Enhancing Lithium-Ion Battery Aging Simulations:

Coupling a High-Resolution, 3D, Grain-Scale Electromechanical Model to a Single-Particle Model

242nd Electrochemical Society Meeting October 9, 2022

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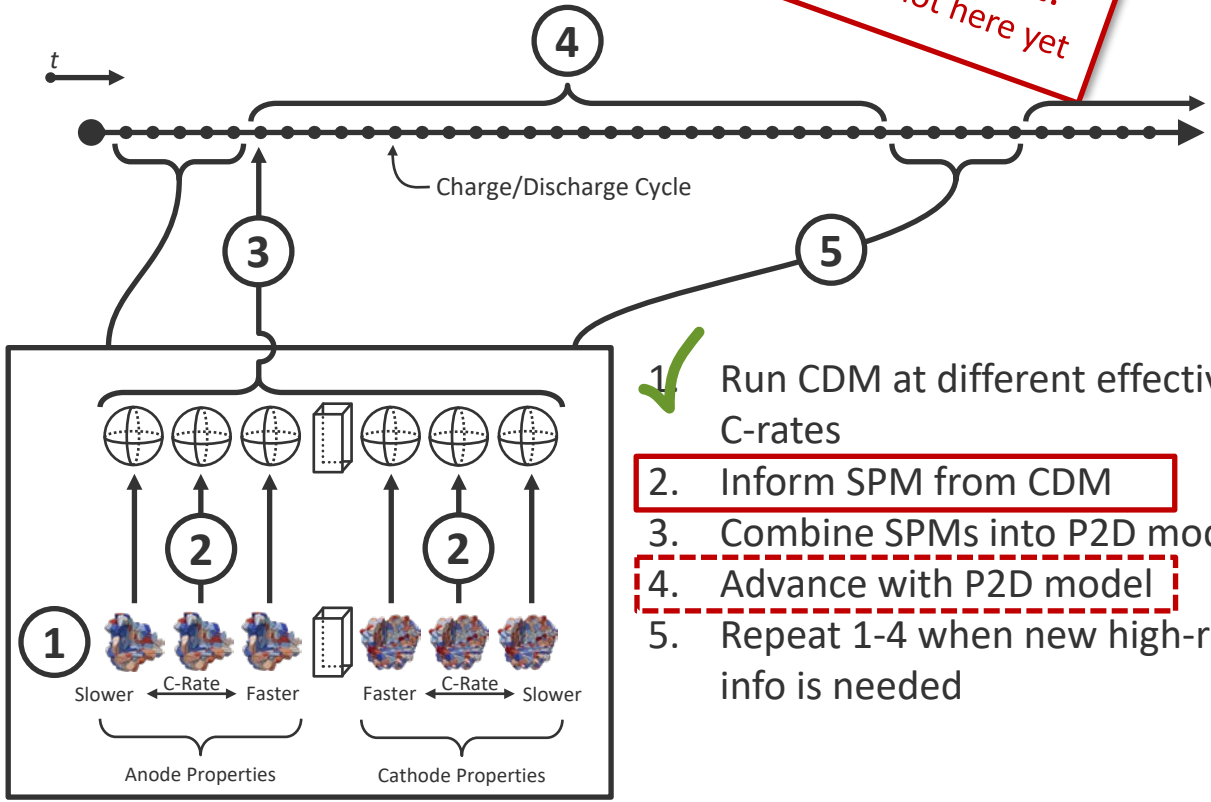
The Ideal Coupled Simulation

- CDM:
  - Continuous Damage Model
  - Micro-scale damage
  - Sub-cycle time scales
- SPM:
  - Single-Particle Model
  - Used to link the CDM to the P2D
- P2D:
  - Pseudo-2D Model
  - Full-cell, macro-scale damage
  - Multi-cycle time scales



Spoiler Alert:
We are not here yet

1. ✓ Run CDM at different effective C-rates
2. Inform SPM from CDM
3. Combine SPMs into P2D model
4. Advance with P2D model
5. Repeat 1-4 when new high-res info is needed

Contents

Grain-Scale 3D Continuum Damage Model – Formulation

- Butler-Volmer kinetics

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

- Anisotropic diffusion

$$\frac{\partial c_s}{\partial t} = -\nabla \cdot N_s \qquad 0 = -\nabla \cdot j_s$$
$$N_s = -D_s \nabla c_s \qquad j_s = -\kappa_s \nabla \phi_s$$

- Anisotropic stiffness and expansion

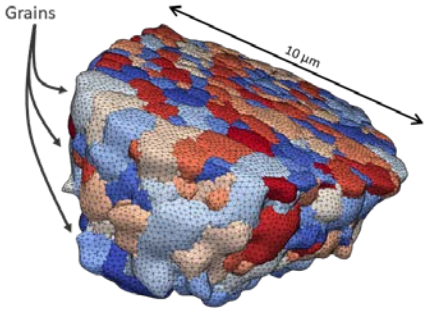
$$\nabla \cdot \sigma = 0, \quad \text{and} \quad \bar{\sigma} = C[\bar{\varepsilon} - \bar{\beta} \Delta c_s], \; \varepsilon = \frac{1}{2}\left(\nabla u + (\nabla u)^T\right)$$

