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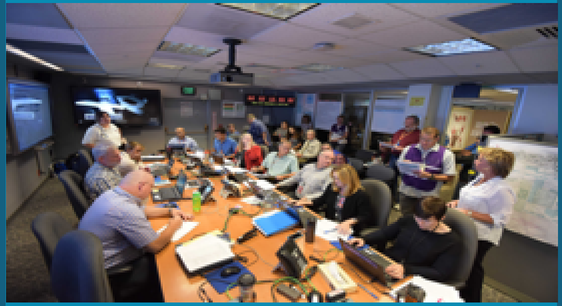
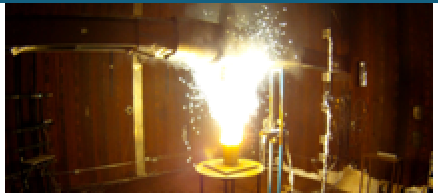
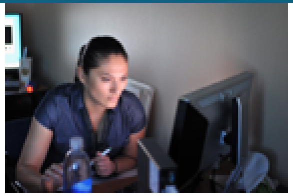
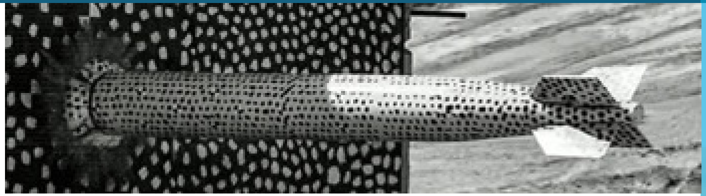


# Pseudo-Two-Dimensional Modeling of Lithium-Ion Conversion Cathode Materials

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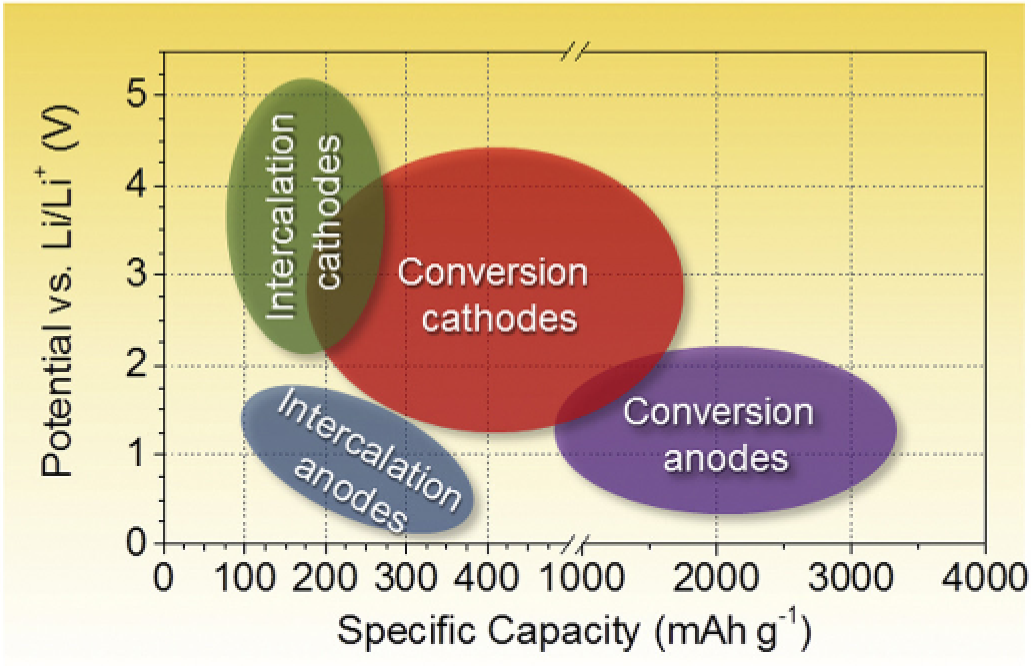
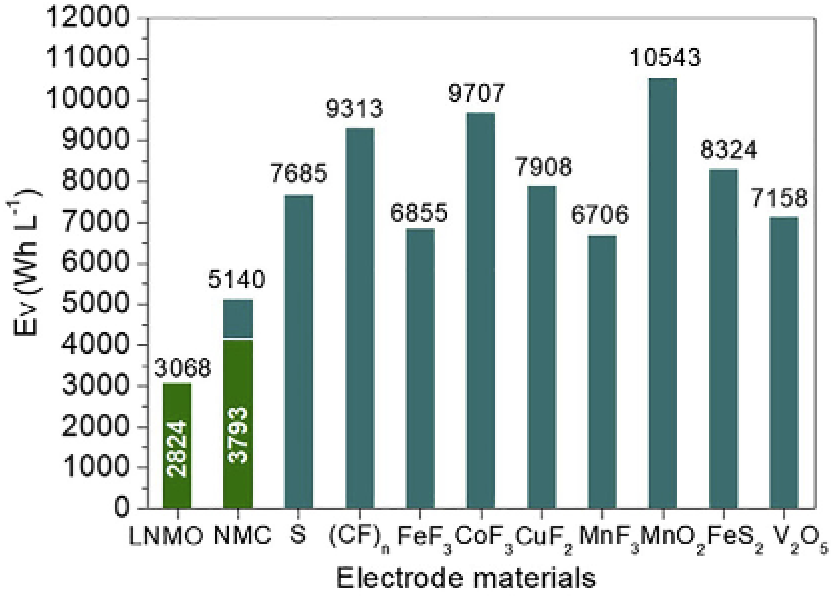
# Conversion Cathode Materials

- Next-generation rechargeable batteries demand increased energy and power density
- Conversion cathode materials undergo a chemical reaction to produce new products
- Typically contain more abundant and safer materials
- Due to the complexity of the reactions, these materials are not fully understood

