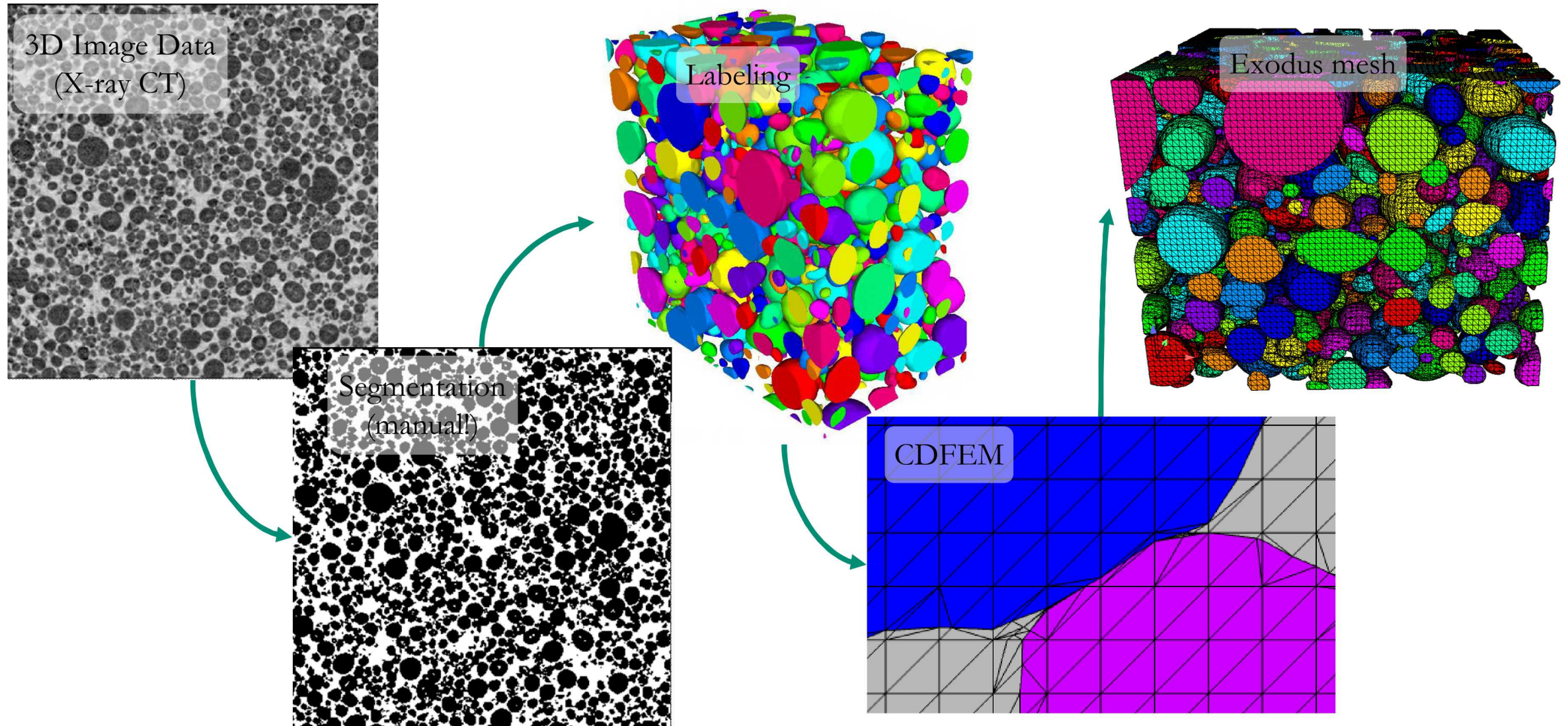


Electrochemical-mechanical discharge sims. of NMC half-cells



Future directions in electrode mesoscale modeling

4 Mesoscale geometry from CT data using CDFEM



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

What about the conductive binder?

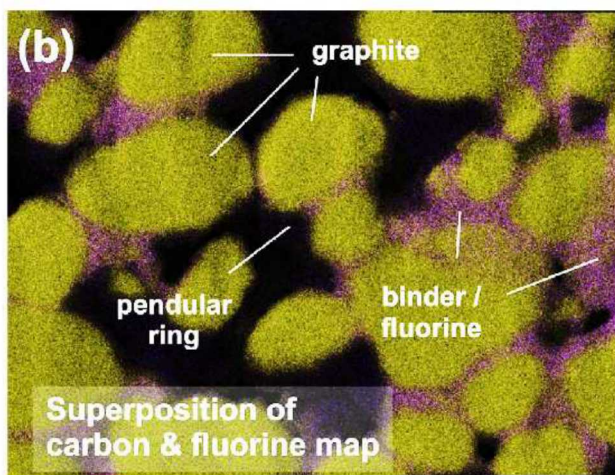
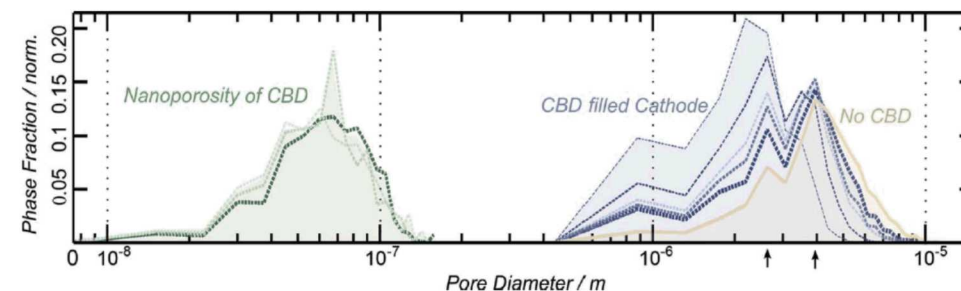
Resolving conductive binder in 3D imaging difficult

- 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

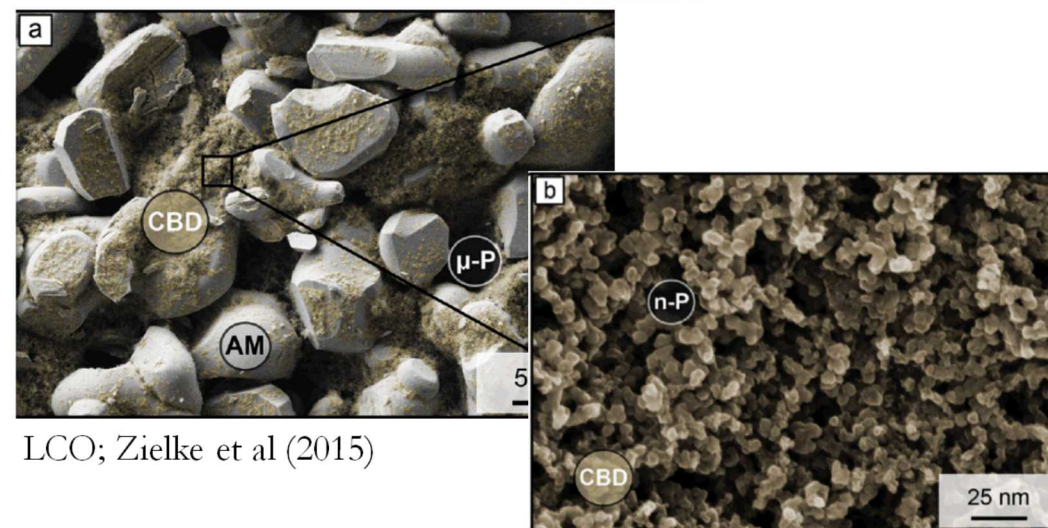
Binder weight fraction	Dense volume binder:particle	Porous volume binder:particle
0.04	0.10	0.15
0.06	0.16	0.23
0.08	0.22	0.31
0.10	0.28	0.40



