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Mesoscale Mechanics: Simulating the Role of Stress on Electrode Electrochemical Performance

PRESENTED BY

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DISTINGUISHED RESEARCH & DEVELOPMENT CHEMICAL ENGINEER
THERMAL/FLUID COMPONENT SCIENCES DEPARTMENTS

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June 22, 2021

U.S. DEPARTMENT OF ENERGY NNSA

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Motivation

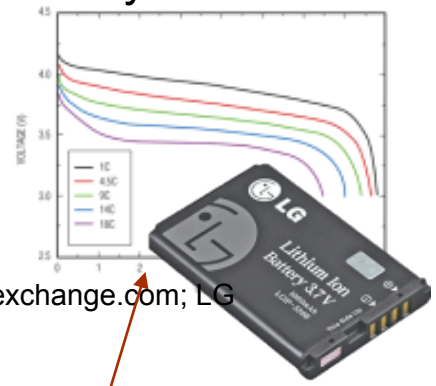
Length scale

Processing

Manufacturing

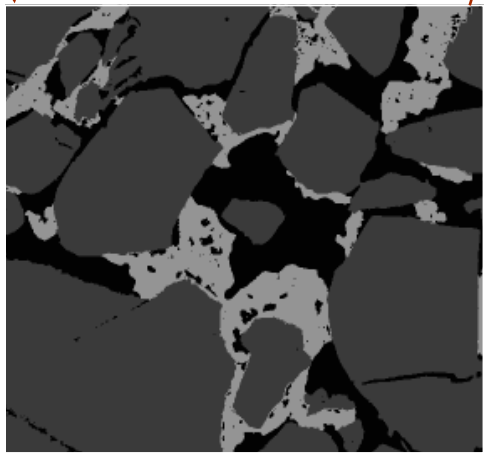
www.targray.com

Battery Performance



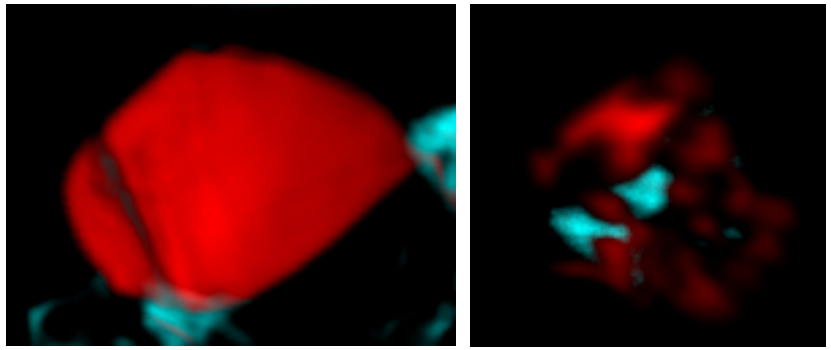
stackexchange.com; LG

Mesostructure



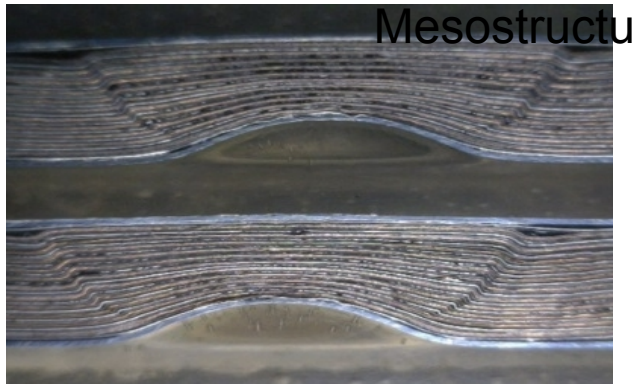
Hutzenlaub (2012)

Lithiation-Induced Fracture

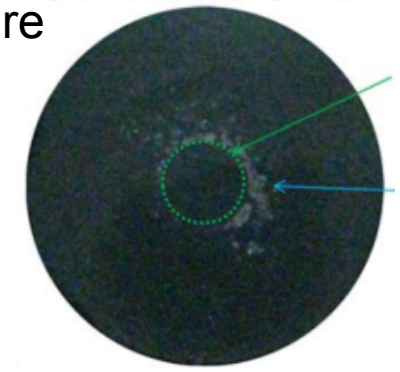


LiCoO2 STXM, Farid El Gabaly Marquez (Sandia)

Mechanical Abuse → Electrochemistry / Mesostructure



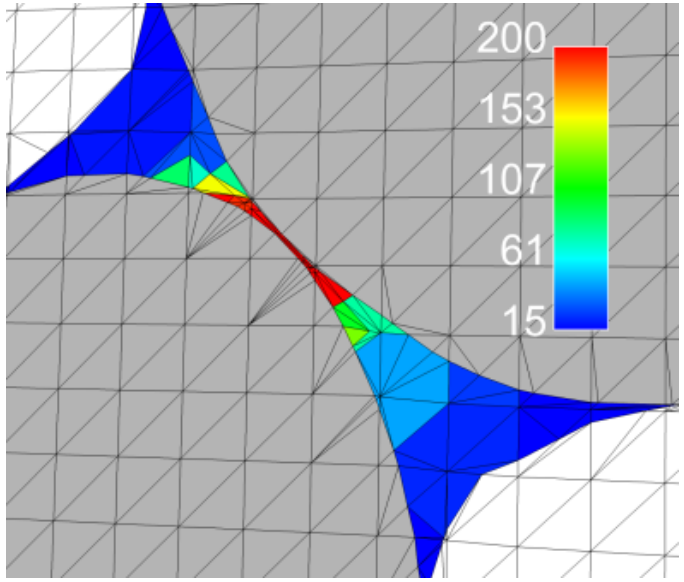
NMC/graphite pouch, H. Wang (ORNL) (2015)



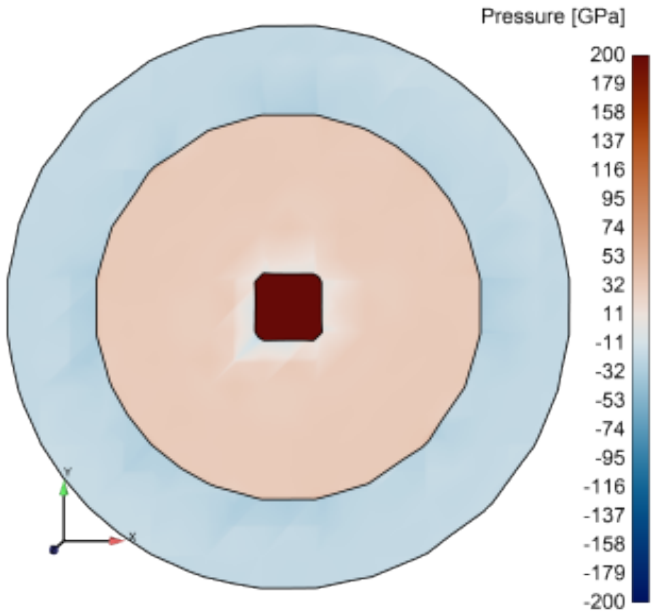
Cannarella/Arnold

Coupled electrochemical-mechanical effects at connect battery manufacturing and performance

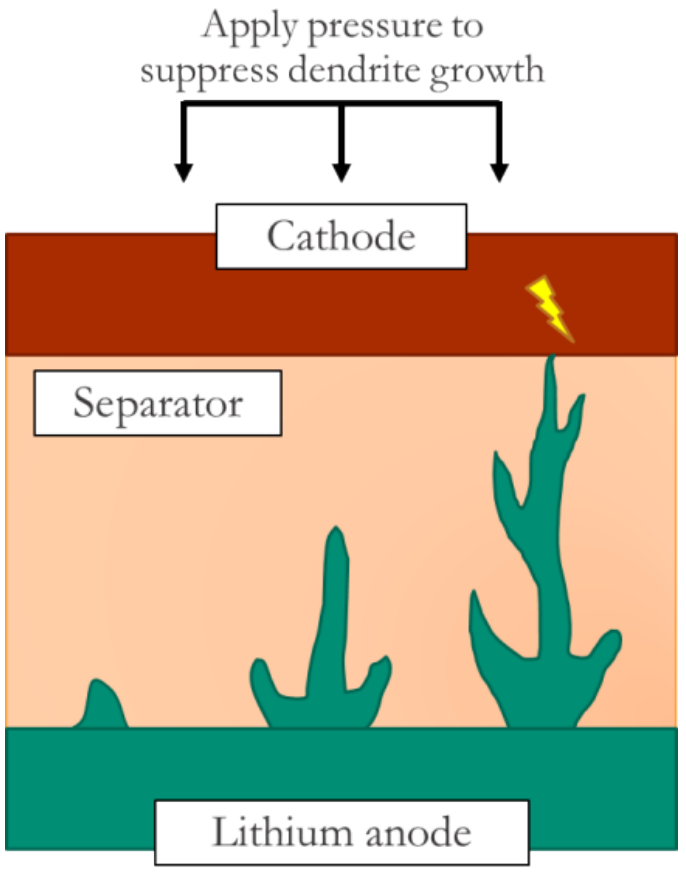
Mechanics in Batteries: 3 Vignettes



Impact of mechanics on binder in intercalating electrodes

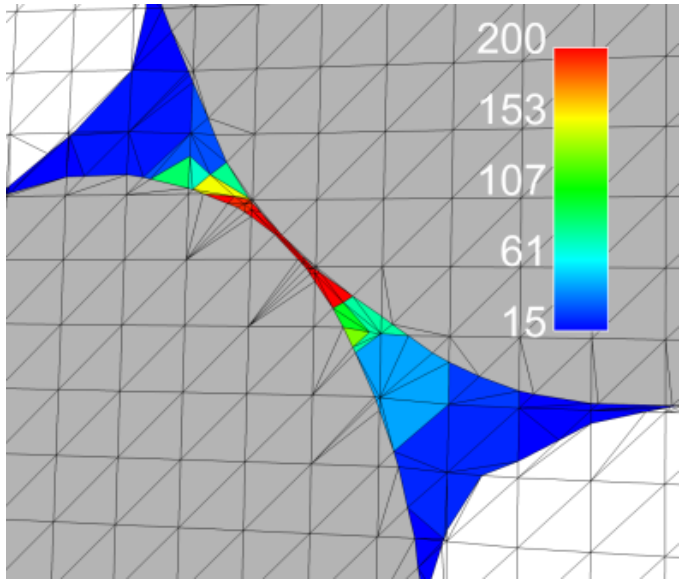


Stress generation in conversion electrode particles



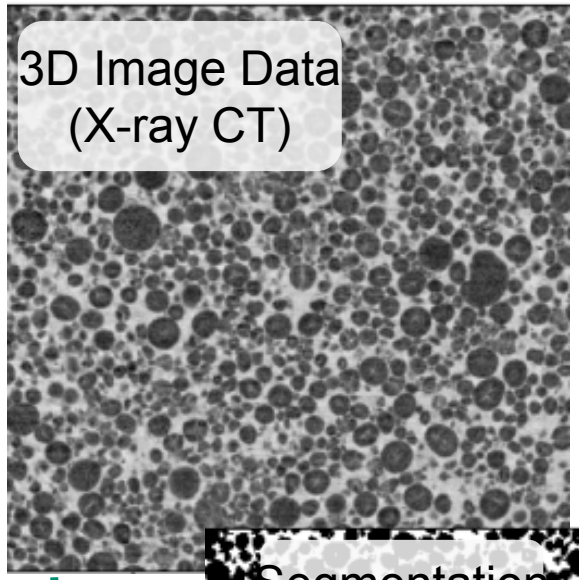
Role of mechanics in mitigating dendrite growth on lithium metal

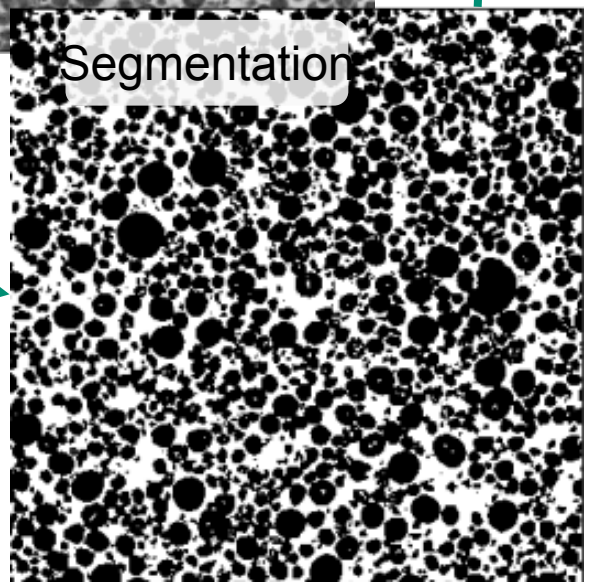
Impact of mechanics on binder in intercalating electrodes

