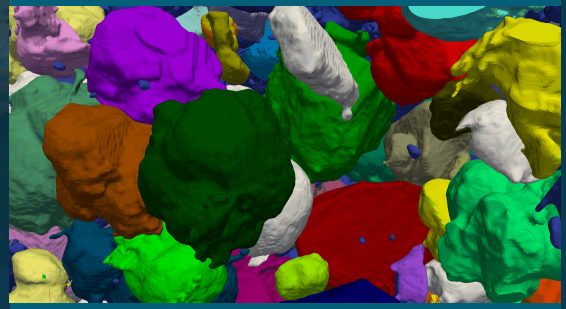
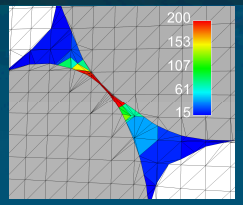
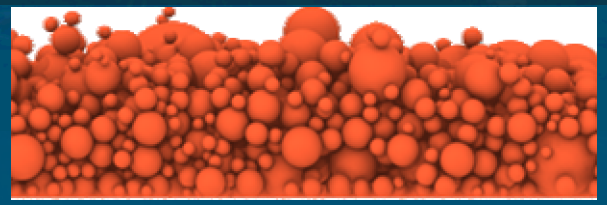
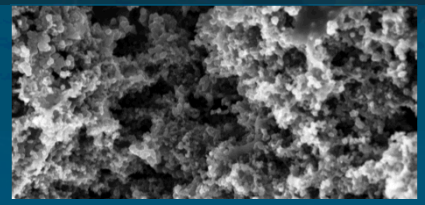
SAND2018-7966PE

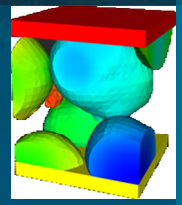
Modeling Mechano-Electrochemical Phenomena from the Mesoscale to the Macroscale











PRESENTED BY

Scott A. Roberts, Ph.D.

- Srikanth Allu (ORNL)
- Victor E. Brunini
- Mark E. Ferraro
- Jeremy B. Lechman
- Aashutosh N. Mistry (Purdue)
- Partha P. Mukherjee (Purdue)
- David R. Noble
- Chance Norris (Purdue)
- Ishan Srivastava
- John Turner (ORNL)
- Bradley L. Trembacki

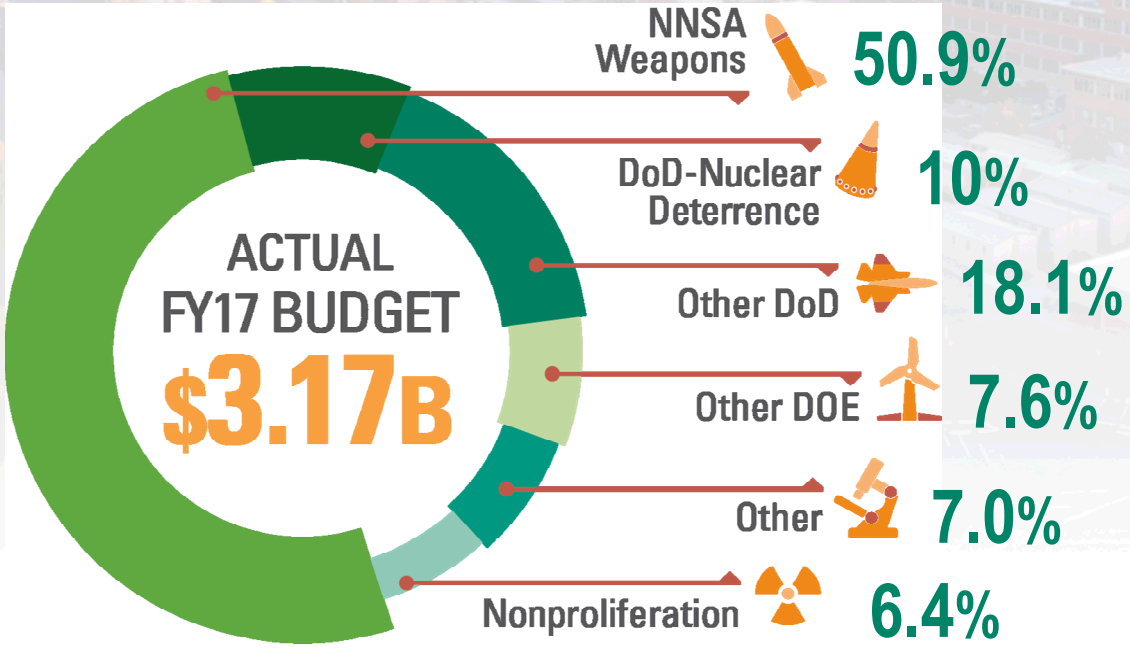
Princeton University Seminar
July 23, 2018

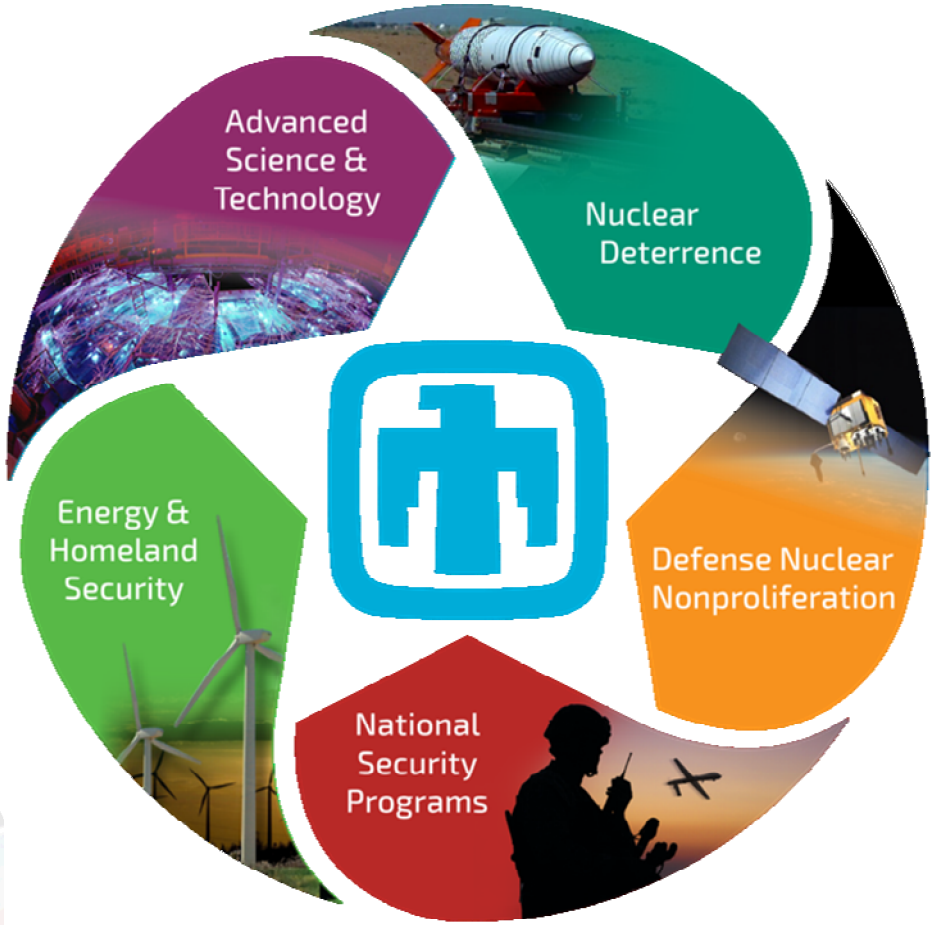
2/27/2018

Sandia National Laboratories

Sandia is the nation's premiere engineering DOE laboratory

- Established in 1949 from Los Alamos Z Division
- Primary locations: Albuquerque, NM; Livermore, CA
- 12,200 employees (52% R&D)



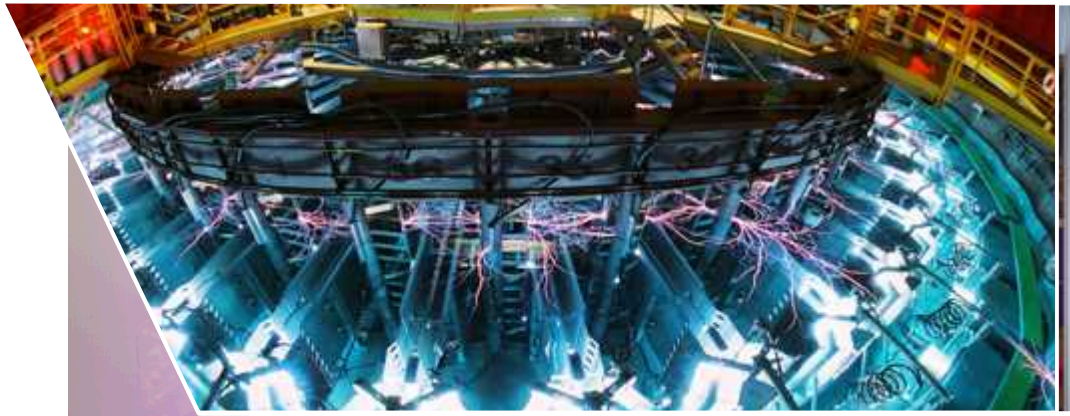


Advanced Science & Technology

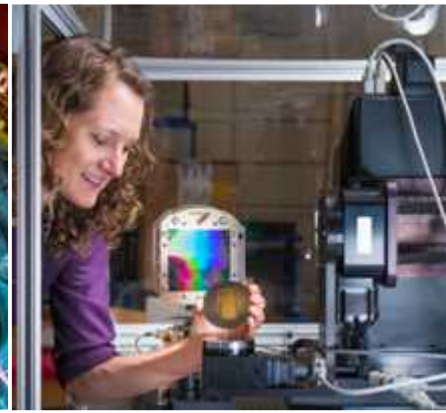
Resear ral role in mission delivery

Nanodevices & Microsystems

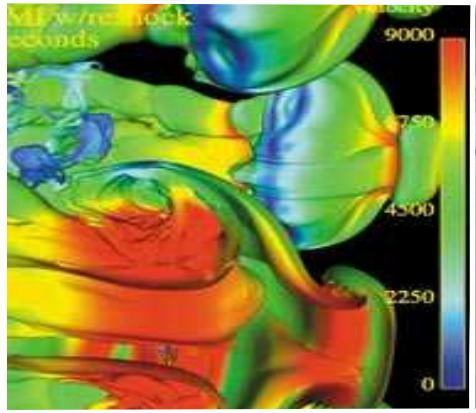
Computing & Informa



Radiation Effects & High Energy Density Science



Materials Science



Engineering Science

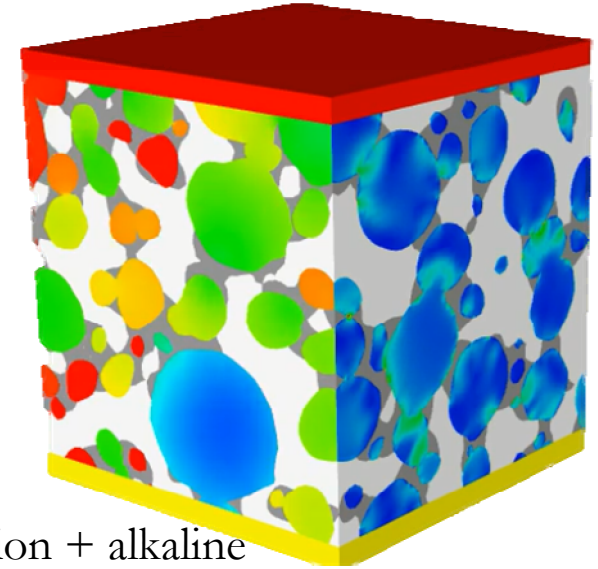
Geoscienc e

Bioscience

Roberts research efforts

Multi-physics, multi-scale applied modeling & simulation

- Lead teams comprised of 14 PhD staff members, 3 post-docs, 2 graduate students, and 4 interns
- $2.9M in FY18 research funding



Li-ion + alkaline battery mesoscale

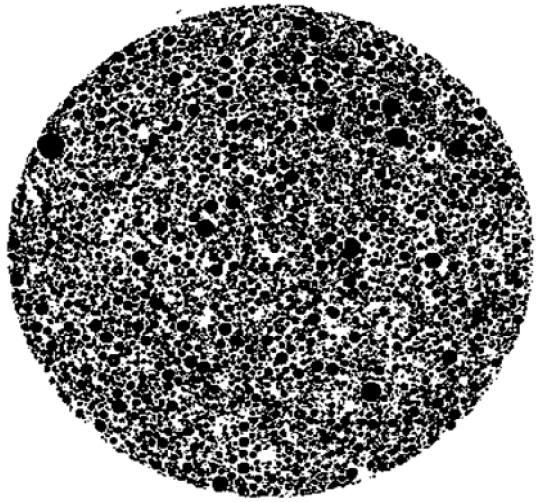
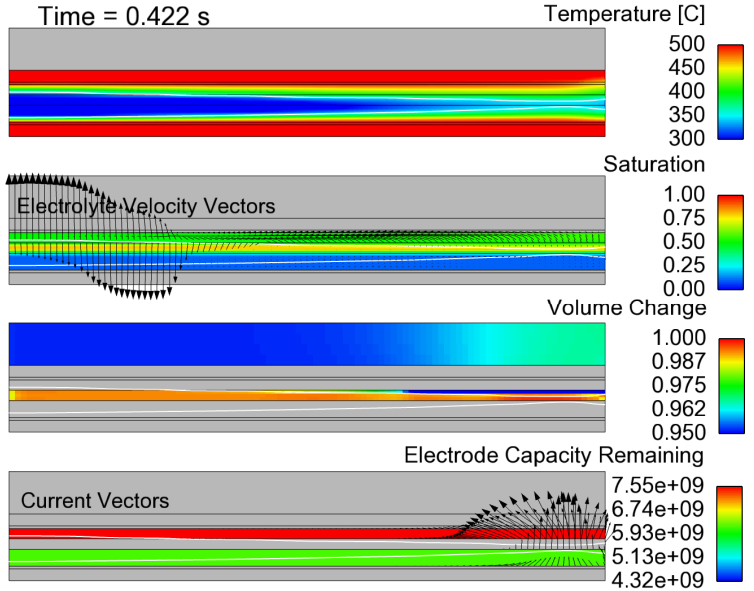
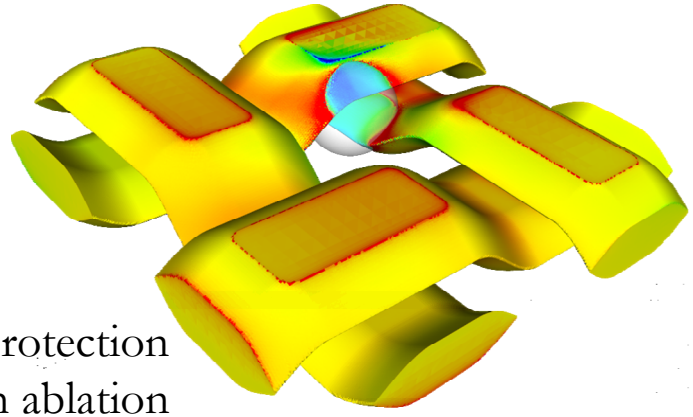


Image-to-mesh with ML/UQ

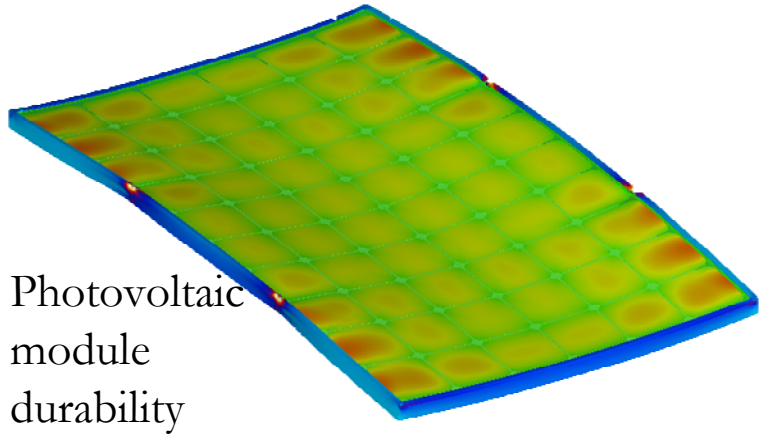


Thermal batteries

EM railgun launcher performance



Thermal protection system ablation



Photovoltaic module durability

Motivation

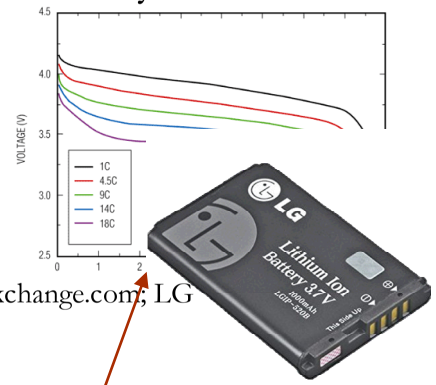
Length scale

Processing

Manufacturing

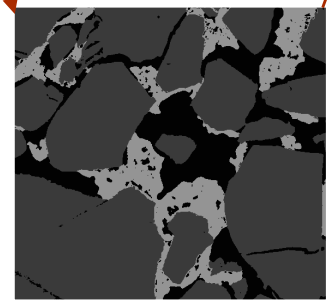
www.targray.com

Battery Performance



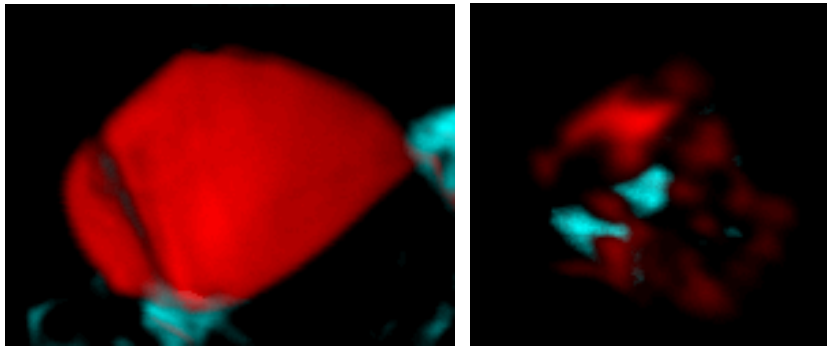
stackexchange.com; LG

Mesostructure



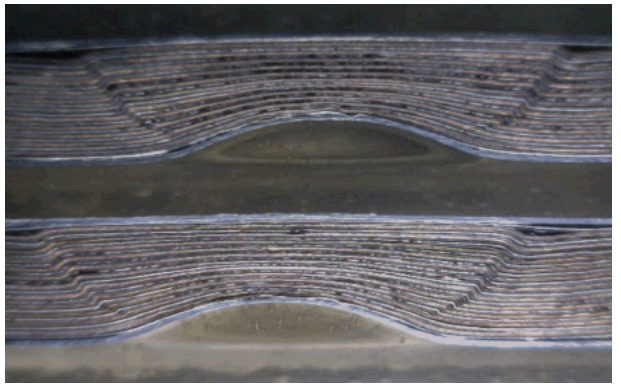
Hutzenlaub (2012)