Graphite; Jaiser et al. (2017)



LCO; Komini Babu et al (2015)

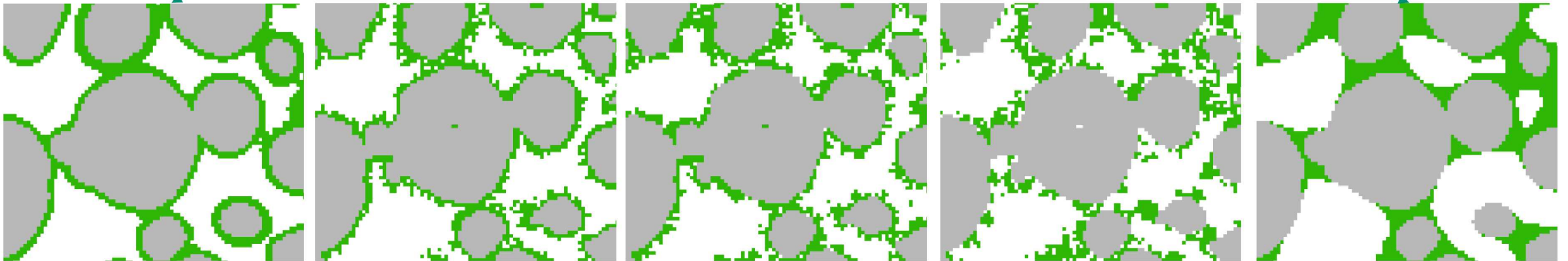
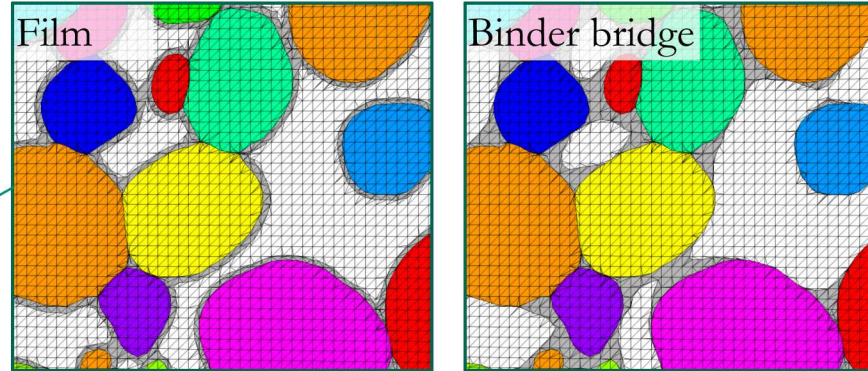


LCO; Zielke et al (2015)

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

Binder bridge morphology approaches

Level-set methods



$\omega = 0.01$

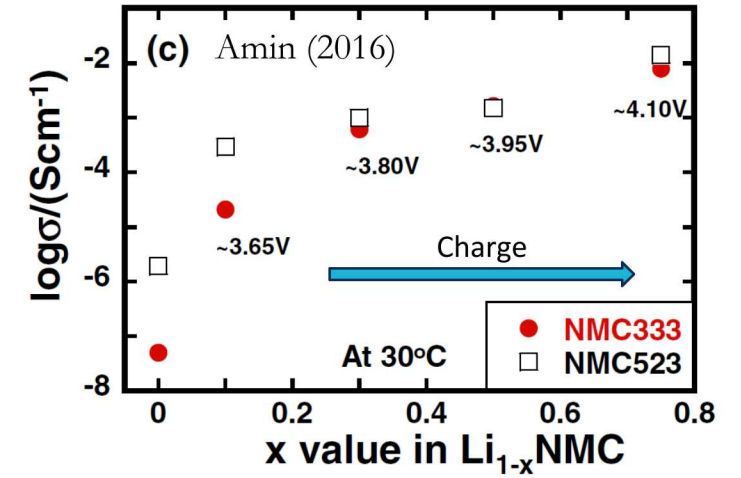
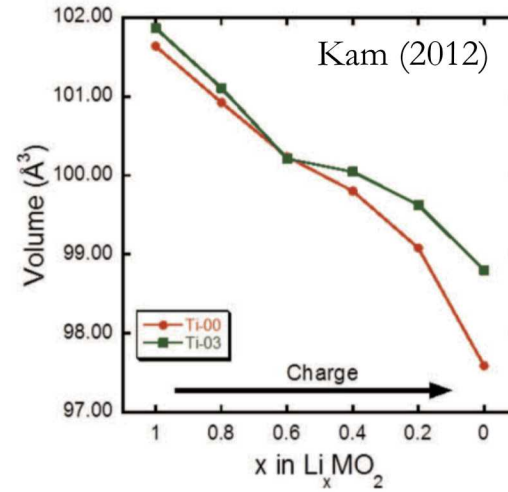
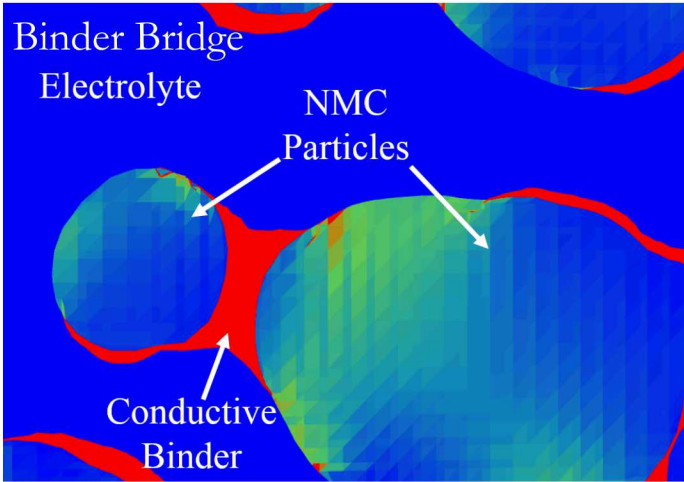
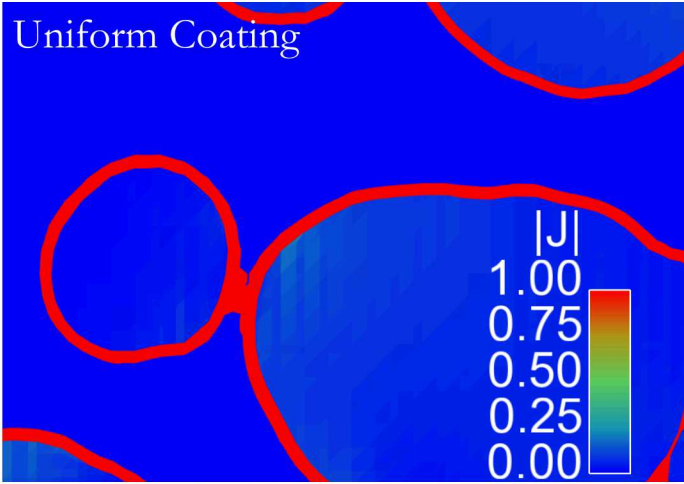
$\omega = 0.50$