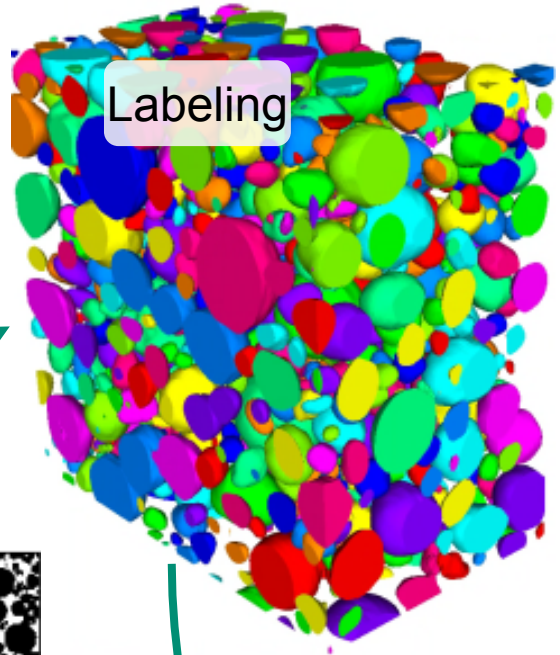


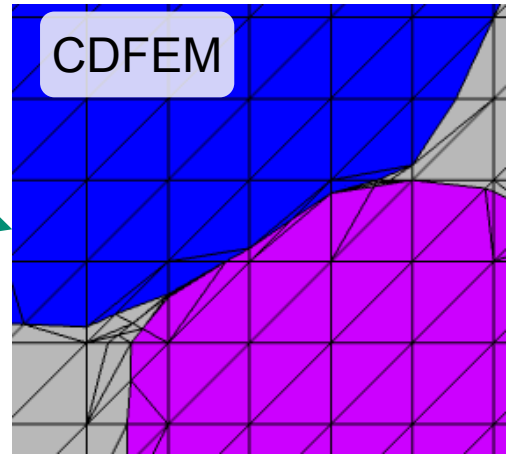
Work in this section with Mark E. Ferraro, former Sandia post-doc

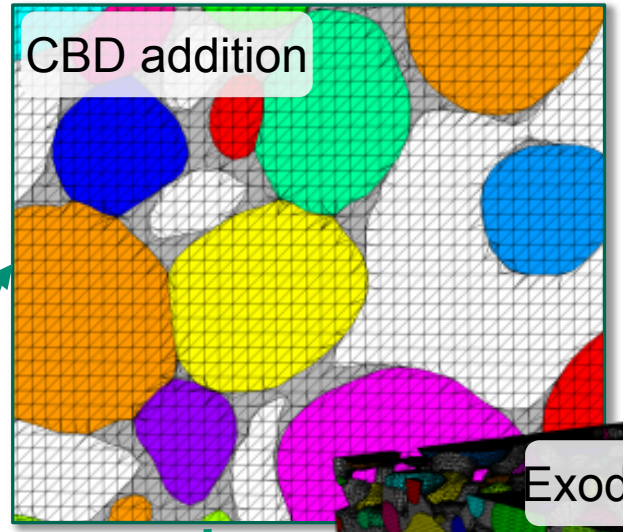
Mesoscale geometry from CT data using CDFEM

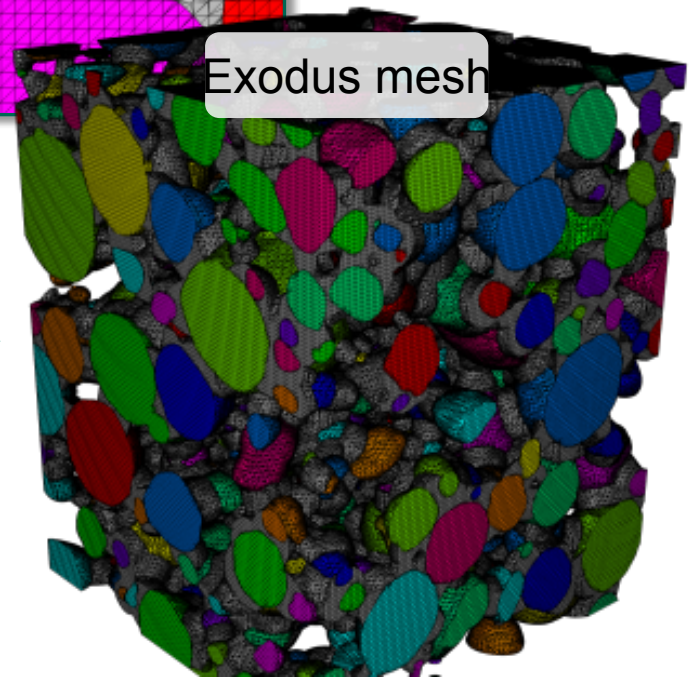






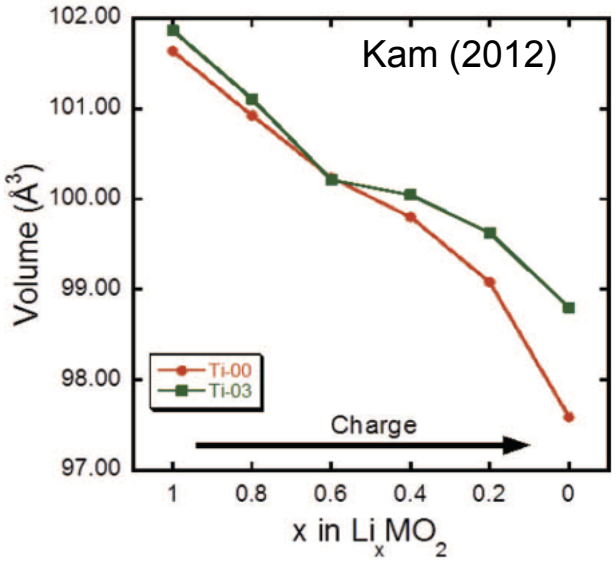


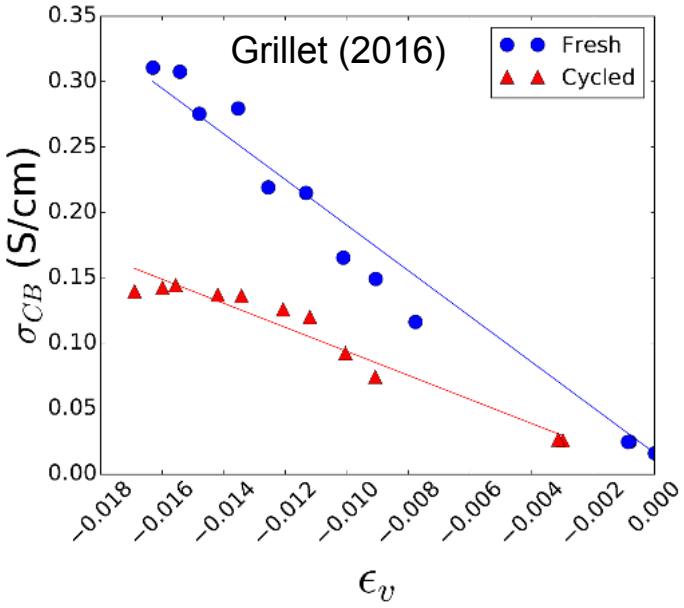




How does mechanics affect NMC electrode modeling?

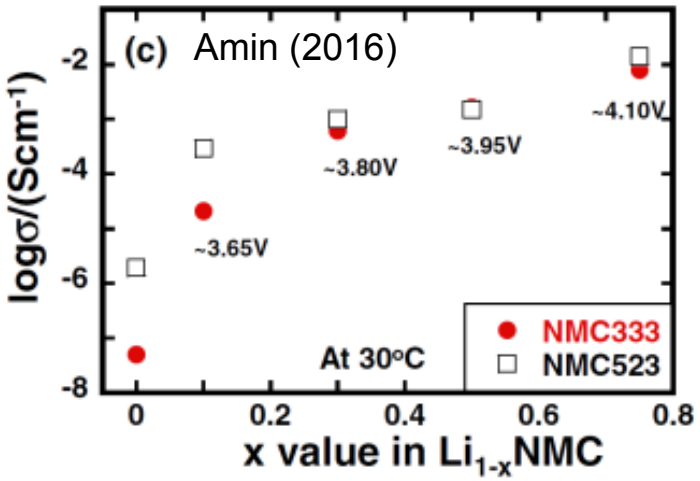
NMC particles expand as they lithiate (discharge)

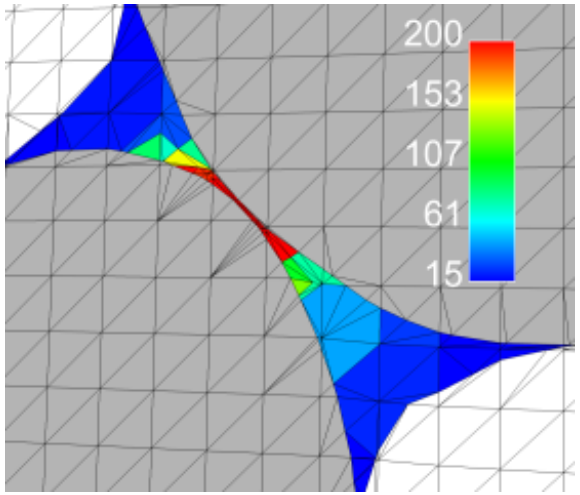




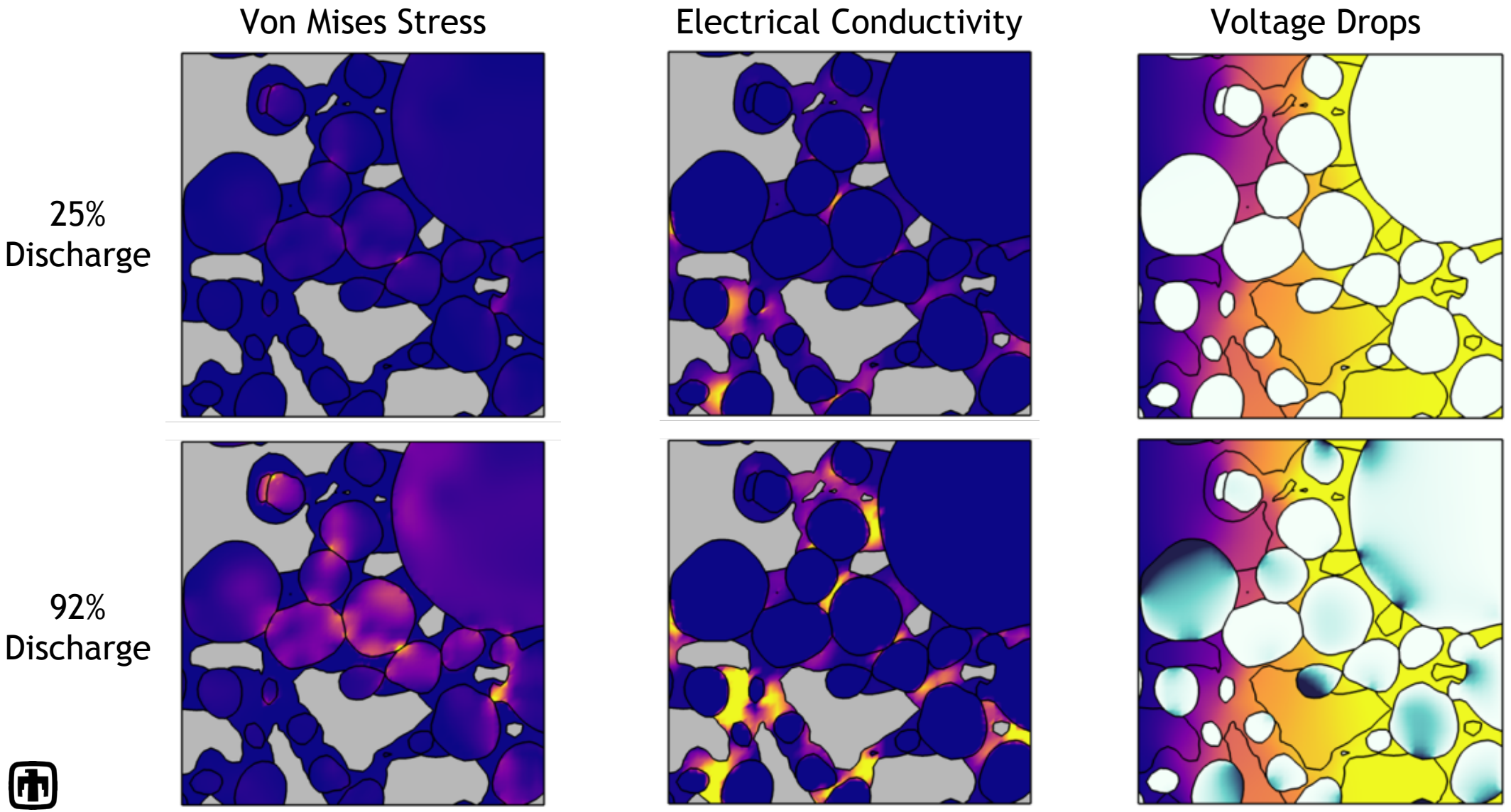
But CBD conductivity increases as it's compressed