- Damage based on equivalent strain
  - Cracks on expansion
  - Does not recover
  - Damage attacks stiffness and diffusion

$$\varepsilon^e_{eq} = \sqrt{\sum_{i=1}^{3} (< \varepsilon^e_i >)^2}$$

$$D = \begin{cases} 0 & \text{if } \varepsilon^e_{eq} < k_i \\ \frac{k_f}{\varepsilon^e_{eq}} \frac{\varepsilon^e_{eq} - k_i}{k_f - k_i} & \text{if } k_i < \varepsilon^e_{eq} < k_f \\ 1 & \text{if } \varepsilon^e_{eq} > k_f \end{cases} \quad \text{and} \quad D_{n+1} = \max(\{D, D_n\})$$

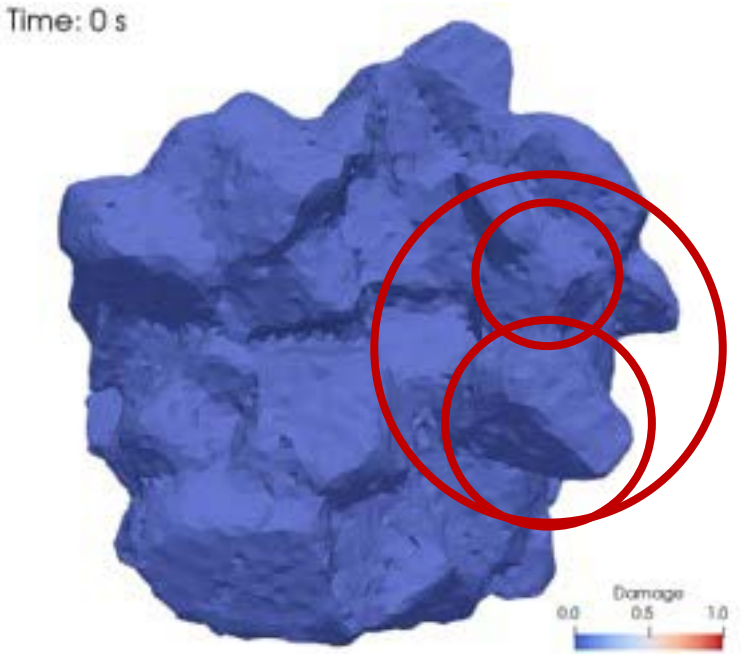
$$\hat{C} = \max((1 - D), 0.1\}) C \quad \text{and} \quad \hat{\mathbf{D}}_s = (1 - D)\mathbf{D}_s$$



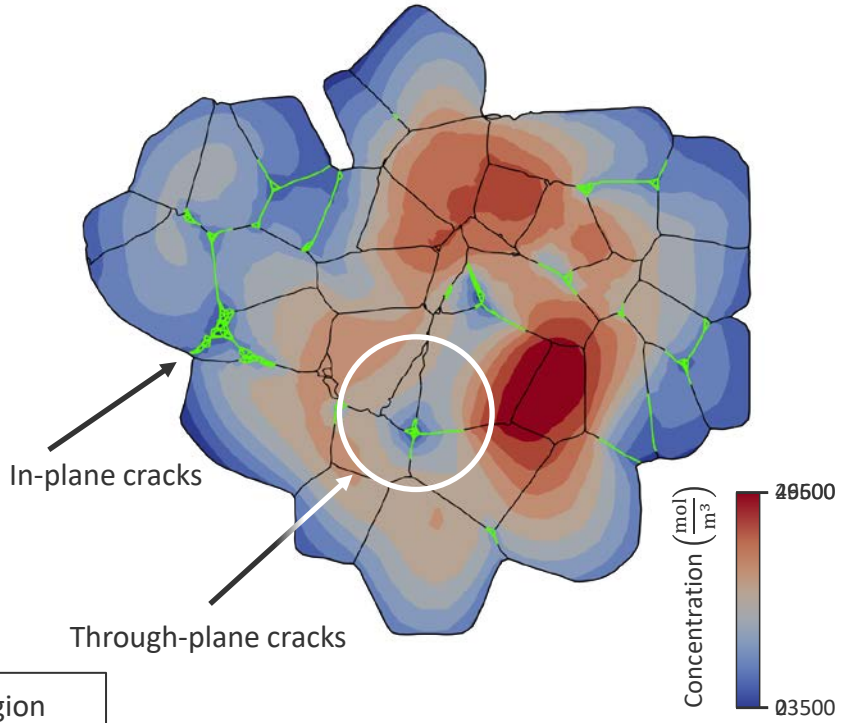
- 3D $Li_yNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ particle, 926k DOFs
- 1 cycle, 1.67 hours w/ 72 processes
- 1.3x to 24x real time (depending on C-rate)
- fenicsproject.org

