



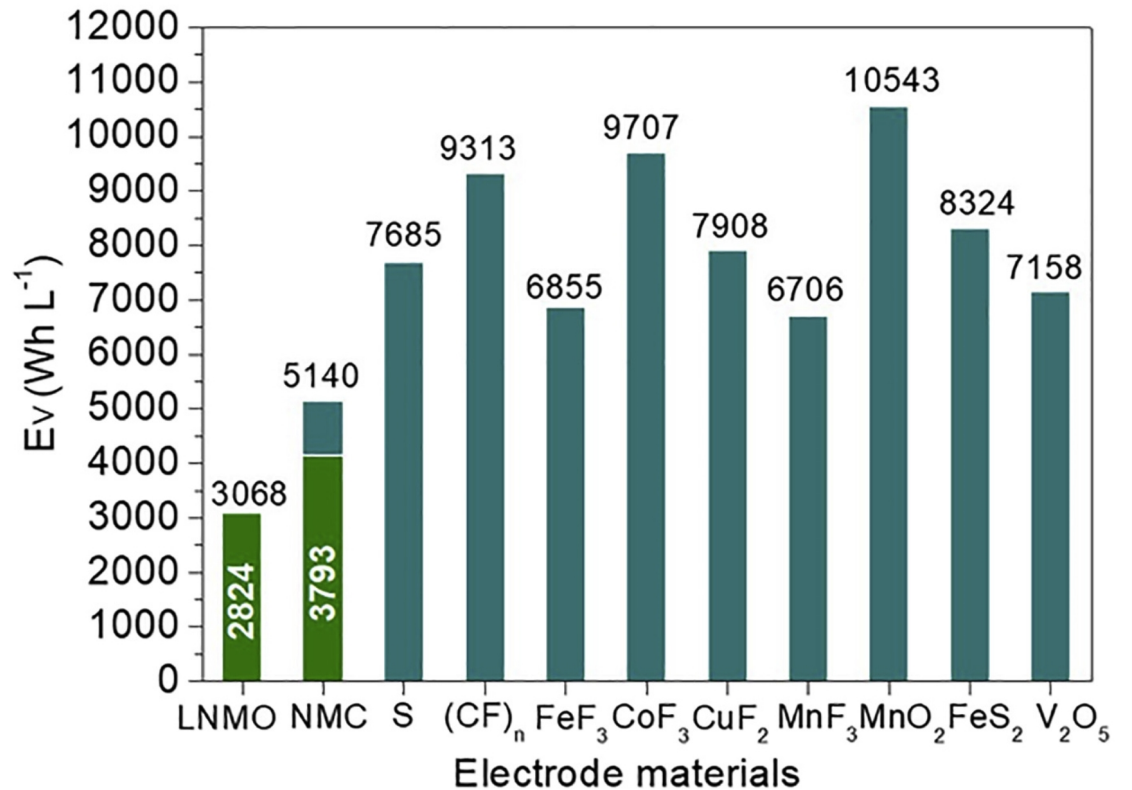
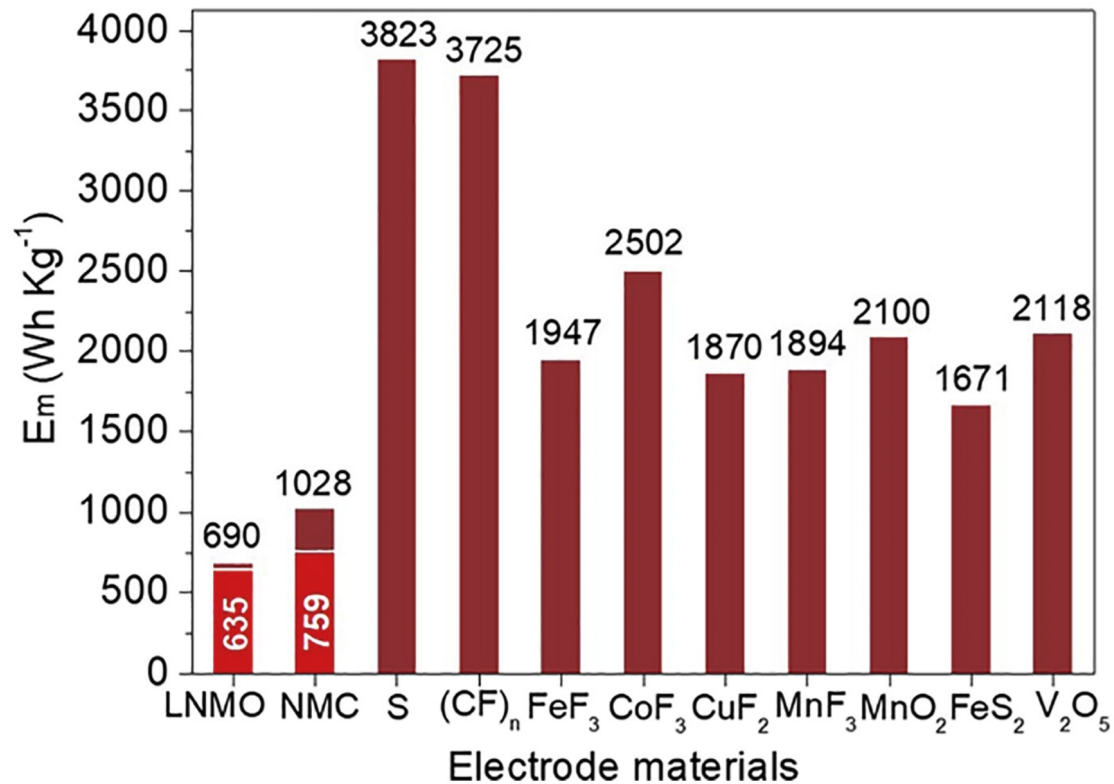
Exceptional service in the national interest

Enabling high-energy-density cathodes by coupling electrochemistry and mechanics across length scales

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March 21, 2023

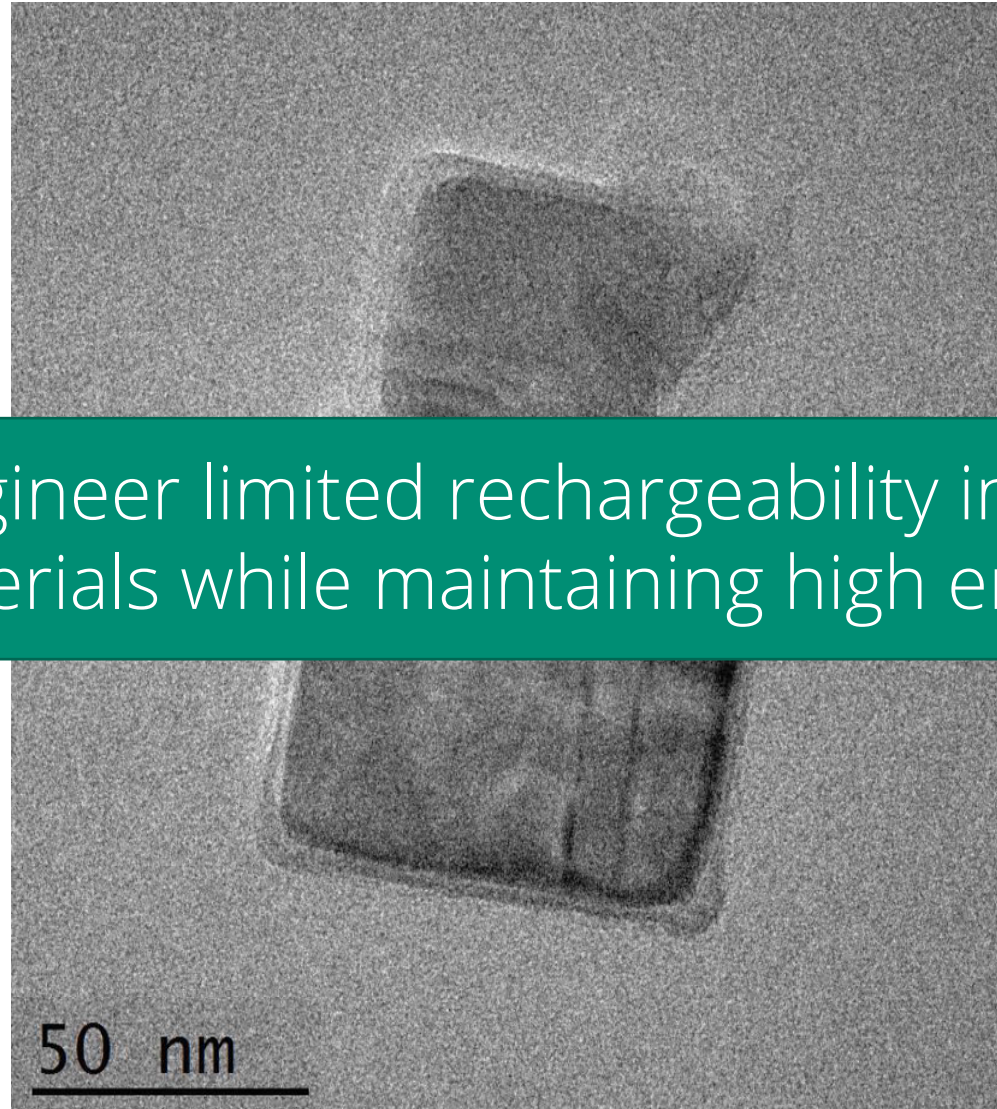
Conversion cathodes hold potential for higher energy densities