Lithiation-Induced Fracture

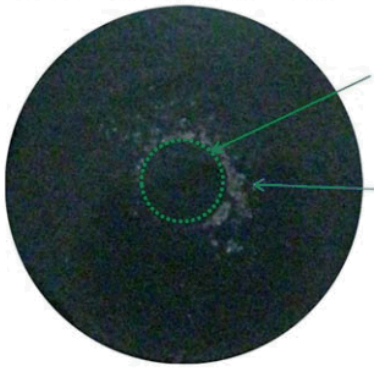


LiCoO2 STXM, Farid El Gabaly Marquez (Sandia)

Mechanical Abuse → Electrochemistry / Mesostructure



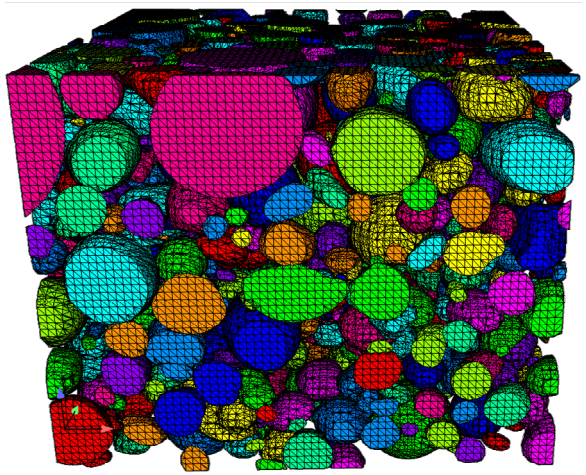
NMC/graphite pouch, H. Wang (ORNL)



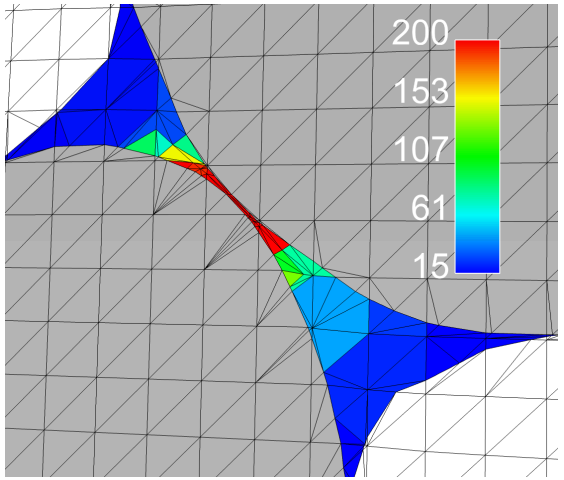
Cannarella/Arnold (2015)

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

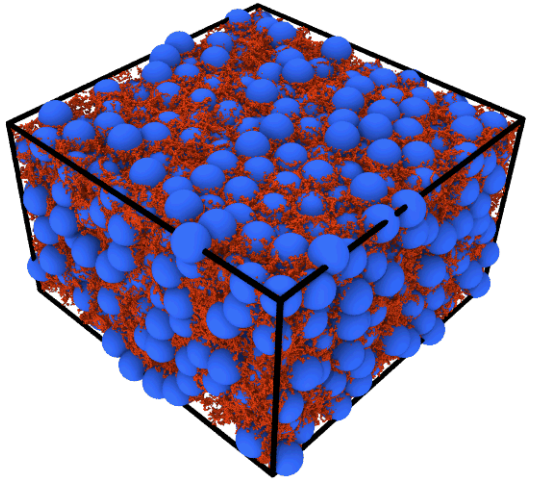
Outline



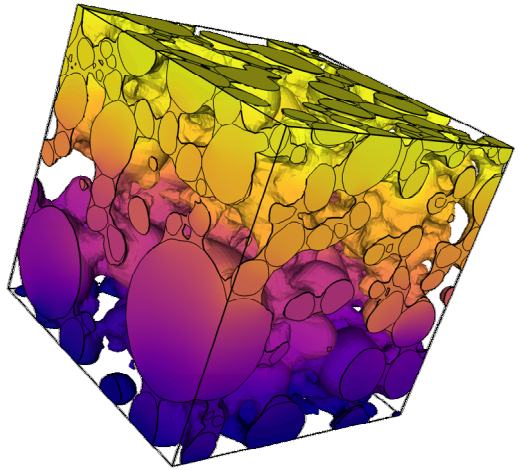
Computational representation of electrode mesostructures



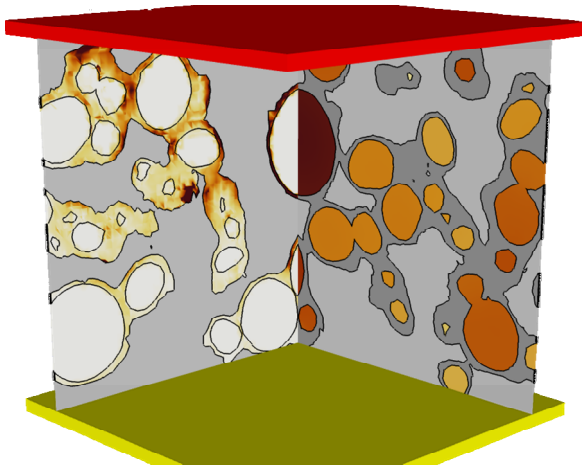
Representation and role of conductive binder morphology



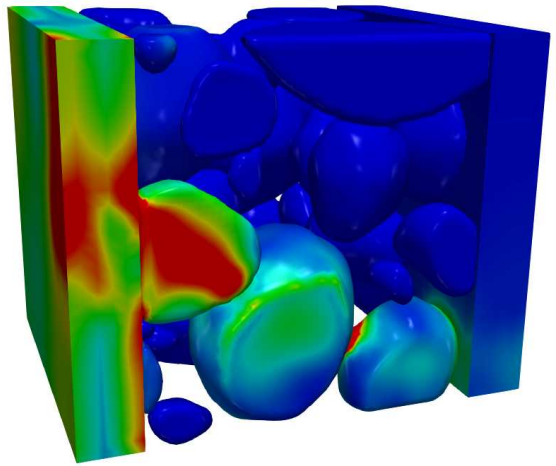
Discrete element method mesostructure generation



NMC cathode effective property prediction and upscaling



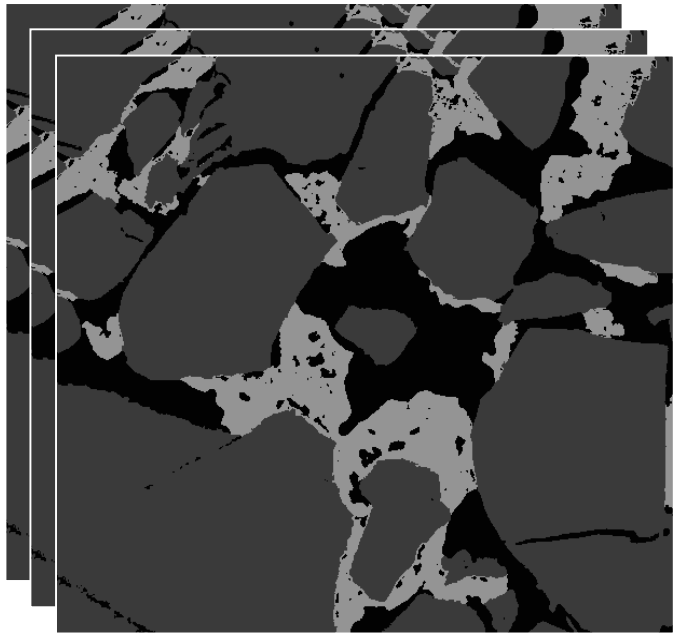
Electrochemical-mechanical discharge sims. of NMC half-cells



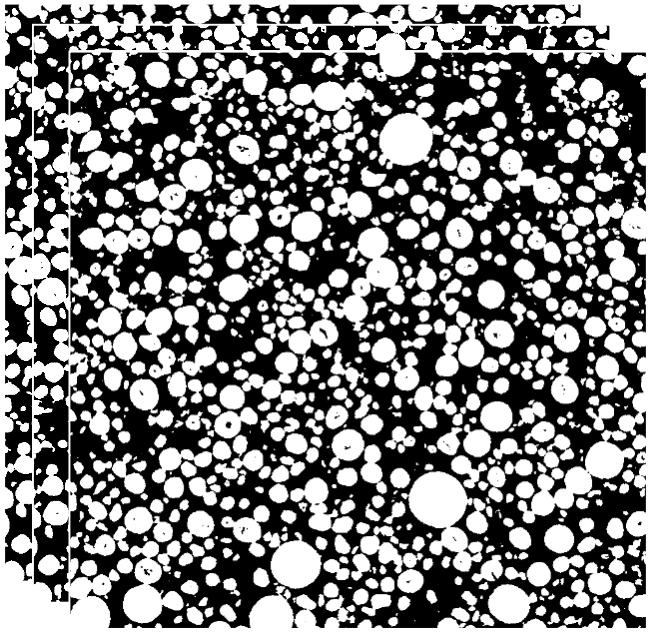
Future directions in electrode mesoscale modeling

Computational representation of electrode mesostructures

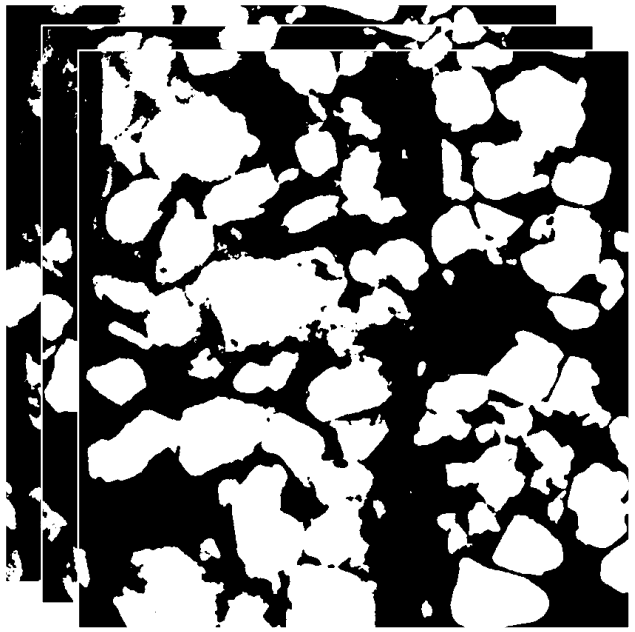
Imaging of cathode mesostructures



LCO with binder from FIB/SEM,
35 nm resolution,
20 μm domain.
Hutzenlaub (2012)



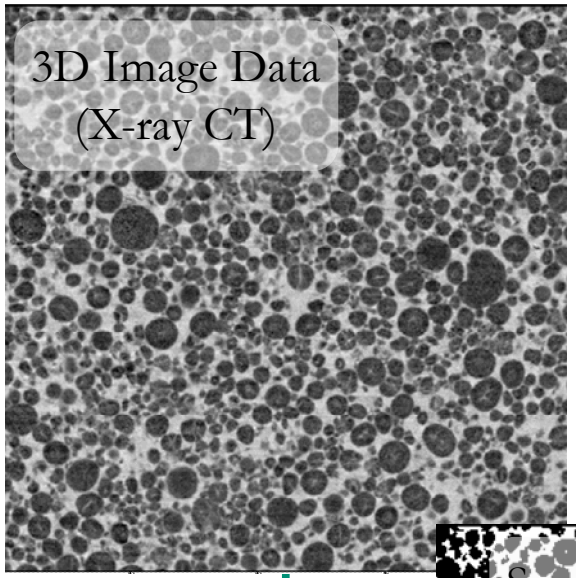
NMC from XRCT,
370 nm resolution,
757 μm domain.
Ebner (2013)

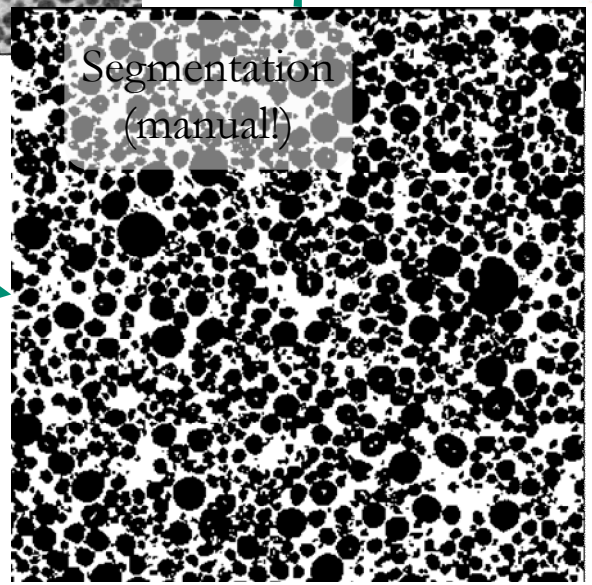


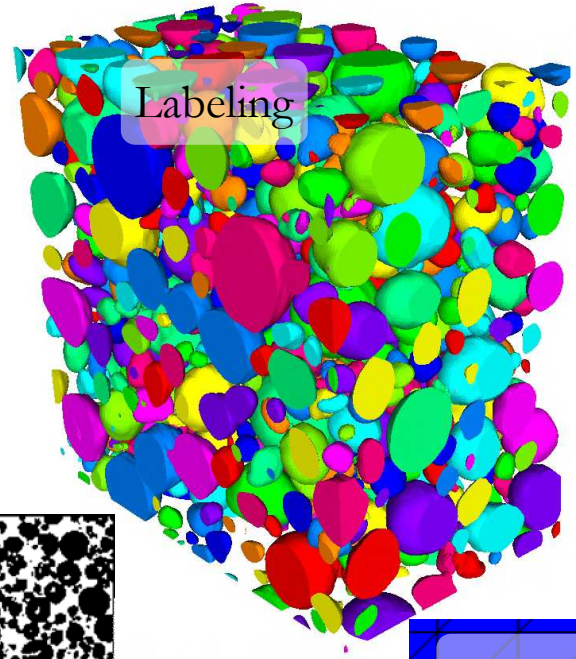
LCO from XRCT,
64 nm resolution,
22 μm domain.
Yan (2012)

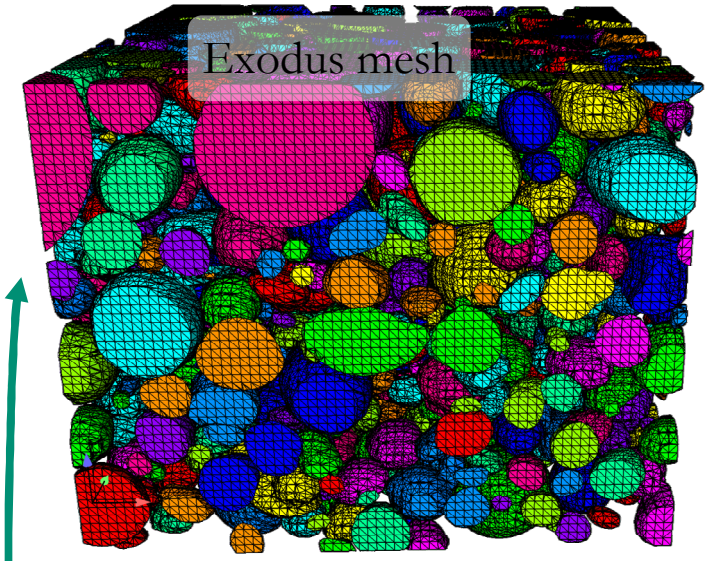
Imaging reveals complex networks; binder can be difficult to detect at scale

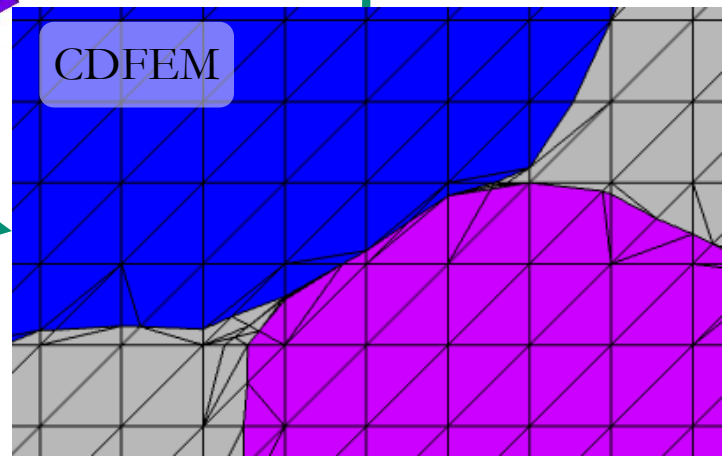
Mesoscale geometry from CT data using CDFEM