$\omega = 0.99$

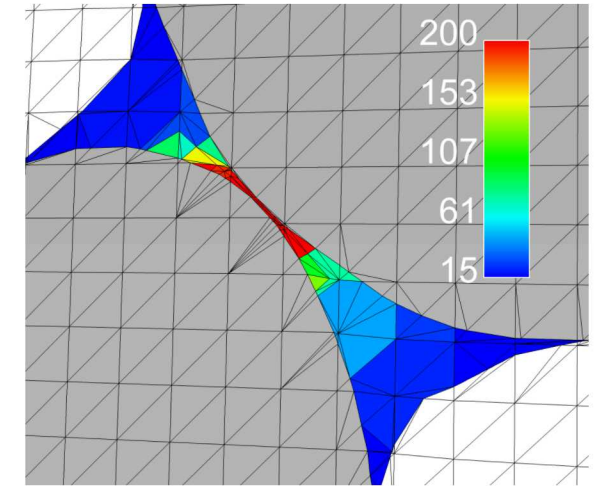
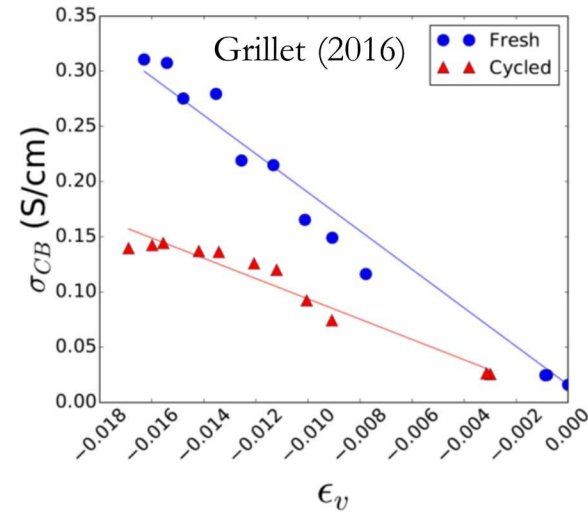
Stochastic method

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

7 Why does the morphology matter?



NMC swells on lithiation, compressing binder



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

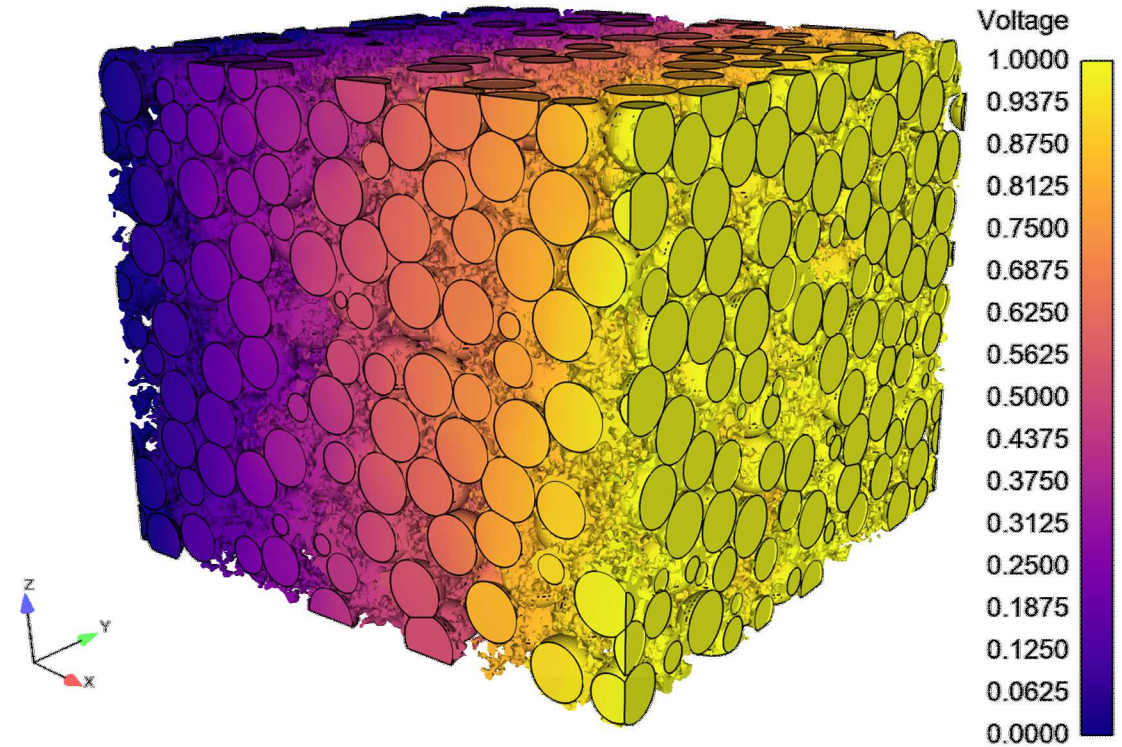
Effective electrode property calculations

Calculate effective transport properties for upscaling

- Particle specific surface area
- Electrical conductivity
- Tortuosity

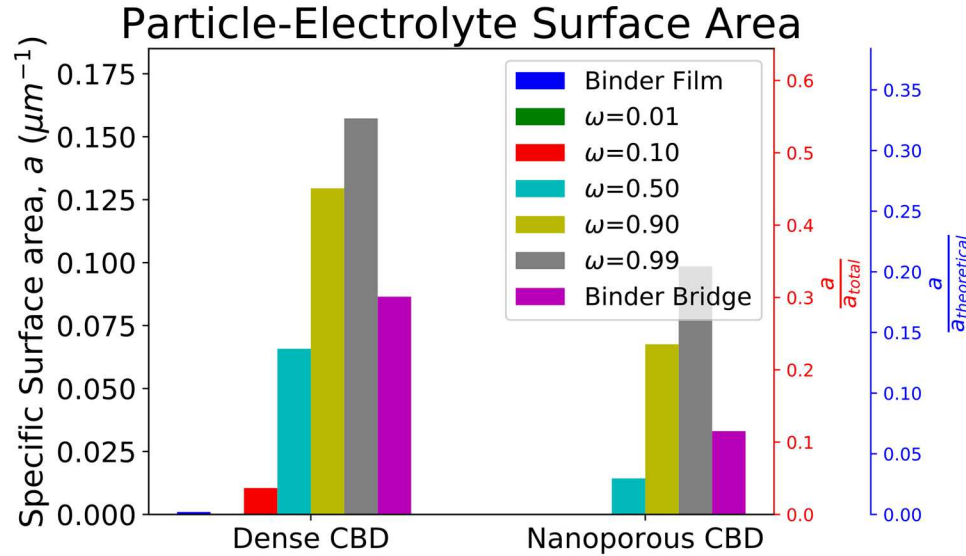
NMC image data from Ebner (2013)

