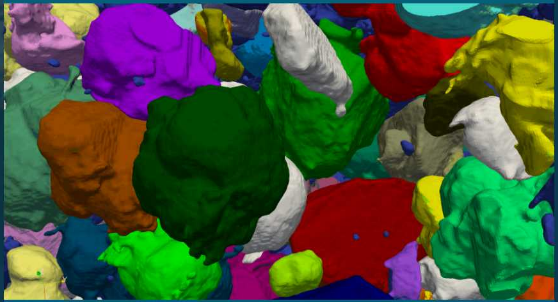
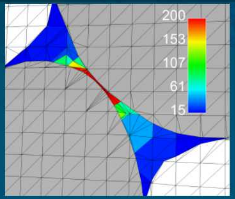
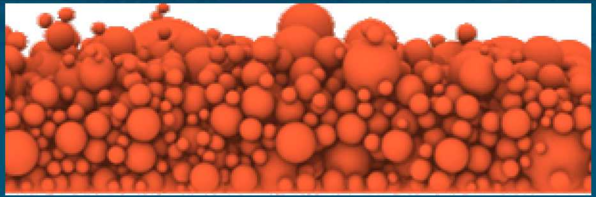
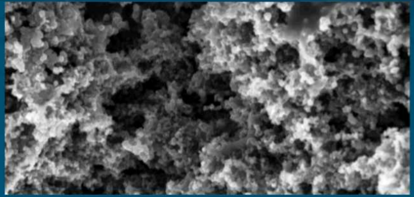
SAND2020-10025C

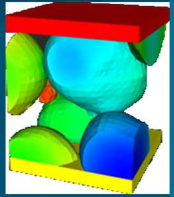
Mesoscale Electrochemical-Mechanical Analyses of Solid-State Non-Planar Conversion Cathodes











Co-Authors:
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- Katharine L. Harrison

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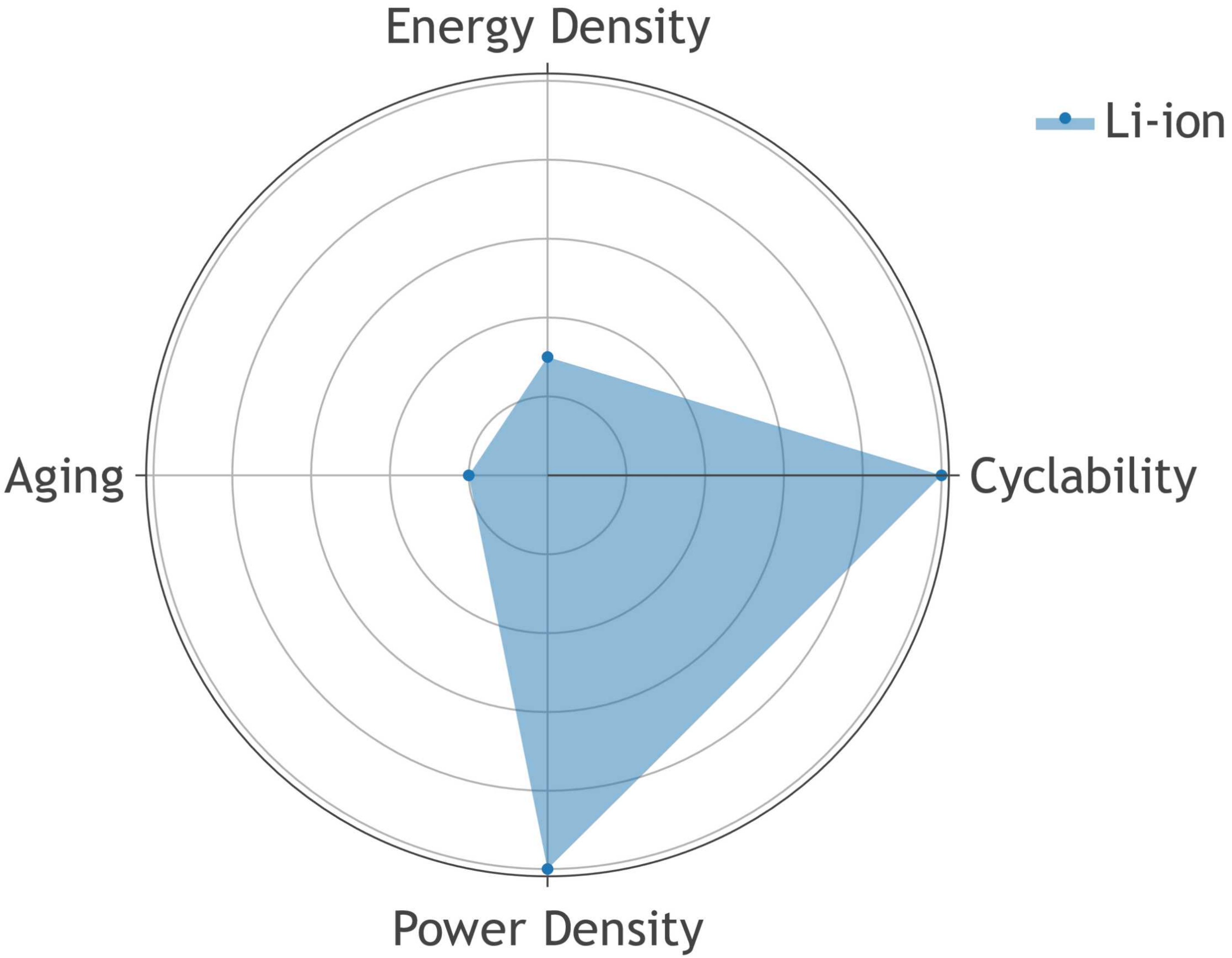
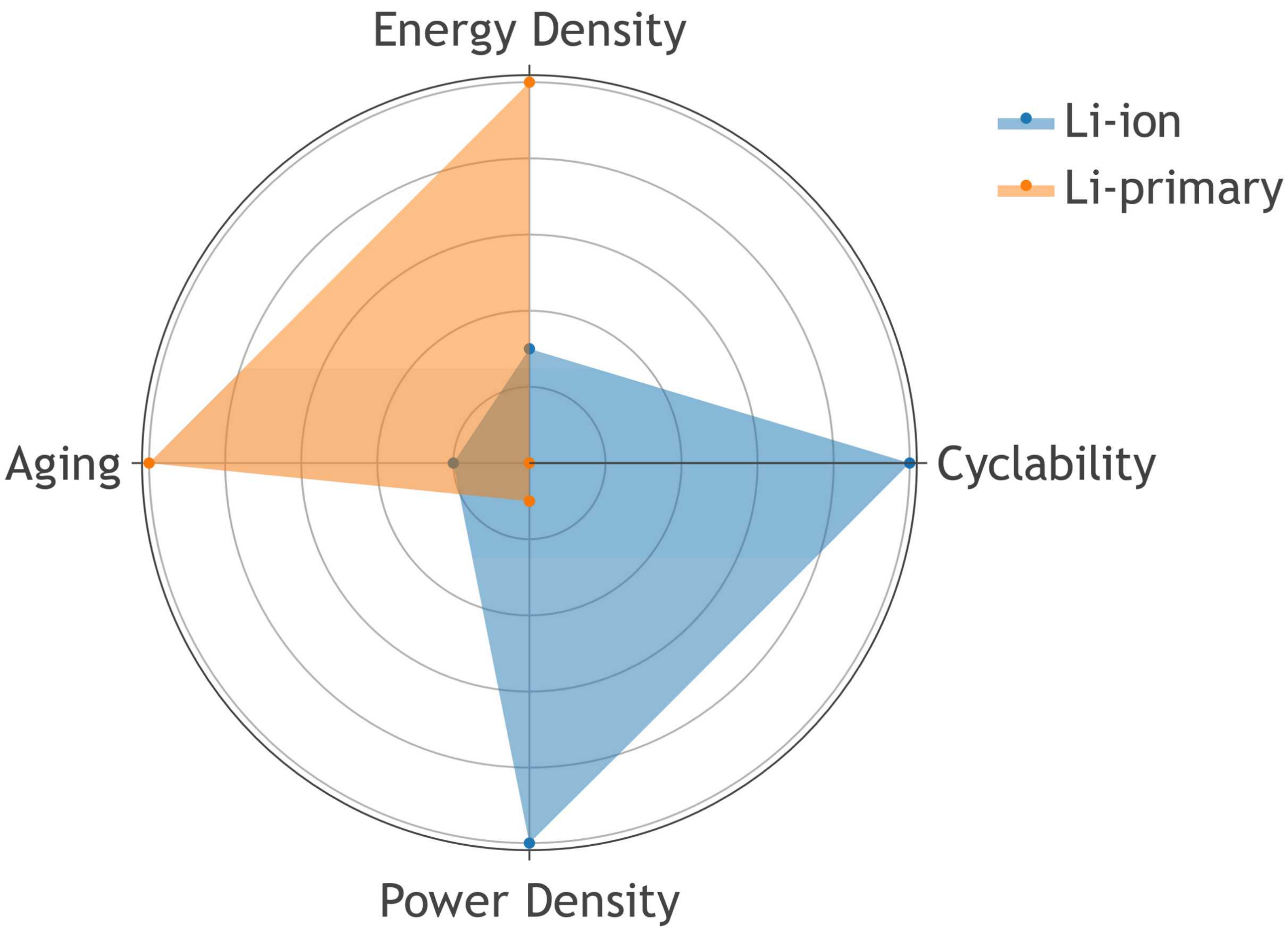
Why study FeS_2 cathodes?