Wang et al., Joule (2019)

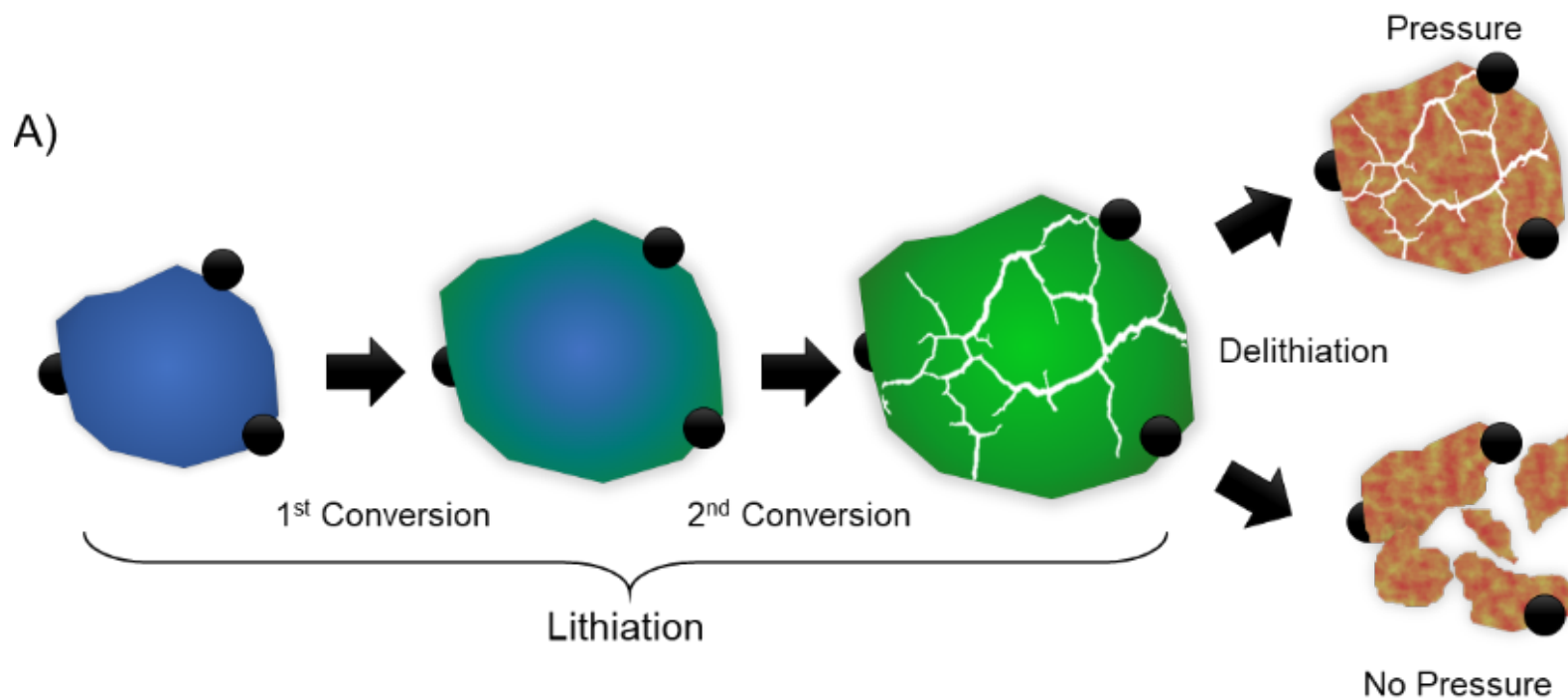
Mechanical degradation can limit conversion secondary cells

Can we engineer limited rechargeability in conversion cathode materials while maintaining high energy density?



Boebinger et al, Joule (2018)

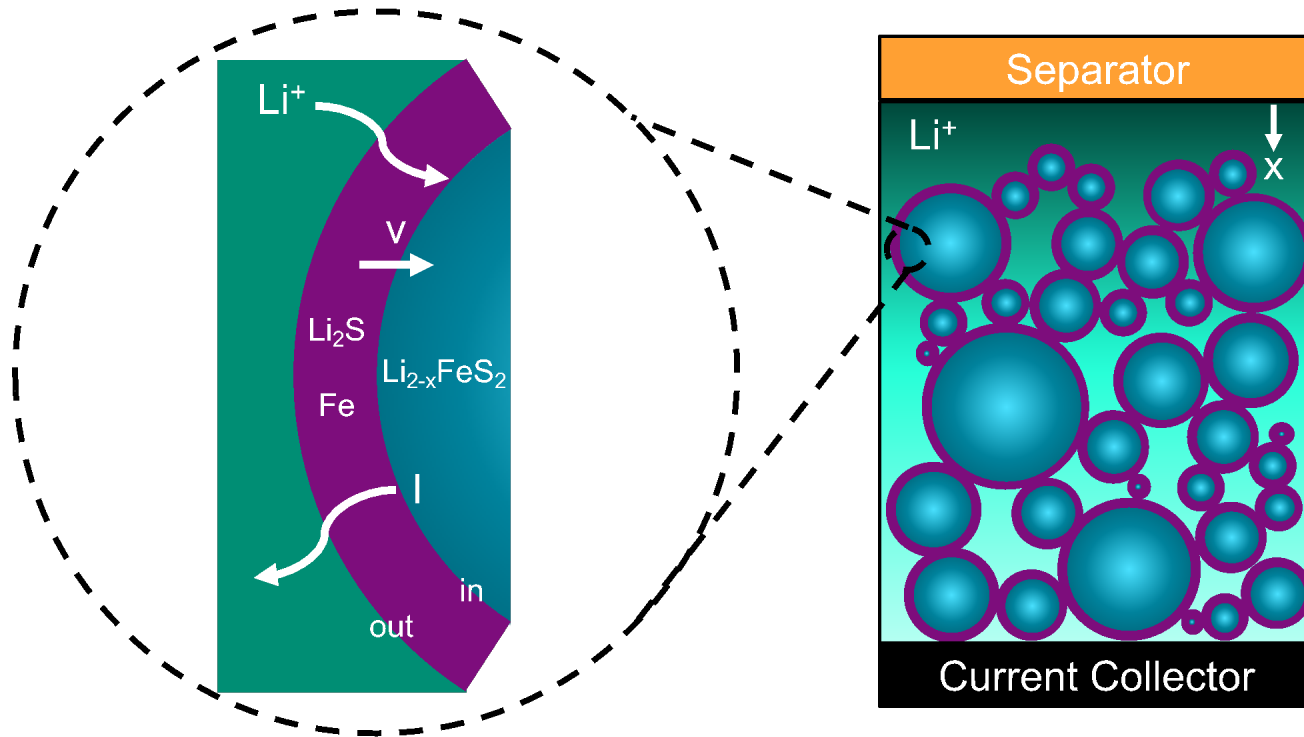
FeS₂ reaction pathways



Generalized Reaction Mechanism

(1)	$\text{FeS} + \text{S} + x \text{Li}^+ + x \text{e}^- \rightleftharpoons \text{FeS} + x \text{Li}_2\text{S}$	Conversion
(2)	$\text{FeS} + x \text{Li}_2\text{S} + y \text{Li}^+ + y \text{e}^- \rightleftharpoons y \text{LiFeS} + x \text{Li}_2\text{S}$	Intercalation
(3)	$y \text{LiFeS} + x \text{Li}_2\text{S} + z \text{Li}^+ + z \text{e}^- \rightleftharpoons \text{Fe}^0 + 2 \text{Li}_2\text{S}$	Conversion

Pseudo 2D model for conversion electrodes



Solid potential (V_s)