- 90, 92, 94, 96 wt% NMC (remainder 1:1 CB:PVDF)
- 0, 300, 600 & 2000 bar calendering
- $100\text{ }\mu\text{m} \times 100\text{ }\mu\text{m} \times 60\text{ }\mu\text{m}$ domain (20 realizations eac
- Binder bridge (porous) morphology approach



Effective properties are an important first step for upscaling mesoscale data

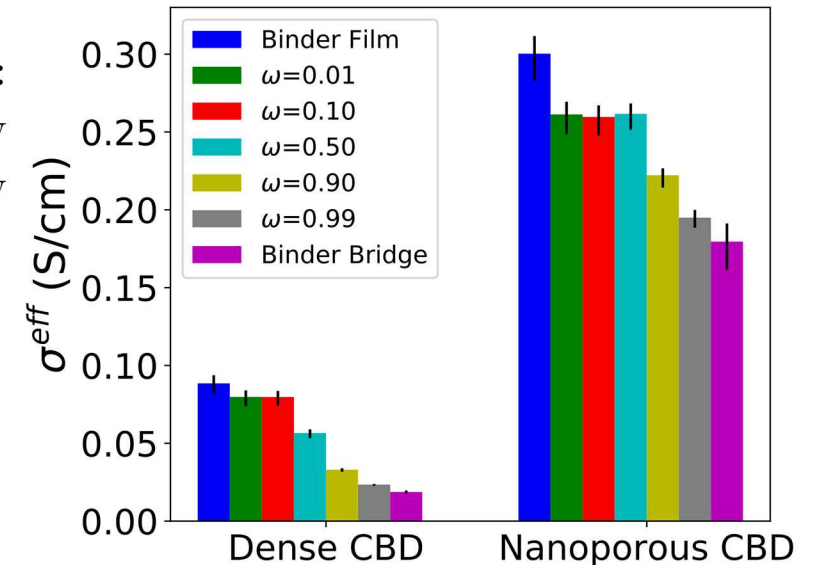
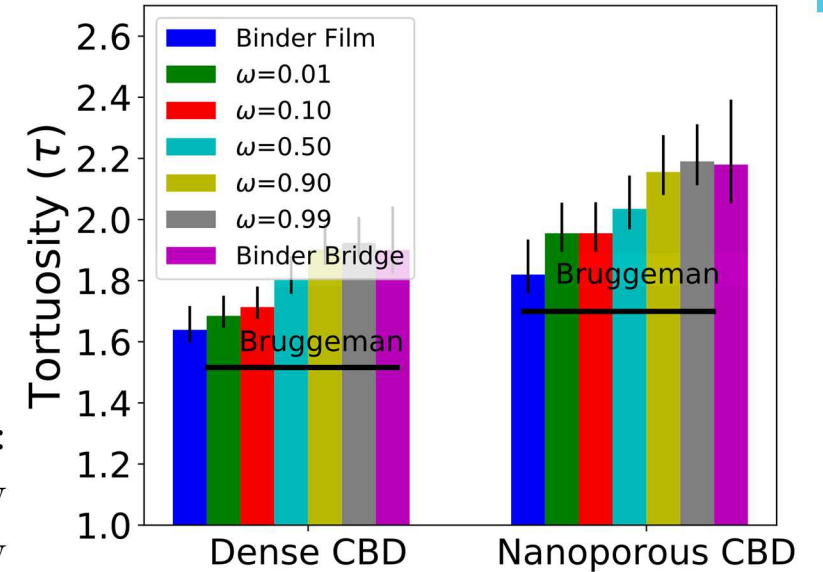
9 Porous binder and morphology considerations