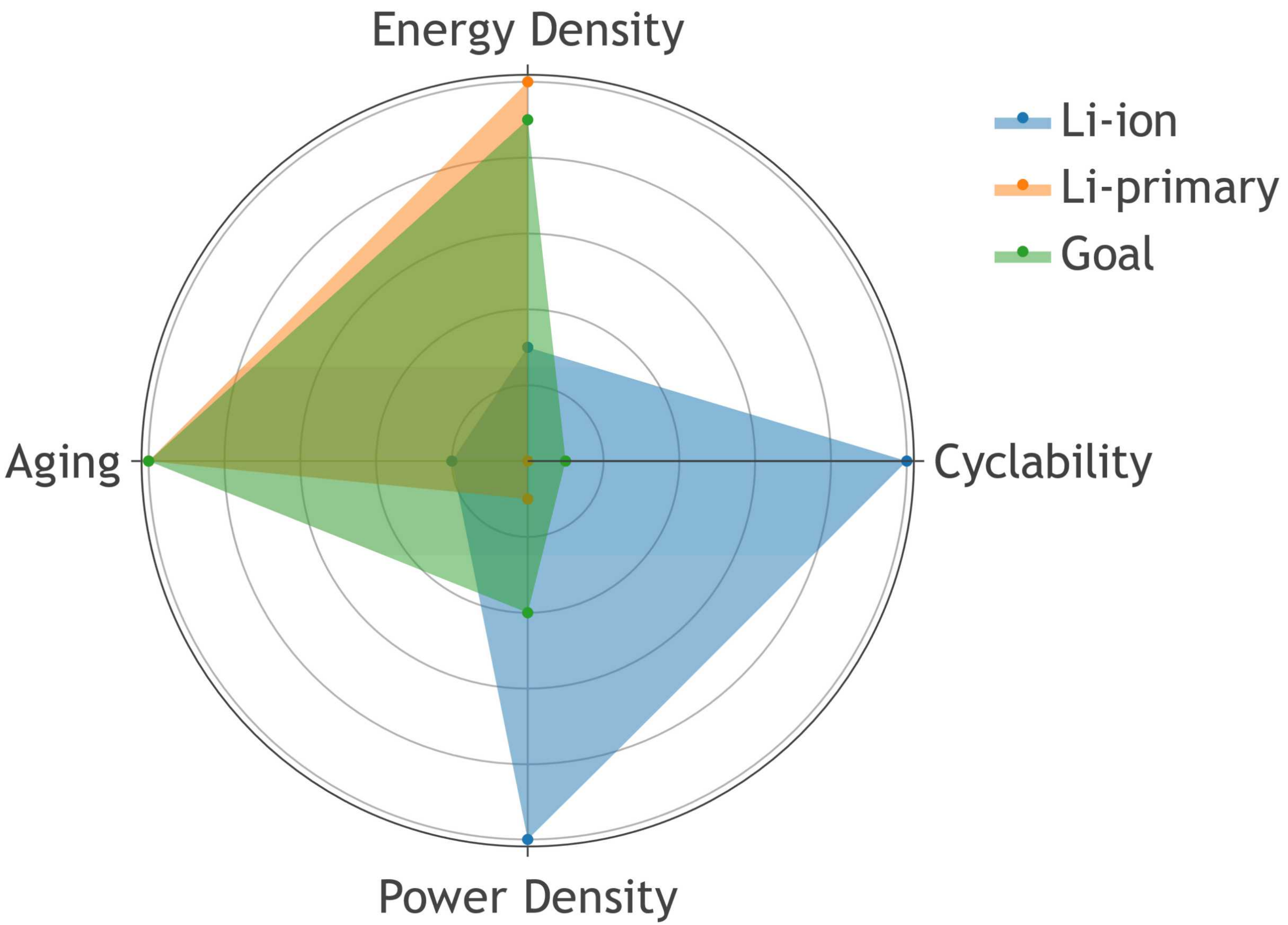
Motivation: High energy-density batteries with limited, tunable cyclability

Why study FeS_2 cathodes?



