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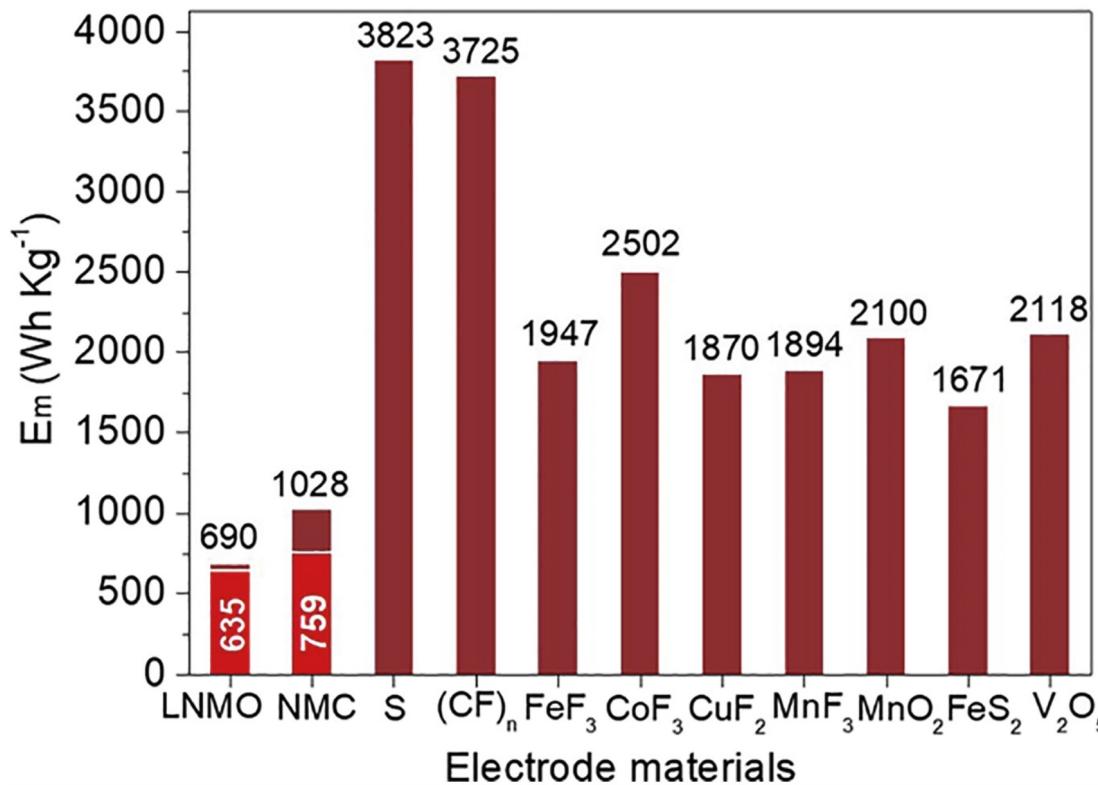
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# Enabling high-energy-density cathodes by coupling electrochemistry and mechanics across length scales

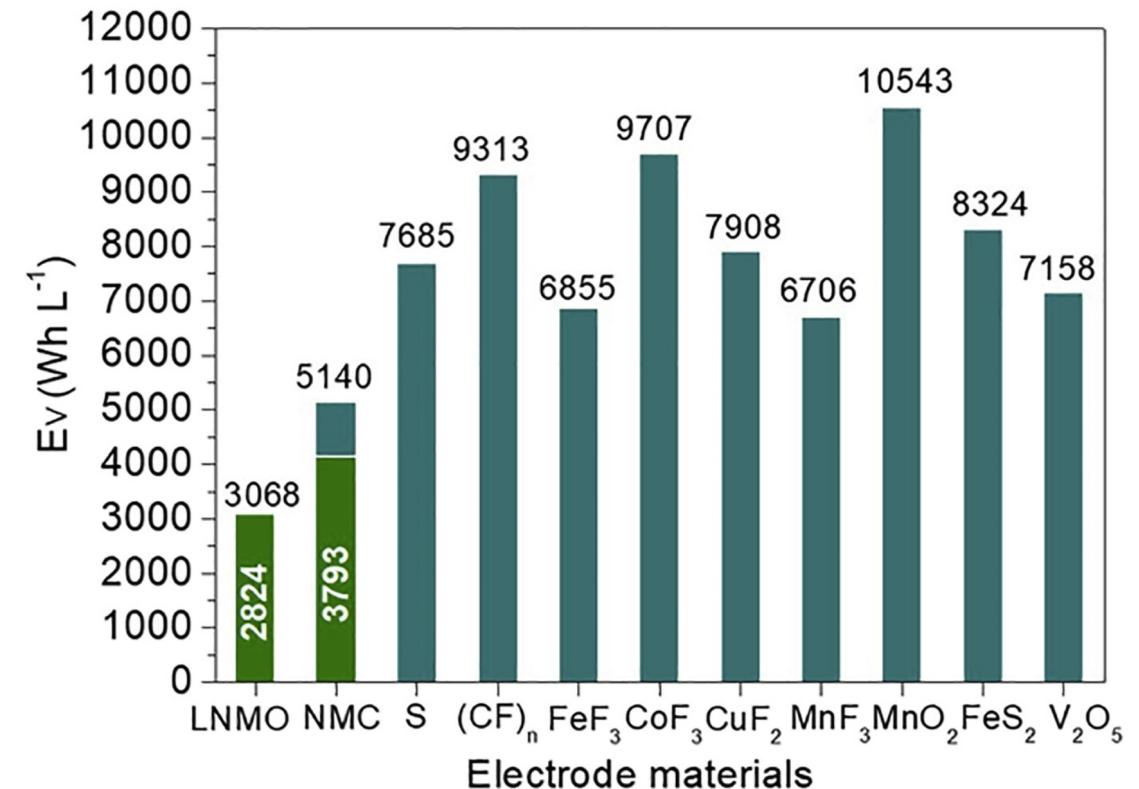
Scott A. Roberts, Jeffrey S. Horner

March 21, 2023

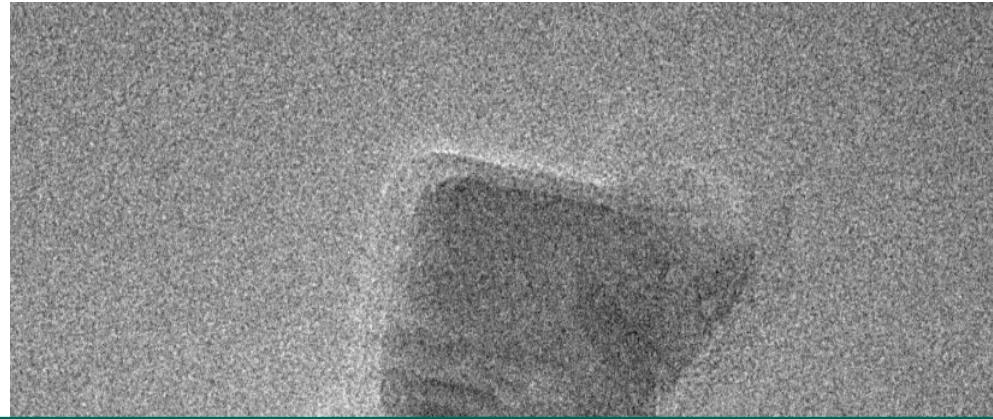
# Conversion cathodes hold potential for higher energy densities



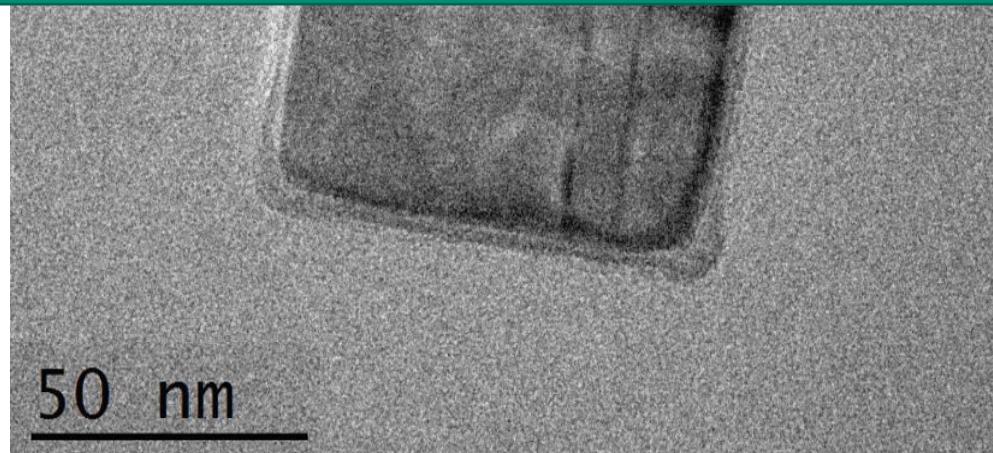
Wang *et al.*, Joule (2019)



