# Micro/Macro-Scale Modeling for Battery Fast Charge Applications

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DOE Vehicle Technologies Office
2018 Annual Merit Review and Peer Evaluation Meeting

# Overview

## Timeline

- Project start date: FY18
- Project end date: FY19
- Percent complete: 30%

## Barriers

- Long charge times for electric vehicles
- Today's fast charge batteries use thin electrodes to avoid electrolyte transport limits and lithium plating
    - Thin electrodes have higher cost and lower energy density however
- Safety and degradation concerns with lithium plating

## Budget

- Total project funding $1.1M
    - DOE share: 100%
    - Contractor share: 0
- Funding for FY 2018: $550k
- Funding for FY 2019: $550k

## Partners

- Lead: Argonne National Laboratory (ANL)
- Interactions/collaborations
    - Idaho National Laboratory (INL)
    - University College of London (UCL)
    - Brigham Young University (BYU)

# Relevance – Prediction of Transport Limits and Consequences for Extreme Fast Charge (XFC)

**1) Li⁺ depletion in electrolyte**
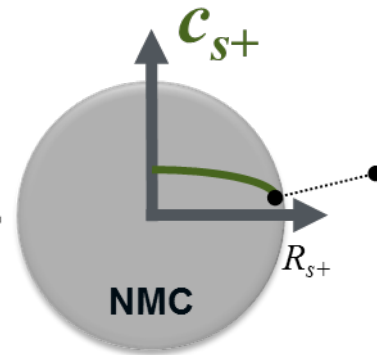
Solubility limit

$c_e$

$x$

0
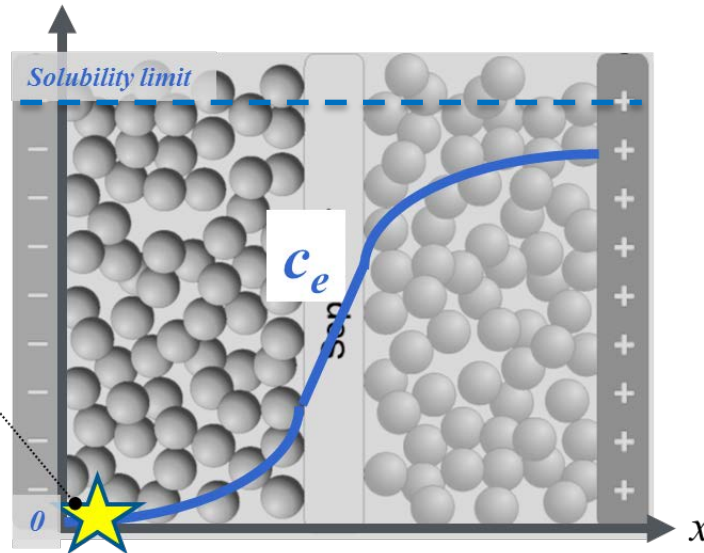
Electrolyte transport is the most common limiter of fast charge rate for energy dense (thick electrode) battery electric vehicle (BEV) cells

*Depletion results in non-uniform current in negative electrode, promoting lithium (Li) plating near separator*

**2) Li saturation @ graphite surface**

$c_{s-}$

max

$R_{s-}$

Graphite

Li⁺

$c_{s+}$

$R_{s+}$

NMC
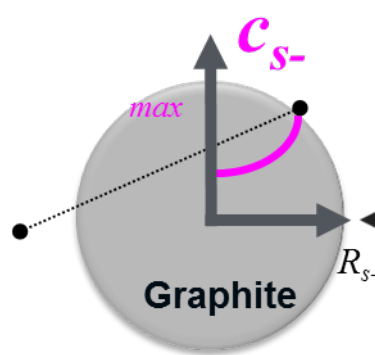
**3) Li depletion @ NMC surface**

Charge

NMC: Nickel-Manganese-Cobalt Oxide

# Relevance – DOE Goals

- Battery goals[1]
  - Cost: $80/kWh
  - Energy: 275 Wh/kg, 550 Wh/L
  - Vehicle range: 300 miles
  - Charge time: 80% ΔSOC in 15 min

- System challenges:
  - Thermal management
  - Safety, controls
  - Infrastructure

- Electrode-level challenges (present focus)

|  | Pros | Cons |
|---|---|---|
| Thick electrodes | Lower battery cost<br>Higher energy density | Increases electrolyte ionic transport distance<br>(leads to polarization, heat, Li plating) |
| Thin electrodes | Capable of fast charge | ~ 2x increase in cell cost<br>(from $103/kWh to $196/kWh)<br><br>~ 20% less energy density<br>(from 220 to 180 Wh/kg) |