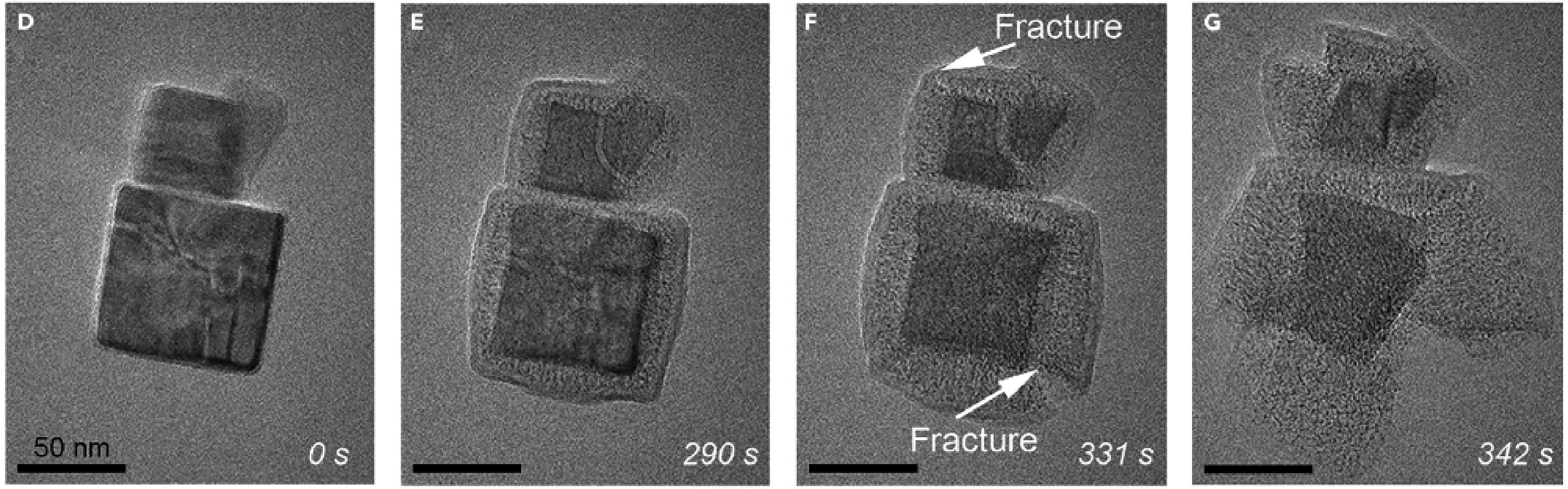


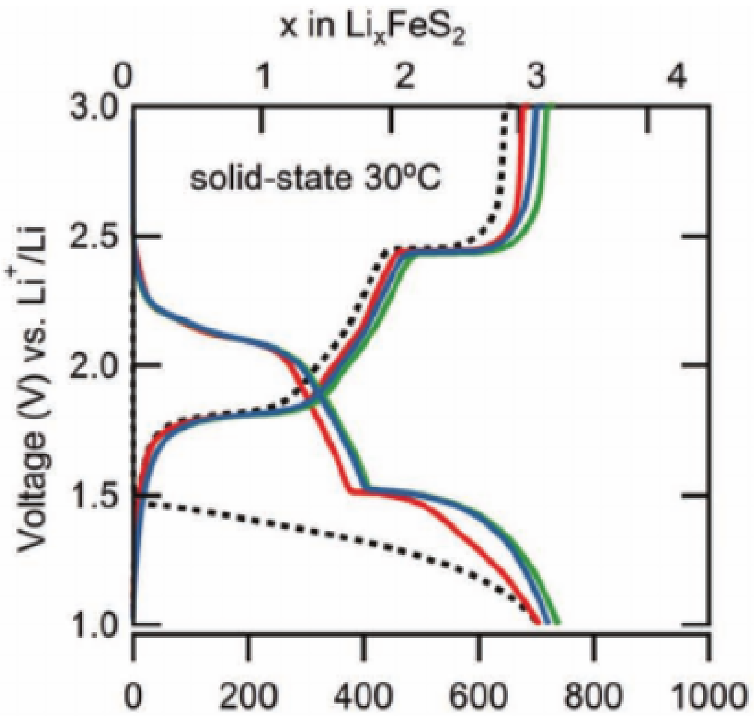




Nitta *et al.*, *Materials Today*, (2015), **18**, 252-264
Wang *et al.*, *Joule*, (2019), **3**, 2086-2102