# Mechanical degradation can limit conversion secondary cells

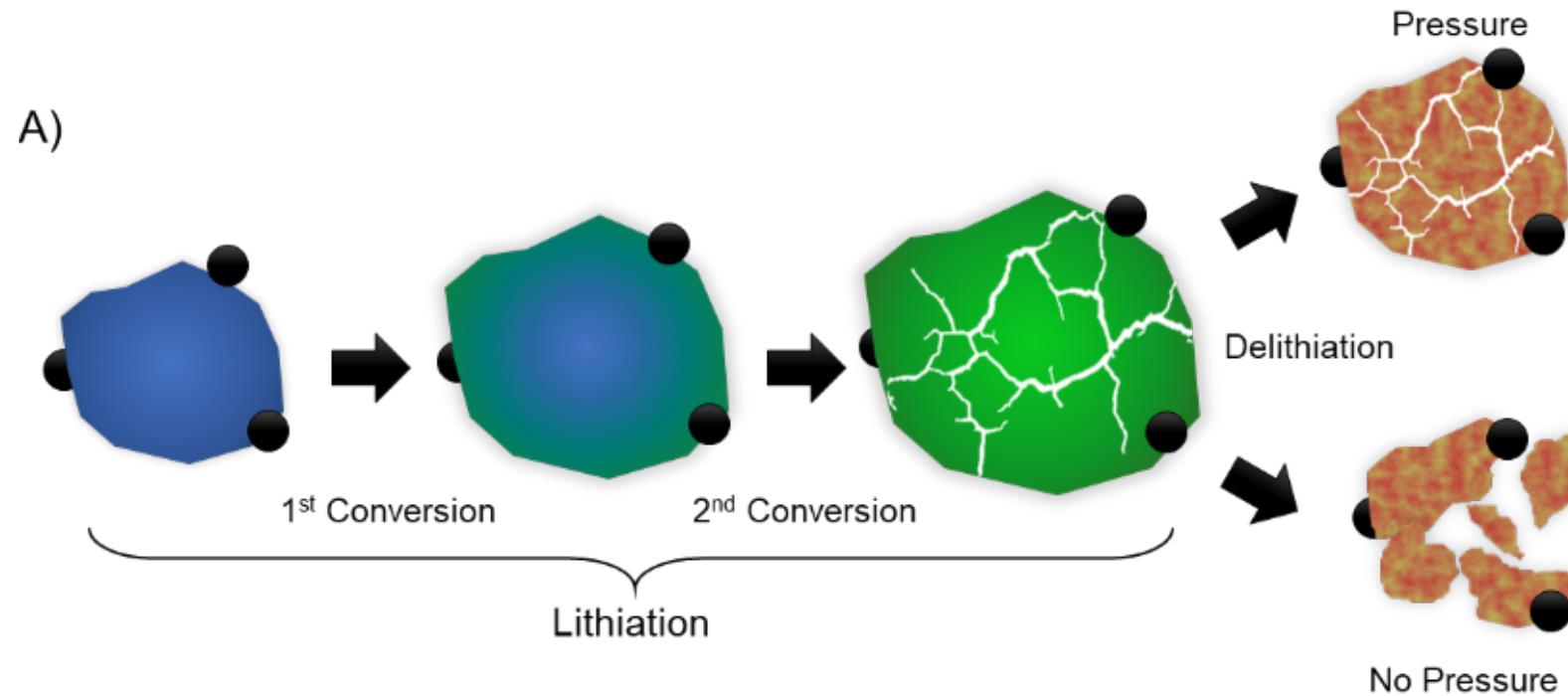


Can we engineer limited rechargeability in conversion cathode materials while maintaining high energy density?



Boebinger et al, Joule (2018)