1. "Enabling Fast Charging: A Technology Gap Assessment" U.S. DOE, October 2017.
SOC: state of charge

# Relevance – Objectives

- Through modeling studies, quantify
  - Limits of today's graphite-based electrode technologies for varying electrode designs (loadings, porosities, etc.)
  - Why some electrodes are better suited to XFC than others
    - Electrode tortuosity based on electrode morphology
  - Electrode and electrolyte improvements needed to enable XFC
- Develop first case studies with 3D microstructure model to explore
  - Interaction of electrode morphology with heterogeneous utilization, increasing probability of degradation

Leverage tools developed under DOE's Computer-Aided Engineering of Batteries (CAEBAT) program for XFC

# Approach

- **Electrochemical modeling tools for XFC**

  - Macro-homogeneous modeling

    - Guide electrode design and electrolyte requirements

  - Microstructure modeling

    - Effective properties determined via homogenization and geometric analysis (tortuosity, surface area, porosity, morphology)

    - 3D electrochemical models assess electrode heterogeneity

- **ANL-CAMP electrodes: Experimental characterization**

  - Related CAEBAT work: Toda NMC532 / Phillips A12 graphite of varying porosity and thickness (Ref. poster bat299)

  - Present XFC project: Extend to additional graphite material types (1 of 6 thus far)

Ref: **ES030** Cell Analysis, Modeling, and Prototyping (CAMP) Research Activities



$0.95 \times c_{s,\mathrm{max}}$

Graphite lithiation

$0.73 \times c_{s,\mathrm{max}}$

# Milestones

| Remaining FY18 milestones | Due (end of quarter) | Go/ No-go | Status |
|---|---|---|---|
| M1. Use **macro model** to determine limits of **varying electrode designs** for accomplishing XFC | Q1 | Yes | Complete |
| M2. Build **first case of microstructure models** for fast charge | Q2 | No | Complete |
| M3. Report summarizing **measurement of electrochemical parameters** for graphitic electrodes and **impact on cell-level performance** | Q3 | No | On track |
| M4. Comparison of **model predictions** against **test data** | Q4 | No | On track |

# Technical Accomplishments: Macro-homogeneous Modeling

# Fast Charging of Full Cell with Thin (~42-µm) Electrodes

A12 Graphite vs. NMC532, Gen2 Electrolyte, Celgard 2325, 2 mAh/cm²
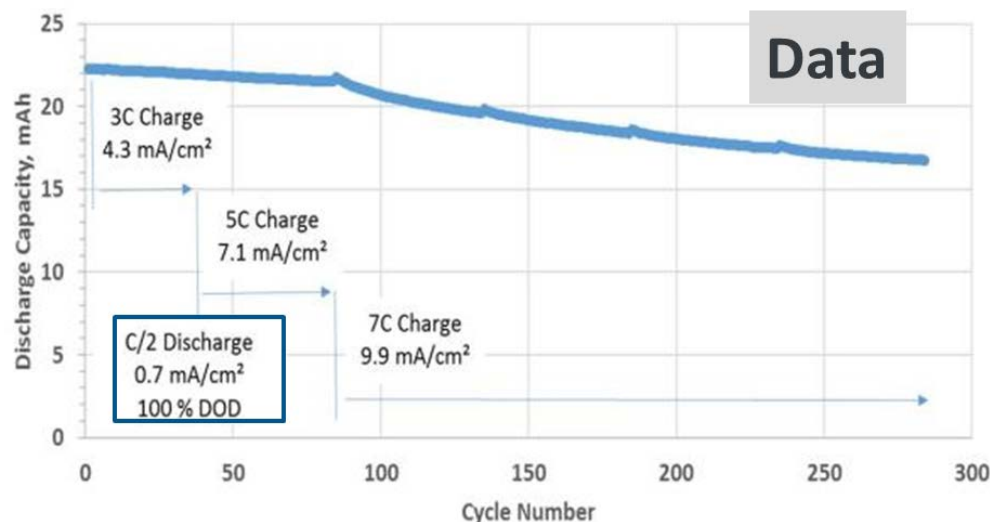


Data: Andy Jansen, Stephen Trask, and Bryant Polzin (ANL)
Model: Andrew Colclasure (NREL)



