Modeling Chemo-Mechanics with Electrolyte Infiltration to Quantify Degradation of Cathode Particles.

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GrainCDM Overview

https://fenicsproject.org/

- Grain-scale Continuum damage model
- Couples electrochemistry and mechanics
- Perform CC-CV charge/discharge cycles
- Parallel implementation:
  - 1 Cycle, 1.67 hours, 926 K DOFS, 72 Procs
  - 1.3x to 24x real time (depending on C-rate)
- Collaborators

NREL: VTO

- Andrew M. Colclasure
- Donal P. Finegan
- Weijie Mai
- Anudeep Mallarapu
- Kandler Smith
- Francois Usseglio-Viretta
- Ankit Verma
- Peter J. Weddle
- Sheila Whitman

Ulm

- Volker Schmidt
- Orkun Furat

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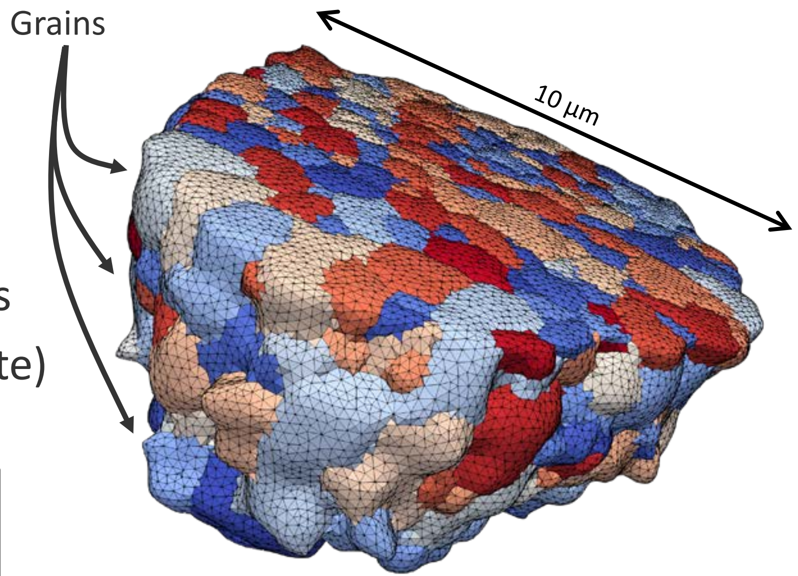
- Tanvir Tanim