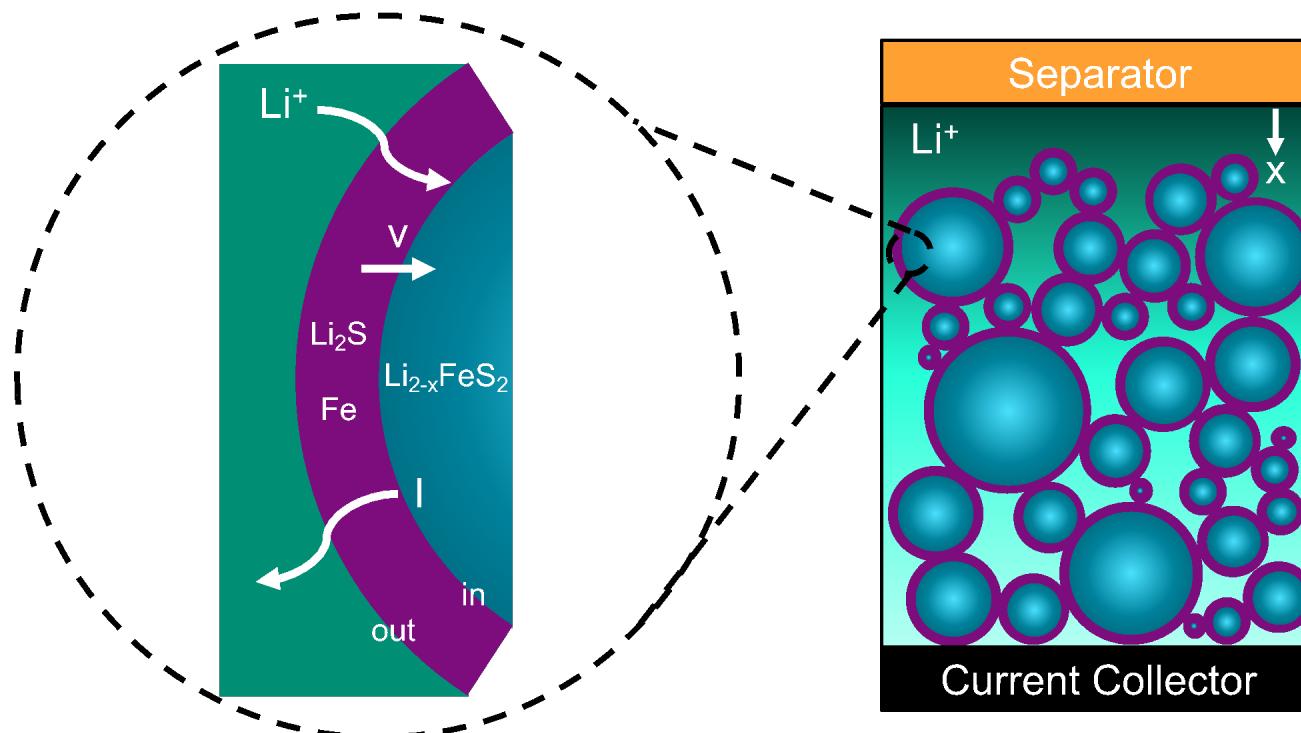
# FeS<sub>2</sub> reaction pathways



## 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 ( $V_s$ )

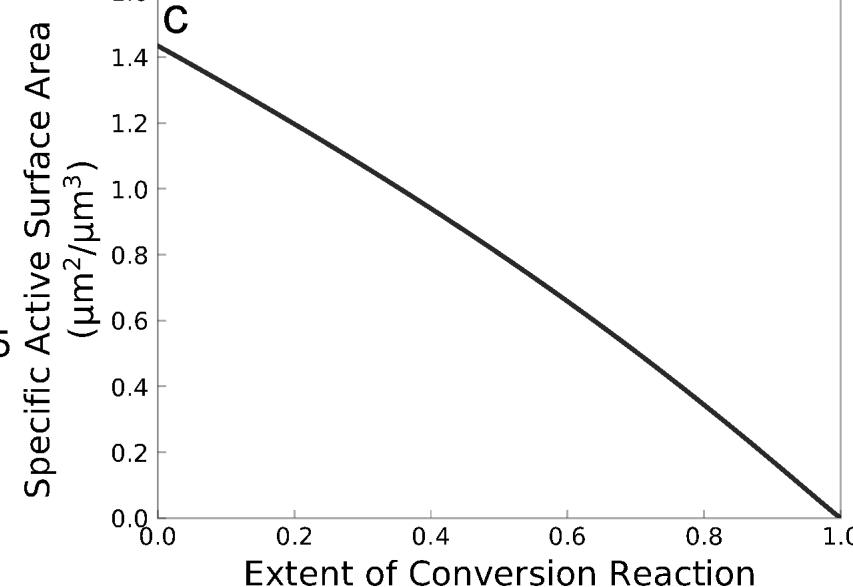
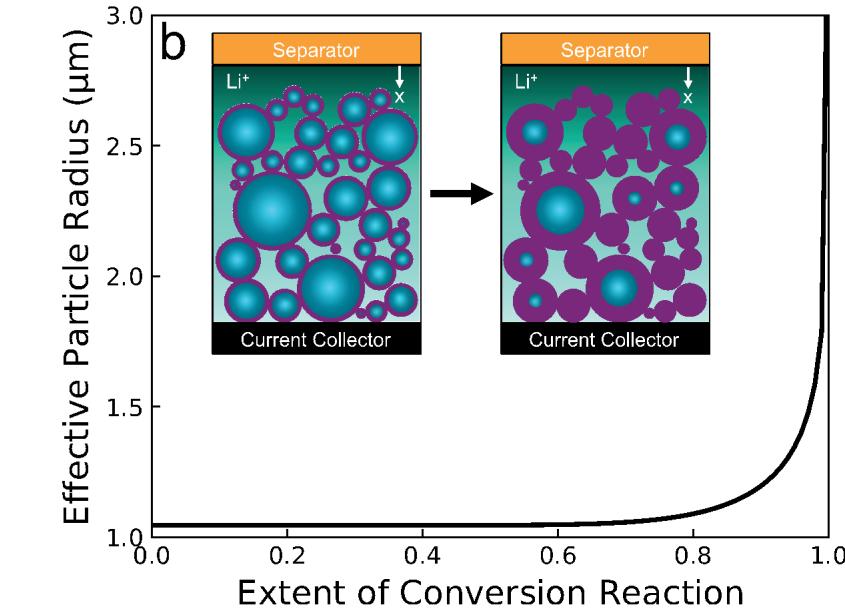
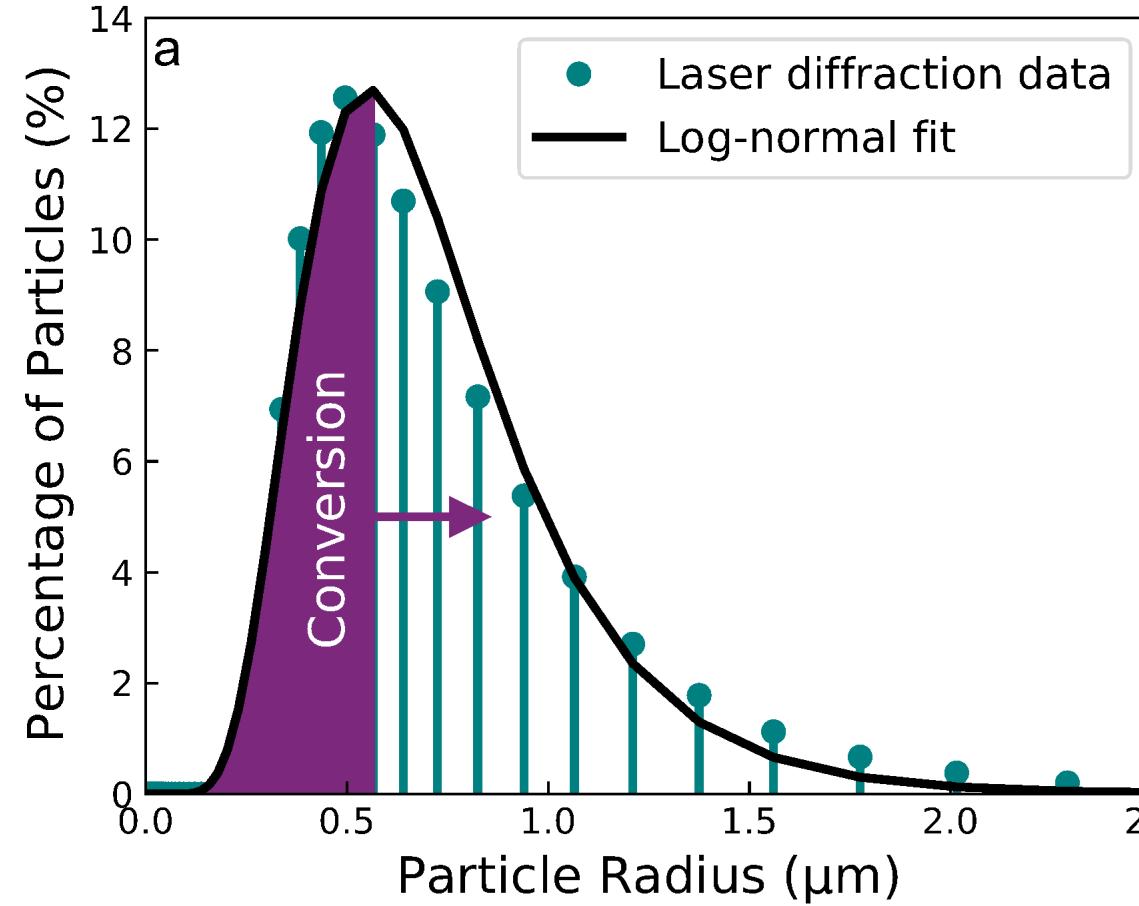
Solid Li concentration ( $C_{\text{Li}}$ )

Electrolyte potential ( $V_l$ )

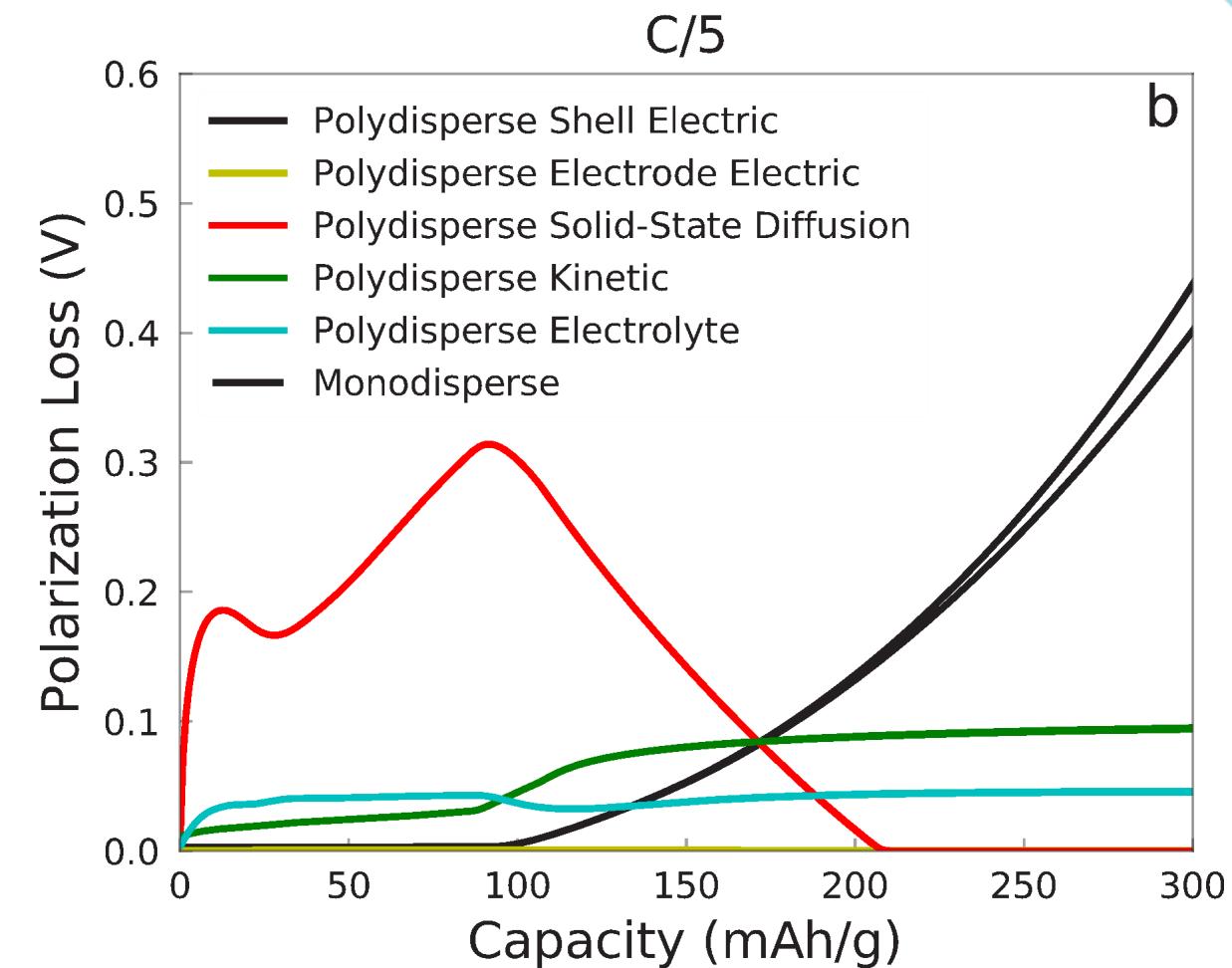
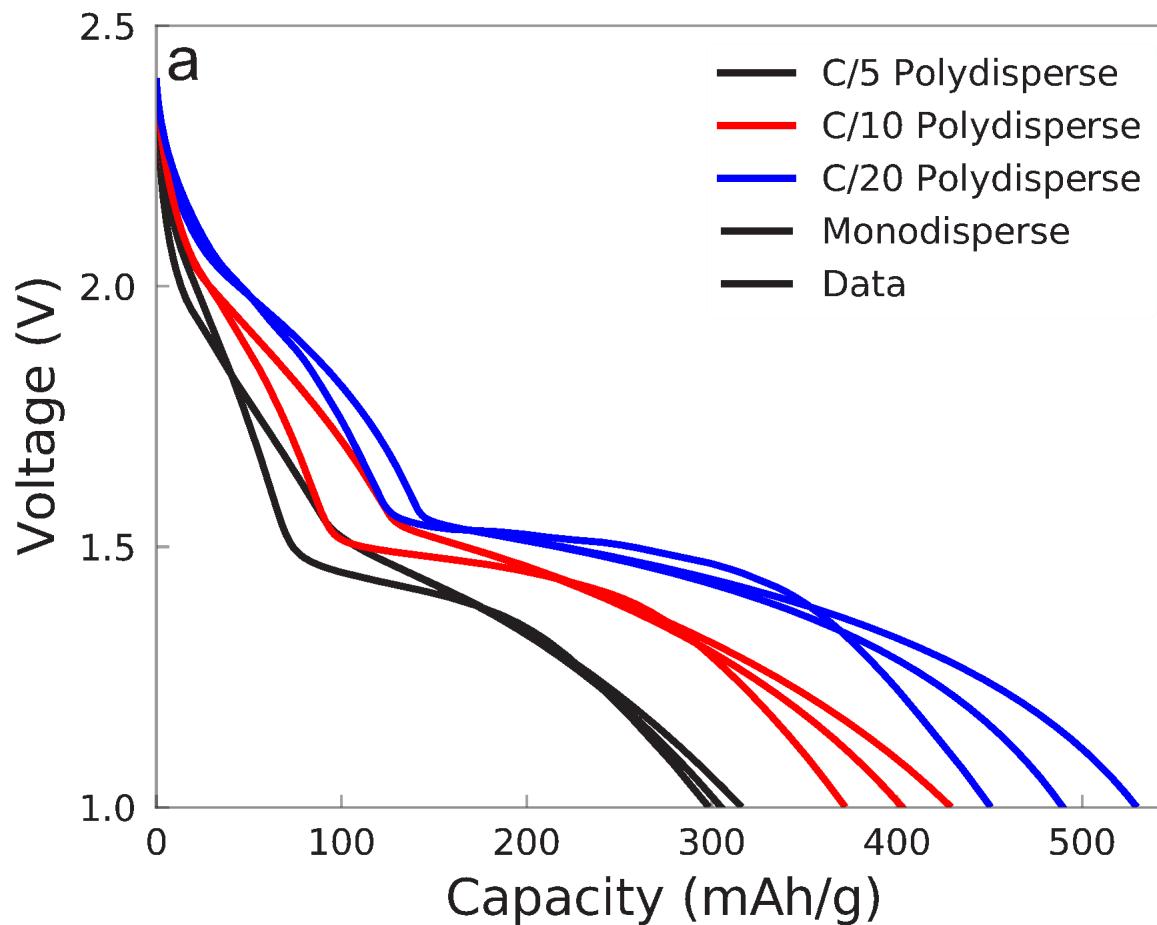
Electrolyte concentration ( $C_{\text{Li}^+}$ )