NMC electrical conductivity also decreases with lithiation

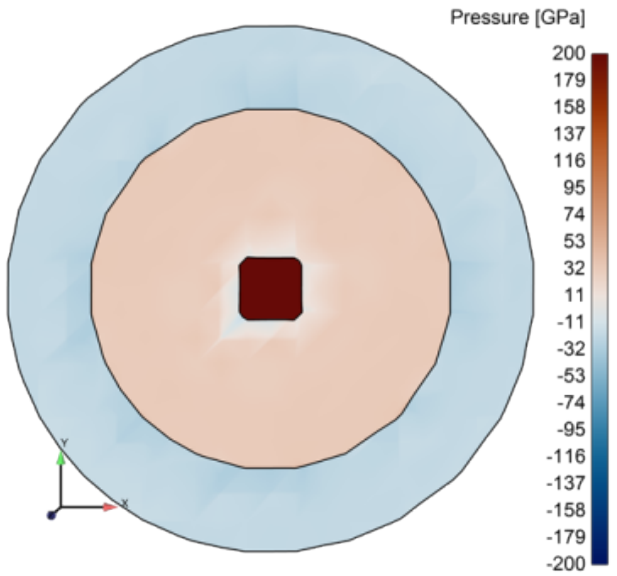




Mechanics of CBD drive current transport

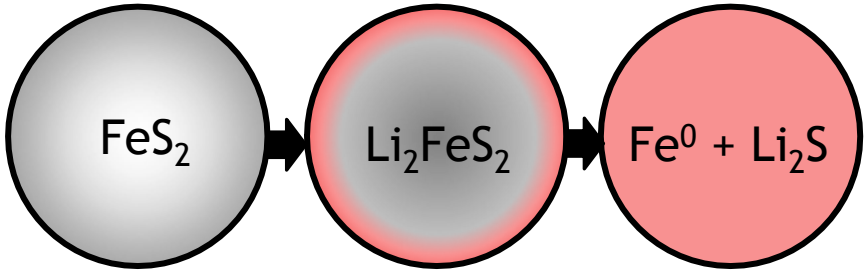


Stress generation in conversion electrode particles

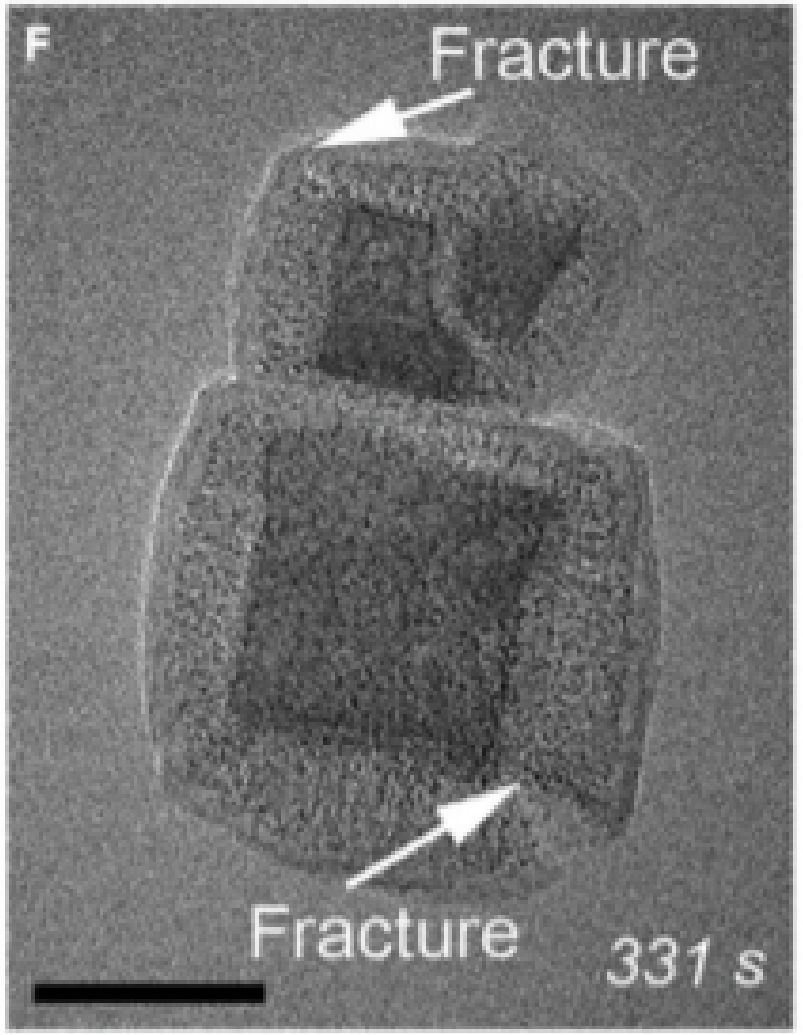


Work in this section with Jeffery S. Horner, Sandia post-doc

FeS_2 – Conversion reactions are brutal

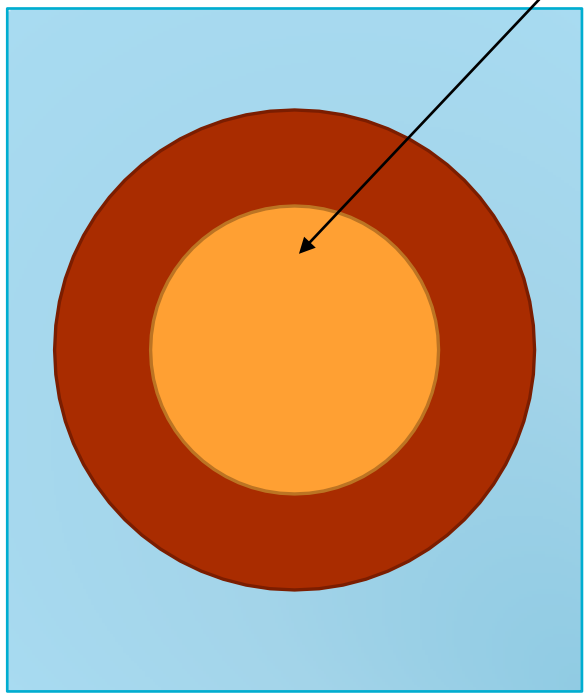


Generalized Reaction Mechanism		
(1)	$FeS_2 + 2Li^+ + 2e^- \rightleftharpoons Li_2FeS_2$	Intercalation
(2)	$Li_2FeS_2 + 2Li^+ + 2e^- \rightleftharpoons Fe^0 + Li_2S$	Conversion



Boebinger Joule (2018)

FeS_2 mathematical model



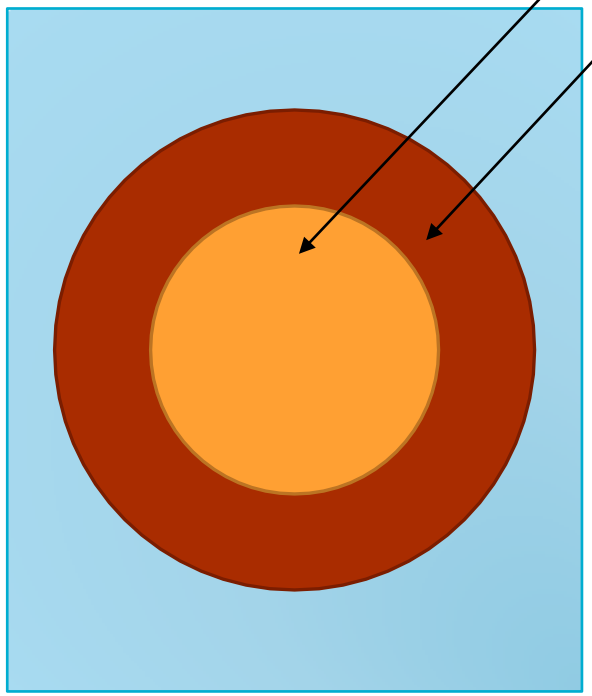
Li_xFeS_2 Particle "Core":

Electrical transport (voltage) – Ohm's Law

Intercalated lithium diffusion (Li_xFeS_2 concentration) – Non-ideal solution transport (i.e. electrochemical potential-driven)

Quasi-static mechanics (stress) – Lithiation-induced swelling

FeS_2 mathematical model



Li_xFeS_2 Particle “Core”:

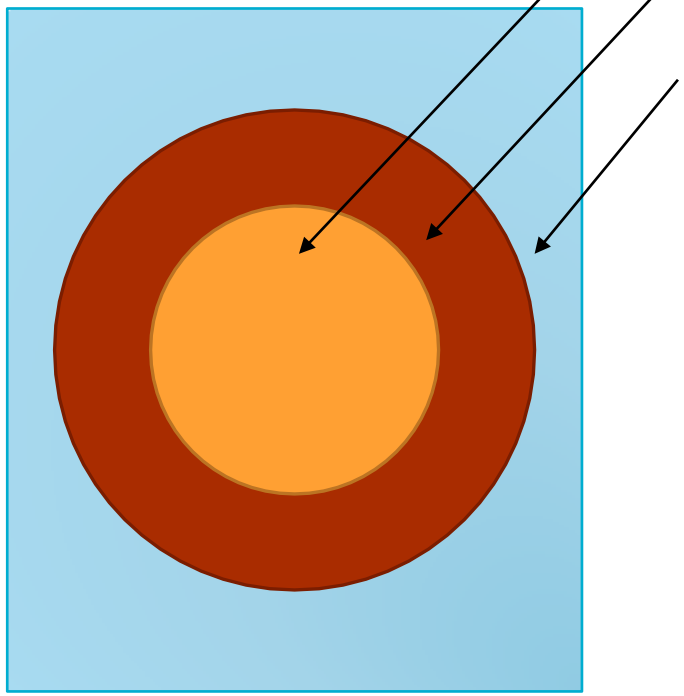
<u>Fe_0 + 2 Li_2S Particle “Shell”:</u>

Electrical transport (voltage) – Ohm’s Law

Lithium ion diffusion (Li+ concentration) – Fick’s Law

Quasi-static mechanics (stress) – Density change vs. Li_xFeS_2

FeS_2 mathematical model



Li_xFeS_2 Particle “Core”:

Fe_0 + 2 Li_2S Particle “Shell”:

<u>LiTFSI in DOL/DME Electrolyte + Diffuse CBD:</u>

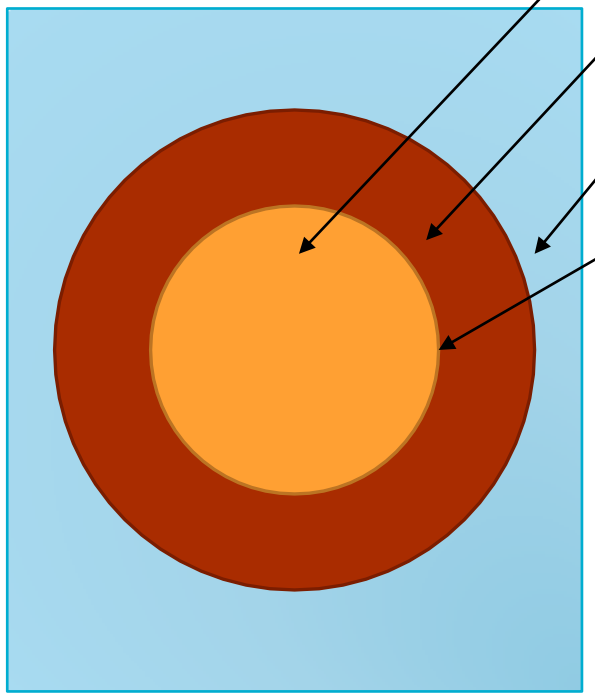
Charge transport (voltage) – Ohm’s Law + Nernst-Planck Flux

Lithium ion diffusion (Li+ concentration) – Fick’s Law + Nernst-Planck

Electrical transport (voltage) – Ohm’s Law

Conductivity set to represent an evenly distributed CBD phase

FeS_2 mathematical model



Li_xFeS_2 Particle “Core”:

Fe_0 + 2 Li_2S Particle “Shell”:

LiTFSI in DOL/DME Electrolyte + Diffuse CBD:

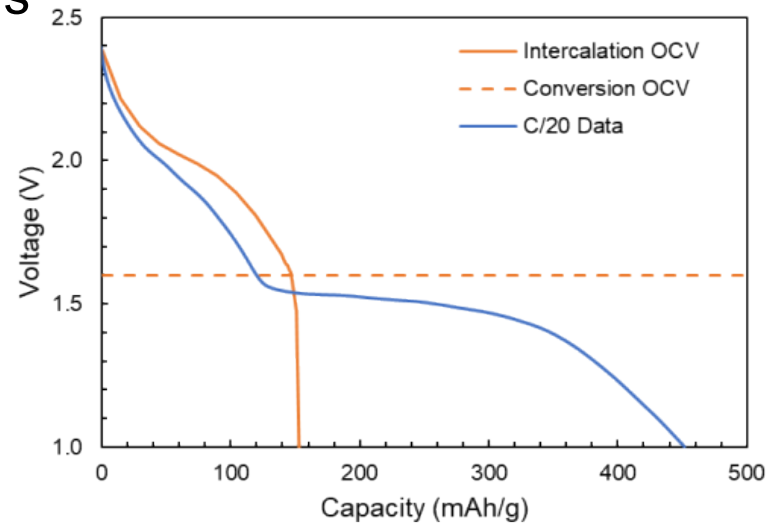
<u>Reaction Surface:</u>

$$i_r = i_{0,r}\left[\exp\left(\frac{\alpha_a F\eta_r}{RT}\right) - \exp\left(\frac{-\alpha_c F\eta_r}{RT}\right)\right]$$

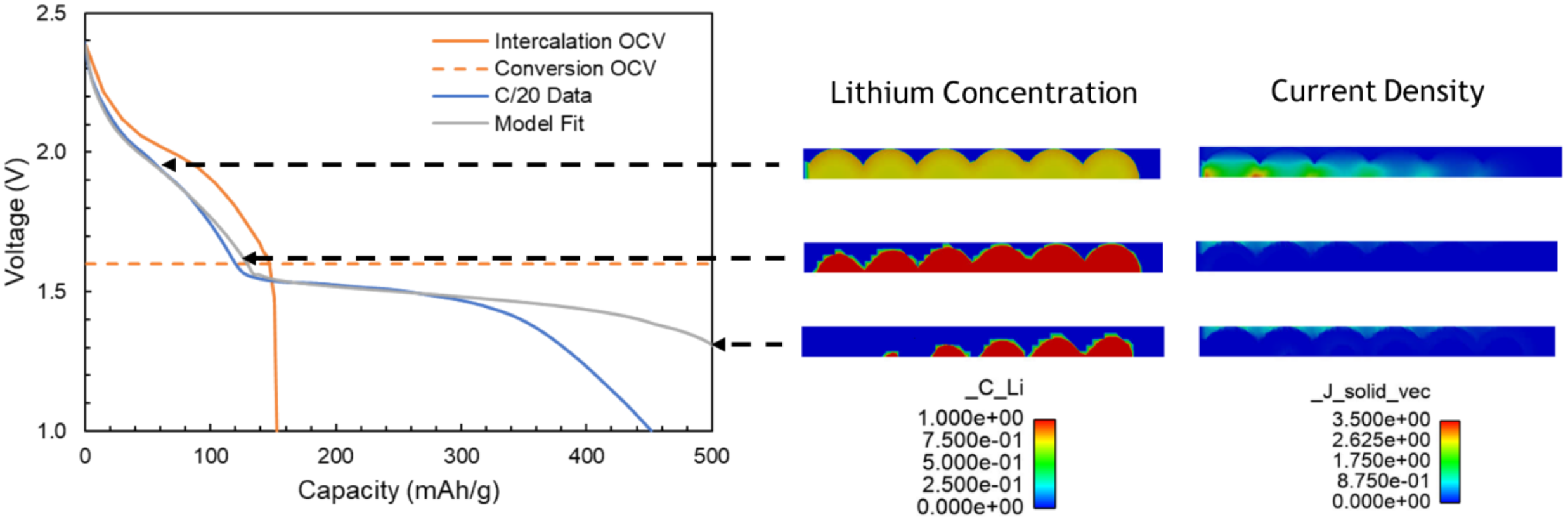
Butler-Volmer reaction kinetics –
2 simultaneous reactions

Reaction surface moves using
level-set field + CDFEM

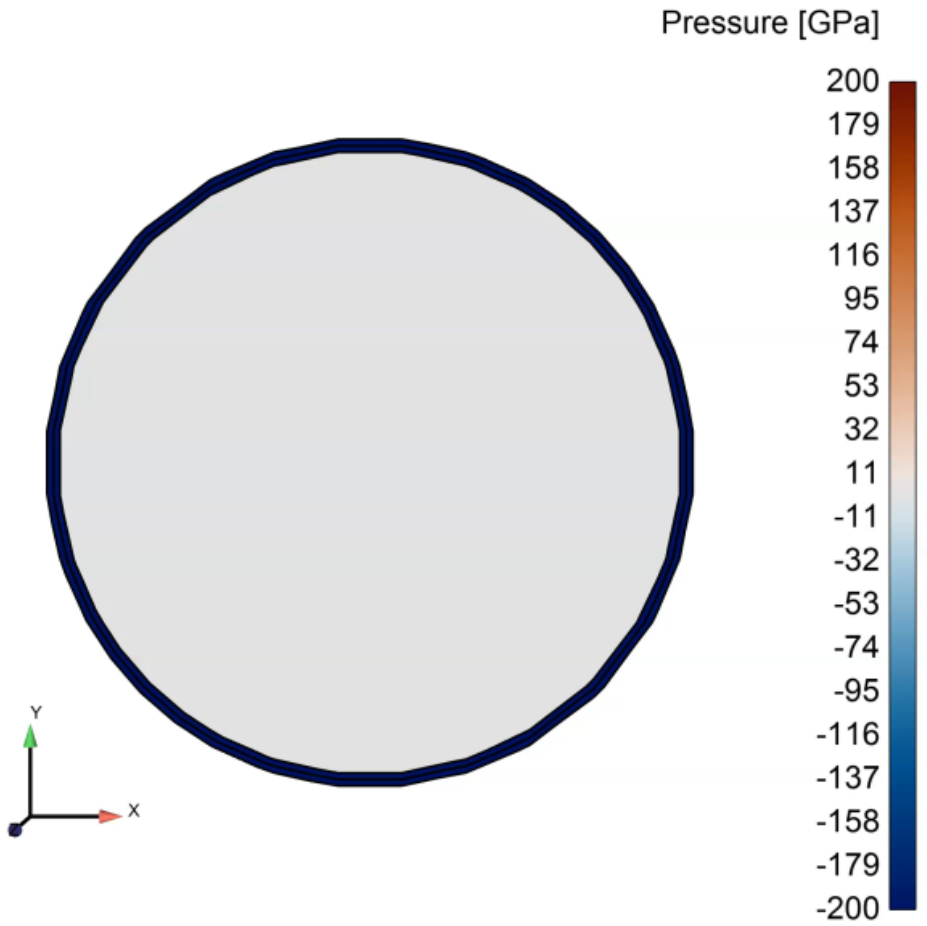
$$v = n \cdot \left(-\frac{i_{conv}}{nF}\frac{M}{\rho}\right)$$

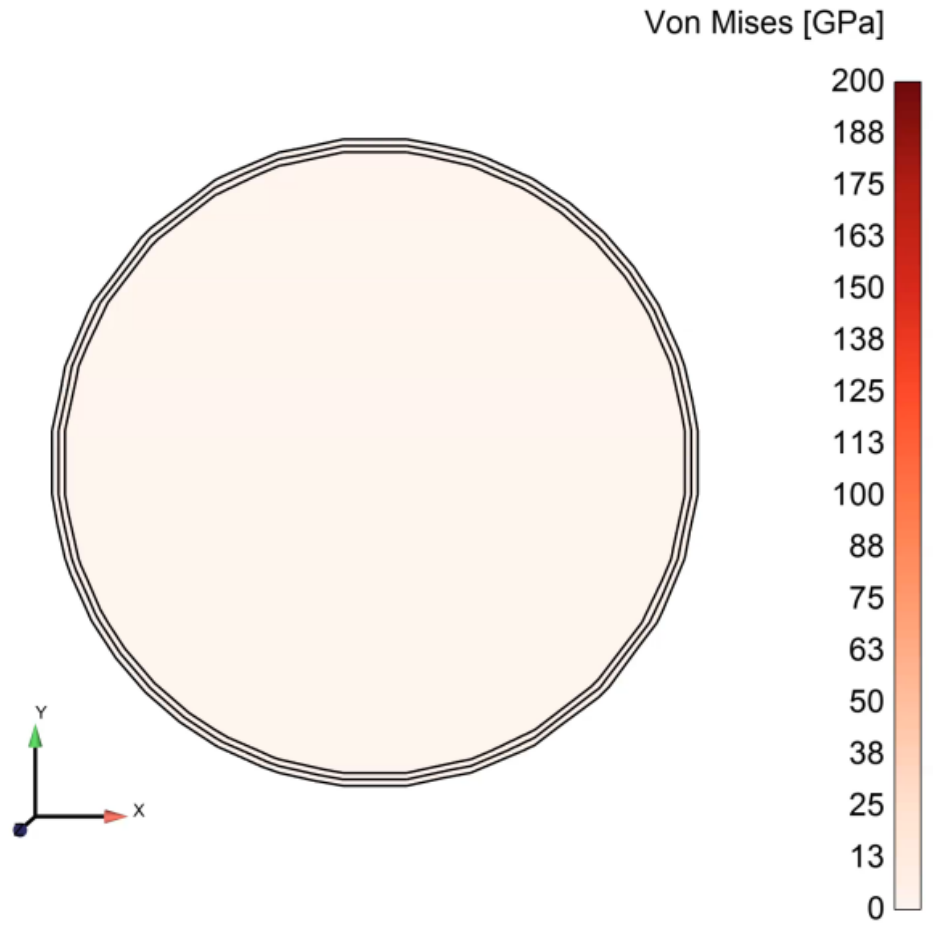


Electrochemical results

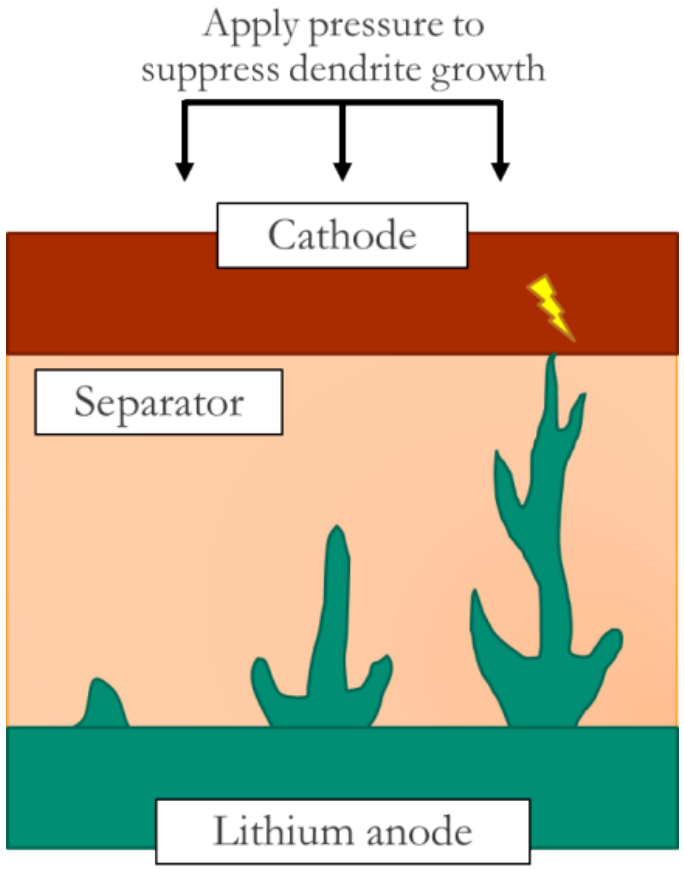


Stress generation in two conversion reactions of FeS_2



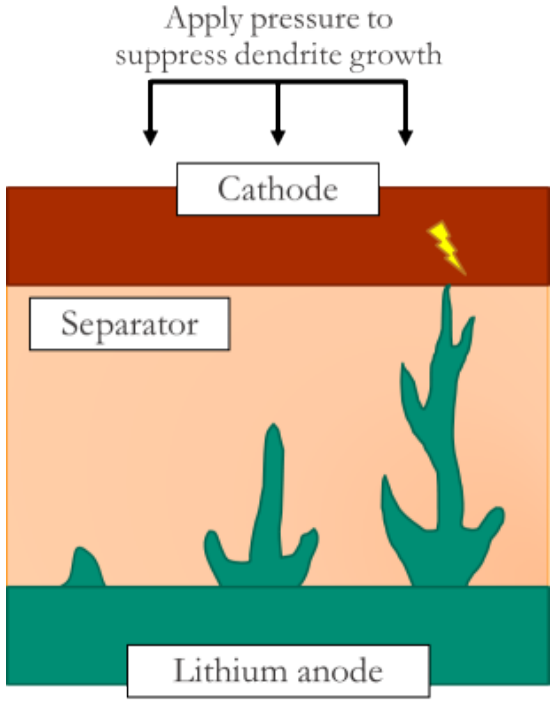


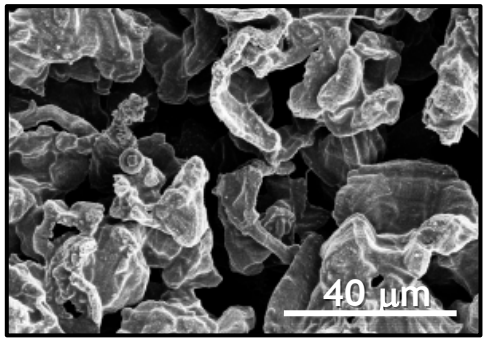
Role of mechanics in mitigating dendrite growth on lithium metal