Reconstructed Cathode Particle

Contents

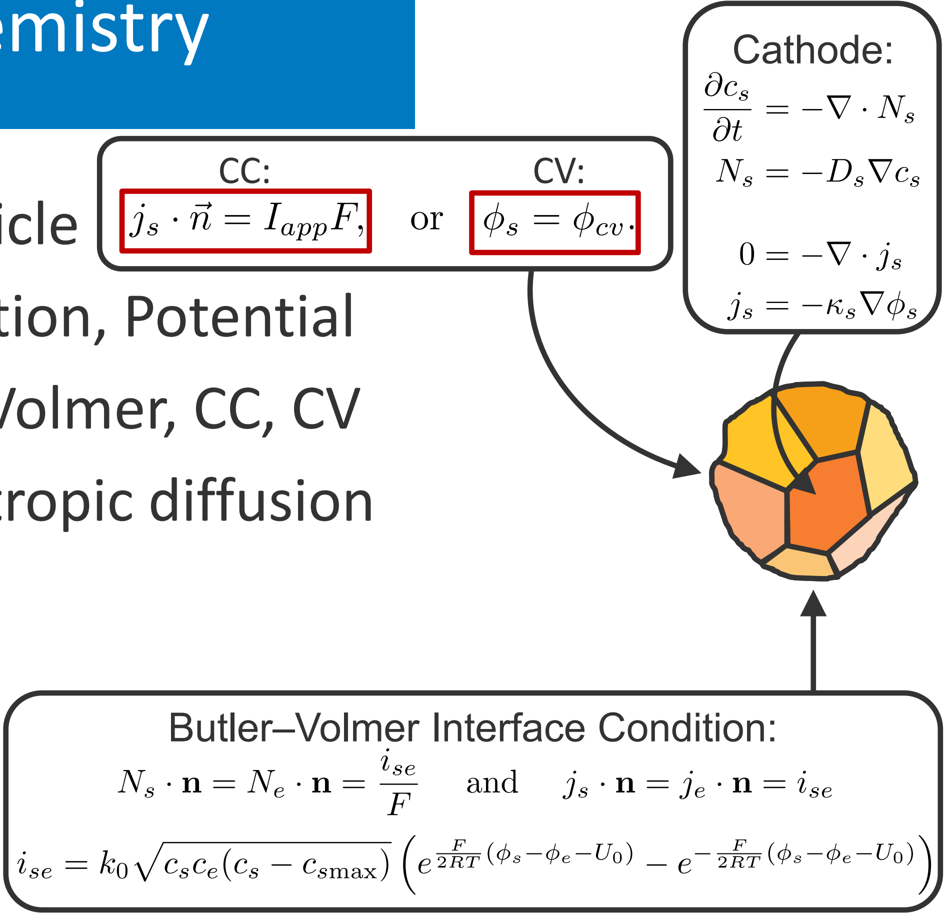
Cathode Electrochemistry

- Domain: single cathode particle
- Bulk equations: Li concentration, Potential
- Boundary condition: Butler-Volmer, CC, CV
- Small modification for anisotropic diffusion within grains:

$$D_s \to -\boldsymbol{R}\boldsymbol{D}_s\boldsymbol{R}^{-1}$$

$$\boldsymbol{D}_s = \begin{bmatrix} s_{xy} & 0 & 0 \\ 0 & s_{xy} & 0 \\ 0 & 0 & s_z \end{bmatrix} D_s$$

$$\boldsymbol{R} = \boldsymbol{R}_z\boldsymbol{R}_y\boldsymbol{R}_x$$



CC: $\boxed{j_s \cdot \vec{n} = I_{app}F,}$ or CV: $\boxed{\phi_s = \phi_{cv}.}$

Cathode:

$$\frac{\partial c_s}{\partial t} = -\nabla \cdot N_s$$

$$N_s = -D_s \nabla c_s$$

$$0 = -\nabla \cdot j_s$$

$$j_s = -\kappa_s \nabla \phi_s$$

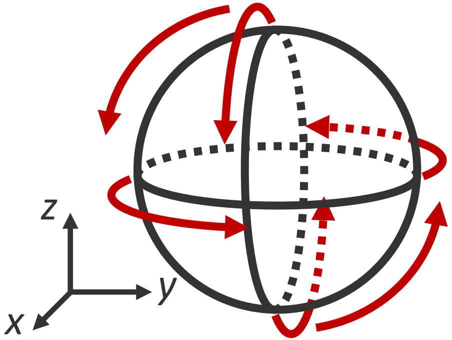
Butler–Volmer Interface Condition:

$$N_s \cdot \mathbf{n} = N_e \cdot \mathbf{n} = \frac{i_{se}}{F} \quad \text{and} \quad j_s \cdot \mathbf{n} = j_e \cdot \mathbf{n} = i_{se}$$

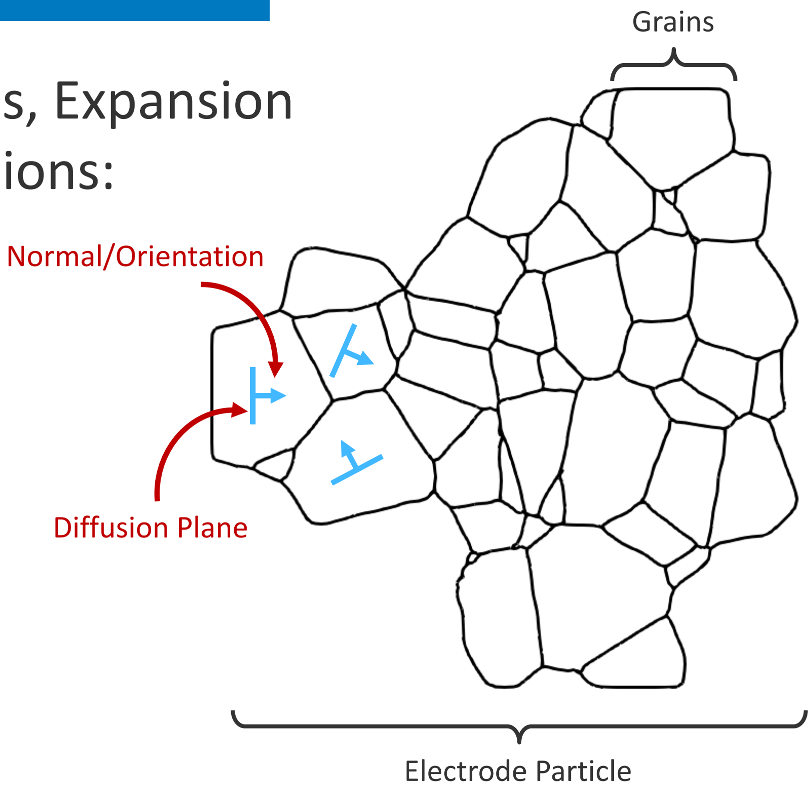
$$i_{se} = k_0\sqrt{c_s c_e (c_s - c_{s\max})}\left(e^{\frac{F}{2RT}(\phi_s - \phi_e - U_0)} - e^{-\frac{F}{2RT}(\phi_s - \phi_e - U_0)}\right)$$