NMC Anisotropic Strain-Induced Damage

3D electrochemo/mechanical model
- Anisotropic transport, exp./contraction
- Butler-Volmer boundary conditions
- Continuum damage → 3D multiple cycles
- Electrolyte infiltration

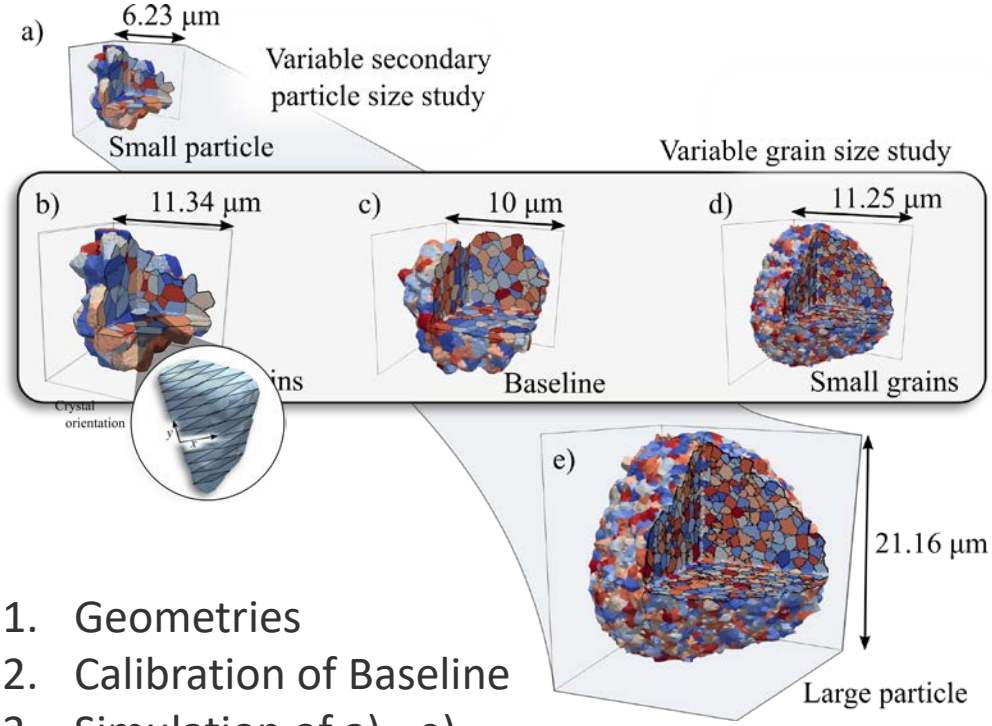


Post Processed Displacement Amplified by 10x



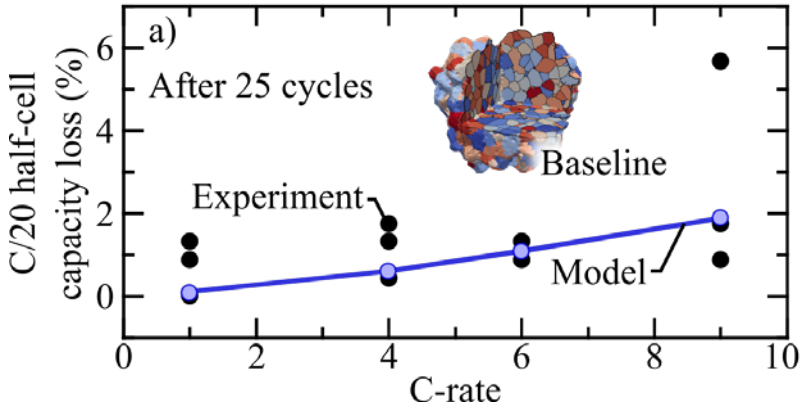
- Fully damaged region
- Surface-connected crack

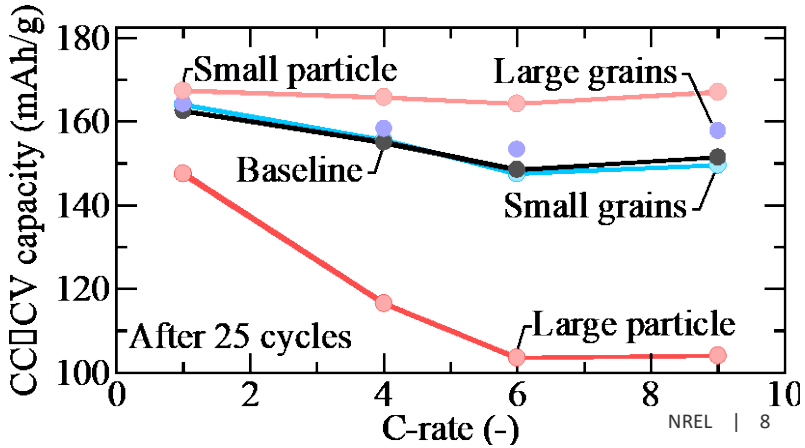
Geometry Study



1. Geometries
2. Calibration of Baseline
3. Simulation of a) - e)
4. Small particles with large grains perform better

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





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SPM -> CDM

- **Goal**: Use the continuous damage model (CDM) to inform parameters in the single-particle model (SPM).
- **Method**: Using the voltage curve from a given CDM simulation, optimize the design variables to minimize the difference in the SPM voltage curve.
- **Design Variables**: diffusion, radius, exchange current density, overpotential