# $FeS_2$ Reaction

No Image

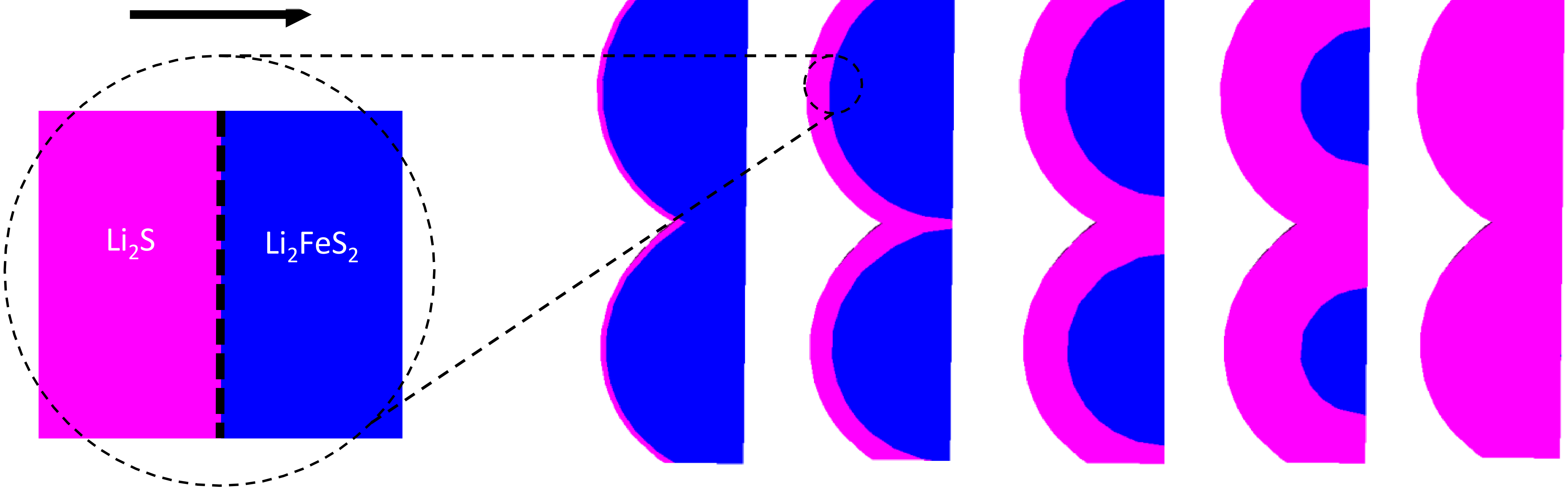



Boebinger *et al.*, *Joule*, (2018), **2**, 1783-1799
Yersak *et al.*, *Advanced Energy Materials*, (2013), **3**, 120-127

