

Predicting Mechanical Stresses in Lithium-Ion Battery Electrodes using Mesoscale Simulations

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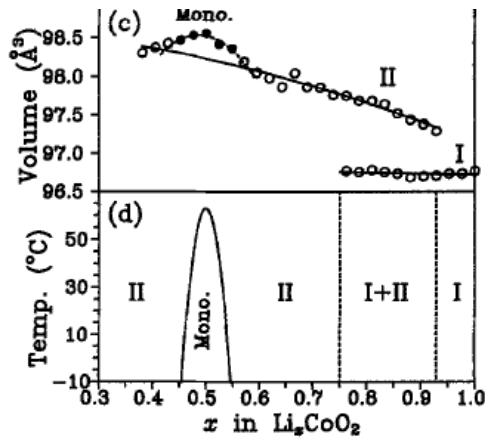
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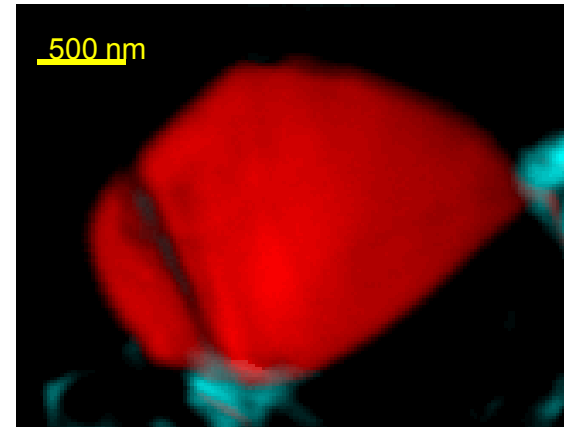
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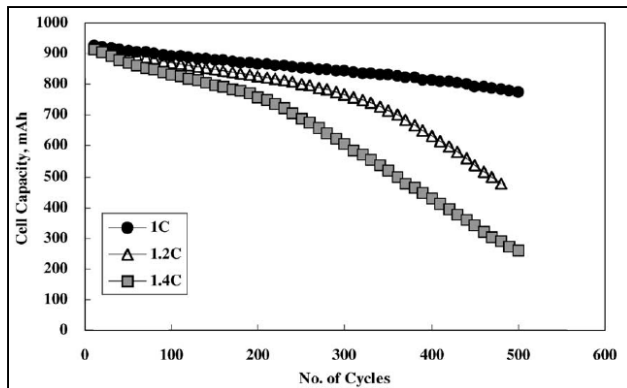
Mechanics of capacity fade in lithium-ion batteries



Li changes lead to strain.
Reimers and Dahn (1992)

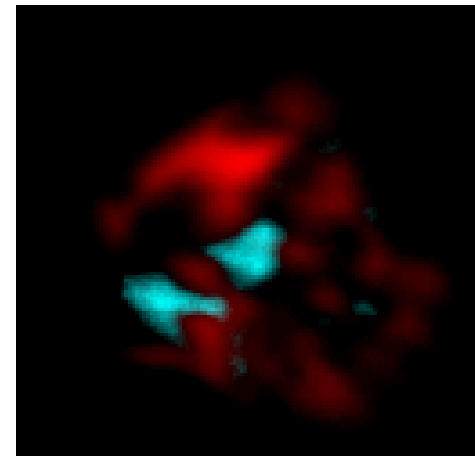


Un-cycled
LiCoO₂



Capacity fades as batteries are cycled

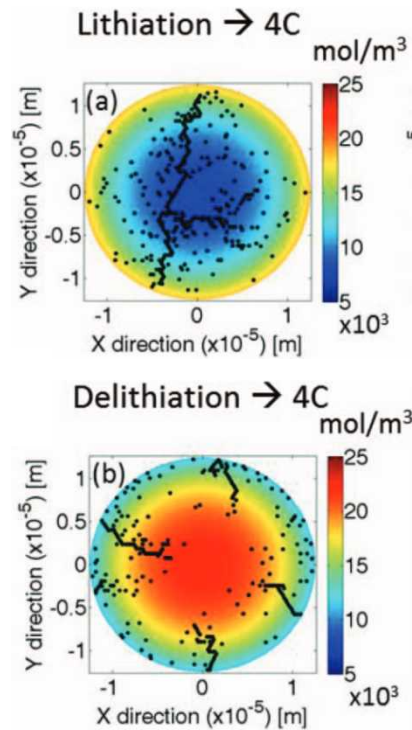
- Faster discharge rates cause greater reductions in cell capacity



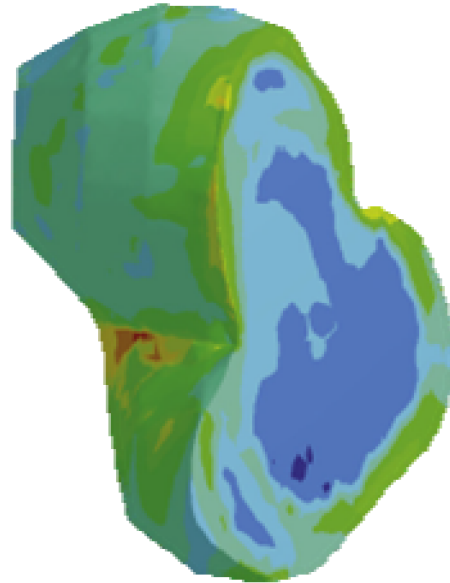
LiCoO₂
after 400
Cycles

Mechanical degradation leads to capacity fade

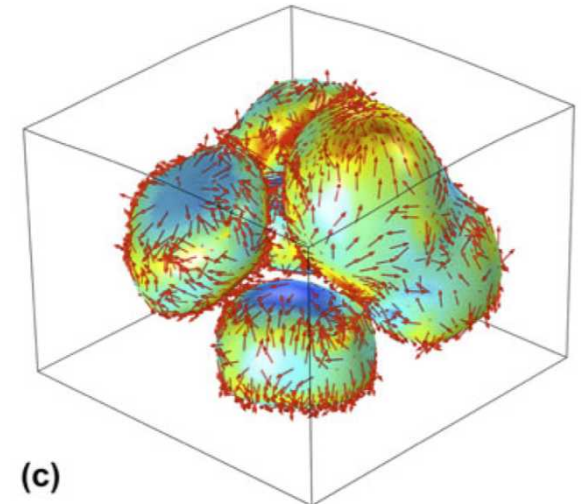
Hypothesis: Capacity fade occurs due to structural damage to electrode network



Lithiation-induced particle fracture. Barai and Mukherjee (2013)



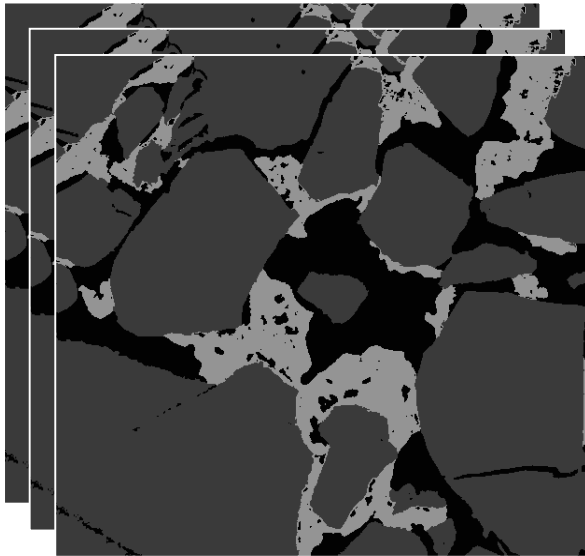
Lithiation-induced swelling, stress concentrators. Malave et al (2014)



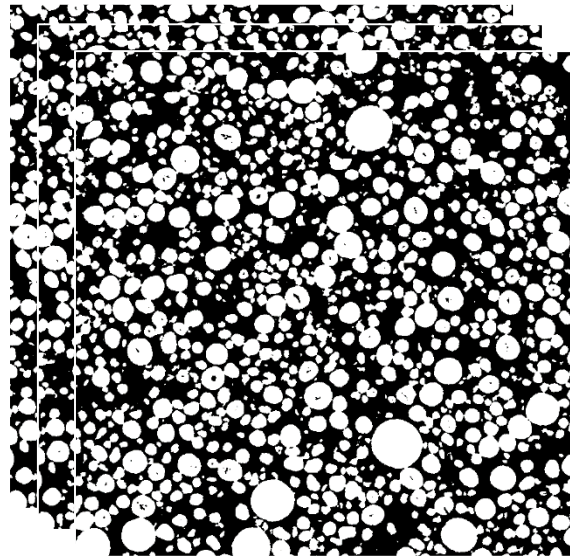
Mean stress contours and Li flux in SnO anodes, swelling 250%. Xu et al. (2016)