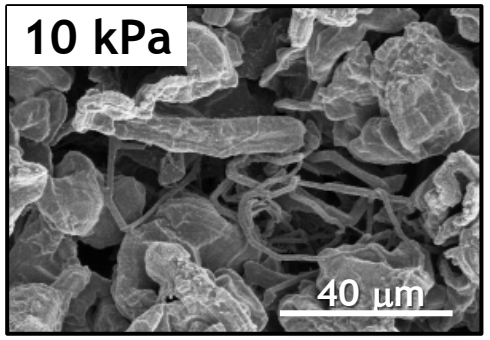


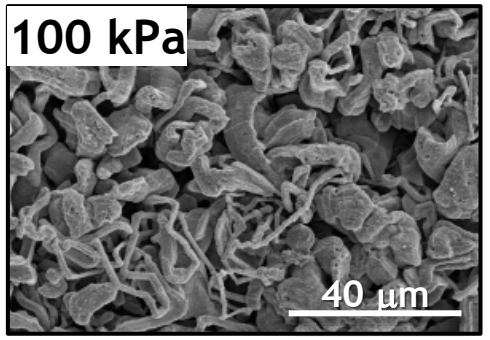
Work in this section with Julia Meyer,
Purdue Ph.D. student with Partha P. Mukherjee

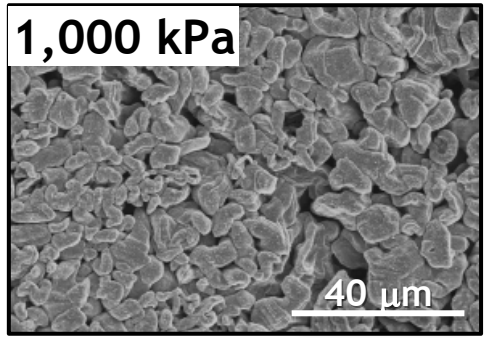
Pressure suppresses dendrite formation in Li metal

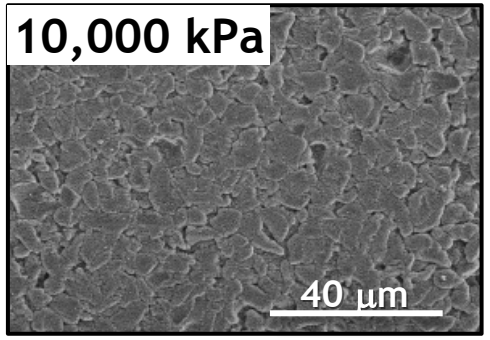












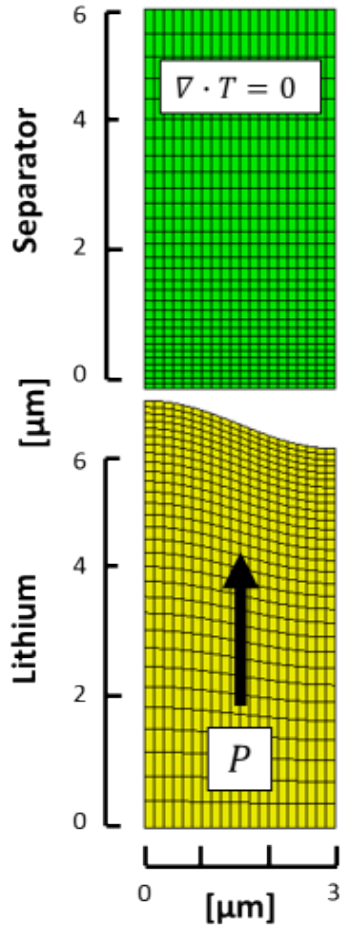
K.L. Harrison, et al., “The Effects of Interfacial Compression on Li Metal Cycling Performance and Morphology in 4M LiFSI in DME,” in press, ACS AMI 2021