# Mesoscale Modeling – Conversion Reaction

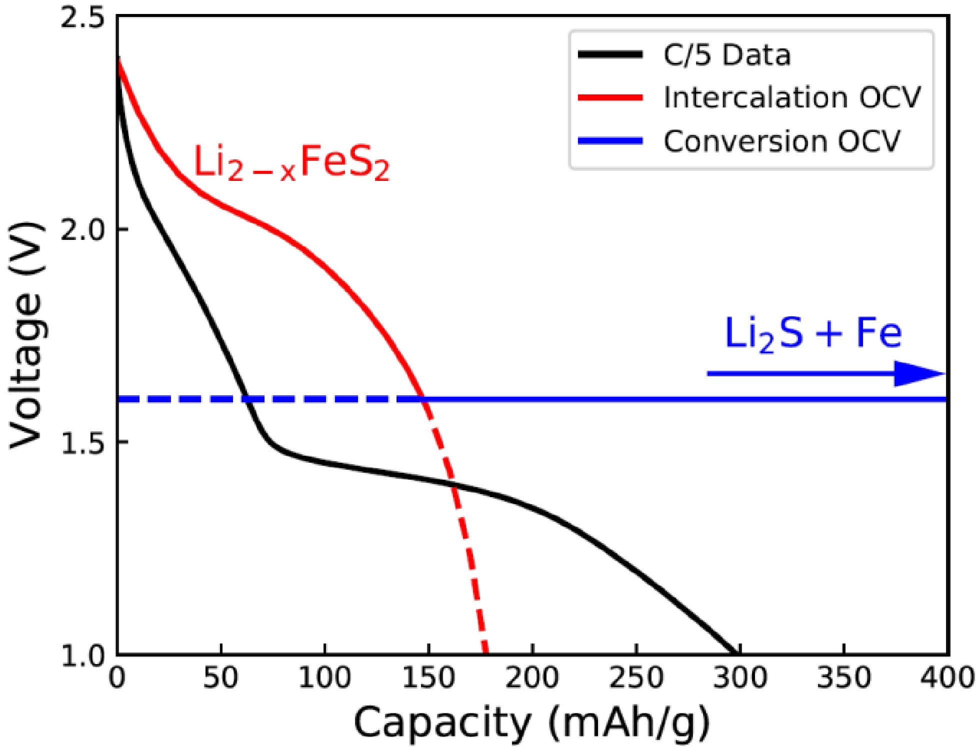


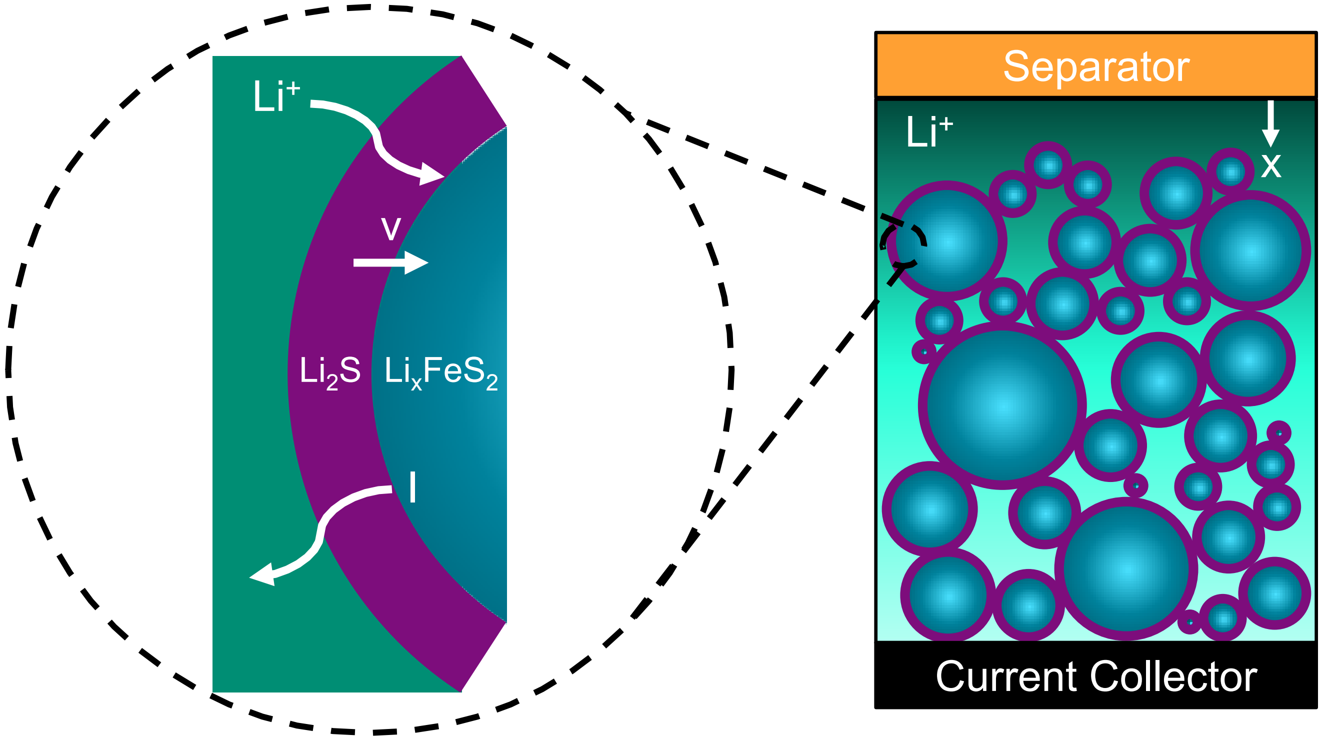


# Pseudo-Two-Dimensional (P2D) Model

- Large mesoscale simulations can be computationally expensive and difficult to run

- We can simplify the process through an adapted pseudo-two-dimensional approach which considers relevant transport both on the electrode and particle scales




Horner *et al.*, *Journal of Power Sources* (Submitted)

# Model Equations and Variables

- Used adapted Doyle-Fuller-Newman (DFN) half-cell model with non-ideal transport for the intercalated lithium and an additional equation that tracks the shell thickness

- The presence of the shell affects the solid potential, electrolyte potential and lithium-ion concentration at the reaction surface as well as the overall electrode conductivity

**Equations**

| | |
|---|---|
| Electrode Potential: | $\frac{\partial}{\partial x}\left((1-\epsilon)^b \kappa_{eff} \frac{\partial V_s}{\partial x}\right) = aFj$ |
| Electrolyte Potential: | $\frac{\partial}{\partial x}\left[\epsilon^b \kappa_l \left(\frac{\partial V_l}{\partial x} - (1-t_+)\frac{2RT}{FC_{Li^+}}\frac{\partial C_{Li^+}}{\partial x}\right)\right] = -aFj$ |
| Electrolyte Concentration: | $\epsilon \frac{\partial C_{Li^+}}{\partial t} = \frac{\partial}{\partial x}\left[\epsilon^b D_{Li^+} \frac{\partial C_{Li^+}}{\partial x}\right] + a(1-t_+)j$ |
| Solid Concentration: | $\frac{\partial C_{Li}}{\partial t} = -\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{D_{Li} F C_{Li}}{RT}\frac{\partial V_{Eq}}{\partial r}\right)$ |
| Shell Thickness: | $\frac{\partial \delta}{\partial t} = -\frac{j_{conv} M}{\rho z\left(2 - \frac{C_{Li}}{C_{max}}\right)}$ |