- 180 Wh/kg, 450 Wh/L design
- Phillips A12 graphite/Toda NMC532 electrochemical parameters taken from CAEBAT project (Ref. bat298 & bat299 posters)
- Tortuosity: 6.0 and 2.9 for anode and cathode, respectively
- Assumes 10% loss of cycle-able lithium due to solid-electrolyte interphase formation
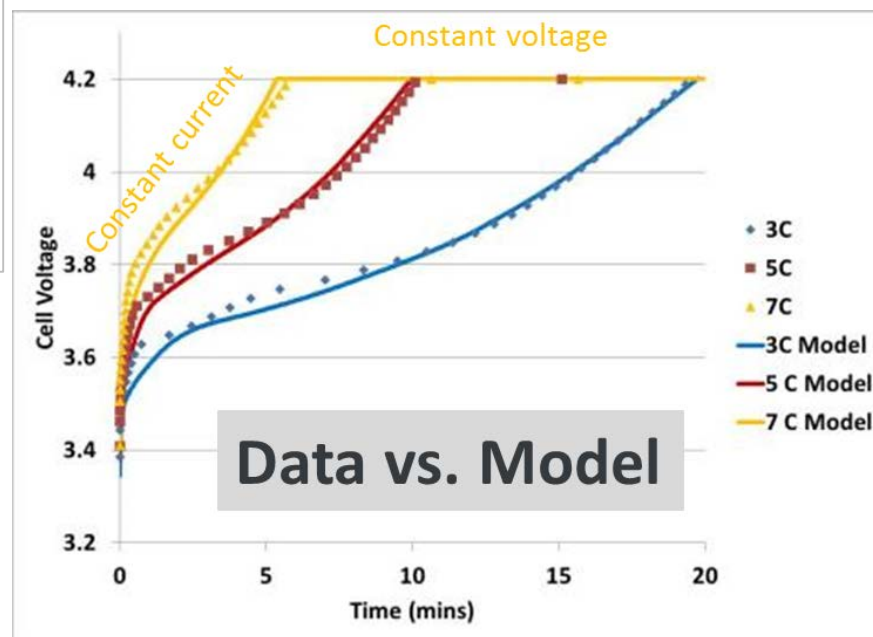
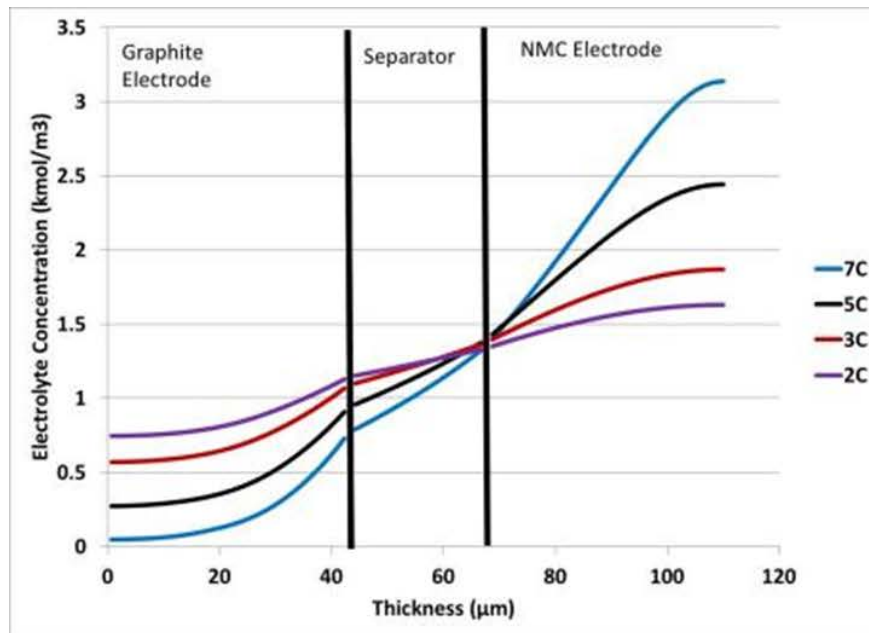# Lithium (Li) Plating Likely Near End of 7C Constant Current Charge
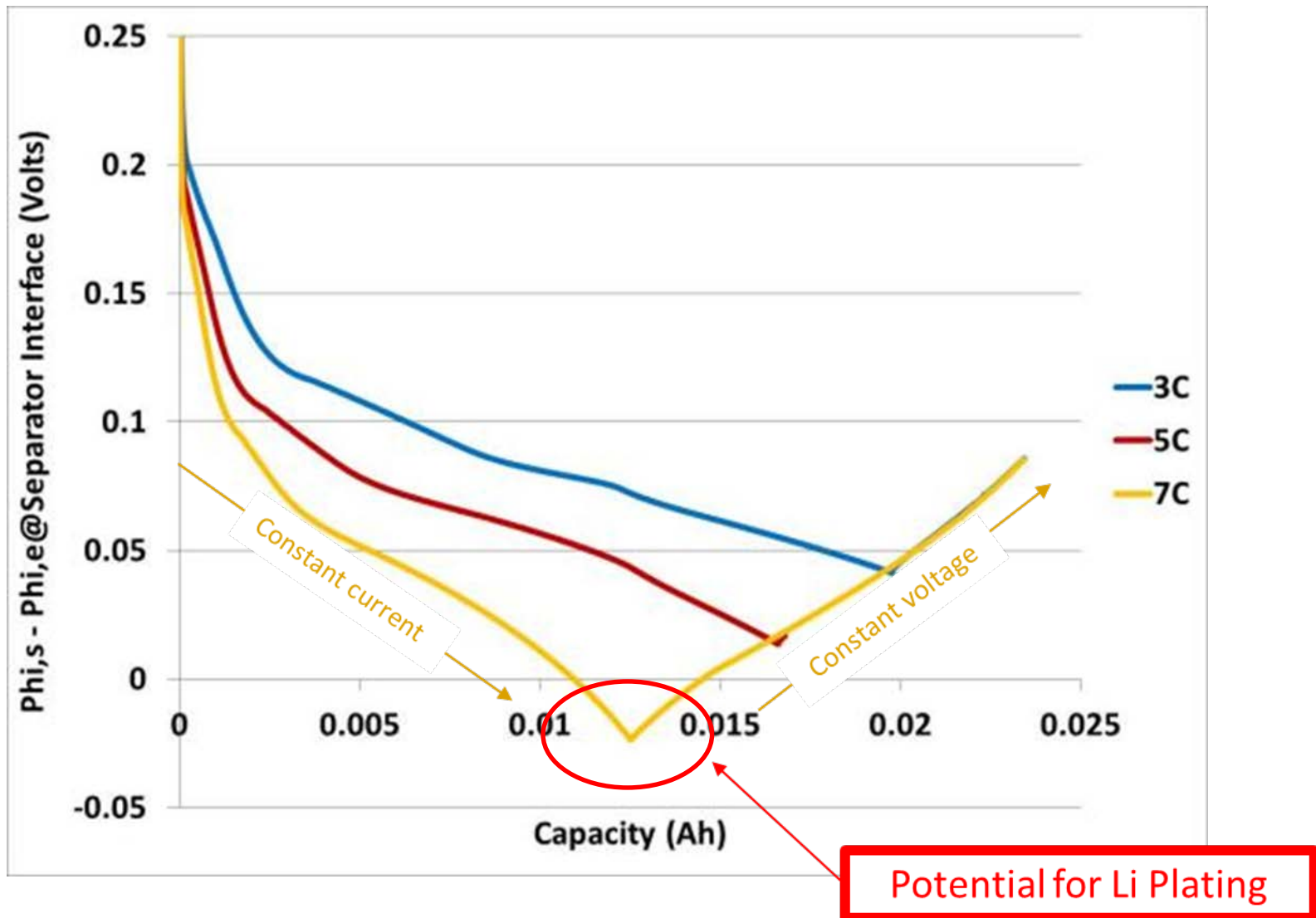
# Electrolyte Li⁺ Concentration Gradients at Transition from Constant Current to Constant Voltage Charge Step