Cryo SEM images courtesy of Katie Jungjohann and Dan Ward

Li model workflow

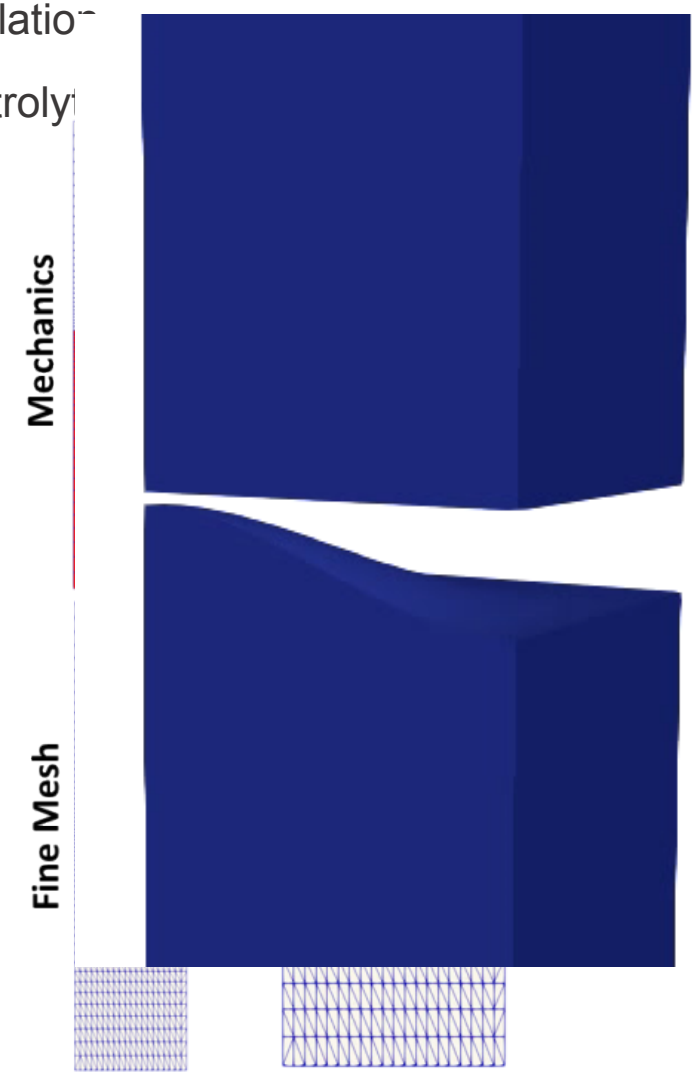
1. Mechanics

- Separator: Celgard 2325
- 3D, linear elastic model



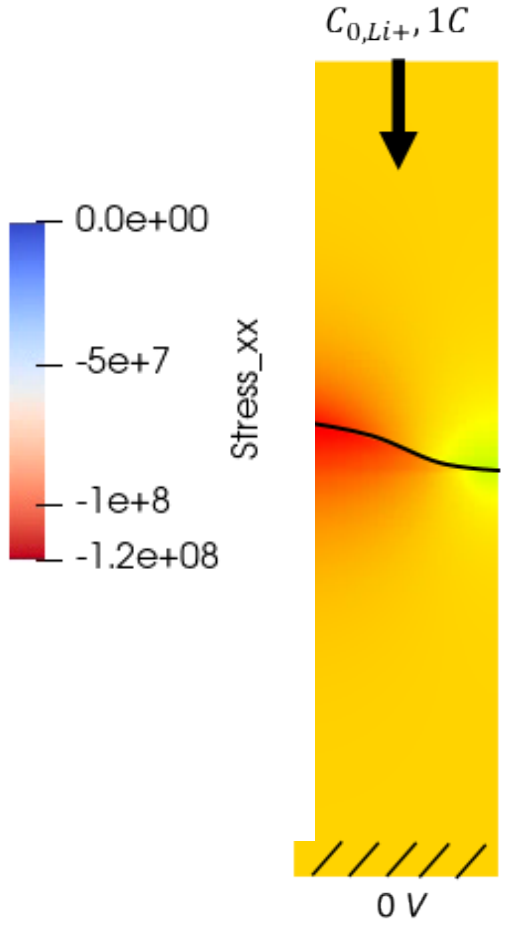
2. Re-Meshing

- Conformal contact after mechanics simulatio
- Electroly

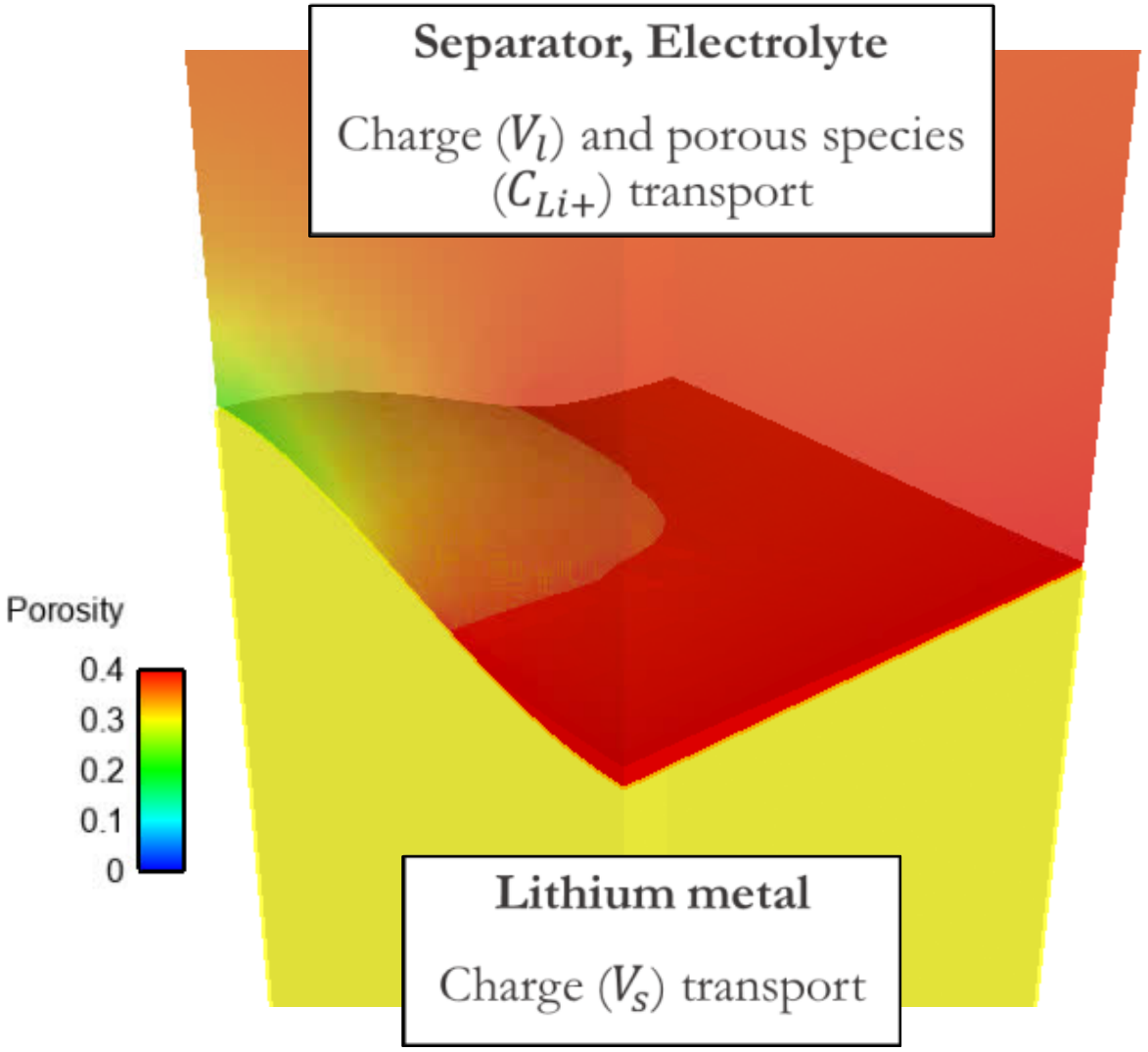


3. Electrochemistry

- Electrochemical response
  stem evaluated



Impact of mechanics on electrochemistry

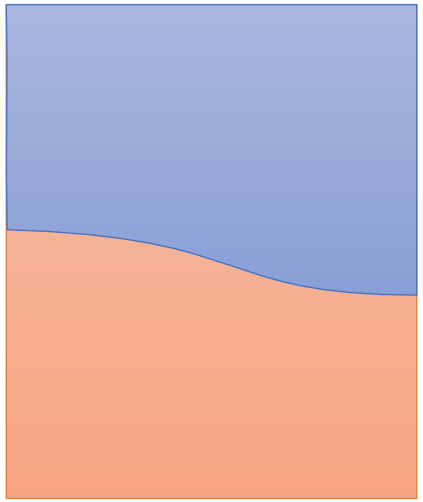


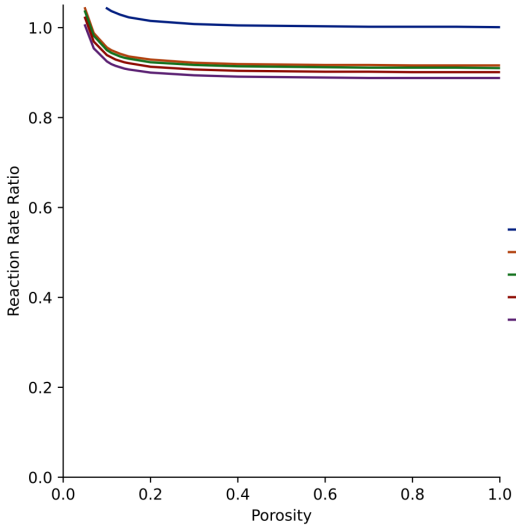
- Celgard tortuosity approximation [1]:
  - $\tau = \epsilon^{-1.5}$
- Effect of strain on separator porosity:
  - $\phi = 1 - \frac{b(1-\phi_0)}{det\langle F \rangle}$
- Reaction rate at interface [2]:
  - $i_n = i_{0,ref}\, exp\left[\frac{(1-\alpha_a)\Delta\mu_{e^-}}{RT}\right]\left[\exp\left(\frac{\alpha_a F\eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta_s}{RT}\right)\right]$
  - $\Delta\mu_{e^-} = -\frac{1}{2}(\bar{V}_{Li} + t_-^0\bar{V}_{LiX}) \times \{-\gamma\bar{\nabla}_s \cdot e_n + e_n \cdot [e_n \cdot (\tau_d^{elec} - \tau_d^{sep})]\} + \frac{1}{2}(\bar{V}_{Li} - t_-^0\bar{V}_{LiX})(\Delta p^{elec} + \Delta p^{sep})$

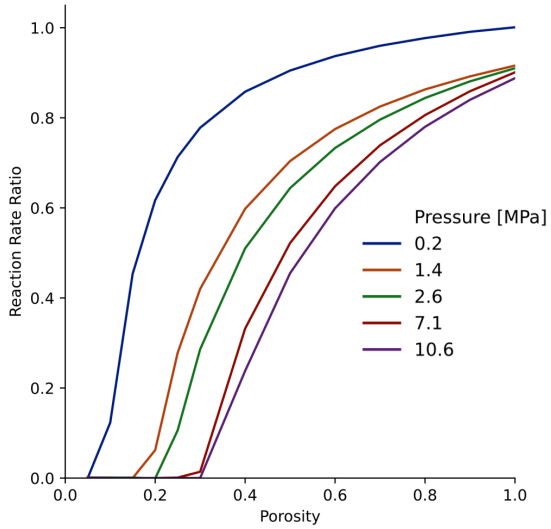
Interplay between pressure, geometry, and compressibility