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

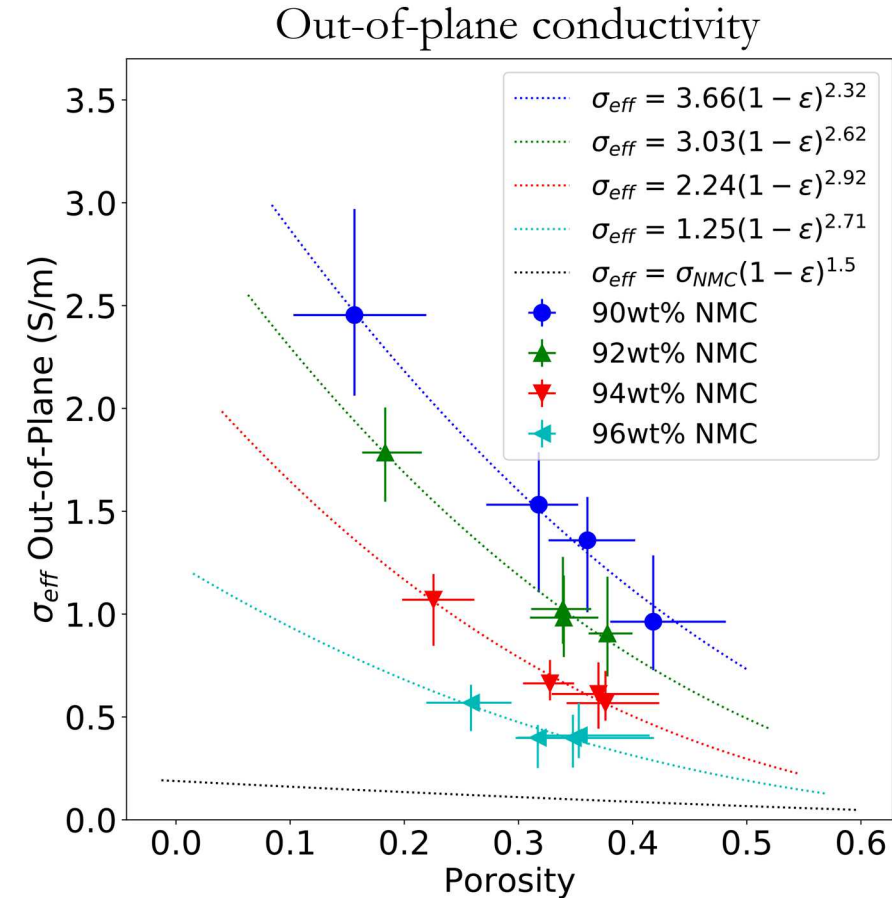
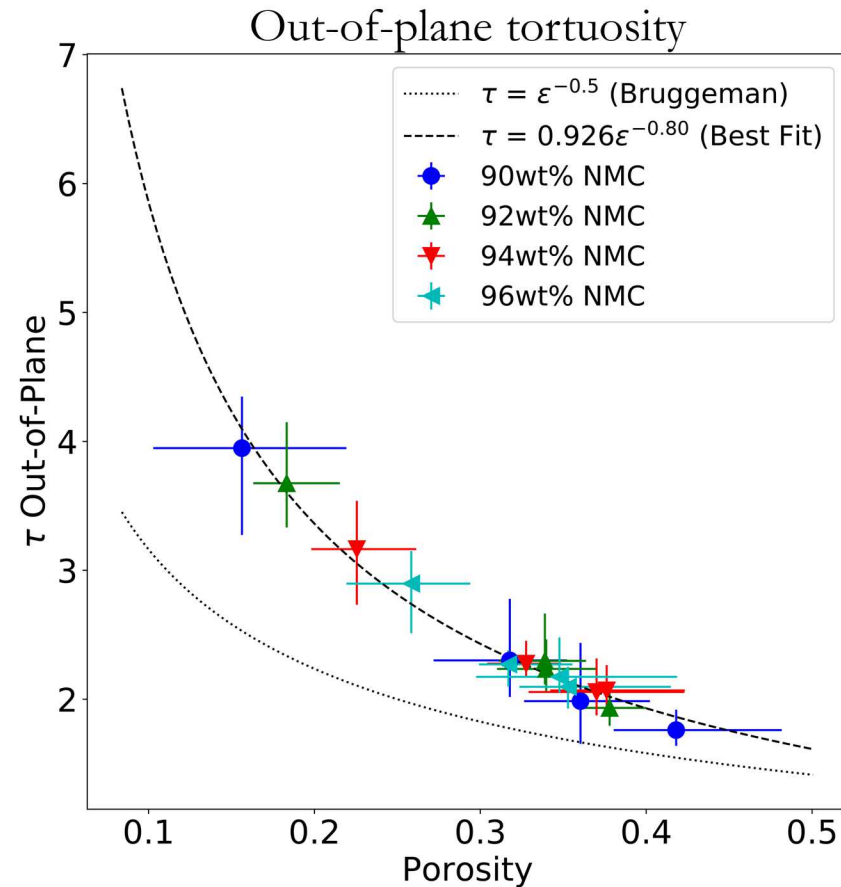
- Non-uniform binder:
- Increases tortuosity
 - Decreases conductivity

- Nanoporosity:
- Increases tortuosity
 - Increases conductivity



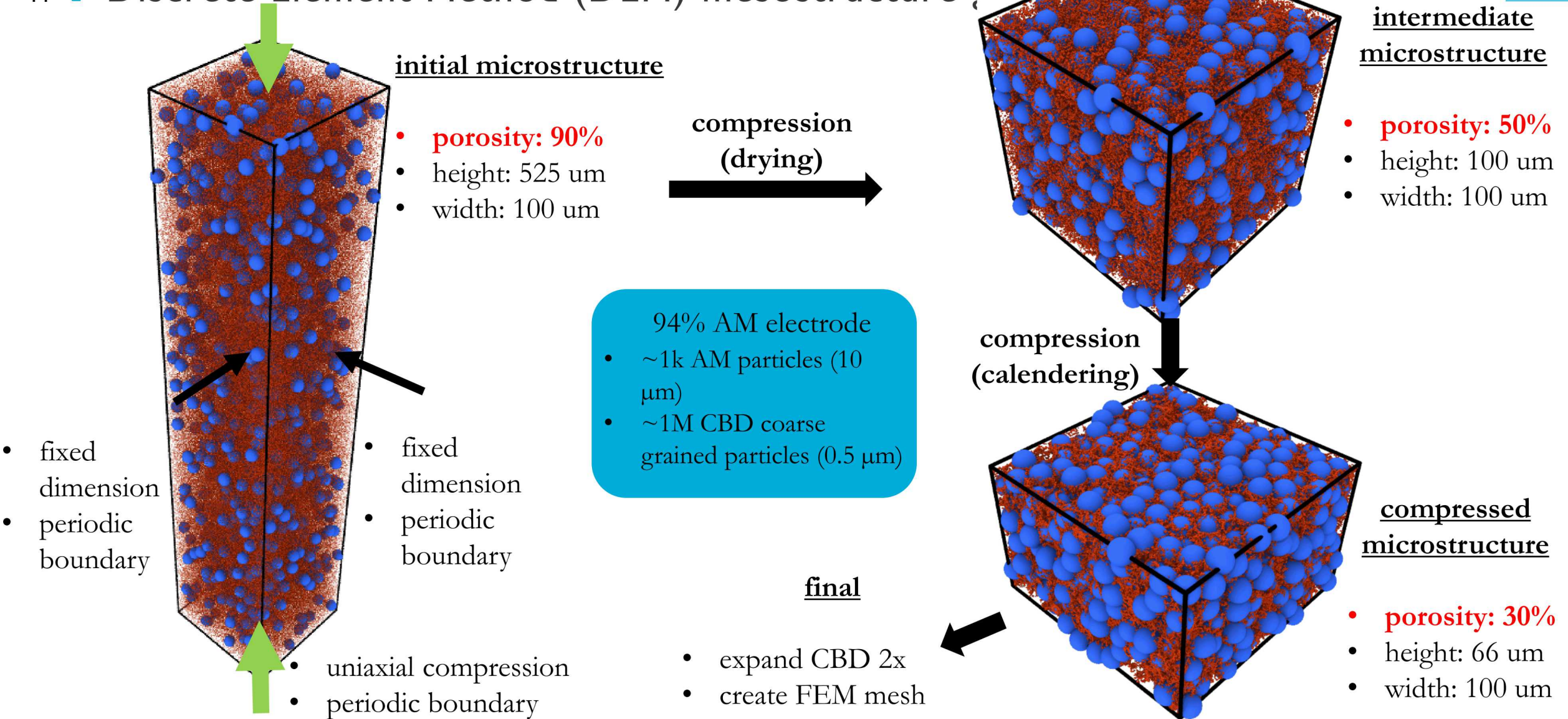
Limiting cases of both morphology methods show similar (but not identical) behavior; nanoporosity is important!