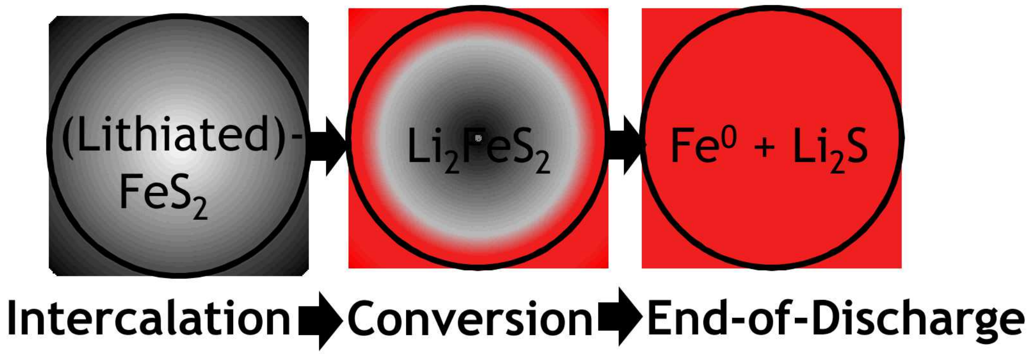
Motivation: High energy-density batteries with limited, tunable cyclability

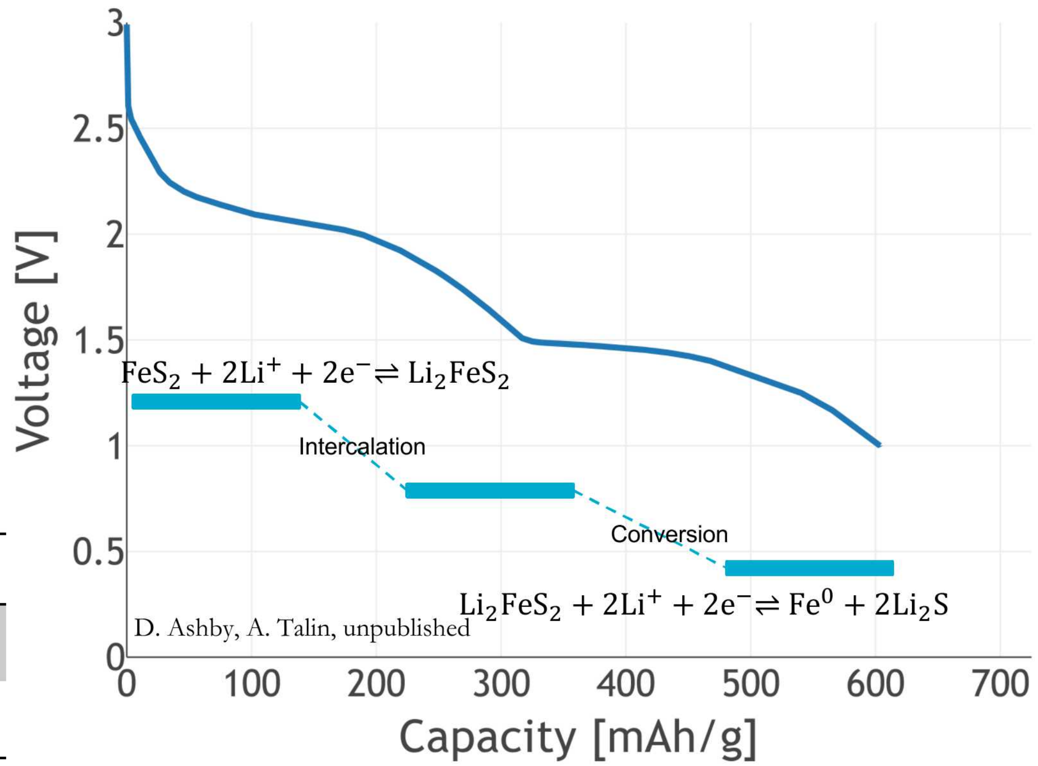
Why study FeS_2 cathodes?



Motivation: High energy-density batteries with limited, tunable cyclability

FeS_2 – A combination of intercalation and conversion



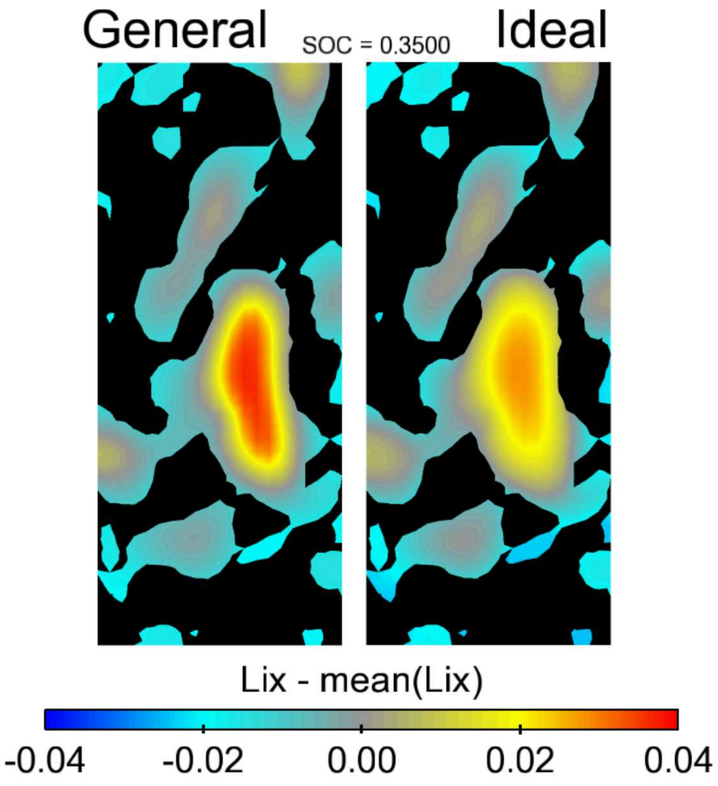


Generalized Reaction Mechanism		
(1)	$FeS_2 + 2Li^+ + 2e^- \rightleftharpoons Li_2FeS_2$	Intercalation
(2)	$Li_2FeS_2 + 2Li^+ + 2e^- \rightleftharpoons Fe^0 + 2Li_2S$	Conversion

T. A. Yersak, et al, Adv. Energy Mat. (2013)

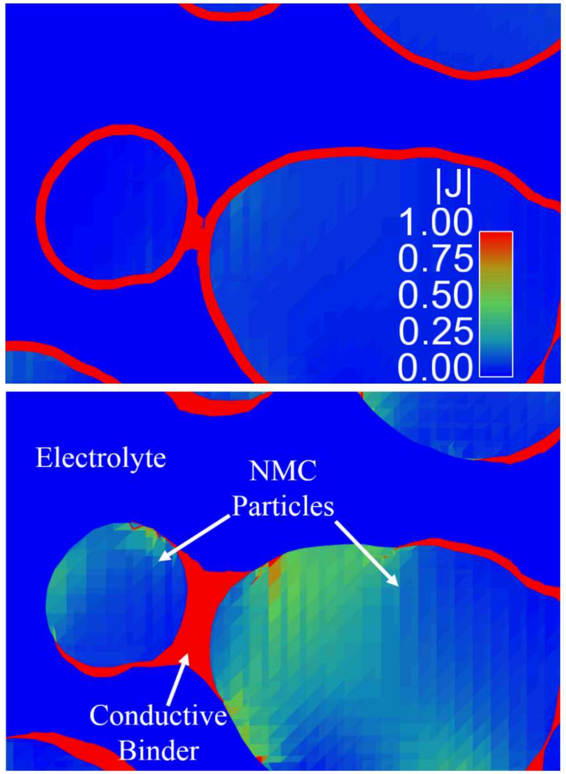
Combined intercalation and conversion is a unique modeling challenge