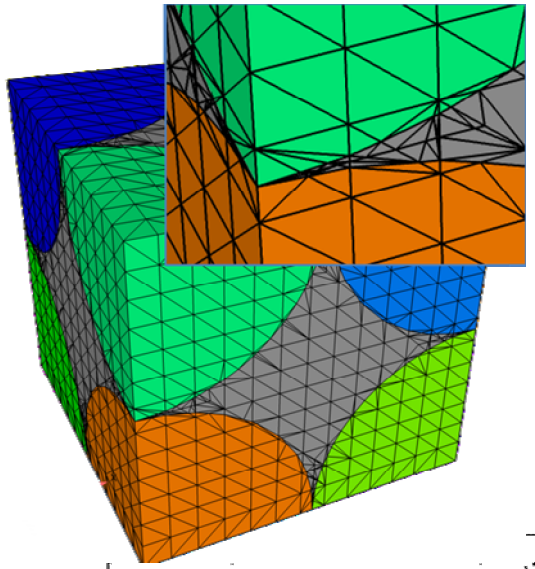


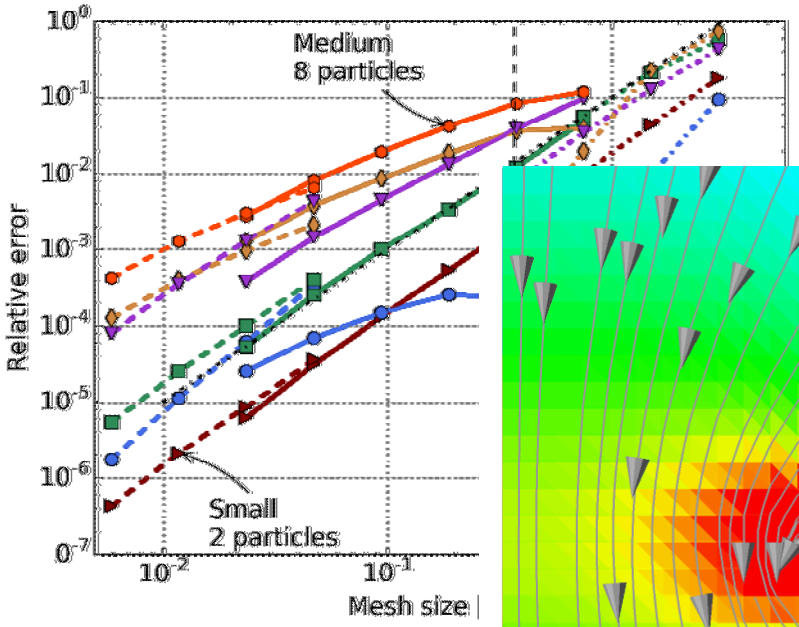


Detailed 3D reconstruction and image processing necessary to get usable mesostructure data

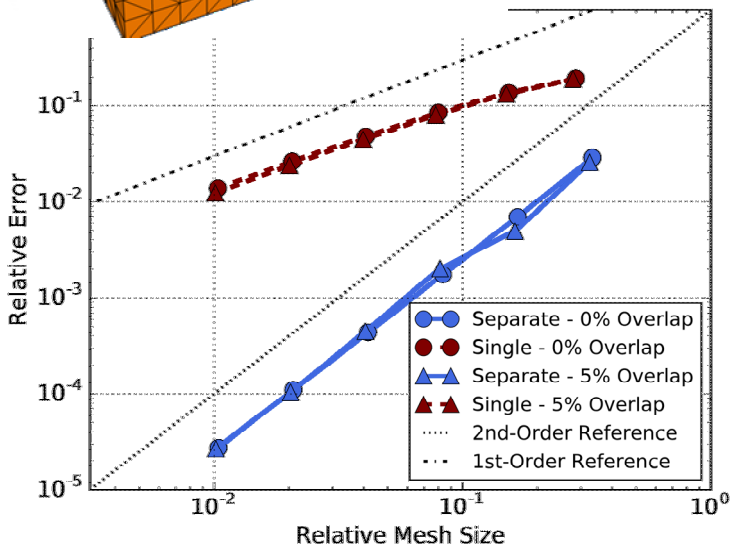
Roberts et al JES 2014, Roberts et al JEECS 2016

Solution verification for credible mesostructure simulations

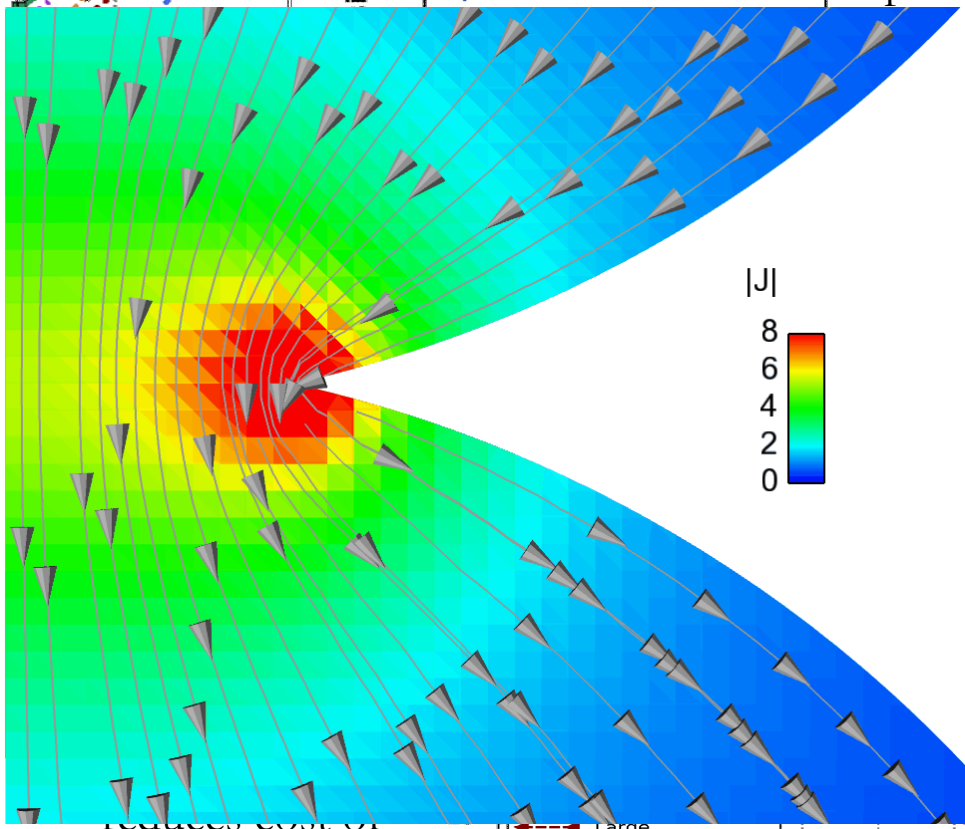




Understand mesh resc
for accurate pred



Separate particle representations required for optimal convergence



Quantify representative element omain

reduces cost of physics solve

Solution verification establishes simulation correctness and domain/mesh size requirements

Roberts, submitted to J. Comp. Phys.

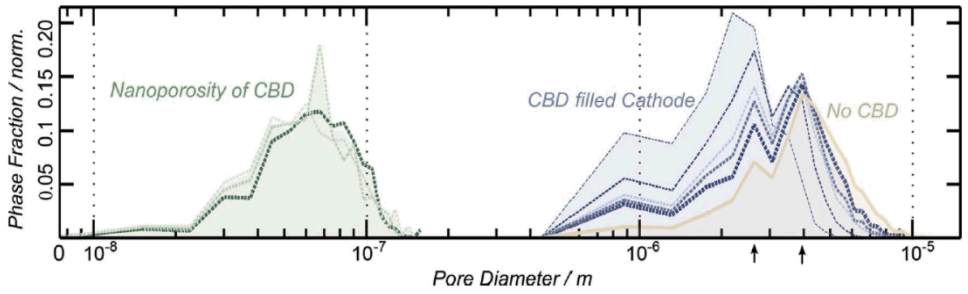
Representation and role of conductive binder morphology

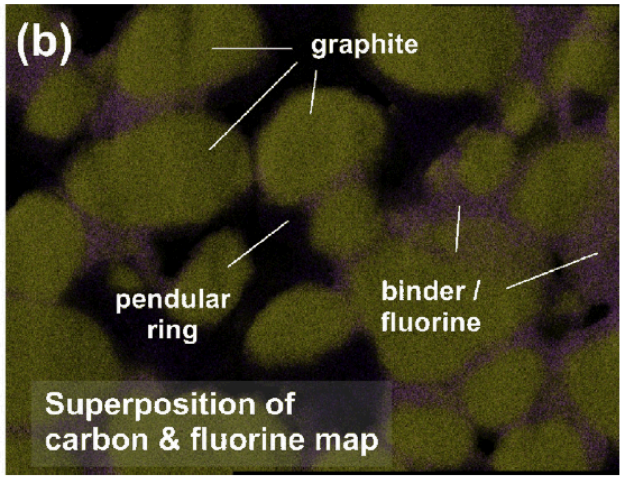
What about the conductive binder?

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

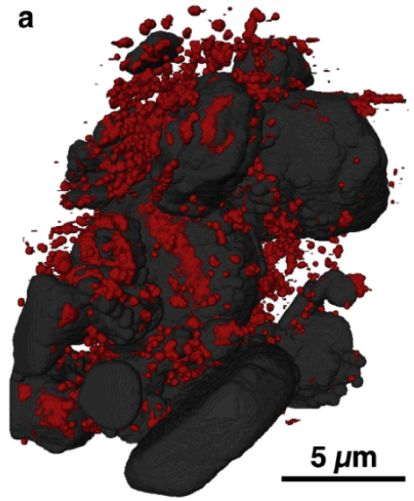
Amorphous binder is significantly nanoporous
- 47% Zielke (2015); 45% Grillet (2016)
- 5% ionic conductivity of pure electrolyte

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

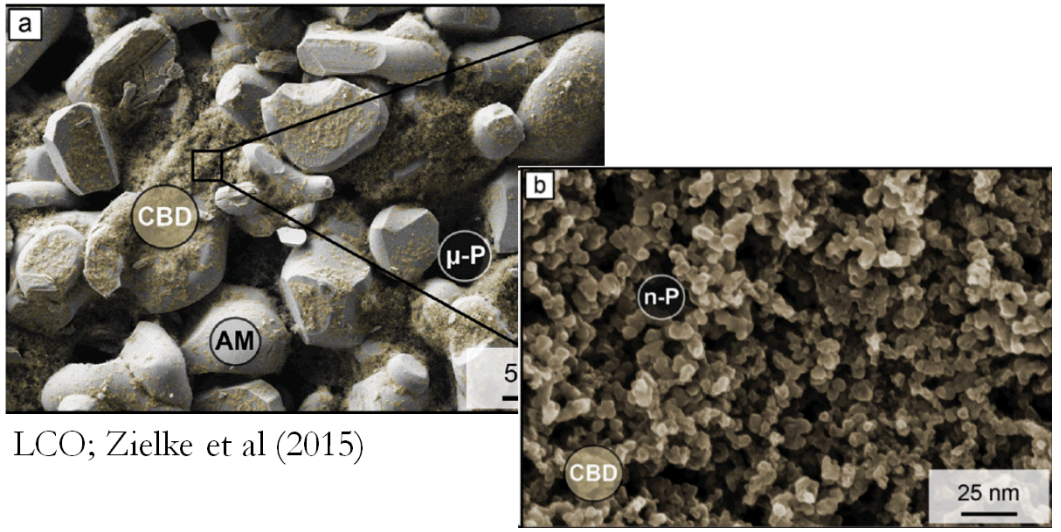




Graphite; Jaiser et al. (2017)



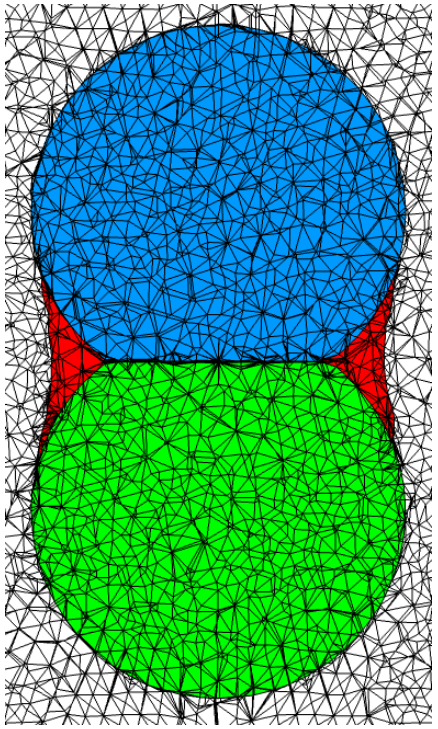
LCO; Komini Babu et al (2015)



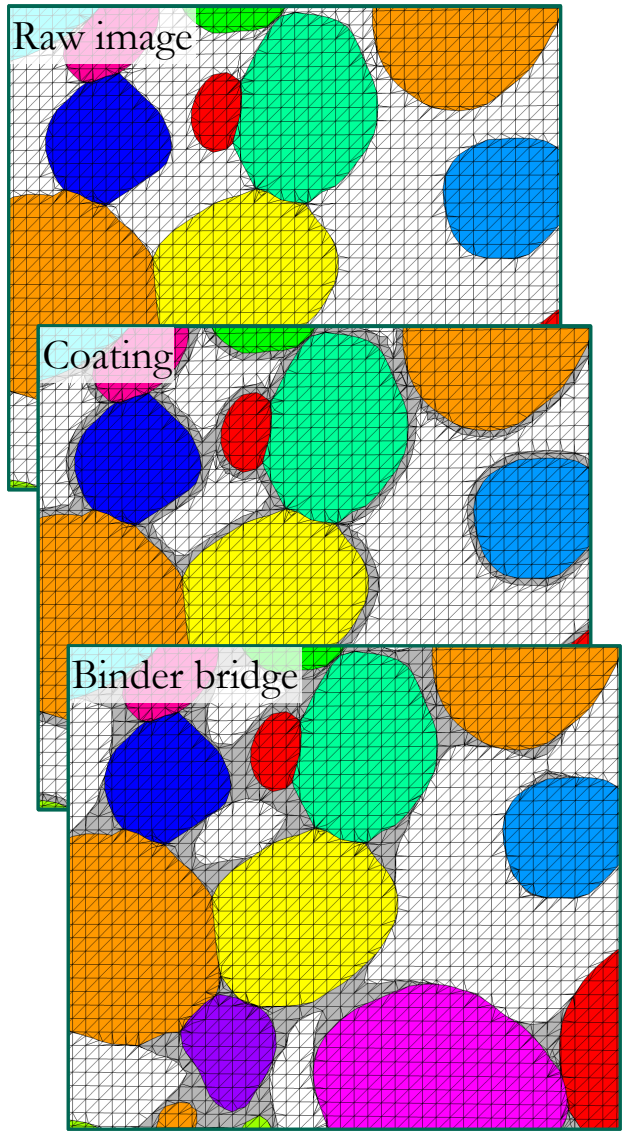
LCO; Zielke et al (2015)

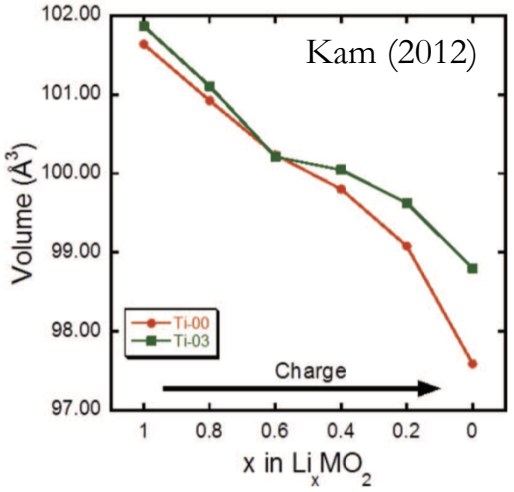
How are electrode-scale properties affected by the inclusion of binder? How does the morphology matter?

