NREL
Transforming ENERGY

Project ID # bat299

DOE Vehicle Technologies Program
2019 Annual Merit Review and Peer Evaluation Meeting

Microstructure Characterization and Modeling for Improved Electrode Design

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National Renewable Energy Laboratory
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Daniel Abraham, Andy Jansen, **Argonne National Laboratory**
Aashutosh Mistry, Ankit Verma, Partha Mukherjee, **Purdue University**

Overview

This project was awarded in response to VTO Fiscal Year (FY) 15 Lab Call.

Timeline

- Project start date: Oct. 2015
- Project end date: Sept. 2019
- Percent complete: 85%

Budget

- Total project funding: $ 3.35M
  - DOE share: 100%
- Funding received in FY 2016: $1.05M
  Funding received in FY 2017: $1.05M
  Funding received in FY 2018: $600k
  Funding received in FY 2019: $650k

Barriers

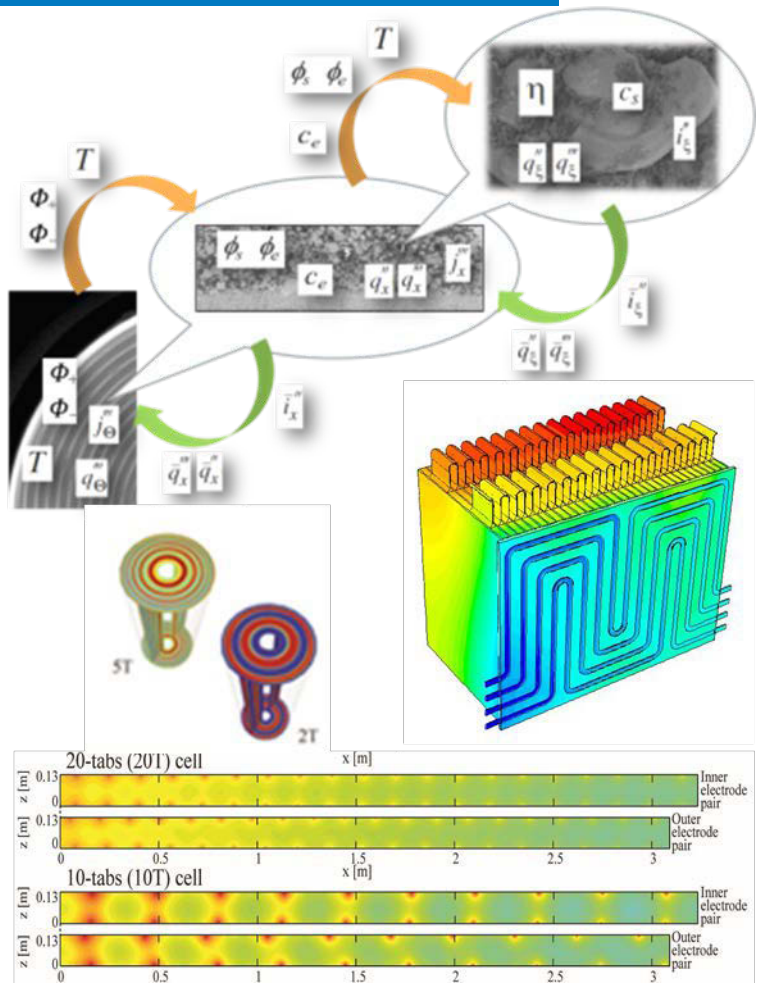
- Gaps between modeling tools and cell design process in the industry
- Lack of simulation models capturing the effect of electrode recipe, including inert components, on performance
- Low-cost, thick electrodes limited by tortuosity

Partners

- Lead: National Renewable Energy Lab (NREL)
  - Microstructure characterization and 3D simulation.
- Argonne National Laboratory (ANL)
  - Graphite/Nickel-Manganese-Cobalt 532 (NMC532) electrode library and electrochemical characterization
- Purdue University
  - Stochastic reconstruction of electrodes and carbon-binder numerical generation
  - Meso-scale modeling of electrode recipes
- University College of London (UCL)
  - X-ray computed tomography imaging
- Brigham Young University (BYU)
  - Tortuosity measurement

Relevance

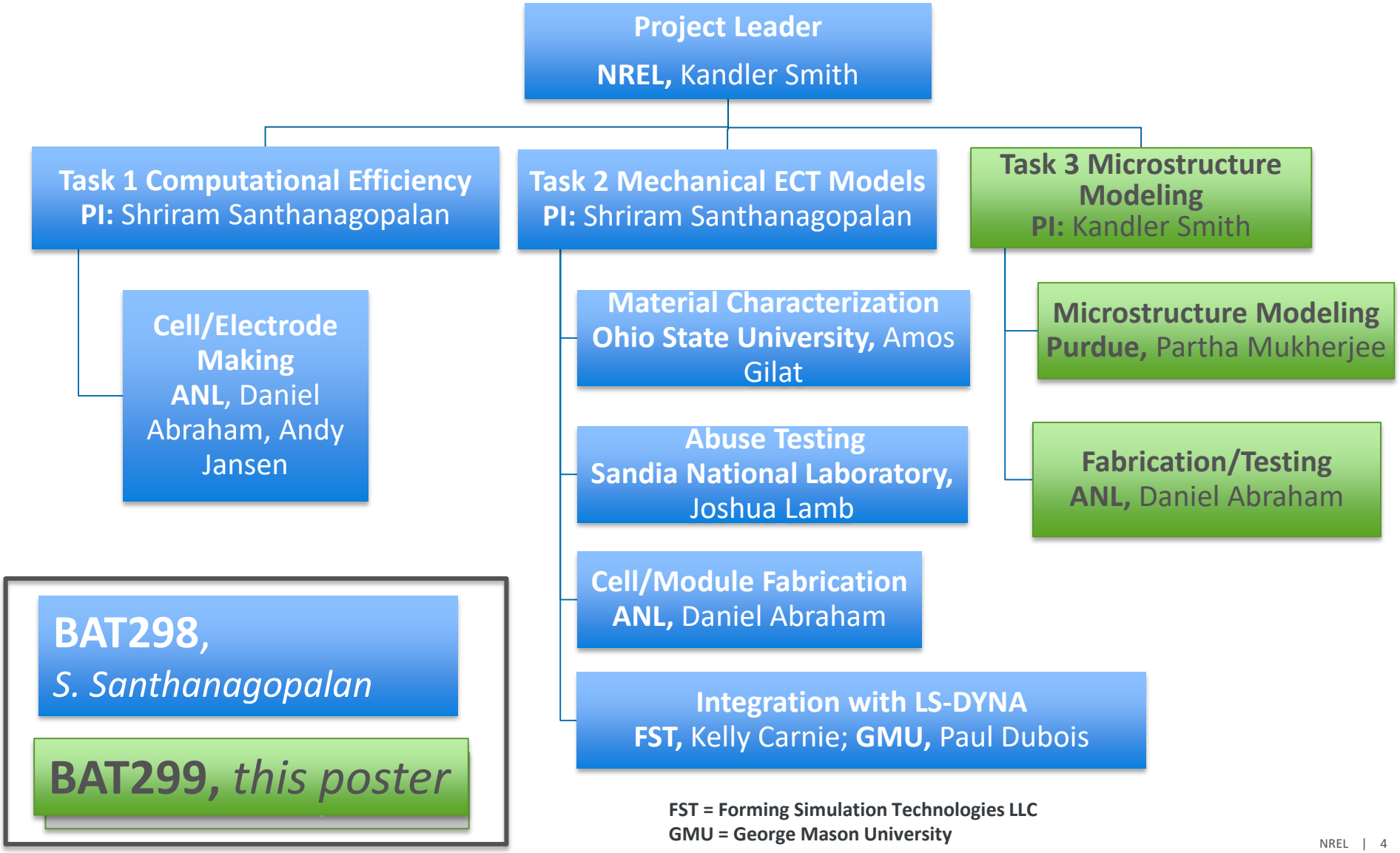
- VTO launched the Computer-Aided Engineering of Batteries (CAEBAT) project to develop validated modeling tools to accelerate development of batteries, in support of vehicle electrification R&D to reduce dependence on imported oil.
- Over 40 different end users from the community have adopted the Multi-Scale Multi-Domain (MSMD) modeling approach developed under CAEBAT.
- Feedback from the first few sets of end users has helped us identify priorities that will enable wider use of model-based design:
  - Standardize identification of the model parameters
  - Increase computational efficiency
  - Extend the models to include mechanical failure of cells and packaging components
  - **Close gaps between materials R&D and CAEBAT modeling tools**
- We are now licensing beta versions of NREL models to the industry and academic partners to identify technical gaps in simulation capabilities.



MSMD models previously developed in CAEBAT have been widely adapted in the community and have helped us identify gaps.

Project Structure

Project Title: Computer-Aided Battery Engineering Consortium

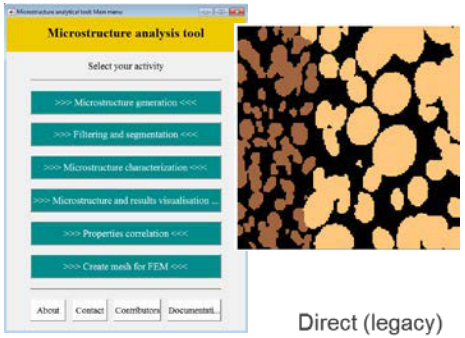


FST = Forming Simulation Technologies LLC
GMU = George Mason University

Relevance – March 2018 to March 2019 Objectives

1) Microstructure analysis:

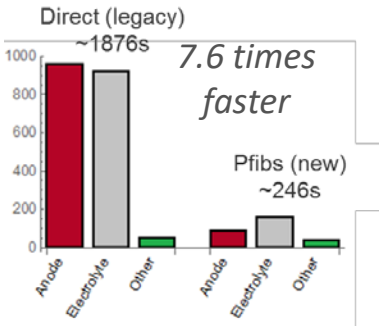
- Build an open-source toolbox to speed up & standardize the macro- and micro-battery modeling workflow
- Develop microstructure generation algorithm dedicated to investigate particle heterogeneities impact on degradation mechanism and alternative electrode design



2) 3D microstructure modeling

- Improve numerical stability and speed up numerical calculation to enable calculations on representative volume

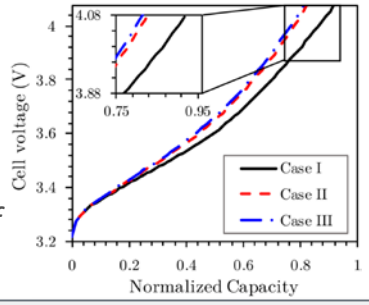
Enables domains 38 times larger



3) Electrochemical macro-homogenous model extension to new physics

- Implement large deformation for silicon anode
- Consider multi-phase, multi-reaction and polycrystalline systems

Impact of Si strain



NMC532 Polycrystalline architecture

Impact: By making disruptive computer-aided engineering (CAE) design tools for use by the battery community, this effort supports the following goals identified by the VTO:

1. Reduce the number and duration of battery test cycles in the industry to enable a path to $80/kWh electric vehicle (EV) battery cost
2. Provide physical insights to optimize thick electrode designs for low-cost, high energy density cells with reliable, high rate performance, considering different chemistry and complex reaction

Milestones

	Milestone Name/Description	Deadline	Milestone Type	Status
Computational Efficiency	M 1.2 MSMD identification and simulation of graphite/NMC532 system	1/31/2017	Quarterly Progress Measure (Qrt. Prog. Meas.)	Done
	M 1.4 Submit journal article on analysis of NMC532 solid state diffusivity concentration dependence from Galvanostatic Intermittent Titration Technique (GITT) experiments	11/30/2017	Qrt. Prog. Meas.	Done
	M 1.5 Report summarizing ability of macro-homogeneous model to predict performance of ANL Cell Analysis, Modeling, and Prototyping (CAMP) electrodes of varying thickness and porosity	3/31/2018	Qrt. Prog. Meas.	Done
Mechanical Abuse	M 2.2 Detailed documentation describing the mechanical tests procedure for development and validation of constitutive models for individual battery components	7/31/2017	Annual SMART	Done
	M 2.3 Interim update on mechanical models demonstrating damage propagation	6/30/2018	Qrt. Prog. Meas.	Done
	M 2.4 Report summarizing model validation for mechanical-electrochemical-thermal (MECT) simulations	9/30/2018	Qrt. Prog. Meas.	Done
	M 2.5 Document implementation of mechanical abuse simultaneous coupling in the form of case studies (.k files) that can be distributed	3/31/2019	Qrt. Prog. Meas.	Done
	M 2.6 Present final report on the MECT models at the Vehicle Technologies Office Annual Merit Review	6/30/2019	Annual SMART	On track
Microstructure	M 3.2 Present microstructure project update at AMR	4/30/2017	Qrt. Prog. Meas.	Done
	M 3.3 Comparison of microstructural model simulations from both stochastic reconstructed (simulated) and tomographic (measured) geometries	9/30/2017	Qrt. Prog. Meas. (Go/No-Go)	Done
	M 3.4 Report on 3D microstructure electrochemical model algorithm enhancements for improved computational speed, accuracy, and scalability	12/31/2018	Qrt. Prog. Meas.	Done
	M 3.5 Demonstrate electrochemical models enhanced with mechanical and/or multi-reaction mechanisms with application to VTO materials research	9/30/2019	Qrt. Prog. Meas.	On track

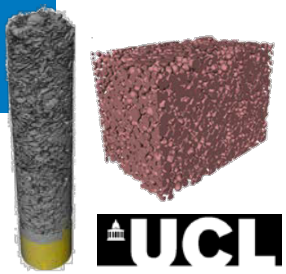
Image credits:
Microstructure – Partha Mukherjee, Purdue
HPC – NREL image gallery

Approach

PURDUE UNIVERSITY

Carbon-Binder Domain (CBD) numerical generation & meso-scale physics

Validation of virtual 3D geometry



UCL

Tomographic measurement

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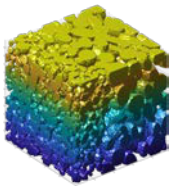
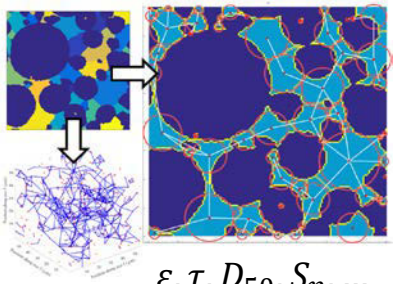
Microstructure analysis

Geometry (generated & tomography-based)

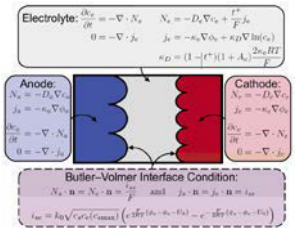


Microstructure characterization



$\varepsilon, \tau, D_{50}, S_p, \ldots$

Physics (electro-chemical model)



High performance computing (HPC)

Argonne NATIONAL LABORATORY

Electrode fabrication, & electrochemical response

UC San Diego

Ni-rich NMC cathodes

BYU

Homogenization experimental verification

Homogenization

Electrochemical simulation

Suggest new design

Linkage to CAEBAT macroscopic simulation toolsets. Implement multi-physics, multi-reaction mechanisms

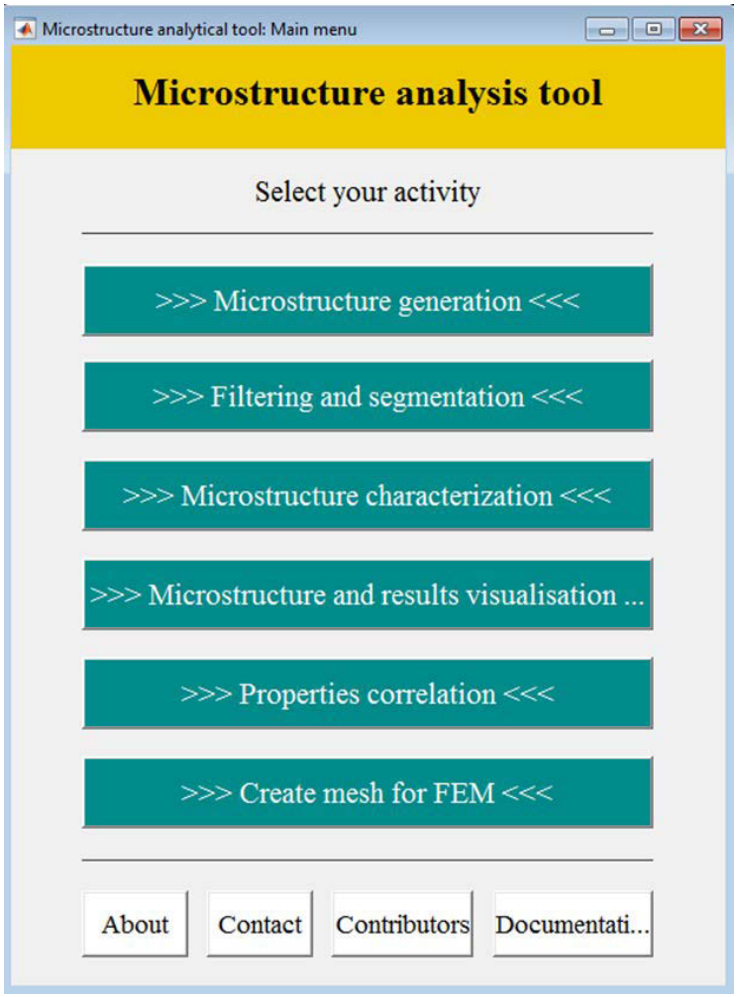
Linkage to extreme fast charge program BAT339

Material Microstructure Analysis

Microstructure Analysis Tool

- Microstructure analysis supports macro-homogenous (provides microstructure parameters) and micro-scale (provide geometry) electrochemical battery models.
- Automated workflow based upon a graphic user-interface (GUI) can **reduce working time, errors, and promote standard analysis beneficial for reproducibility and comparability.**
- NREL is developing a MATLAB user-friendly GUI microstructure analysis open-source toolbox, which covers most of the microstructure-related tasks:
  - 3D microstructure generation
  - 3D microstructure filtering and segmentation
  - 3D microstructure characterization and properties correlation
  - 3D microstructure meshing (Iso2mesh third-party open-source code)

Tool not restricted to battery microstructure. Applicable to any other porous materials (e.g., fuel cell electrodes)



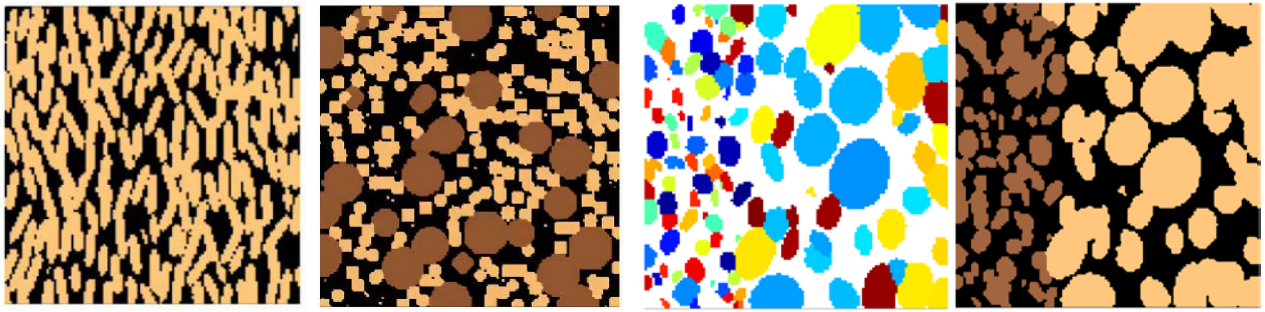
Algorithms 95% done

GUI 70% done

On track to be published open-source this year at https://www.nrel.gov/transportation/data-tools.html

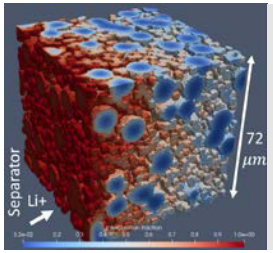
Examples and Applications: 3D Volumes

- Investigate “what if” electrodes (microstructure generation)



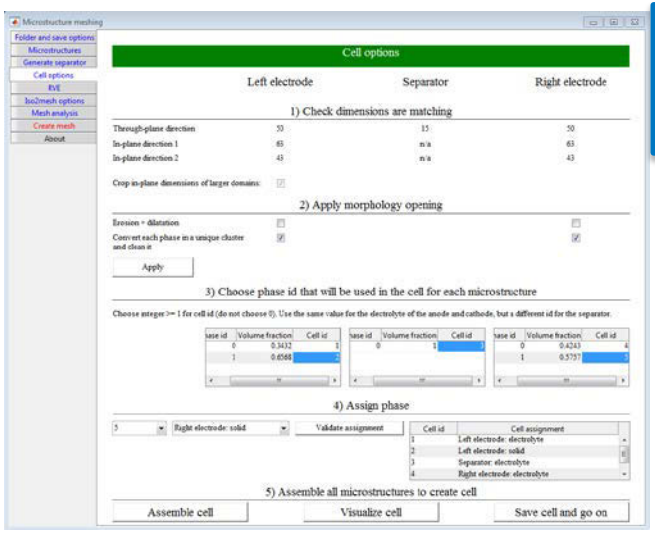
  - Variable particle morphology/orientation/size distribution
  - Multi-layer and/or graded electrodes