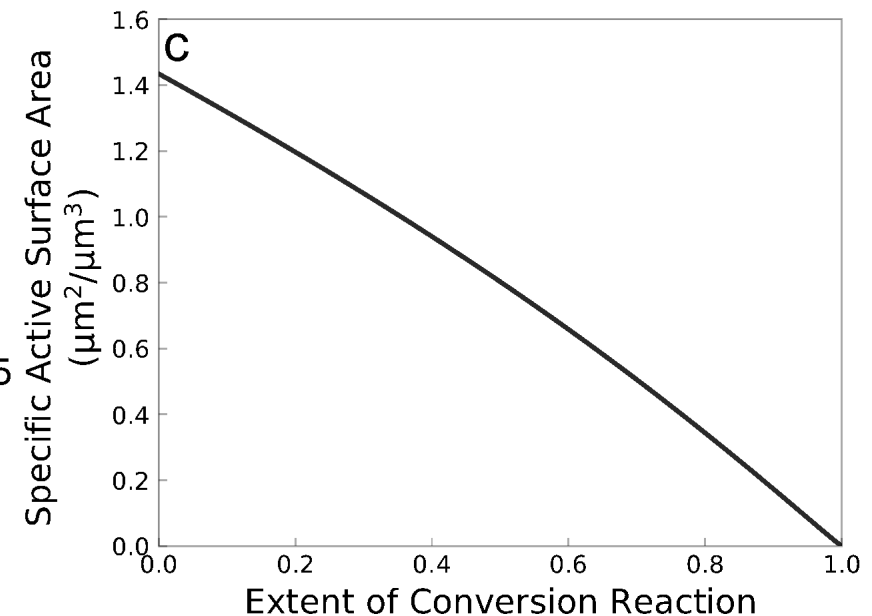
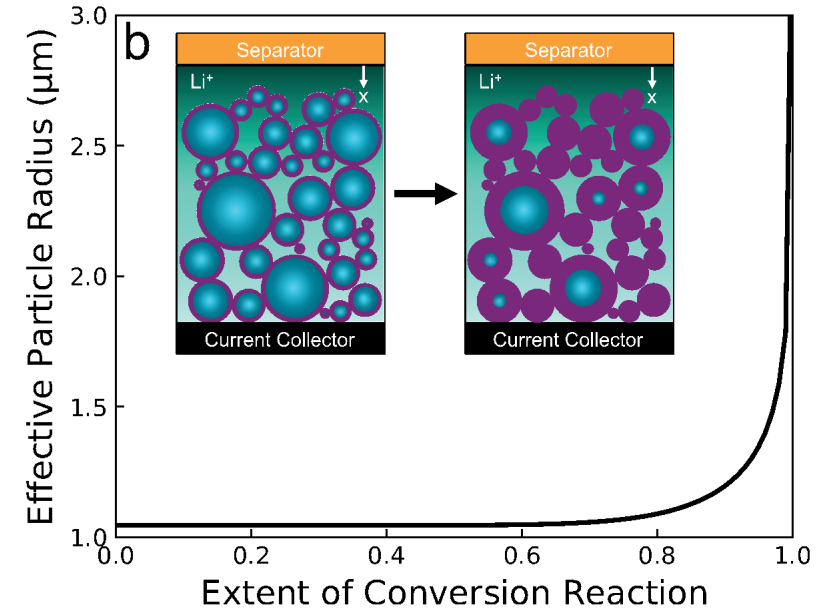
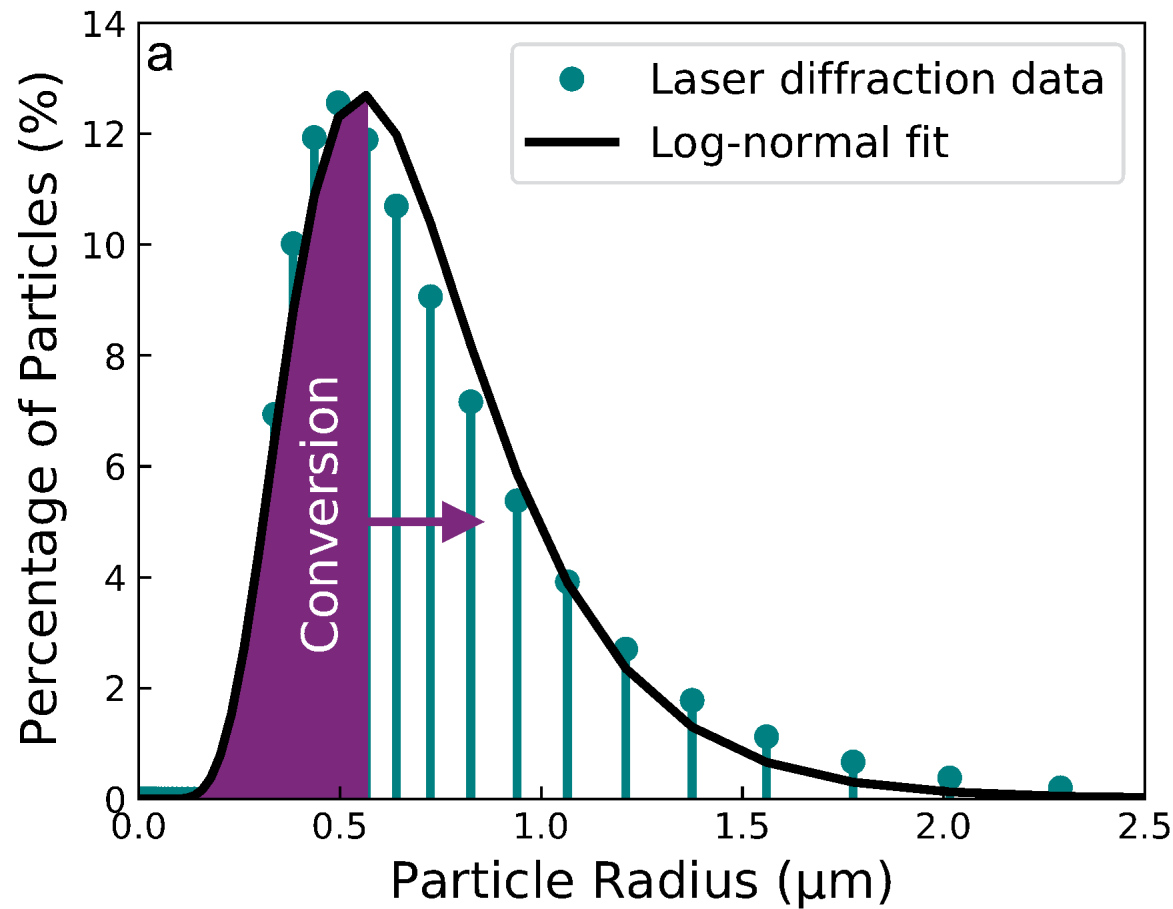
Solid Li concentration (C_{Li})

Electrolyte potential (V_l)

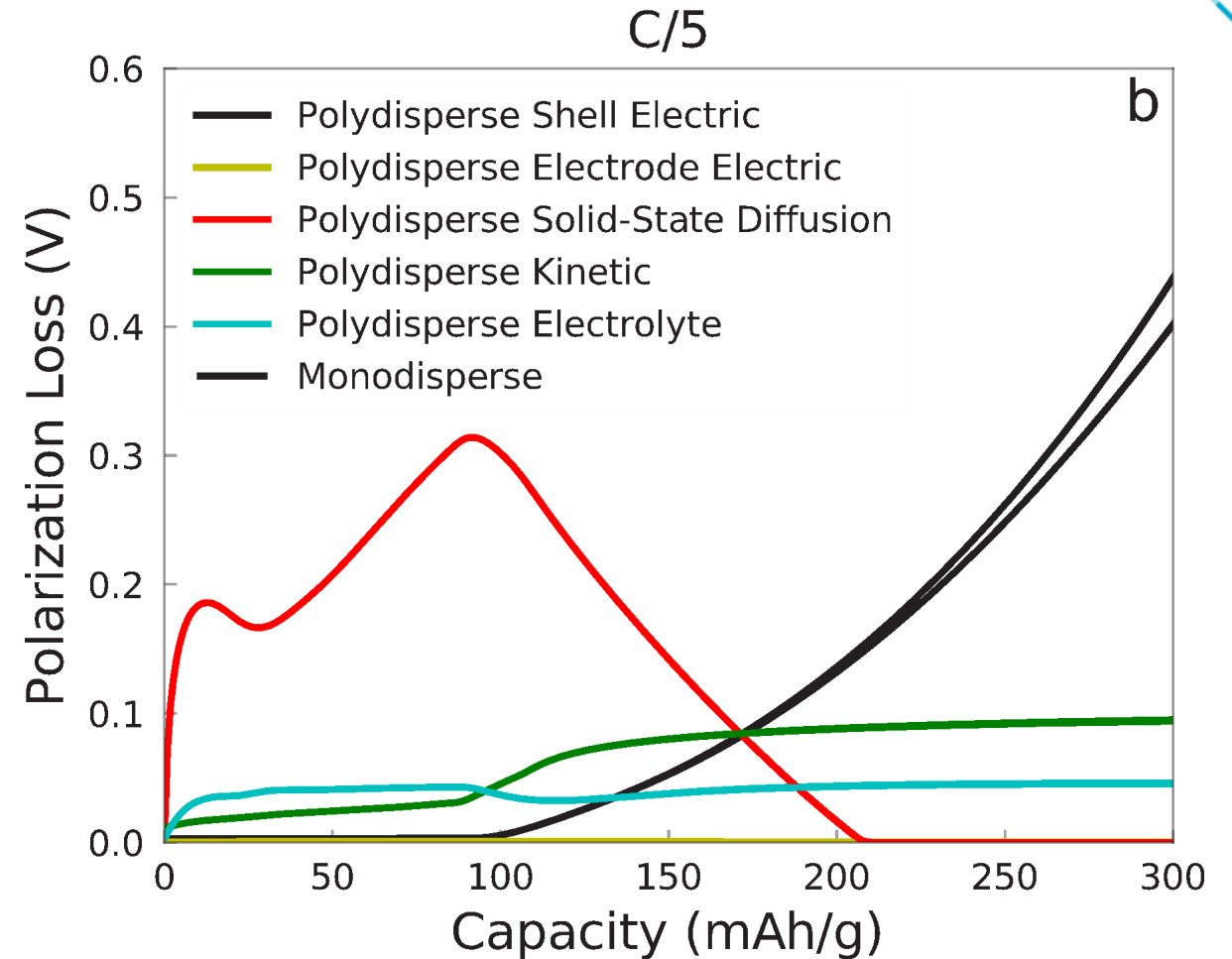
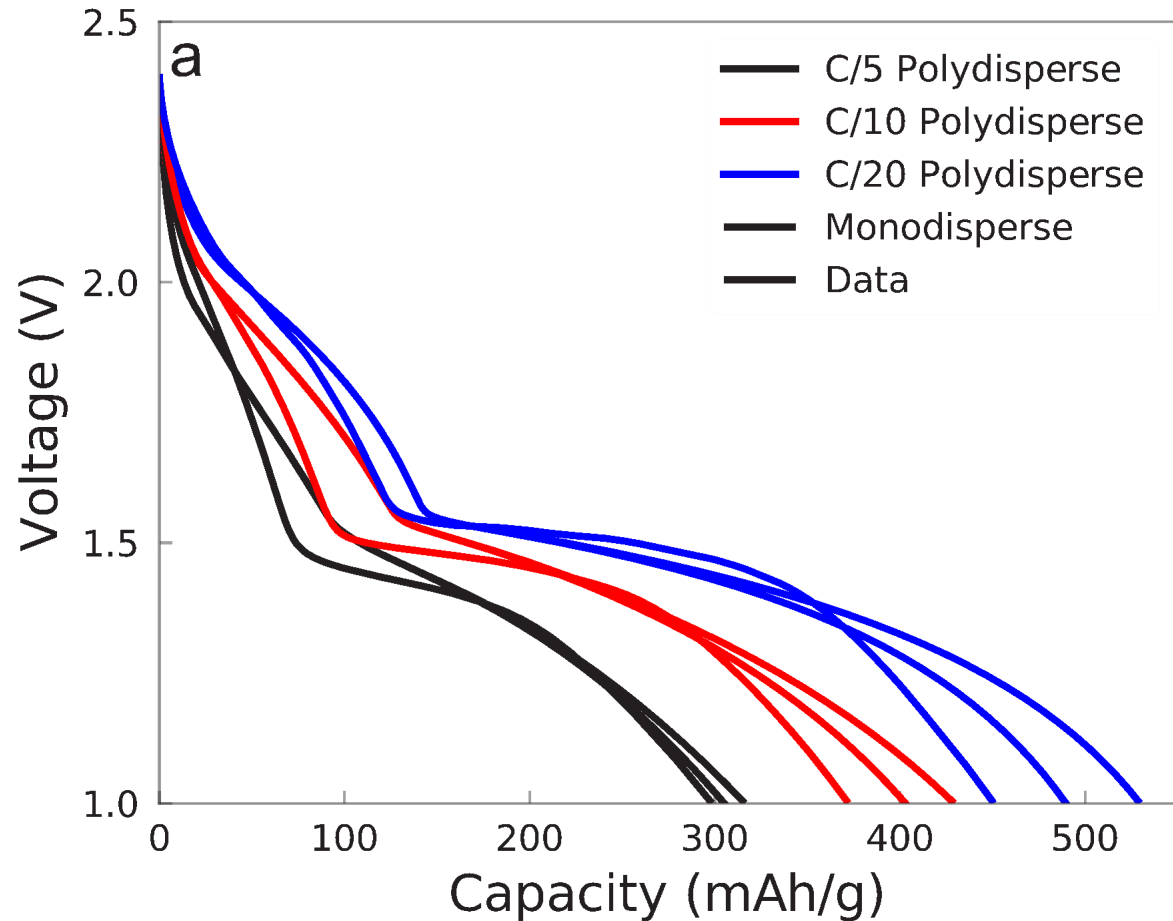
Electrolyte concentration (C_{Li^+})