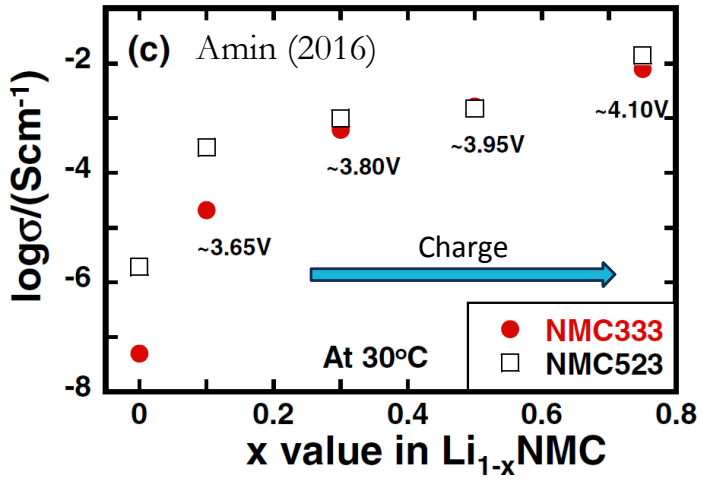
Binder bridge morphology approach



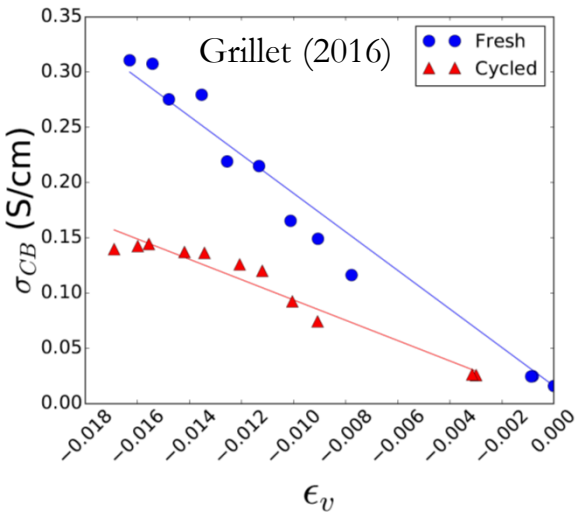
Mathematical description of "binder bridges"

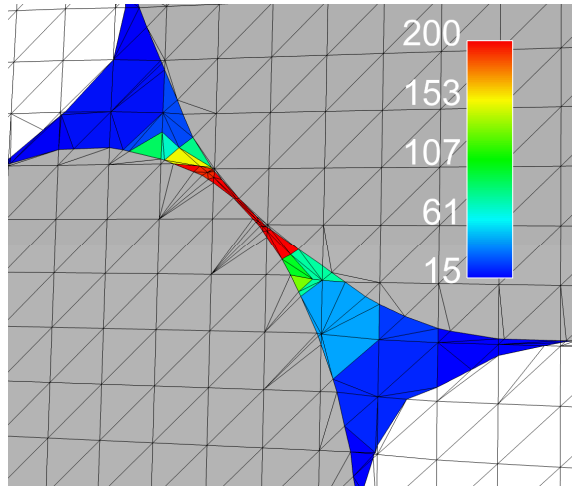






NMC has lithiation-dependent properties



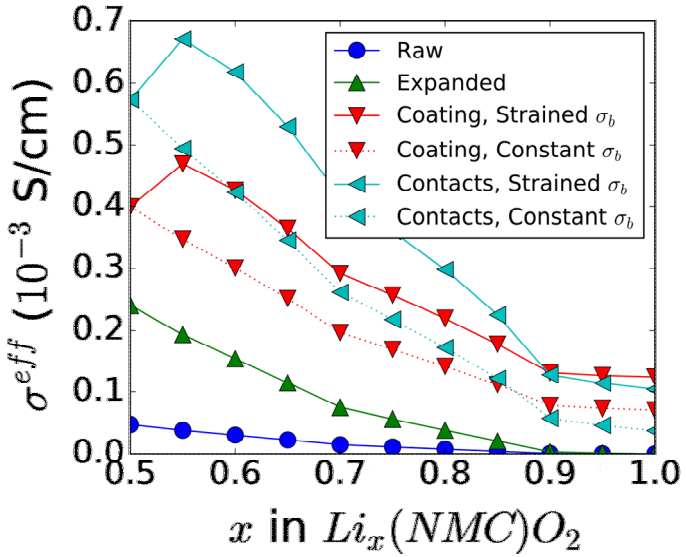


Binder has strain- (e.g. lithiation-) dependent properties

Binder bridge mimics experimental observations; properties are lithiation-dependent

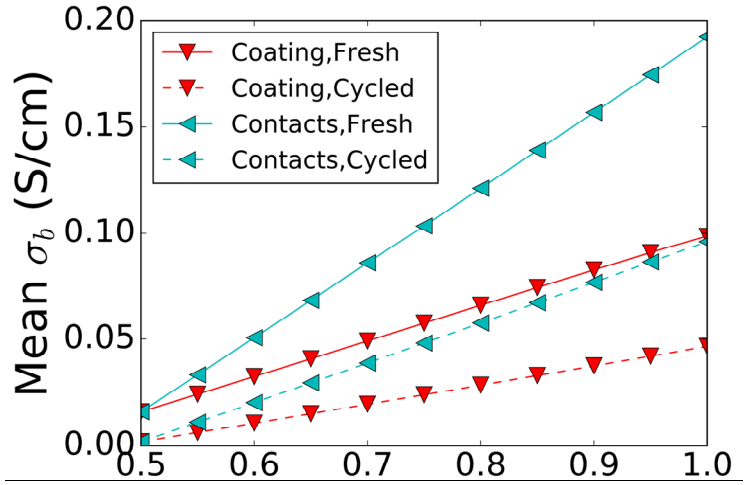
Trembacki (2017)

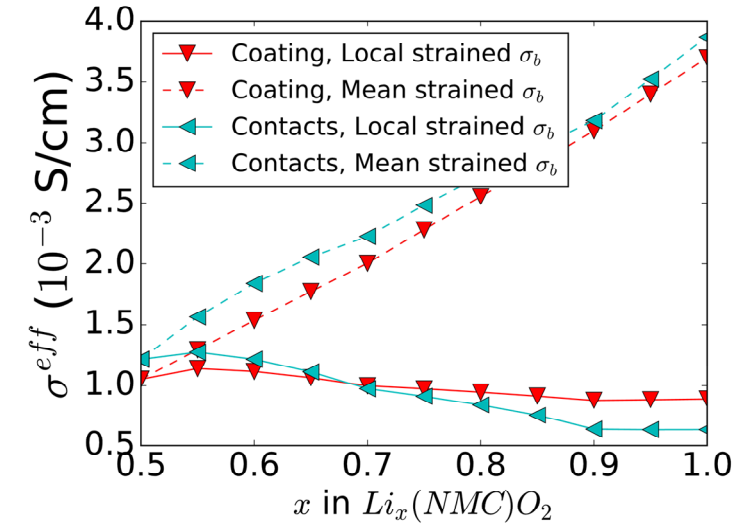
Effect of including binder on effective properties

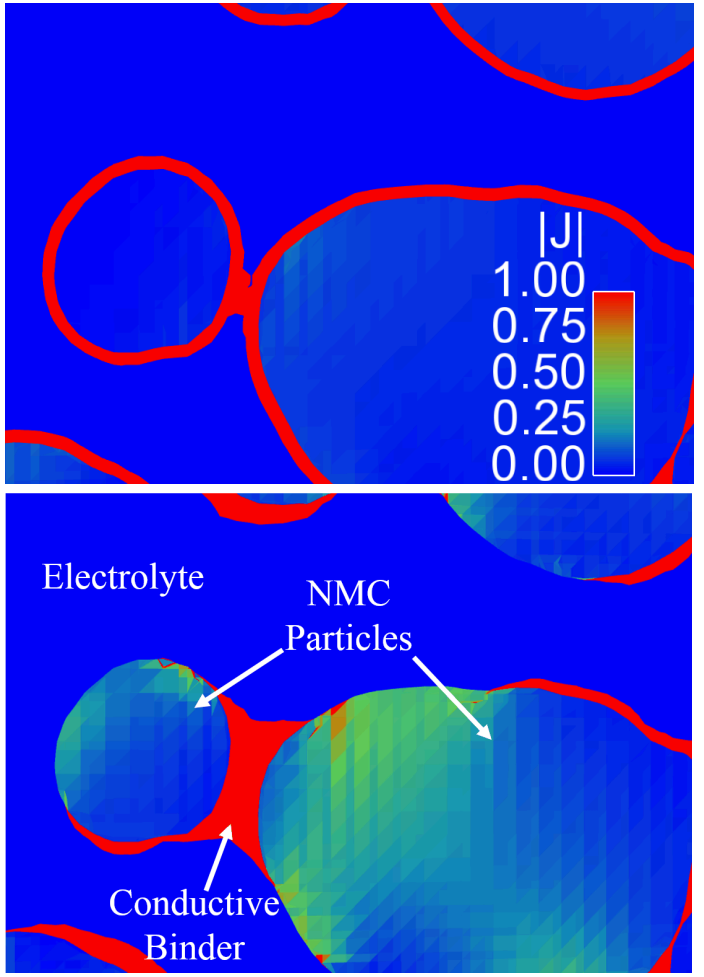


Presence of binder increases electrical conductivity. Mechanics further increase conductivity.

Binder morphology and current localization matters. Binder bridge forces current flow through particles.



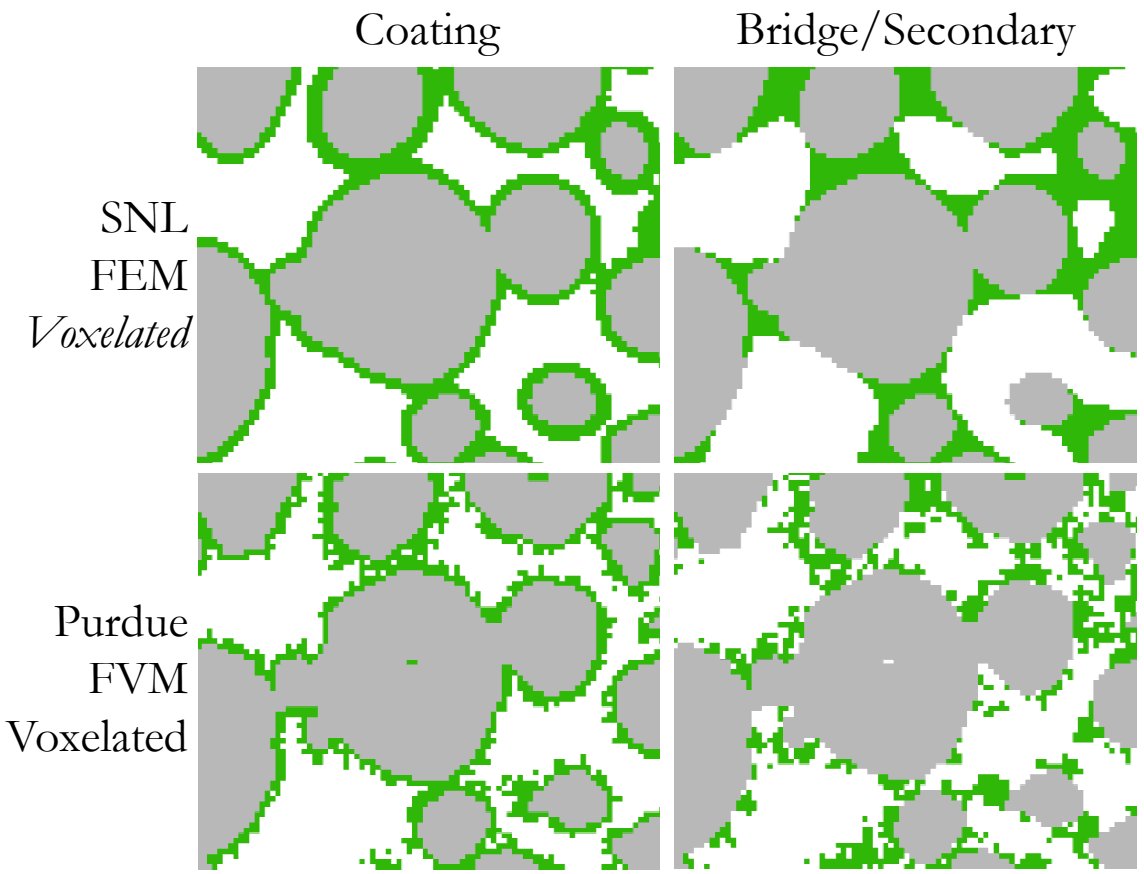


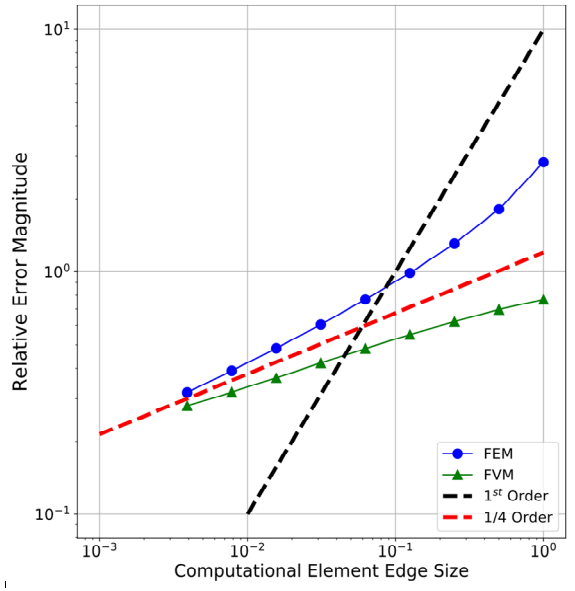


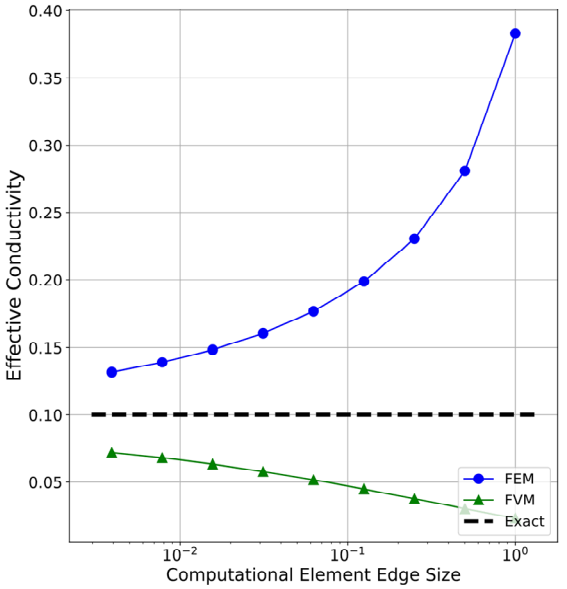
Binder morphology and mechanical coupling have a significant impact on effective properties; localization matters!

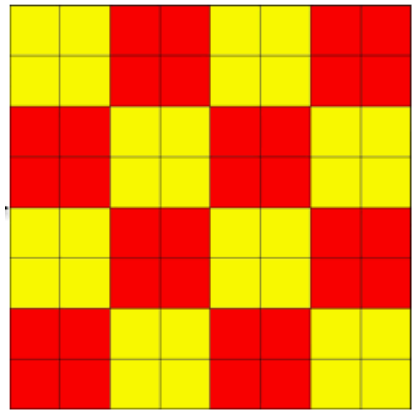
Trembacki (2017)

What about other morphologies and numerical methods









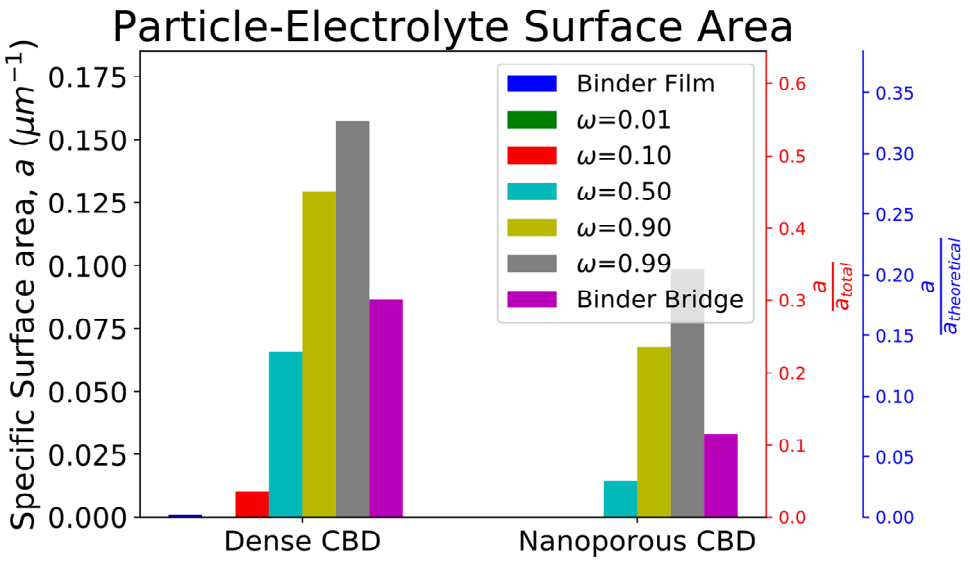
Both methods convergent on voxelated meshes, but:

- At slow rates (1/4-order)
- From different directions
- Unrefined results 10x different

Care must be taken when comparing results generated using different numerical methods; likely not converged!

Trembacki, in preparation

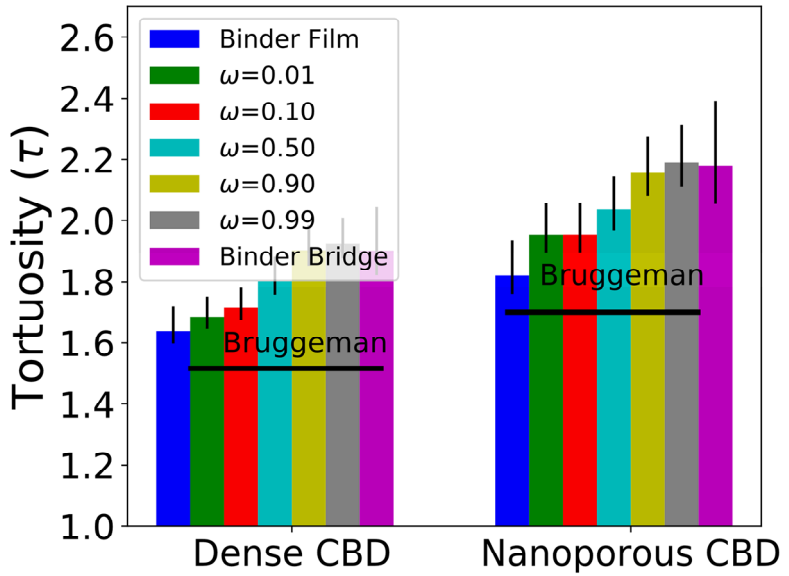
Porous binder and morphology considerations



- 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

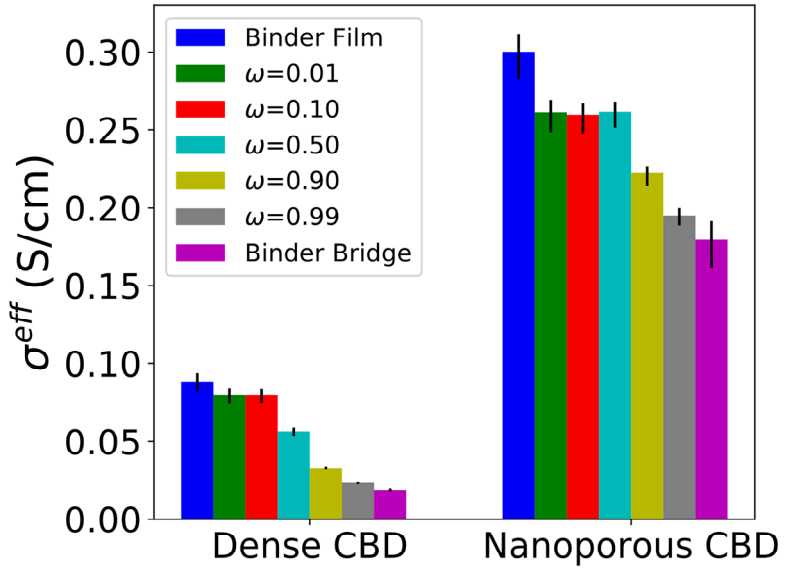
Non-uniform binder:

- Increases tortuosity
- Decreases conductivity



Nanoporosity:

- Increases tortuosity
- Increases conductivity



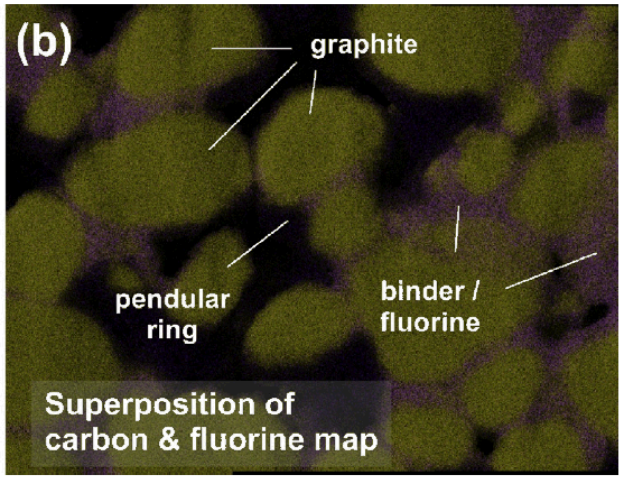
Limiting cases of both morphology methods show similar (but not identical) behavior; nanoporosity is important!

