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Chemo-Mechanical Model of Lithium Dendrite Growth Impacted by External Pressure

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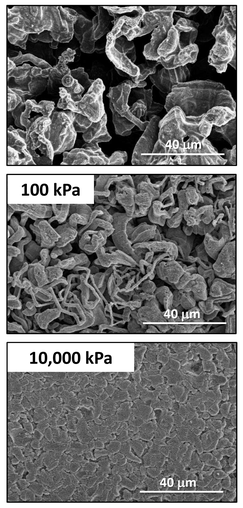
MOTIVATION

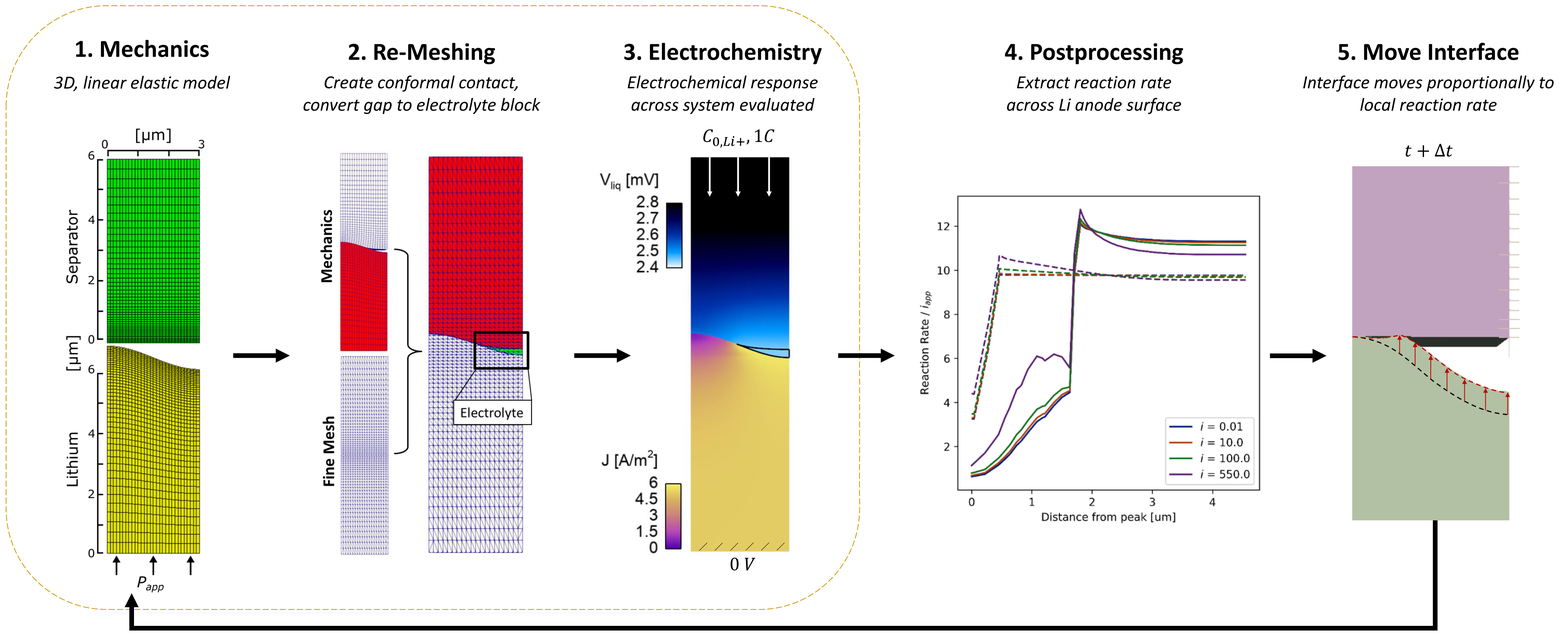
- Dendrite formation within Li-ion batteries during cycling leads to poor performance, safety problems
  - Prior research has shown that Li morphology greatly improves with stack pressure (up to 10 MPa)
  - Excessive pressure causes high overpotential, likely from transport limitations
- Li anode roughness influences stress and overpotential distributions
- Primary focus: Exploring the impact of mechanical stress and roughness on electrochemical reactions and plating on lithium metal anodes
  - Developed high-fidelity, 3D model of mechanics and electrochemistry at lithium-separator interface



