Battery Electrode Simulation Toolkit using MFEM (BESFEM)

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2. Department of Chemical Engineering & Materials Science

Michigan State University

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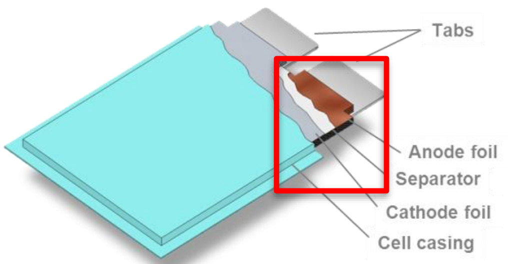
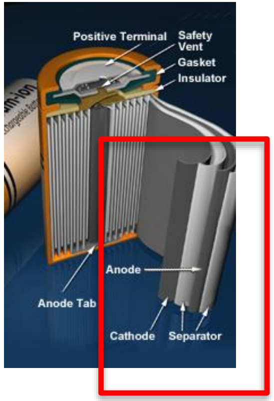
Coin cell

Pouch cell



Swiss-roll cells



Images from internet

Complexity in battery simulations

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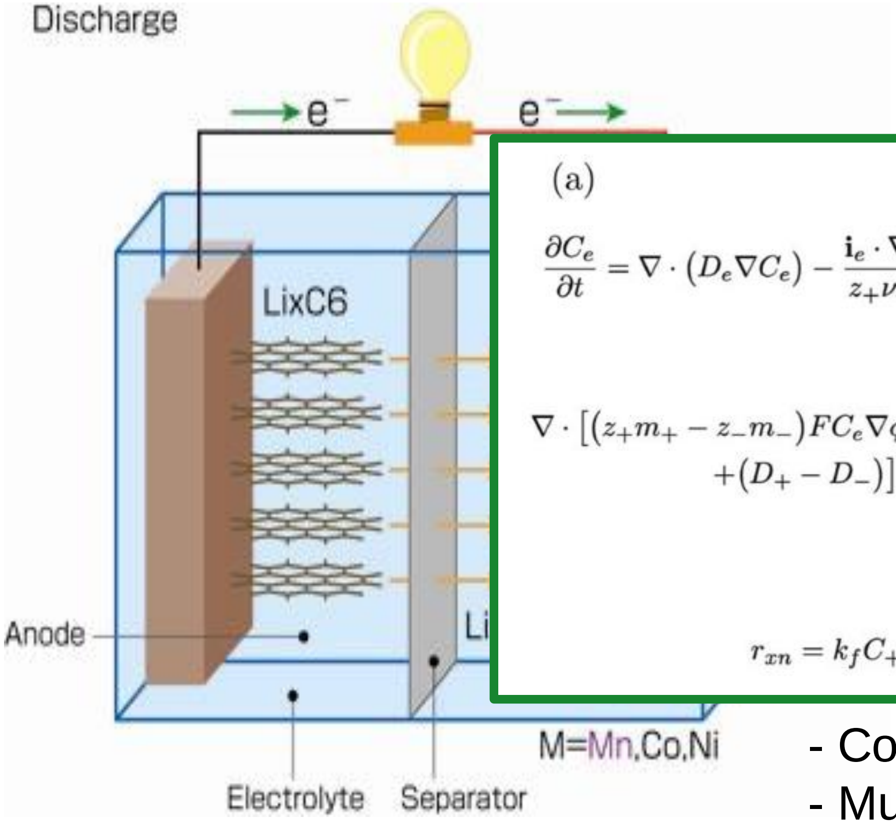
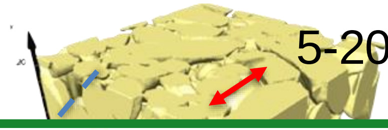


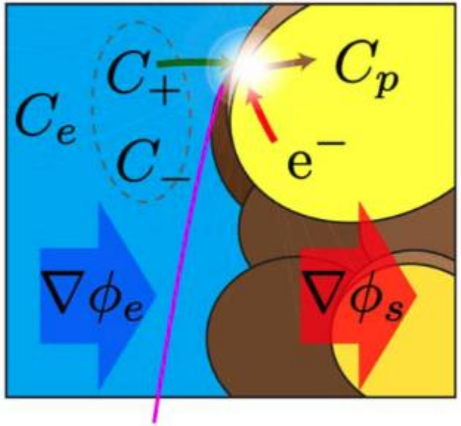


5-20 μm

(a)

$$\frac{\partial C_e}{\partial t} = \nabla\cdot(D_e\nabla C_e) - \frac{\mathbf{i}_e\cdot\nabla t_+}{z_+\nu_+F}$$

$$\nabla\cdot[(z_+m_+ - z_-m_-)FC_e\nabla\phi_e + (D_+ - D_-)] = 0$$



$$\frac{\partial C_p}{\partial t} = \nabla\cdot(D_p\nabla C_p)$$

$$\nabla\cdot(\kappa_s\nabla\phi_s) = 0$$

$$r_{xn} = k_f C_+ \exp\left(\frac{-\alpha z_+ F}{RT}[\phi]_e^p\right) - k_b C_p \exp\left(\frac{(1-\alpha)z_+F}{RT}[\phi]_e^p\right)$$

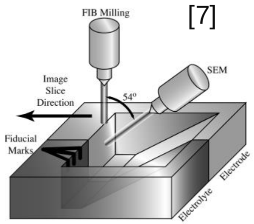
- Complex geometries
- Multiphysics

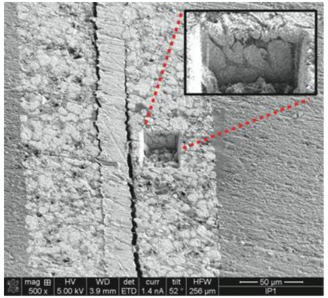
http://www.eco-aesc.com/en/liion.html;

Microstructure reconstruction via serial sectioning

FIB-SEM

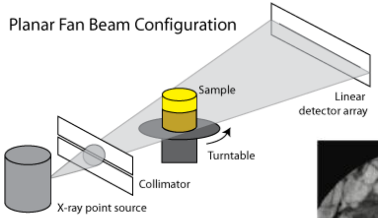
[7]

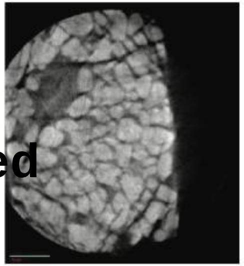




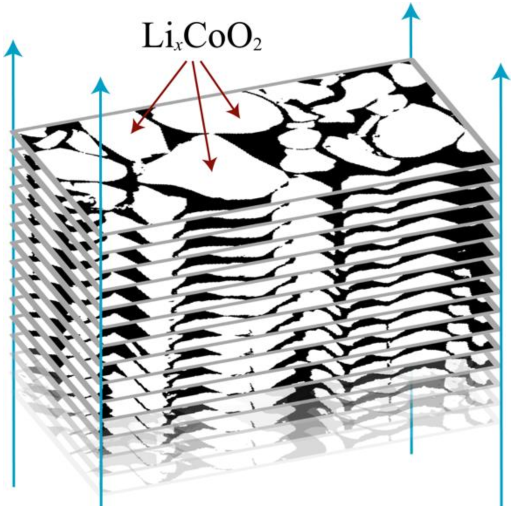
X-ray computed tomography

[8]

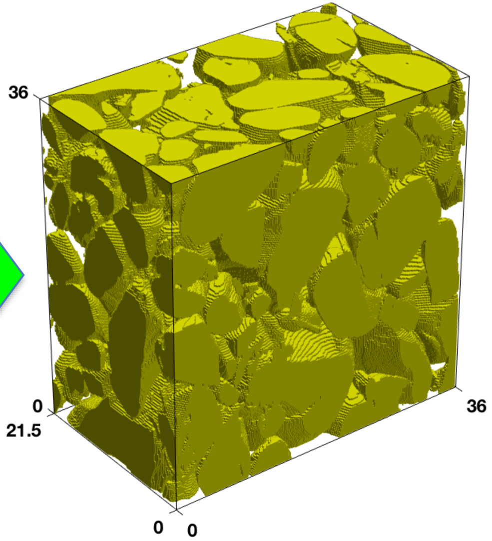




Combing series of images



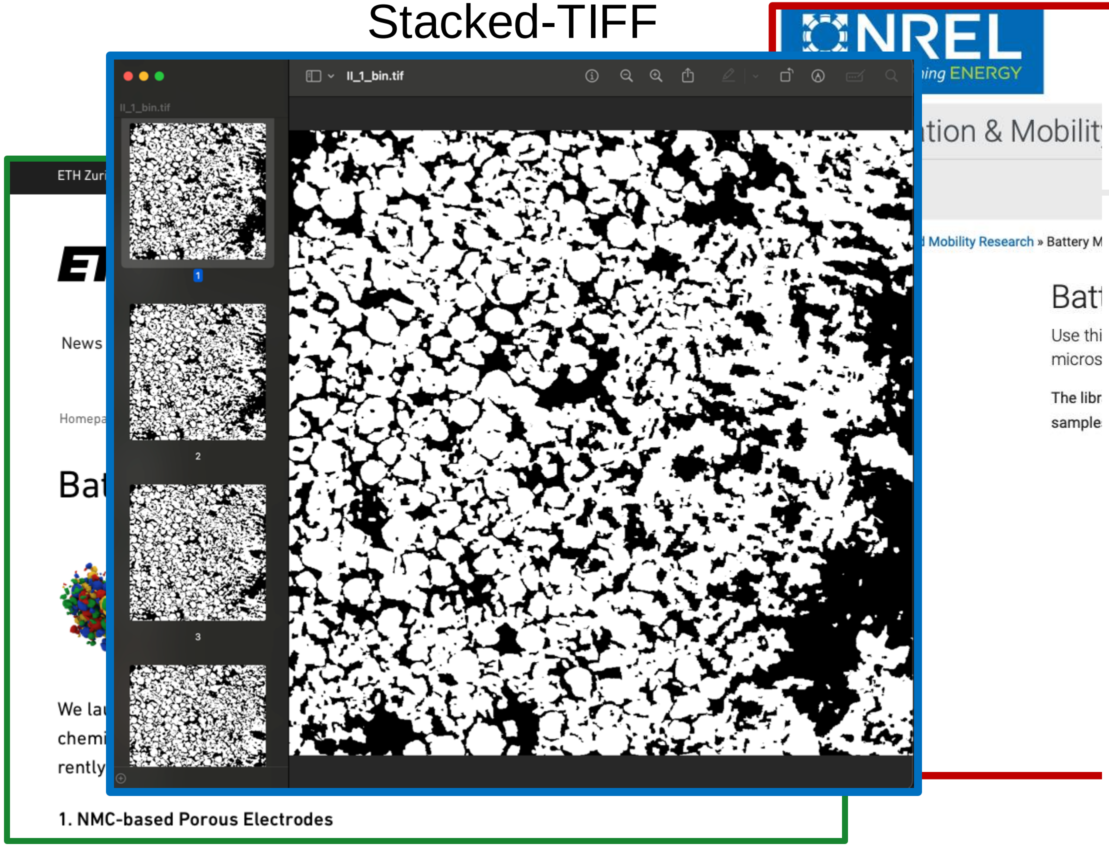
Voxel microstructure



[7] J. Wilson *et al.*, *ECS Trans* 7 (2007) 1879; [8] B Yan et al, *Journal of The Electrochemical Society*, **159** (10) A1604-A1614 (2012)