Single-Particle Model

- Concentration:

$$\frac{\partial c}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial c}{\partial r}\right)$$

- Potential:

$$0 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(\kappa_s r^2 \frac{\partial \phi}{\partial r}\right)$$

- Boundary Condition:

$$F\nabla c \cdot \vec{n} = \nabla \phi \cdot \vec{n} = i = 2i_0(c)\sinh\left[\frac{F}{RT}\left(\phi - E^{\mathrm{eq}}(c)\right)\right]$$

Single-Particle Model (Modified)

- Concentration:

$$\frac{\partial c}{\partial t} = \frac{1}{{R_f}^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_f D_s r^2 \frac{\partial c}{\partial r}\right)$$

- Potential:

$$0 = \frac{1}{{R_f}^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(\kappa_s r^2 \frac{\partial \phi}{\partial r}\right)$$

- Boundary Condition:

$$F\nabla c \cdot \vec{n} = \nabla \phi \cdot \vec{n} = i = 2I_f i_0(c) \sinh\left[\frac{F}{RT}\left(\phi - E^{\mathrm{eq}}(c) - U_f\right)\right]$$

Optimization

- Objective Function:

$$J = \|\phi_{SPM}(t) - \phi_{CDM}(t)\|_2 \qquad \text{for } \phi_{CDM}(t) < 4.2 \text{ V}$$

- Design Variables:

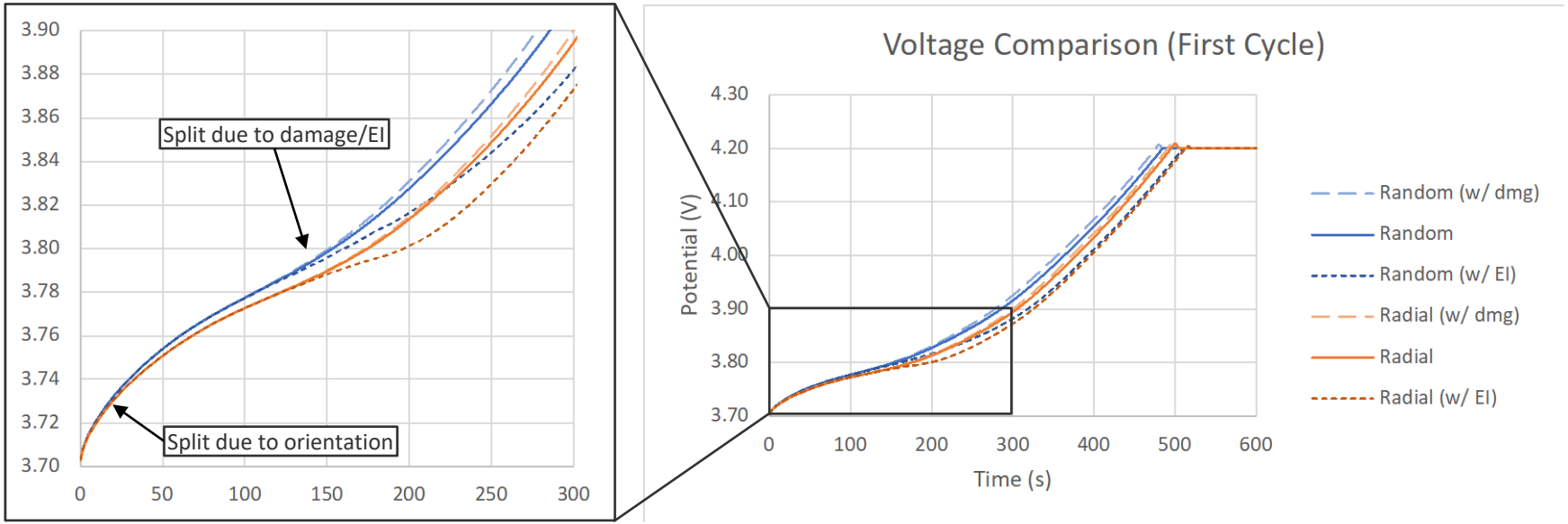
$$D_f - \text{Diffusion Factor}$$
$$R_f - \text{Radius Factor}$$
$$I_f - \text{Exchange Current Factor}$$
$$U_f - \text{Overpotential Offset}$$