Shell thickness (δ)

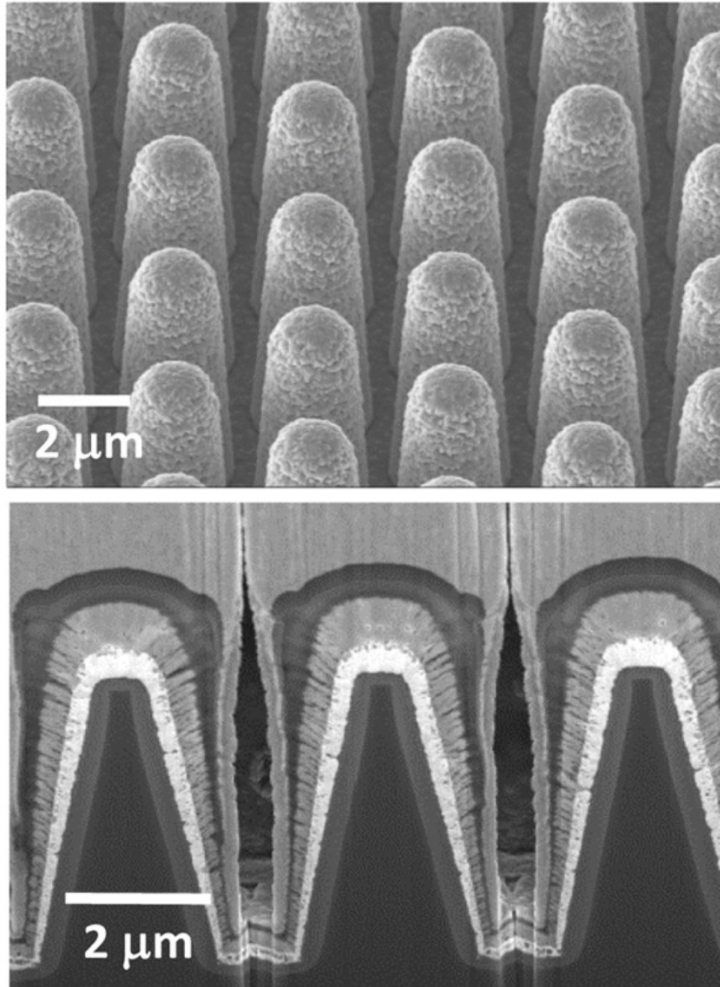
Effective particle size increases as cathode discharges