Effective electrode property calculation results – Transport

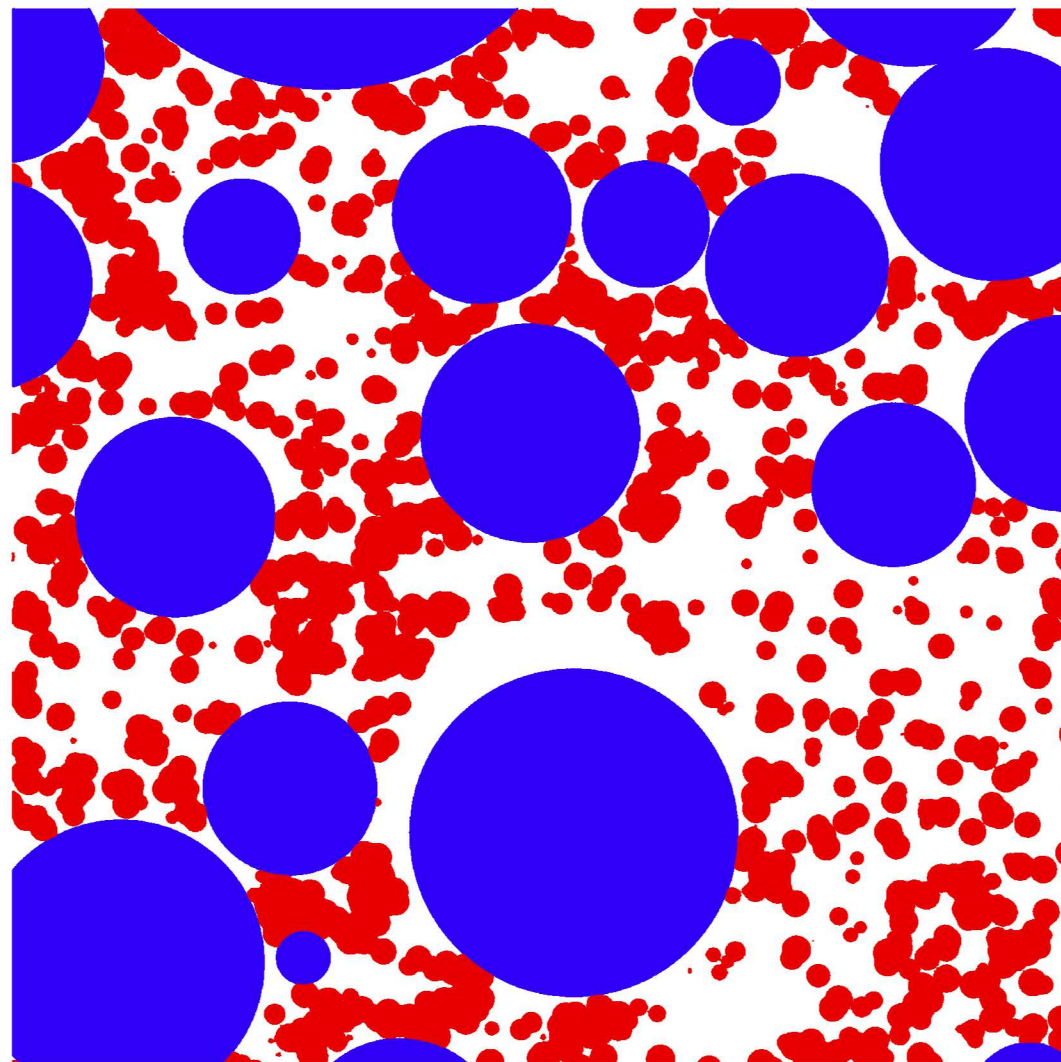
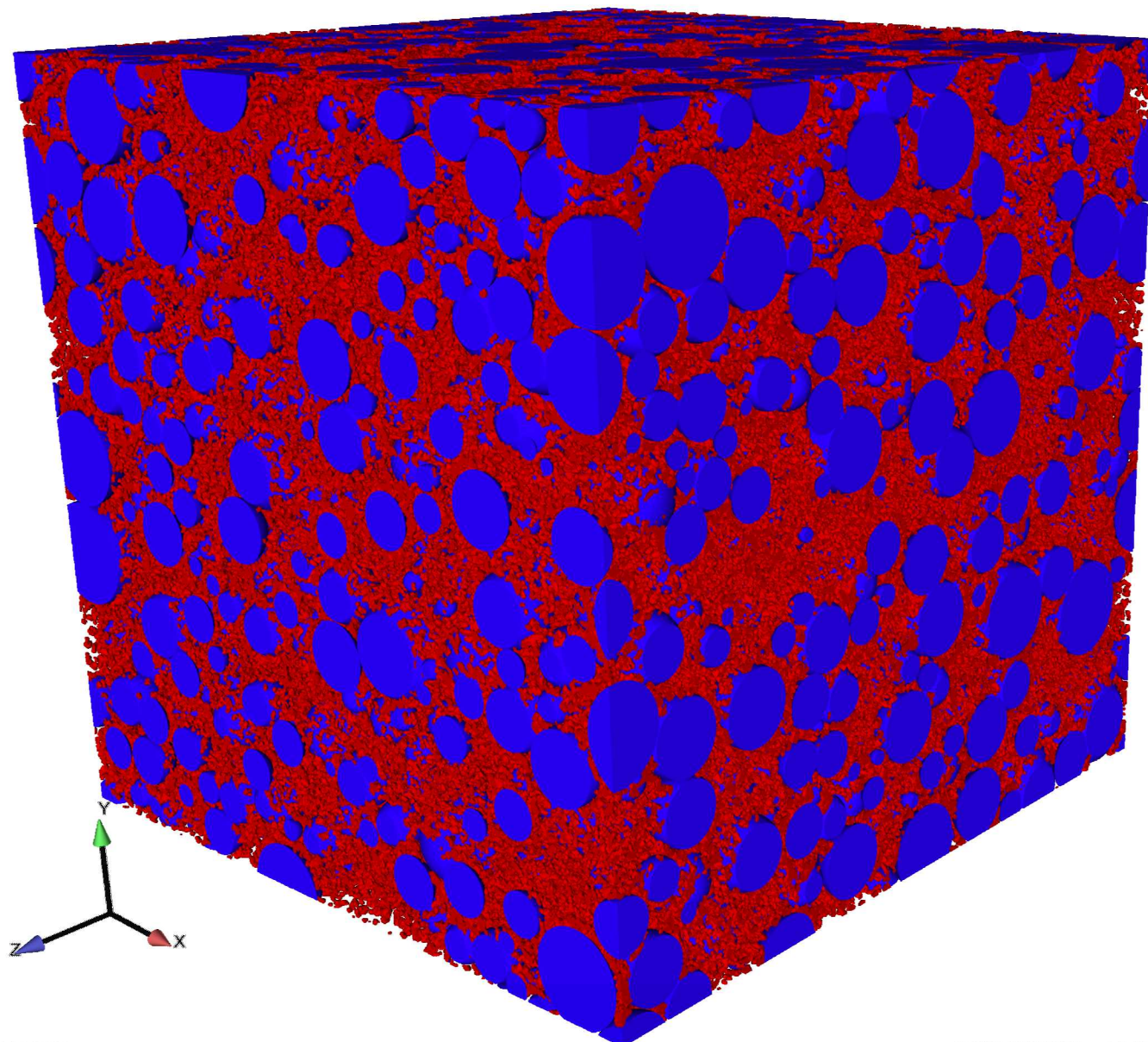