Shell thickness ( $\delta$ )

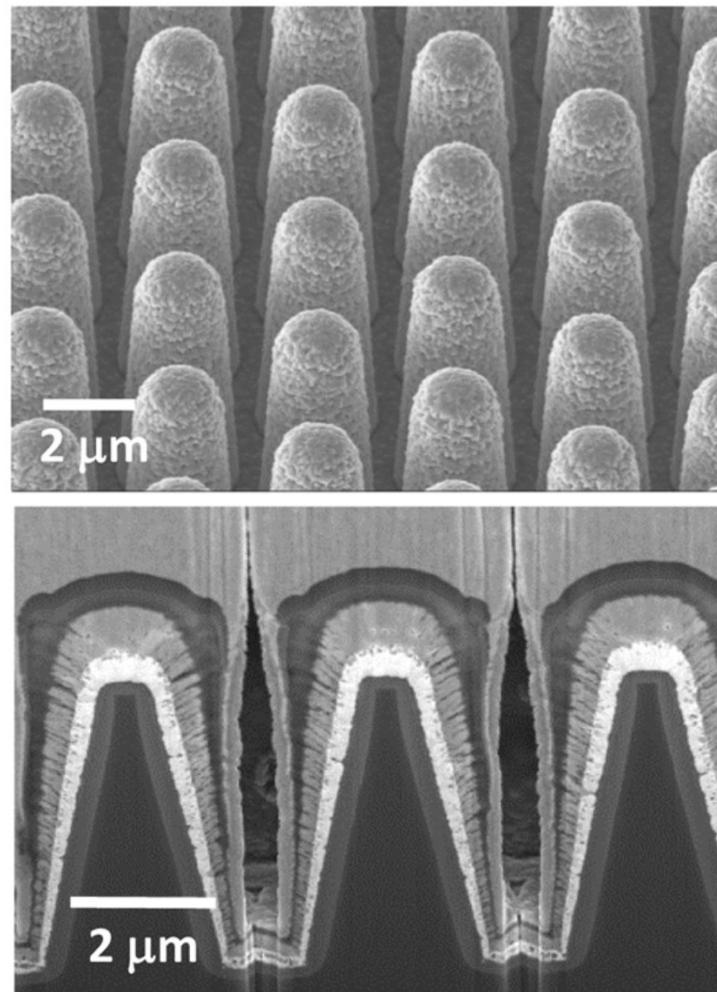
# Effective particle size increases as cathode discharges



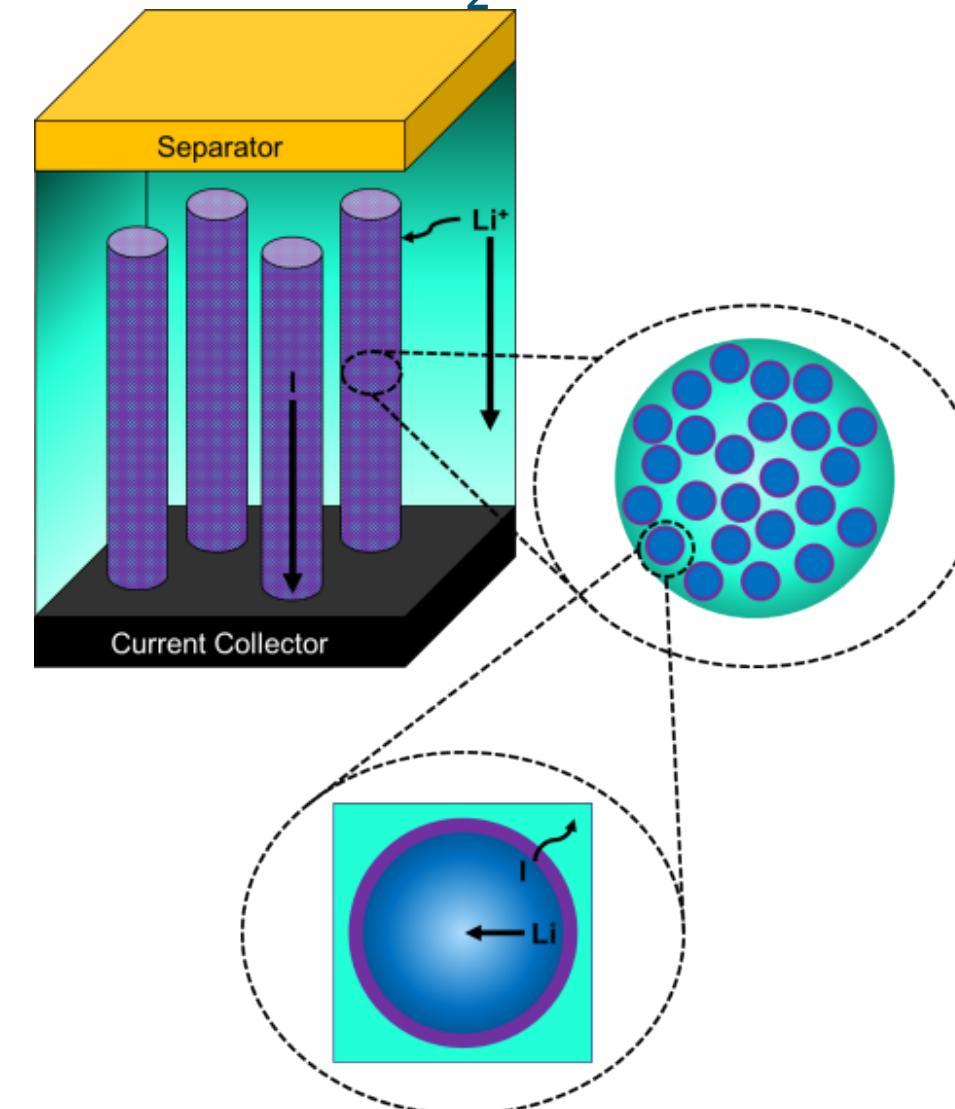
# FeS<sub>2</sub> leading loss mechanisms