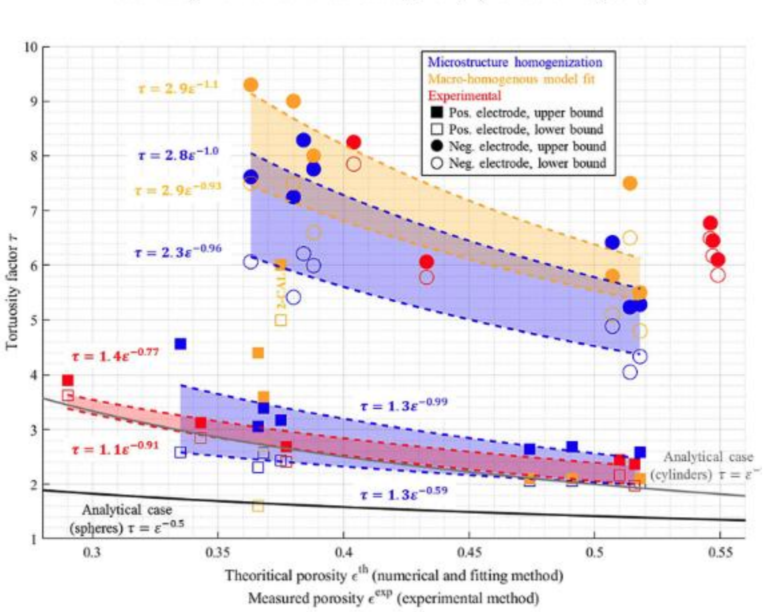
Electrode microstructure databases

Stacked-TIFF



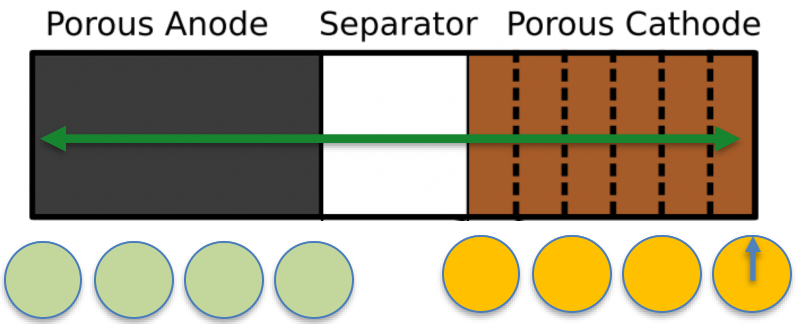
These microstructure data are used mostly for structure analysis, hardly for electrochemical simulations.

Journal of The Electrochemical Society, 165 (14) A3403-A3426 (2018)



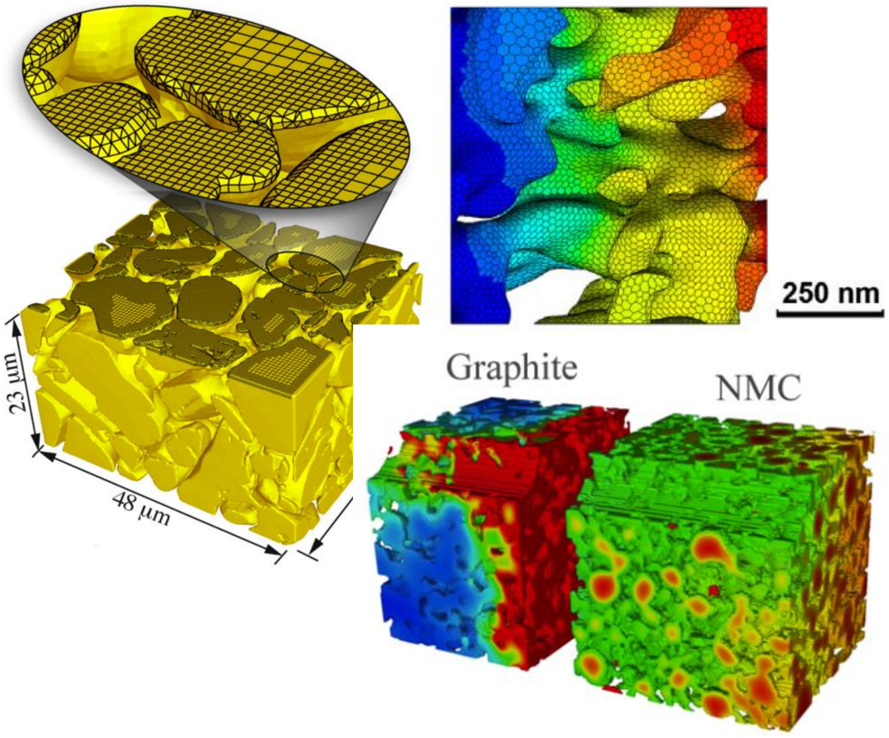
https://www.nrel.gov/transportation/microstructure.html; https://made.ee.ethz.ch/research/open-source-data-and-software/battery-microstructure-project.html

Porous electrode theory, PET (pseudo-2D, P2D) model, pioneered by J Newman.



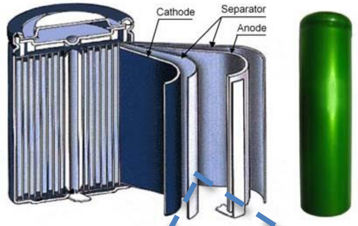
- 1D equation (longitudinal) for C_e, ϕ_e, ϕ_s. Using **homogeneous effect properties**: D_e^{eff}, κ_e^{eff}, κ_s^{eff}.
- 1D equation (radial) for C_s

Conventional 3D simulations

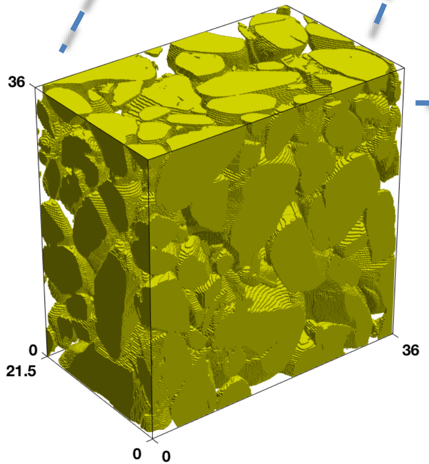


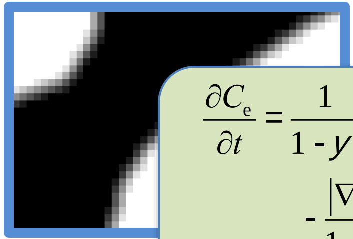
Wiedemann et al., *Electrochimica Acta* 88 (2013) 580–588; S.J. Cooper et al., *Journal of Power Sources* 247 (2014) 1033-1039;
V. De Lauri et al, *Applied Energy Materials*, **4** (12) 13847-13859 (2021)

SBM Formulated electrochemical governing equations



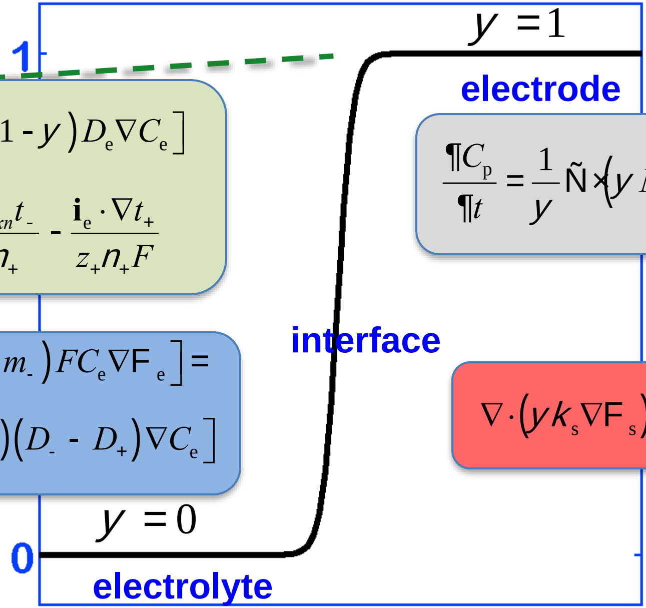
$$R_{xn} = k_f^a a_+ \exp\left(\frac{-\alpha z_+ F}{RT}[\Phi]_e^p\right) - k_b^a a_p \exp\left(\frac{(1-\alpha) z_+ F}{RT}[\Phi]_e^p\right)$$





$$\frac{\partial C_e}{\partial t} = \frac{1}{1-\psi}\nabla\cdot\left[(1-\psi)D_e\nabla C_e\right] - \frac{|\nabla\psi|}{1-\psi}\frac{R_{xn}t_-}{n_+} - \frac{\mathbf{i}_e\cdot\nabla t_+}{z_+ n_+ F}$$

$$\nabla\cdot\left[(1-\psi)(z_+\mu_+ - z_-\mu_-)FC_e\nabla\Phi_e\right] = |\nabla\psi|\frac{R_{xn}}{n_+} + \nabla\cdot\left[(1-\psi)(D_- - D_+)\nabla C_e\right]$$



$$\frac{\partial C_p}{\partial t} = \frac{1}{\psi}\nabla\cdot\left(\psi M_p \nabla\mu_p\right) + \frac{|\nabla\psi|}{\psi}\frac{R_{xn}}{\rho_p}$$

$$\nabla\cdot\left(\psi k_s \nabla\Phi_s\right) = -|\nabla\psi| z_+ F R_{xn}$$

Voxel intensity: ψ

Malik, A. & Yu, H.-C. *Journal of the Electrochemical Society* **169**, 070527 (2022).