Anisotropic Properties

- Anisotropic Values: Diffusion, Stiffness, Expansion
- Achieved by applying a series of rotations:
    - Roll
    - Pitch
    - Yaw



- Different values defined in each grain
- Currently random
- Eventually empirically determined



Mechanical Model

- Mechanics (Linear elasticity with infinitely small-strain theory)

$$\nabla \cdot \sigma = 0, \quad \text{and} \quad \bar{\sigma} = C[\bar{\varepsilon} - \bar{\beta}\Delta c_s], \ \varepsilon = \frac{1}{2}\left(\nabla u + (\nabla u)^T\right)$$

- Anisotropic Stiffness and Expansion Tensors:

$$C = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{C_{11}-C_{12}}{2} \end{bmatrix}$$

$$\beta = \begin{bmatrix} \beta_t & 0 & 0 \\ 0 & \beta_t & 0 \\ 0 & 0 & \beta_n \end{bmatrix}$$

$$\beta_t = \frac{a_s - a_0}{a_0}$$

$$\beta_n = \frac{c_s - c_0}{c_0}$$

Damage Calculation

- Damage based Equivalent Strain (Cracks when expanding)

$$\varepsilon_{eq}^{e} = \sqrt{\sum_{i=1}^{3} (< \varepsilon_i^e >)^2}$$

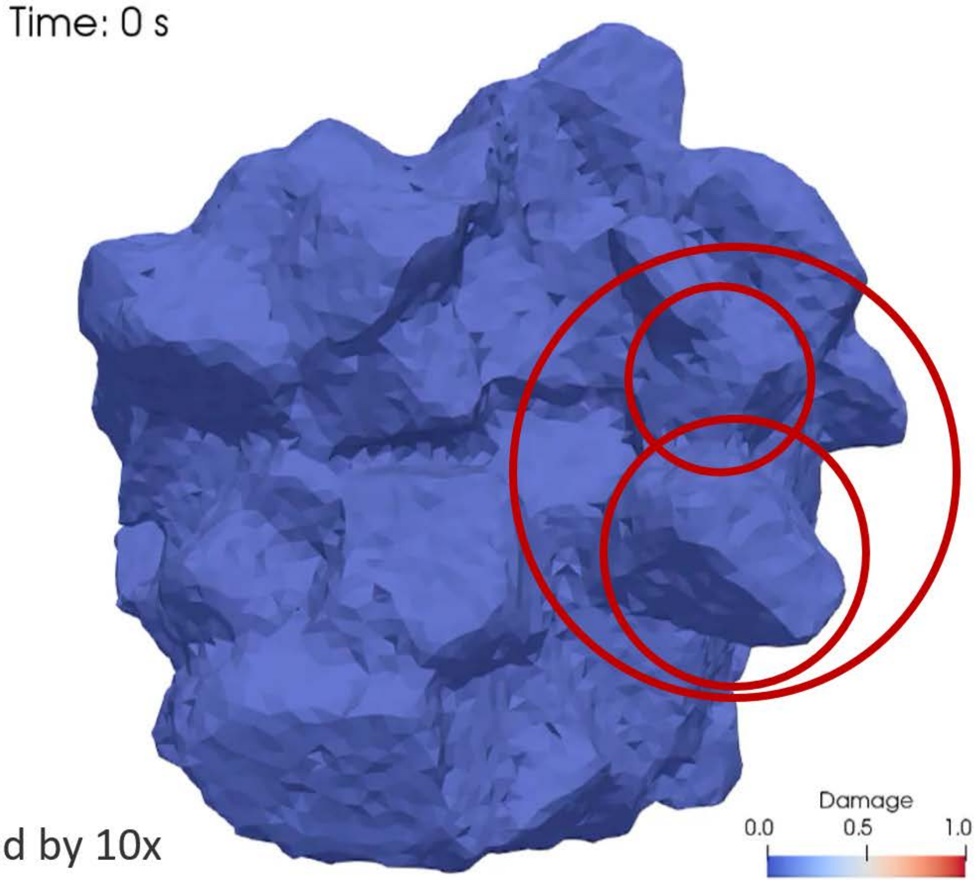
- Damage Thresholding (does not recover)

$$D = \begin{cases} 0 & \text{if } \varepsilon_{eq}^{e} < \boxed{k_i} \xrightarrow{} \text{Crack Initiation} \\ \frac{k_f}{\varepsilon_{eq}^{e}} \frac{\varepsilon_{eq}^{e} - k_i}{k_f - k_i} & \text{if } k_i < \varepsilon_{eq}^{e} < k_f \\ 1 & \text{if } \varepsilon_{eq}^{e} > \boxed{k_f} \xrightarrow{} \text{Complete Failure} \end{cases} \quad \text{and} \quad D_{n+1} = \max\left(\{D, D_n\}\right)$$