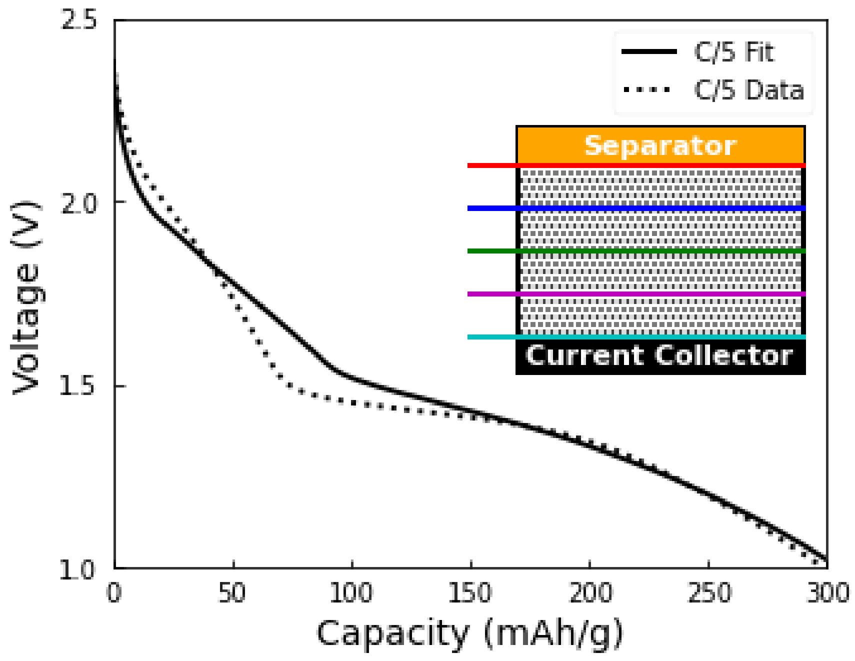
**Variables**

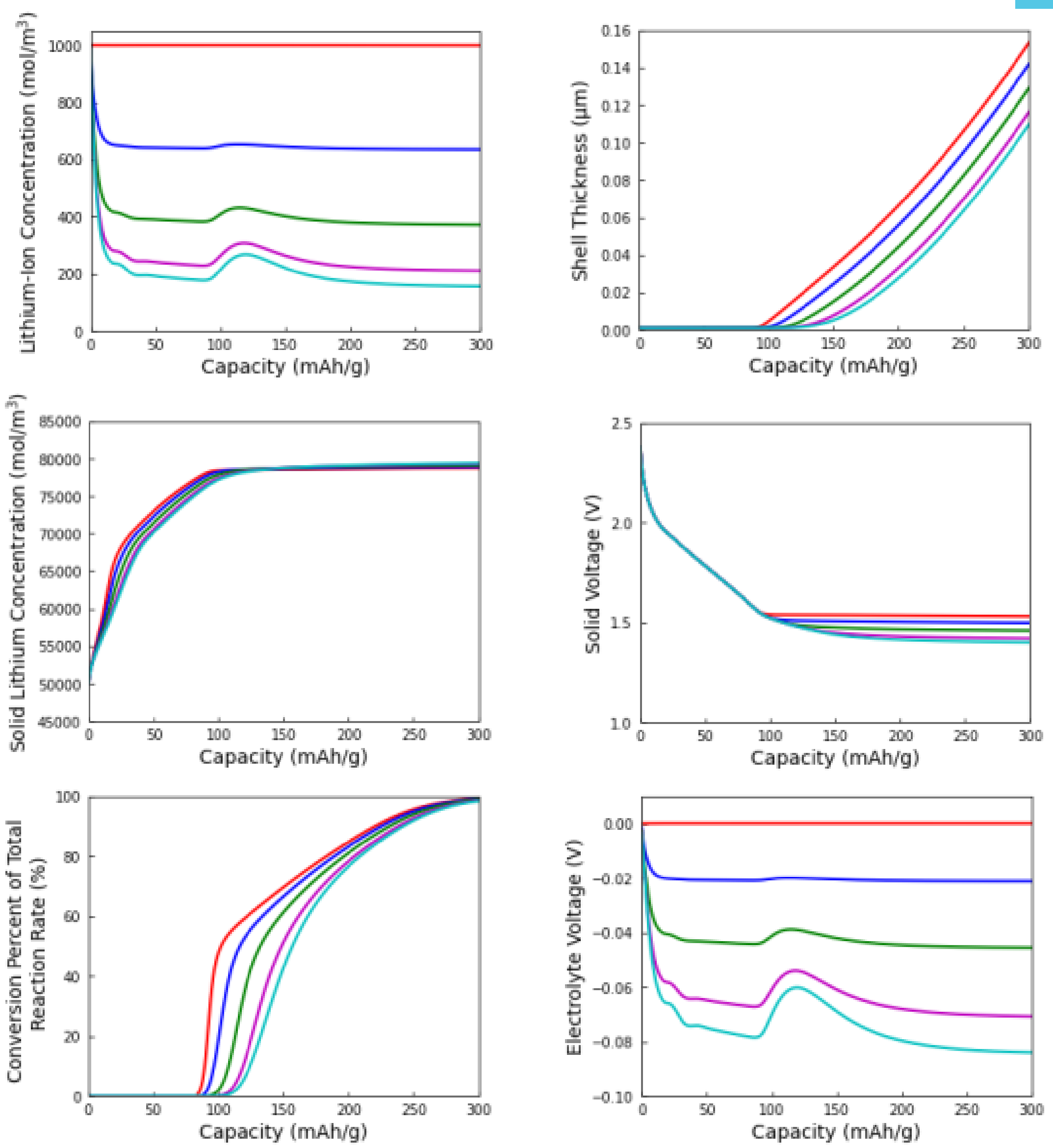
| | |
|---|---|
| Effective Electrode Conductivity: | $0 = \sum_i \phi_i \frac{\kappa_i - \kappa_{eff}}{\kappa_i + 2\kappa_{eff}}$ |
| Inner Solid Potential: | $V_{s,in} = V_{s,out} - \frac{jFR_c^2}{\kappa_{shell}}\left(\frac{1}{R_c} - \frac{1}{R_p}\right)$ |
| Inner Electrolyte Potential: | $V_{l,in} = V_{l,out} + \ln\left(\frac{C_{Li^+,in}}{C_{Li^+,out}}\right)\frac{RT}{F}$ |
| Inner Lithium-Ion Concentration: | $C_{Li^+,in} = C_{Li^+,out} + \frac{jR_c^2}{2D_{shell}}\left(\frac{1}{R_c} - \frac{1}{R_p}\right)$ |
| Overpotential: | $\eta = V_{s,in} - V_{l,in} - V_{Eq}$ |


Horner *et al.*, *Journal of Power Sources* (Submitted)
Marquis et al., *Journal of the Electrochemical Society*, (2019), **166**, A3693
Stroud, *Superlattices and Microstructures*, (1998), **23**, 567-573

# P2D C/5 Model Results

- We fit the model to C/5 data to identify the remaining unknown transport parameters
- Quantities associated with the conversion reaction and the electrolyte exhibit polarization across the electrode