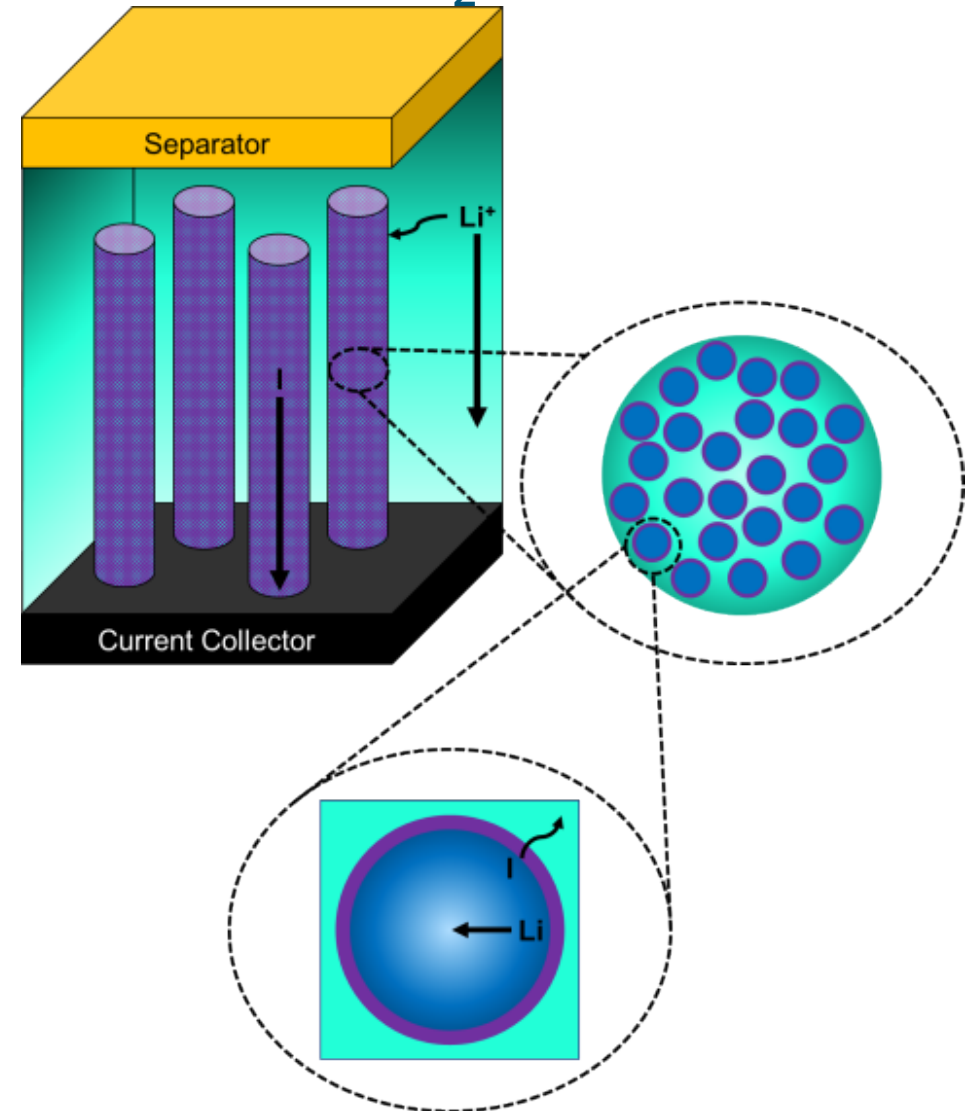
FeS₂ leading loss mechanisms



Extending the P2D model to 2.5D features: P3.5D FeS₂ models

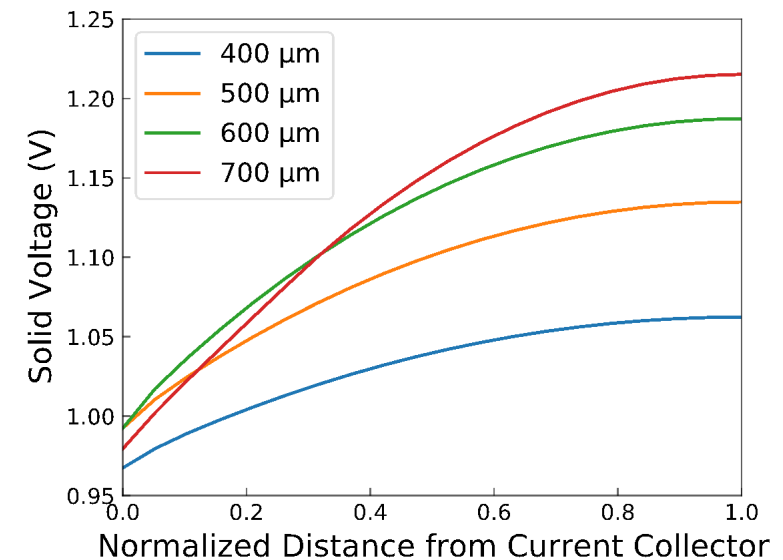
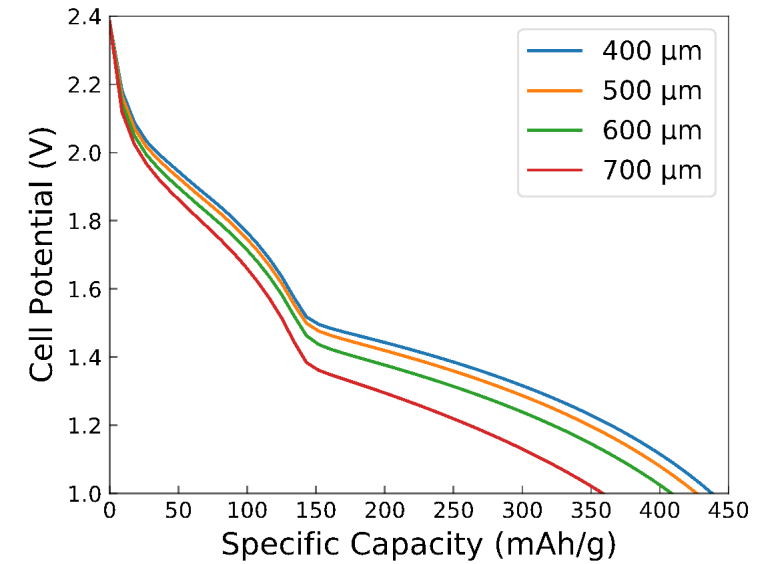
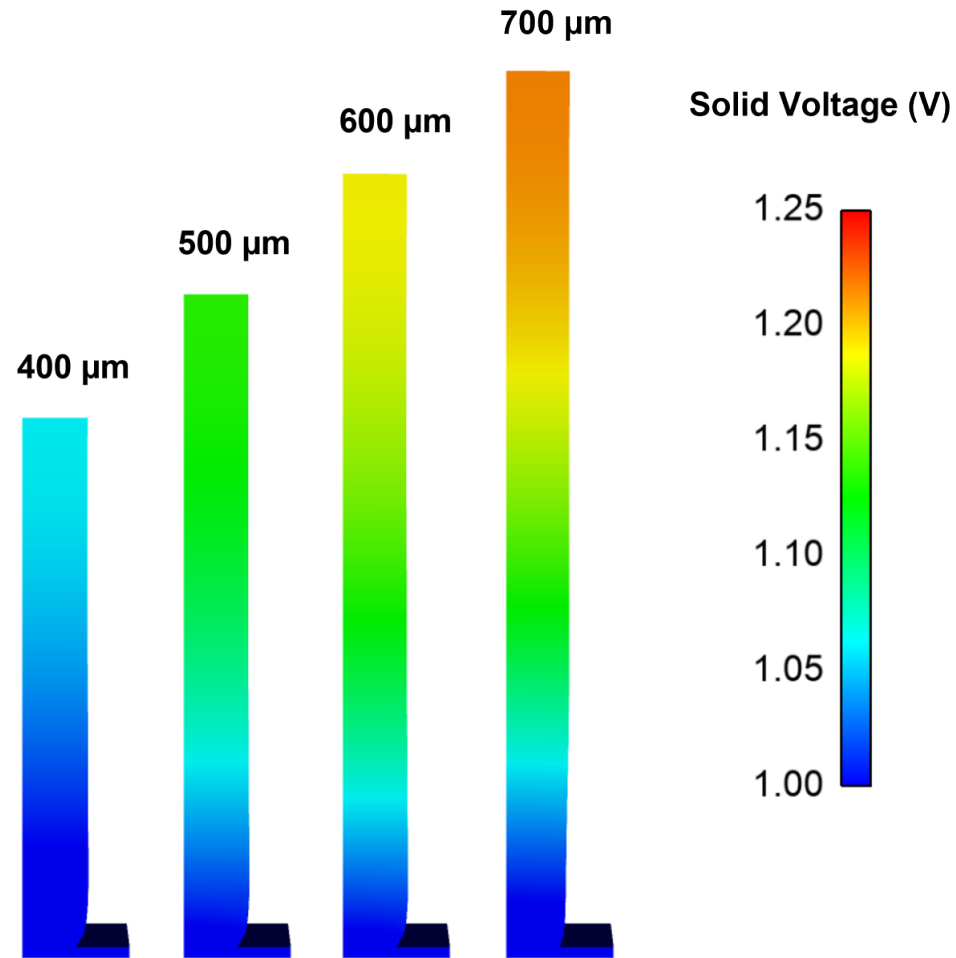


Talin et al, ACS AMI (2016)



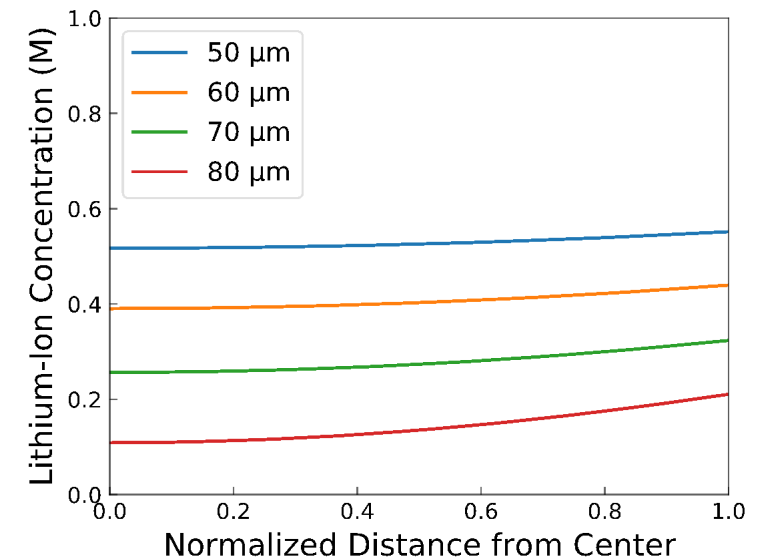
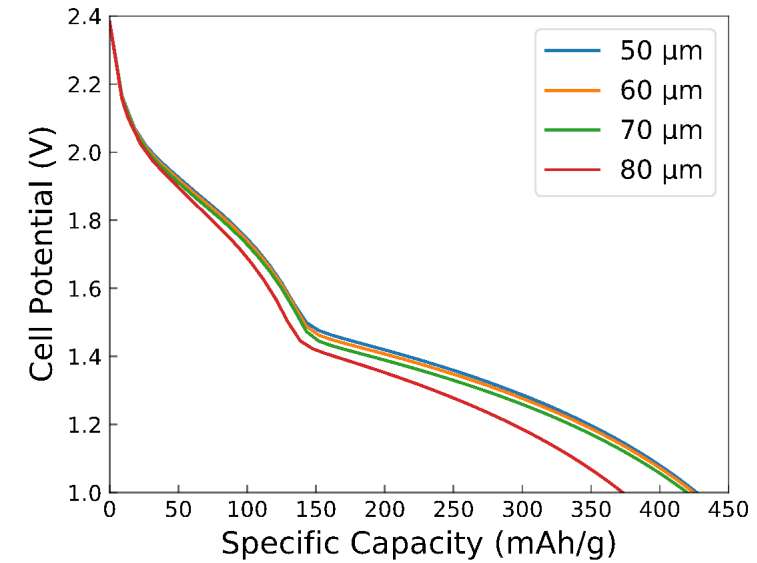
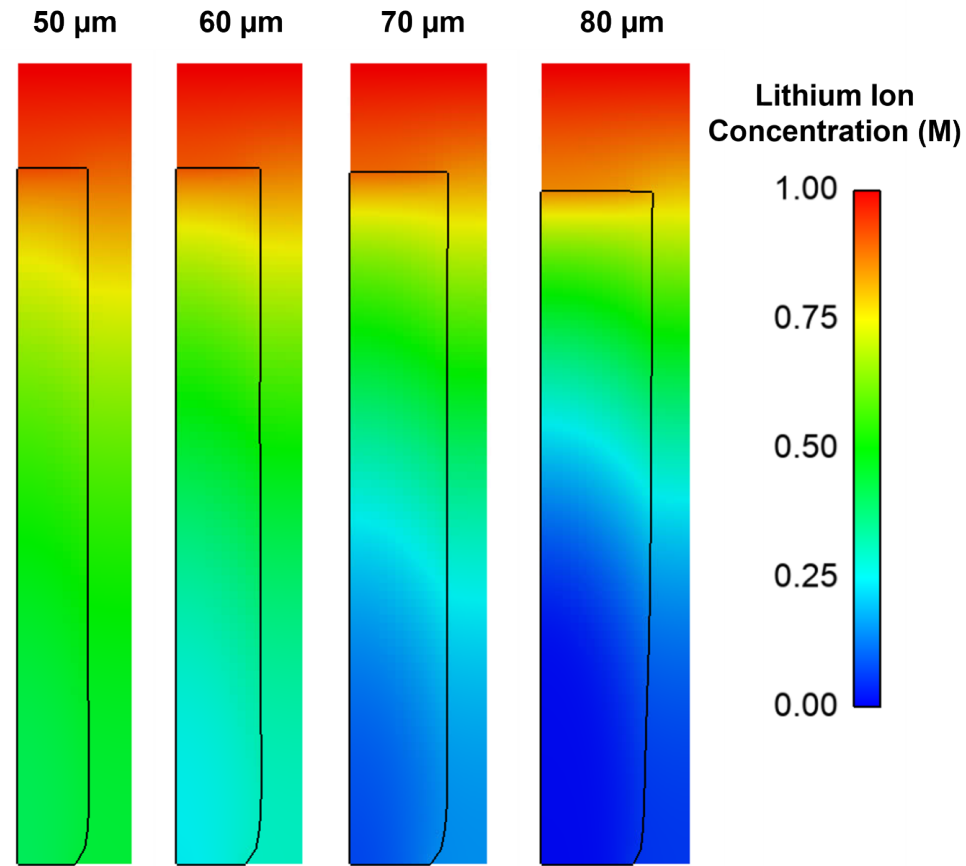
2.5D architected cells can provide high power and energy density solutions