Phase separating electrode (graphite)

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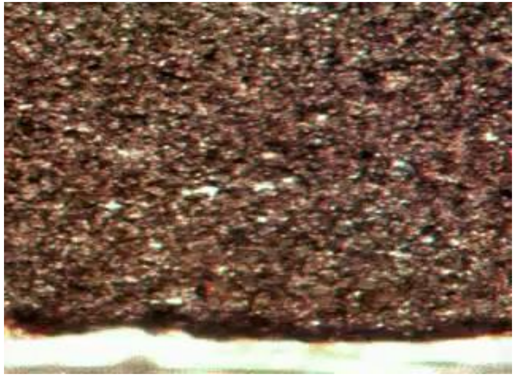
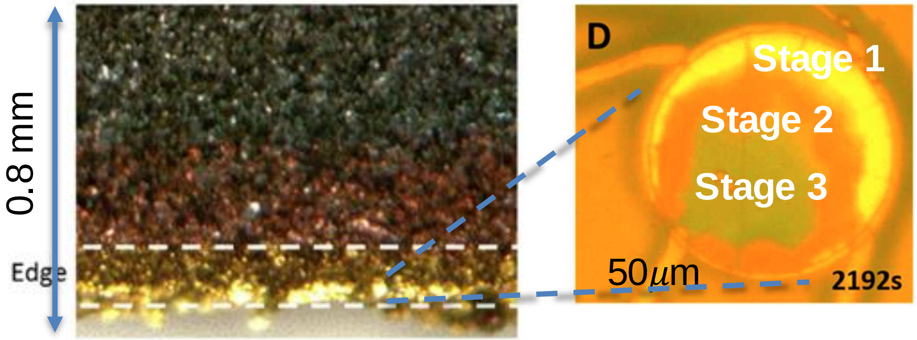
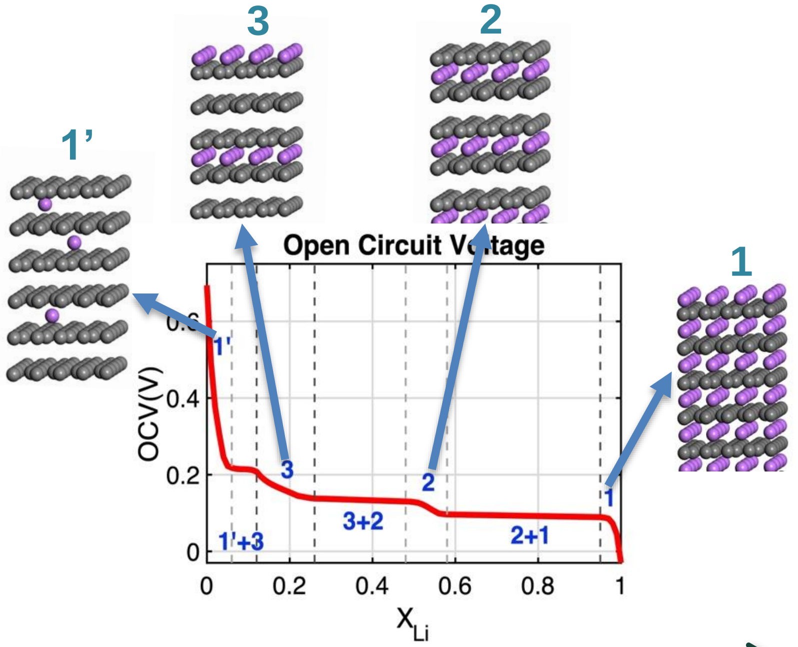
As more and more Li gets intercalated into Graphite, it goes through phase transformations.

$$\frac{\partial X_g}{\partial t} = \nabla \cdot \left[M_g(X_g) \nabla \left(\frac{\partial f}{\partial X_g} - \varepsilon \nabla^2 X_g \right) \right]$$

Cahn-Hilliard Eq (phase-field model)

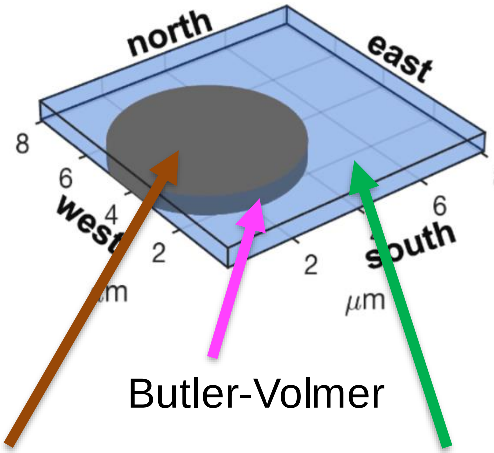




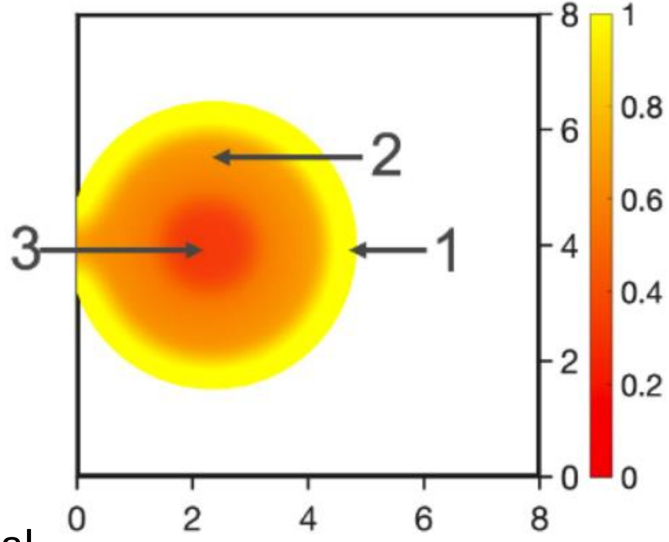


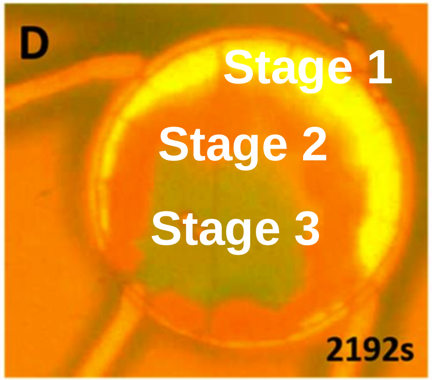
[1] Harris *et al.*, Direct in-situ measurements of Li transport in Li-ion battery negative electrodes, 2009; [2] Ender et al., Anode microstructures from high-energy and high-power lithium-ion cylindrical cells obtained by X-ray nano-tomography, 2014

Single Disk simulation



Butler-Volmer





Phases in a single graphite disk

Phase transition
Electropotential

$X_p \quad \phi_p$

Salt diffusion
Electropotential

$C_e \quad \phi_e$

[3] Guo et al., Li Intercalation into Graphite: Direct Optical Imaging and Cahn−Hilliard Reaction Dynamics, 2016

Open voxel microstructure data.

ETH Zurich › D-ITET › IfE › MaDE Group

ETH zürich Materials and Device Engineering Group

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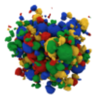
Battery Microstructure Project



The microstructure of lithium ion battery (LIB) electrodes and separators can influence battery performance. The LIB community has traditionally relied on a simplified picture of microstructure or computer generated microstructures due to a lack of available experimental microstructural data.

We launched the **Battery Microstructure Project** to provide 3D microstructural and electrochemical data on porous electrodes and separators. The following microstructures are currently available.