Trembacki, in preparation

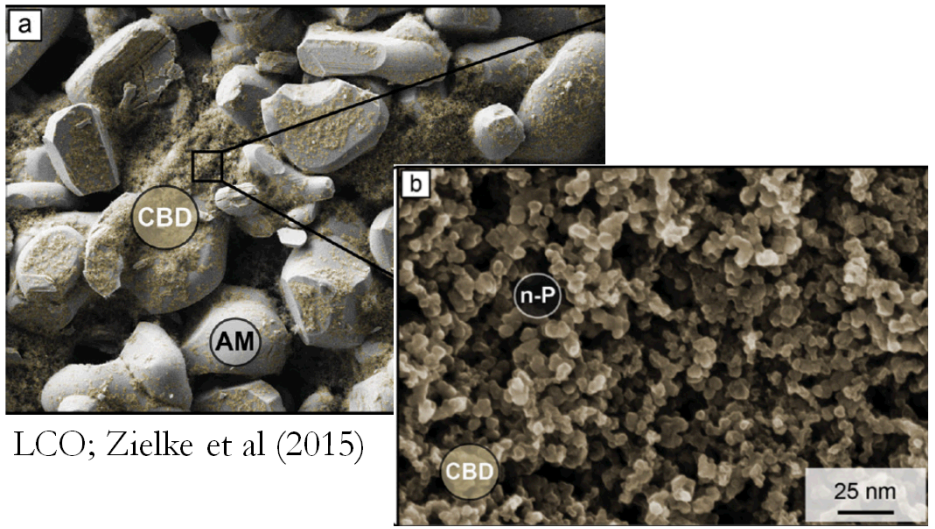
Challenges with using CT mesoscale data

3D CT image data:

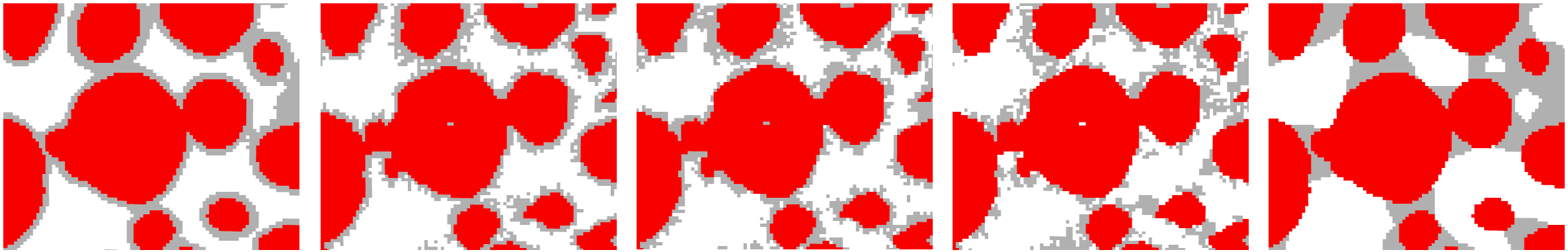
- Expensive
- Time consuming
- Conductive binder not visible



Graphite; Jaiser et al. (2017)



LCO; Zielke et al (2015)



Hypothesis: Use DEM simulations to create AM+CBD mesostructures and CDFEM for physics predictions

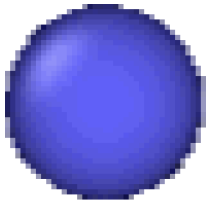
Trembacki et al *in preparation*

Discrete Element Method (DEM) setup

LAMMPS solves Langevin equation for inertial Brownian motion

- 94:3:3 AM:CB:PVDF weight ratio
- (~100 μm)^3 domain at 50% porosity
- 1,000 AM particles, 800,000 CBD particles

Active Matter (AM): NMC particle [10 microns]



Carbon black + PVDF binder (CBD) particle [500 nm]

Inter-particle interactions

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

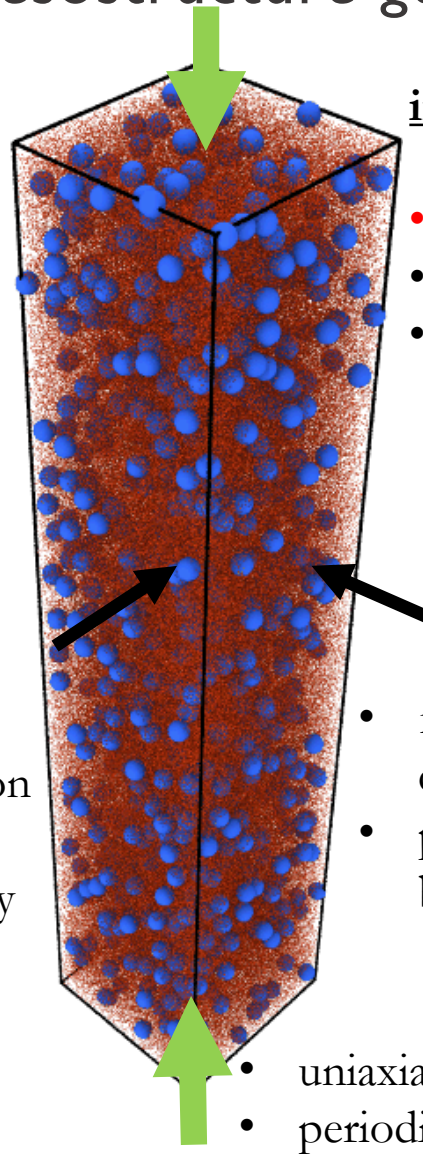
$$F_{\text{JKR}} = \left(\frac{4E\delta^3}{3a} - 2\pi\delta^2 \sqrt{\frac{4\gamma_c E}{\pi\delta}} \right)$$

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

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

Granular + Brownian motion to enable study of AM consolidation and CBD aggregation

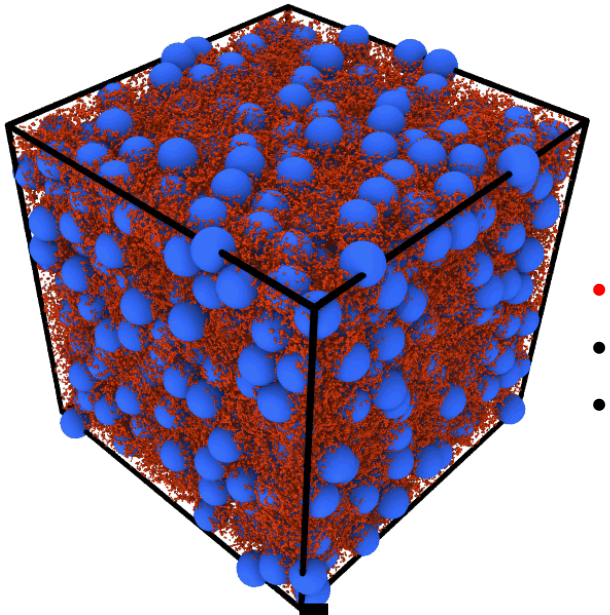
Mesostructure generation: Uniaxial compression



initial microstructure

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

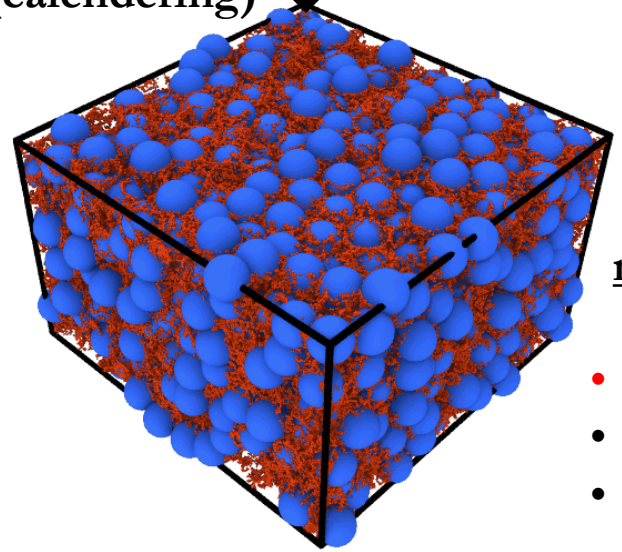
compression (drying)



intermediate microstructure

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

compression (calendering)



compressed microstructure

- **porosity: 20%**
- height: 66 um
- width: 100 um

- fixed dimension
- periodic boundary

- fixed dimension
- periodic boundary

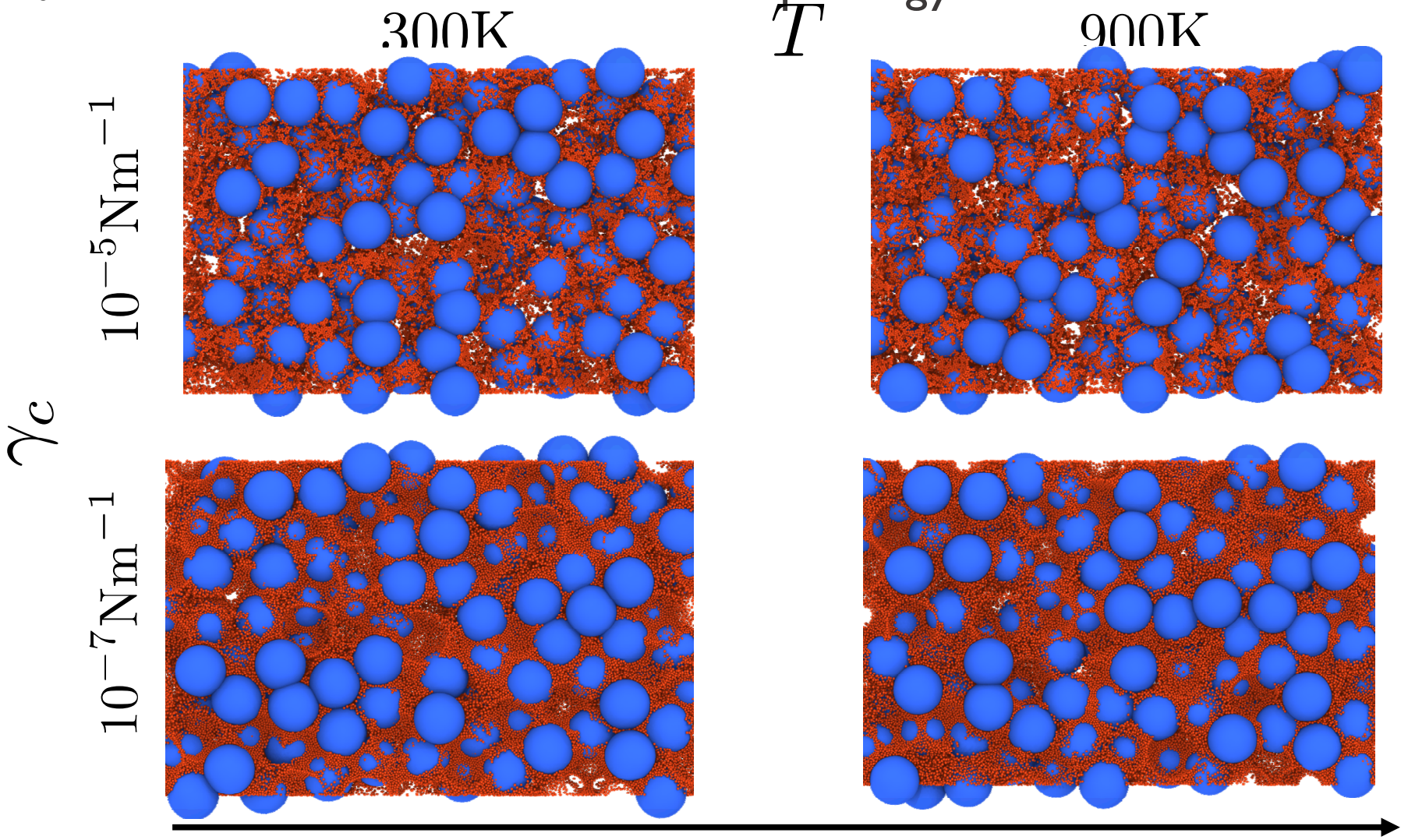
- uniaxial compression
- periodic boundary