Microstructural details can have a significant effect on particle network degradation

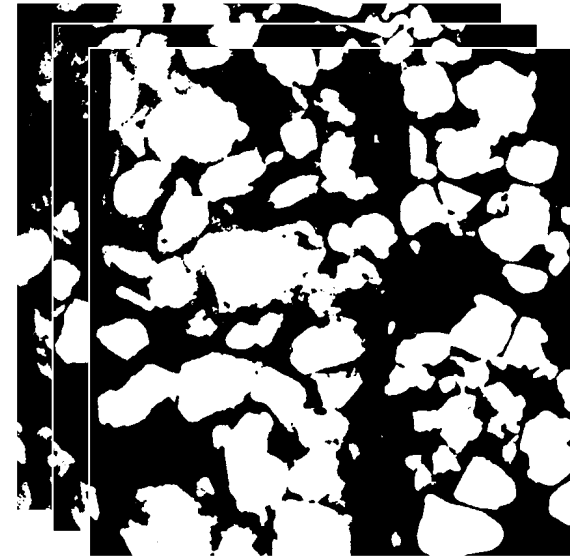
- Imaging and reconstruction of cathode microstructures
 - Conformal Decomposition Finite Element Method (CDFEM)
 - Verification: Mesh and domain size requirements
 - Representing the active binder
- Effective electrode properties
- Coupled electrochemical-mechanical simulations
- Summary and a look forward



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



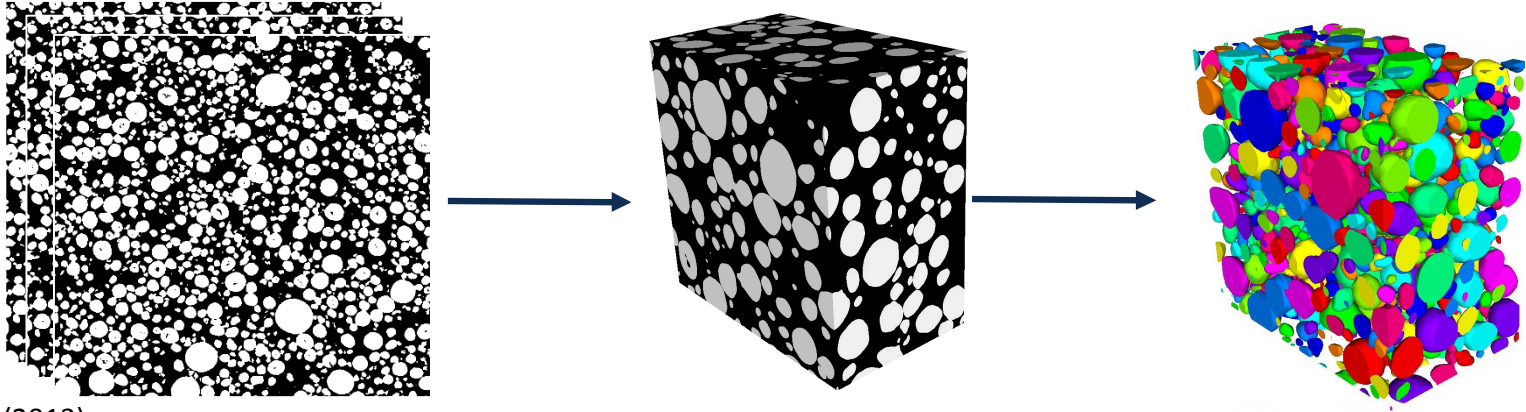
NMC from XRCT,
370 nm resolution,
757 μm domain.
Ebner et al (2013)



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

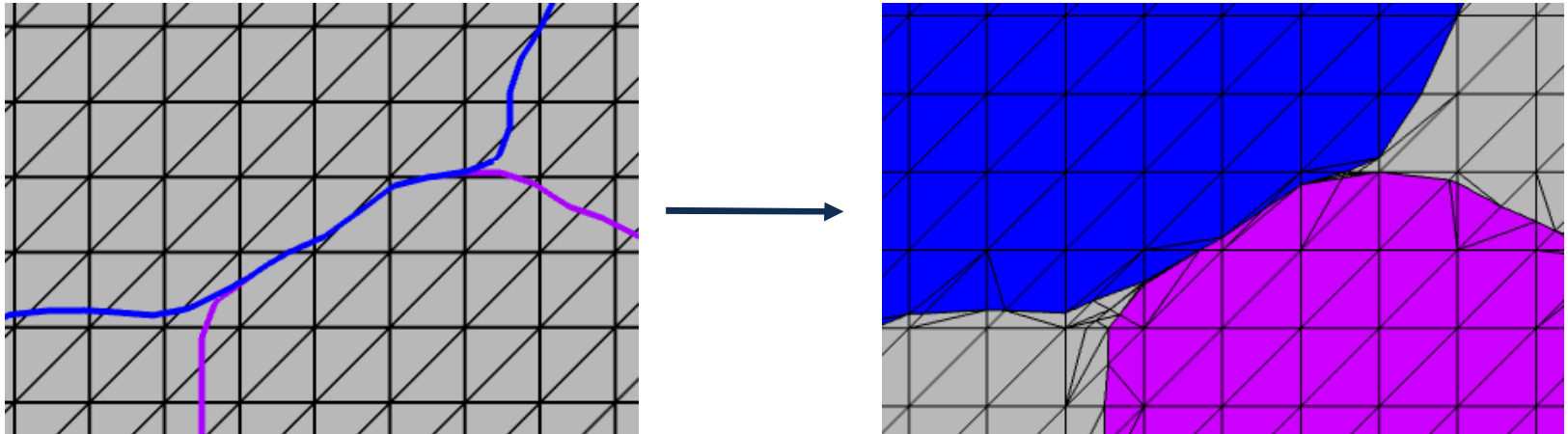
Imaging reveals complex networks; binder can be difficult to detect at scale

- Binarize and label individual particles, surface mesh to STL files (Avizo software)

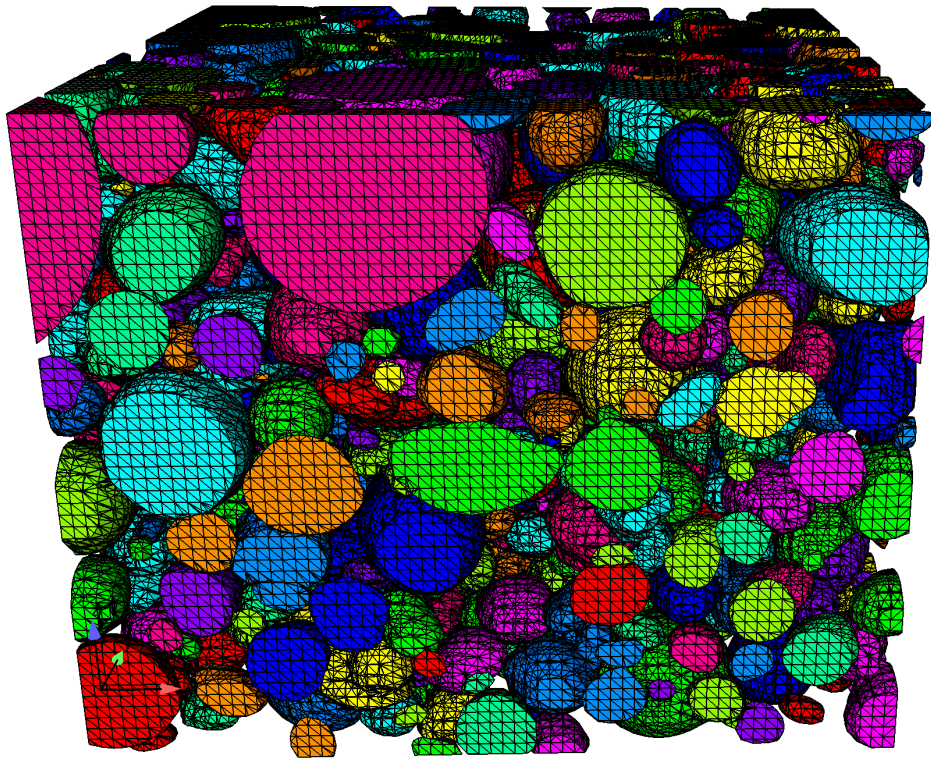


Ebner (2013)