- Four Parings:

$$(D_f,\ R_f),\ (D_f,\ I_f),\ (D_f,\ U_f),\ (R_f,\ I_f)$$

Also referred to as DR, DI, DU, and RI cases

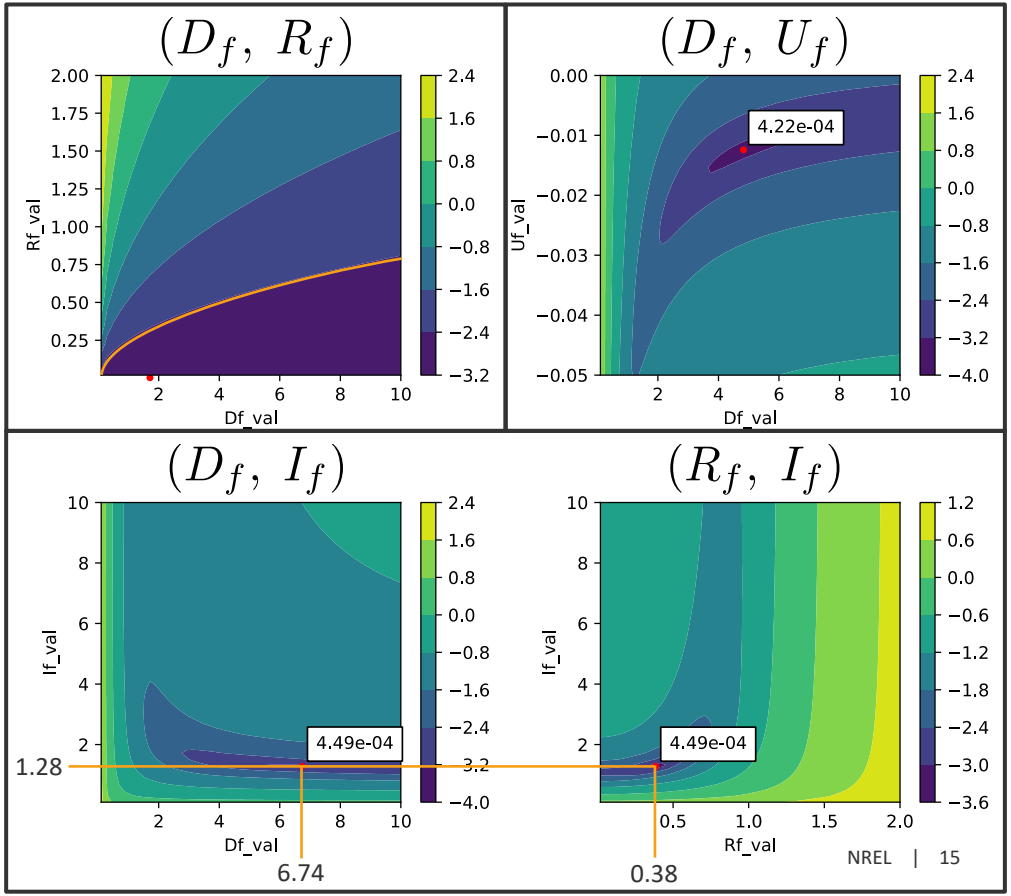
Target Voltages (CDM)



EI = Electrolyte infiltration, dmg = Damage is turned on

CDM: Radial Orientation + Damage On

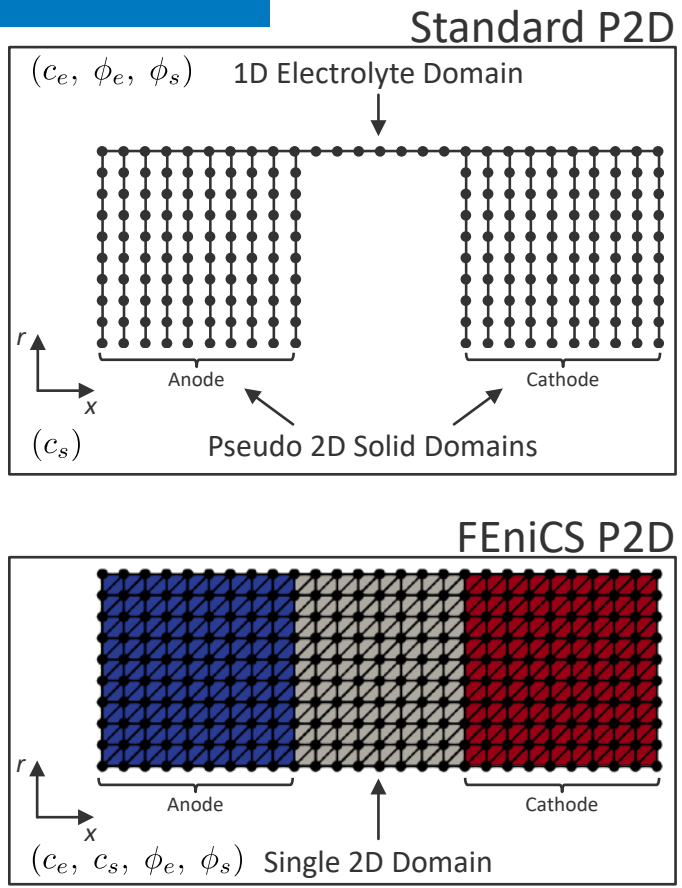
- Lowest resistance case
- DR case does not have a unique minimum
- Side note: DR case exhibits sqrt type behavior
- DU case gets best match but is not physically defendable
- DI and RI have similar minima and are technically identical for the SPM
- Note: 1/sqrt(6.74) ≈ 0.38
- Clearly, we should use DI or RI