## Extending the P2D model to 2.5D features: P3.5D $\text{FeS}_2$ models

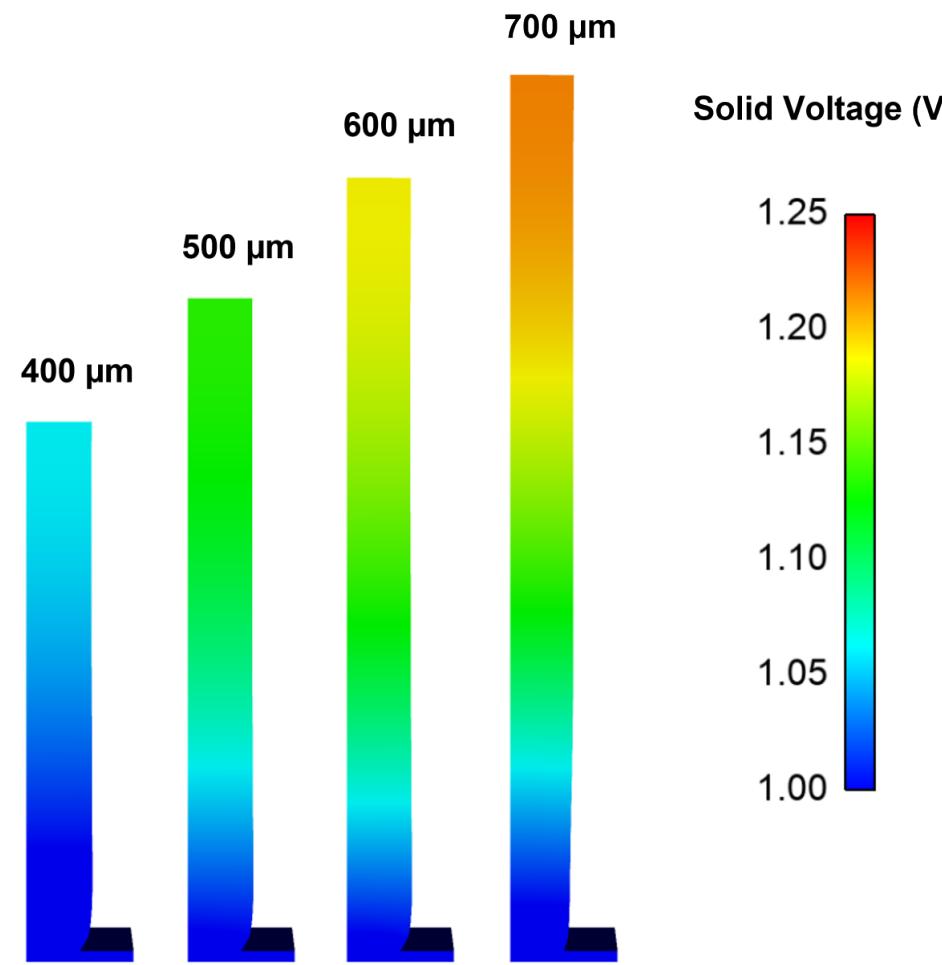


Talin et al, ACS AMI (2016)

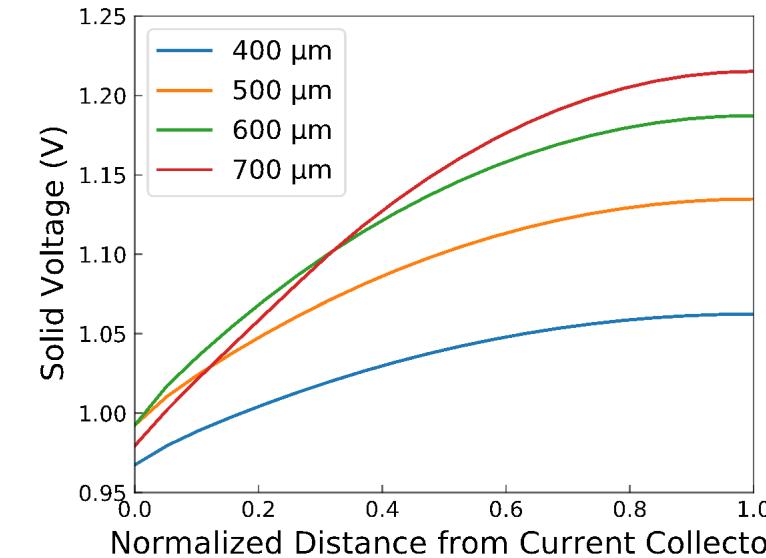
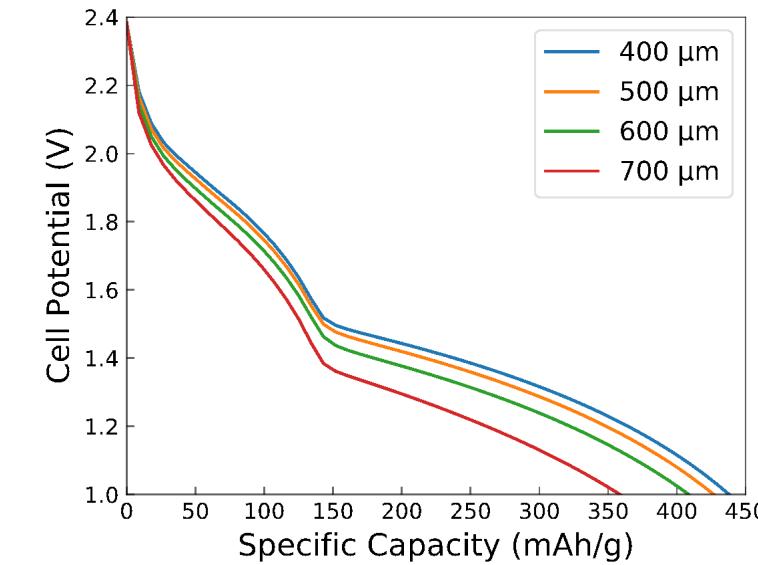


2.5D architected cells can provide high power and energy density solutions

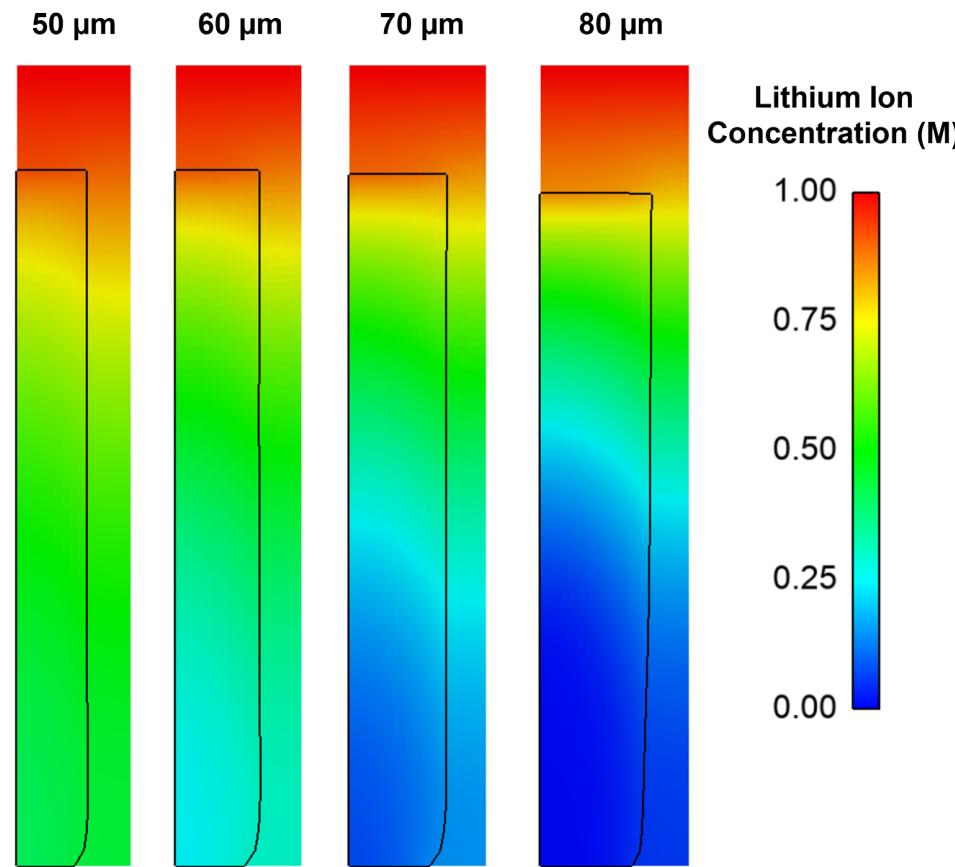
# Pillars can be very tall before limiting performance