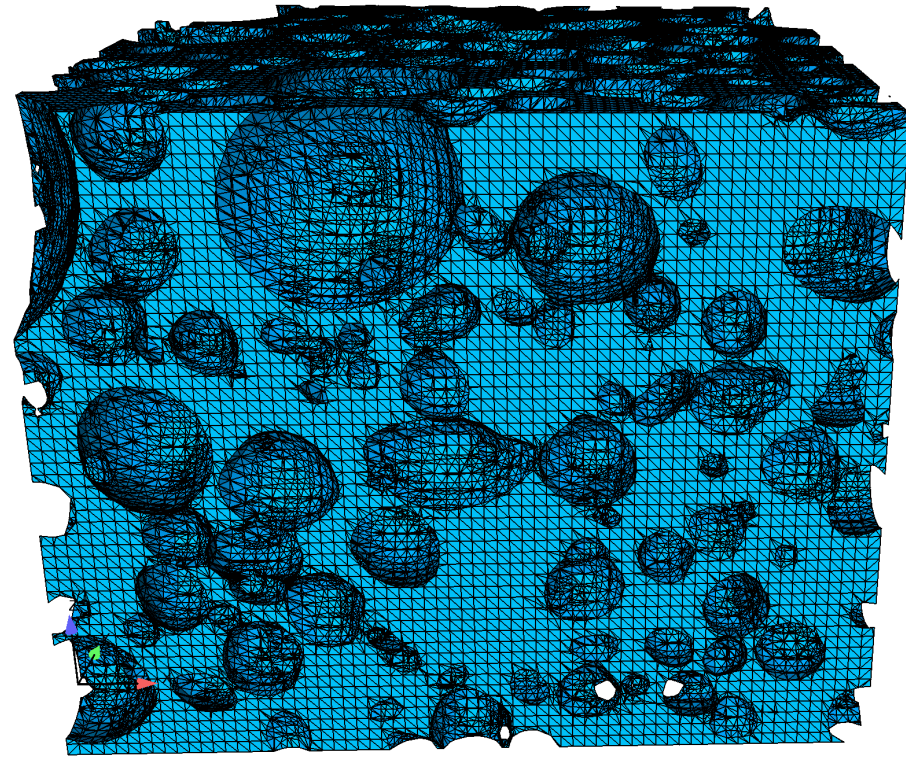
- CDFEM creates level-set field, cuts background mesh to create conformal mesh



Efficient algorithm to go from images to conformal, multi-phase mesh



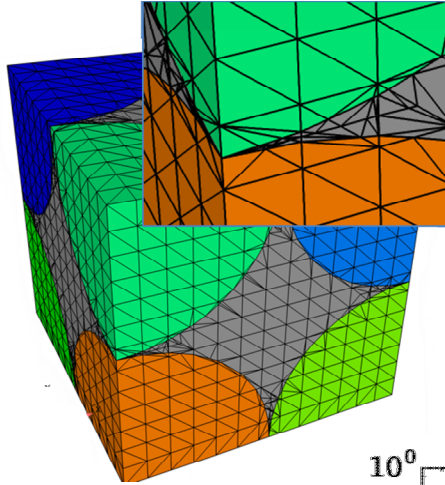
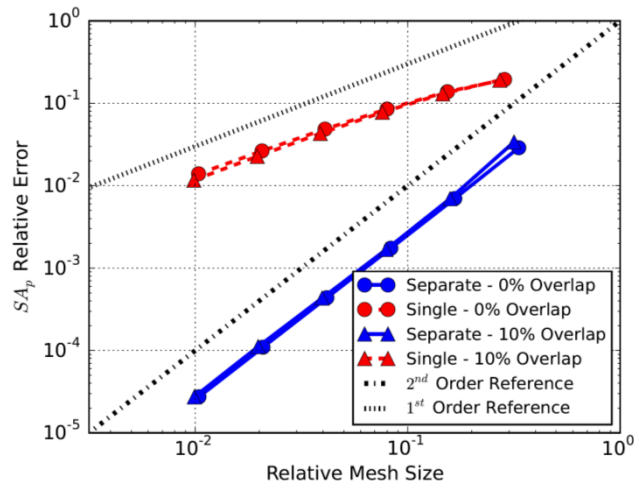
Particles



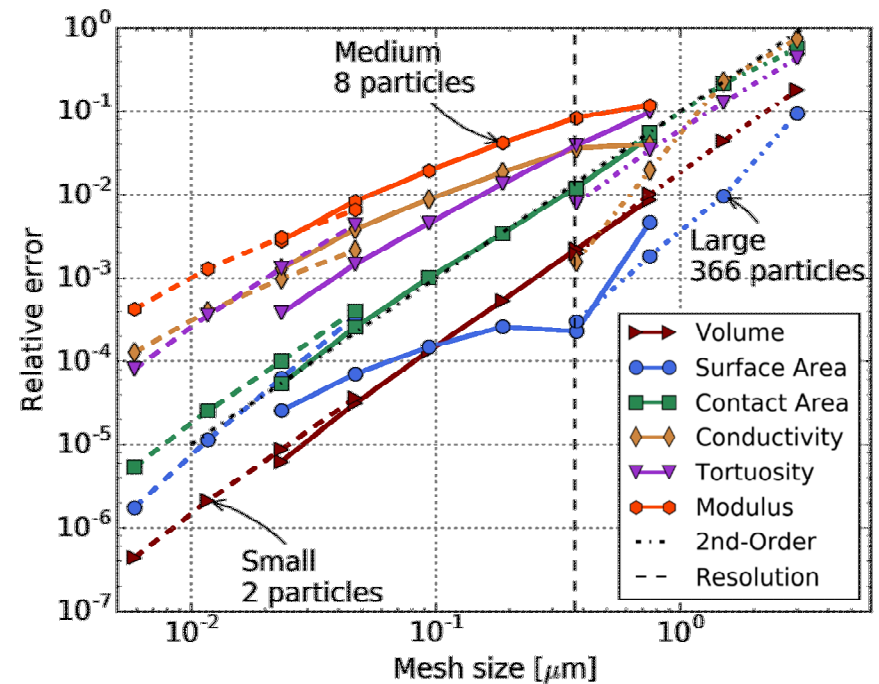
Electrolyte

Efficient algorithm to go from images to conformal, multi-phase mesh

Requirements for meshing accuracy

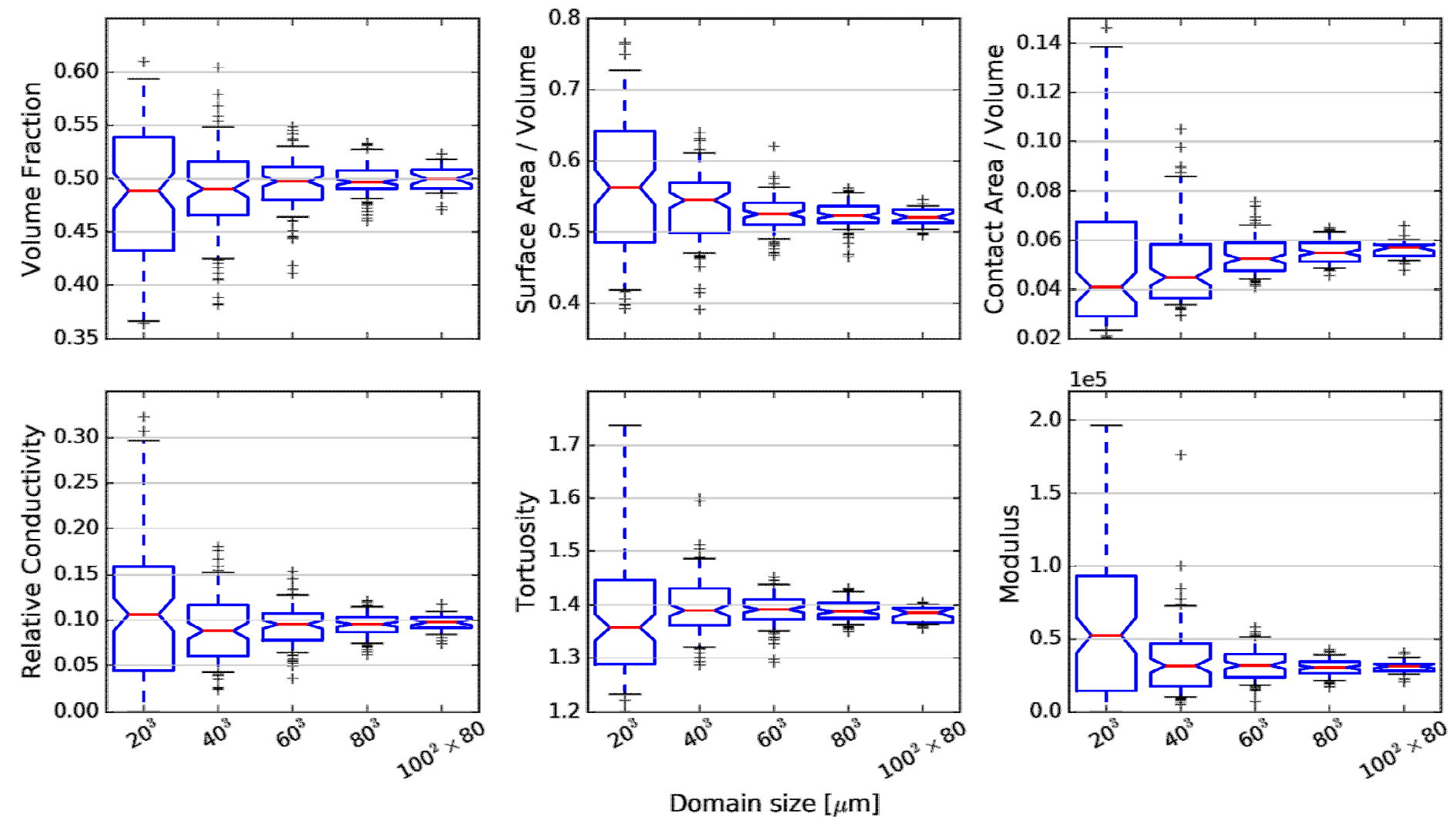


Labeled particles enable additional physics (anisotropic expansion, contact) while improving mesh convergence