1. **NMC-based Porous Electrodes**

M

Mat

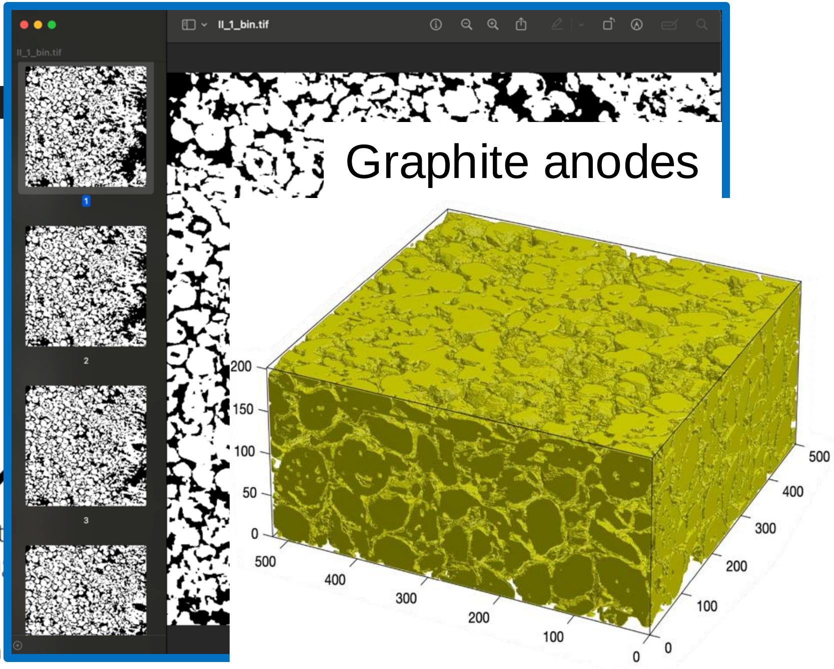
En

Cha

Prof. Dr. Vanessa Wood

VP Knowledge Transfer and Corporate Relations

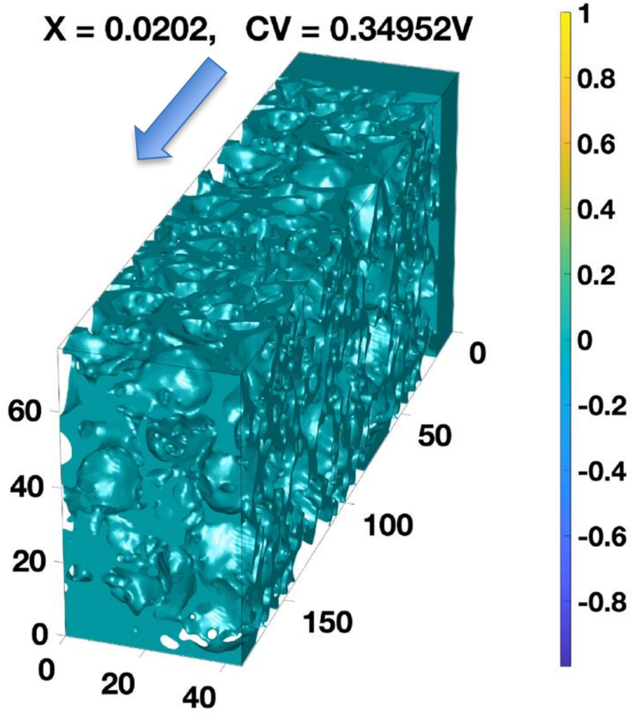
Stacked-TIFF

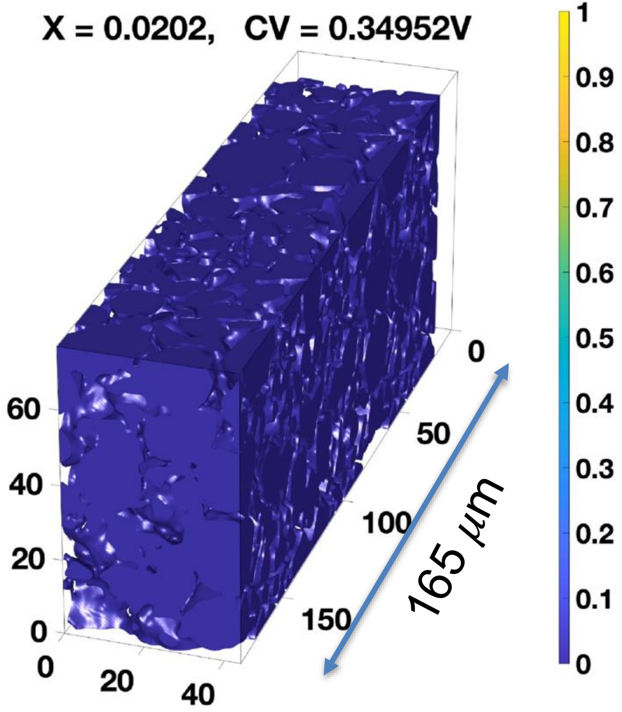


Electrode IIa

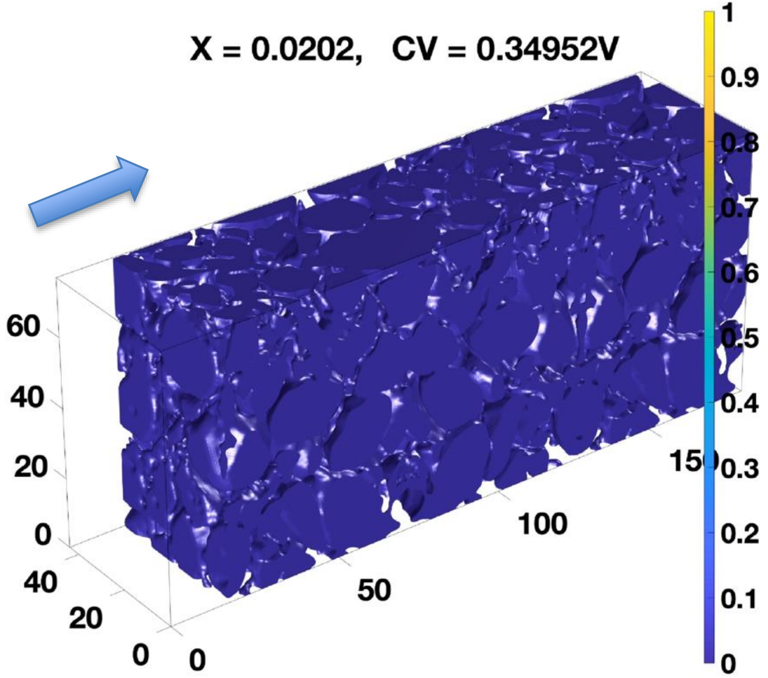
Simulated Li concentration in electrolyte and graphite particles

6C charge: complete charge 6 times in 1 hour, i.e., 10 mins per complete charge

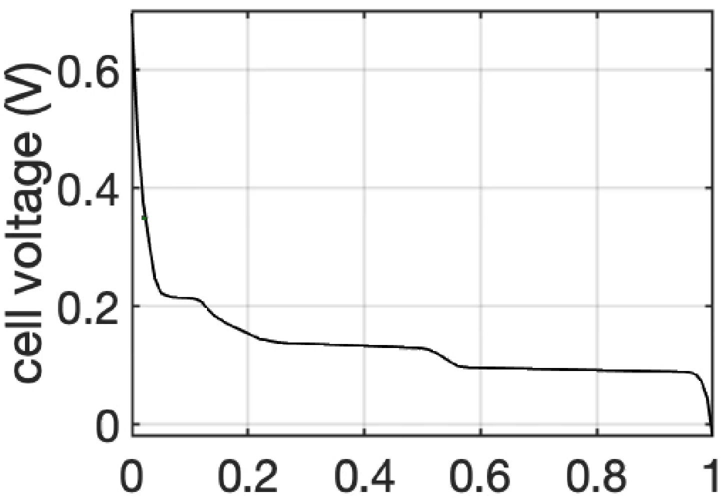




Graphite anode simulations



Simulated cell voltage



SoC = 0.39

Li plating: $\phi_p - \phi_e < 0$, fire/explode. Only a small fraction of thick electrode is utilized.

Thick electrodes

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PROGRESS REPORT

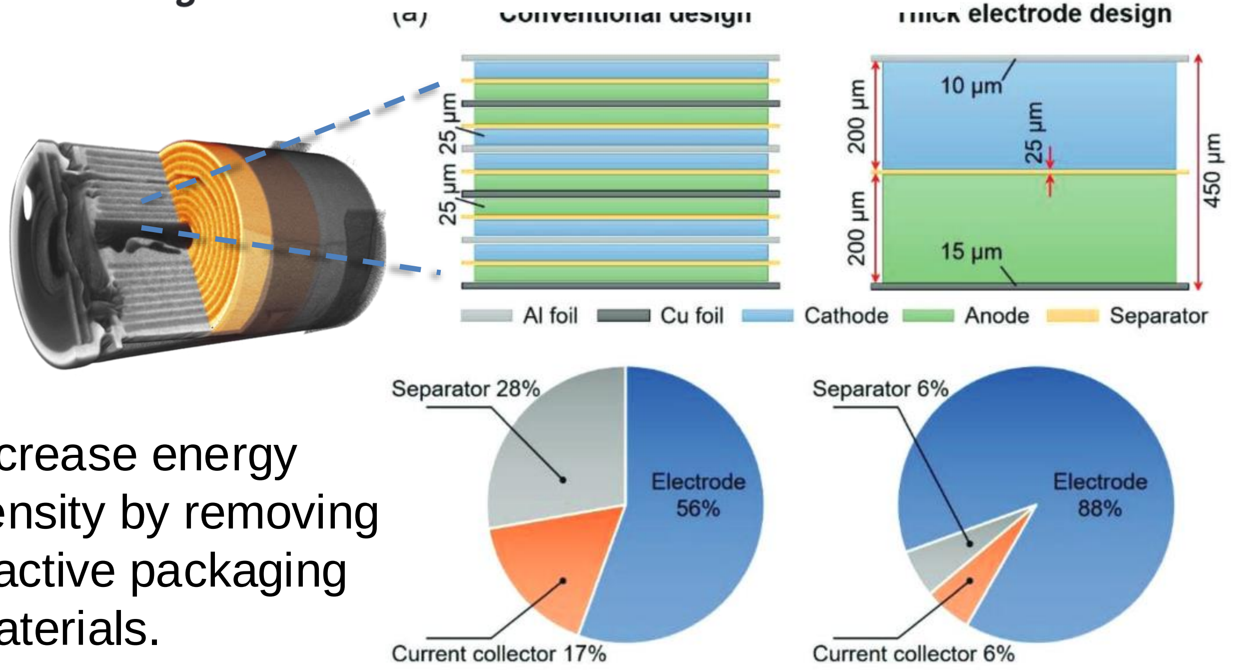
ADVANCED ENERGY MATERIALS

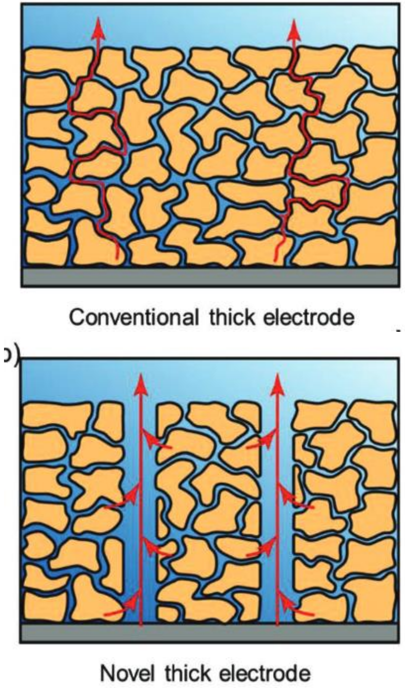
Electrode Materials

www.advenergymat.de

Thick Electrode Batteries: Principles, Opportunities, and Challenges

Yudi Kuang, Chaoji Chen, Dylan Kirsch, and Liangbing Hu**



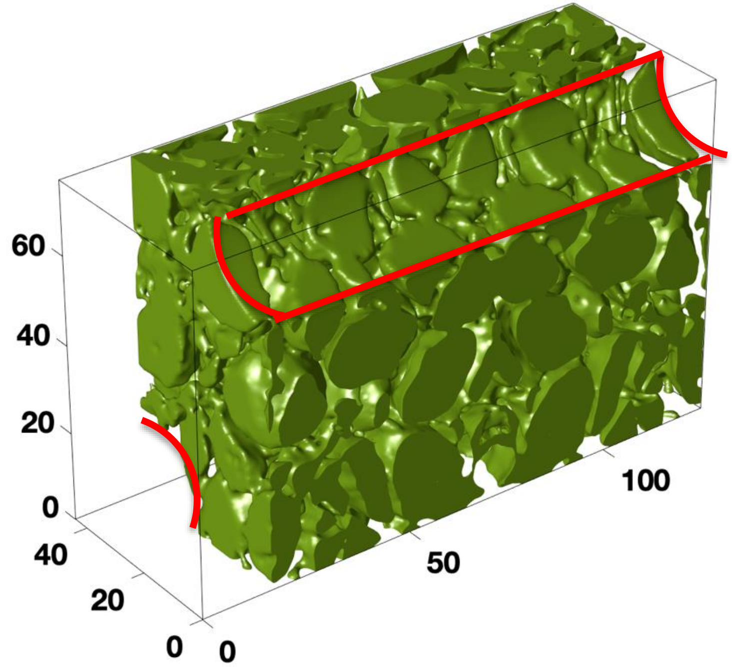


Increase energy density by removing inactive packaging materials.

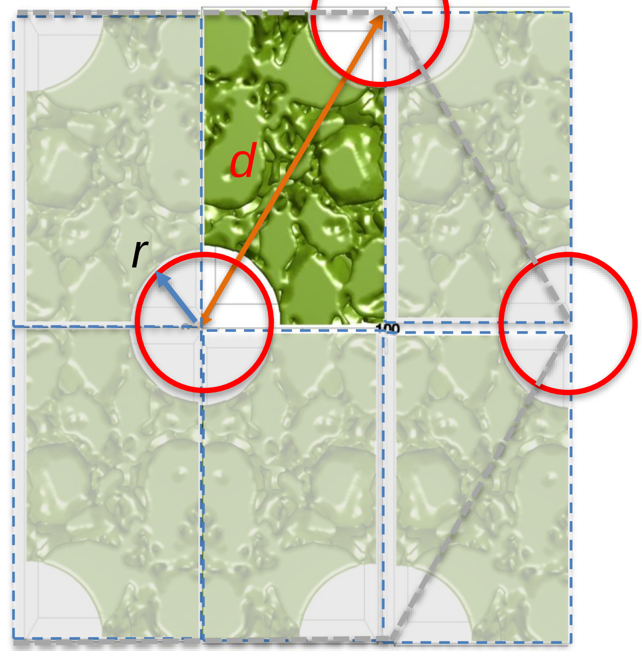
Create tunnels on voxel microstructures: **setting voxel value to be zero**.