$\phi = \phi_0$ $\phi = \phi(p)$

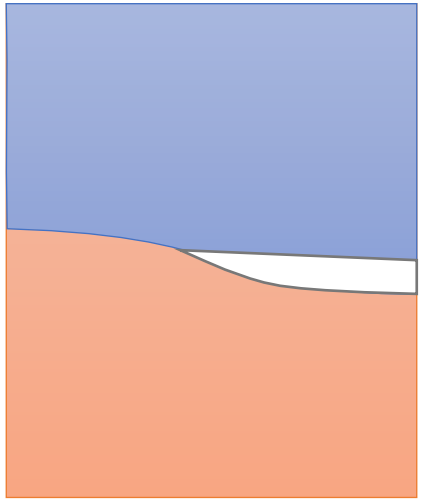
Separator only

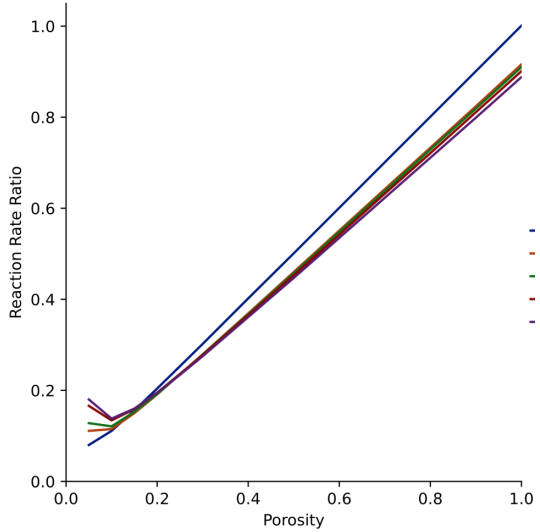


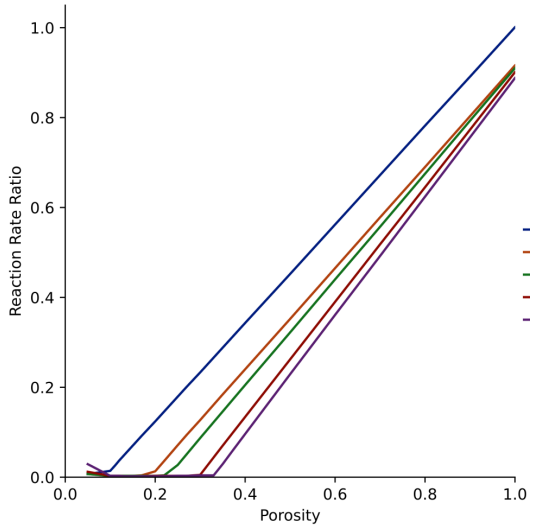




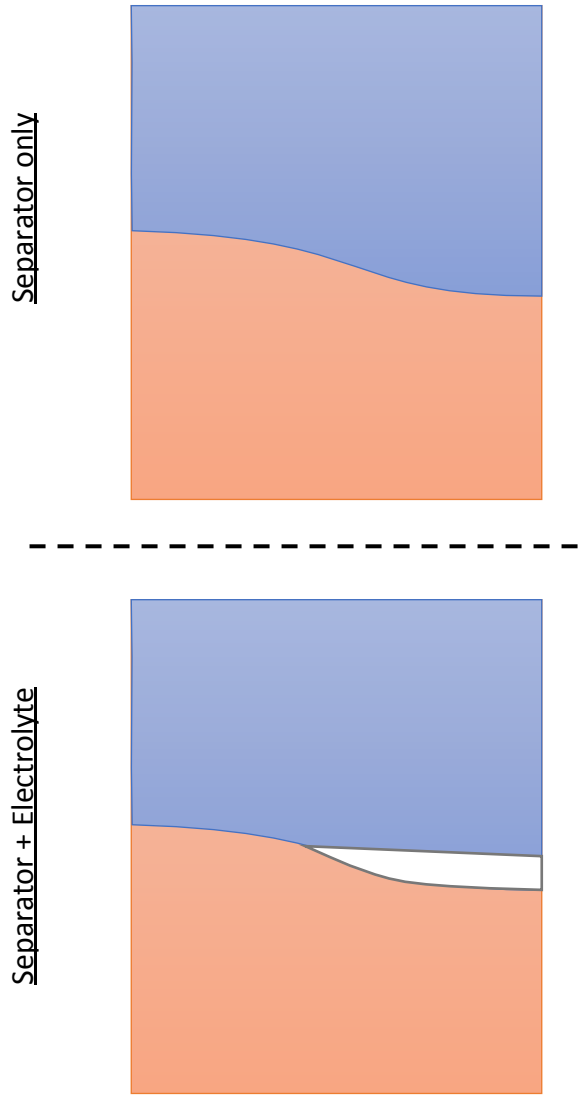
Separator + Electrolyte

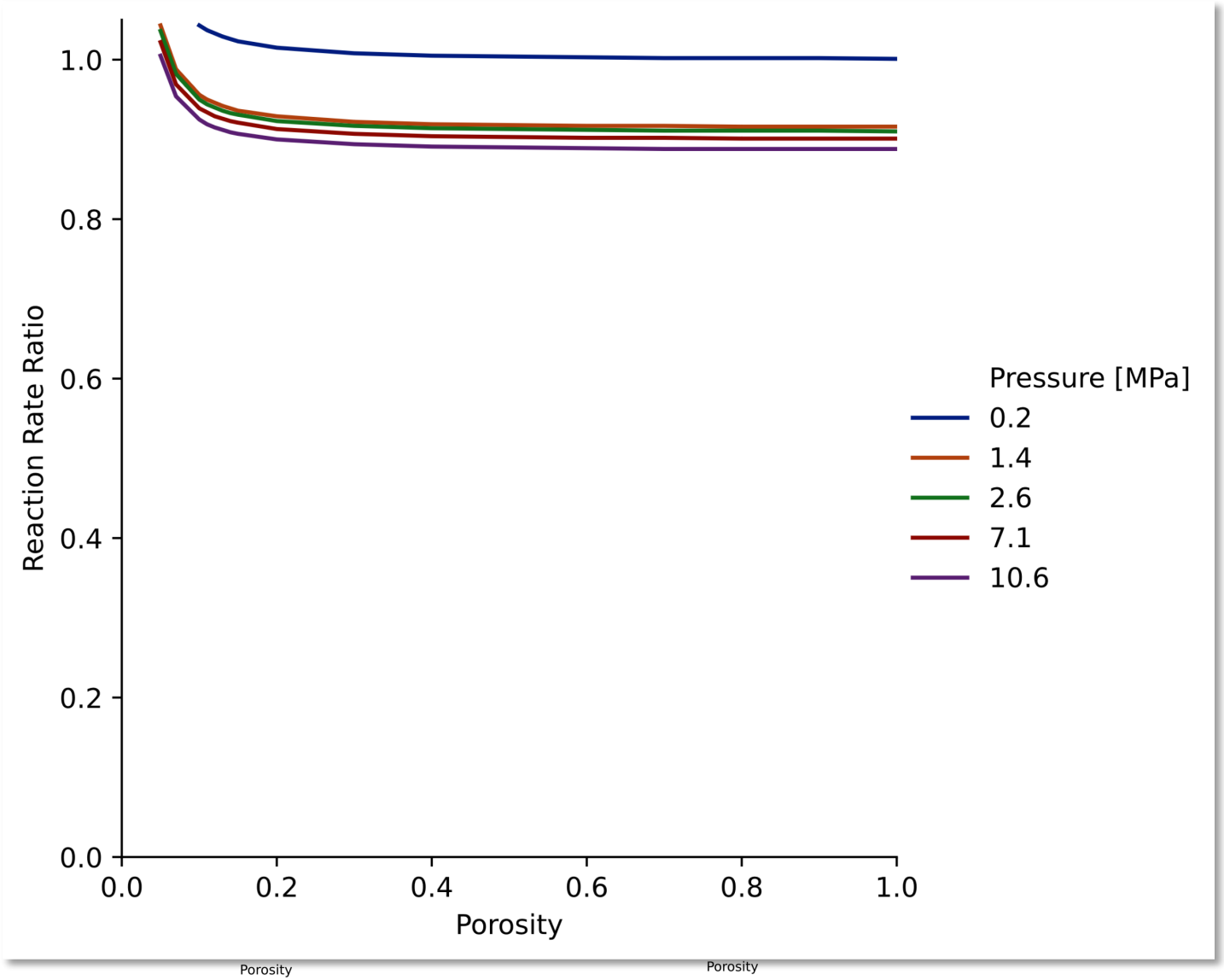




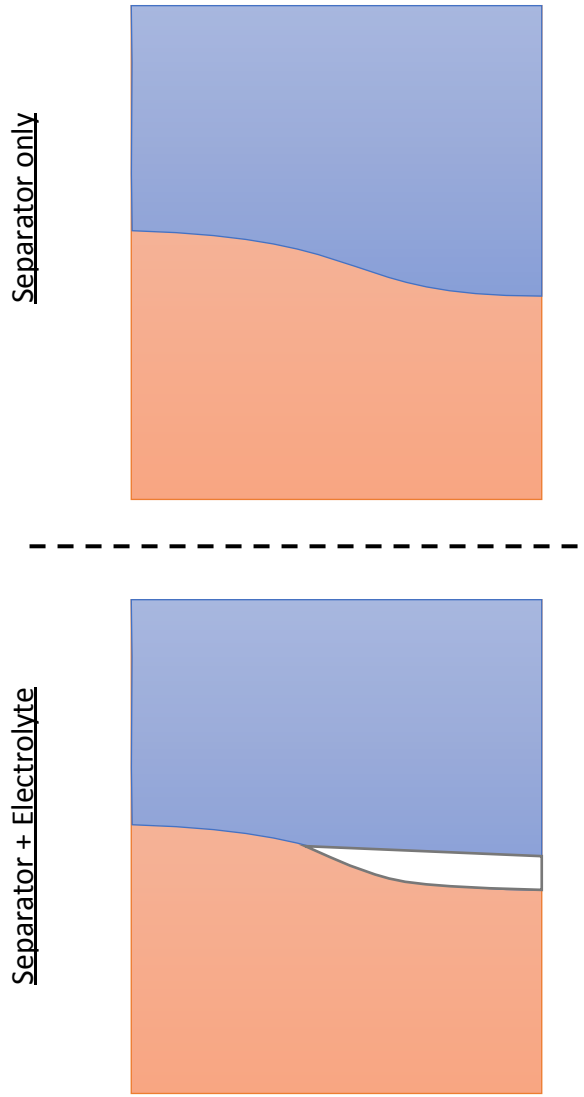


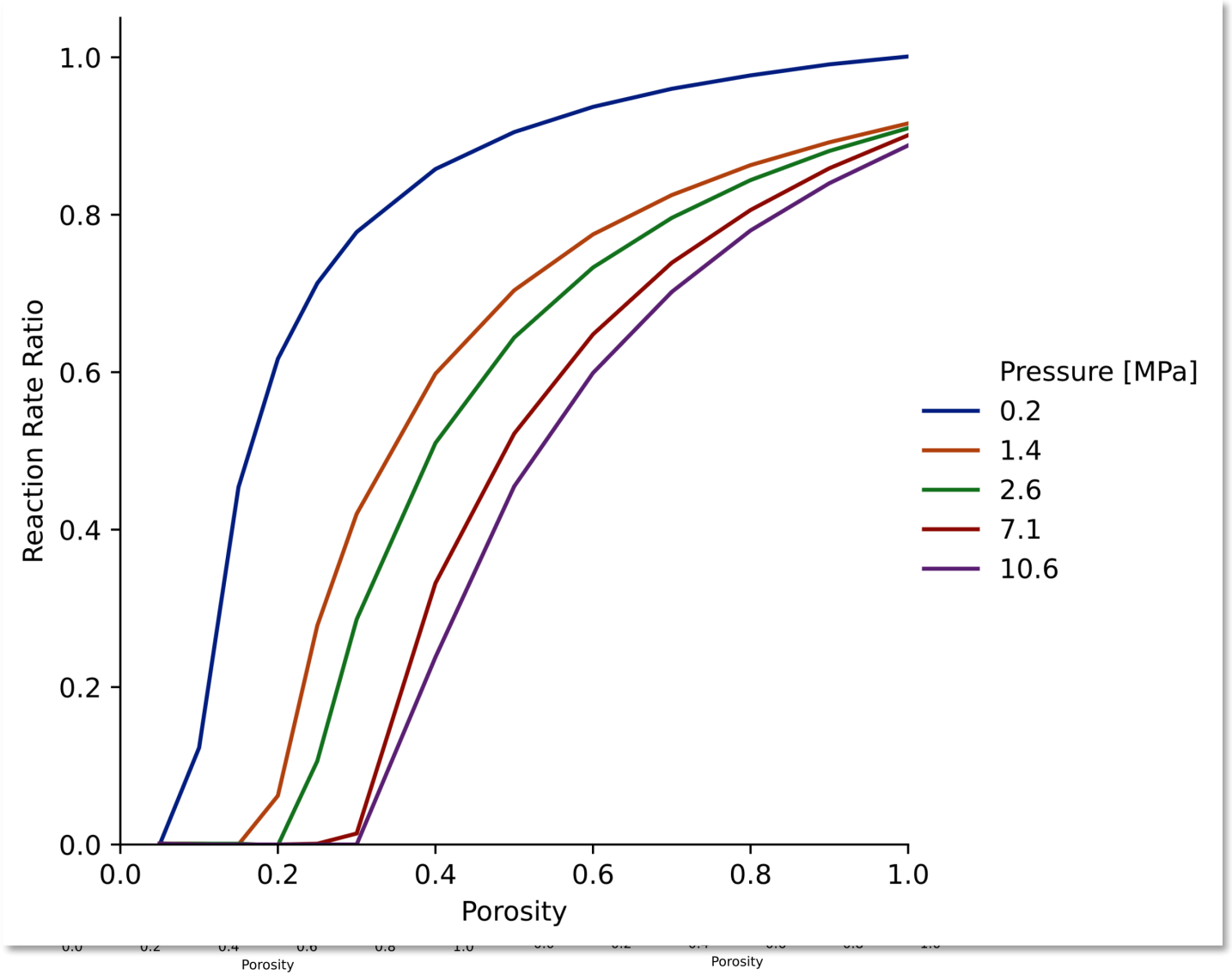
Interplay between pressure, geometry, and compressibility



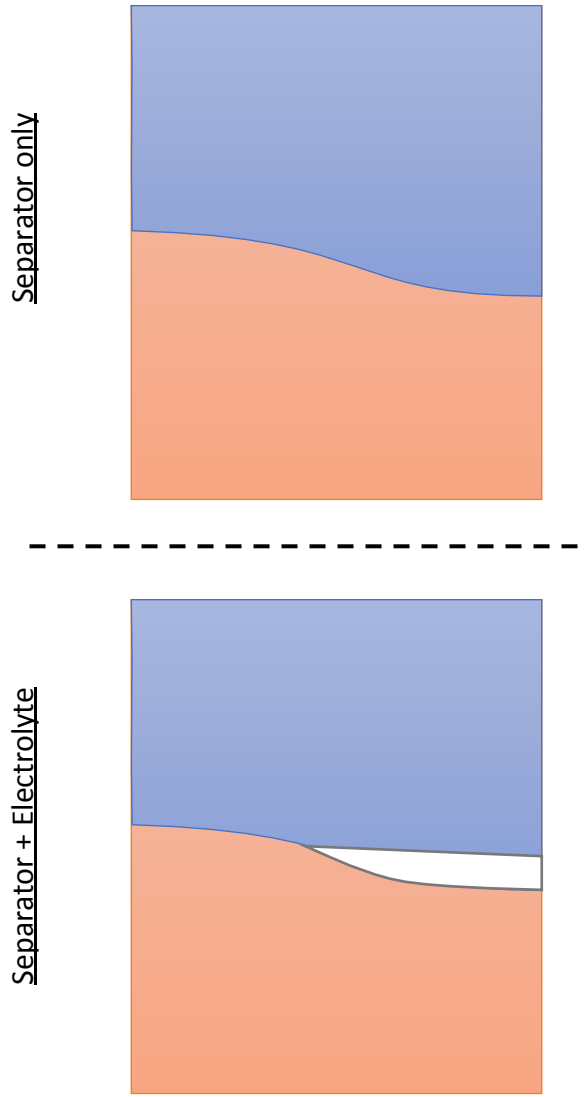


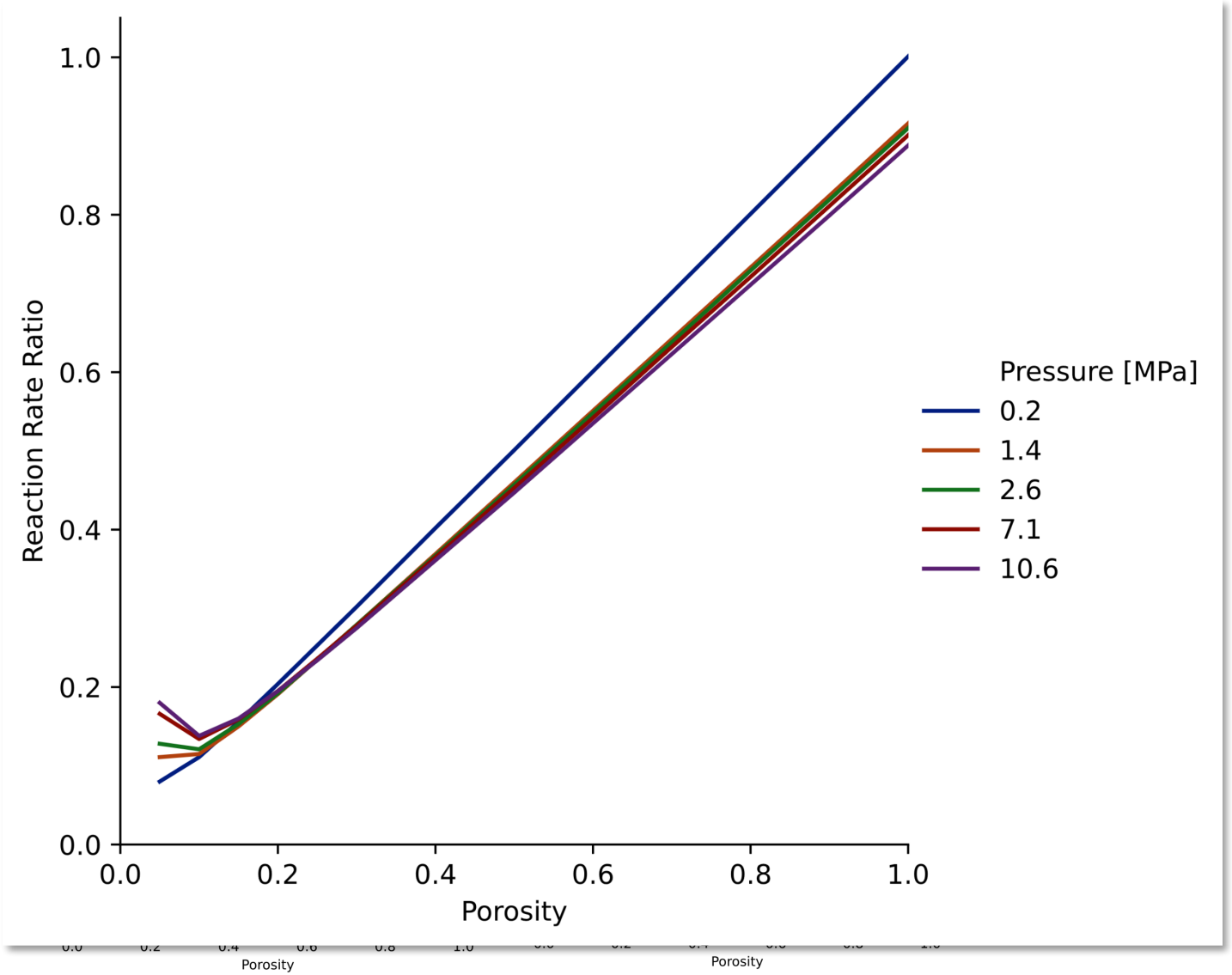
Interplay between pressure, geometry, and compressibility