- Solution verification (mesh refinement) shows:
- 1) 2nd order convergence
 - 2) Faster convergence for geometry vs. physics
 - 3) Recommend mesh size \approx voxel size
 - 4) Mesh primarily required at particle contacts

Focus mesh resolution near particle contacts



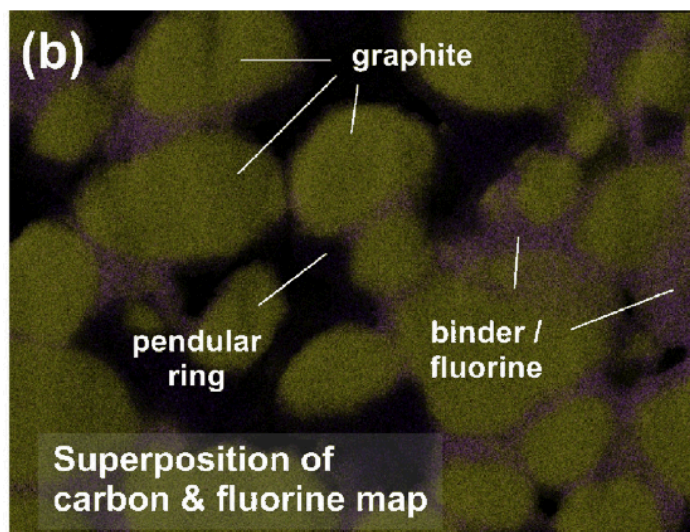
Investing in larger domain / RVE more important than refined mesh

What about the active (conductive) binder?

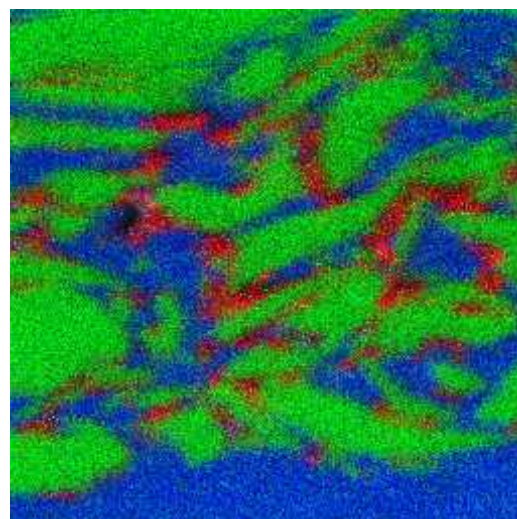
- Resolving the location of active binder (PVDF + CB) is much more difficult than particle image segmentation.
- Binder is often neglected, assuming non-active void space is entirely electrolyte.
- Limited imaging results can hint at binder location

CB/PVDF wt %	NMC/AB Volume Ratio
2-2 wt%	9.62
3-3 wt%	6.23
4-4 wt%	4.61
5-5 wt%	3.61

CB = carbon black
AB = active binder =
PVDF + CB



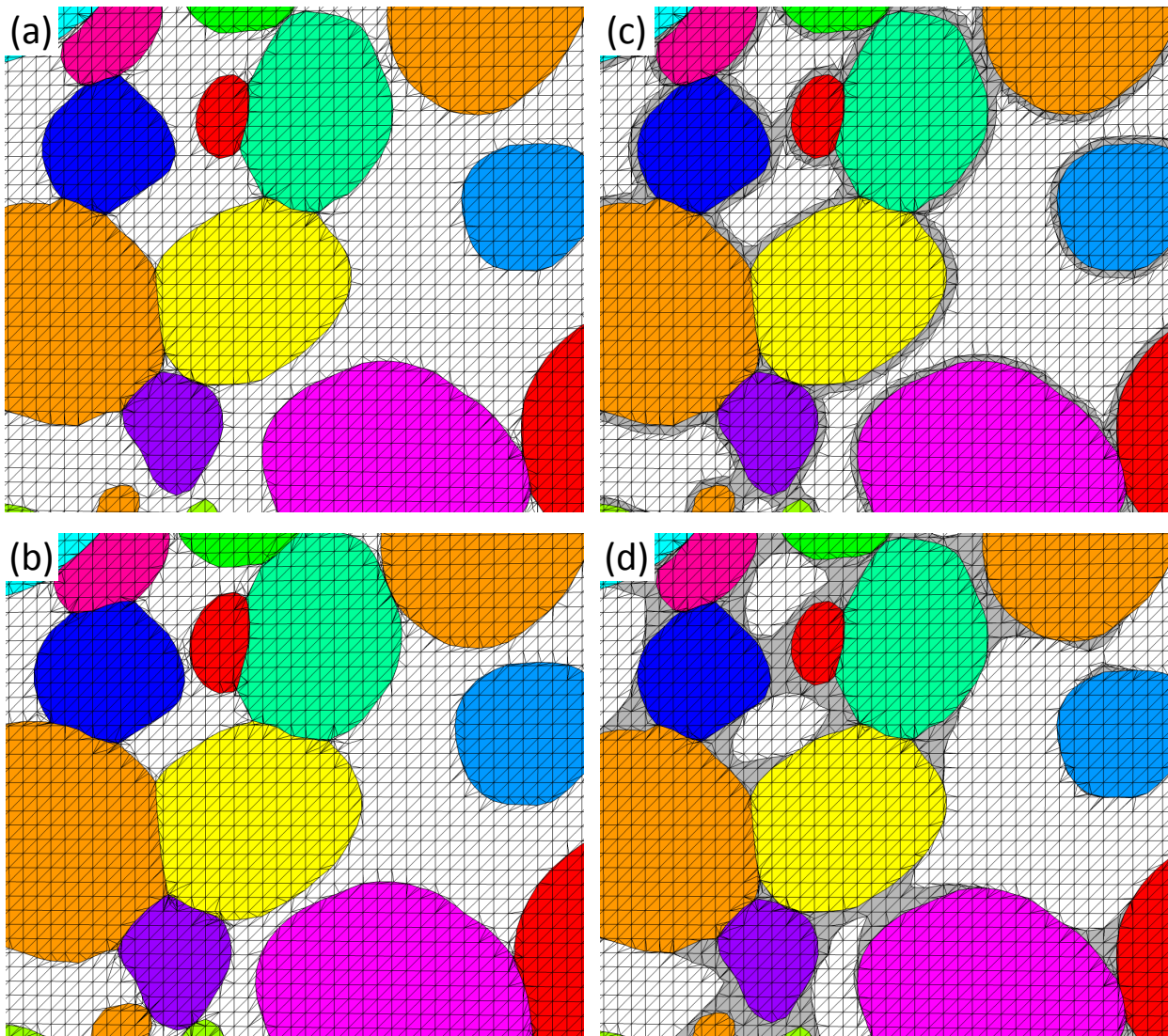
Jaiser et al. (2017)



TOF-SIMS for
graphite anode
(Tony Ohlhausen)

Red: PVDF
Green: Carbon
Blue: Epoxy (Voids)

How are electrode-scale properties affected by inclusion of binder?