Mesoscale modeling



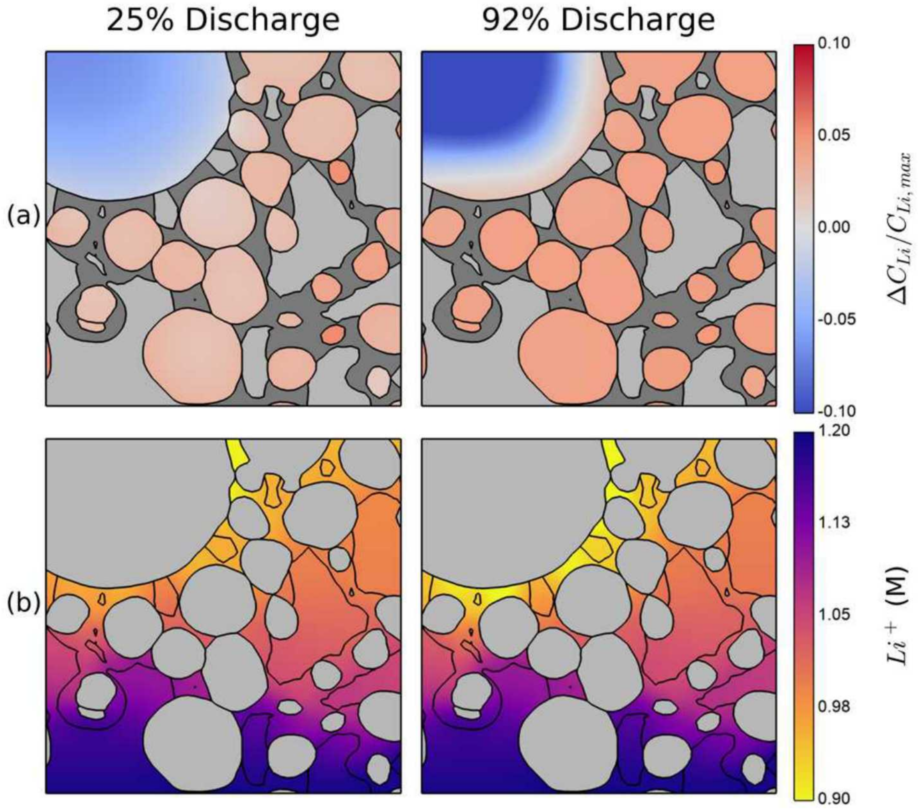
LCO image-based studies

Mendoza et al, J. Electrochem. Soc. (2016)



CBD morphology impacts

Trembacki et al, J. Electrochem. Soc. (2017)

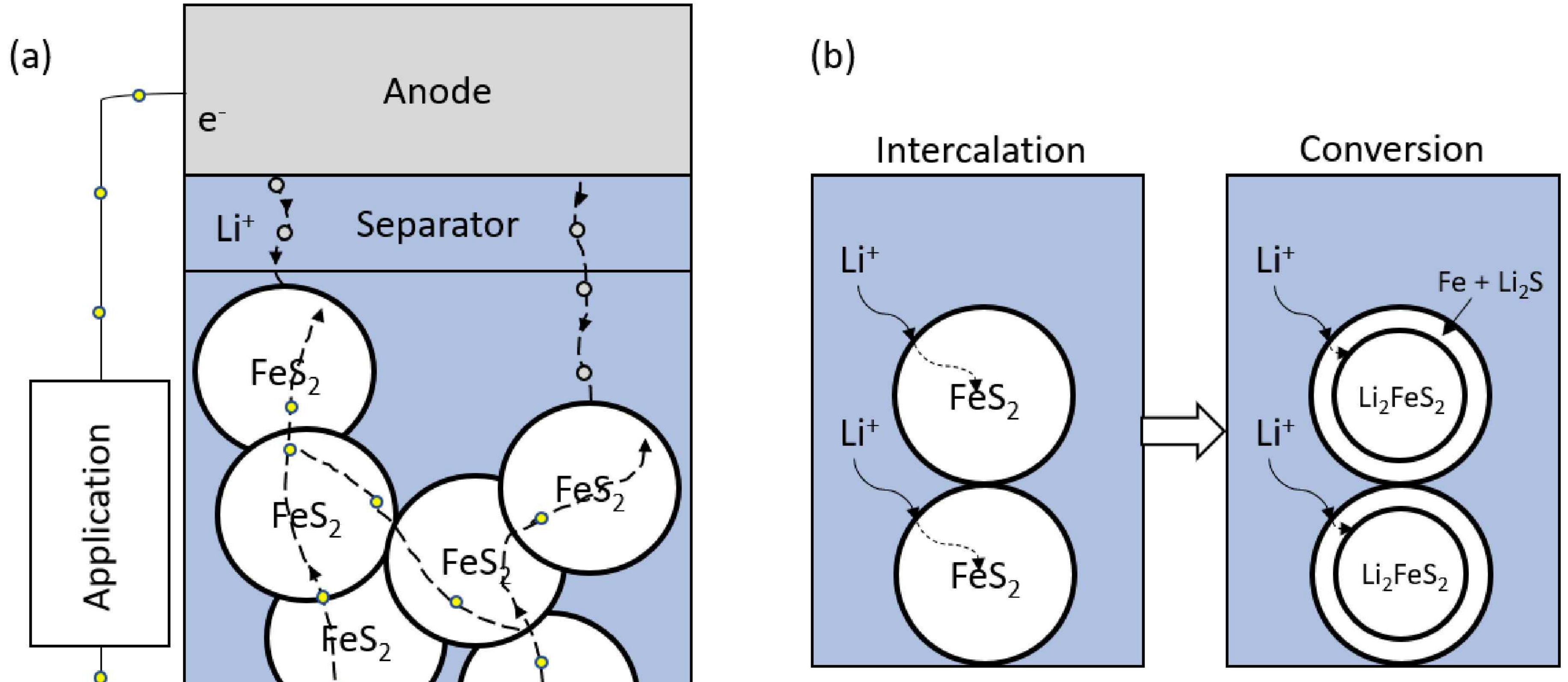


High-fidelity NMC per-particle analyses

Ferraro et al, J. Electrochem. Soc. (2020)

Mesoscale modeling provides detailed insights into coupled-physics behaviors

Mesoscale geometry

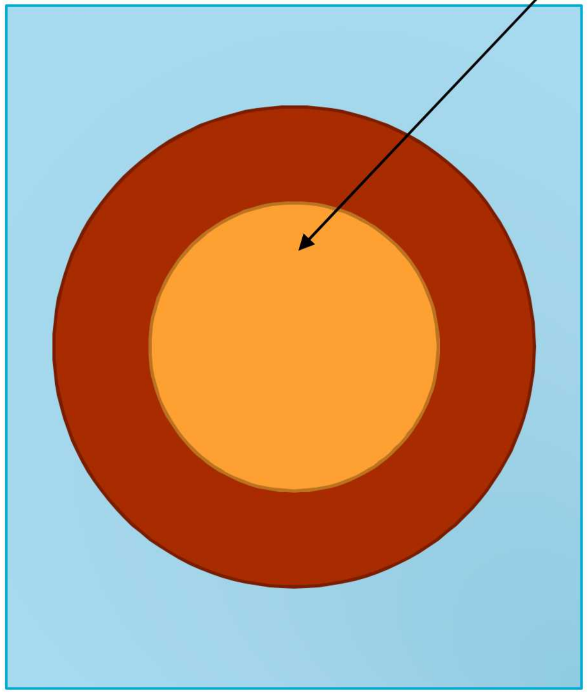


$FeS_2 + 2Li^+ + 2e^- \leftrightharpoons Li_2FeS_2$	$Li_2FeS_2 + 2Li^+ + 2e^- \leftrightharpoons Fe + Li_2S$
• Insertion via solid-state Fickian diffusion	• Phase separation via shrinking core mechanism