d: inter-tunnel distance

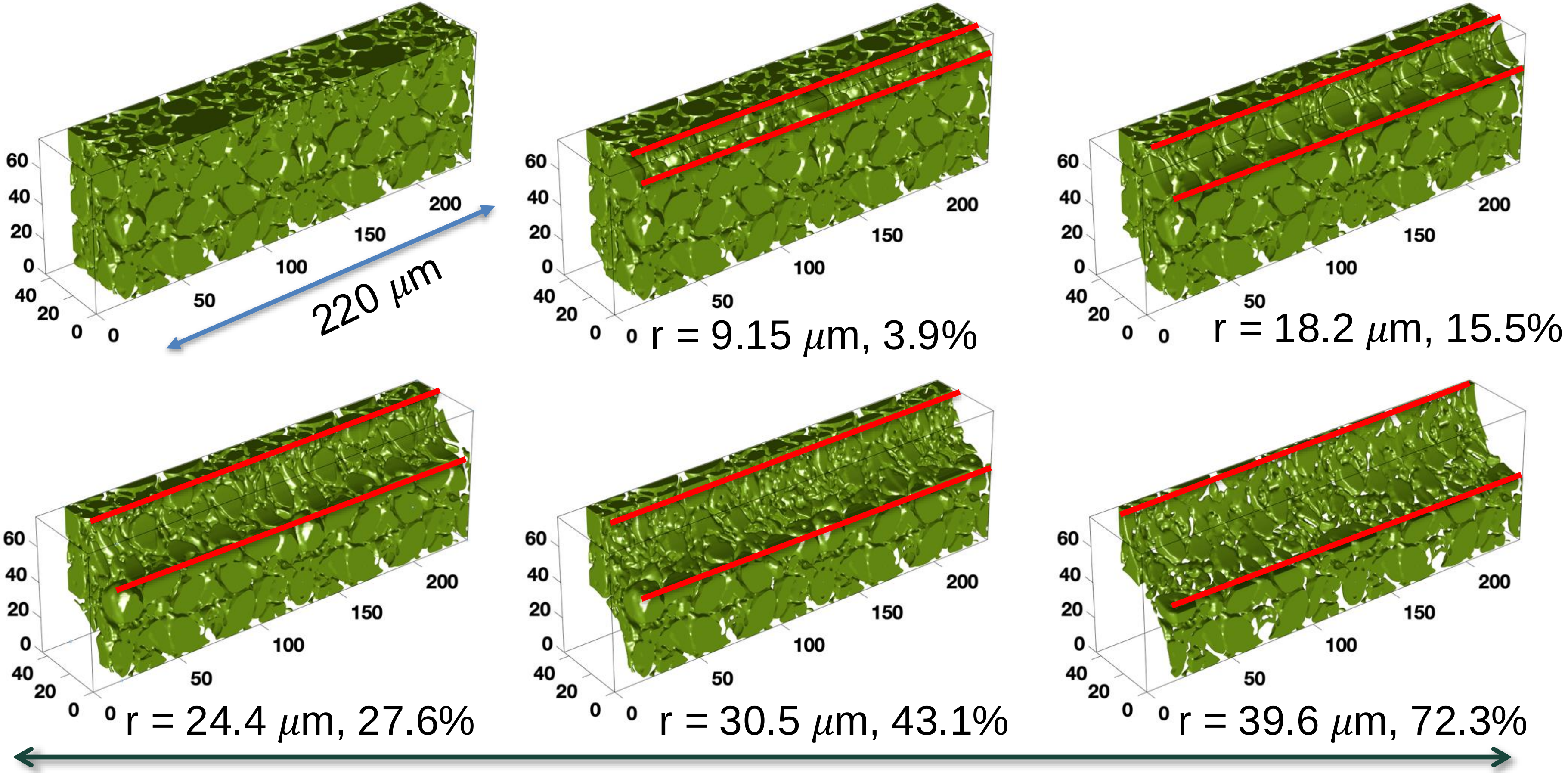
r: tunnel radius

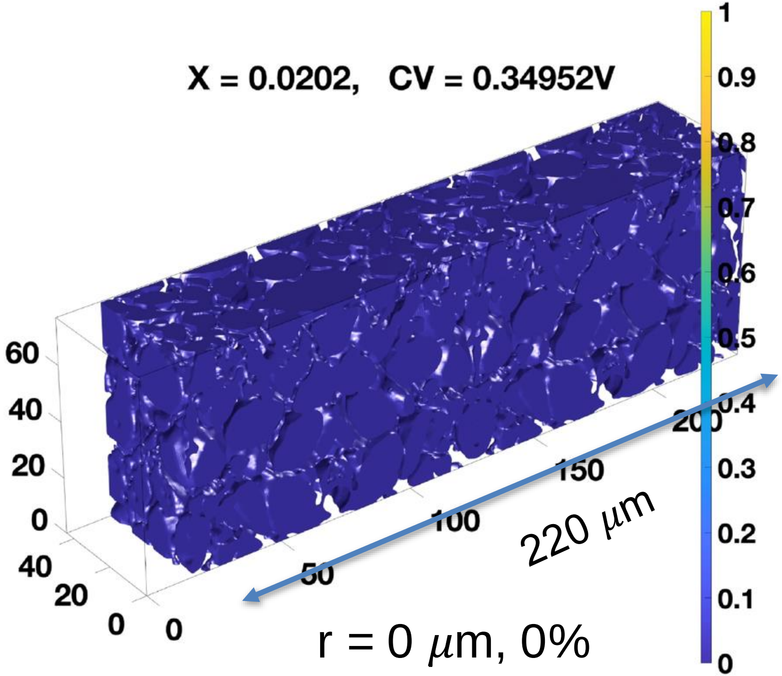


Hexagonal-patterned tunnel array



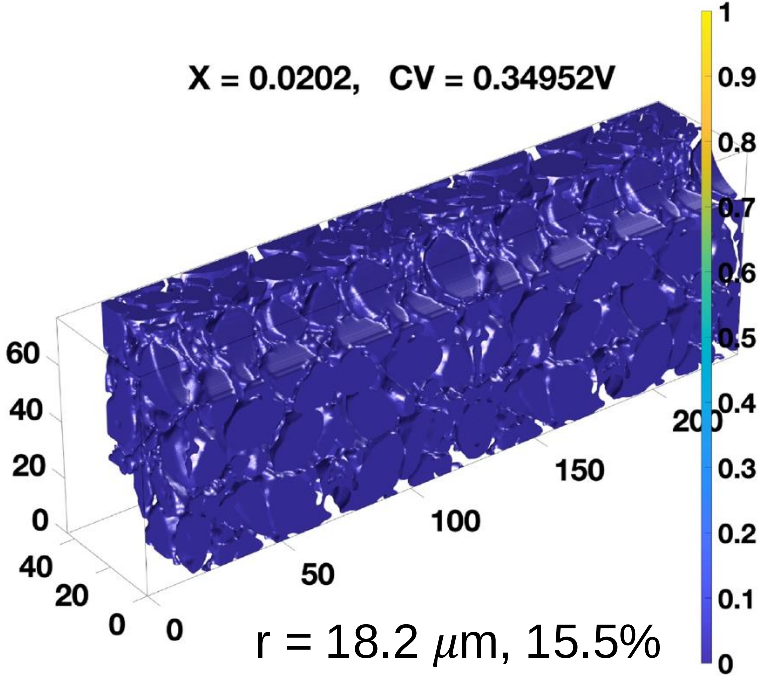
Perforated microstructures





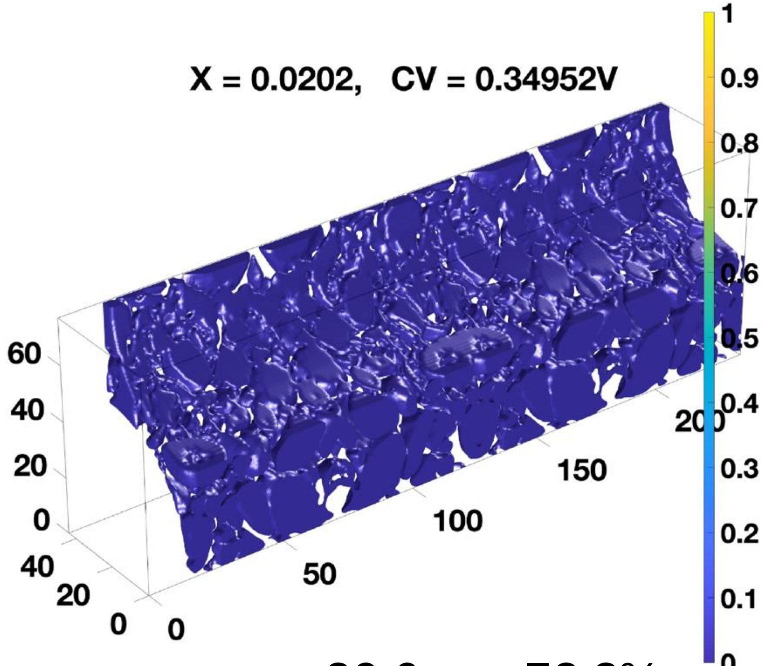
r = 0 μm, 0%

SoC: 0.23; 3.53e-9 mol



r = 18.2 μm, 15.5%

SoC: 0.60; 7.66e-9 mol



r = 39.6 μm, 72.3%

SoC: 0.71; 2.68e-9 mol

Optimal achieved capacity

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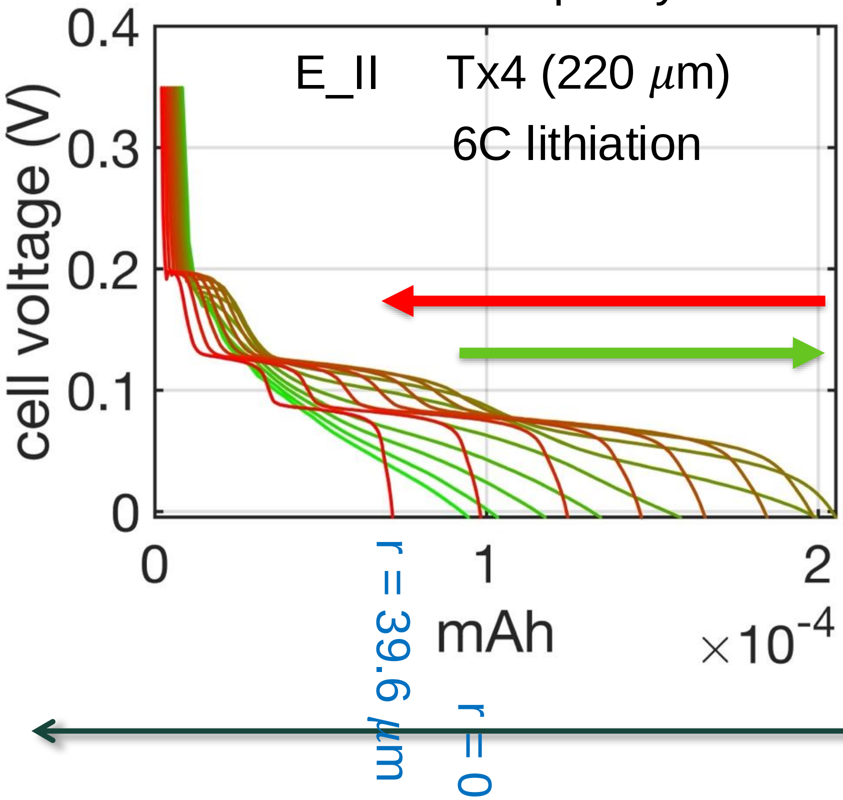
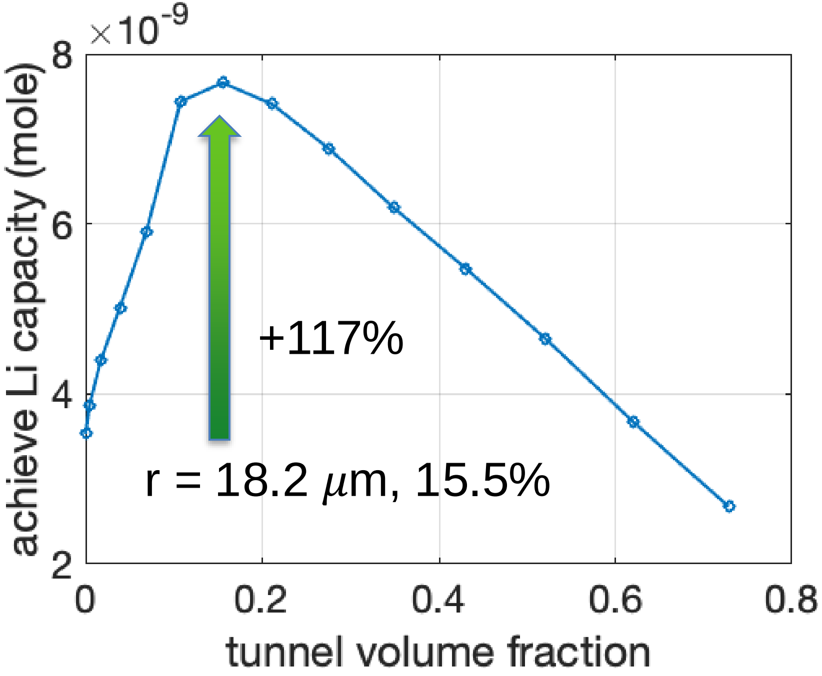
Hexagonal arrang., d = 87.7 μm