Bruggeman relationships must be re-calibrated to fit simulated data

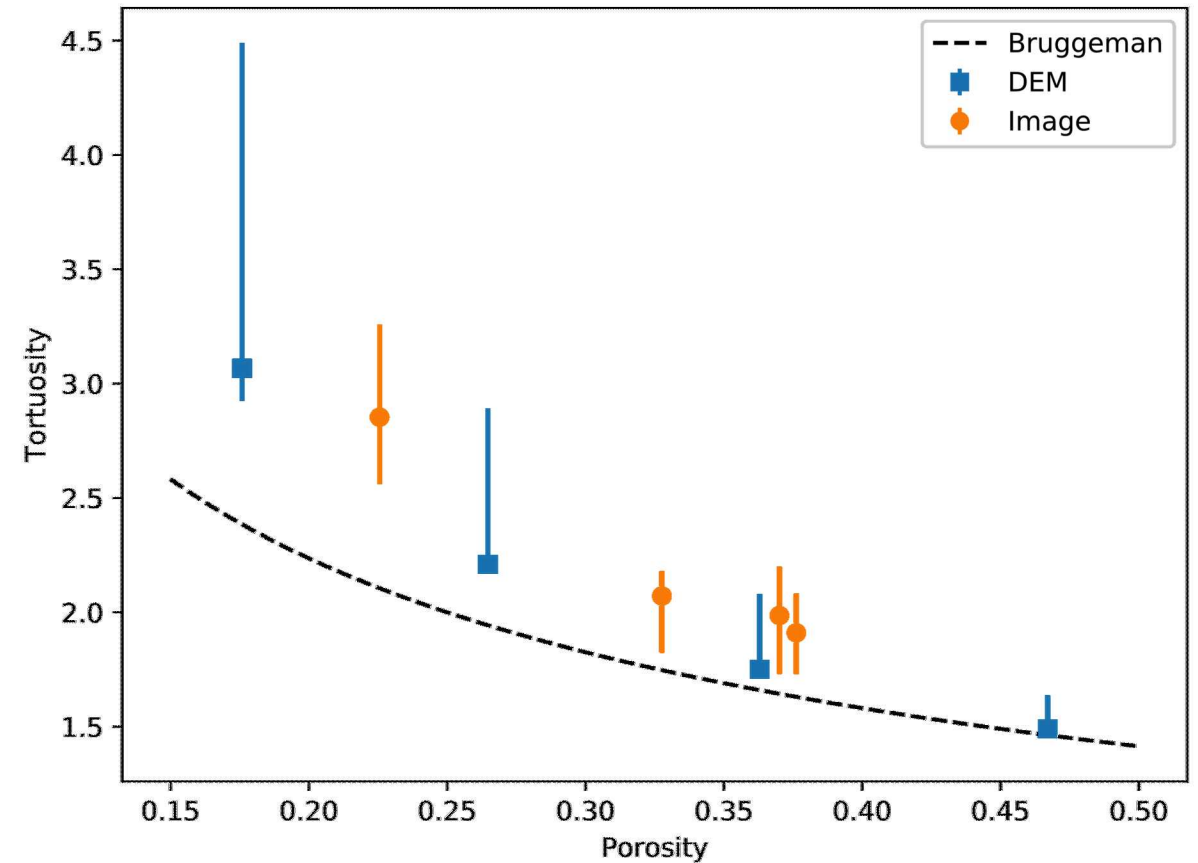
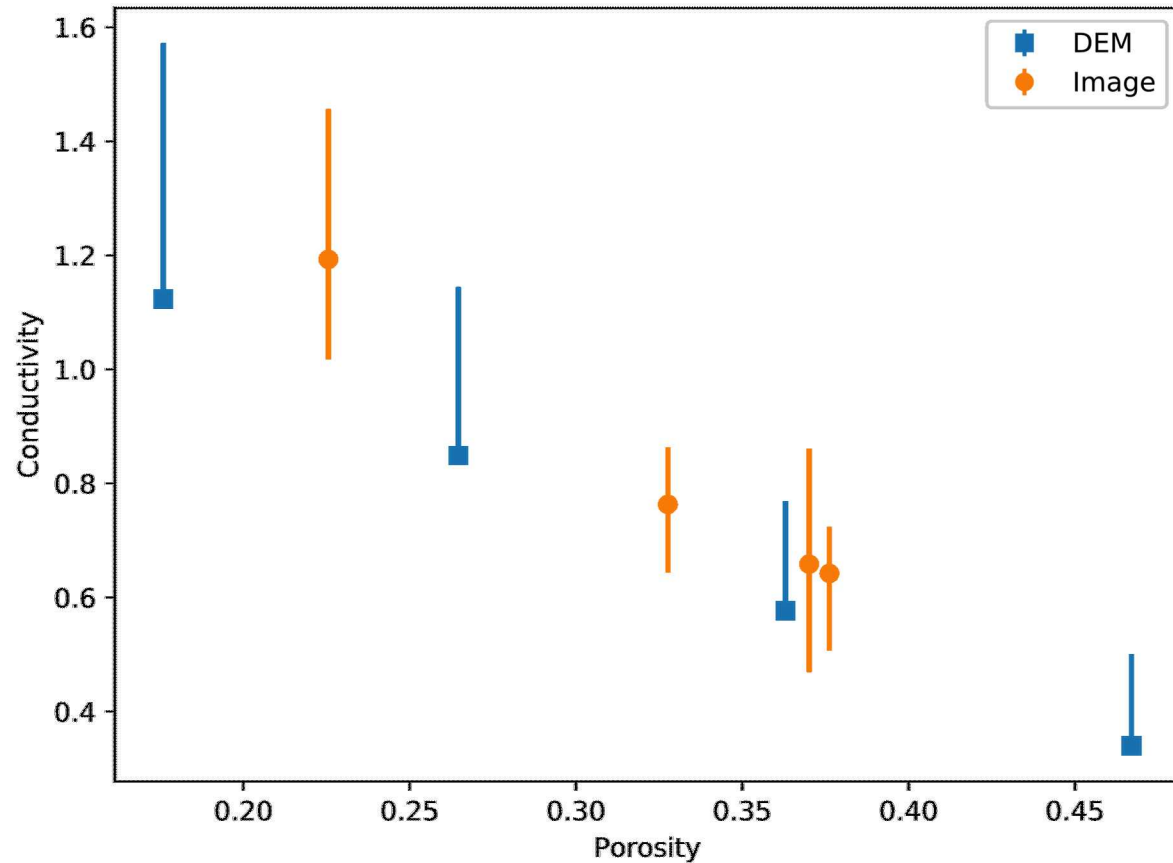
Discrete Element Method (DEM) mesostructure



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



Comparison of image- and DEM-based mesostructures



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

Calendaring $\rightarrow$ lower porosity $\rightarrow$ more CBD connectivity $\rightarrow$ higher conductivity and tortuosity