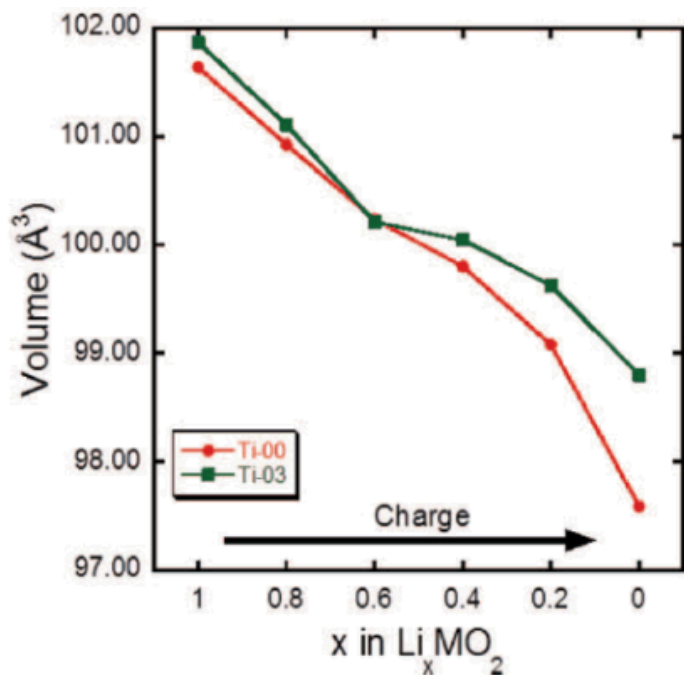


Multiple binder approaches:

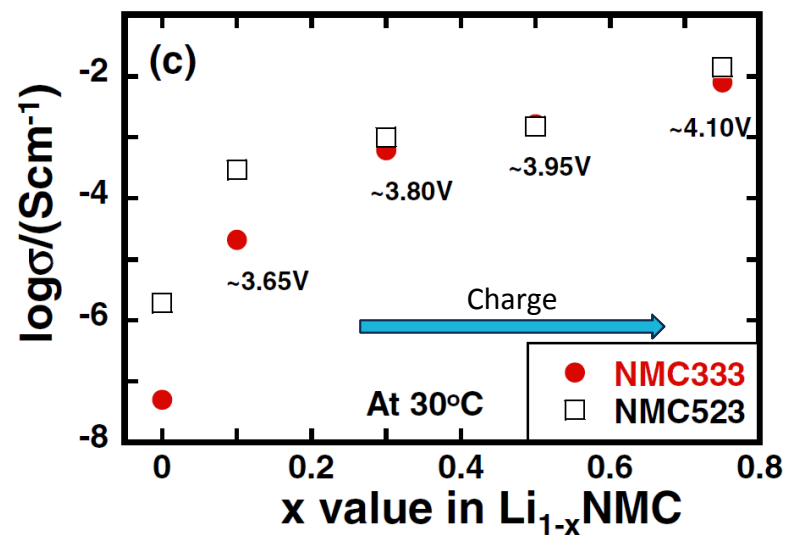
- (a) **Raw:** No binder, just particles
- (b) **Expanded:** Expand particles to give correct porosity
- (c) **Coating:** Coat particles with uniform binder layer to give correct porosity
- (d) **Contacts:** Novel algorithm to place binder near particle contacts, giving correct porosity

New contact method gives binder morphology most similar to imaging

NMC has lithiation-dependent properties



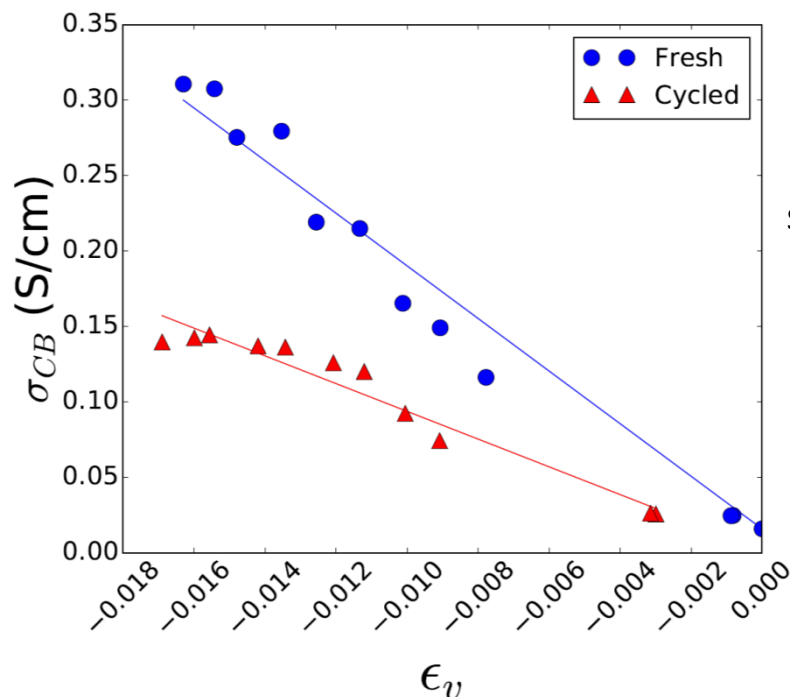
NMC particles swell as battery is discharged (Li added)



NMC electrical conductivity decreases during discharge

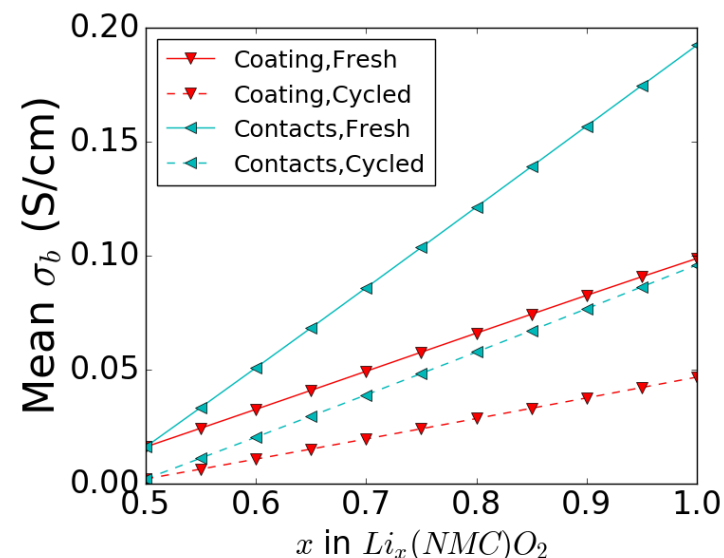
During discharge, conductivity decreases while swelling stresses binder

Active binder has lithiation-dependent properties

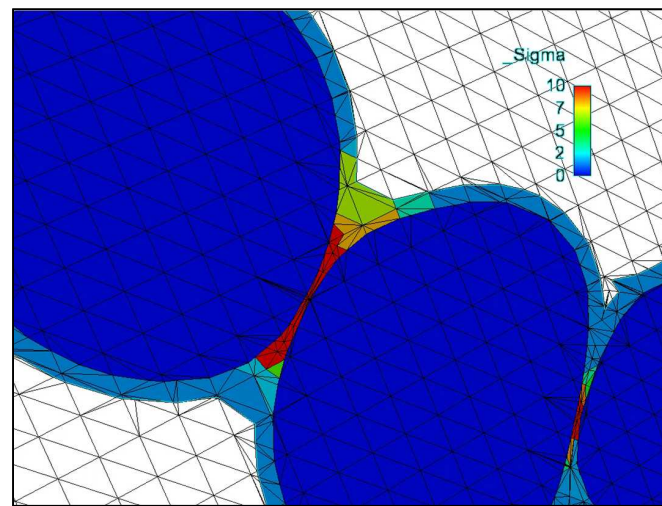


Active binder electrical conductivity increases under compression; carbon particles come into closer contact; degrades under mechanical cycling

Localized conductivity has significant impact on global conductivity; depends on morphology