Plotted vs capacity





Thickness effect

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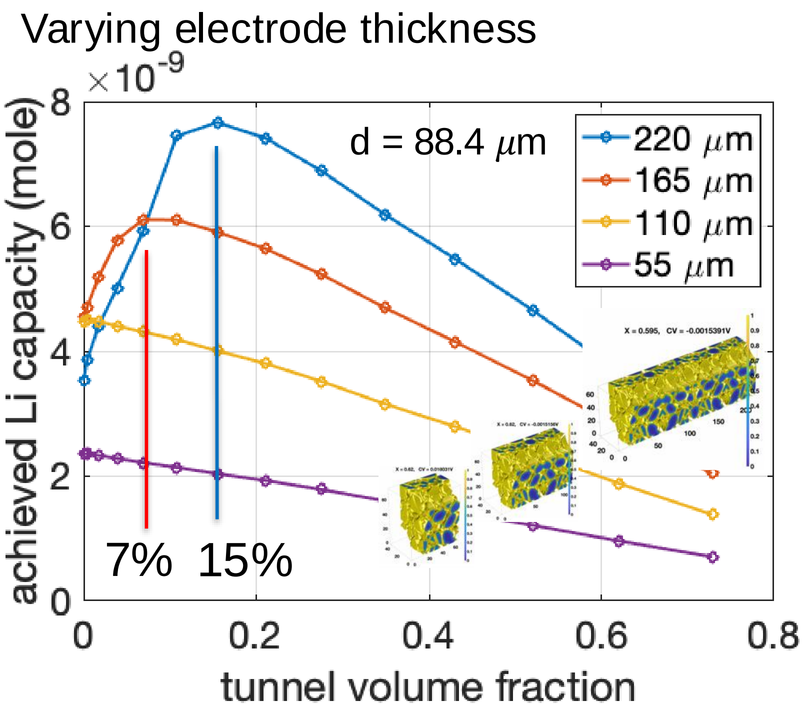

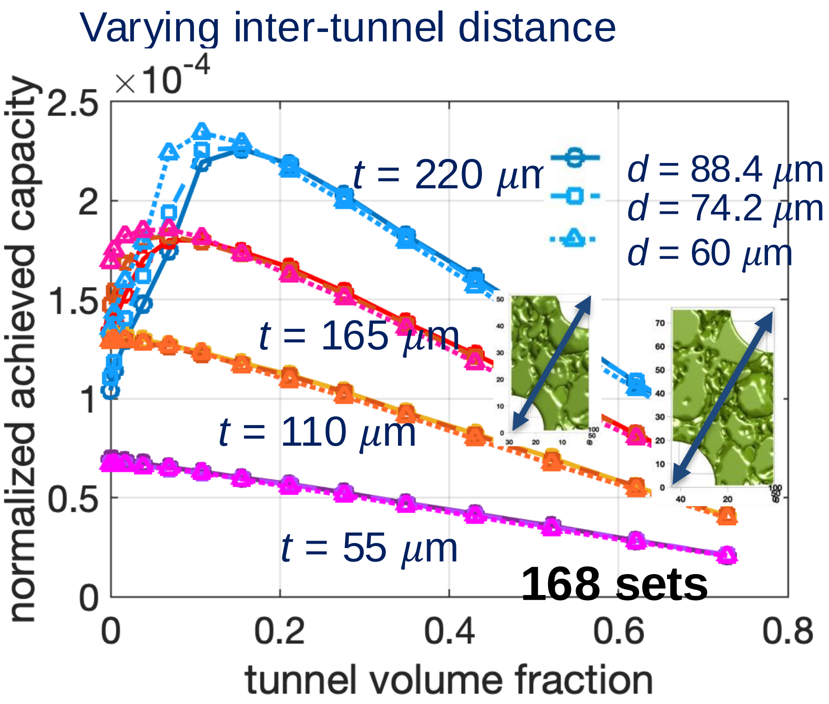

- For anodes of thickness < 110 μm, tunnels do not enhance electrode performance.
- A smaller *d* increases achieved capacity and it decreases the optimal radius.

Voxel-based microstructure simulations

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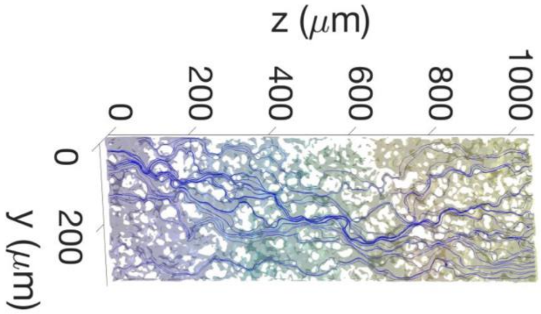
Our group has been developing voxel-based simulation libraries

- In-house code:
  - FORTRAN 90, 08; MPI
  - Finite difference method
- BESFEM:
  - MFEM solver
  - Basic electrochemical process – battery electrodes



- A. Malik, K. Snyder, M. Liu, H.-C. Yu, *Journal of Energy Storage* **77**, 109937 (2024). – **Phase transition** in complex microstructure.
- A. Malik, H.-C. Yu, *Journal of the Electrochemical Society* **169**, 070527 (2022). – SBM with AMR
- D. Qu, H.-C. Yu, *Acs Appl Energy Mater* **6**, 3468–3485 (2023). – **EIS** of complex microstructures
- R. Termuhlen, K. Fitzmaurice, H.-C. Yu, *Comput Method Appl M* **399**, 115312 (2022). – SBM for **Navier-Stokes**
- D. Qu, R. Termuhlen, H.-C. Yu, *Journal of The Electrochemical Society* **167**, 140515–12 (2020). – **Diffuse double layer**
- H.-C. Yu, D. Taha, T. Thompson, N. J. Taylor, A. Drews, J. Sakamoto, K. Thornton, *Journal of Power Sources* **440**, 227116 (2019). – **Linear elasticity**
- H.-C. Yu, M.-J. Choe, G. G. Amatucci, Y.-M. Chiang, K. Thornton, *Computational Materials Science* **121**, 14–22 (2016). – **Grain boundary diffusion**

Elements: Open-Source **B**attery **E**lectrode **S**imulation Toolkit using **MFEM** (BESFEM)
NSF CSSI, # OAC2311466

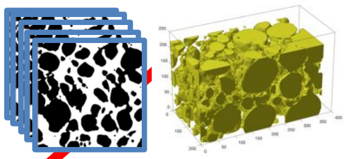
Software development

Community building

Preprocessing

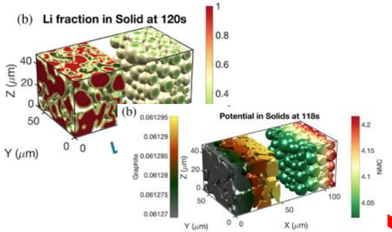
Multiphys. modeling

Postprocessing



TimeDepedentOperator()

CGSolver()



TIFF import
Domain parameter

CnC
CnE
CnA

potC
potE
potA

RxC
RxA

Data visualization
Data analysis

Github
Webpage
Manual
Tutorial
Workshop

Sequential BESFEM -- Benchmarking

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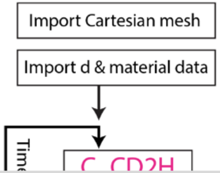
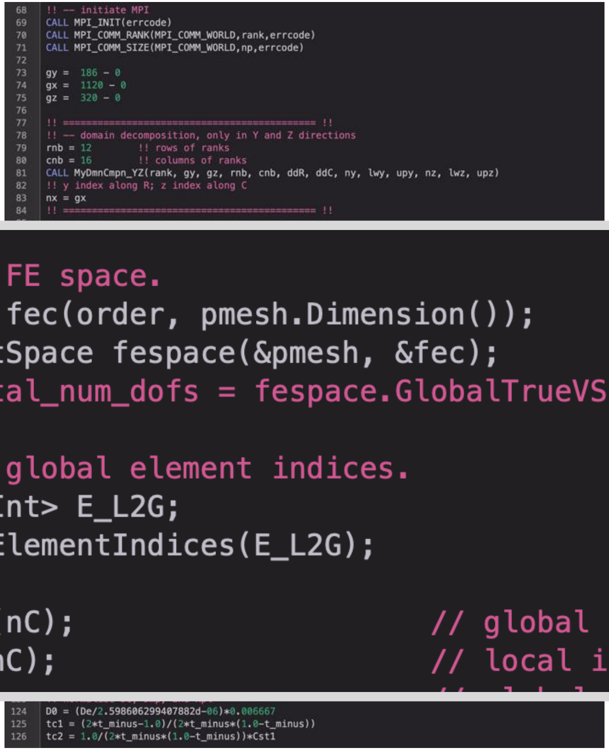
flowchart