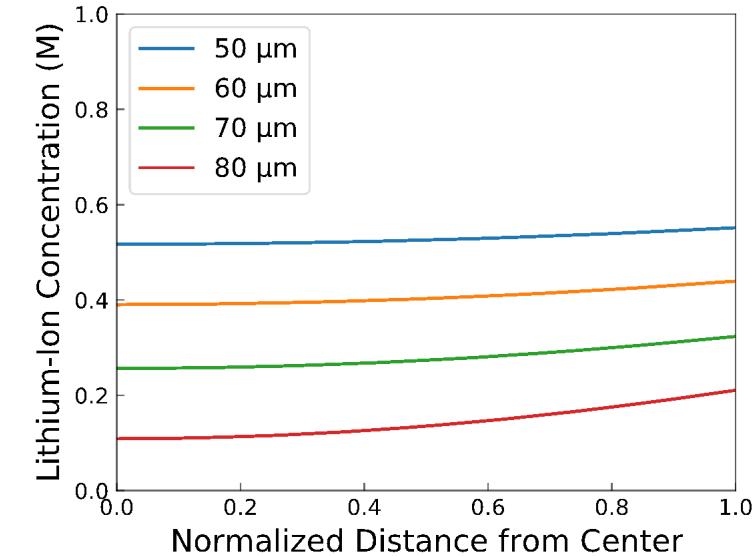
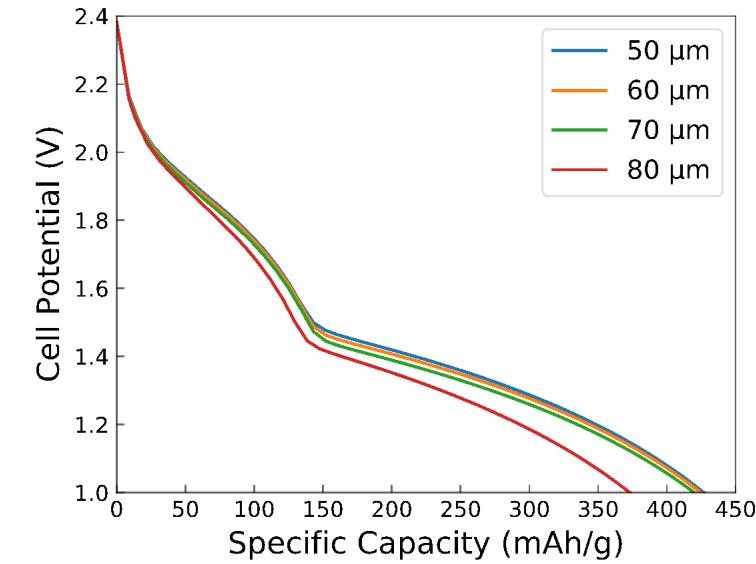
Pillar radius and gap are 50  $\mu\text{m}$ , C/20 discharge



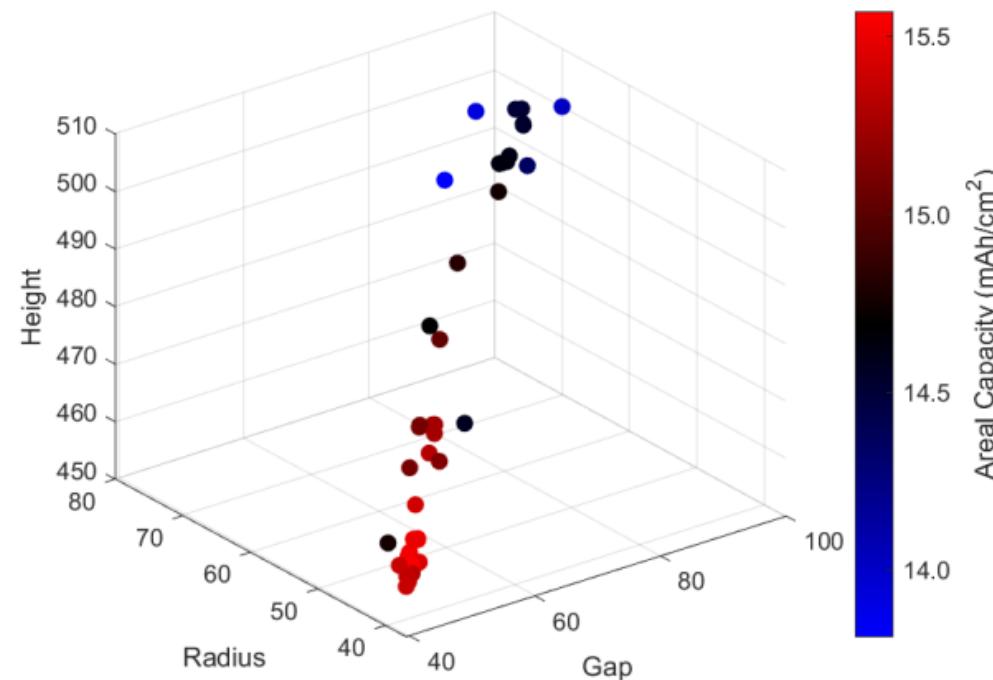
# Pillars rely on radial transport to maintain performance



Pillar gap is 50  $\mu\text{m}$  and height is 500  $\mu\text{m}$  , C/20 discharge

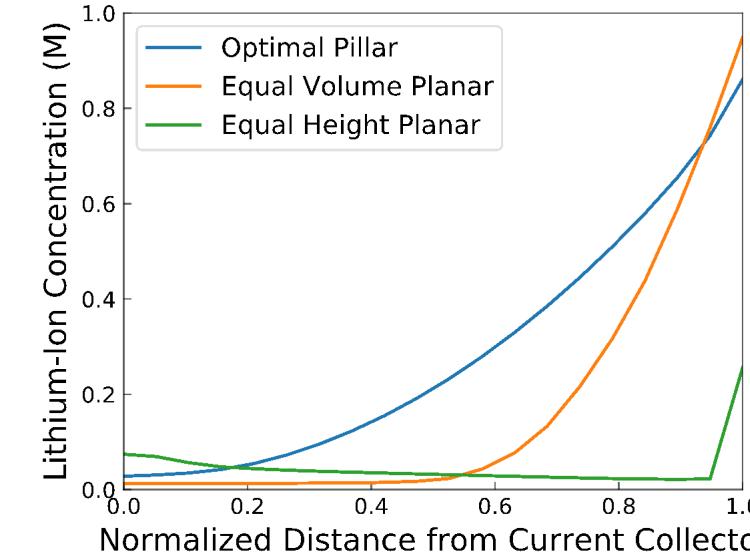
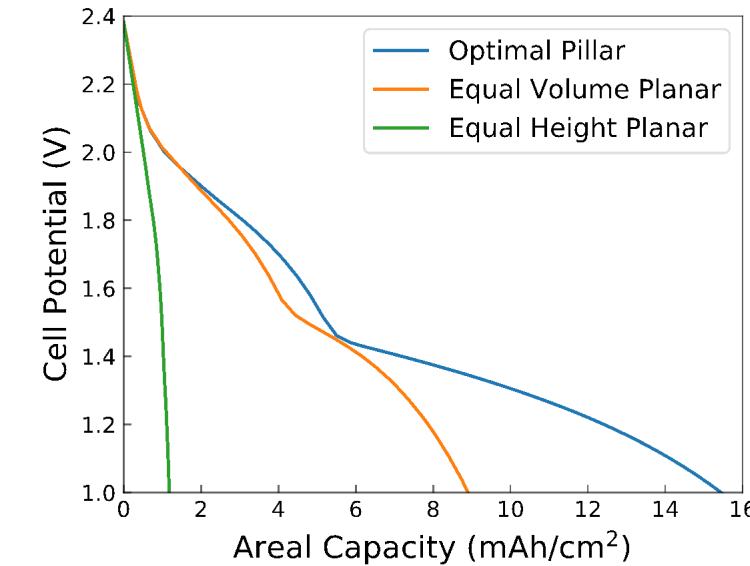