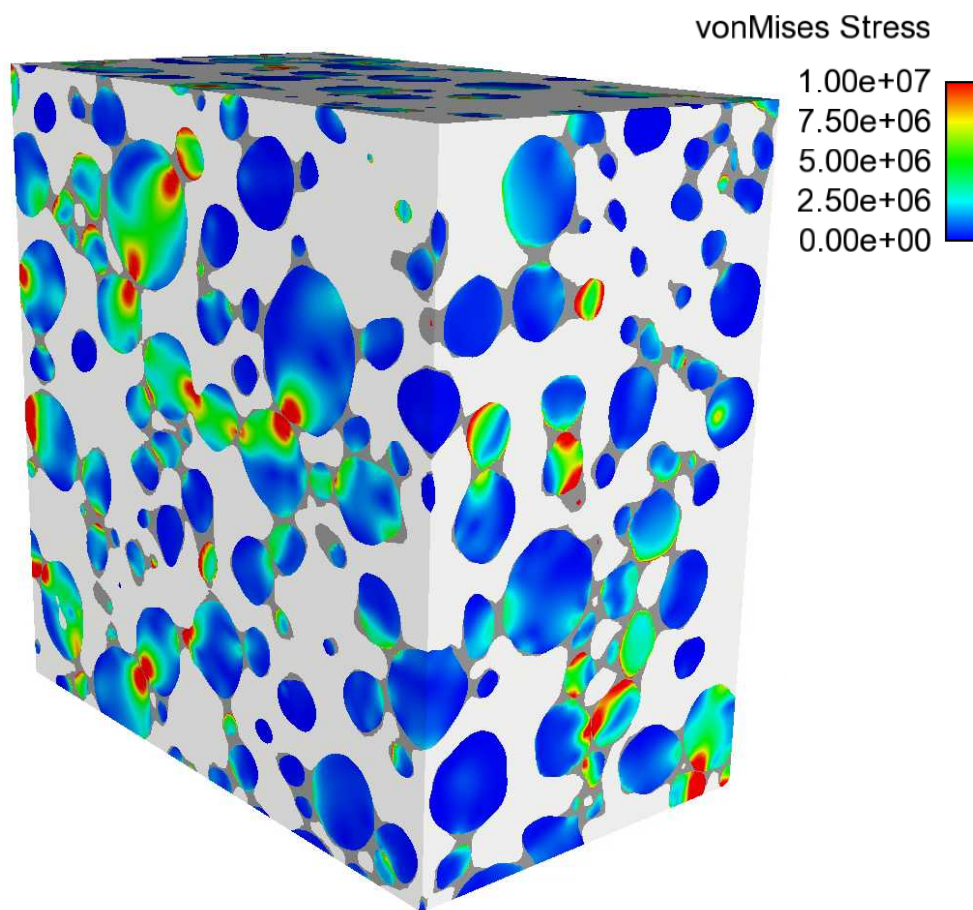


Stress localization during swelling leads to localized increase in conductivity

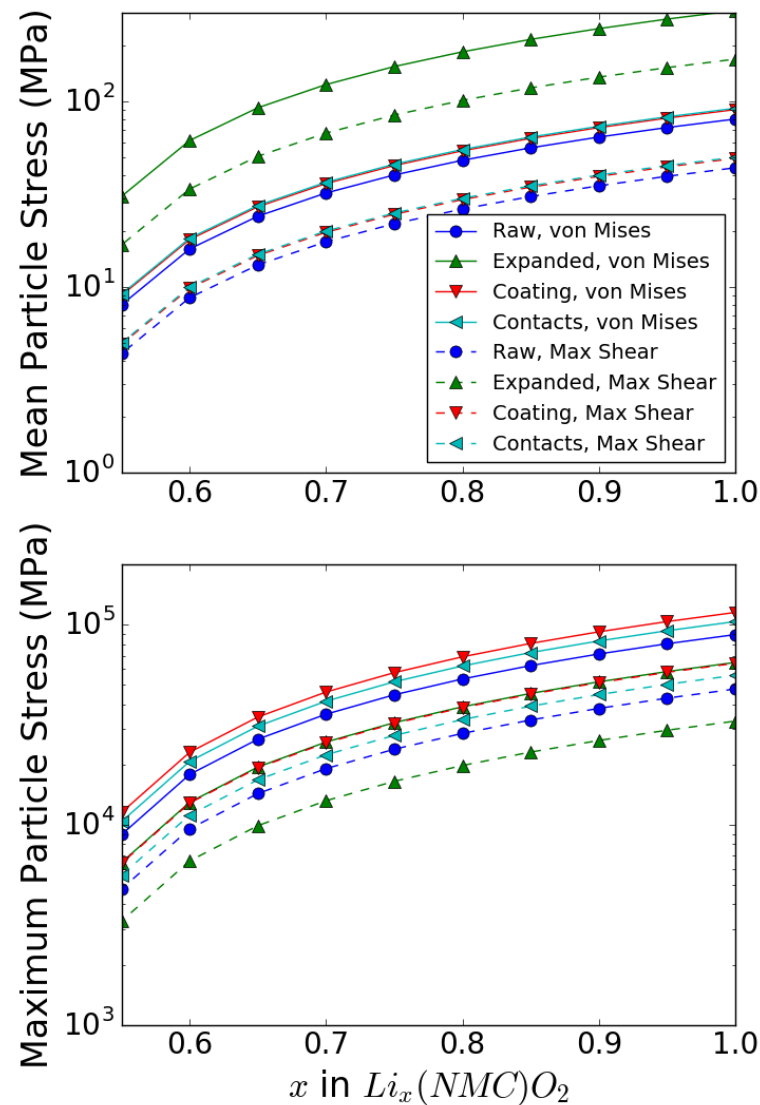


Active binder has important electro-mechanical effects

Active binder impacts: Mechanical stresses



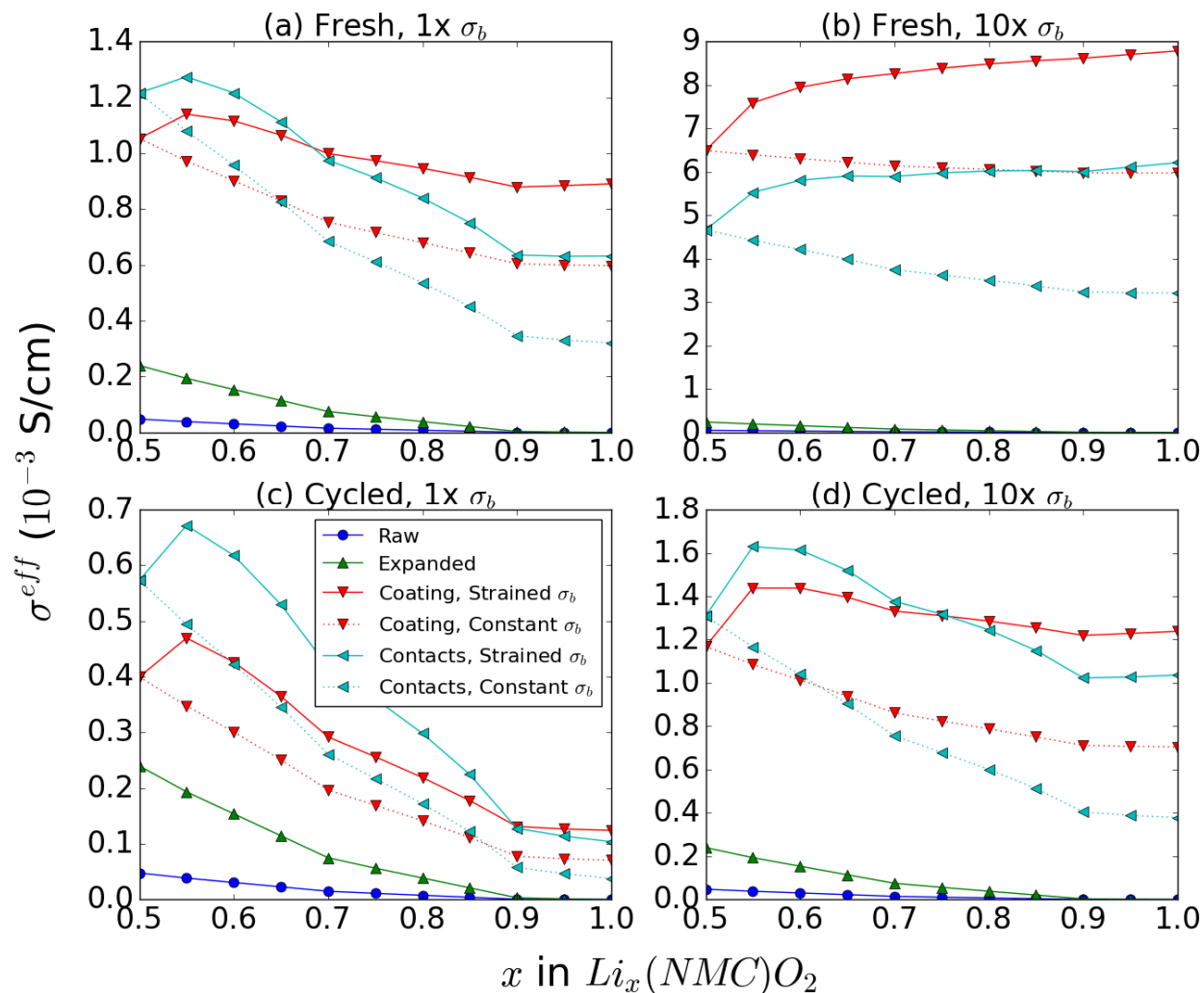
Binder undergoes compressive stress during discharge



Binder significantly mitigates stress vs. hard particle contacts

Active binder impacts: Electrical conductivity

- During battery discharge
 - Lithium added ($x \uparrow$)
 - NMC cond. decreases
 - Binder stress increases
 - Binder cond. increases
- Competing effects lead to nonlinear behaviors
- Aging/cycling drastically reduces conductivity
 - Harder to discharge fully
- Using larger binder conductivity modified trends for fresh batteries, less for cycled