- Coupling by attacking Stiffness and Diffusion

$$\hat{C} = \max\left((1-D), 0.1\}\right) C \quad \text{and} \quad \hat{\mathbf{D}}_s = (1-D)\mathbf{D}_s$$

Large Grain at 6C



Displacement Amplified by 10x

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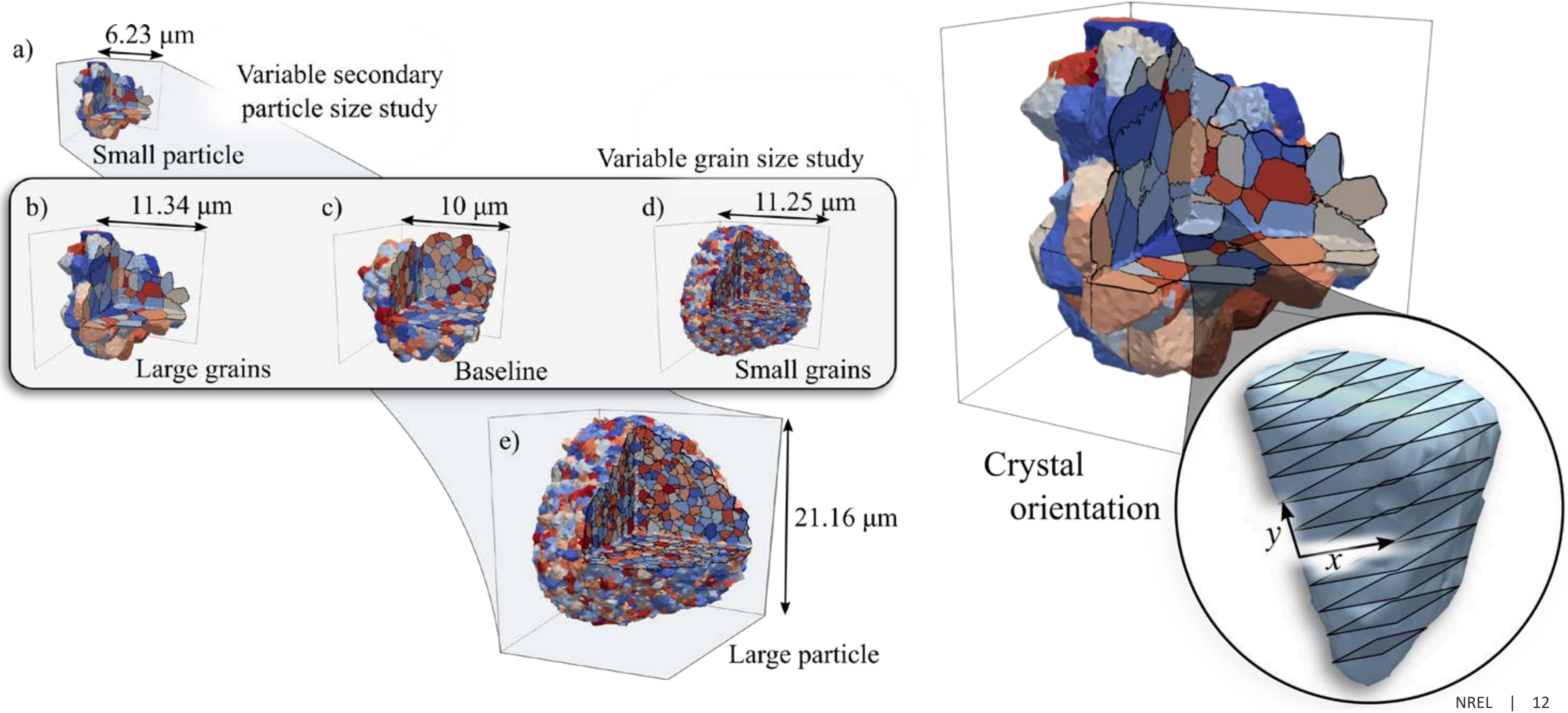
Generated Particles