K.L. Harrison, et al., *ACS Appl. Mater. Interfaces*, 2021

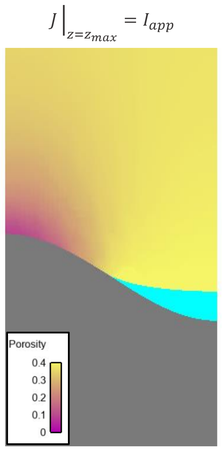
Cryo SEM images courtesy of Katie Jungjohann and Dan Ward

WORKFLOW



MODEL

$$J\big|_{z=z_{max}} = I_{app}$$



Ion Flux

$$J_i = -\frac{\varphi D_i}{\tau} \times \left[z_i C_i \left(\frac{F}{RT}\right) \nabla\phi_l + \nabla C_i\right]$$

Conservation of Mass

$$\varphi \frac{\partial C_{Li+}}{\partial t} + \nabla \cdot J_{Li+} = 0$$

Conservation of Charge

$$\nabla(J_{Li+} - J_{FSI-}) = 0$$

Separator: Celgard 2325
- Porous polymer separator
- $E_{sep} = 344.4\ MPa$ [1]
- $\varphi_0 = 0.39$ [2]

Electrolyte: 4M LiFSI-DME
- Favored for high salt concentration
- $D_e = 3.12 \times 10^{-11}\ m^2/s$

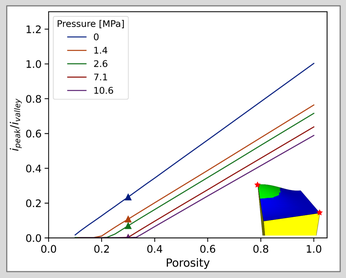
Lithium metal
- $H_0 = 0.8\ \mu m$
- $E_{Li} = 7.8\ GPa$ [3]

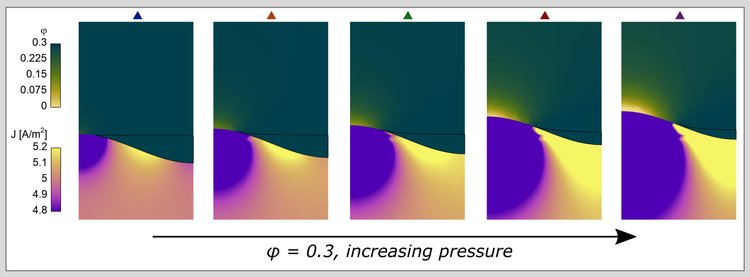
$$V_S\big|_{z=0} = 0$$

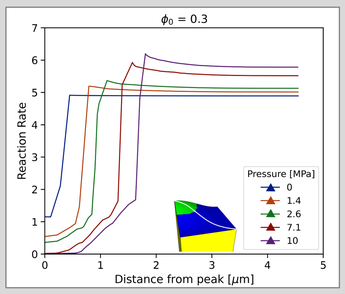
[1] Kalnaus et al., *J. Power Sources* (2017)
[2] Finegan et al., *J. Power Sources* (2016)
[3] Zhang et al., *JES* (2019)

RESULTS

- Ratio between peak and valley reaction rates depends heavily on local porosity
- Below: effect of porosity on ion transport through interface, as stack pressure increases from 0 to 10 MPa

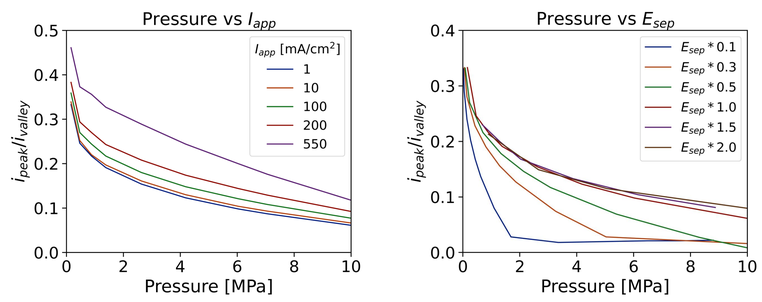






- Reaction rate as function of distance from protrusion peak
  - Ion transport completely inhibited at peak
  - Outside of this region, spike in current density occurs
  - In electrolyte-filled valley, reaction rate approaches constant