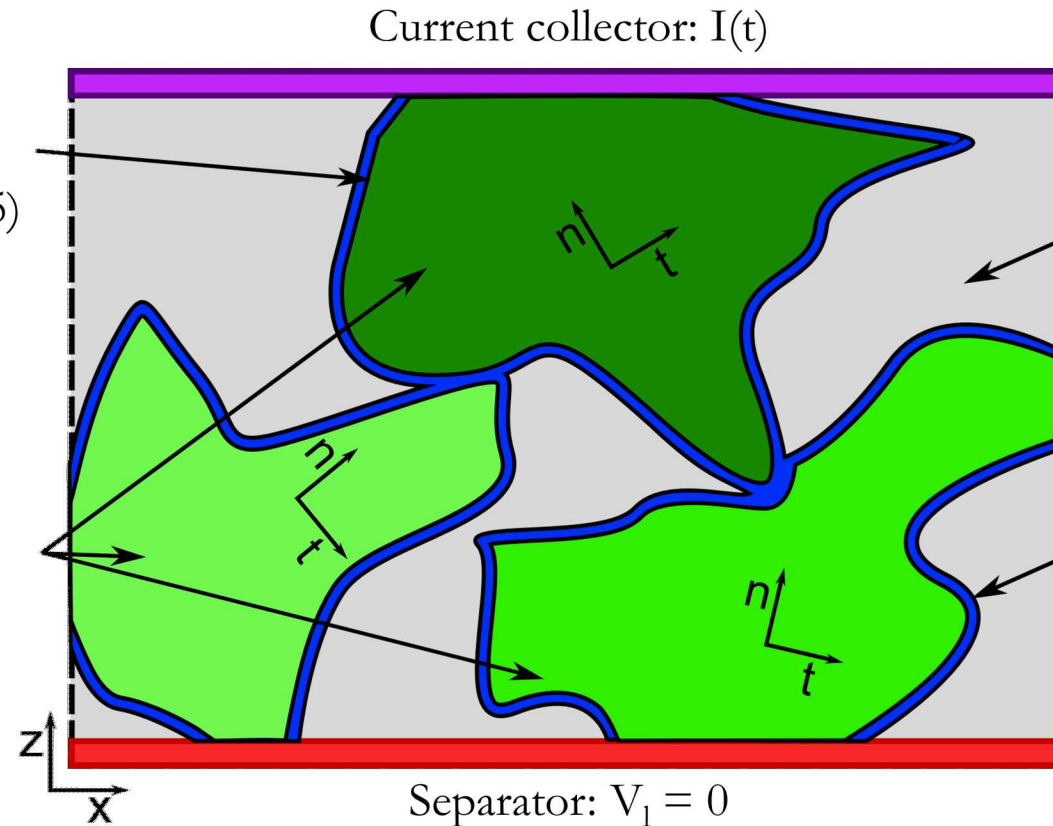
Coupled electrochemical-mechanical half-cell discharge simulations

Particle Interface:

- Butler-Volmer reaction
- OCV from Smekens (2015)

Particles:

- Species – Li tr
 - Chemical
 - Stress pc
- Electrical – ϕ
- Mechanics - E
 - Li-induc



Electrolyte:

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

Conductive binder:

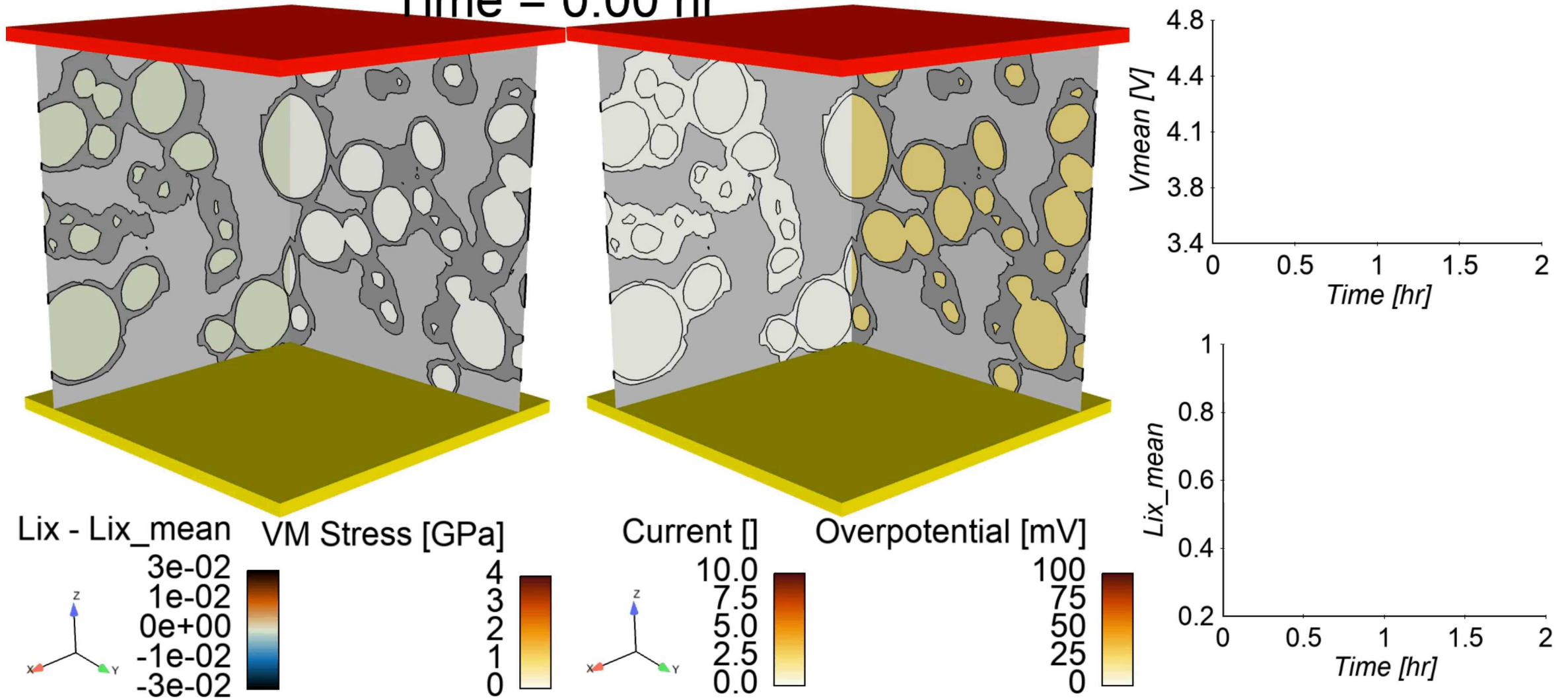
- Species – Porous Li^+ transport
- Electrical
 - Solid: Porous Ohm's law
 - Strain-dependent electrical conductivity
 - Liquid: Ionic conservation & electroneutrality
- Mechanics – Elastic

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

Time = 0.00 hr



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

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



Questions?

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