Contents

Setting up a P2D model in FEniCS

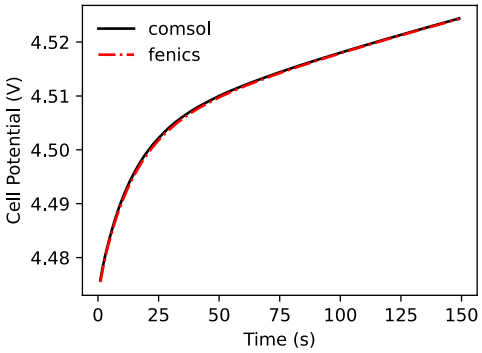
- P2D model is closer to a series of weakly linked ODEs
- FEniCS works best with PDEs on a single domain
- This results in extra overhead associated with the FEniCS model
- This also gives access to dolfin_adjoint for optimization

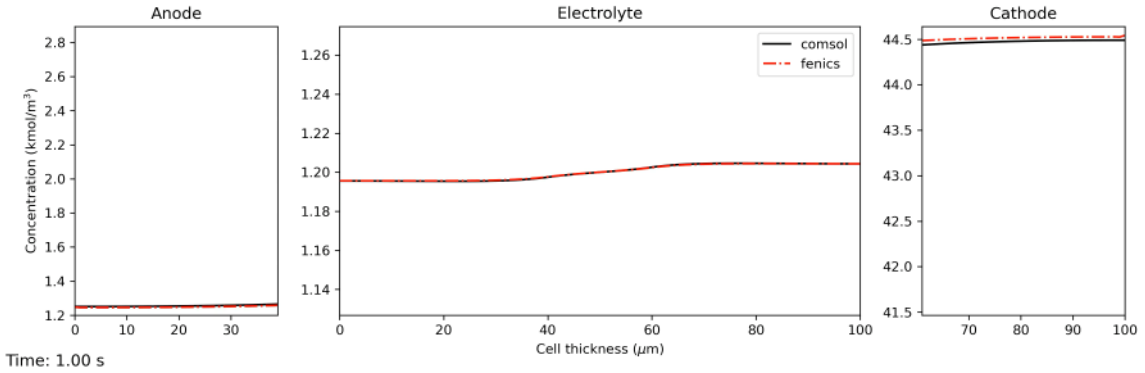


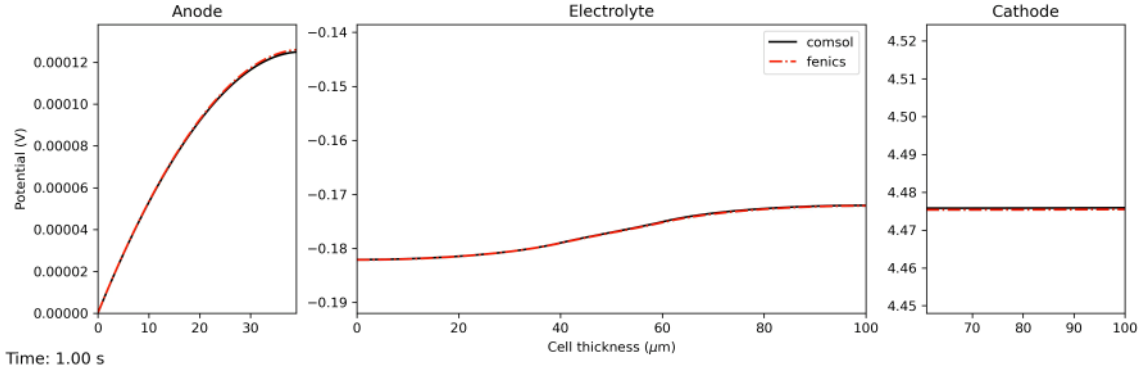
Standard P2D graphic inspired by C. Macklen, Continuum-Scale Lithium-Ion Battery Cell Model in FEniCS, 2019

P2D Verification

- Simple parameters simulated in both COMSOL and FEniCS
- Cell potential and surface concentration/voltage compared