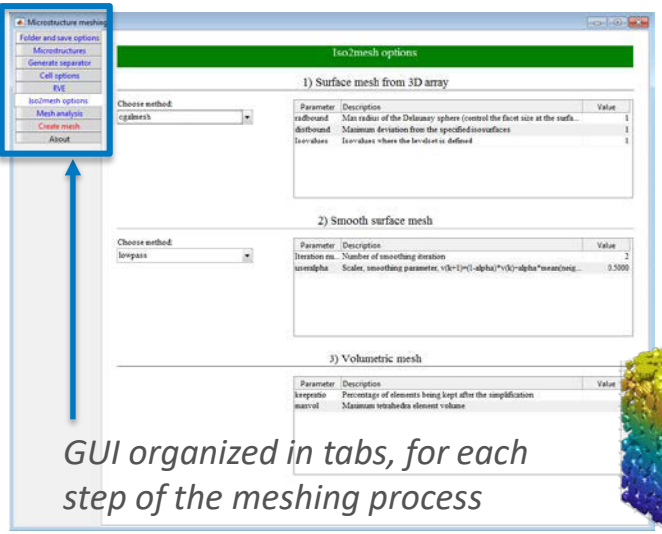
Impact of particle heterogeneities on lithium plating and lithium plating mitigation through graded electrodes



Support DOE extreme fast charge program BAT339

- Provide high quality, non-structured, tetrahedron-based meshes, simply from standard .tif files of the 3D segmented volumes





GUI organized in tabs, for each step of the meshing process

- Region Of Interest (ROI), rescaling
- Morphology opening
- Control mesh density and surface smoothness
- Clean vertex-2-vertex and line-2-line contact
- Calculate mesh quality
- Export vertex and cell connectivity

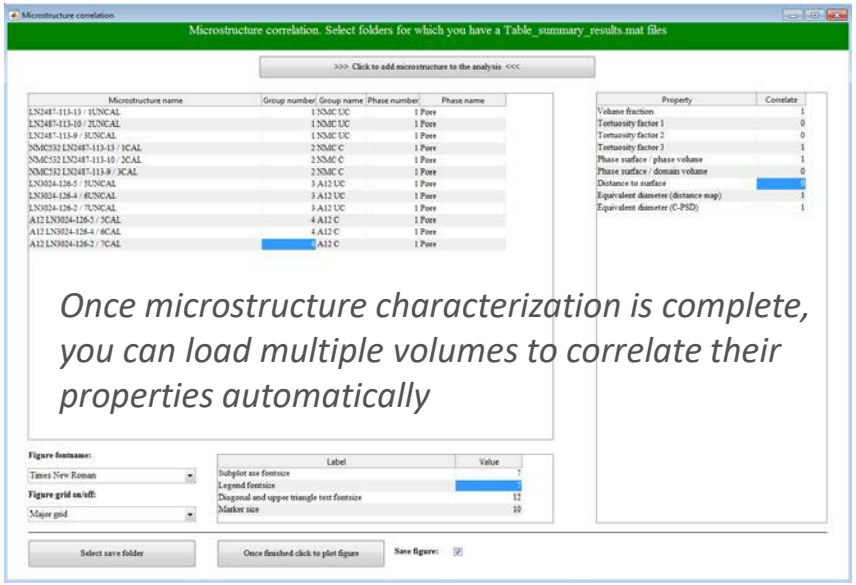
Examples and Applications: Microstructure Parameters

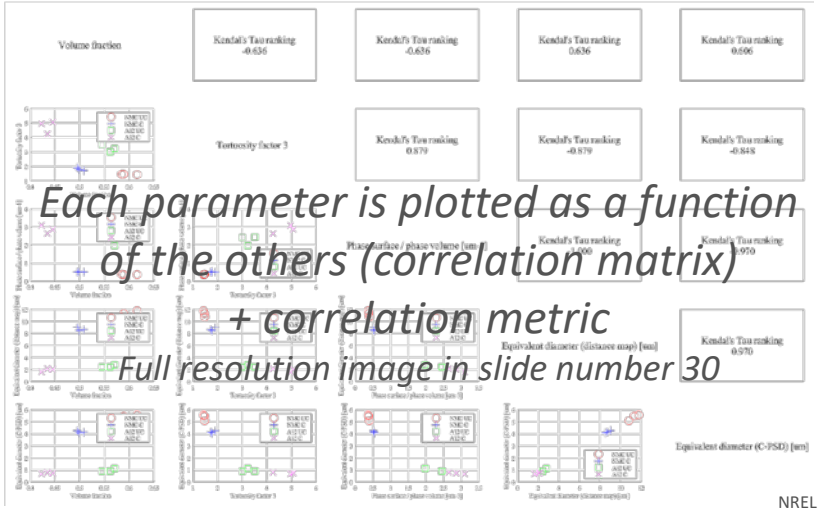
- Microstructure characterization

- Volume fractions, particle size distribution and morphology, tortuosity factor *(third-party open-source Taufactor)* geometric tortuosity & skeletonization, surface area
- Characterize multiple volumes sequentially
- Parameters plotted along position to investigate variation along thickness (graded materials)
- **Automated Representative Volume Element** (RVE) analysis*, with control of the subvolumes aspect ratio
- **Automated image resolution dependence** analysis*
- Results (.png, .fig, .xls) carefully sorted

**Saves manual setting of hundreds of calculations per volume & provides error estimation*

- Microstructure parameters correlation





High Performance Computing of Batteries

Creating a Scalable, Iterative Solver Package for the Microstructure Model

Problem:

- First iteration of the microstructure electrochemical model relied on direct solver (robust, but slow) as iterative solvers (faster, memory-cheap, but require well-conditioned systems to converge) proved to be unstable
- As a result, investigated volumes were too small (to keep central processing unit CPU time acceptable) and model could not be predictive (volumes not representative)

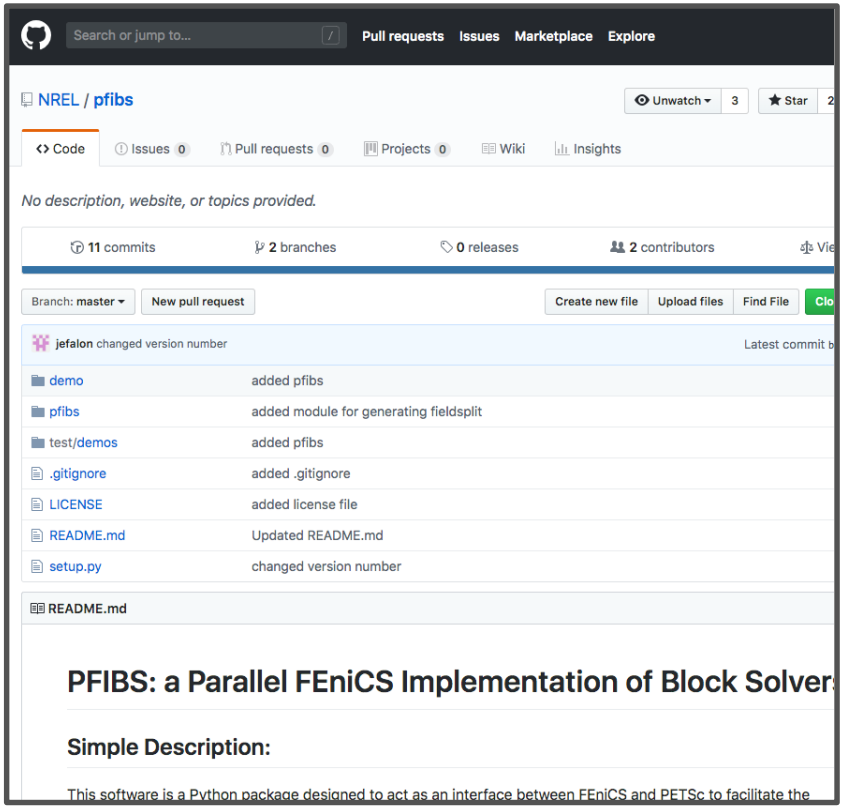
Solution & approach

- Create a **scalable, iterative solver** package capable of handling **large meshes**
- Leverage the Portable, Extensible Toolkit for Scientific Computation (PETSc) backend to customize preconditioners to handle the poorly conditioned electrochemical model

pFibs: a Parallel FEniCS Implementation of Block Solvers

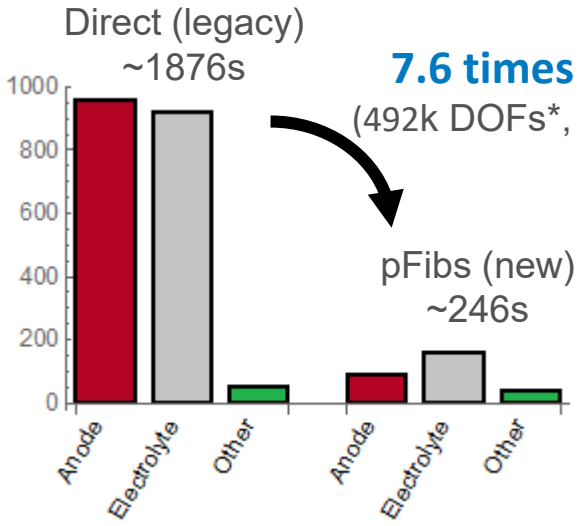
- ➢ Provides easy access to PETSc's more advanced features
- ➢ Automatically sets up the block iterative solver for the electrochemical model

Open-source, available at https://github.com/NREL/pfibs



Iterative Solver Impact on the Microscale Model's Time to Solution

Average Wall Clock Time (s) per Time Step:



pFibs is even faster (up to 33 times) for larger domains for which the direct solver can only solve few step times (due to excessive CPU time).

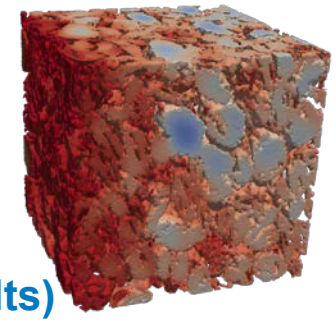
Direct Mumps (legacy):

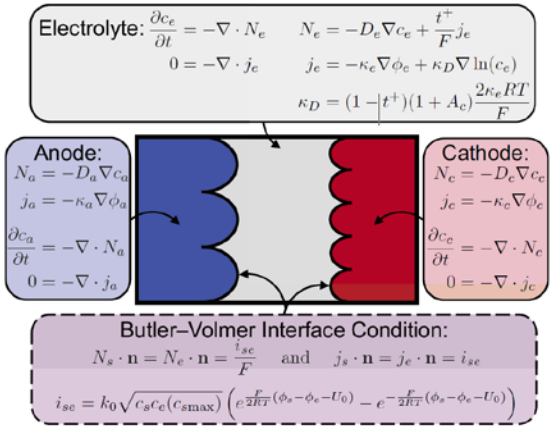
- Small Domains
- 492k DOFs*
- 13.6 x 13.6 x 54.4 μm^{-3}

Volumes ~38 times larger, DOFs x19

pFibs, iterative (now):

- Large Complex Domains
- 9.2 Millions DOFs*
- 74 x 74 x 69.5 μm^{-3}
- **Representative volume (enables predictive results)**