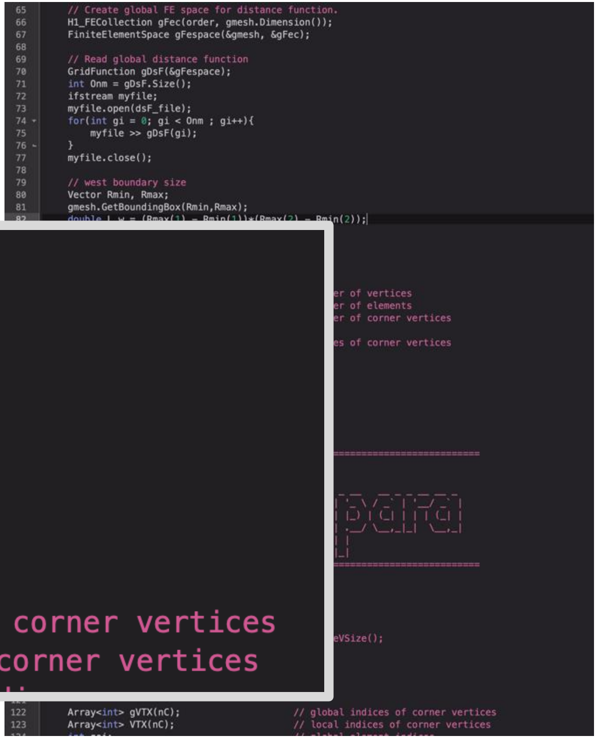


In-house FORTRAN 90 code



```
!! -- initiate MPI
CALL MPI_INIT(errcode)
CALL MPI_COMM_RANK(MPI_COMM_WORLD,rank,errcode)
CALL MPI_COMM_SIZE(MPI_COMM_WORLD,np,errcode)

gy =  186 - 0
gx =  1120 - 0
gz =  320 - 0

!! ========================================== !!
!! -- domain decomposition, only in Y and Z directions
rnb = 12         !! rows of ranks
cnb = 16         !! columns of ranks
CALL MyDmnCmpn_YZ(rank, gy, gz, rnb, cnb, ddR, ddC, ny, lwy, upy, nz, lwz, upz)
!! y index along R; z index along C
nx = gx
!! ========================================== !!
...
D0 = (De/2.598606299407882d-06)*0.006667
tc1 = (2*t_minus-1.0)/(2*t_minus*(1.0-t_minus))
tc2 = 1.0/(2*t_minus*(1.0-t_minus))*Cst1
```

C++ code using MFEM solver

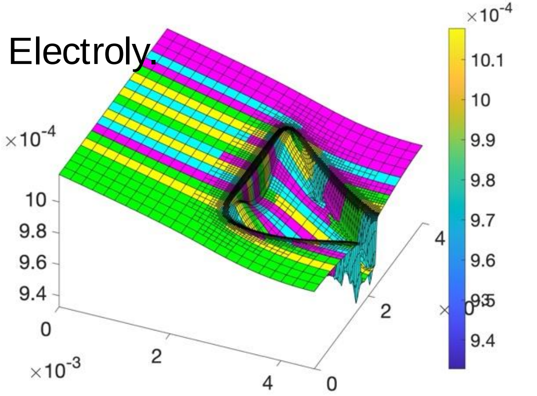


```
// Create global FE space for distance function.
H1_FECollection gFec(order, gmesh.Dimension());
FiniteElementSpace gFespace(&gmesh, &gFec);

// Read global distance function
GridFunction gDsF(&gFespace);
int Onm = gDsF.Size();
ifstream myfile;
myfile.open(dsF_file);
for(int gi = 0; gi < Onm ; gi++){
    myfile >> gDsF(gi);
}
myfile.close();

// west boundary size
Vector Rmin, Rmax;
gmesh.GetBoundingBox(Rmin,Rmax);
...
Array<int> gVTX(nC);          // global indices of corner vertices
Array<int> VTX(nC);           // local indices of corner vertices
```

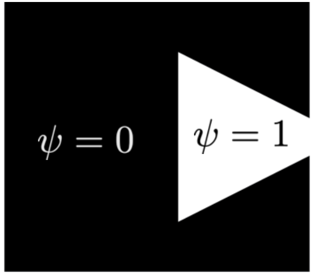
```
    // Create local FE space.
    H1_FECollection fec(order, pmesh.Dimension());
    ParFiniteElementSpace fespace(&pmesh, &fec);
//  HYPRE_BigInt total_num_dofs = fespace.GlobalTrueVSize();

    // Map local to global element indices.
    Array<HYPRE_BigInt> E_L2G;
    pmesh.GetGlobalElementIndices(E_L2G);

    Array<int> gVTX(nC);                    // global indices of corner vertices
    Array<int> VTX(nC);                     // local indices of corner vertices
```

Sequential BESFEM – 2D test

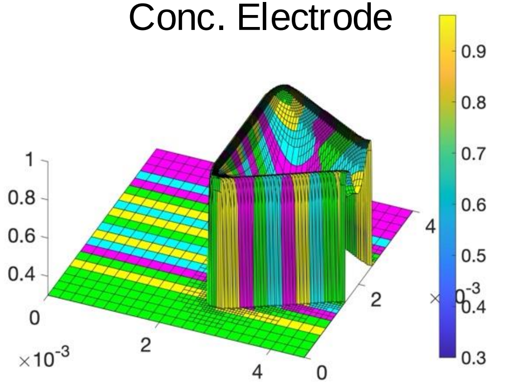
Conc. Electroly.



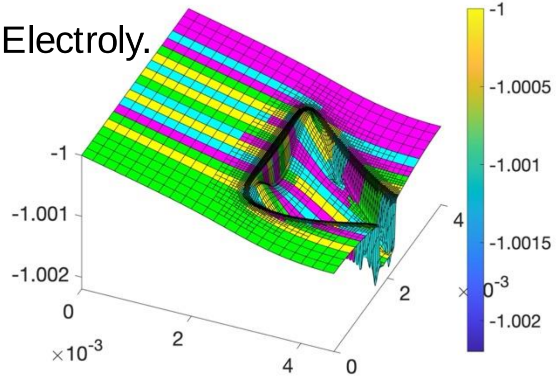
2D image: a single triangular particle



Conc. Electrode

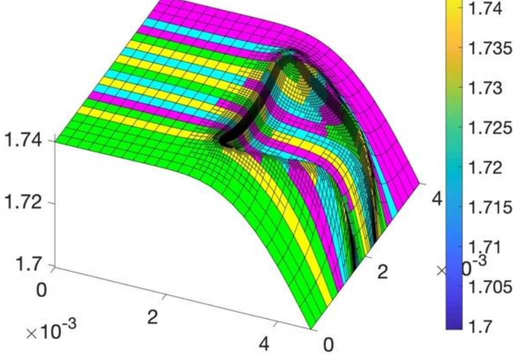


Pot. Electroly.



Pmesh()
RefineByError()
HypreParMatrix()
HypreParVector()
T_Solver()
CGSolver()

Pot. Electrode

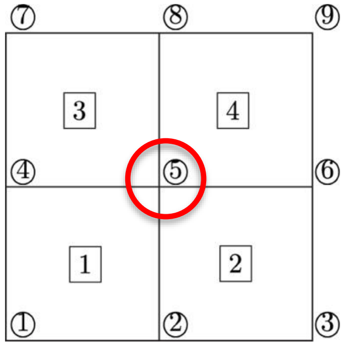


FEM vs FDM

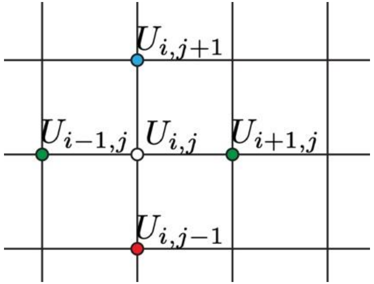
FEM:
- High accuracy
- High computational cost (slow)

e.g., default Laplace operator, ∇^2

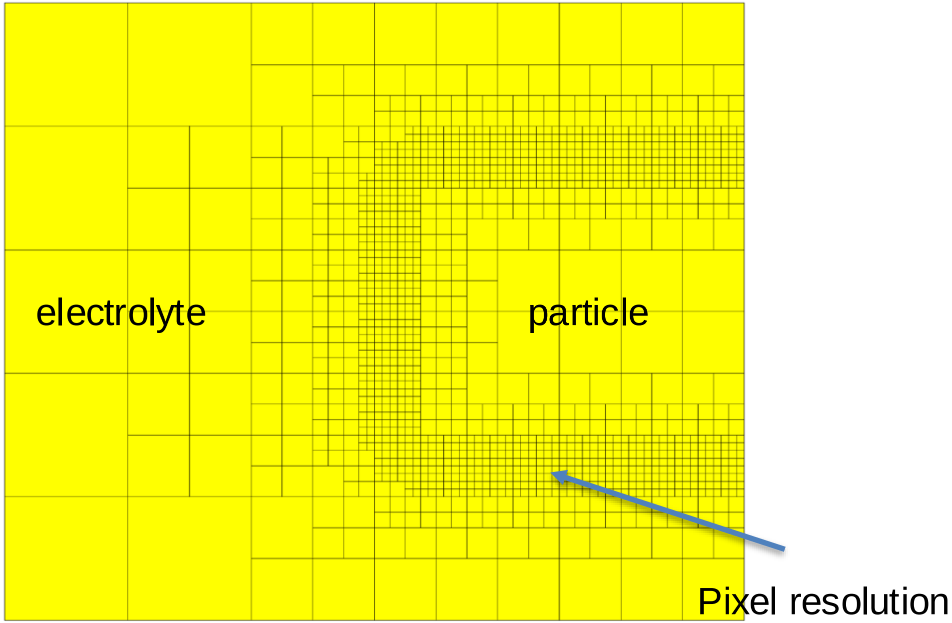
FEM: 9 points



FDM: 5 points



- In terms of speed, MFEM is out-performed by in-house FDM code in original pixel resolution
- Strategy: use coarse mesh away from the bulk.
- Weighing computing costs against accuracy



BESFEM software development status

MICHIGAN STATE UNIVERSITY

- Jan–May 2024: sequential code
- May—present: OOP

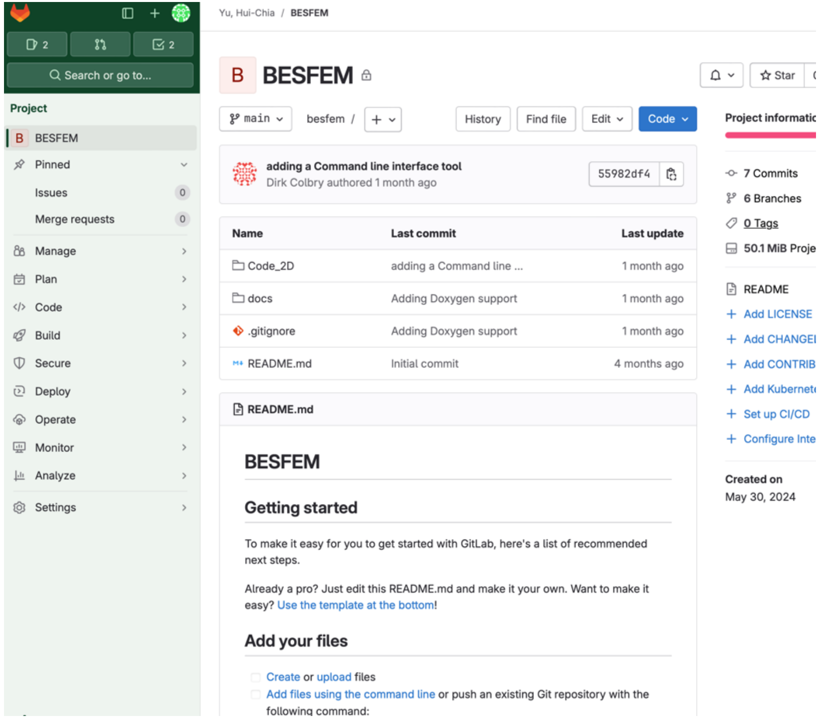
Work in progress

Preprocessing units
- TIFF importer -- ✓
- Pixel intensity smoother
  - Sequential -- ✓
  - OOP – in progress
- Mesh coarsener

Modeling units

Class:
- Concentration
- Electro-potential
- Reaction calc.