Pillars can be very tall before limiting performance



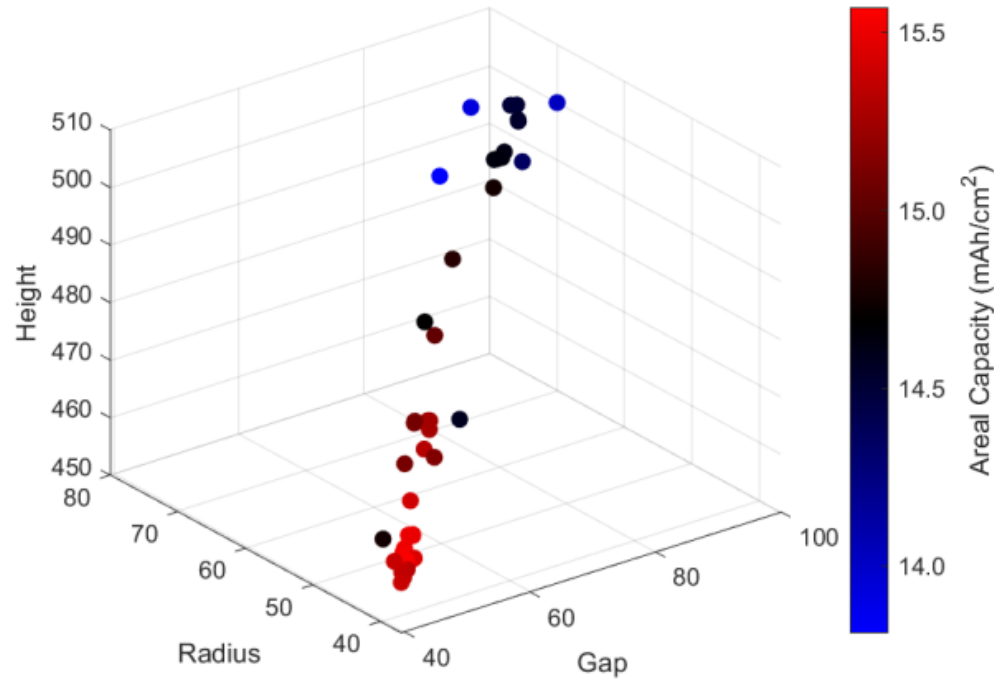
Pillar radius and gap are 50 μm, C/20 discharge

Pillars rely on radial transport to maintain performance



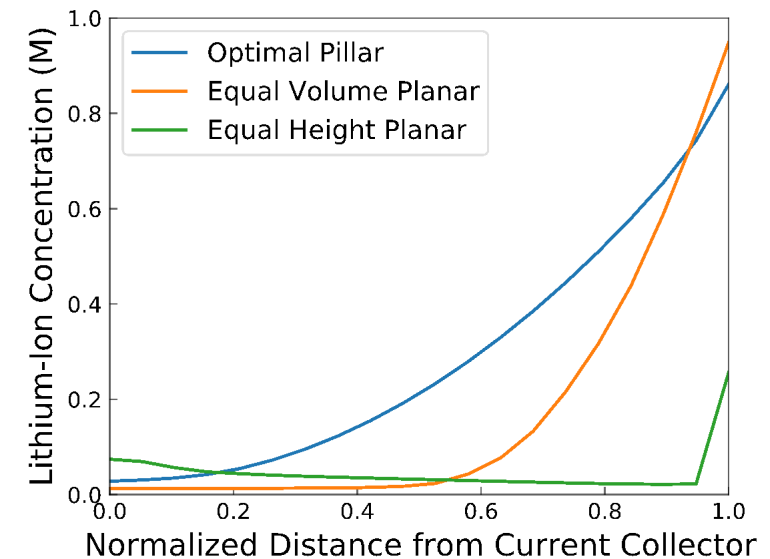
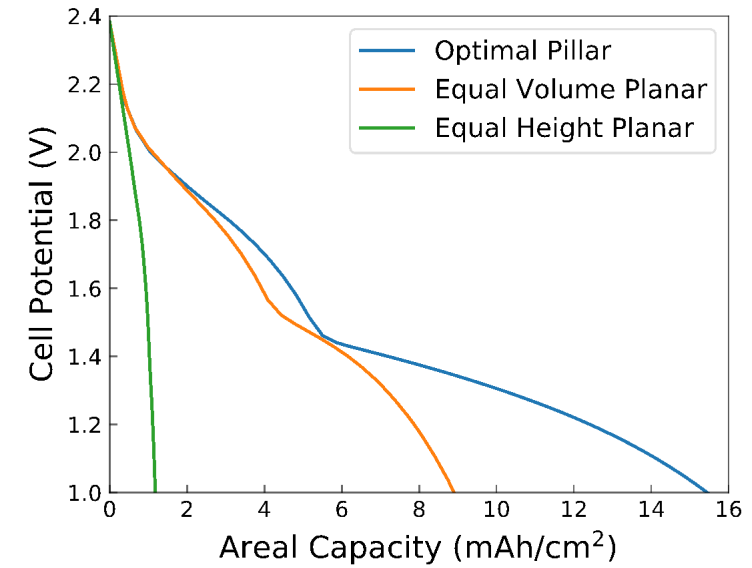
Pillar gap is 50 μm and height is 500 μm , C/20 discharge

Optimal pillar geometry greatly improves performance compared to planar electrodes