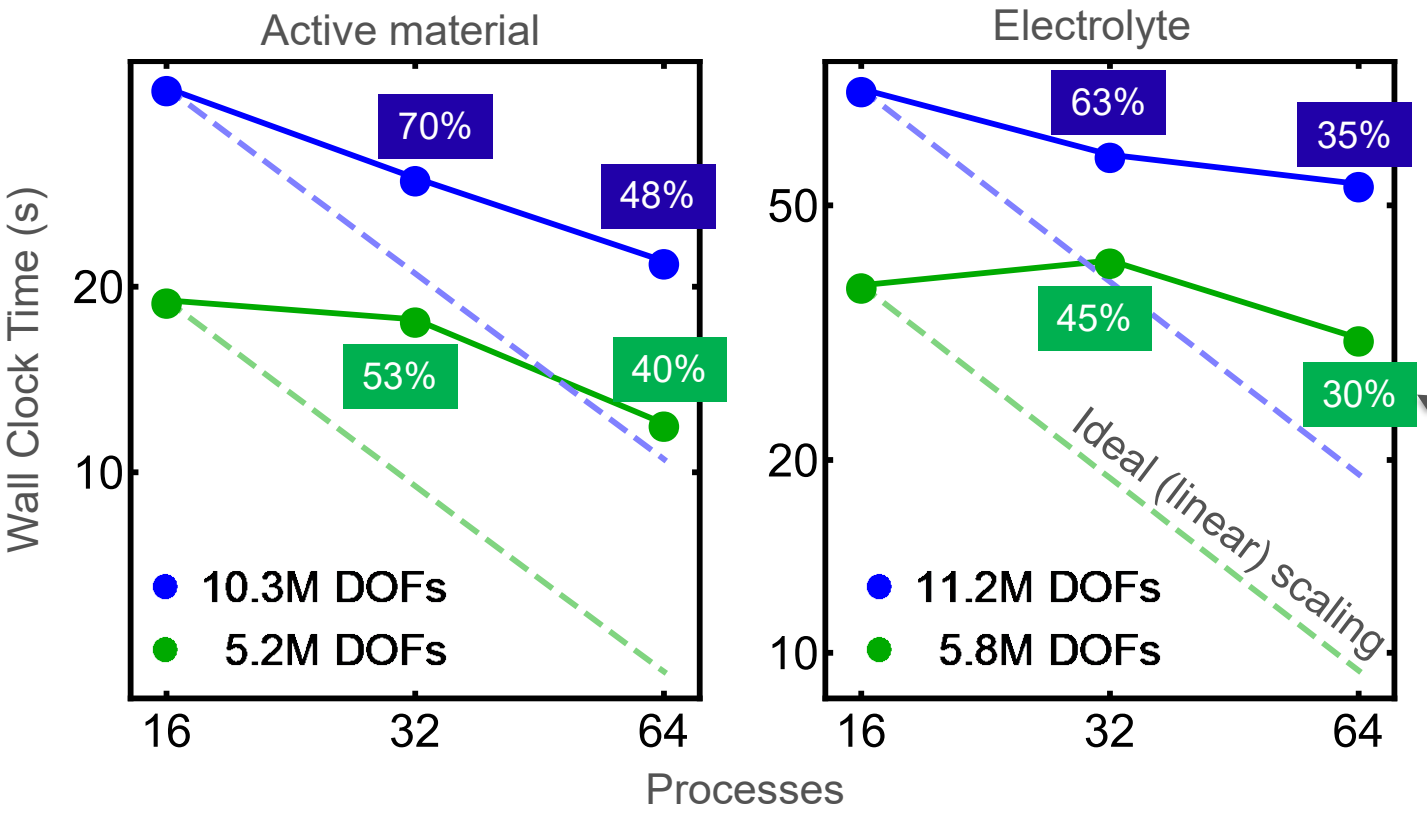




- 6C CC (Constant Current) charge simulation performed on a **representative half-cell volume** (74 x 74 x 69.5+20 μm^3, 9.2 Million DOFs*) now takes ~5 days with old-generation HPC, 32 cores.
- Model **tested up to 45 Million DOFs*** and is stable, **enables future full-cell calculation.**

*DOF: Degree Of Freedom

Strong Scaling Parallel Performance with pFibs



Scaling (parallelism performance) analysis performed on tomography-based anode volumes

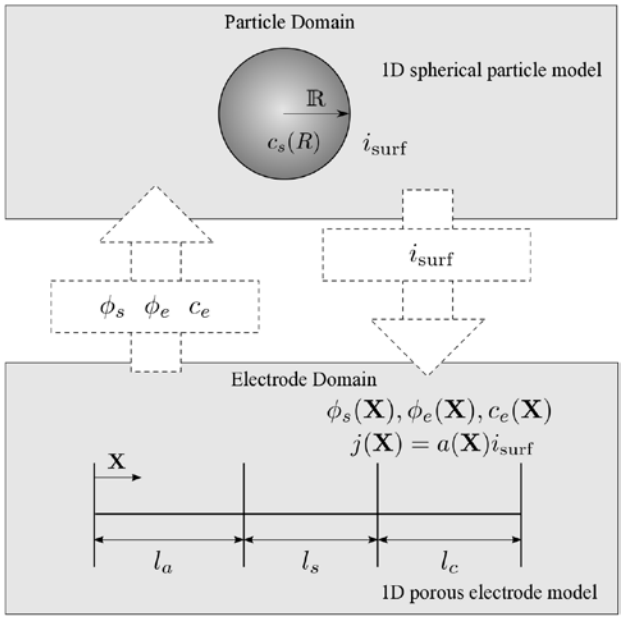
Scaling efficiency

Strong scaling: (number of DOFs constant & variable number of processes)

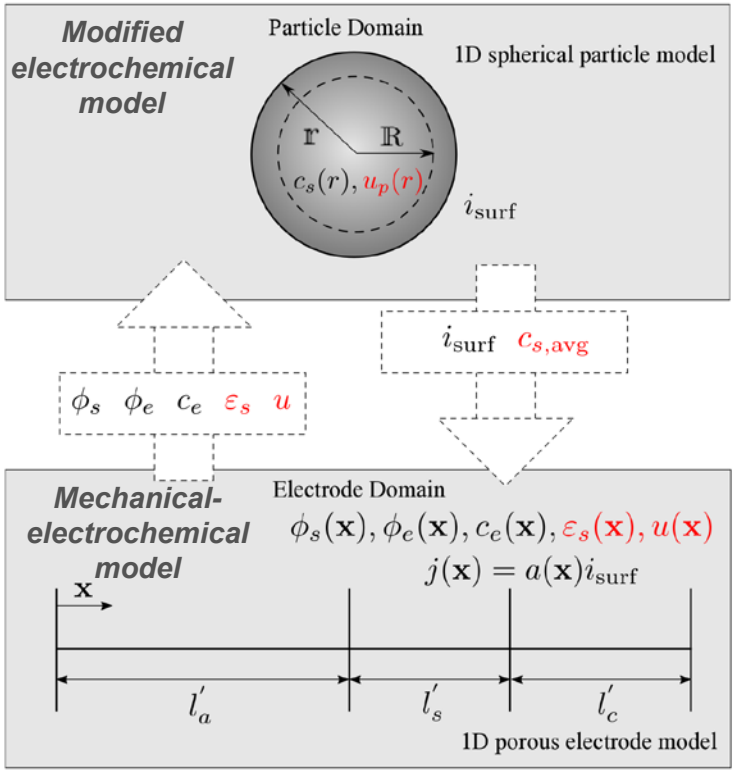
- pFibs achieves parallel speedup. **Scaling efficiency is increasing with domain size.**
- Static scaling analysis (technical back-up slide 32) indicates **larger domain will benefit from 64+ processes.**
- The electrolyte domain scales less well than the active material.

Extension for Large Deformation Materials

Incorporating Particle/Electrode Mechanical Deformation into the Pseudo2D Electrochemical Model



P2D Newman model



P2D model coupling large deformations

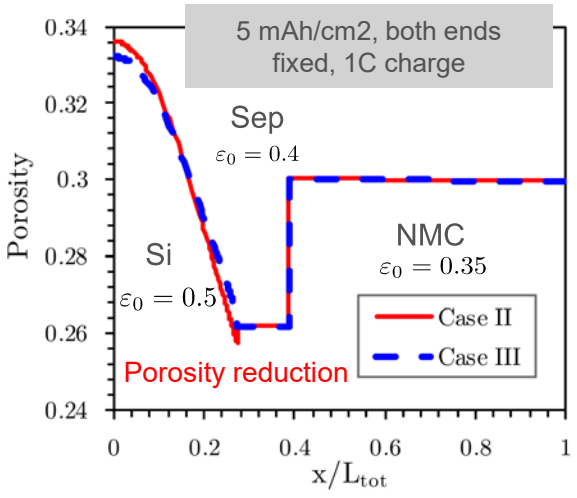
c_s: Li concentration
i_{surf}: surface current density
$u_p(r)$: particle displacement

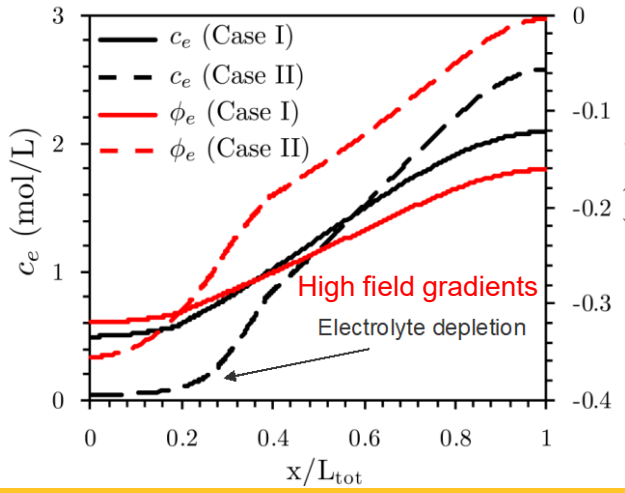
ϕ_s: solid potential
ϕ_e: electrolyte potential
c_e: electrolyte concentration
ε_s: solid volume fraction
u: electrode domain displacement

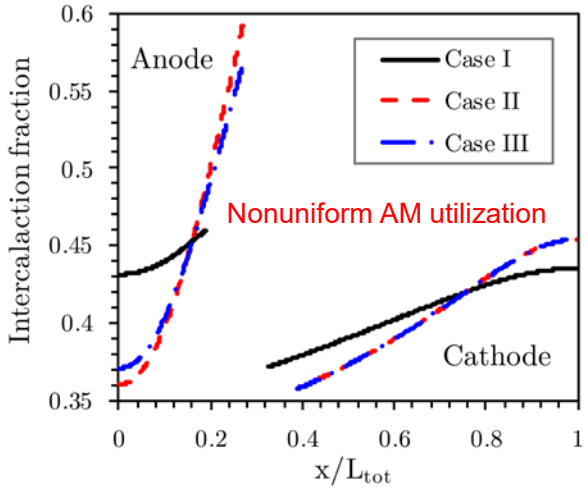
- High-capacity materials (Silicon, Tin) subject to large deformation
- **Goal**: consistently incorporate deformations based on the Pseudo2D (P2D) framework
- **Challenge**: infinitesimal deformation assumption inapplicable
- **Approach**: finite strain theory + reference frame reformulation of mass & charge conservation governing equations