Effect of binder treatment on electrical conductivity is significant

In the particle

- Ohm's Law

$$\underline{\nabla} \cdot (\sigma \underline{\nabla} \phi_s) = 0$$

- Intercalated Li conservation

$$\frac{\partial C_{\text{Li}}}{\partial t} + \underline{\nabla} \cdot [-MC_{\text{Li}} \underline{\nabla} (\mu_{\text{Li}}^{\text{chem}} + \mu_{\text{Li}}^{\text{stress}})] = 0$$

At the interface

- Butler-Volmer reaction rate

$$\underline{J} \cdot \underline{n} = j_0 \left[\exp \left(\frac{\alpha_a F (\phi_s - \phi_l - \phi_{\text{eq}})}{RT} \right) - \exp \left(\frac{-\alpha_c F (\phi_s - \phi_l - \phi_{\text{eq}})}{RT} \right) \right]$$

In the electrolyte

- Current conservation

$$\underline{\nabla} \cdot \left[F \left(\underline{J}_{\text{Li}^+} - \underline{J}_{\text{PF}_6^-} \right) \right] = 0$$

- Nernst-Planck fluxes

$$\underline{J}_i = -D_i \left(z_i C_i \frac{F}{RT} \underline{\nabla} \phi_l + \underline{\nabla} C_i \right)$$

- Li+ conservation

$$\frac{\partial C_{\text{Li}^+}}{\partial t} + \underline{\nabla} \cdot \underline{J}_{\text{Li}^+} = 0$$

- Electroneutrality

$$C_{\text{PF}_6^-} = C_{\text{Li}^+}$$

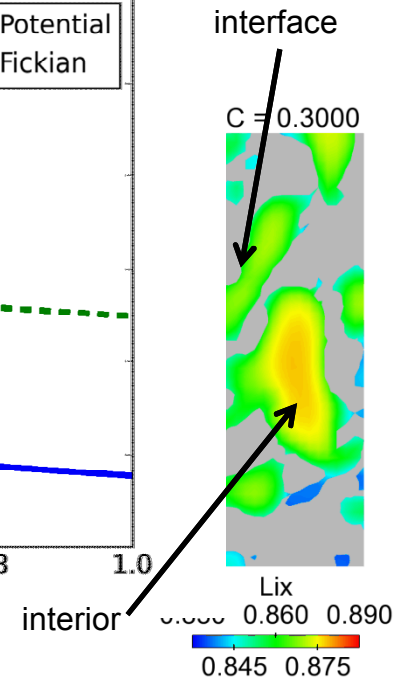
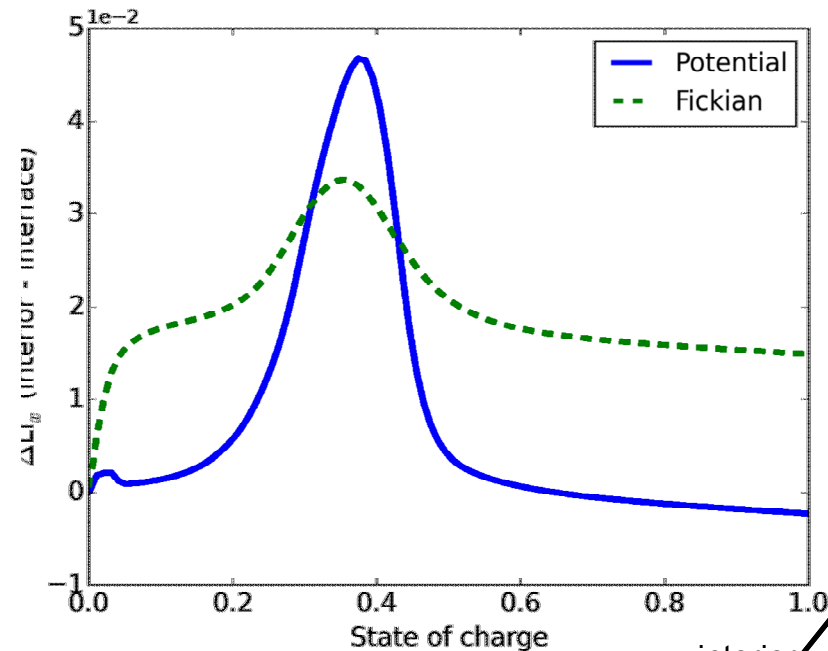
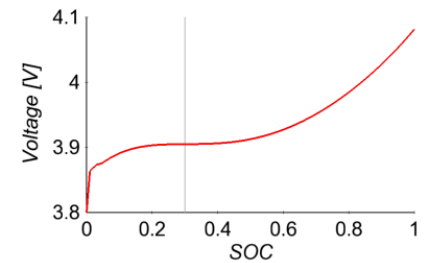
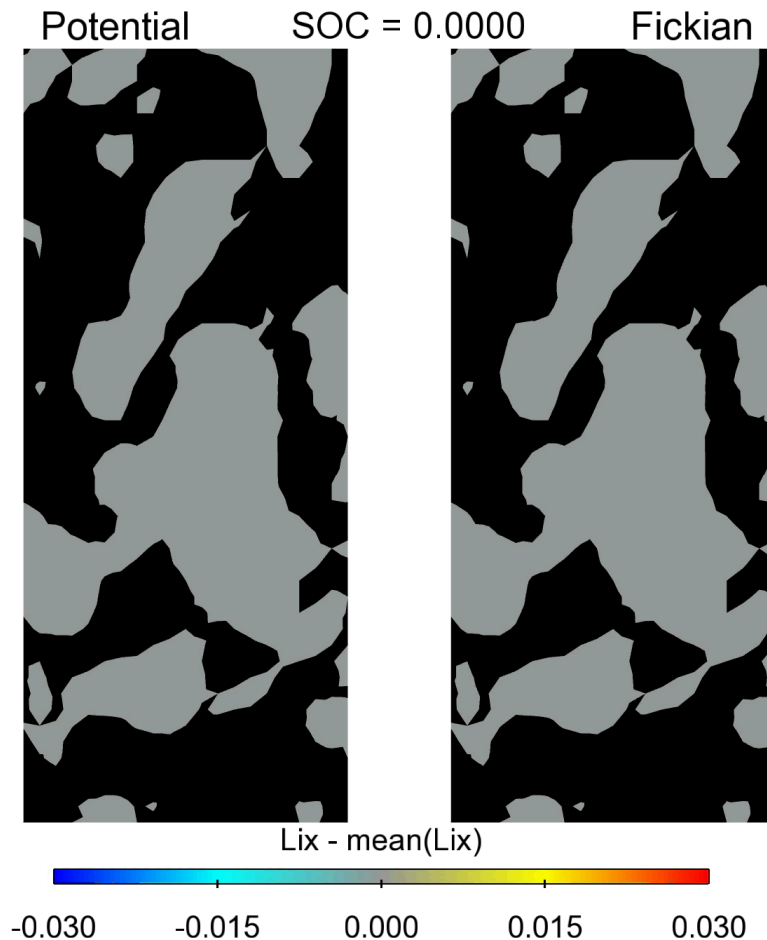
Well-defined mathematical model at the mesoscale

- Ideal transport (Fickian) model:

$$\underline{J}_{\text{Li}} = -D \nabla C_{\text{Li}}$$

- Non-ideal (potential) model:

$$\underline{J}_{\text{Li}} = -MC_{\text{Li}} \nabla \mu_{\text{Li}}^{\text{chem}}$$



Ideal transport model shows unrealistically high concentration gradients

- Intercalation-induced swelling causes a volumetric strain

$$\begin{aligned}\underline{\underline{\mathbf{E}}} &= \underline{\underline{\mathbf{E}}}_{\text{elastic}} + \underline{\underline{\mathbf{E}}}_{\text{swelling}} \\ &= \underline{\underline{\mathbf{E}}}_{\text{elastic}} + \underline{\underline{\alpha}} \Delta C_{\text{Li}}\end{aligned}$$

- For a linear elastic constitutive behavior, swelling is converted to stress
 - Analogous to standard “coefficient of thermal expansion” (e.g. Vegard’s law)

$$\begin{aligned}\underline{\underline{\boldsymbol{\sigma}}} &= \underline{\underline{\mathbf{C}}} : \underline{\underline{\mathbf{E}}}_{\text{elastic}} \\ &= \underline{\underline{\mathbf{C}}} : \underline{\underline{\mathbf{E}}} - \underline{\underline{\mathbf{C}}} : \underline{\underline{\alpha}} \Delta C_{\text{Li}} \\ &= \underline{\underline{\mathbf{C}}} : \underline{\underline{\mathbf{E}}} - \underline{\underline{\beta}} \Delta C_{\text{Li}}\end{aligned}$$