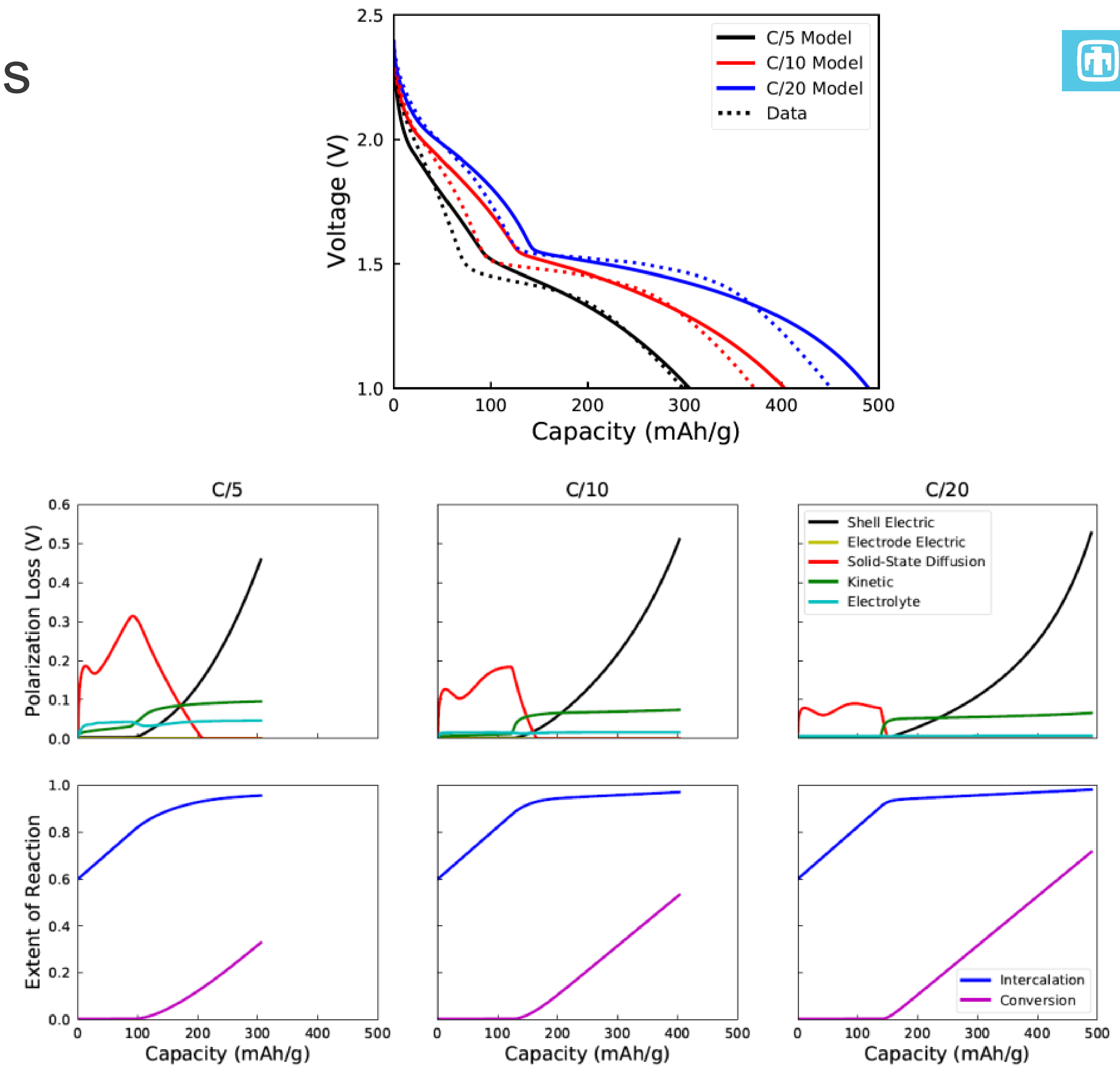



Horner *et al.*, *Journal of Power Sources* (Submitted)

# Leading Loss Mechanisms

- The P2D model enables us to identify the leading loss mechanisms for the cell
- At slow c-rates, solid-state diffusion and shell electrical conductivity are the leading loss mechanisms
- At faster c-rates, additional losses including kinetic and electrical conductivity through the electrode become relevant