Deformation, Stress, and Effects on Cell Performance

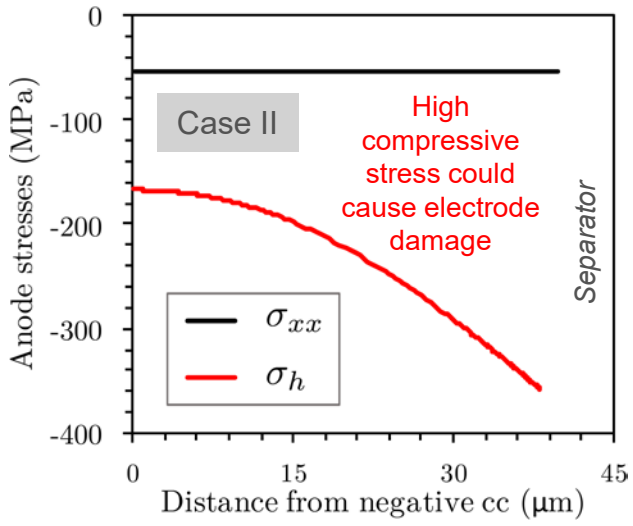
Case I: P2D (ref) **Case II**: P2D+deformations **Case III**: Case II + stress-dependent Open Circuit Potential of Si

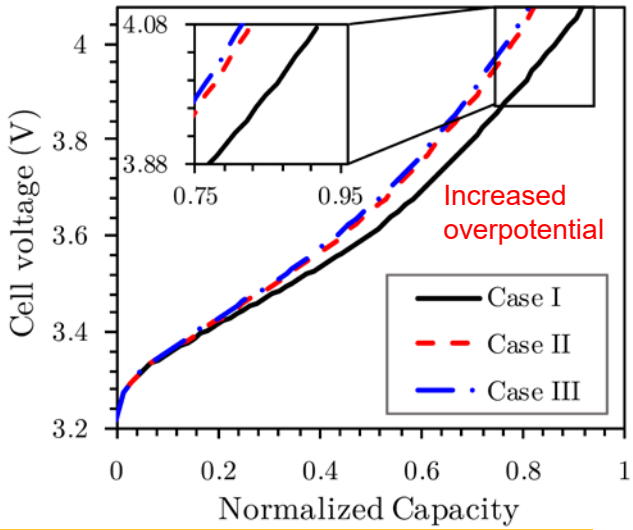






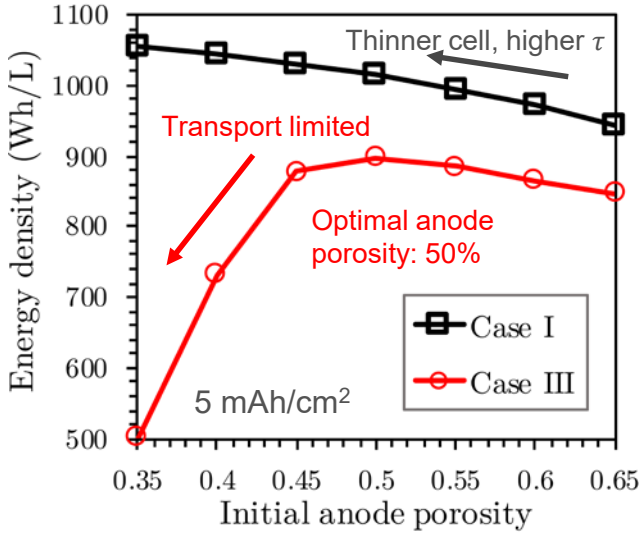
- Particle expansion → porosity reduction → increased cell-level inhomogeneity

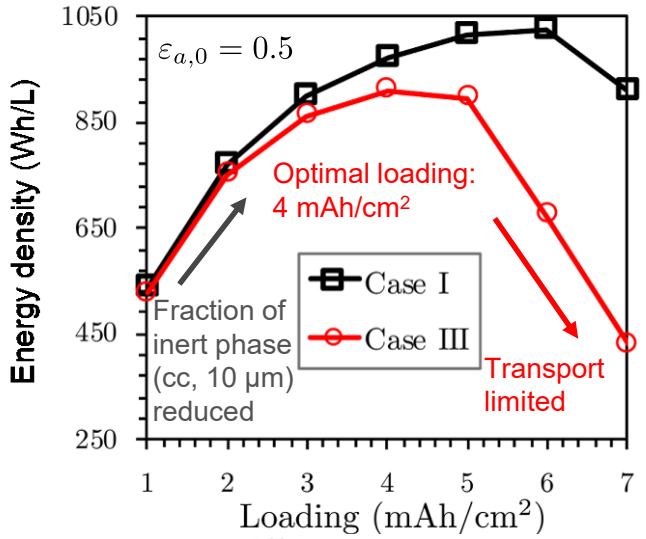


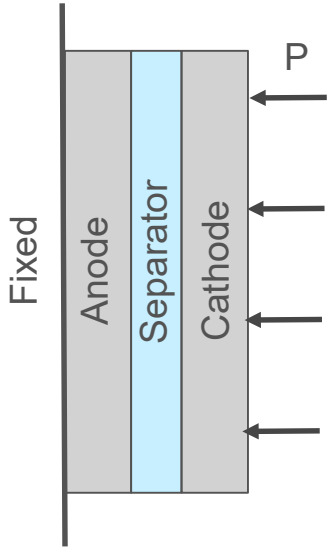


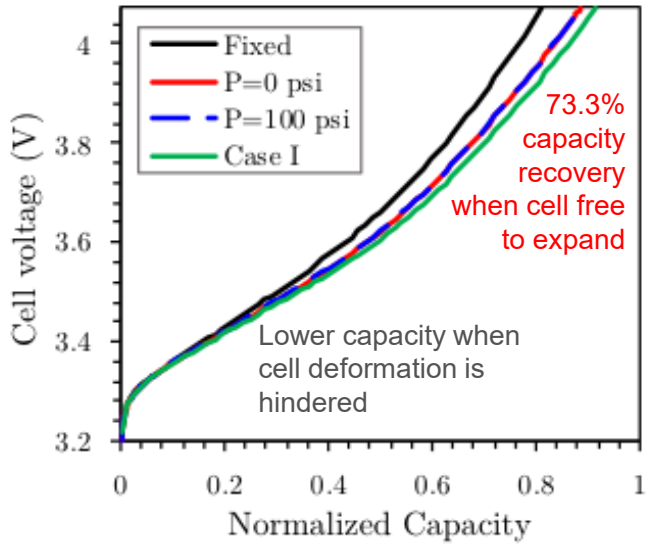
- High compressive stress; cell capacity reduced by 9.16%

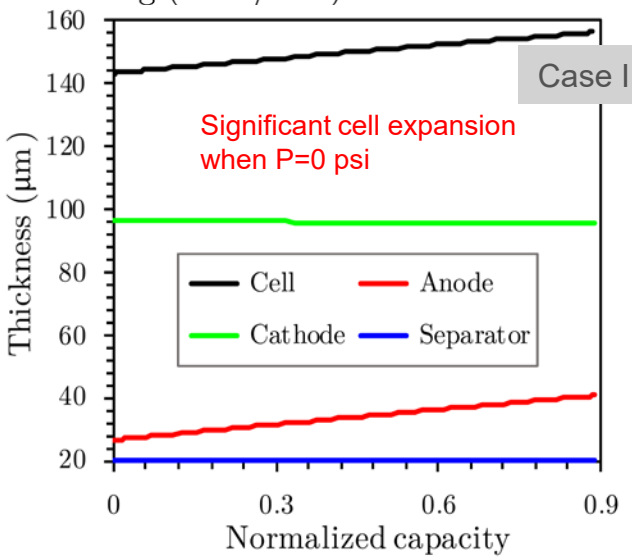
Model Guidance on Optimal Cell Design











- Incorporation of deformations significantly affects model prediction
- Free cell expansion: capacity ↑ 9.86% but cell thickness ↑ 9.1%

Extension to Multi-Phase Multi-Reaction and Polycrystalline Systems

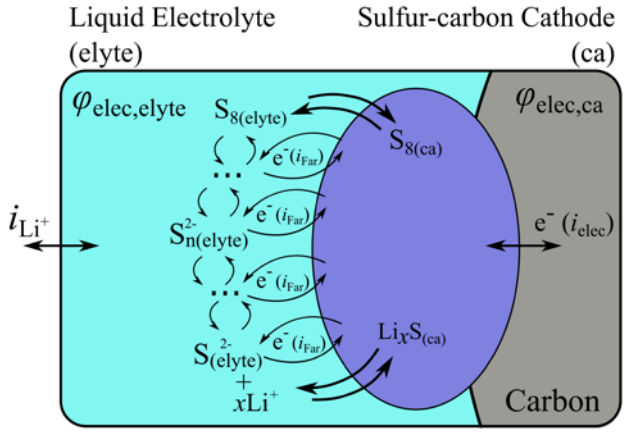
Integrating Physics to Tackle Challenges of New Material Systems (initiated January 2019)

Path for integrating complex chemistry and mechanical evolution into HPC toolset

1) Multi-phase multi-reaction

Li-sulfur system

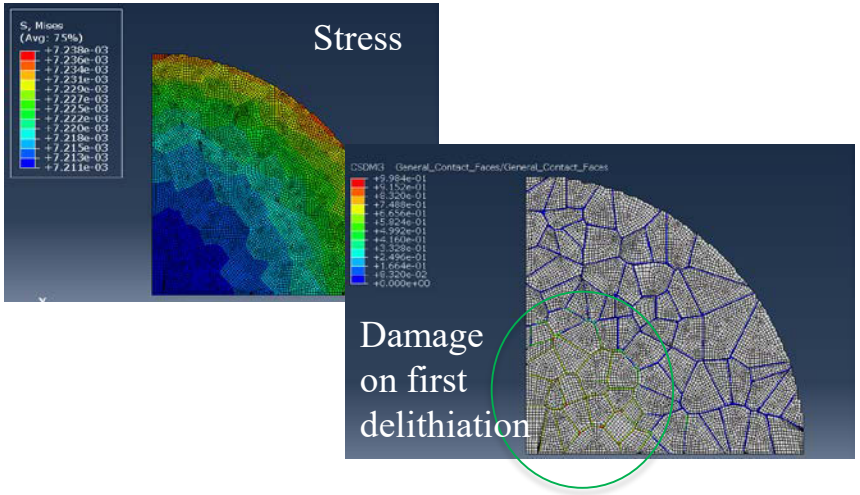
Professor Steven Decaluwe
Colorado School of Mines



- Cantera open-source software treating generalized electrochemical-thermo-kinetic reactions
- Develop, validate electrochemical mechanism to identify dominant Li-S reaction pathways, species, thermodynamics
- Help assess mitigation strategies for poly-sulfide shuttling

2) Polycrystalline architectures

High voltage NMC811



- Grain/particle geometry, anisotropic properties
- Model tracks cracking and surface area evolution of polycrystalline particles with cycling
  - Important for aging of NMC811
- Use model to clarify benefits of alternate particle architectures

Responses to Previous Year Reviewers' Comments

- Comment: The effects of electrode thickness on microstructural-resistance analysis and rate capability need to be considered
- Response: We agree. This is an important consideration and has been captured in the models. Tortuosity is the primary parameter capturing ionic resistance across a thick electrode. Under this CAEBAT project, the microstructure model predictions of tortuosity – including carbon/binder effects – have been validated versus direct measurements and electrochemical rate capability experiments. That work was published in FY 19 in the Journal of The Electrochemical Society. Under the extreme fast charge program, BAT339, the models have been further validated at up to 9C charge rates and for electrodes with different active material morphologies (platelet, ellipsoid, sphere).