constant strain-rate compression

$$\dot{\gamma} = 4\mathrm{s}^{-1}$$

Uniaxial compression represents both drying and calendering

Role of cohesion in CBD morphology



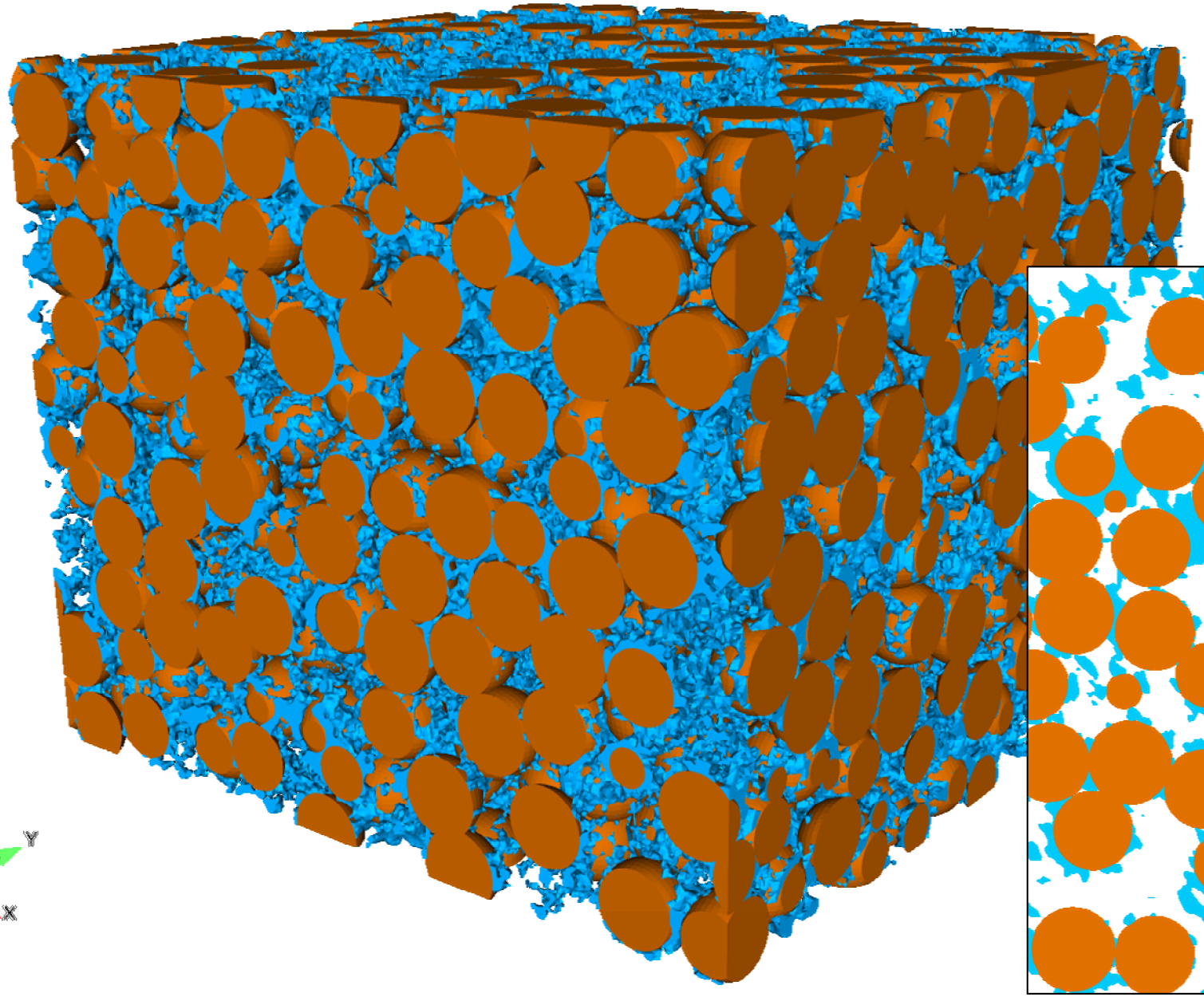
governing parameter

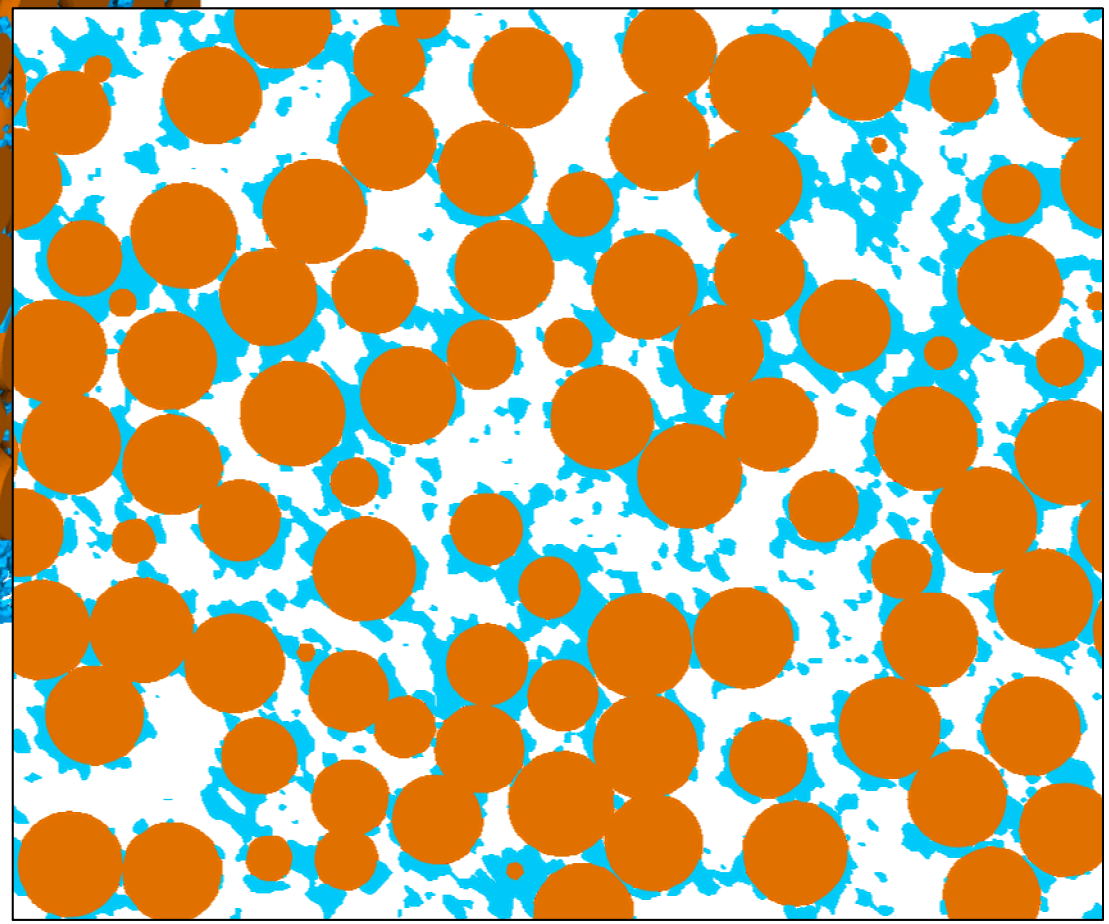
$$\frac{\gamma_c a^2}{kT}$$

increased string-like fractal microstructure of CBD particles resulting in non-uniform coating around AM particles. CBD phase behaves like a sticky fluid

Cohesive surface energy drastically alters CBD morphology

Conformal Decomposition Finite Element Method (CDFEM)





NMC cathode effective property prediction and upscaling

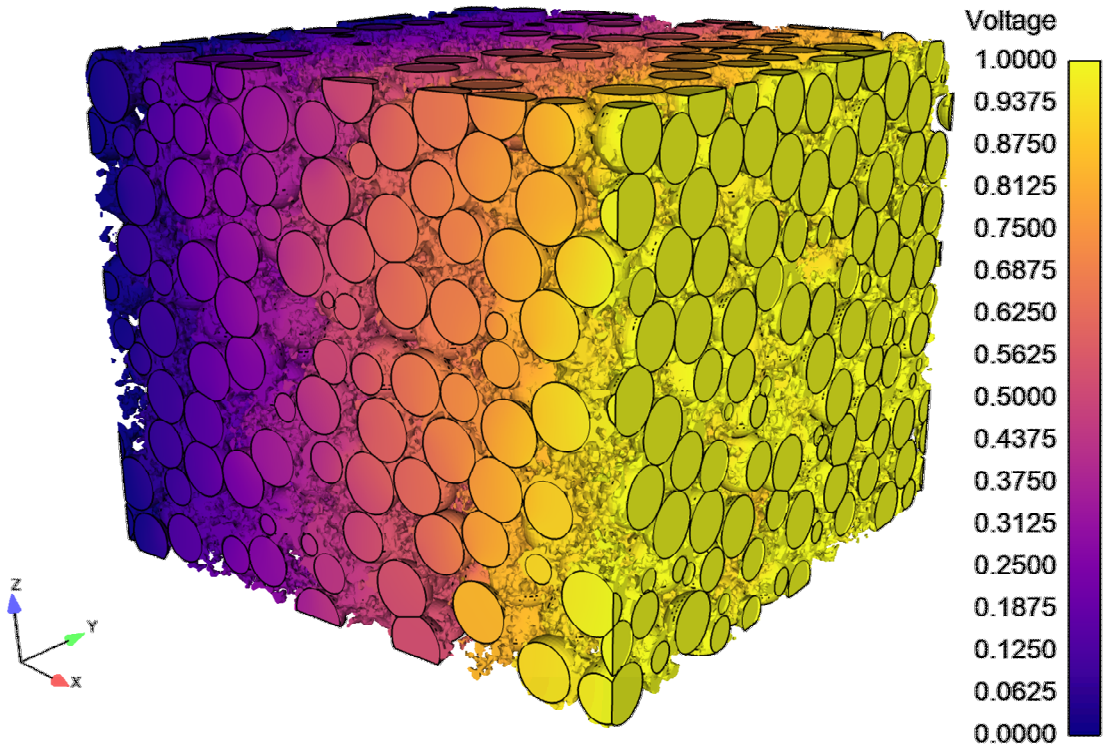
Effective electrode property calculations

Calculate effective transport properties for upscaling

- Particle specific surface area
- Electrical conductivity
- Tortuosity

NMC image data from Ebner (2013)

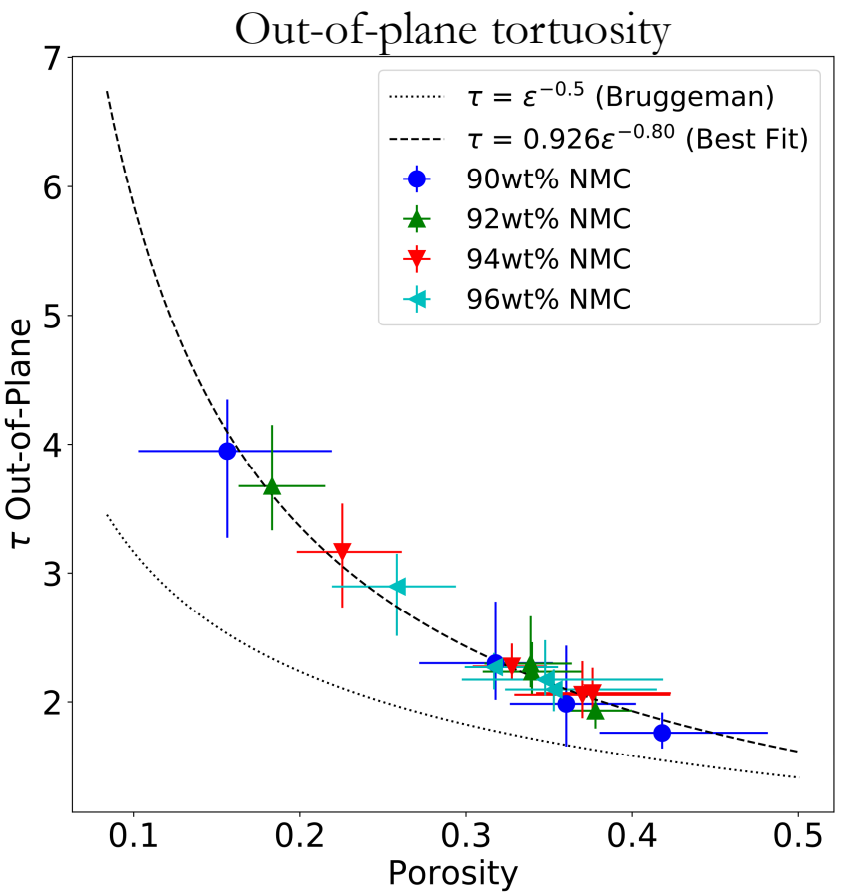
- 90, 92, 94, 96 wt% NMC (remainder 1:1 CB:PVDF)
- 0, 300, 600 & 2000 bar calendering
- 100 µm x 100 µm x 60 µm domain (20 realizations eac
- Binder bridge (porous) morphology approach

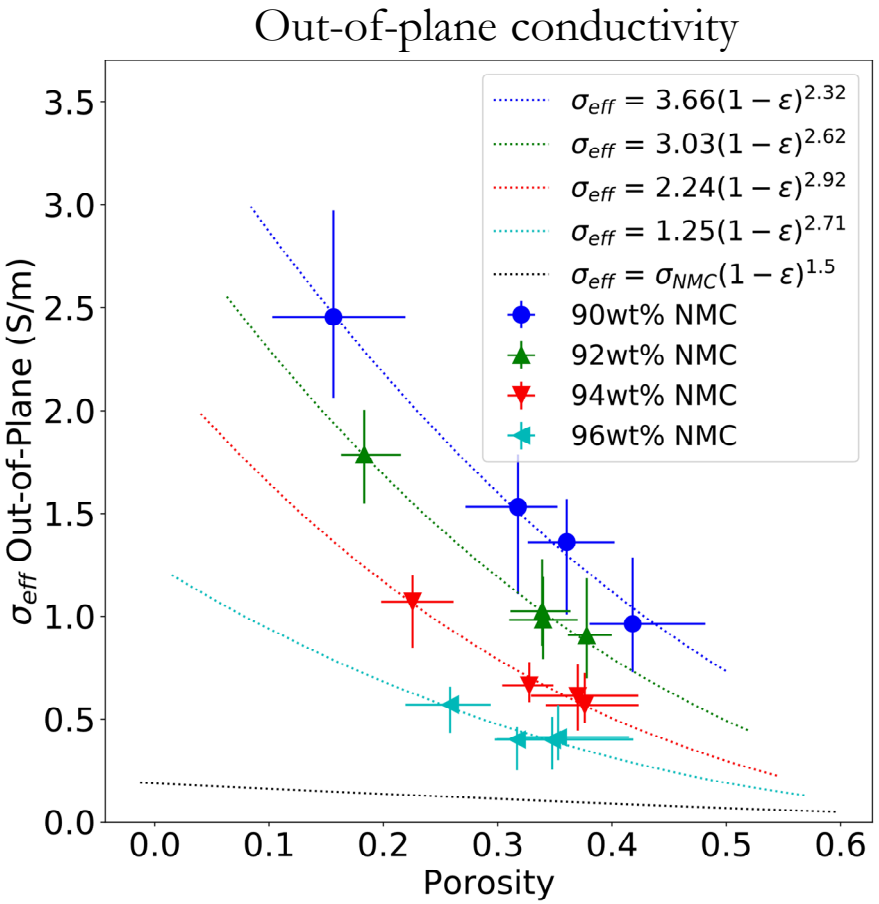


Effective properties are an important first step for upscaling mesoscale data

Ferraro, in preparation

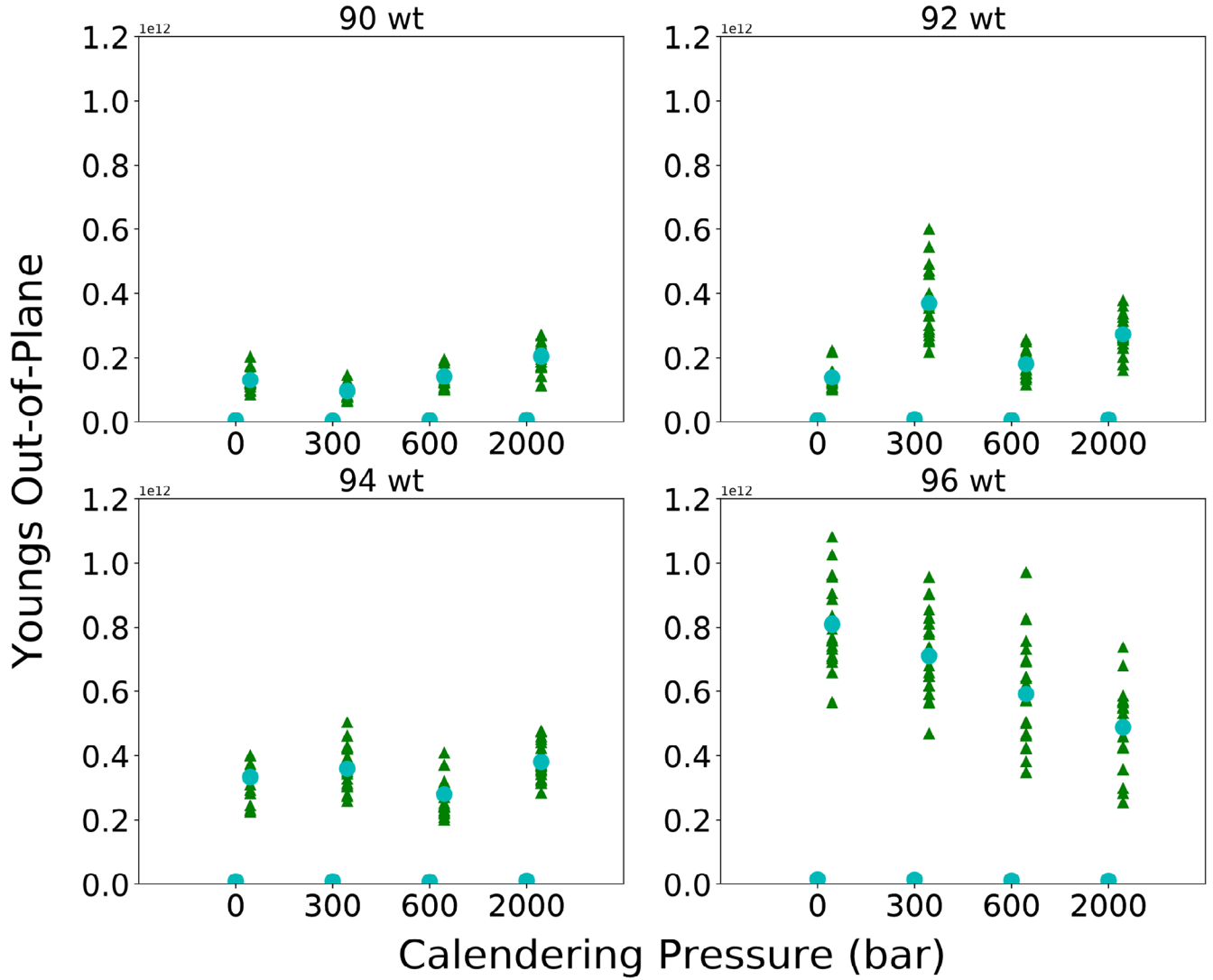
Effective electrode property calculation results – Transport





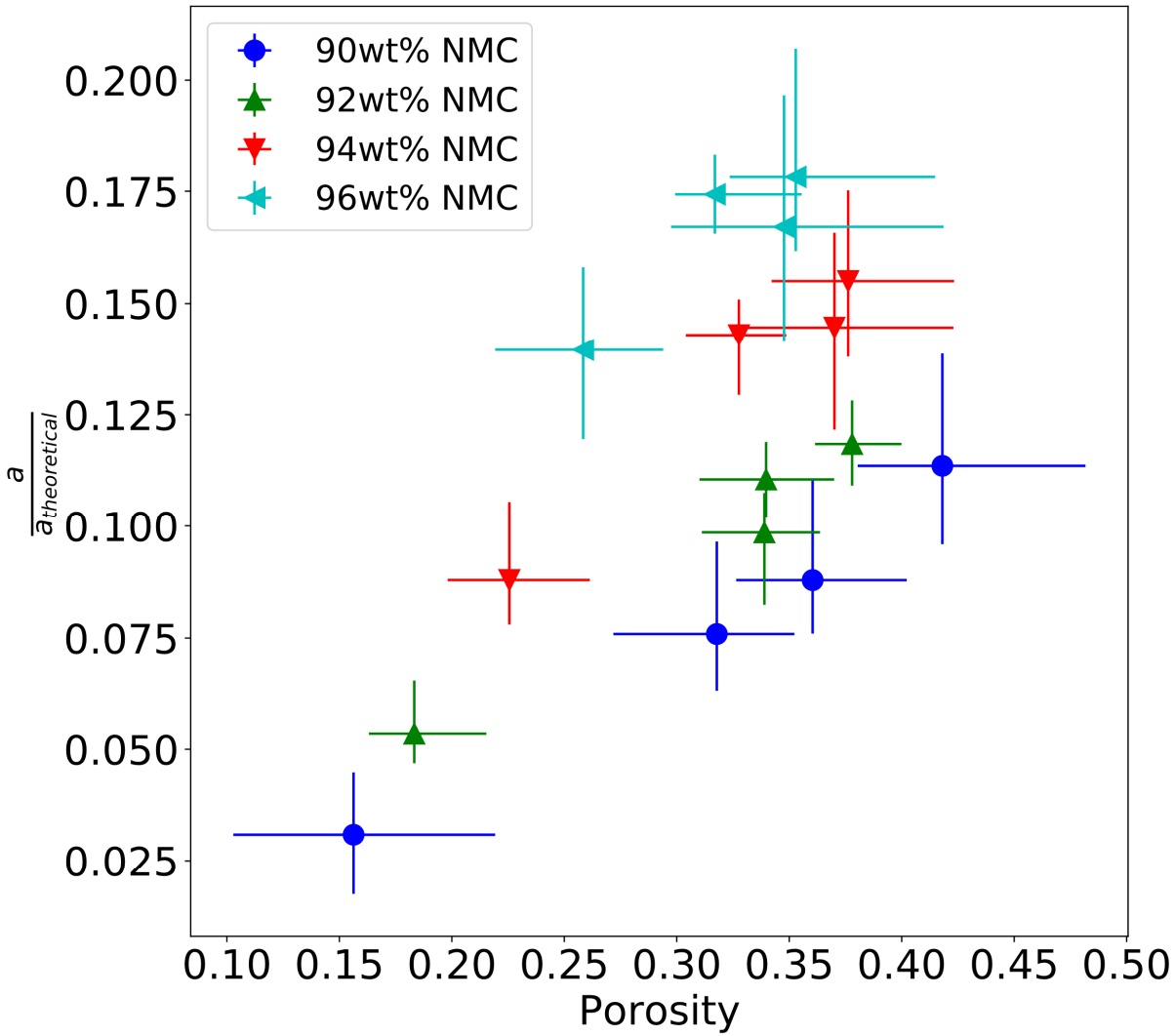
Bruggeman relationships must be re-calibrated to fit simulated data