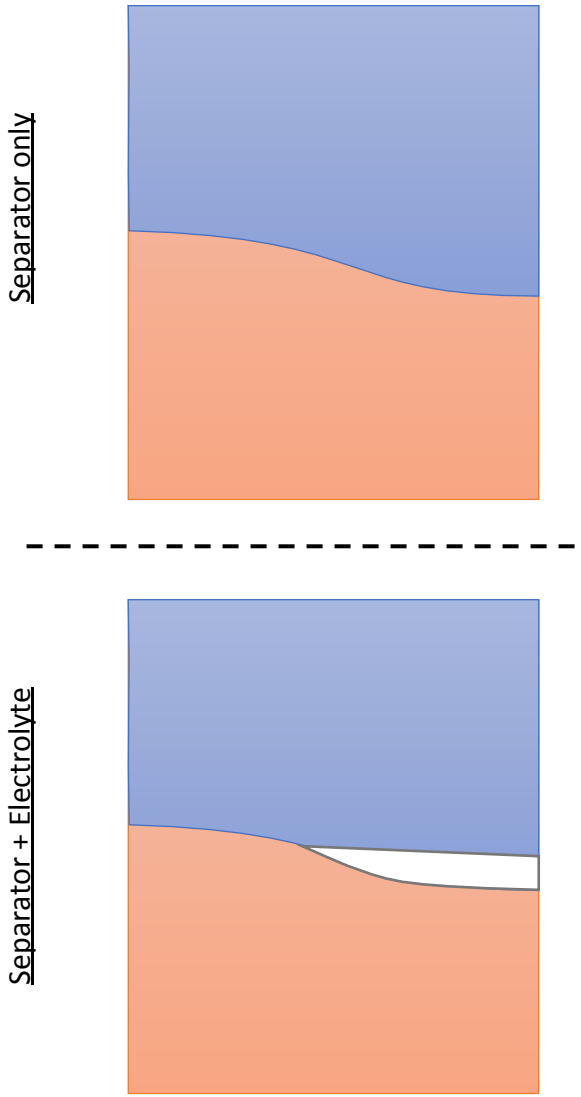


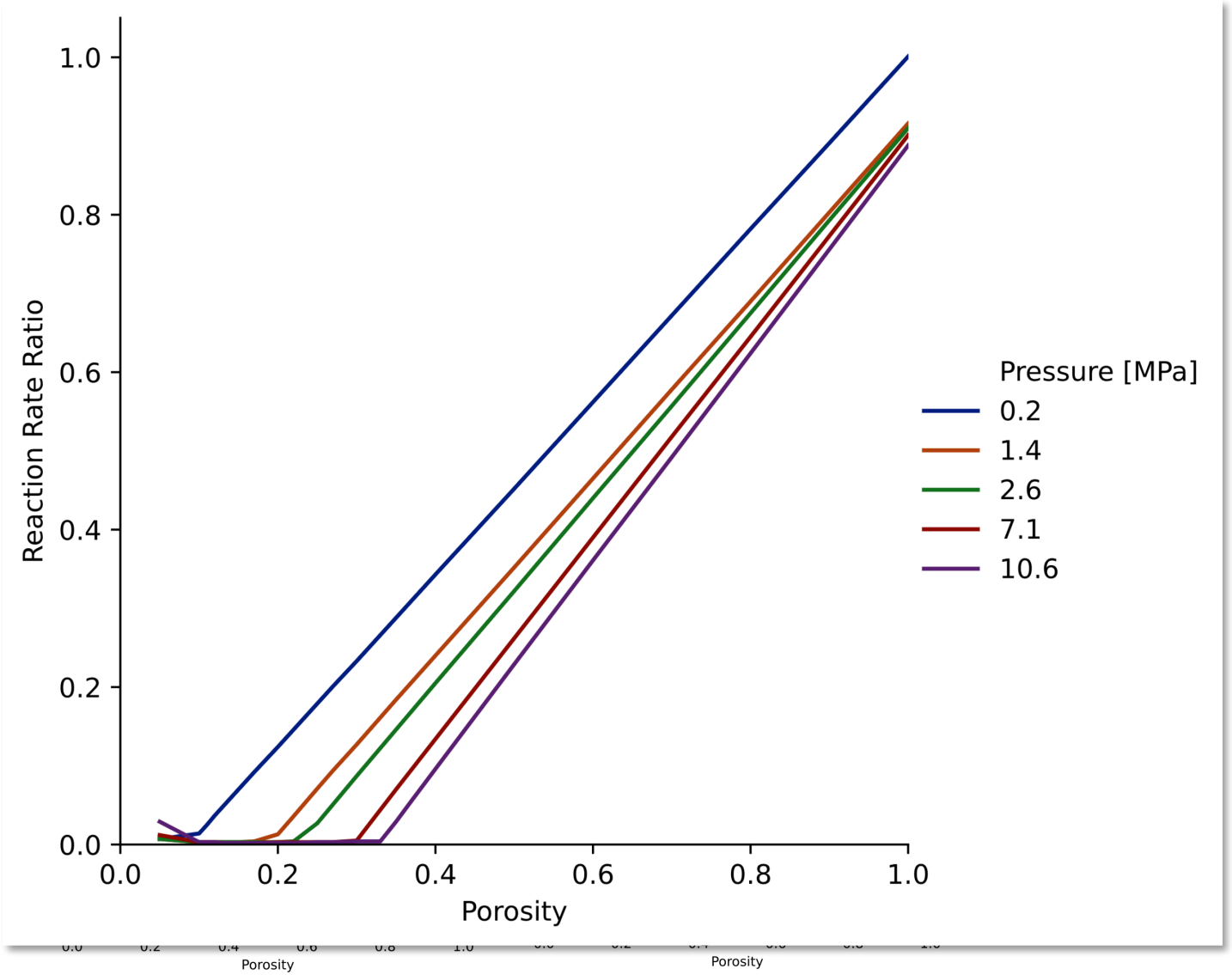
Interplay between pressure, geometry, and compressibility



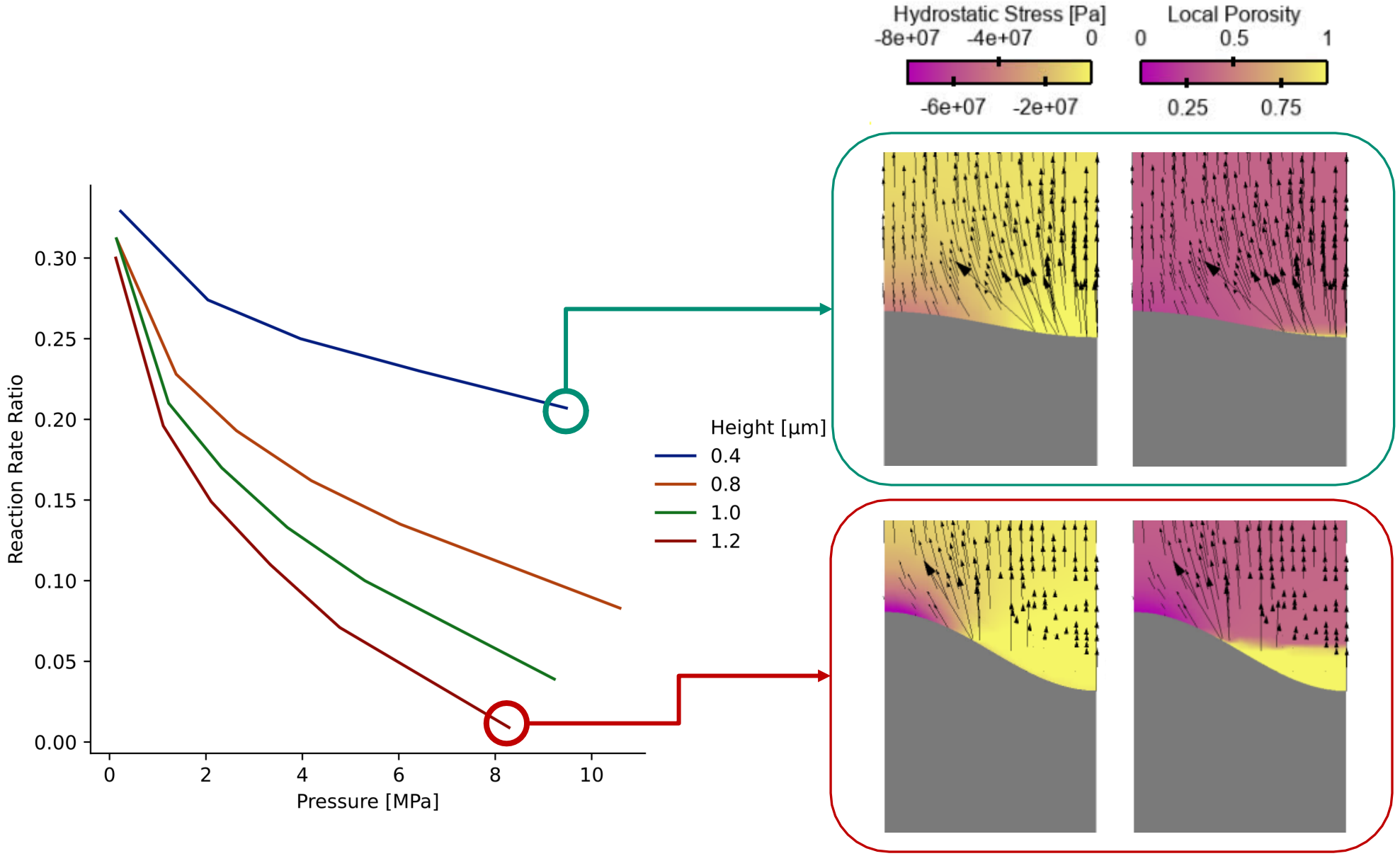


Interplay between pressure, geometry, and compressibility

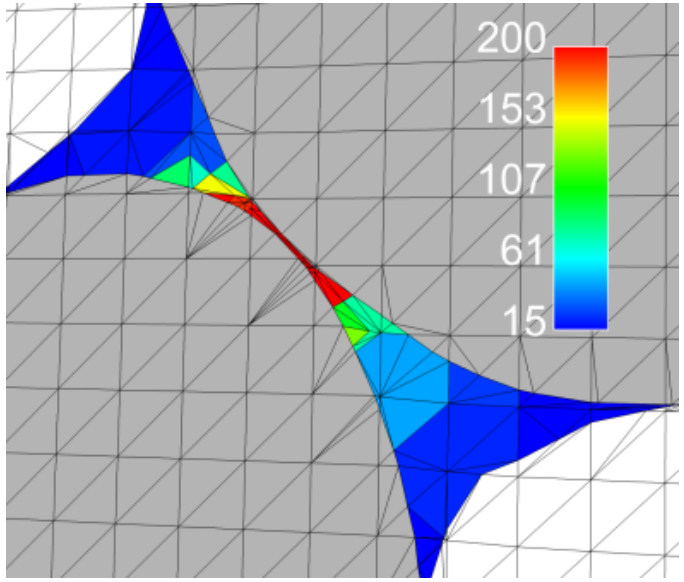




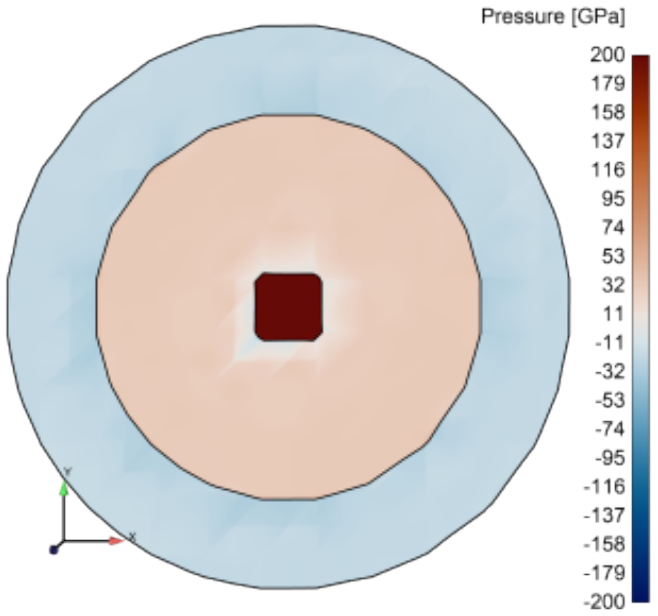
Taller protrusions increase mechanics impact



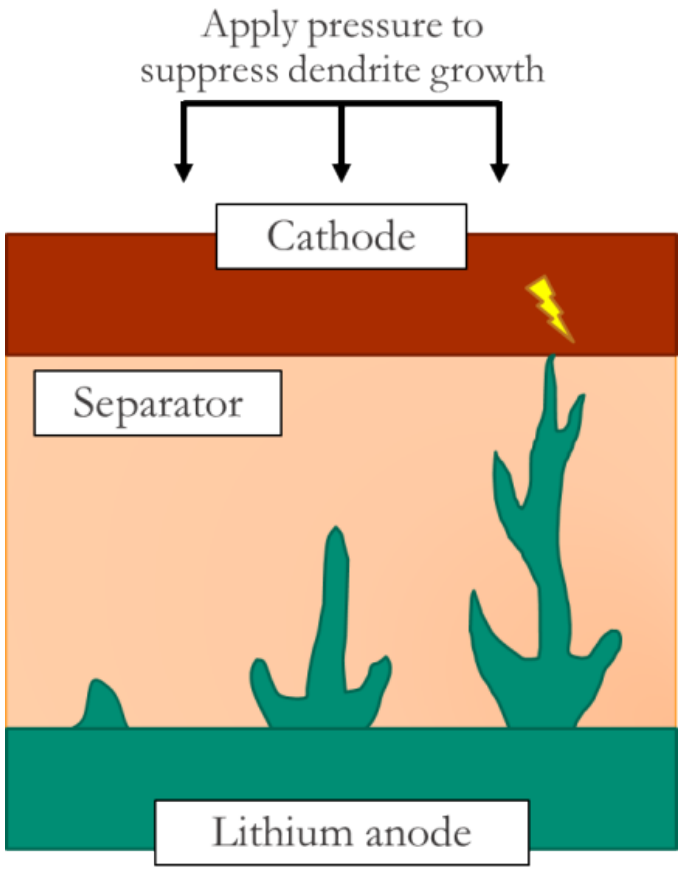
Mechanics in Batteries: 3 Vignettes



Impact of mechanics on binder in intercalating electrodes



Stress generation in conversion electrode particles



Role of mechanics in mitigating dendrite growth on lithium metal

Sandia National Laboratories

Exceptional service in the national interest

Thank you

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