- Comment: The reviewer suggested looking at temperature-dependent materials models and how they might be implemented.
- Response: The electrochemical macro-homogenous model has been updated from isothermal to lumped thermal. Experimental determination of temperature-dependent coefficients (activation energies) is ongoing.

Collaboration and Coordination with Other Institutions

Category	Institution		Role
National Laboratories	Argonne NATIONAL LABORATORY	Argonne National Lab[1]	Electrode/cell prototyping and characterization
Universities	PURDUE UNIVERSITY	Purdue University (sub to NREL CAEBAT)	Stochastic electrode reconstruction & CBD generation for microstructure studies. Mesoscale electrode modeling
	UCL	University College of London[2]	Nano and micro X-ray computed tomography
	BYU	Brigham Young University[2]	Tortuosity measurement
	UC San Diego	University of California San Diego[2,3]	NMC811 samples with different size distribution & mud-cracking

1. Part of DOE Vehicle Technologies Office
2. Informal collaboration
3. Batt500 Energy Storage Program team member

Remaining Challenges and Barriers

- Complexity of modeling volume change, phase evolution, chemistry of future battery material systems
- Linking first principles calculations with continuum scale models to better represent reactions and transport processes
- Obtain 3D images of CBD with sufficient field of view and resolution to validate morphology, including surface coverage and nano porosity
- Enhance stochastic reconstruction of CBD to capture mechanics
- Develop appropriate identification and validation experiments

Future Work

- Enhance models as described above, including particle, carbon-binder, new chemistries, and electrode mechanics/degradation mechanisms. Validate.
- Investigate subparticle heterogeneities (e.g., crystal orientation) and their impact on degradation onset
- Apply models to electrode design studies for new materials, 3D architectures and applications, e.g., fast charge

Any proposed future work is subject to change based on funding levels

Summary

- Developed open-source microstructure analysis open-source toolbox
  - Performs segmentation, generation, characterization, correlation, Representative Volume Analysis (RVA) and meshing (Supports extreme fast charge program BAT339)
  - To be released this summer together with already published open-source battery microstructure library
- Improved robustness and speed of 3D microstructure high-performance computing model
  - Developed pFibs: a Parallel FEniCS Implementation of Block Solvers
    - Speed-up problem solve by 8-33 times. Domain size 38 times larger, DOFs up to 45 Millions
  - Enables representative volume simulations that elucidate the impact of heterogeneity on electrode performance and degradation
    - Fully-resolved half cell simulation (e.g. 6C charge of 74 x 74 x 69.5+20 μm^3 volume; 9.2M degrees of freedom in ~5 days)
    - Performing quantitative analysis and electrode design recommendations (Supports extreme fast charge program BAT339)
- Reformulated classical Pseudo2D electrochemical model to efficiently incorporate large deformation at particle and electrode levels. Studied silicon anode system
  - Non-uniform stress along the anode thickness, with high compression near separator
  - Induces anode porosity variation that aggravates electrolyte depletion (transport limitation)
  - Free cell expansion mitigates anode porosity variation, thus allowing recovery of most of the lost capacity (~73%) due to the silicon strain, but increases cell thickness (~+9.1%)
- Multi-phase multi-reaction chemistry and evolution of mechanical damage are being incorporated into models to aid development of emerging Li-sulfur and NMC811 systems

Acknowledgements

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  - Brian Cunningham
  - Samuel Gillard
  - Steven Boyd

Thank You

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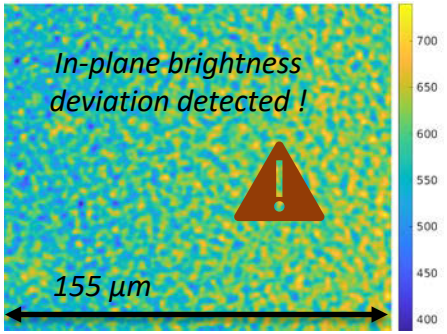
Technical Back-Up Slides

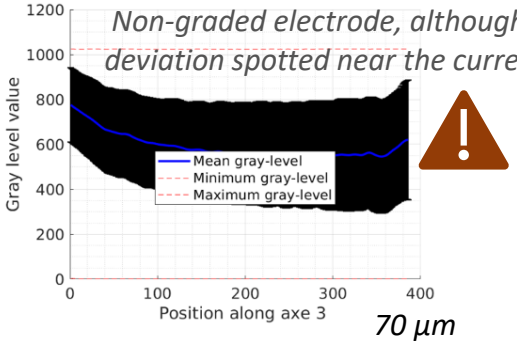
Microstructure Analysis Workflow: Volume Preparation

1) Image diagnosis

Grey level projection



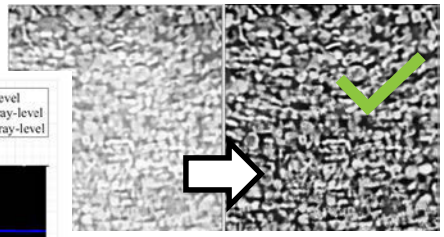
Grey level variation along thickness

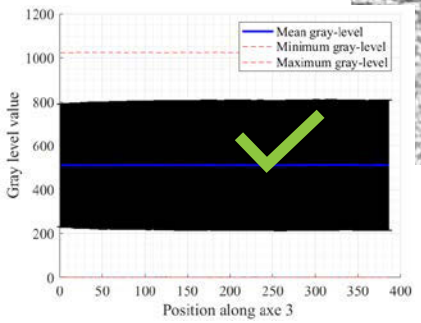


- "Simple" segmentation but in-depth analysis approach
- Performed with the NREL microstructure analysis tool

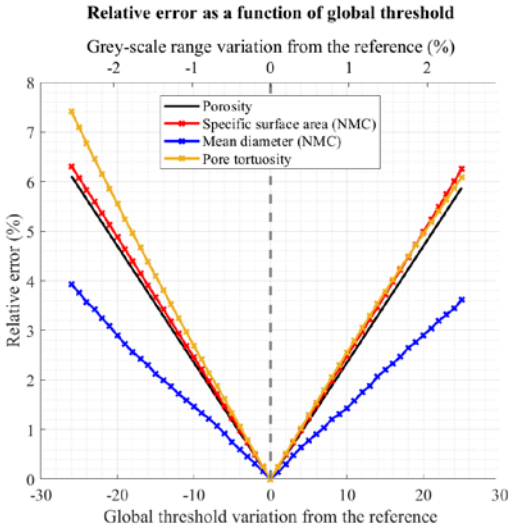
Illustrated with SLC1506T2 (70 µm thick, 144 x 155 µm² Field Of View FOV)

2) Image contrast correction





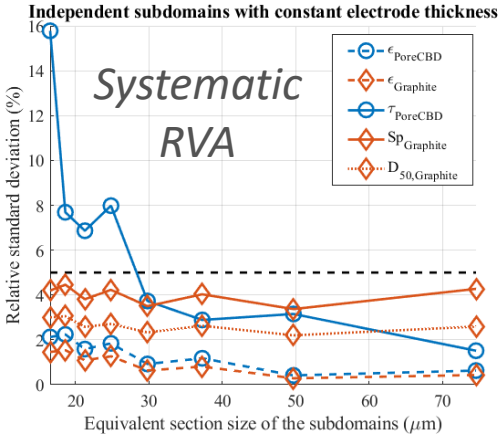
3) Image segmentation & segmentation error estimation

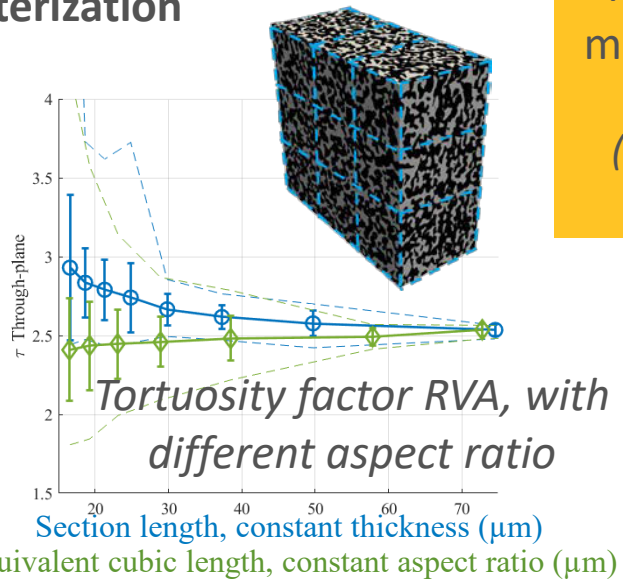


Microstructure Analysis Workflow: Volume Characterization

3b) Image segmentation or microstructure generation

4a) Microstructure characterization





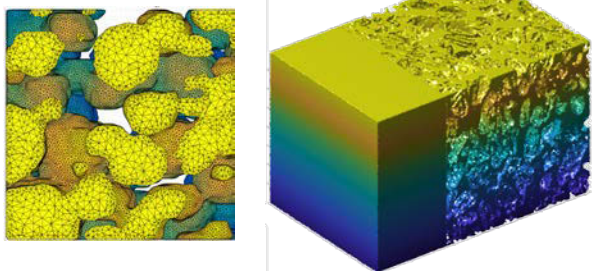
Performed with the NREL microstructure analysis tool
Illustrated with SLC1506T2 (70 µm thick, 144 x 155 µm² FOV)

Macro-homogenous modeling **relevance** of the microstructure parameters is known

Microstructure parameters used for macro-homogenous are thoroughly evaluated (accuracy estimation)