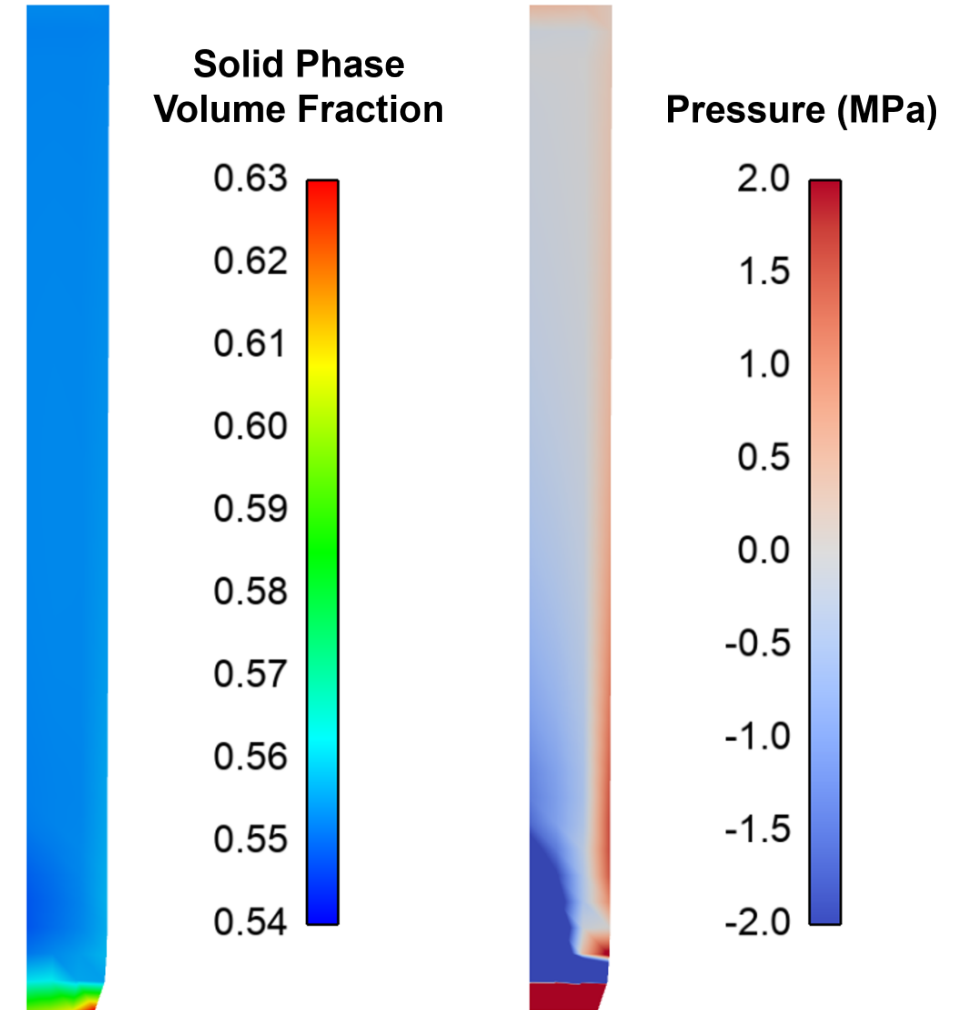
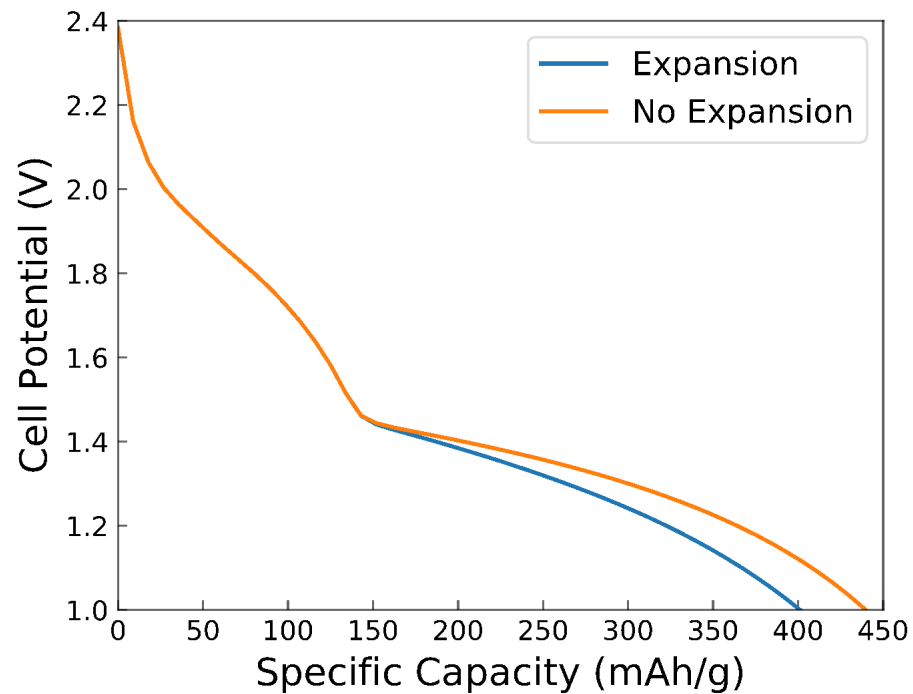


Optimal geometry, C/20

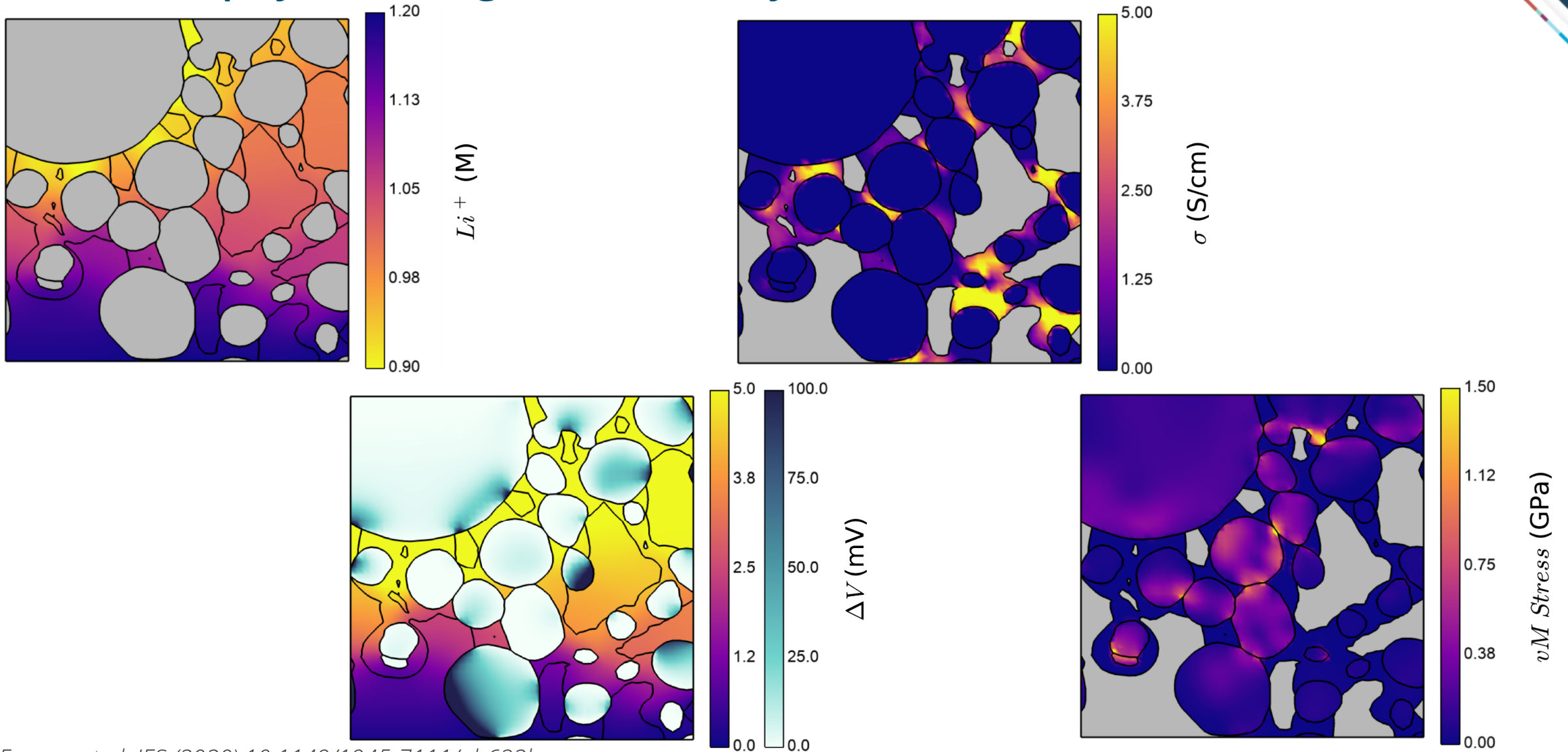
Dimension	μm
Height	460
Radius	37
Gap	40