# Optimal pillar geometry greatly improves performance compared to planar electrodes

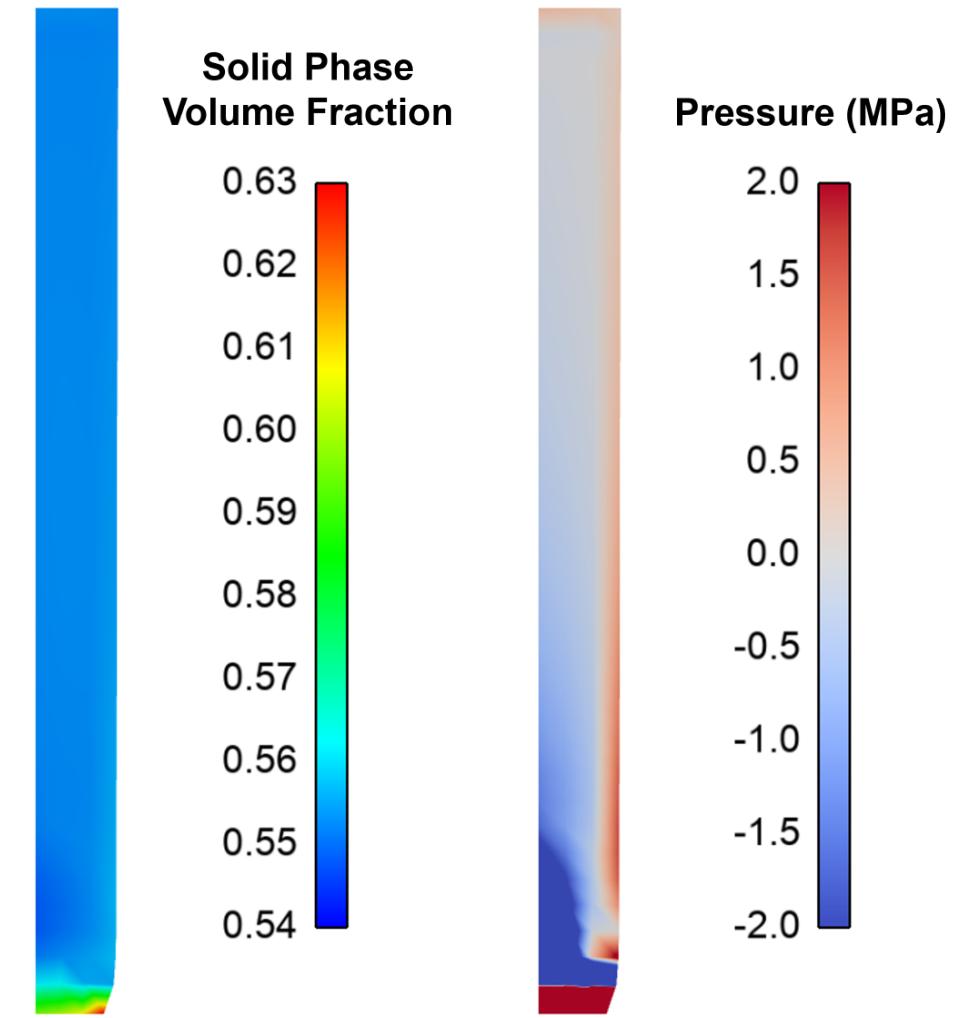
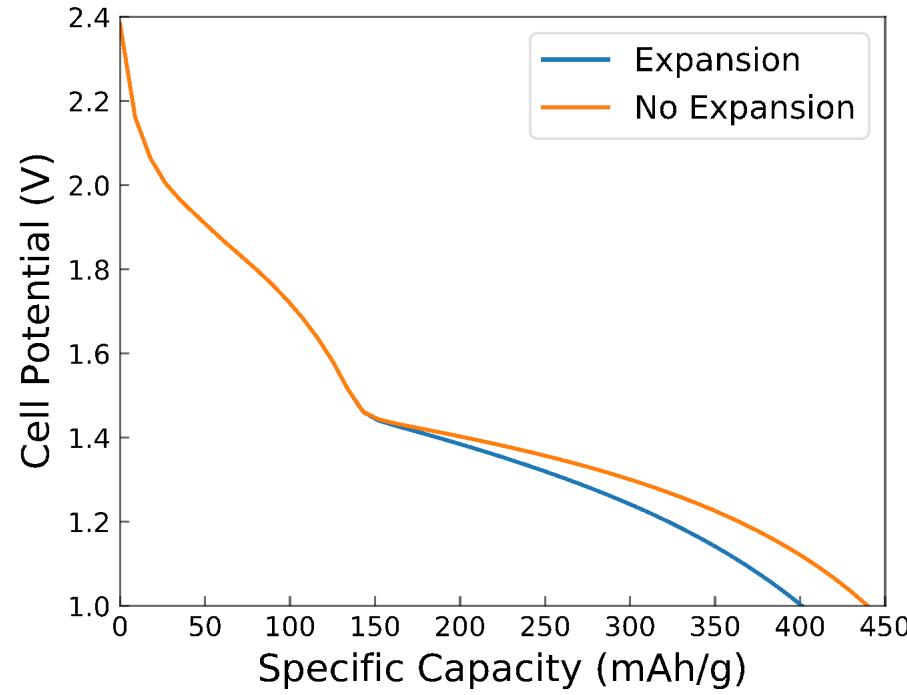


Optimal geometry, C/20

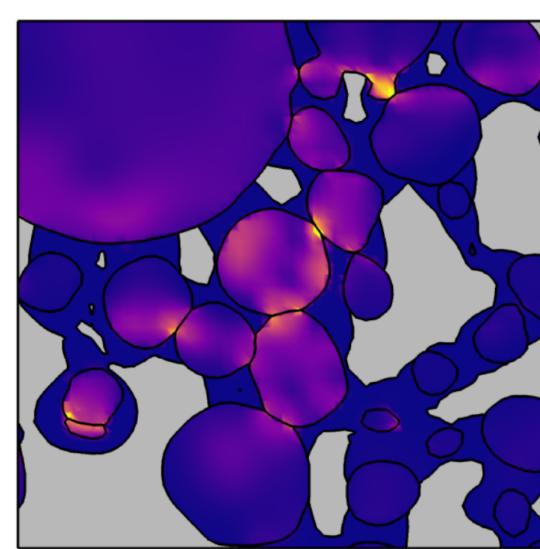
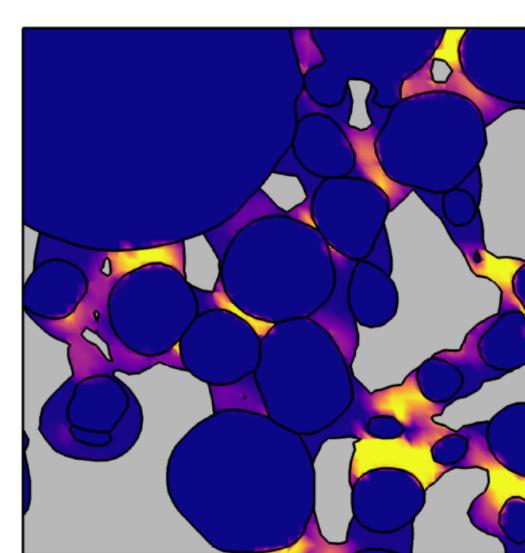
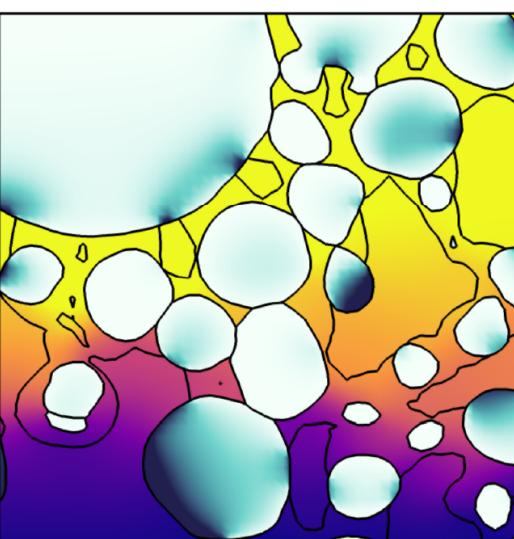
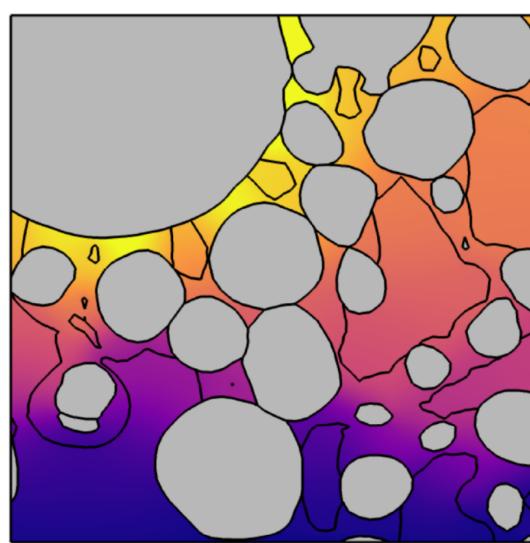
Dimension	$\mu\text{m}$
Height	460
Radius	37
Gap	40