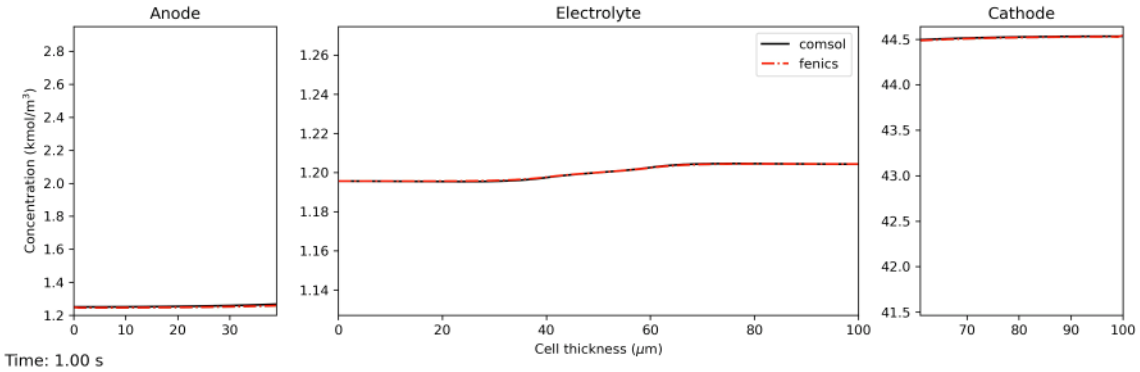


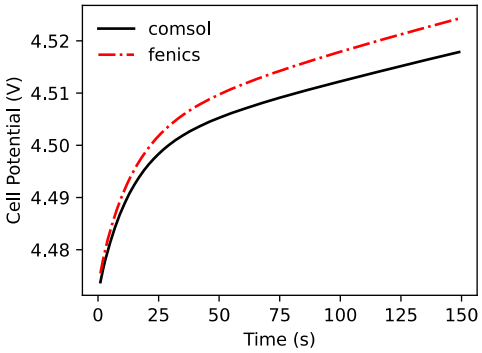


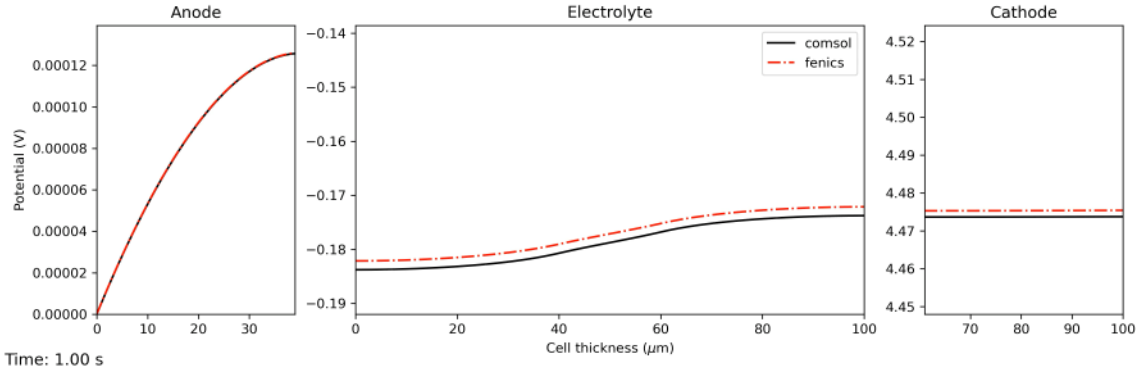
Surface Values

P2D Modification

- Parameters modified in COMSOL model
- Anode: $I_f = 1.2$
- Cathode: $D_f = 2.0$