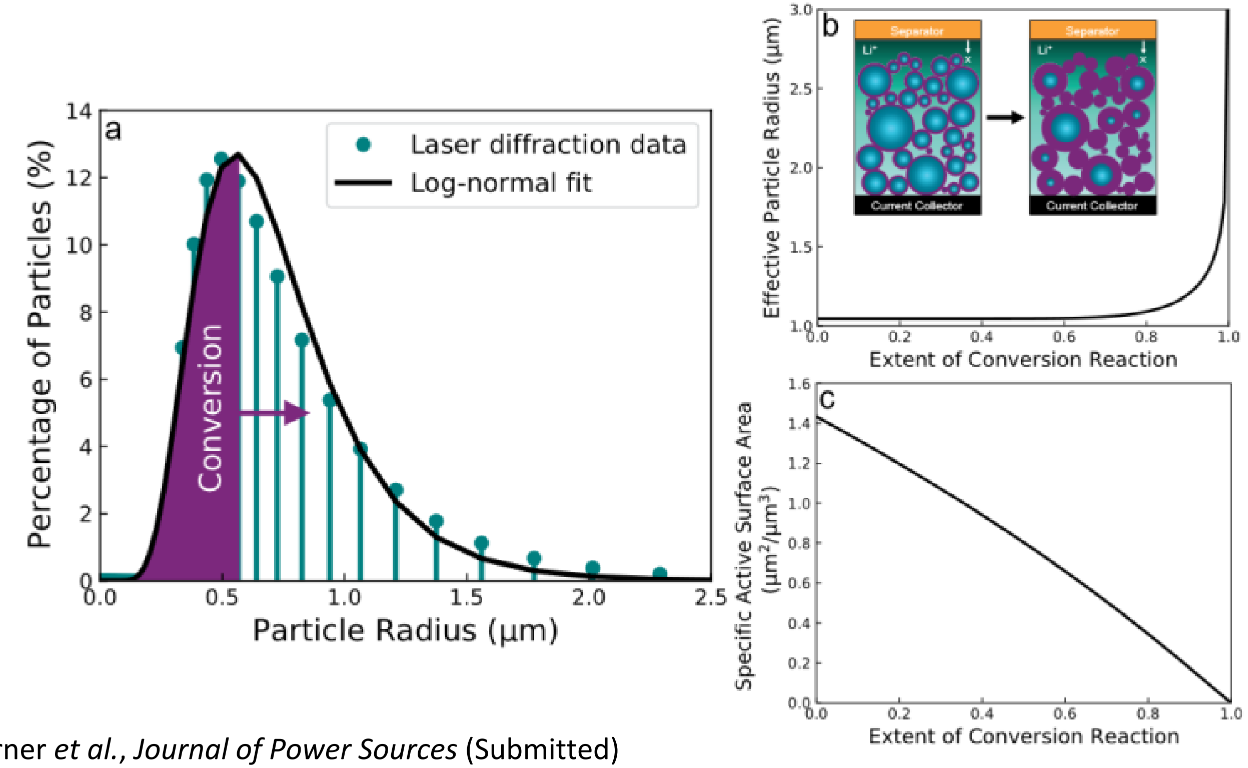


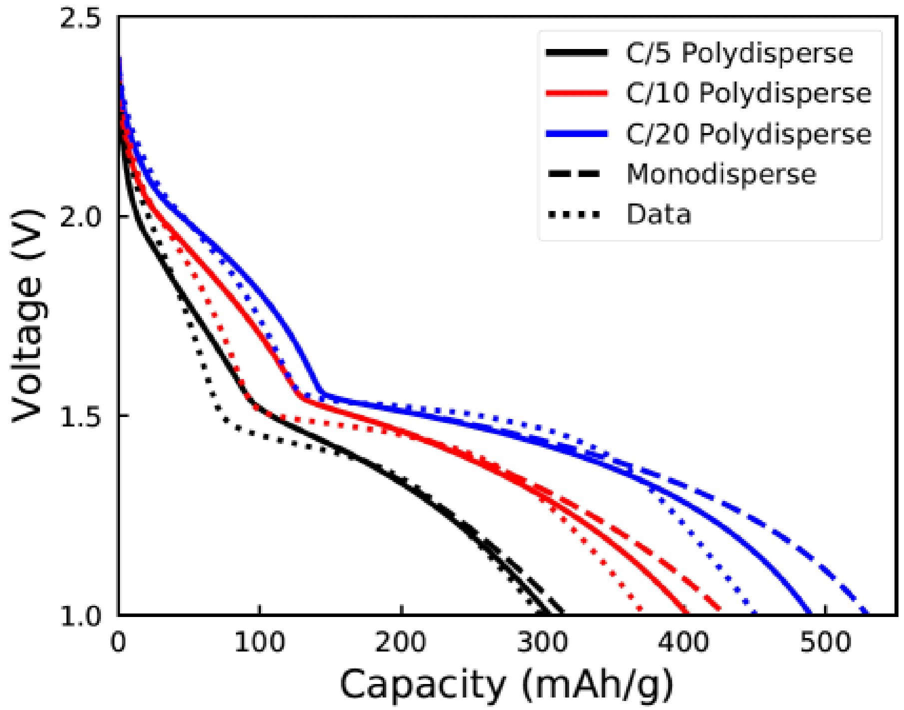

Horner *et al.*, *Journal of Power Sources* (Submitted)

# P2D Model Polydispersity

- We include polydispersity by introducing a variable effective particle radius and specific active surface area

- Inclusion of polydispersity results in a lower capacity in the conversion regime, particularly at slow c-rates, when compared to a single particle approach