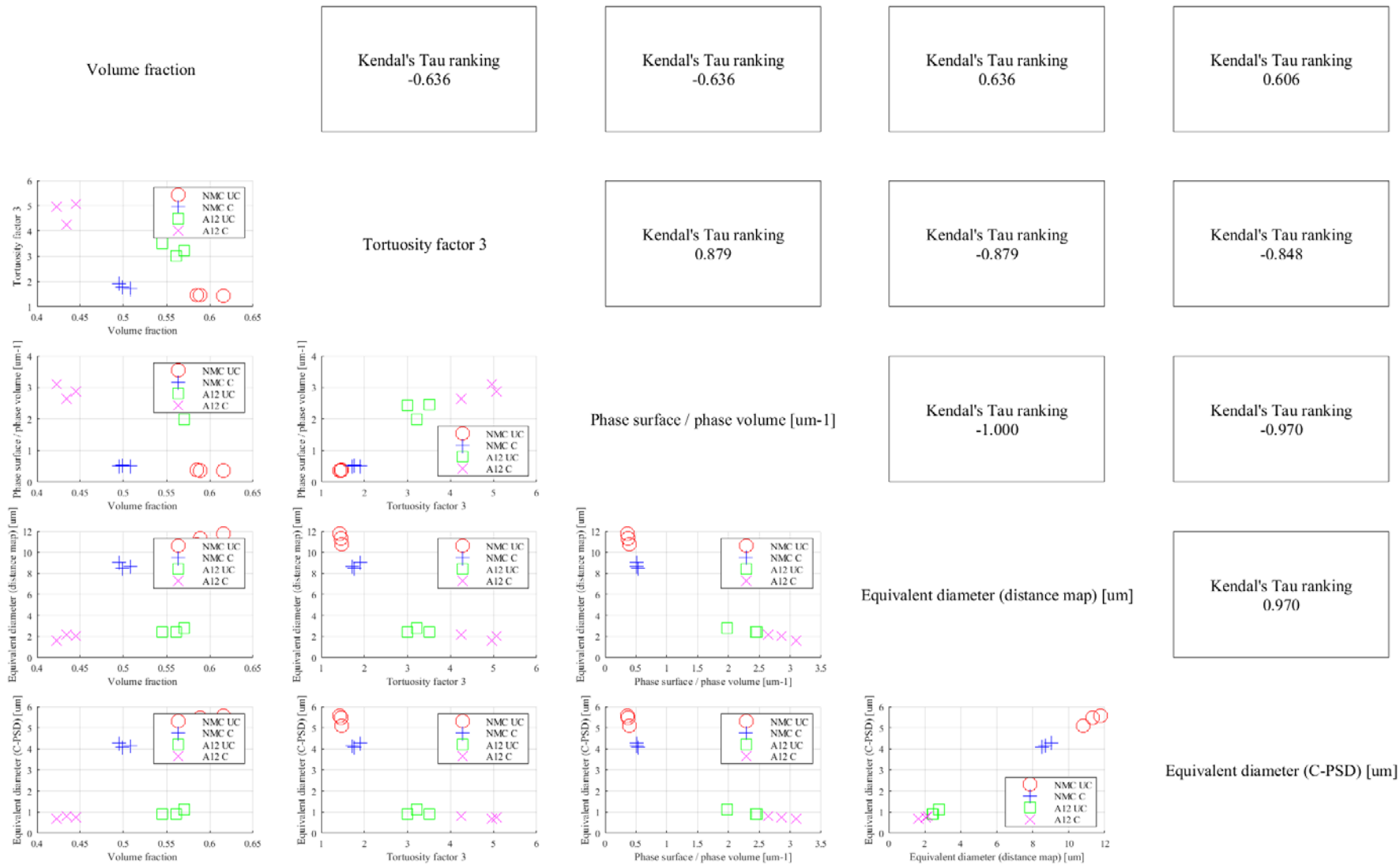
- **Different numerical methods → property bounds estimation**
- **RVA → representativeness evaluation**
- **Voxel size dependence → error/extrapolation**

4b) Microstructure meshing



Micro-homogenous modeling

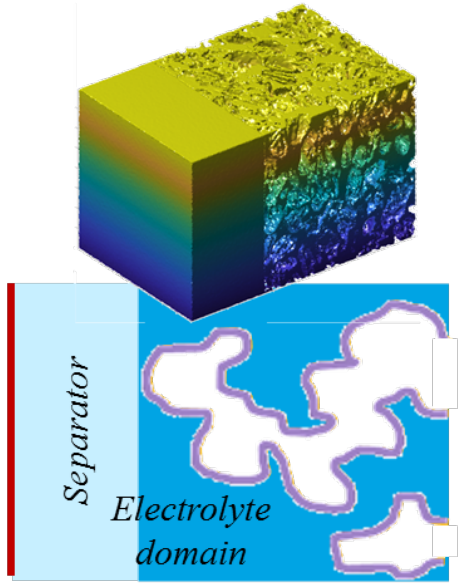
Correlation Matrix for 14 Electrodes (7 Graphite, 7 NMC) Automatically Generated with the Microstructure Analysis Toolbox



Objective: quickly identify if parameters are positively correlated (Kendal's tau ranking >0), negatively correlated (<0), or not correlated (=0)

Microstructure Electrochemical Model

Segregated model: solid and electrolyte domains are solved sequentially

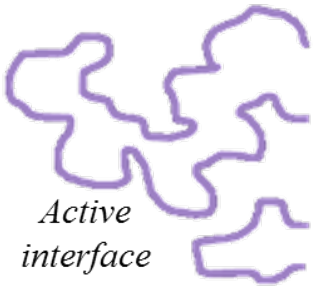


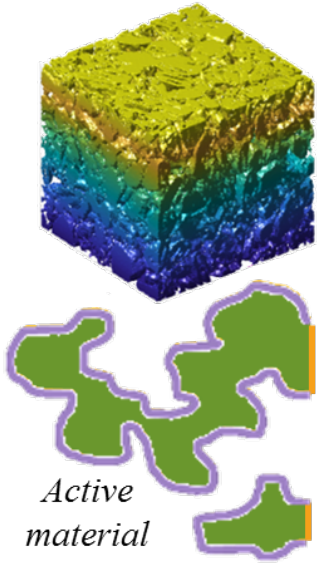
Boundary conditions at the interface separator lithium plate

$\phi_s = \phi_{reference}$

$\overline{N_e}.\bar{n} = \frac{j_{se}}{F}$

$\bar{j}_e.\bar{n} = j_{se}$





Boundary conditions at the interface solid current collector

$\bar{j}_s.\bar{n} = j_{applied}$

$\overline{N_s}.\bar{n} = 0$

Charge conservation: $\nabla \bar{j}_e = 0$

With $\begin{cases} \bar{j}_e = -K_e \bar{\nabla}\phi_e - K_D \bar{\nabla} \ln C_e \\ K_D = \frac{2K_e RT}{F}(t_+^0 - 1) \text{ and assuming } \frac{\partial ln\, f_\pm}{\partial ln\, C_e} = 0 \end{cases}$

Mass conservation: $\frac{\partial (C_e \varepsilon)}{\partial t} = -\nabla \overline{N_e}$

With $\overline{N_e} = -D_e \bar{\nabla} C_e + \frac{t_+^0}{F}\bar{j}_e$

Multiscale model

$$\varepsilon(x) = \begin{cases} \varepsilon_{sep} & \text{if } x \in \text{separator} \\ 1 & \text{otherwise} \end{cases}$$

$$X_e(x) = \begin{cases} \frac{\varepsilon_{sep}}{\tau_{sep}} X_{e,dense}(C_e) & \text{if } x \in \text{separator} \\ X_{e,dense}(C_e) & \text{otherwise} \end{cases}$$

With $X_e = D_e$ and K_e and τ the tortuosity factor

Boundary conditions at the interface solid-electrolyte (charge transfer)

$\overline{N_e}.\bar{n} = \overline{N_s}.\bar{n} = \frac{j_{se}}{F}$

$\bar{j}_e.\bar{n} = \bar{j}_s.\bar{n} = j_{se}$

with

$$\begin{cases} j_{se} = i_0 \left\{ exp\left(\frac{(1-\alpha)F\eta}{RT}\right) - exp\left(-\frac{\alpha F \eta}{RT}\right) \right\} \\ \alpha = 0.5 \\ \eta = \phi_s - \phi_e - OCP \\ i_0 = F k_0 \sqrt{C_e}\sqrt{C_s}\sqrt{C_{s,max} - C_s} \end{cases}$$

No side reactions.

Charge conservation: $\nabla \bar{j}_s = 0$

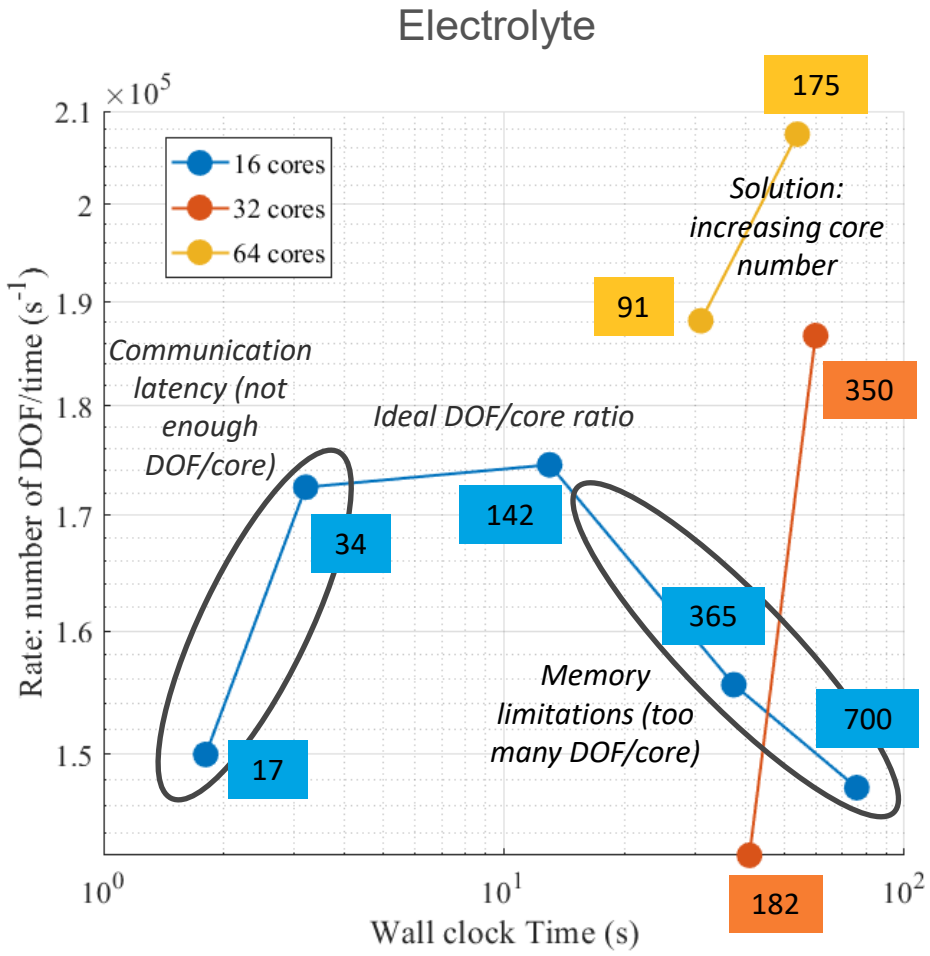
With $\bar{j}_s = -K_s \bar{\nabla}\phi_s$