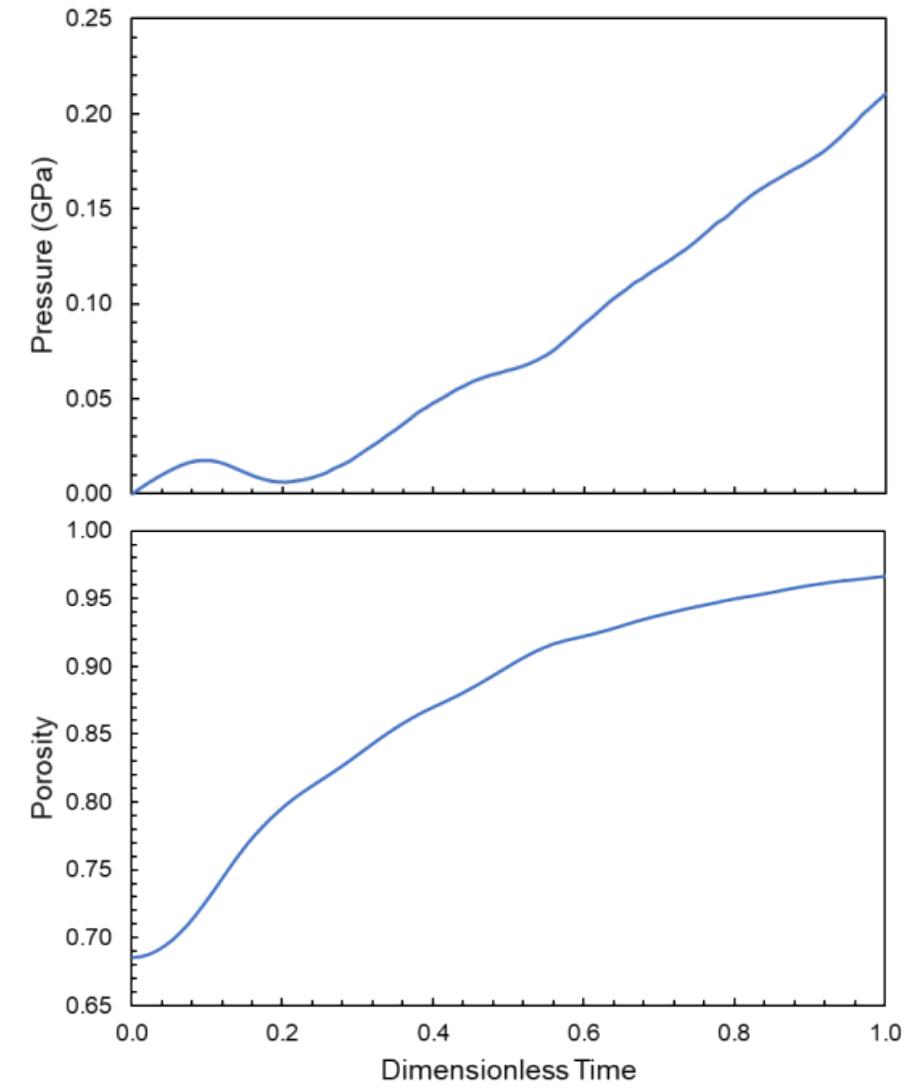
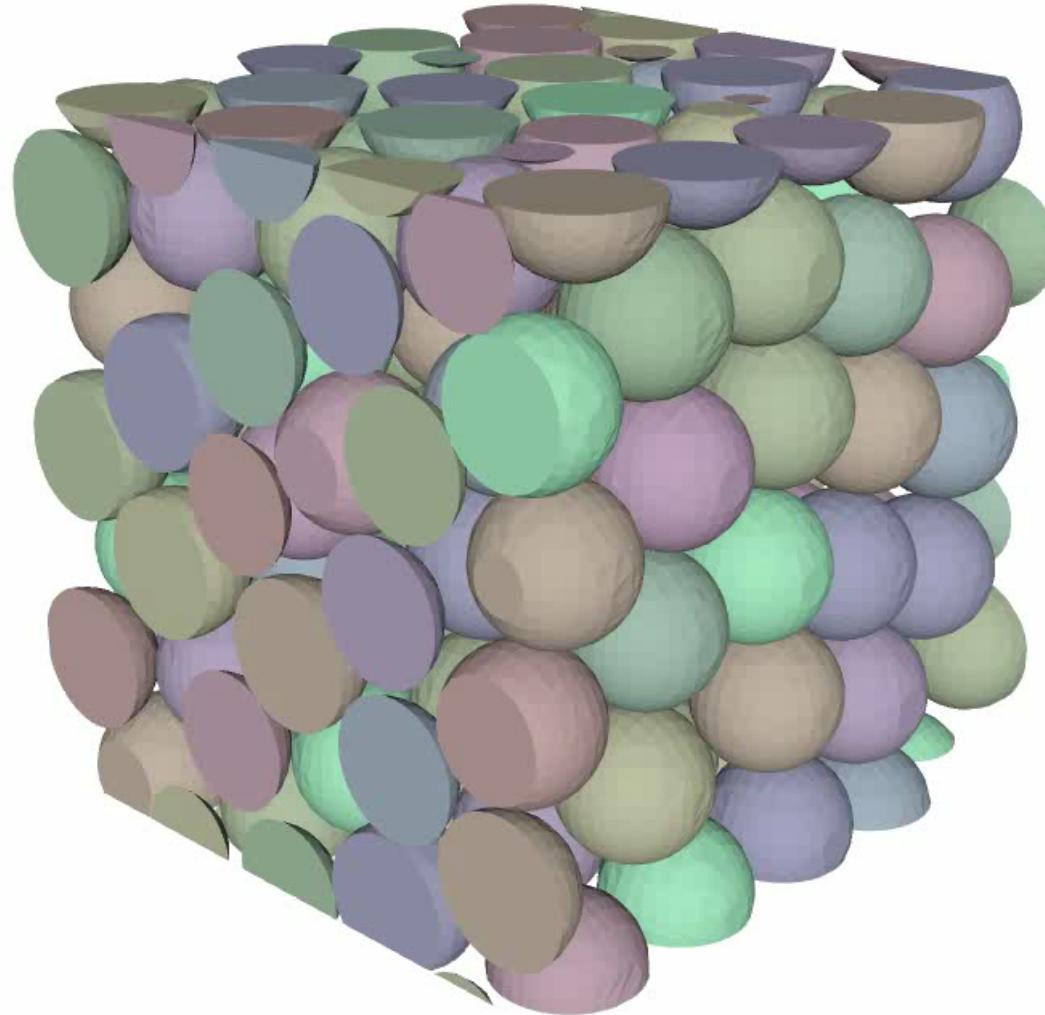
# Consideration of particle swelling and mechanical constraints decreases available capacity



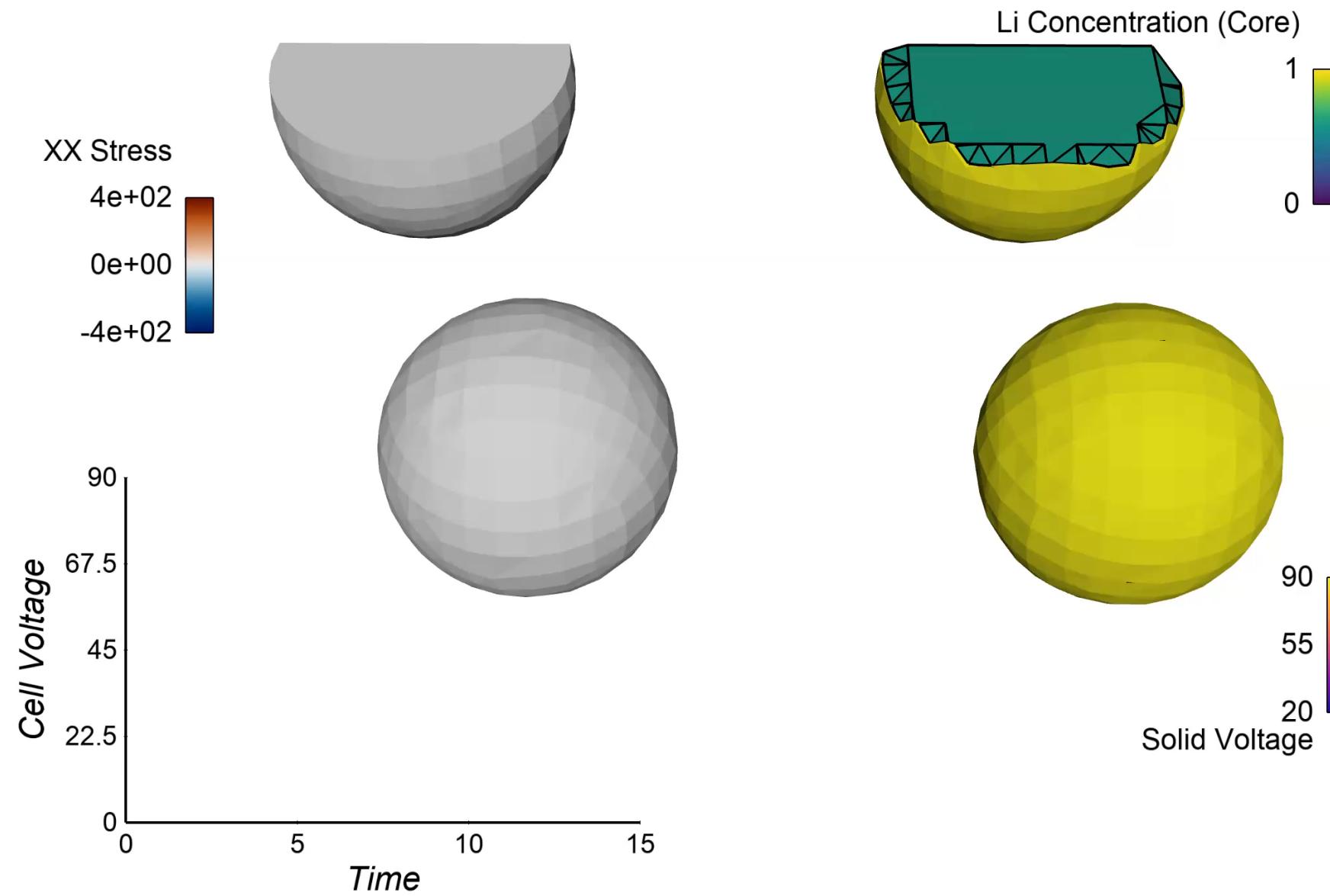
# Volume averaging is nice, but mesoscale models can provide additional physical insight and fidelity



# Swelling of $\text{FeS}_2$ particles impacts ionic transport



# Early work towards a coupled electrochemical-mechanical model of $\text{FeS}_2$ that includes intercalation and conversion



# THANK YOU!

**Scott A. Roberts, Ph.D.**  
Distinguished R&D Chemical Engineer  
Thermal/Fluid Component Sciences (1513)

Phone: (505) 844-7957

Email: [sarober@sandia.gov](mailto:sarober@sandia.gov)

Web: <https://www.sandia.gov/-sarober>