PARAMETRIC STUDIES



- Parametric studies investigated impact of pressure along with various material and electrochemical properties
- Protrusion height, separator modulus impact pore closure
- Certain ranges of electrolyte diffusivities, current densities for which plating is suppressed

EFFECT OF STACK PRESSURE

- Pressure induces interfacial stress
  - Deforms separator, leading to decrease in porosity, tortuosity

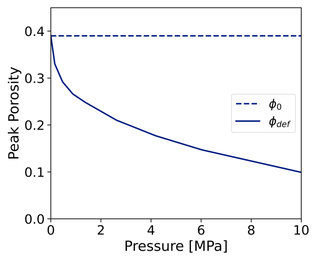
$$\varphi_{def} = 1 - \frac{1 - \varphi_0}{det\langle F\rangle}$$

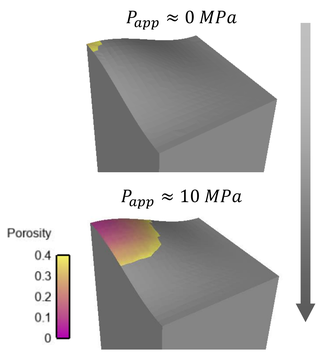
$$\tau_{def} = \phi_{def}^{-1.5}\ [1]$$

  - Increases Li-separator contact area, through which ion transport is limited
  - Impacts exchange current density through Butler-Volmer equation: [2]

$$i_n = i_{0,ref}\varphi \exp\left[\frac{(1-\alpha_a)\Delta\mu_{e^-}}{RT}\right] \times \left[\exp\left(\frac{\alpha_a F\eta_s}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta_s}{RT}\right)\right]$$

$$\Delta\mu_{e^-} = -\frac{1}{2}(\bar{V}_{Li} + t^0_{-}\bar{V}_{LiX}) \times \{-\gamma\bar{\nabla}_s \cdot e_n + e_n \cdot [e_n \cdot (\tau_d^{elec} - \tau_d^{sep})]\} + \frac{1}{2}(\bar{V}_{Li} - t^0_{-}\bar{V}_{LiX})(\Delta p^{elec} + \Delta p^{sep})$$

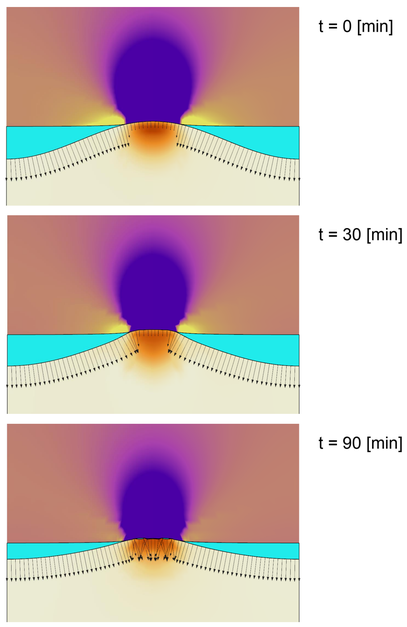




[1] Landesfeind et al., *JES* (2016)
[2] Monroe and Newman, JES (2005)

MOVING INTERFACE

- Second phase of model simulates Li plating
  - State of stress changes as interface evolves
  - Previous work has not taken complexity of separator morphology, electrolyte into account
- Plating and stripping may be modeled over full charge period
  - $P_{app} = 1\ MPa$
  - $I_{app} = 0.5\ mA/cm^2$
  - $\sigma_{Li,yield} = 16\ MPa$
- Applied pressure, current density, and Li yield stress are parameters of interest



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