Develop model on a simplified geometry to allow detailed focus prior to scaling up

B. Ng et al, in preparation

Mathematical model

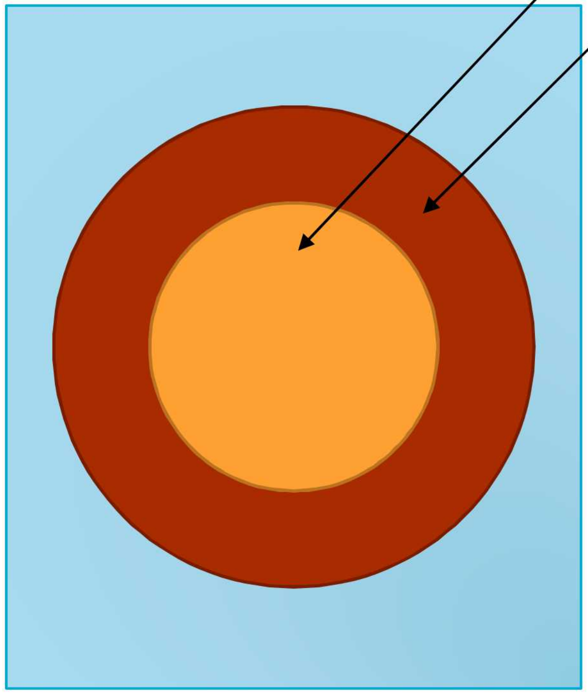


Li_xFeS_2 Particle "Core":

Electrical transport (voltage) – Ohm's Law

Intercalated lithium diffusion (Li_xFeS_2 concentration) – Fick's Law

Mathematical model



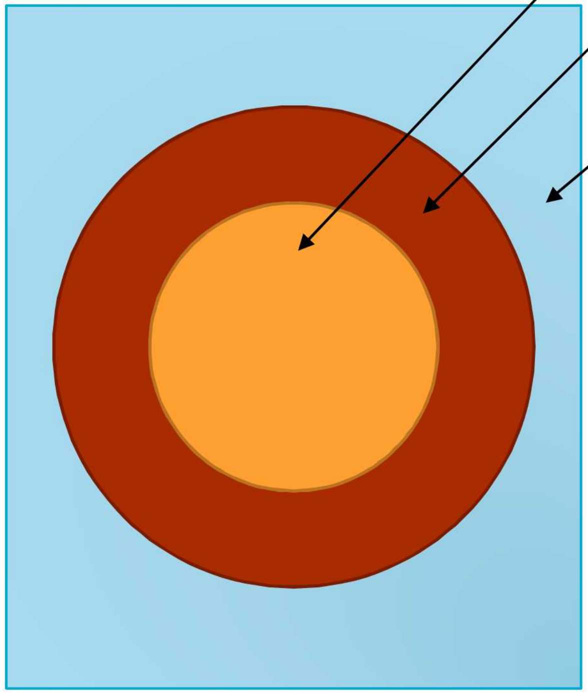
Li_xFeS_2 Particle "Core"

<u>Fe^0 + 2 Li_2S Particle "Shell":</u>

Electrical transport (voltage) – Ohm's Law

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

Mathematical model



Li_xFeS_2 Particle "Core"

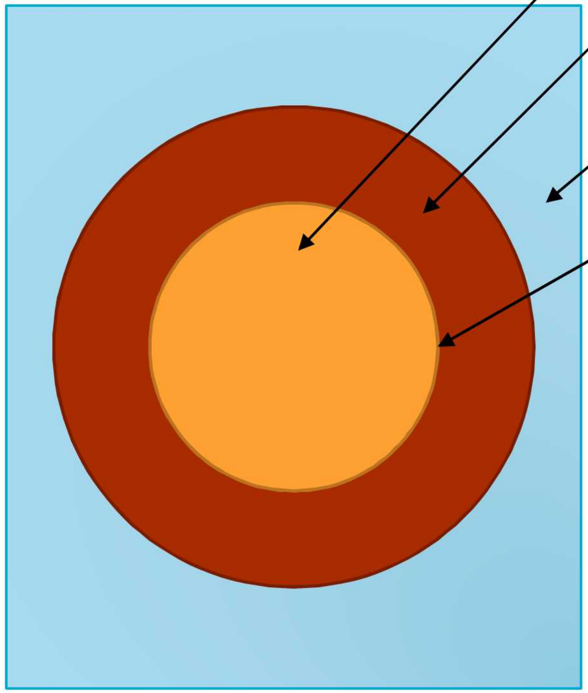
$Fe^0 + 2\ Li_2S$ Particle "Shell"

LiTFSI in DME Electrolyte:

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

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

Mathematical model



Li_xFeS_2 Particle "Core"

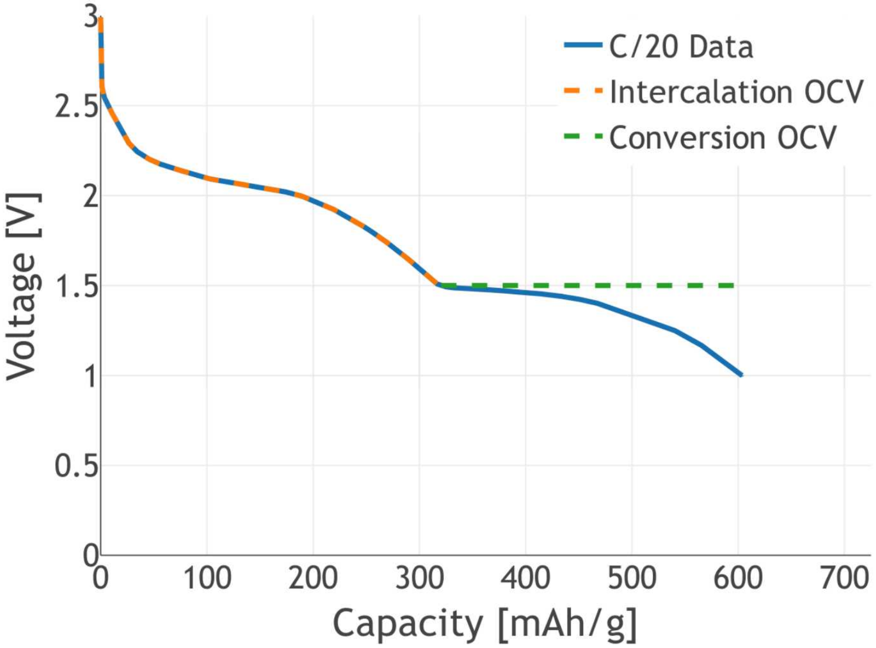
$Fe^0 + 2\ Li_2S$ Particle "Shell"

LiTFSI in DME Electrolyte

Reaction Surface:

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

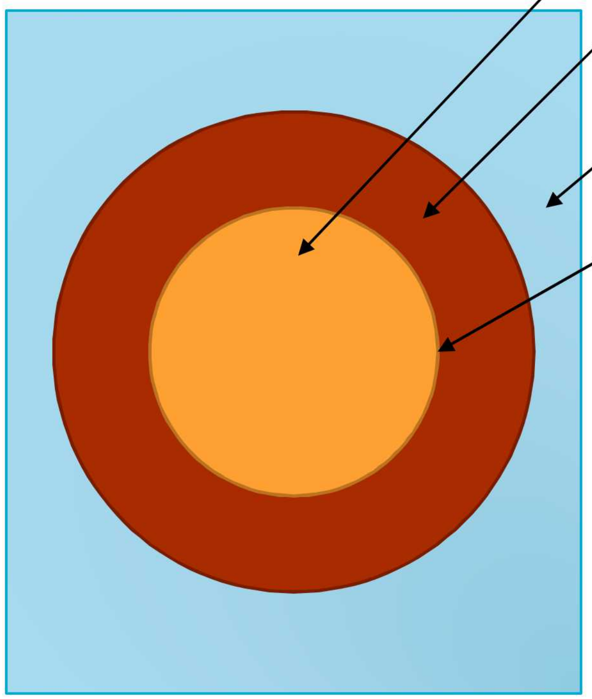
Butler-Volmer reaction kinetics – 2 simultaneous reactions



Reaction surface moves using level-set field

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

Mathematical model



Li_xFeS_2 Particle "Core"

$Fe^0 + 2\ Li_2S$ Particle "Shell"

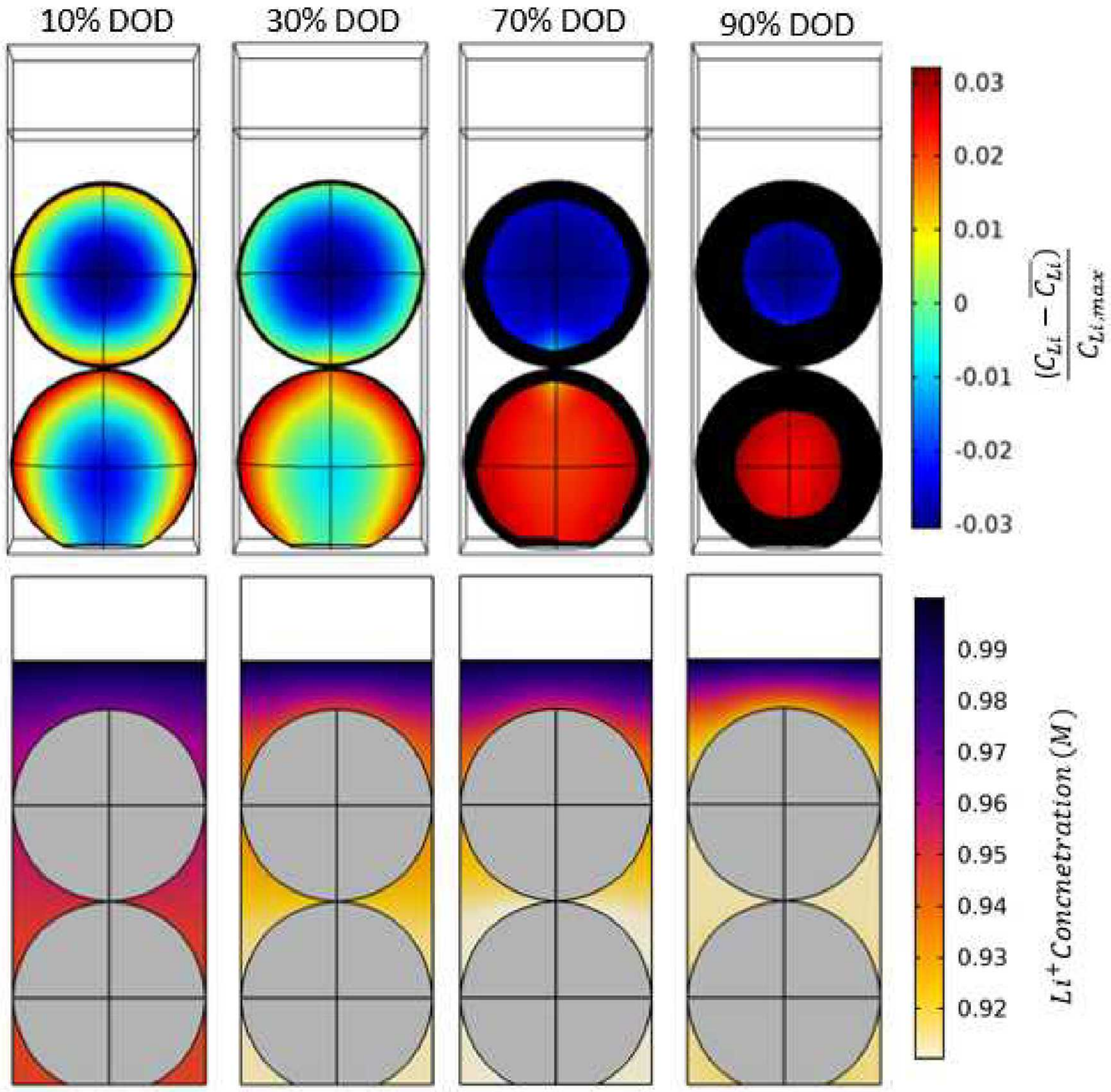
LiTFSI in DME Electrolyte

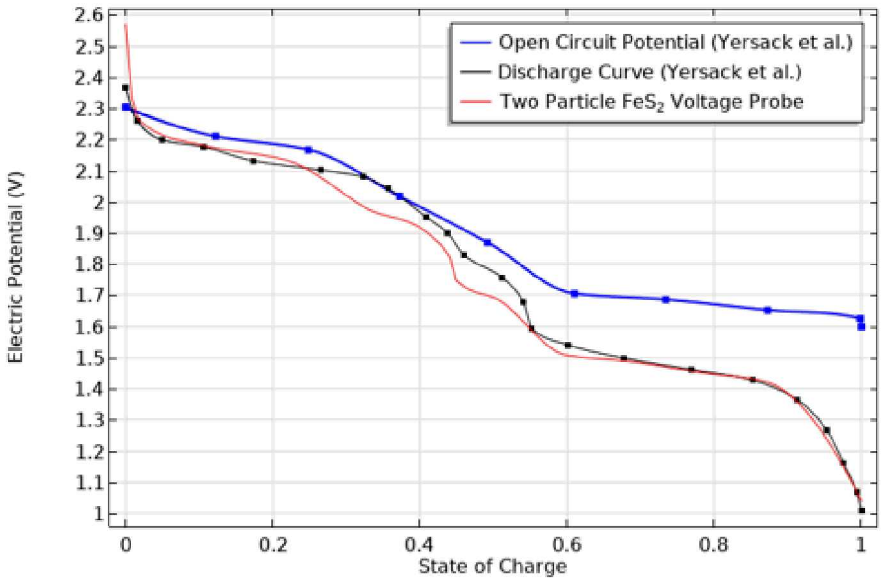
Reaction Surface:

<u>Key Assumptions:</u>

- Isothermal (but temperature-dependent)
- Infinite Li^+ source at separator
- Perfect electrical transport at collector
- Polysulfide shuttle not considered
- No capacity loss mechanisms

Nominal simulation

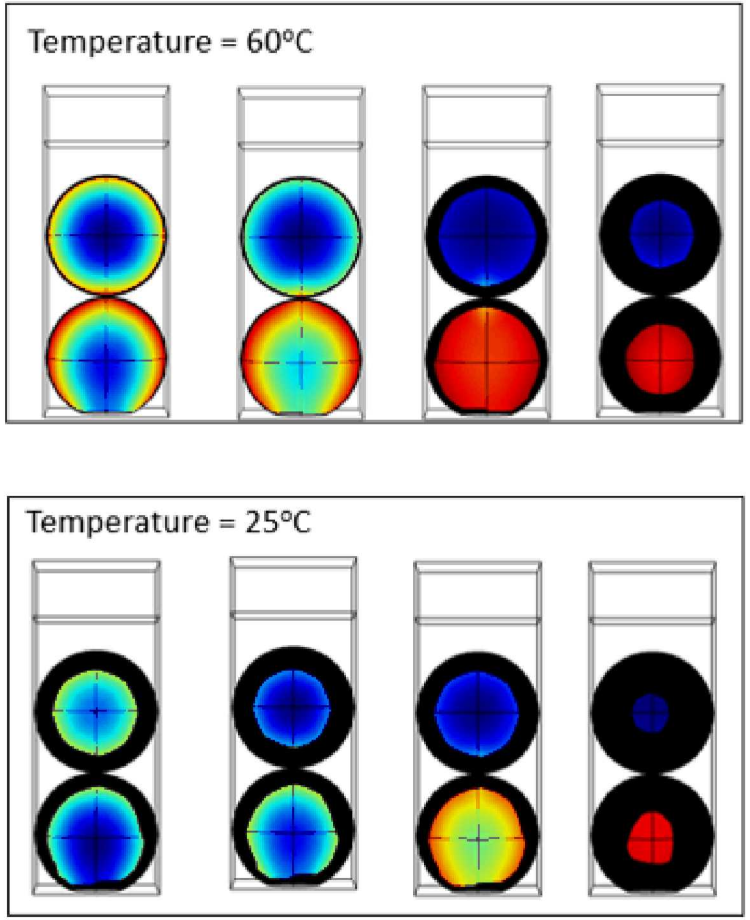


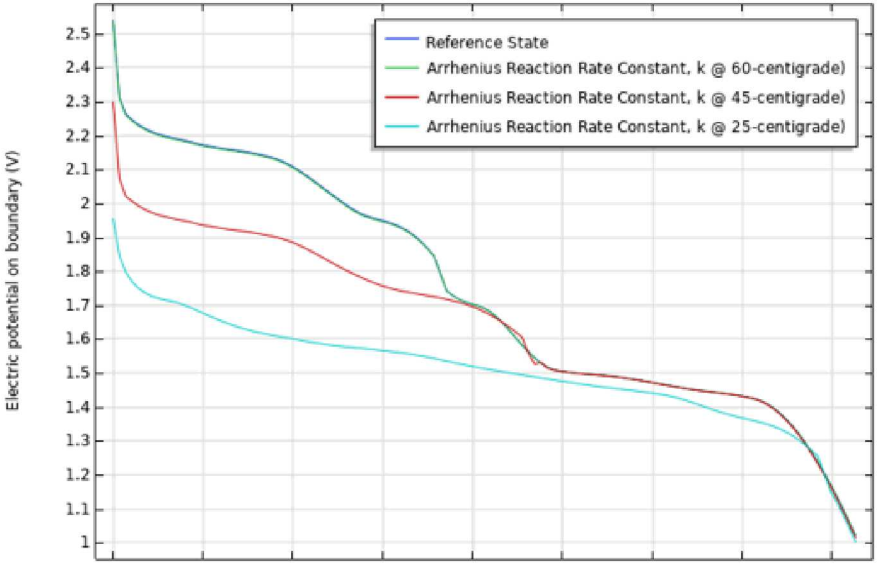


Clear distinction between intercalation and conversion regimes; reasonable match to data

Temperature dependence

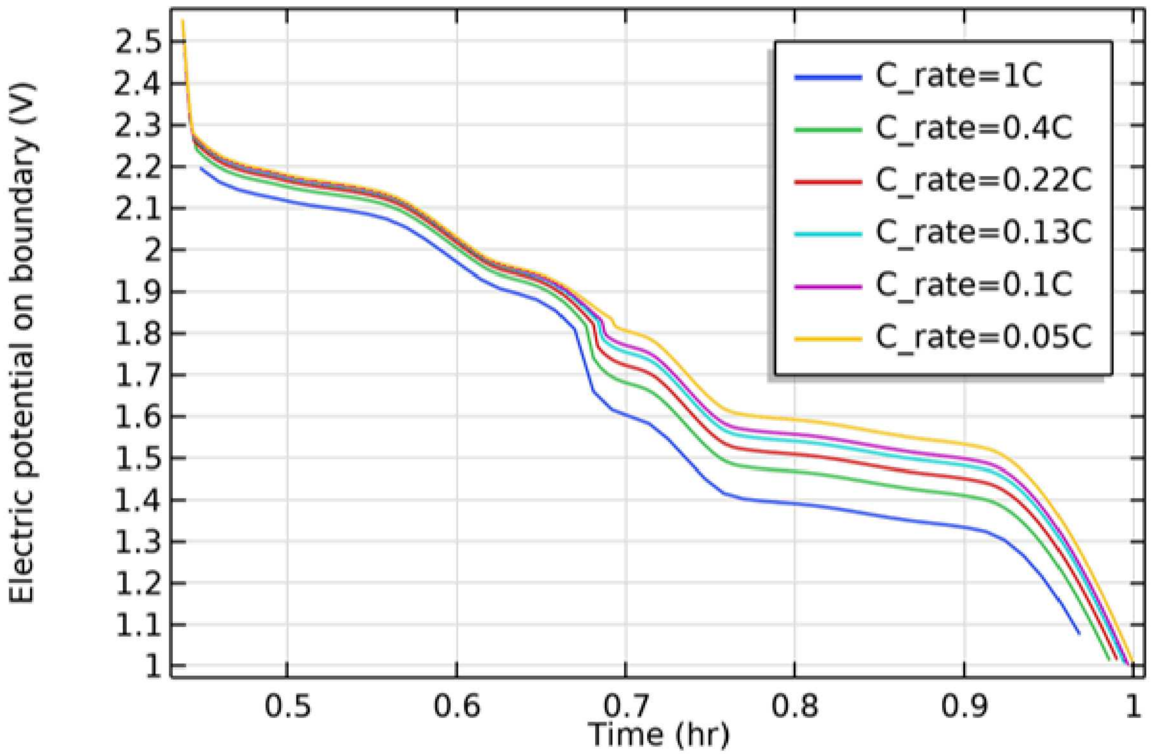
Arrhenius temperature dependence of solid-state diffusivity, electrical conductivity, and intercalation OCV