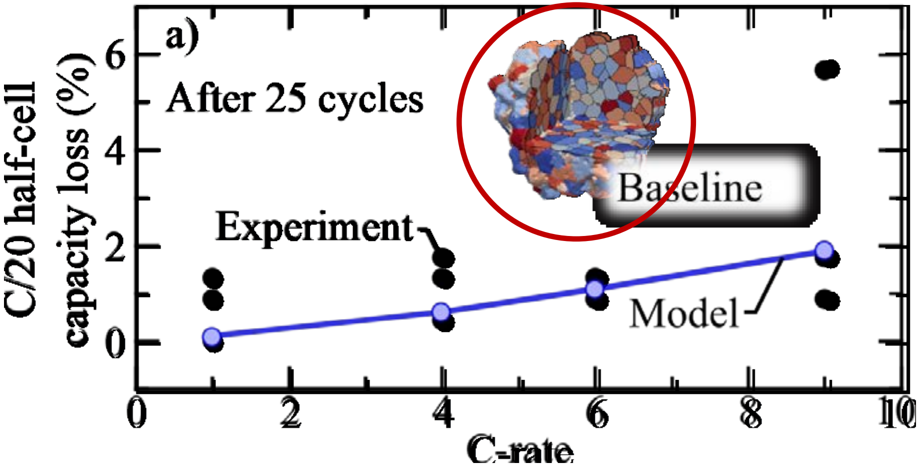


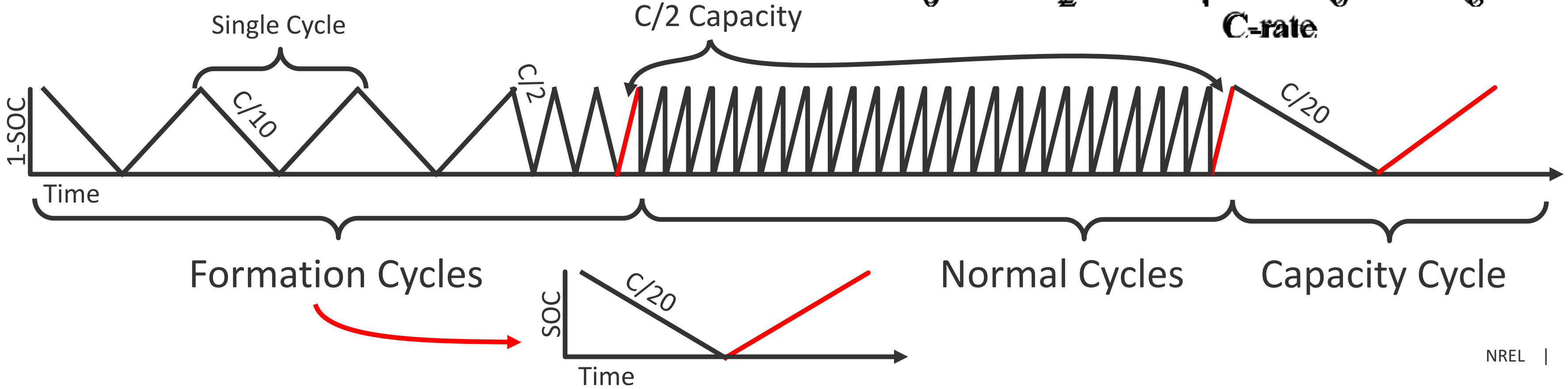
Data Calibration for k_i (NMC532)

(data from T. Tanim, et. al., 2021)