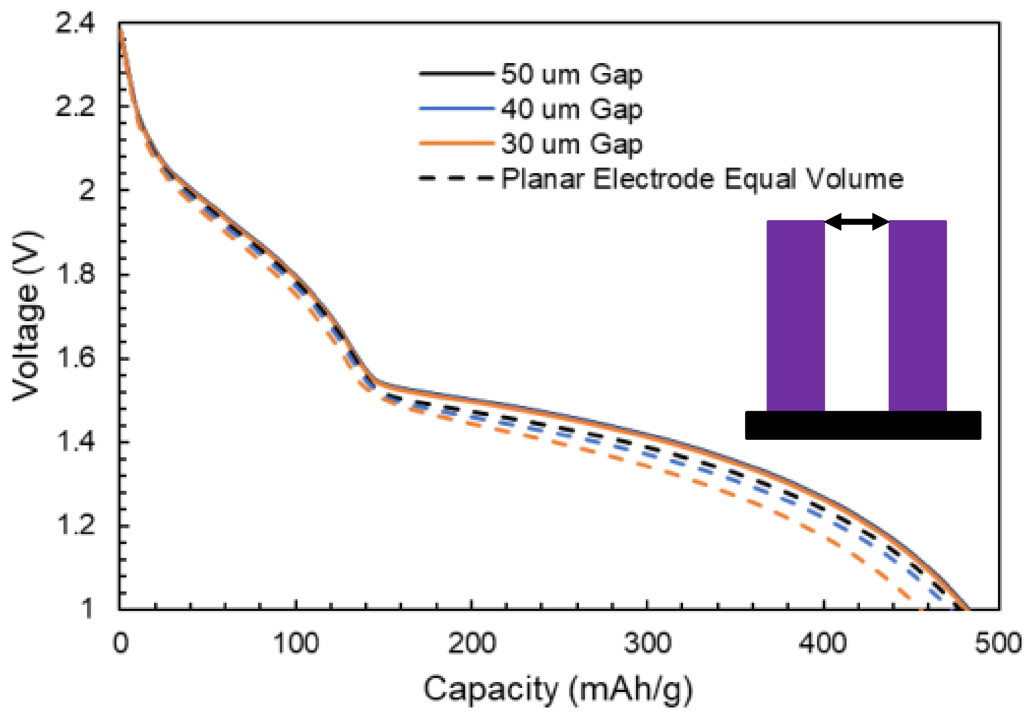


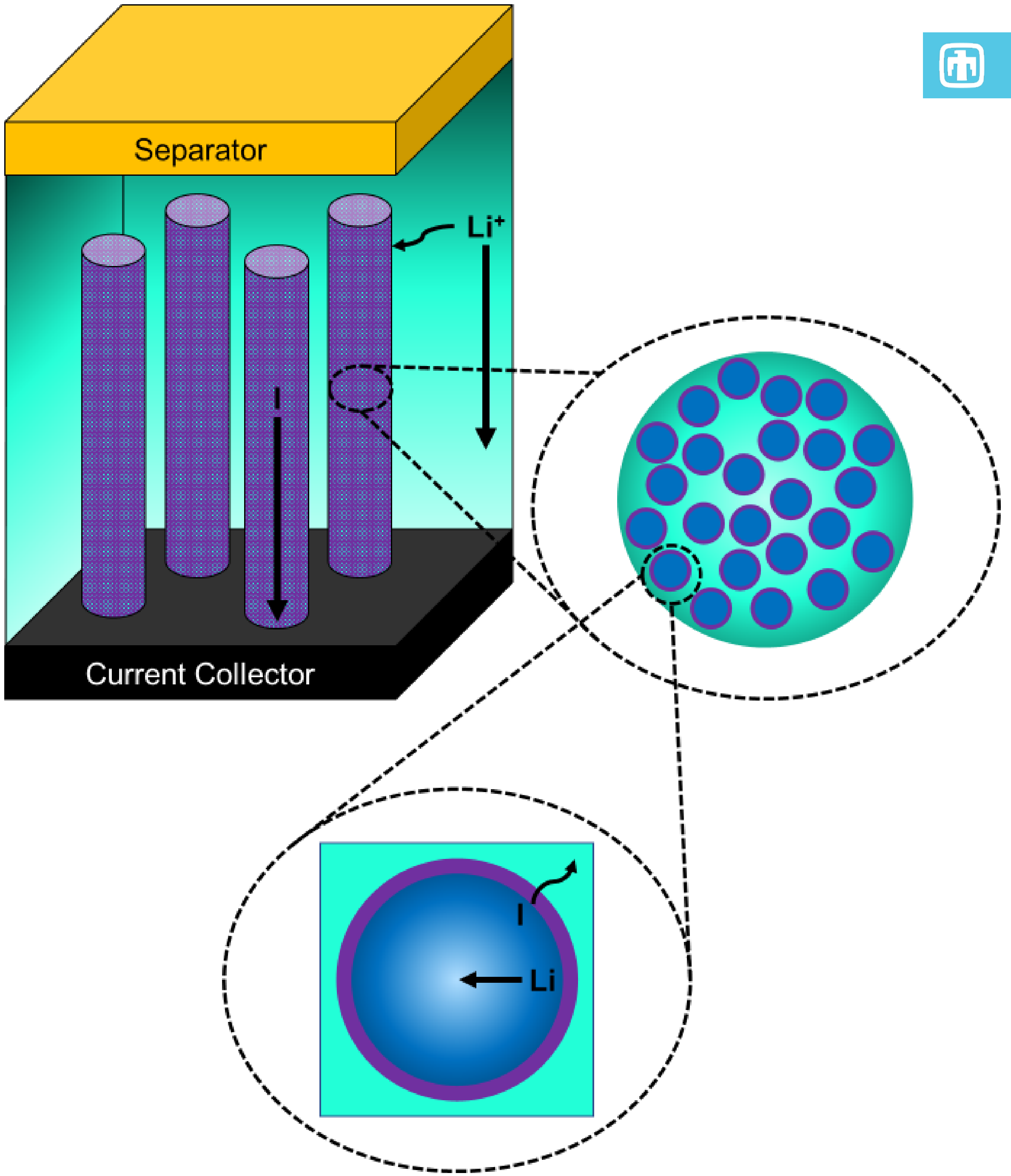




Horner *et al.*, *Journal of Power Sources* (Submitted)
Horner *et al.*, *ACS Applied Energy Materials*, (2021), **4**(10), 11460-11469

# Three-Dimensional Electrodes

- Three-dimensional electrodes are intriguing due to their potential to outperform planar electrodes
- By extending the P2D approach to three-dimensional electrodes, we can validate this assertion for $FeS_2$



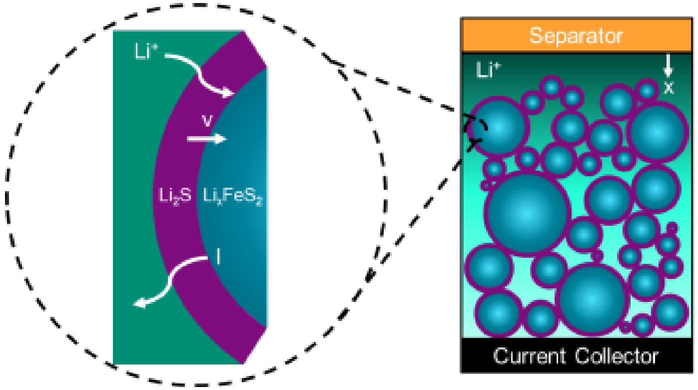



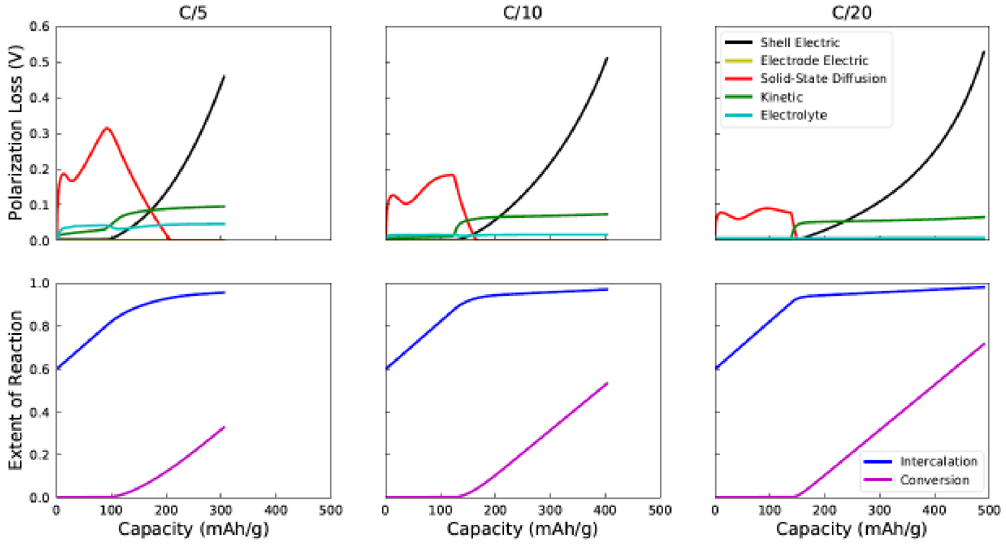
# Conclusions and Acknowledgements

- We developed a polydisperse, P2D model to represent the full behavior of $FeS_2$ during lithiation

- The model helped to identify solid-state diffusion and shell electrical conductivity as the leading loss mechanisms

- Incorporation of polydispersity led to decreased capacity in the conversion regime





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  - Katharine Harrison
  - Ben Ng
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Horner *et al.*, *Journal of Power Sources* (Submitted)