Effective electrode property calculation results – Mechanical



Stiffness increases with NMC content but also varies with calendaring

Effective electrode property calculation results – Surface area

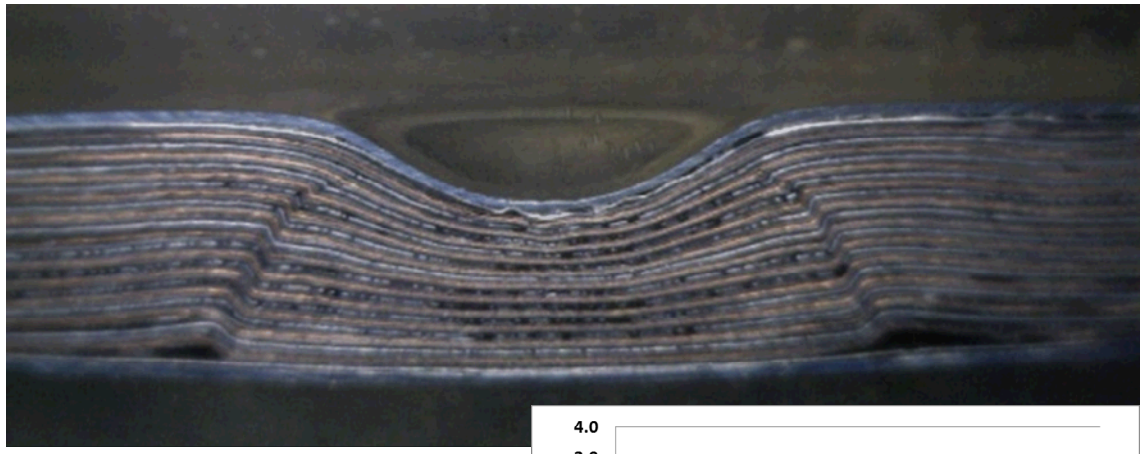


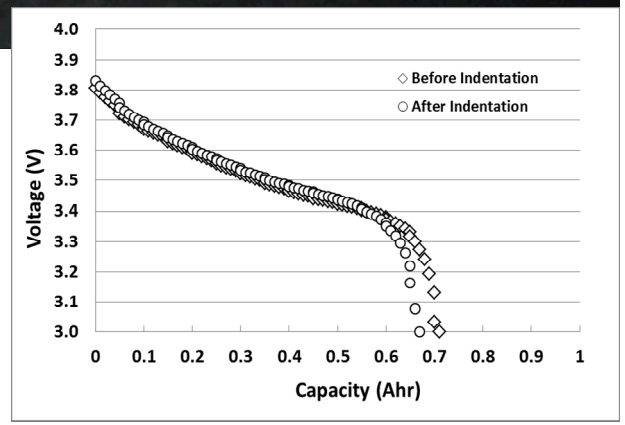
Binder morphology significantly reduces particle surface area available for chemical reaction

Upscaling effective properties for pouch-level modeling

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

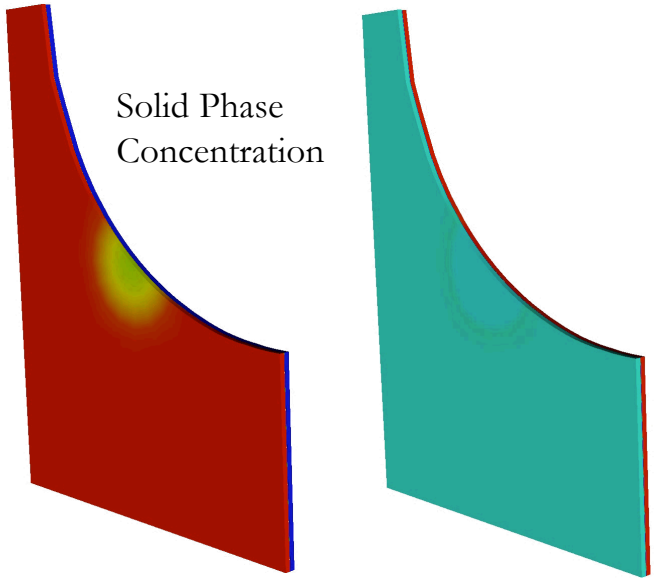
- 10 cell pouch with 80 μm electrodes
- Indented with 13 mm diameter spherical indenter
- Modeled mechanics of indentation (porosity change)
- Simulated 1C discharge

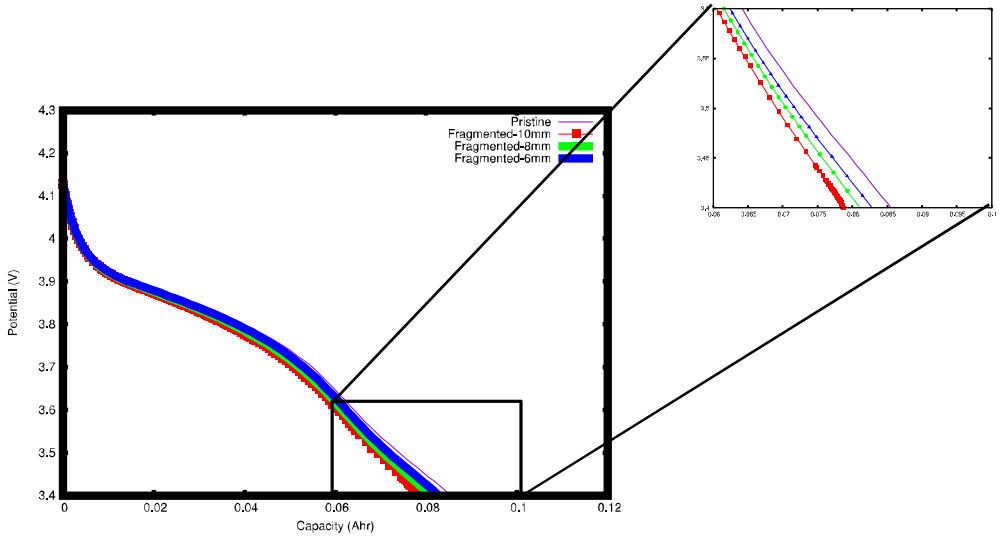




Solid Phase Potential

Solid Phase Concentration

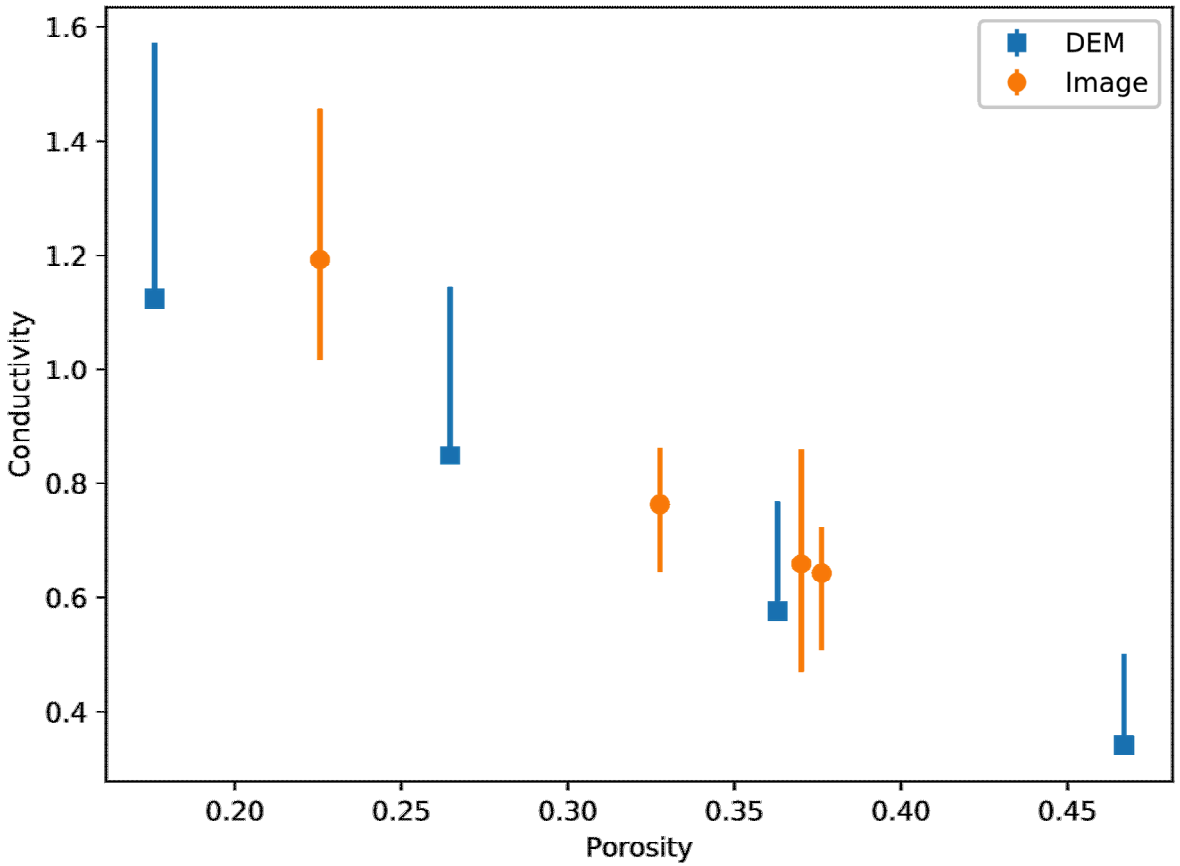


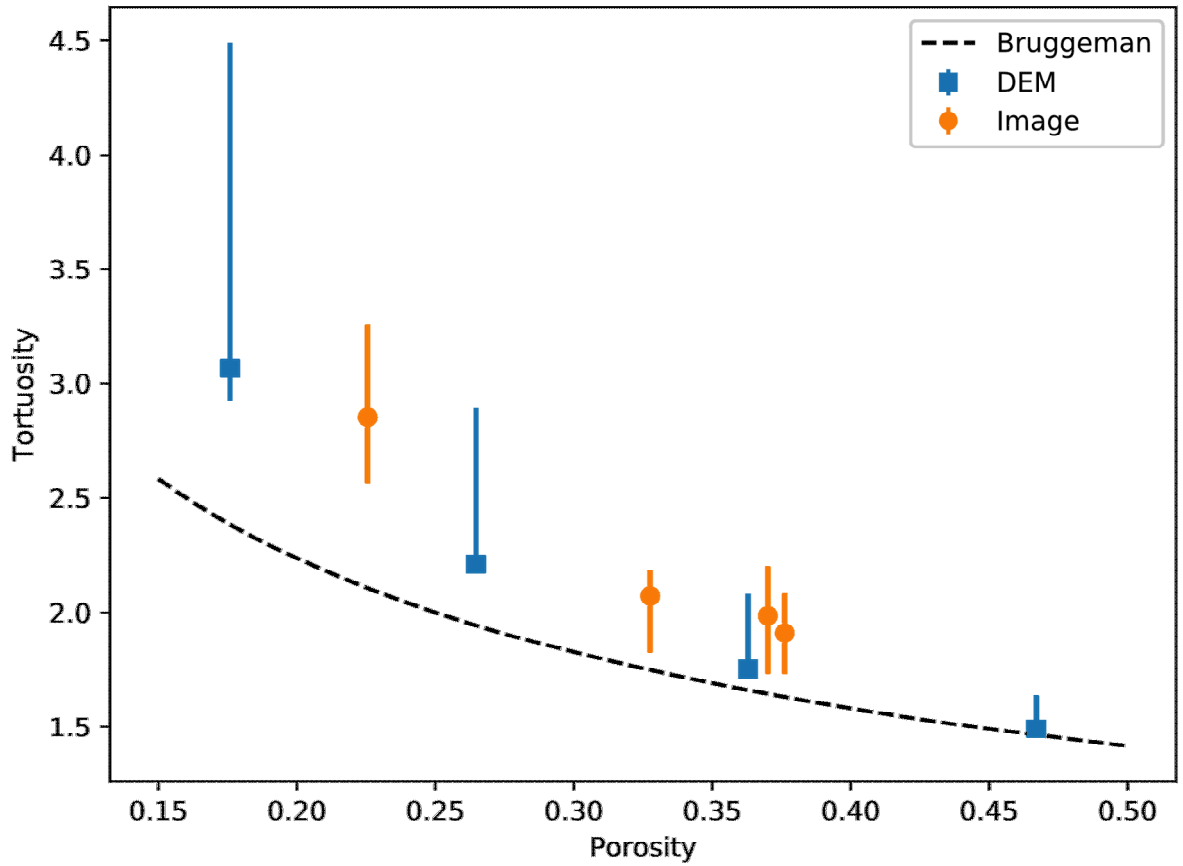


Pouch simulation with effective properties shows similar-scale capacity decrease; demonstrates mesoscale integration

Allu, in preparation

Comparison of image- and DEM-based mesostructures





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

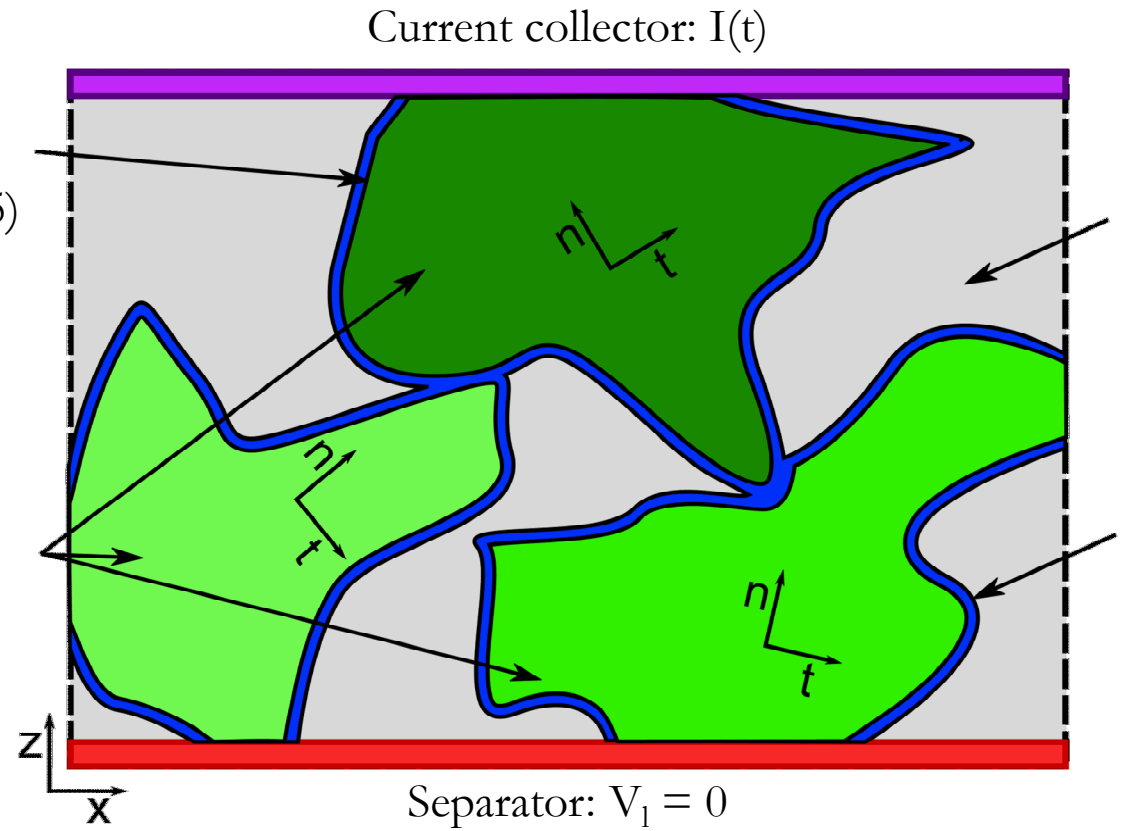
Calendaring → lower porosity → more CBD connectivity → higher conductivity and tortuosity