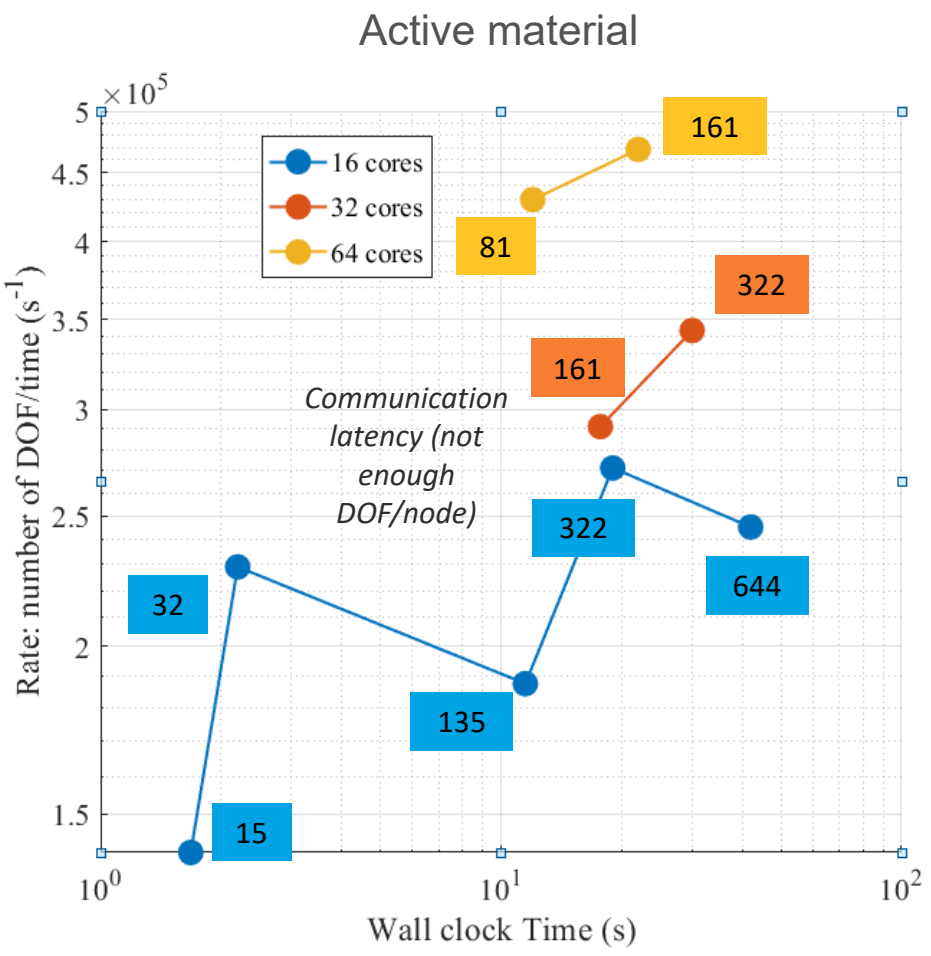
Mass conservation: $\frac{\partial (C_s)}{\partial t} = -\nabla \overline{N_s}$

With $\overline{N_s} = -D_s \bar{\nabla} C_s$

Finite Element open-source package **FEniCS** runs with **NREL High-Performance Computing** (up to 45 M degrees of freedom)

Static Scaling Parallel Performance with pFibs



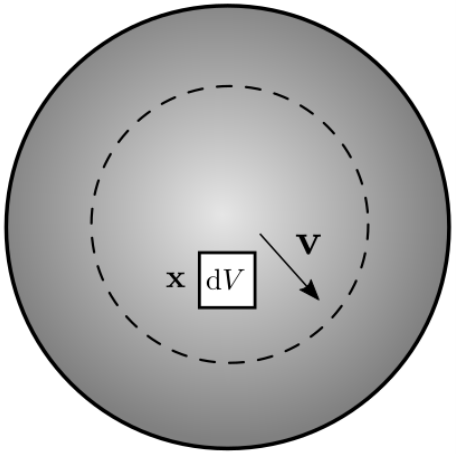


x *Number of DOF in thousands per core*

Static scaling holds the number of processes constant and varies DOFs. Electrolyte poor scalability can be enhanced by increasing number of core to prevent memory limitation for large domain size.

Reference Frame Formulation of Conservation Laws

❑ Eulerian conservation law

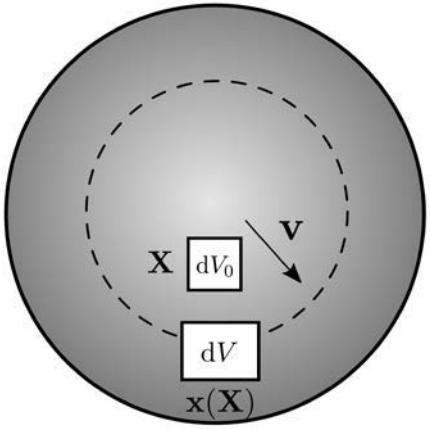


$$\frac{\partial c(\mathbf{x})}{\partial t} = -\nabla_x \cdot \mathbf{N}(\mathbf{x}) + R(\mathbf{x})$$

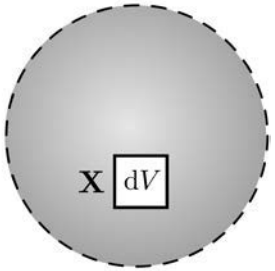
$$\mathbf{N}(\mathbf{x}) = -D\nabla_x c(\mathbf{x}) + c(\mathbf{x})\mathbf{v}(\mathbf{x})$$

- Volume element (fixed in space)
- Need to include a convection term
- Need to explicitly keep track of the deformation

❑ Lagrangian conservation law



Deformed configuration



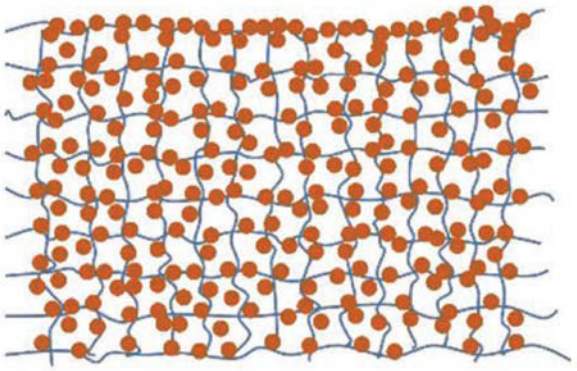
Reference configuration

$$\frac{\partial}{\partial t}\Big[c(\mathbf{X})J(\mathbf{X})\Big] = -\nabla_X \cdot \mathbf{N}(\mathbf{X}) + R(\mathbf{X})J(\mathbf{X})$$

$$\mathbf{N}(\mathbf{X}) = -J\mathbf{F}^{-1}D\mathbf{F}^{-T}\nabla_X c(\mathbf{X}) = -D_X\nabla_X c(\mathbf{X})$$

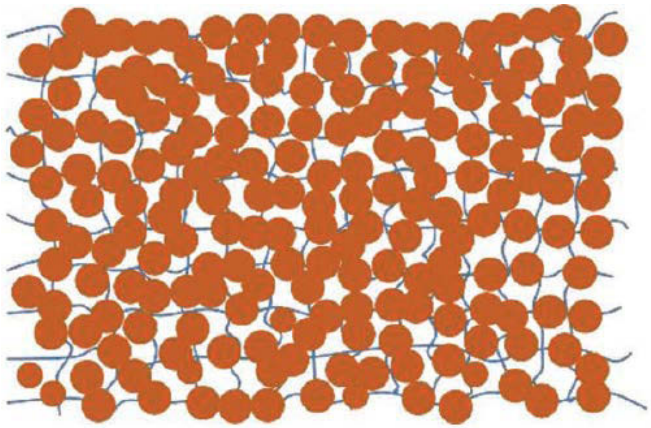
- Approximate field distributions in the undeformed geometry
- Material volume: $\mathrm{d}V_0(\mathbf{X}) \rightarrow dV(\mathbf{x}(\mathbf{X}))$
- Effect of deformation on conservation is embodied in deformation gradient tensor $\mathbf{F}$

Example Formulation: Porosity Variation



Lithiation

Wang et al. Advanced Energy Materials (2018)



- Active material (AM) expansion causes porosity reduction and electrode deformation

$$\underbrace{\frac{\partial \varepsilon_s}{\partial t}}_{\text{Variation rate of solid volume fraction}} + \underbrace{\nabla \cdot (\varepsilon_s \mathbf{v})}_{\text{Electrode deformation rate}} = \underbrace{-\frac{s\Omega_e}{nF} j}_{\text{Increase rate of AM volume}}$$

ε_s : volume fraction of solid phase

Ω_e : partial molar volume of Li in electrode

$\mathbf{v}$: local electrode velocity vector

$j = a(\mathbf{x}) i_{\text{surf}}$: volumetric current source

- Ratio of porosity reduction and electrode deformation depends on fixture condition
- Reference frame reformulation

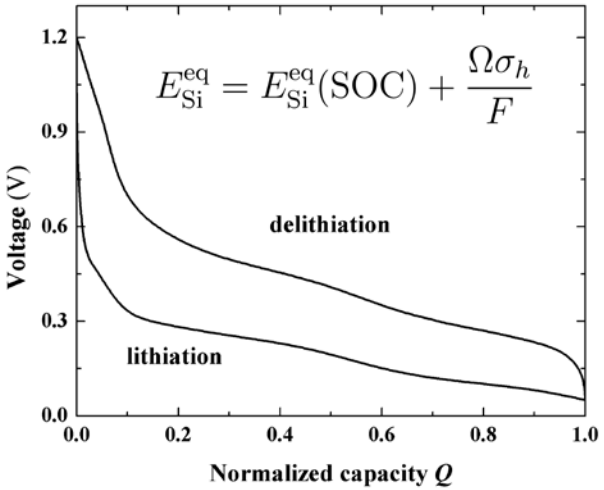
$$\frac{\partial (\varepsilon_s J)}{\partial t} = -\frac{s\Omega_e}{nF} j J$$

$$\varepsilon_e = 1 - \varepsilon_s$$

Additional Multiphysics Coupling and Assumptions

❑ Stress-dependent OCP

Lu et al. Physical Chemistry Chemical Physics (2016)



Voltage hysteresis of LixSi system due to the effect of stress

❑ Porosity-dependent mechanical properties

Kovacik et al. Journal of materials science letters (1999)

$$E = E_s(1 - \frac{\varepsilon_e}{\varepsilon_0})^n$$

$$\nu = \nu_s + \frac{\varepsilon_e}{\varepsilon_1}(\nu_0 - \nu_s)$$

❑ Specific surface area

$$a = \frac{3\varepsilon_s}{\mathbb{r}(x)} = \frac{3\varepsilon_s}{\mathbb{R}} J_p^{-\frac{1}{3}}(x)$$

Couples particle deformation and porosity reduction

❑ Assumptions

- All deformations are elastic and nondestructive
- Uniform and isotropic deformation within each particle
- Negligible in-plane electrode deformation (thin electrode is well adhered to strong metal foil cc)
- Electrolyte moves out/into a material volume only in the out-of-plane direction
- Electrode is composed of only active material and electrolyte