Use the following example codes
- Ex16p
- Ex6p

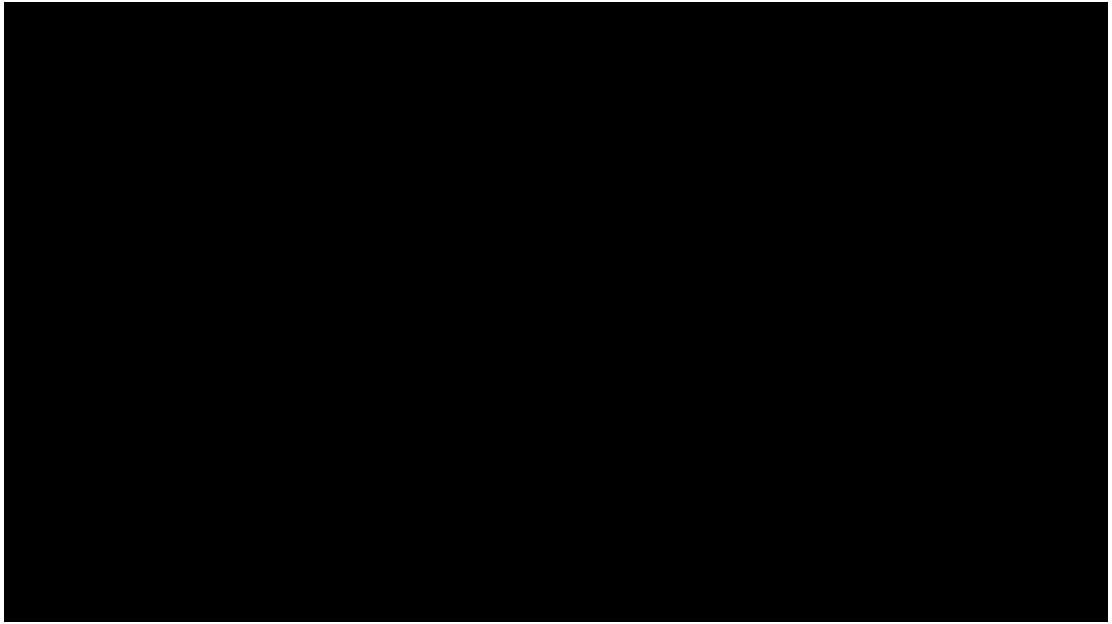


Spin-off (potential miniapps)
- Macro-homogeneous PET simulation
- Microstructure tortuosity calculator

Fun REU project

Sean Gibson,
Sanika Kapre

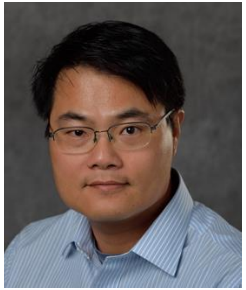
VR set



VR visualization of battery electrode simulations

Team members



- Ph.D. student: Anna Brandl (brandlan@msu.edu)
- Fixed term Asst. Prof. Robert Termuhlen (termuhle@msu.edu)
- Sr Specialist Dirk Colbry (colbryd@msu.edu)
- Asso. Prof. Hui-Chia Yu (hcy@msu.edu)

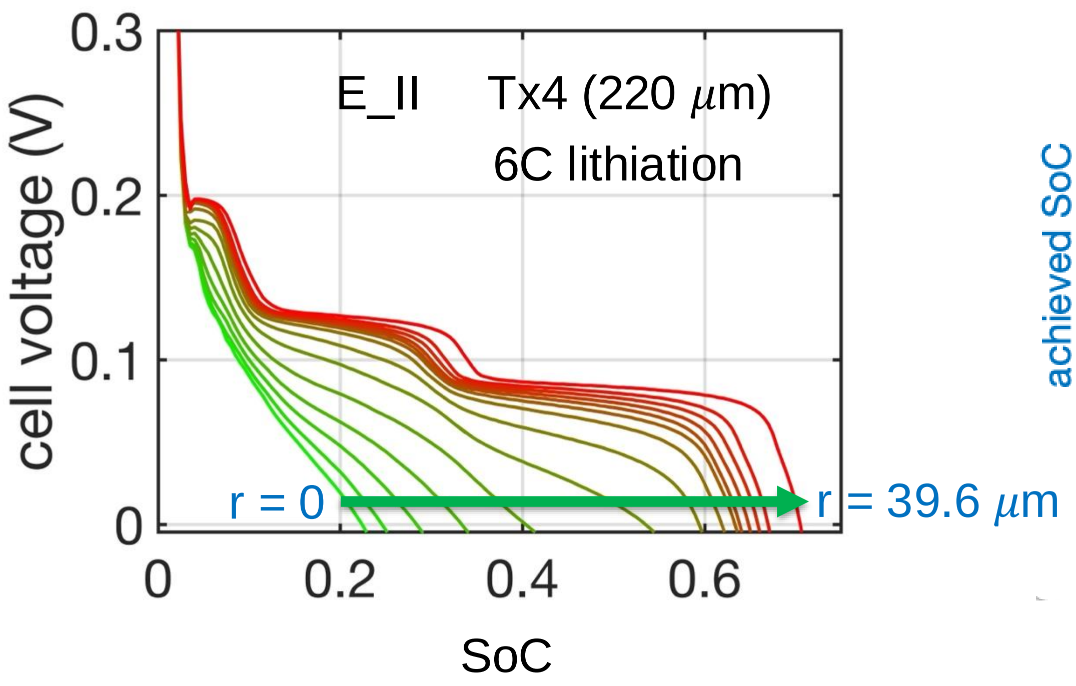
Collaborators/co-developers are WELCOME!!

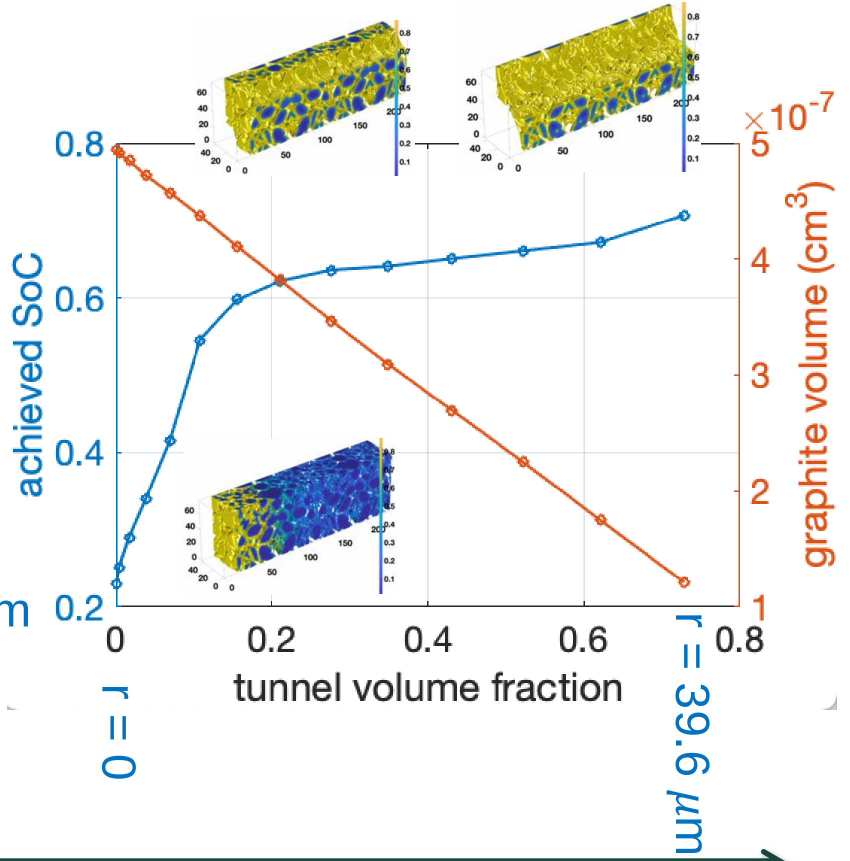
-- hcy@msu.edu, colbryd@msu.edu

Potential add-ons:
Aging model (side reaction), cycling stress, thermal simulations, Li metal plating, characterization (EIS), PET (P2D), etc.

Tunnel effect

Hexagonal arrang., d = 88. μm

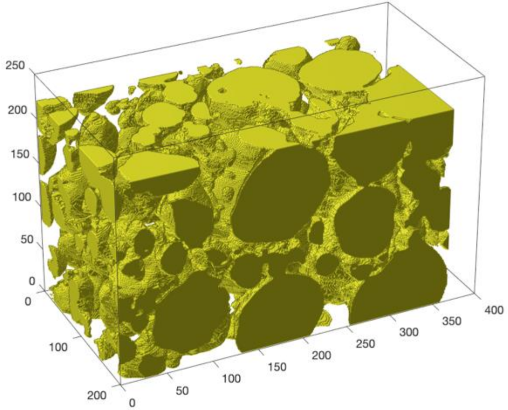




Direct image-based simulation of NMC111 cathode

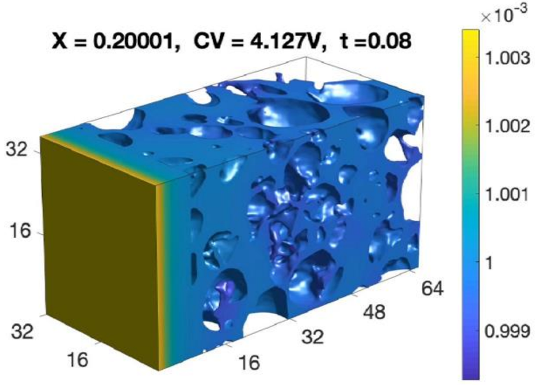
Ming Tang, Rice Univ

Stacked tiff file

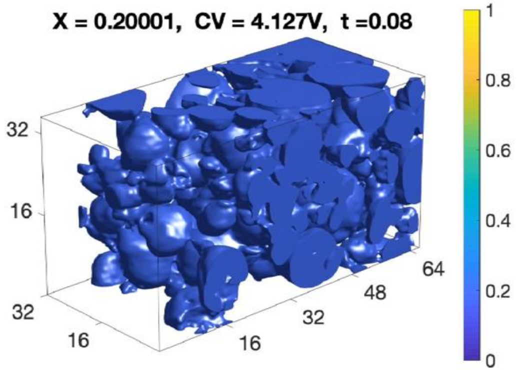


Voxel representation of FIB-SEM reconstructed NMC cathode

Image-based simulation



Salt conc



Li frax