Electrochemical-mechanical discharge simulations of NMC half-cells

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

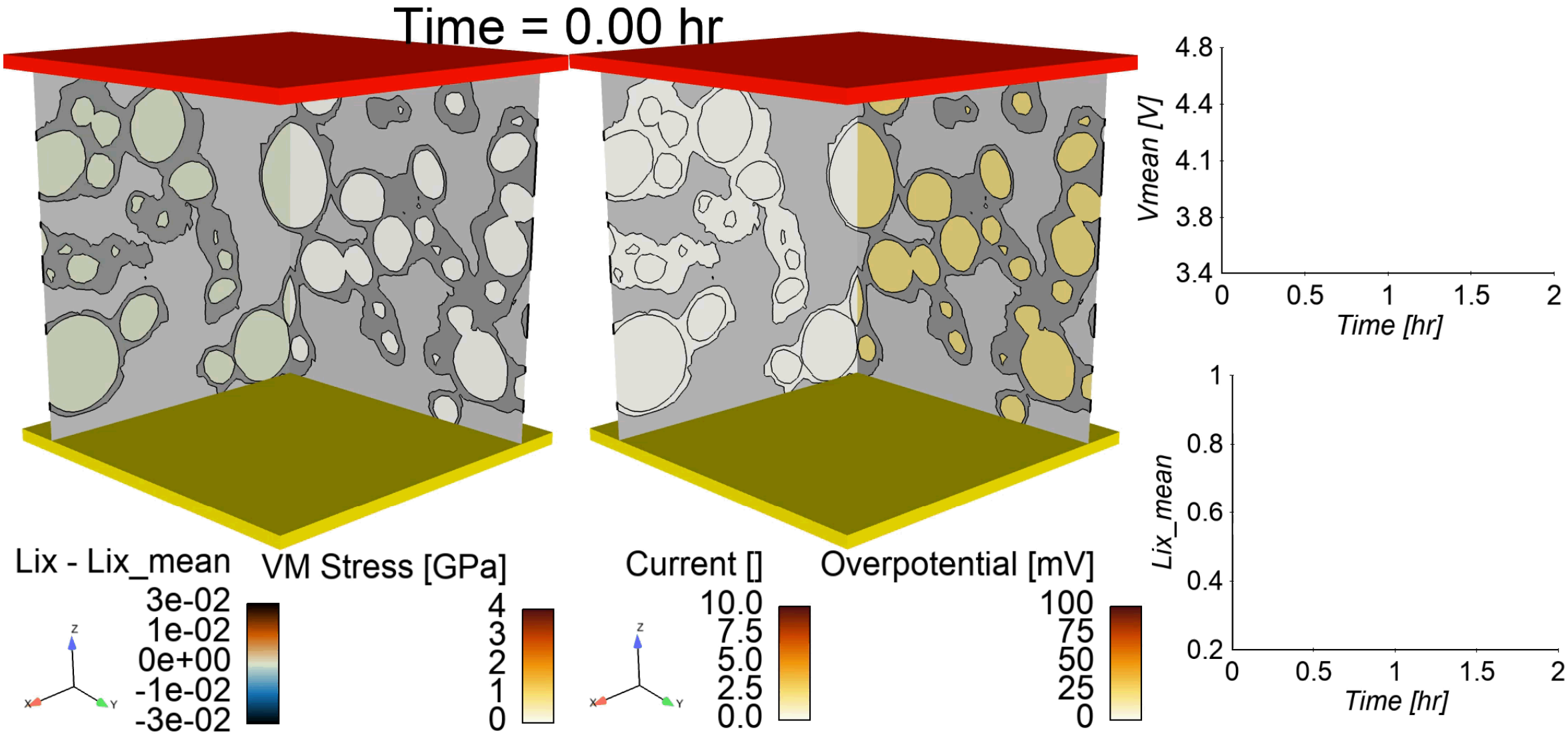
Conductive binder:
- Species – Porous Li^+ transport
- Electrical
  - Solid: Porous Ohm's law
    - Strain-dependent electrical conductivity
  - Liquid: Ionic conservation & electroneutrality
- Mechanics – Elastic

Mathematical formulation builds off of Mendoza (2016) LCO studies

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

Ferraro, in preparation

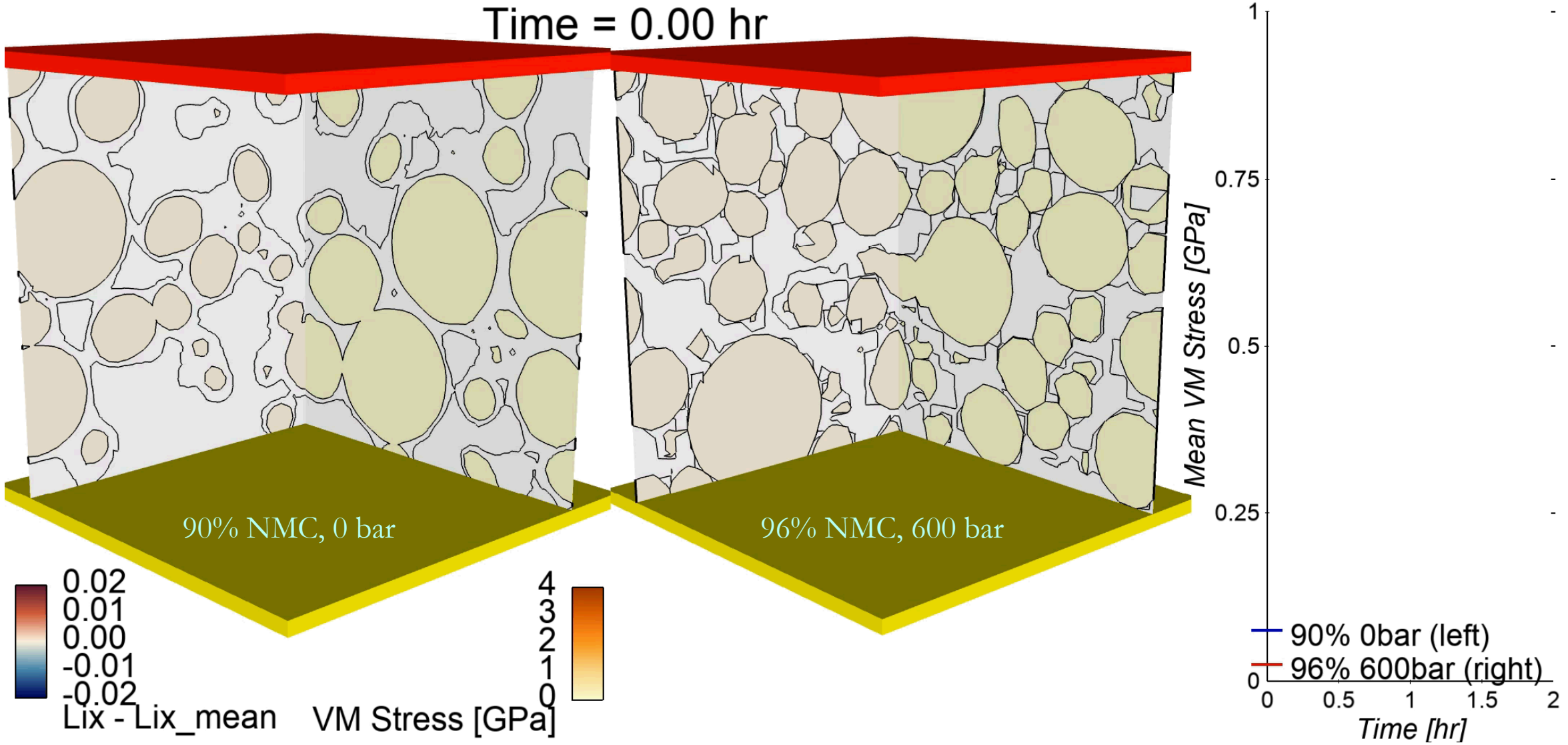
Demonstration of NMC half-cell discharge simulation at C/2



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

Ferraro, in preparation

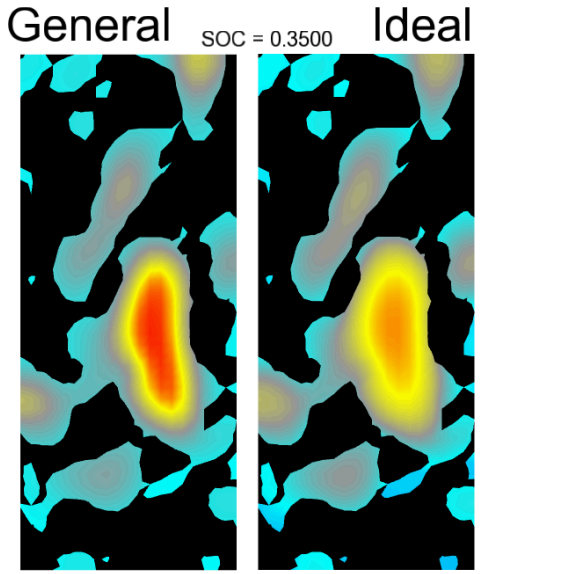
Effect of solids loading, calendering pressure

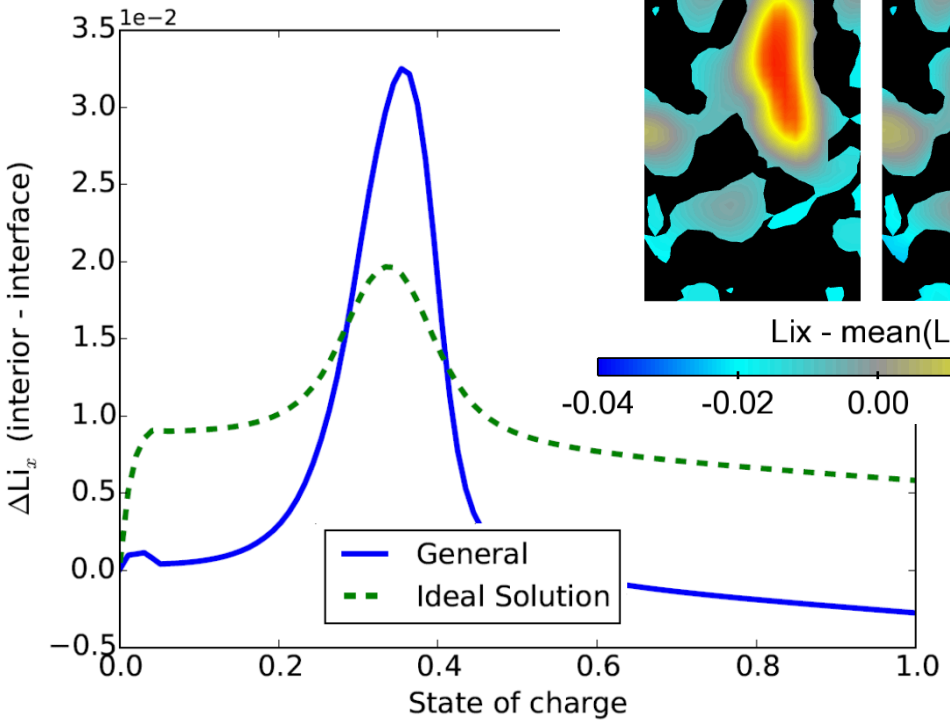


Significantly higher mechanical stresses for higher NMC loadings and higher calendering pressures

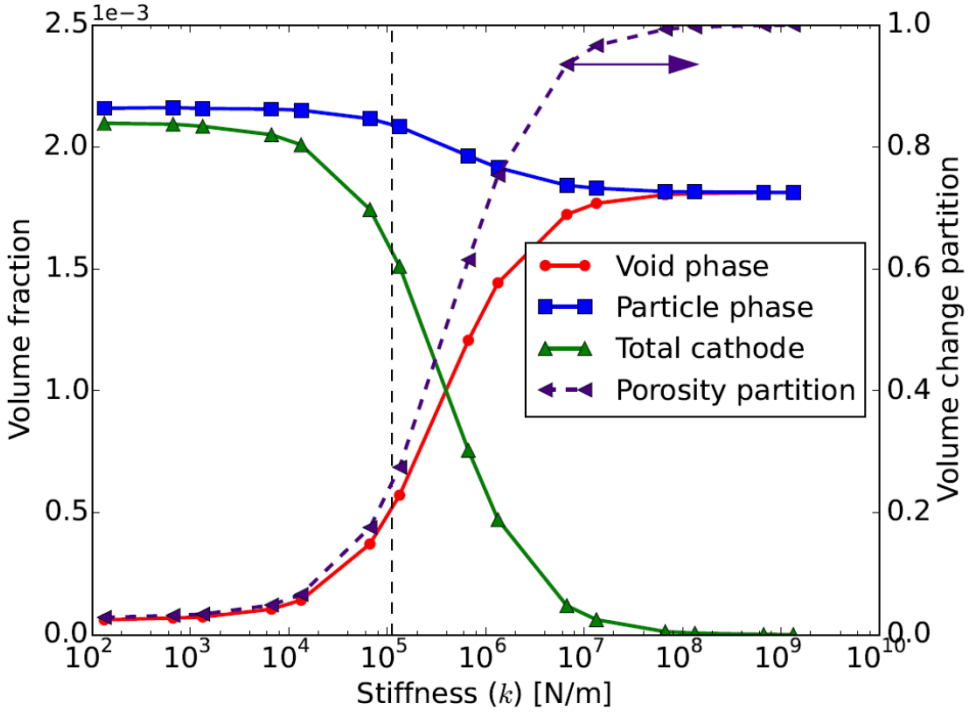
Ferraro, in preparation

What can you learn from coupled half-cell simulations? LCO





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!

Mendoza (2016)

Future directions in electrode mesoscale modeling

Future extensions of current work

Effective property calculation, correlation, and upscaling
- Effective properties for all 16 NMC data sets from Ebner (2013)
- Effective properties from DEM simulations, validation to experiment

Graphite anode mesoscale analysis (current student with P. Mukherjee)
- Recent image data from V. Wood group

Coupled electrochemical-mechanical simulations
- Study of binder fraction, calendering, and discharge rate
- More appropriate boundary conditions (separator/collector stiffness/transport, V. Wood/C. Arnold)
- Multiple charge-discharge cycles
- Full-cell (cathode, separator, anode) analysis

Upscaling and integration with cell-level codes (i.e. CAEBAT/OAS/VIBE)

Automated image-to-simulation – machine learning (LDRD just funded)

Silicon anode mesoscale analysis
- Inelastic binder mechanics (viscoelasticity, delamination, etc.)
- Large deformation multi-physics framework

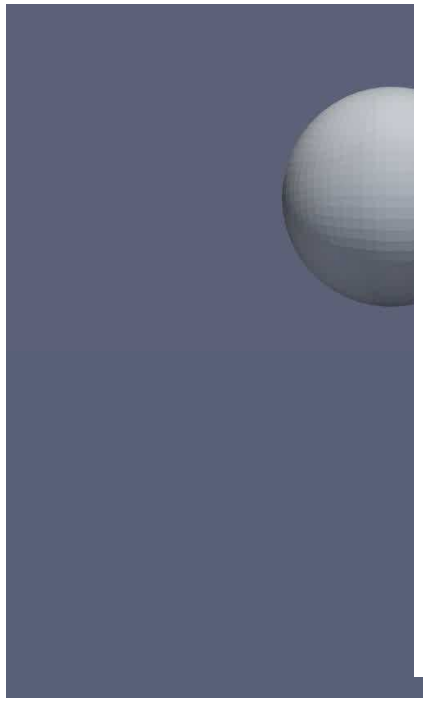
Application to 3D printed batteries, lithium plating and growth (2 current proposals to EERE/VTO)

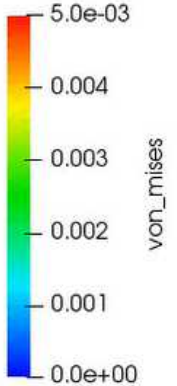
There's still much work to be done in the areas discussed here

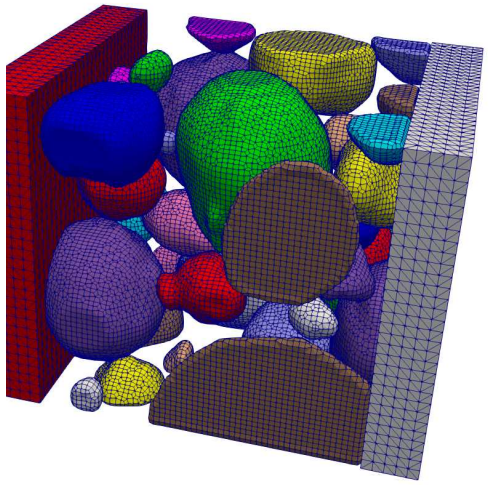
Large deformation multi-physics formulation

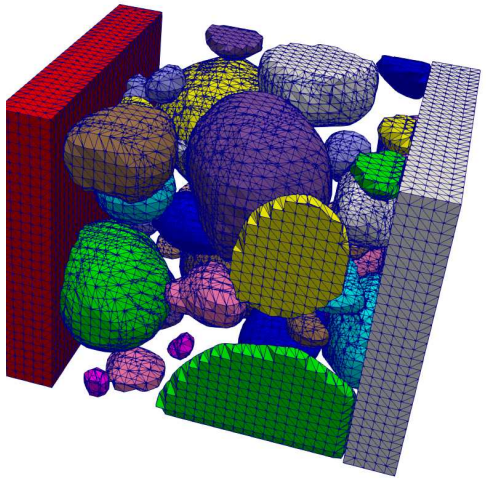
Concept:

- Solid mechanics c
- Transport/electrc
- Transfer displacer









Demonstrated two-way coupling between mechanics and transport codes; developing robust particle contact

Brunini, unpublished

References and acknowledgments

Publications

- Roberts *et al.*, "A Framework for Three-Dimensional Mesoscale Modeling of Anisotropic Swelling and Mechanical Deformation in Lithium-Ion Electrodes", J. Electrochem. Soc. (2015) 10.1149/2.0081411jes
- Mendoza *et al.*, "Mechanical and Electrochemical Response of a LiCoO2 Cathode using Reconstructed Microstructures," Electrochim. Acta (2016) 10.1016/j.electacta.2015.12.224
- Roberts *et al.*, "Insights into lithium-ion battery degradation and safety mechanisms from mesoscale simulations using experimentally-reconstructed mesostructures," J. Electrochem. En. Conv. Stor. (2016) 10.1115/1.4034410
- Trembacki *et al.*, "Mesoscale Effective Property Simulations Incorporating Conductive Binder," J. Electrochem. Soc. (2017) 10.1149/2.0601711jes

Data

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

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- Sandia's Laboratory Directed Research and Development (LDRD) program – 2013-2016
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Questions?

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