## Electrolyte transport severely limits charging rate at higher loadings
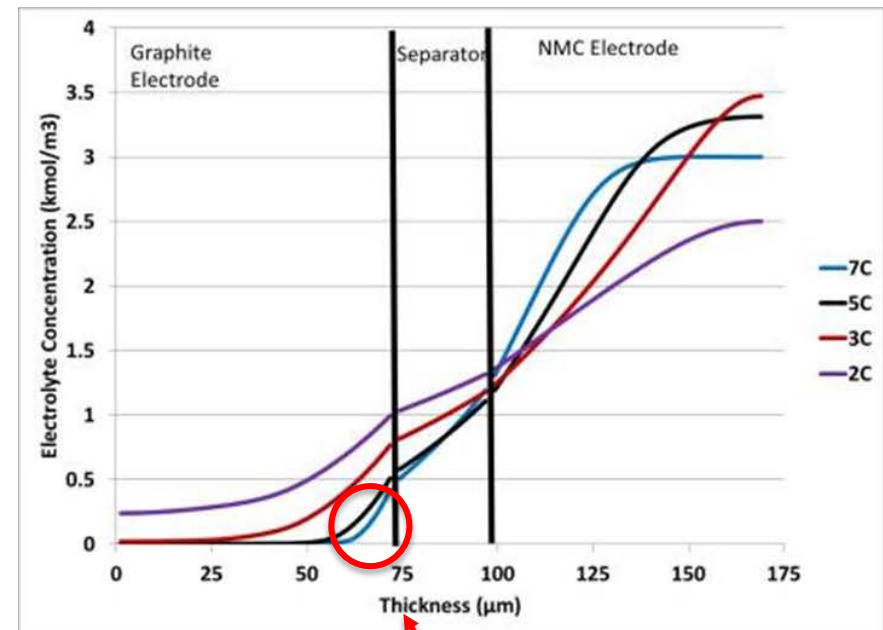
**Low Electrode Loading**
1.5 mAh/cm² cathode (42 μm)
1.84 mAh/cm² anode (43 μm)