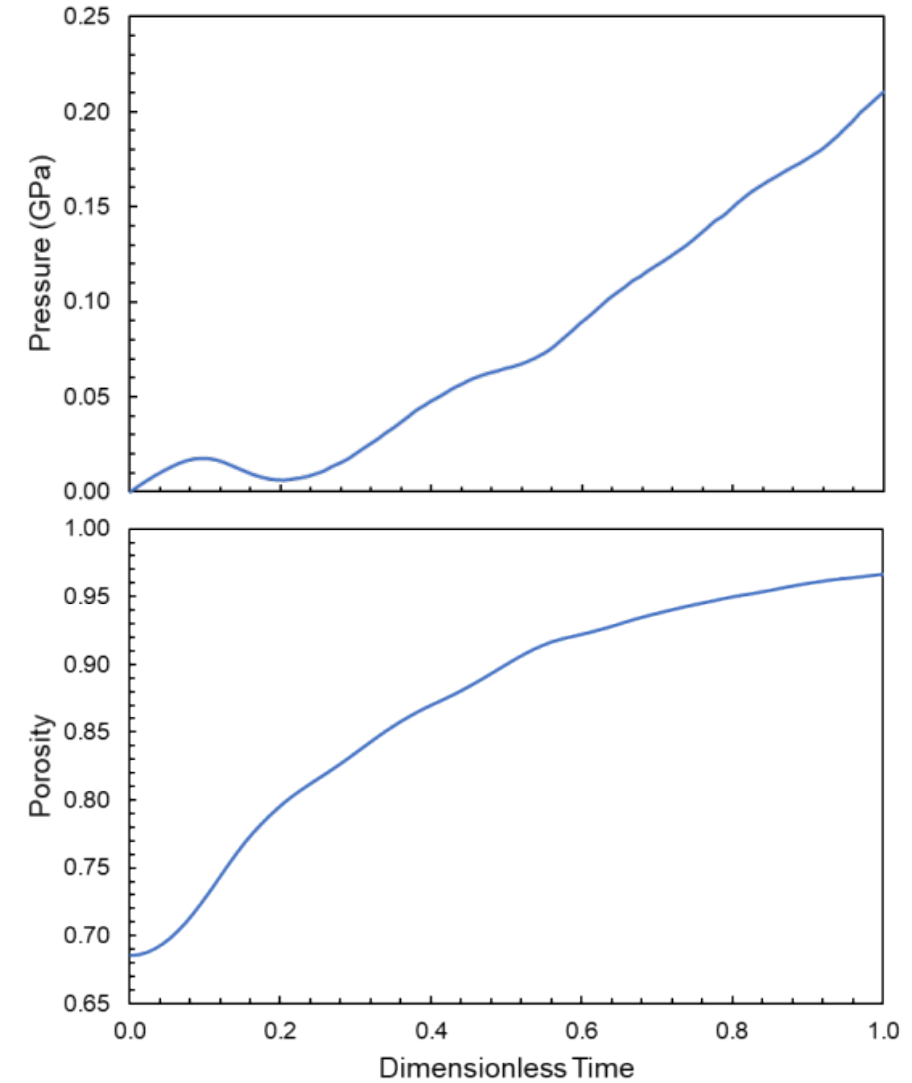
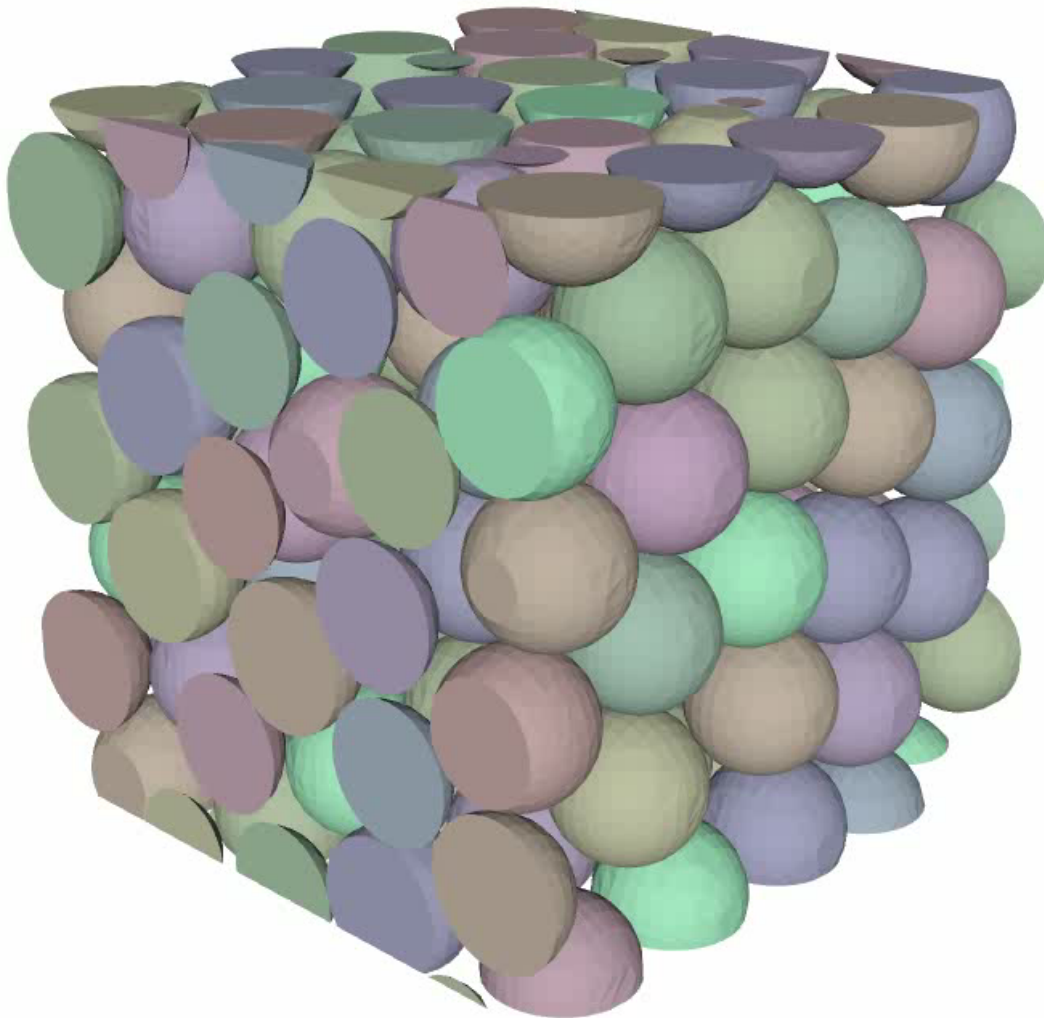
Consideration of particle swelling and mechanical constraints decreases available capacity



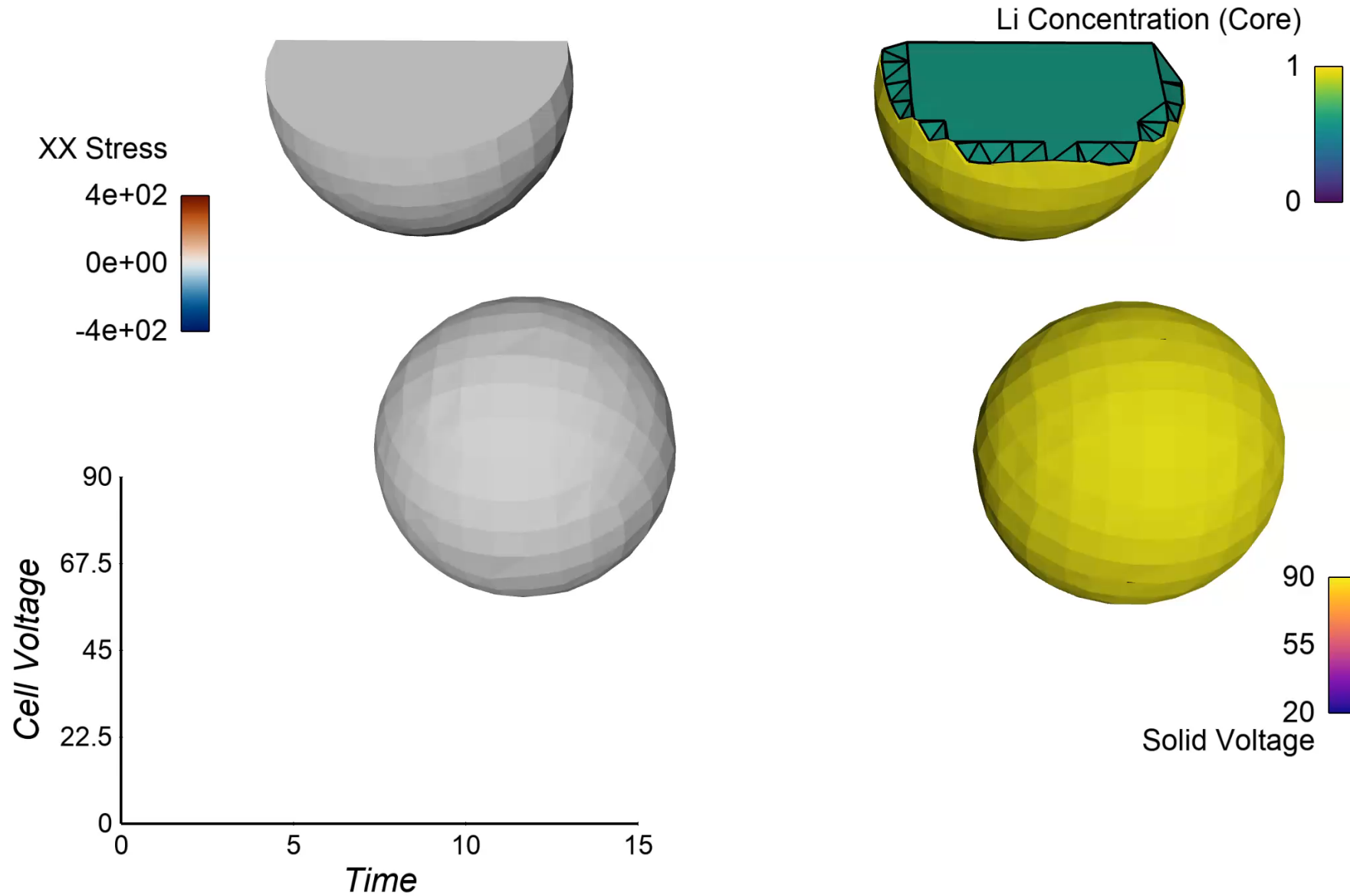
Volume averaging is nice, but mesoscale models can provide additional physical insight and fidelity



Swelling of FeS_2 particles impacts ionic transport



Early work towards a coupled electrochemical-mechanical model of FeS_2 that includes intercalation and conversion



THANK YOU!

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