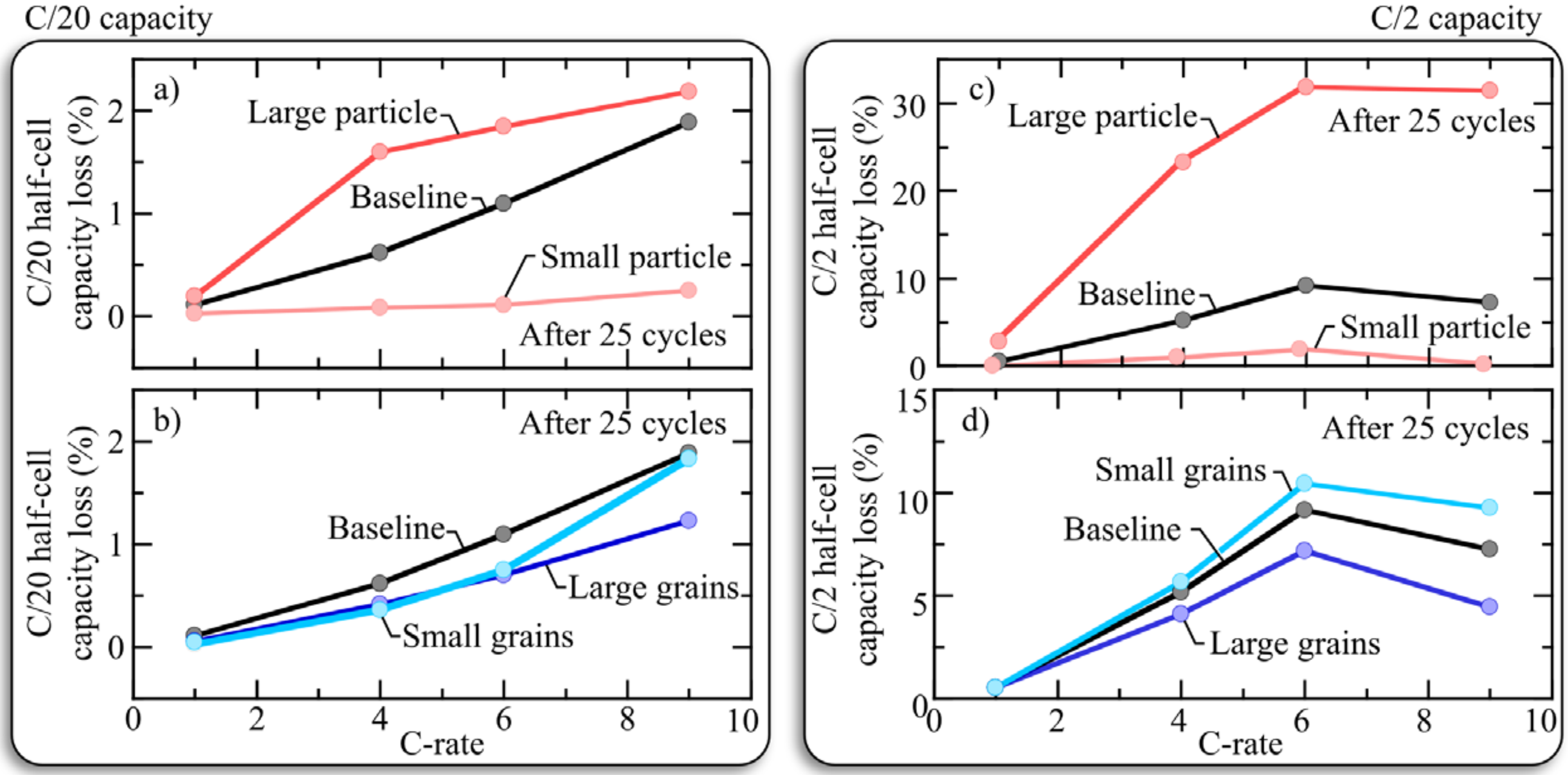
Structure of Simulation:

1. Performed Formation Cycle
2. Cycled 25 time at 1, 4, 6, 9 C
3. Calculate C/20 capacity loss





Capacity Loss



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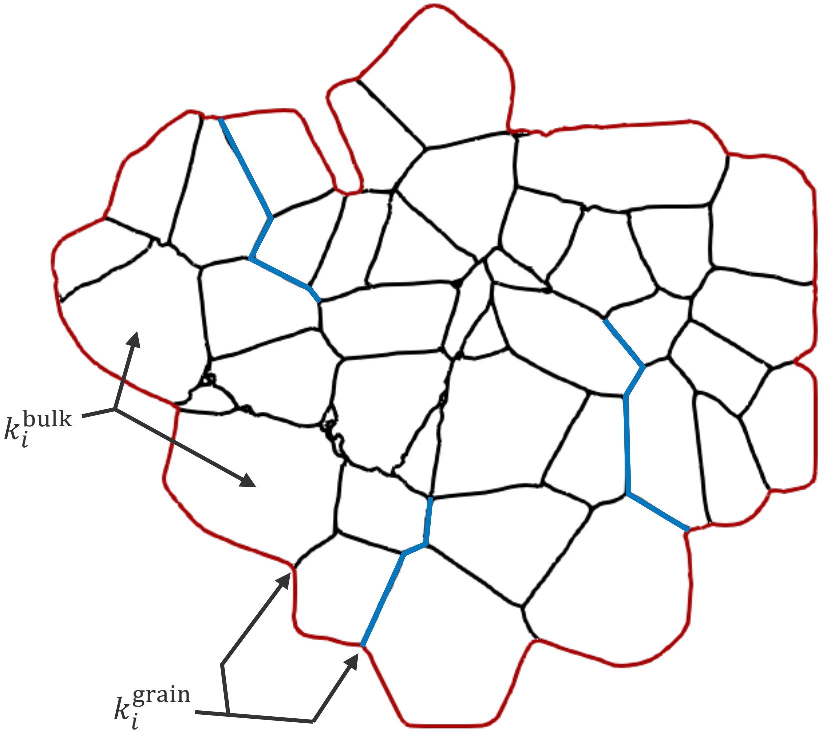
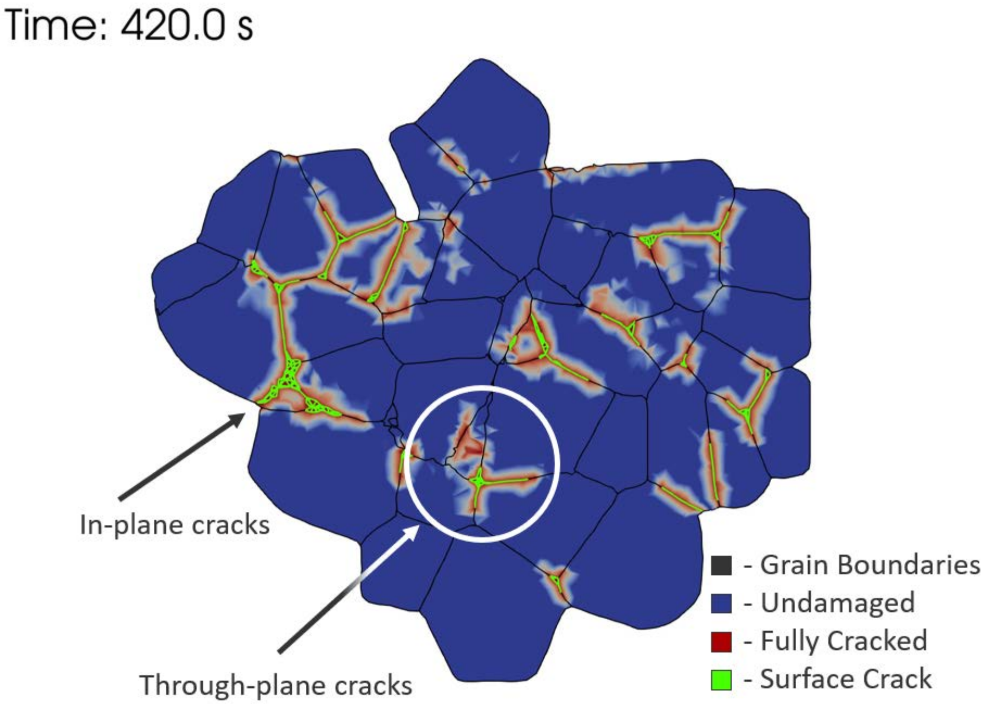
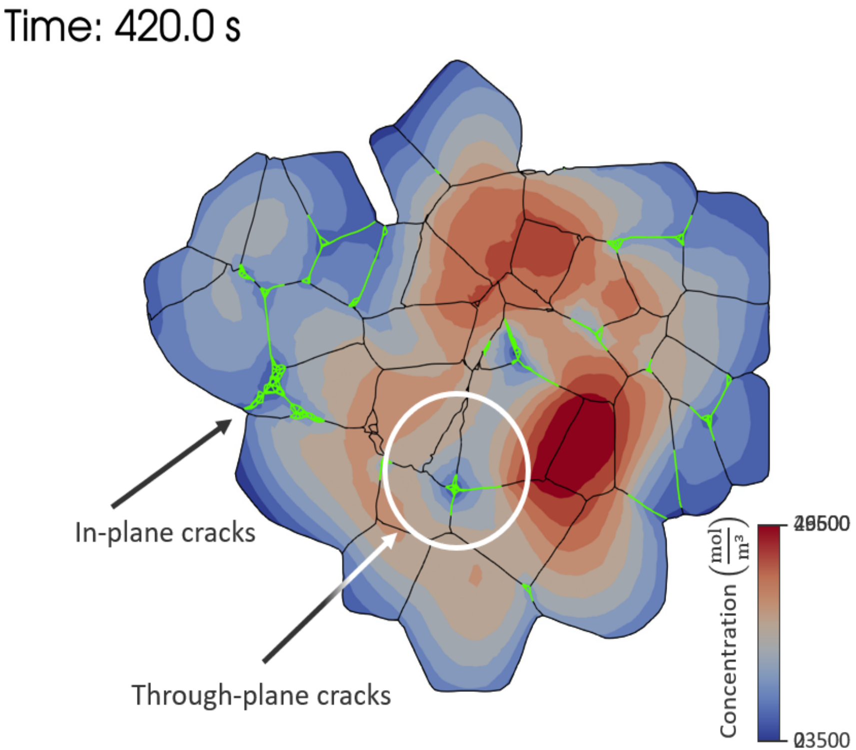
Modeling Electrolyte Infiltration