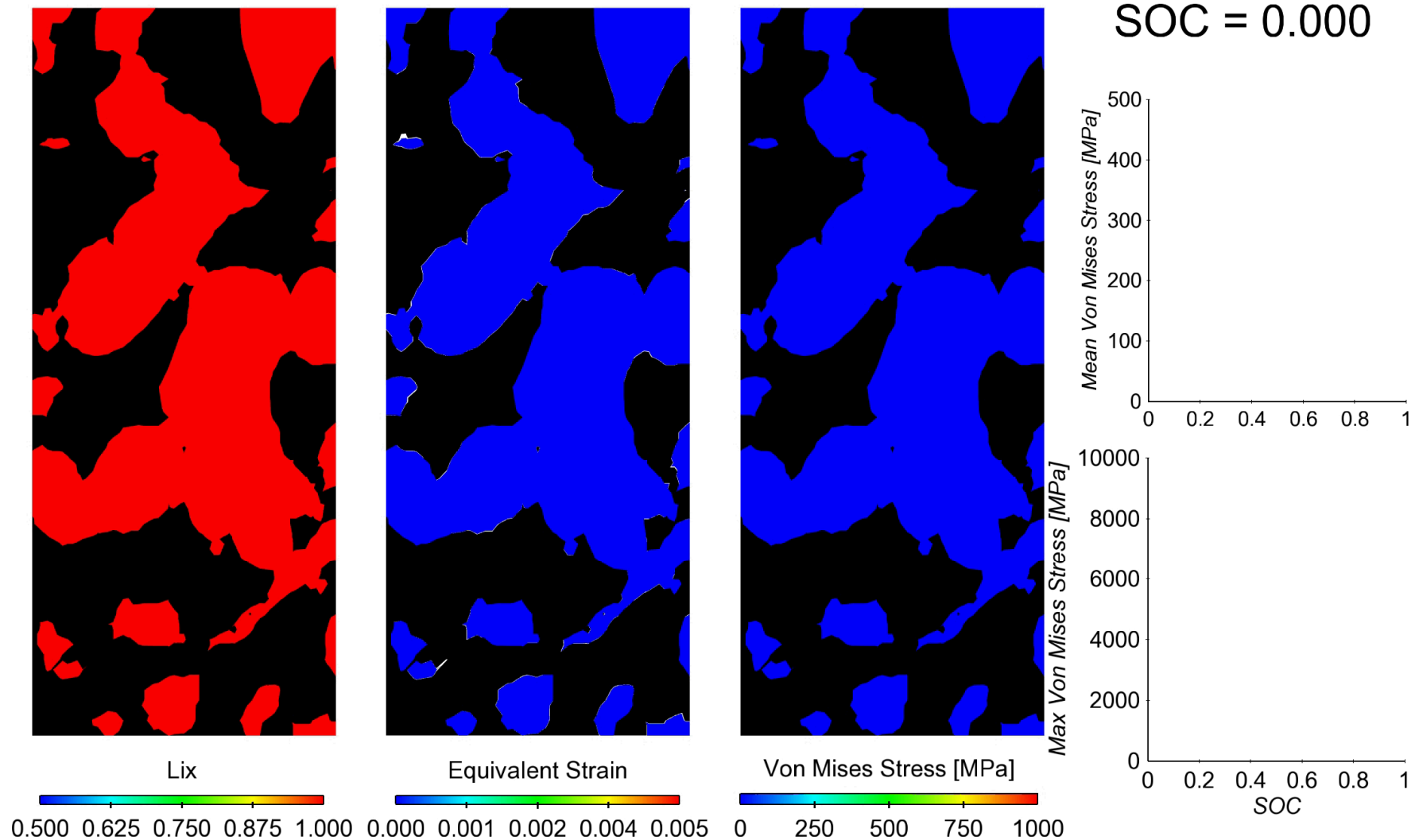
- Generally, volumetric strain is isotropic

$$\underline{\underline{\beta}} = \underline{\underline{\beta}} \delta$$

- Stress governed by quasi-static momentum conservation

$$\underline{\underline{\nabla}} \cdot \underline{\underline{\boldsymbol{\sigma}}} + \underline{\underline{\mathbf{F}}} = \underline{\underline{\mathbf{0}}}$$

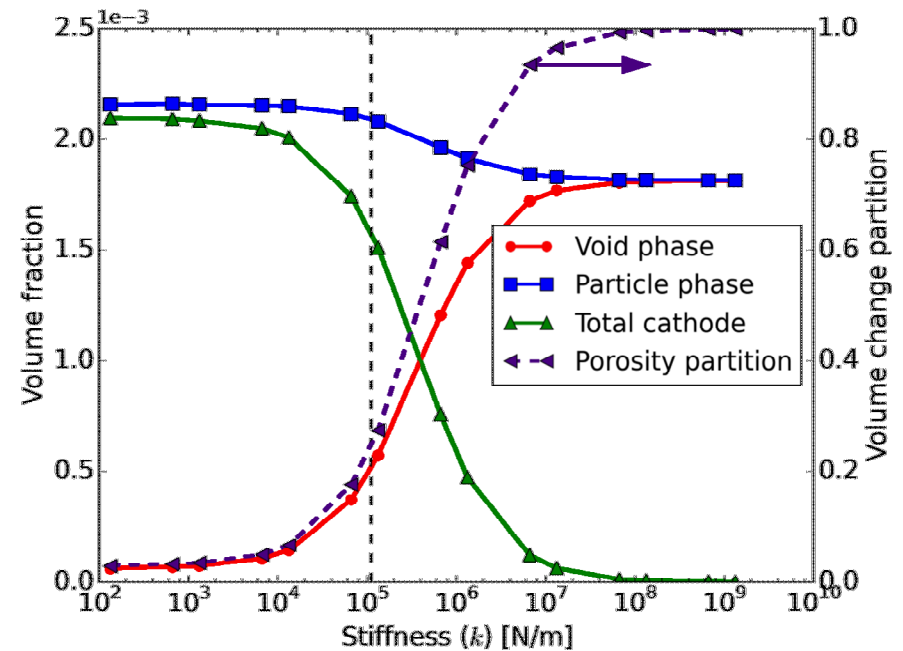
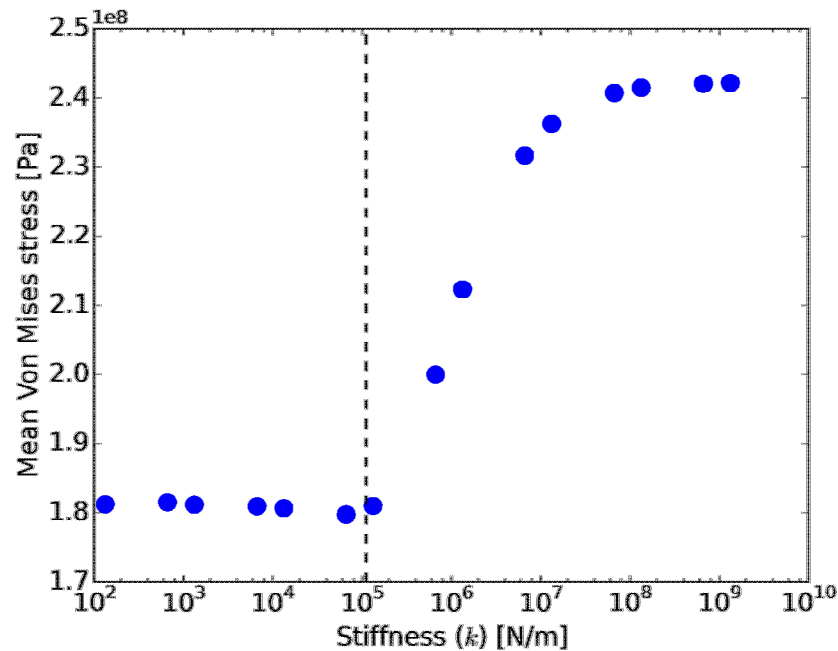
Well-defined mathematical model at the mesoscale



Particle confinement leads to 100x higher stress than observed in isolated particles

Electrode breathing: Effect of flexible boundaries

- Jellyroll boundary conditions can allow macroscopic swelling (breathing)
- Mimic this effect by controlling stiffness of upper boundary (collector)



Allowing electrode breathing changes volume partitioning and reduces stress by 1/3

- Conclusions
 - Lithiation-induced swelling can lead to significant mechanical forces, degradation
 - Polymeric active binder plays a critical role in electrical transports, stress generation
 - Effective property calculations useful links to battery-scale models

- Future work
 - Coupled electrochemical-mechanical simulations in large NMC domains with binder
 - Upscaling results into table look-ups or curve fits for battery-scale models
 - Direct integration into battery-scale models; multi-scale approach

- Acknowledgments
 - CAEBAT-III program, DOE Vehicle Technologies Office, Brian Cunningham
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