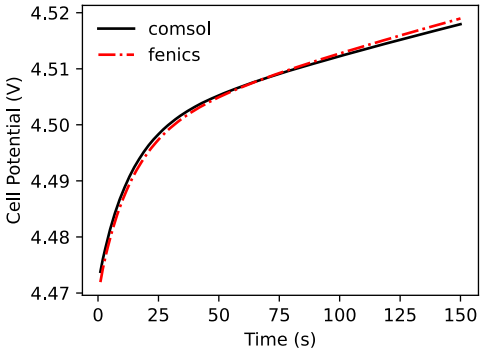


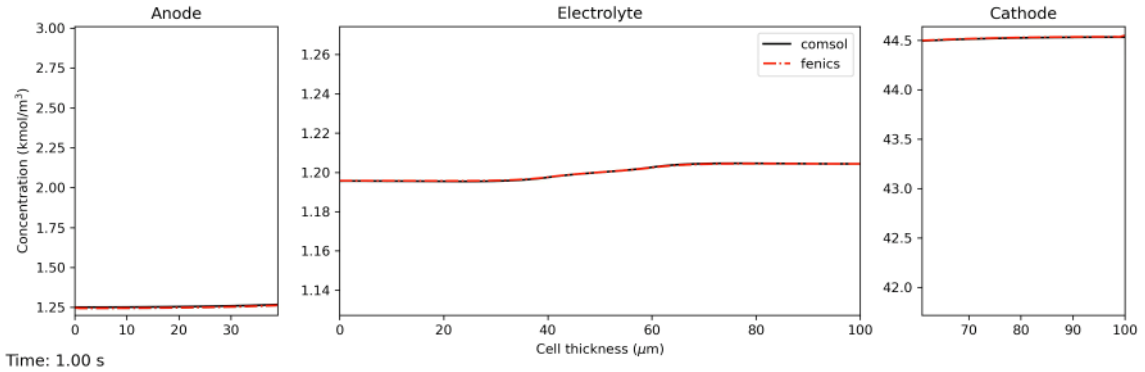


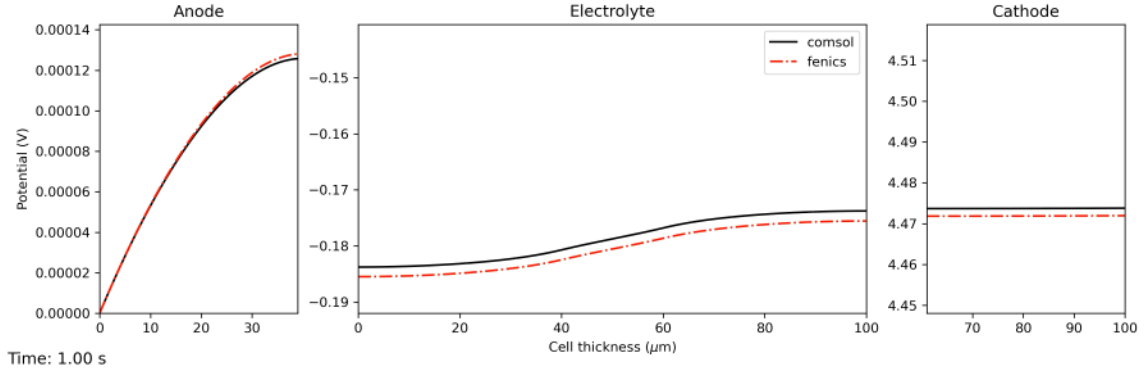


P2D Optimization

- Minimized error in cell voltage over 150 s
- Anode: $I_f = 1.49002658$
- Cathode: $D_f = 1.28533679$
- Local minimum







Contents

Conclusions and Future Work

- Conclusions:
  - Each model works individually.
  - Optimizations can be used to link models, either directly or by informing a relationship between parameters
- Future work:
  - Refine P2D model to include realistic parameters
  - Expand the type of P2D optimization (charging profiles?)
  - Couple all three parts to enable lifetime aging simulations

Thanks for coming!

Questions?

NREL/PR-2C00-83439

This work was authored in part by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308, and in part by Idaho National Lab, United States, operated by Battelle Energy Alliance for the U.S. Department of Energy under contract DE-AC07-05ID14517. Funding provided by the U.S. DOE Vehicle Technologies Office Energy Storage Program, eXtreme Fast Charge and Cell Evaluation of Lithium-Ion Batteries (XCEL) Program, program manager Samuel Gillard. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

A portion of This research was performed using computational resources sponsored by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy and located at the National Renewable Energy Laboratory.

Our Papers

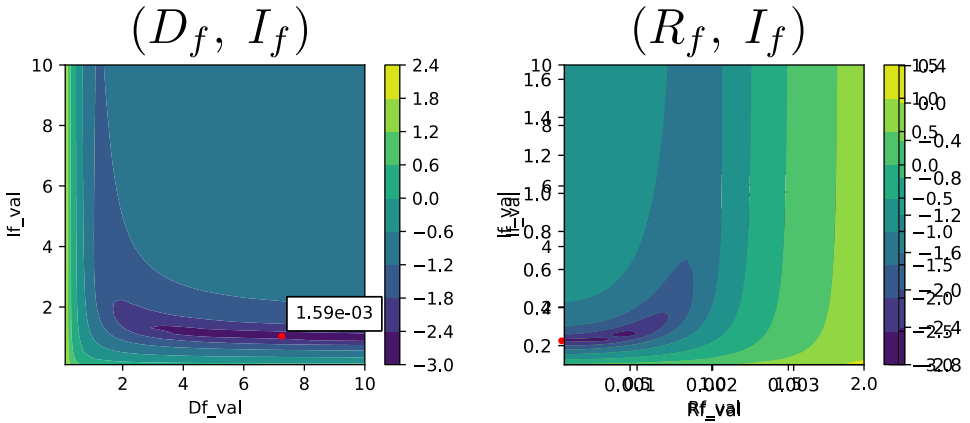
Funded through VTO

[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).

[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).

Which to choose: DI or RI

- **Problem with DI**: solid diffusion is not factored into electrolyte for P2D
- **Problem with RI**: numerically unstable
- **Solution**: Preform the DI optimization and then compute the corresponding $R_f = 1/\text{sqrt}(D_f)$



- CDM Case: Random Orientation + Damage On
- DI results in $D_f = 7.25$
- This should yield $R_f = 0.37$ based on 1/sqrt(*Df*)
- RI optimization yields $R_f = 0.00203$
- Initial condition shoot R_f to lower boundary (0.002)
- Locally insensitive to changes in R_f stall optimizer

Justification

The R_f in the potential equation can be ignored since that equation equals zero, so lets look at the concentration equation:

$$\frac{\partial c}{\partial t} = \frac{1}{{R_f}^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_f D_s r^2 \frac{\partial c}{\partial r}\right)$$

Since D_f is constant with respect to r:

$$= \frac{D_f}{{R_f}^2}\frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial c}{\partial r}\right)$$

Now, set $C_f = \frac{D_f}{{R_f}^2}$,

$$= C_f \frac{1}{r^2}\frac{\partial}{\partial r}\left(D_s r^2 \frac{\partial c}{\partial r}\right)$$

and optimize for C_f and I_f. To recover R_f, set $D_f = 1$ and use

$$R_f = 1/\sqrt{C_f}$$