- Limit cracks to grains boundaries using k_i^{bulk} and k_i^{grain}
- Track which cracks are connected to surface
- Treat surface cracks as new boundary conditions (scaled by new surface area)
- Assumptions:
  - Electrolyte instantly fills cracks
  - Li⁺ immediately available
  - Li⁺ Does not deplete



Modeling Electrolyte Infiltration



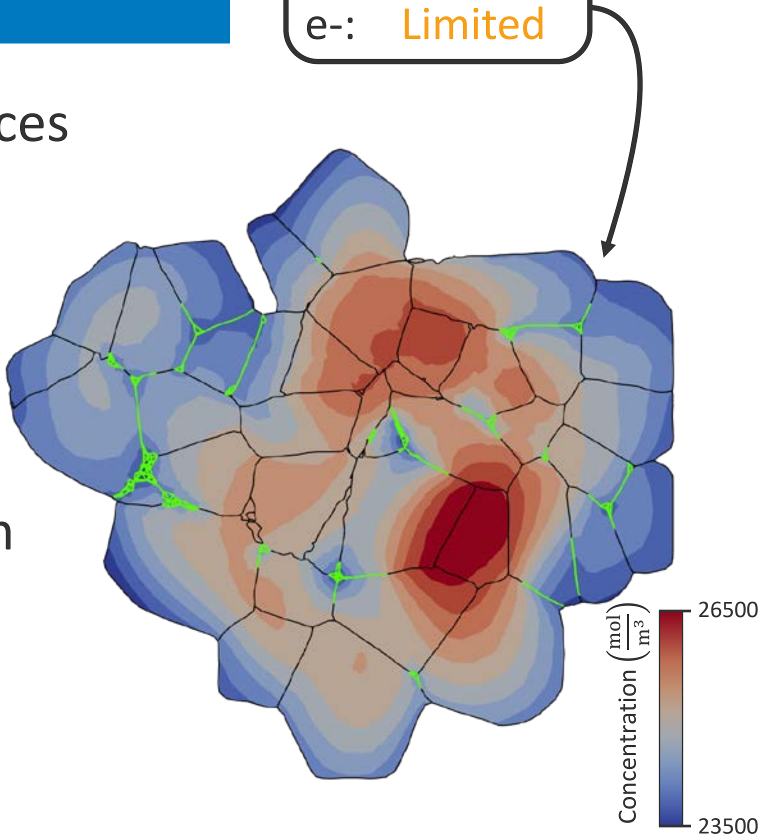


Rescale colorbar for more detail

Unexpected Complications

- Adding EI significantly reduces resistances
- Damage is now a benefit
- More damage leads to higher capacity
- To remedy this, we are investigating Electrical Isolation:
  1. Use realistic conductivity, e-
  2. Remove the potential flux BC from surface cracks
  3. Damage affects conductivity
- We are currently working on implementing this

Within Cracks:
Li+: Available
e-: Limited



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Conclusions & Future Work

- Conclusions:
  - Without EI, smaller particles with larger grains experience reduced capacity loss
  - EI allows Lithium to penetrate deeper into the bulk of a particle
- Future Work:
  - Investigate if EI can explain why NMC811 has resilient capacity despite significantly cracking
  - Looking to couple this high-fidelity model to a reduced-order model to facilitate full life-time simulations.

Thanks for coming!

Questions?

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[1] **J. Allen**, P. Weddle, A. Verma, A. Mallarapu, F. L. E. Usseglio-Viretta, D. Finegan, A. Colclasure, O. Schmidt, V. Furat, D. Diercks, and K. Smith. *Quantifying the influence of charge rate and cathode-particle architectures on degradation of Li-ion cells through 3D continuum-level damage models.* Journal of Power Sources, (2021, under review).

[2] **J. Allen**, J. Chang, F. L. E. Usseglio-Viretta, P. Graf, and K. Smith. *A segregated approach for modeling the electrochemistry in the 3-D microstructure of Li-ion batteries and its acceleration using block preconditioners.* Journal of Scientific Computing, 10.1007/s10915-021-01410-5, (2021).