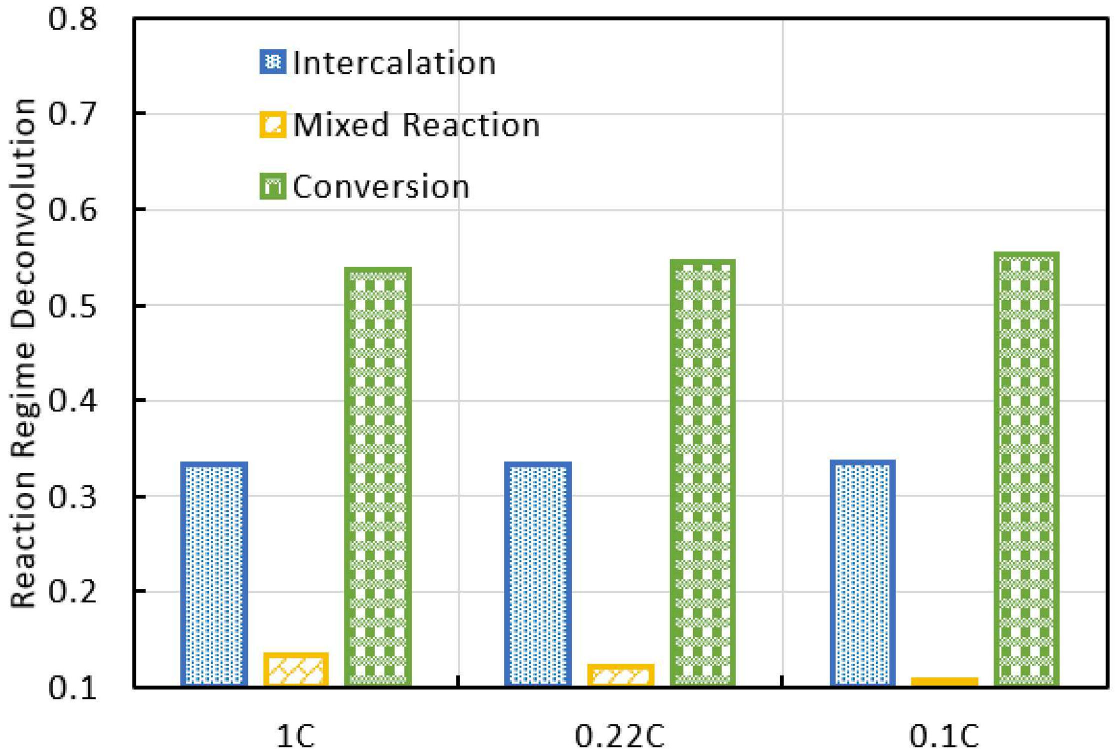




Lower temperatures lead to a larger mixed reaction zone (simultaneous intercalation and conversion)

Reaction rate dependence





Higher current densities lead to a slightly larger mixed reaction zone, lower overall voltage

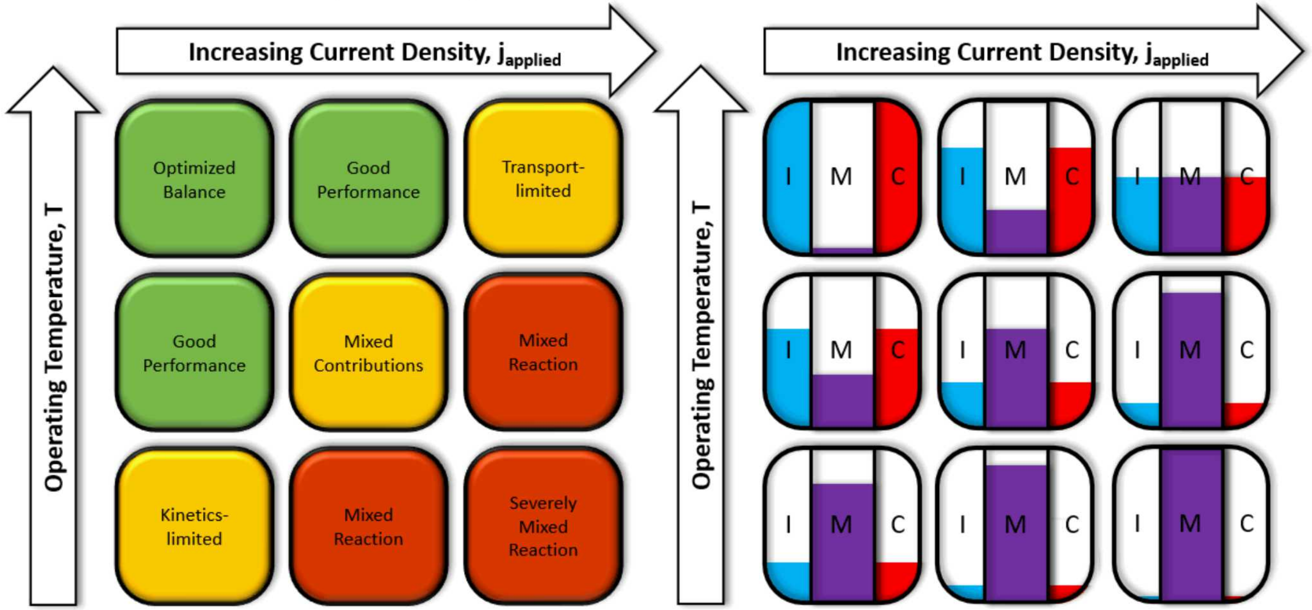
Summary and future directions

Novel mesoscale model combining intercalation and conversion reactions in FeS2

Studied temperature- and reaction rate-dependences

Future directions

- Additional parametric studies – particle size, electrode thickness, porosity
- Scale up to realistic particle mesostructures
- Heat generation and transport
- Stress generation and degradation



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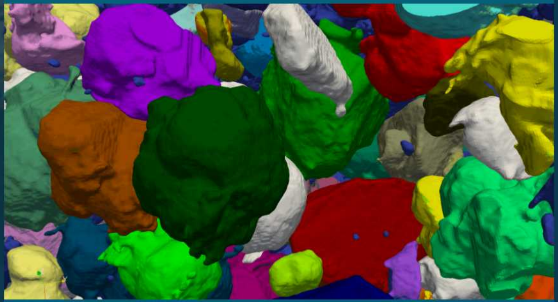

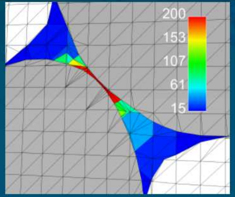

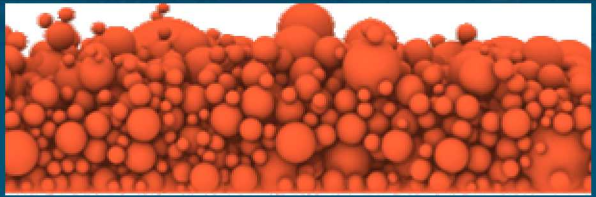

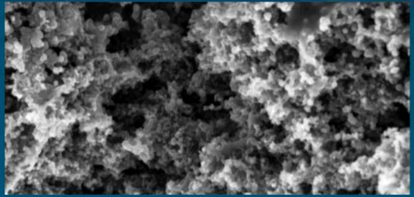

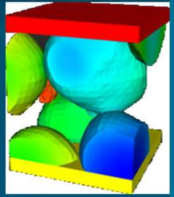

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