**Medium Electrode Loading**
2.5 mAh/cm² cathode (71 μm)
3.07 mAh/cm² anode (87 μm)



When electrolyte is depleted at the back of the electrode, only the front portion of the electrode remains active. Excessive local C-rates lead to Li plating near the separator.

# Projections Next-Generation (NG) Electrolyte

Reduced chance of Li plating with hypothetical "NG" electrolyte
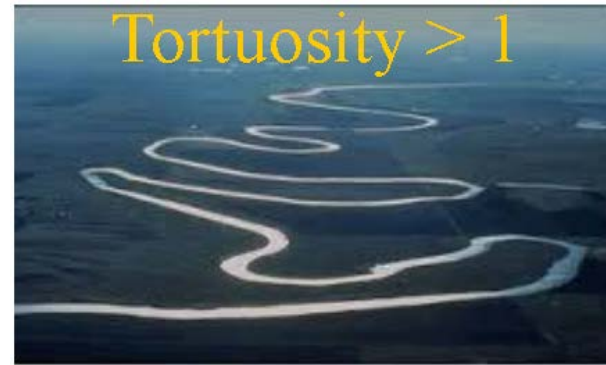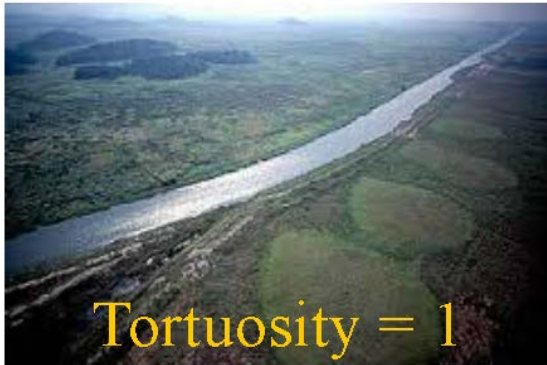
- Anode tortuosity same as cathode ($\tau_- = 6.0 \rightarrow 2.85$)
- Electrolyte with 1.5x conductivity, 3x diffusivity, and $t^+$ improved by 0.1 (baseline: κ=10 mS/cm, $D_e$=1.6E-6 cm$^2$/s, and $t^+$=0.46 @ 1M)
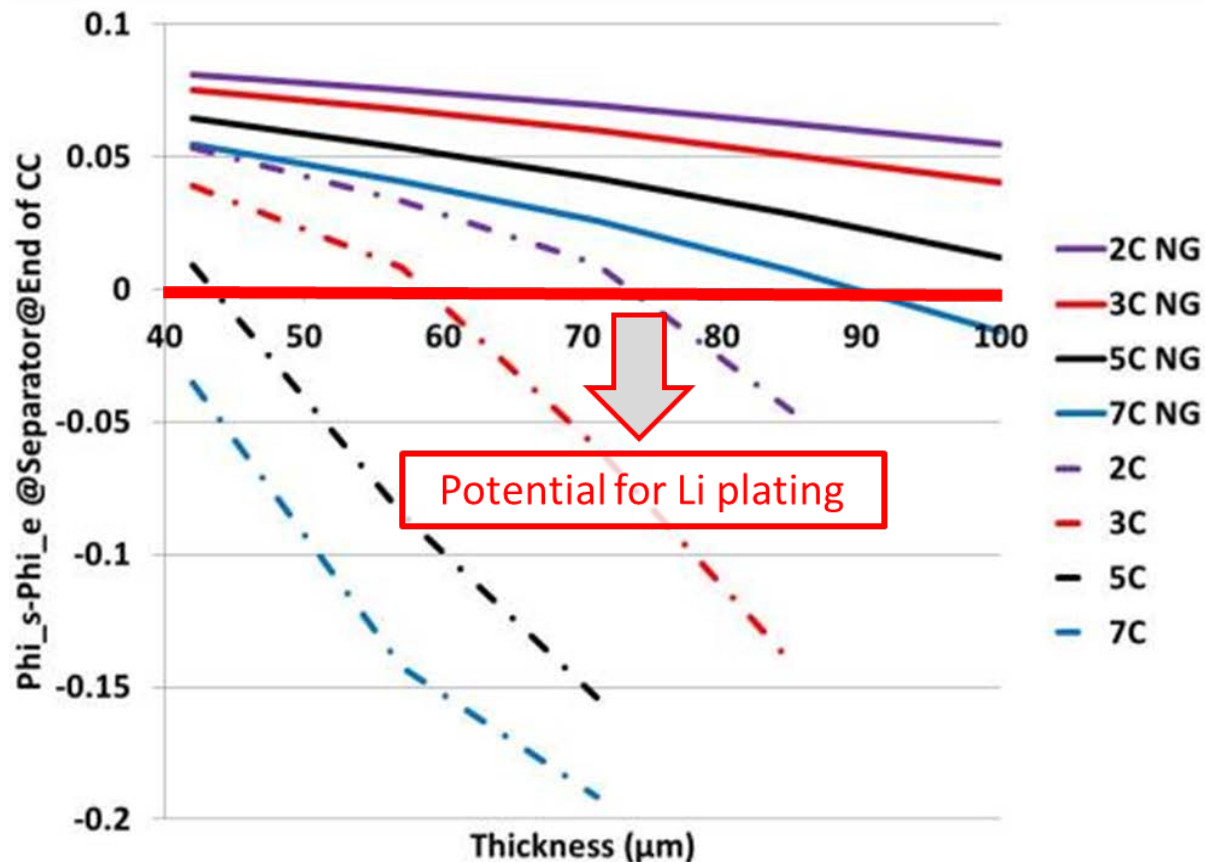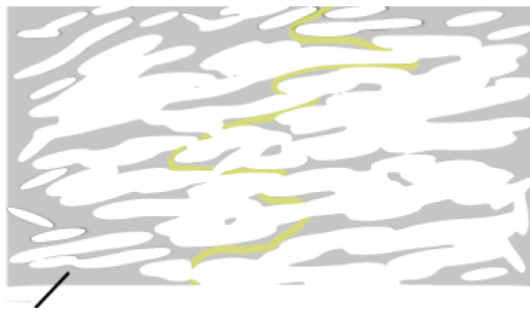
# Technical Accomplishment: Prediction of Microstructure Tortuosity

- What is tortuosity, $\tau$?



Tortuosity = 1



Tortuosity > 1

- Homogenization calculation

Credit: Tommaso Magrini



$D_0$ (bulk diffusion coefficient)

$$\varepsilon, \tau =$$
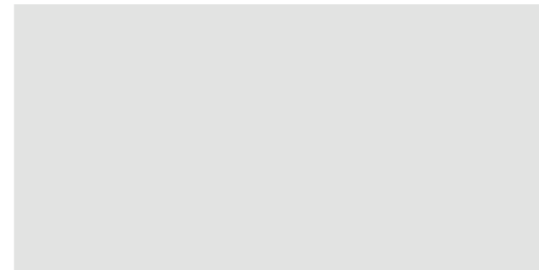
$D_{eff}$ (effective diffusion coefficient)

$$D_{eff} = \frac{\varepsilon}{\tau} D_0$$

Images: Juliette Billaud et al. (ETHzürich) "Enhanced Rate Performance in Electrode Materials for Lithium-ion Batteries," International Battery Seminar & Exhibit, March 20-23, 2017.
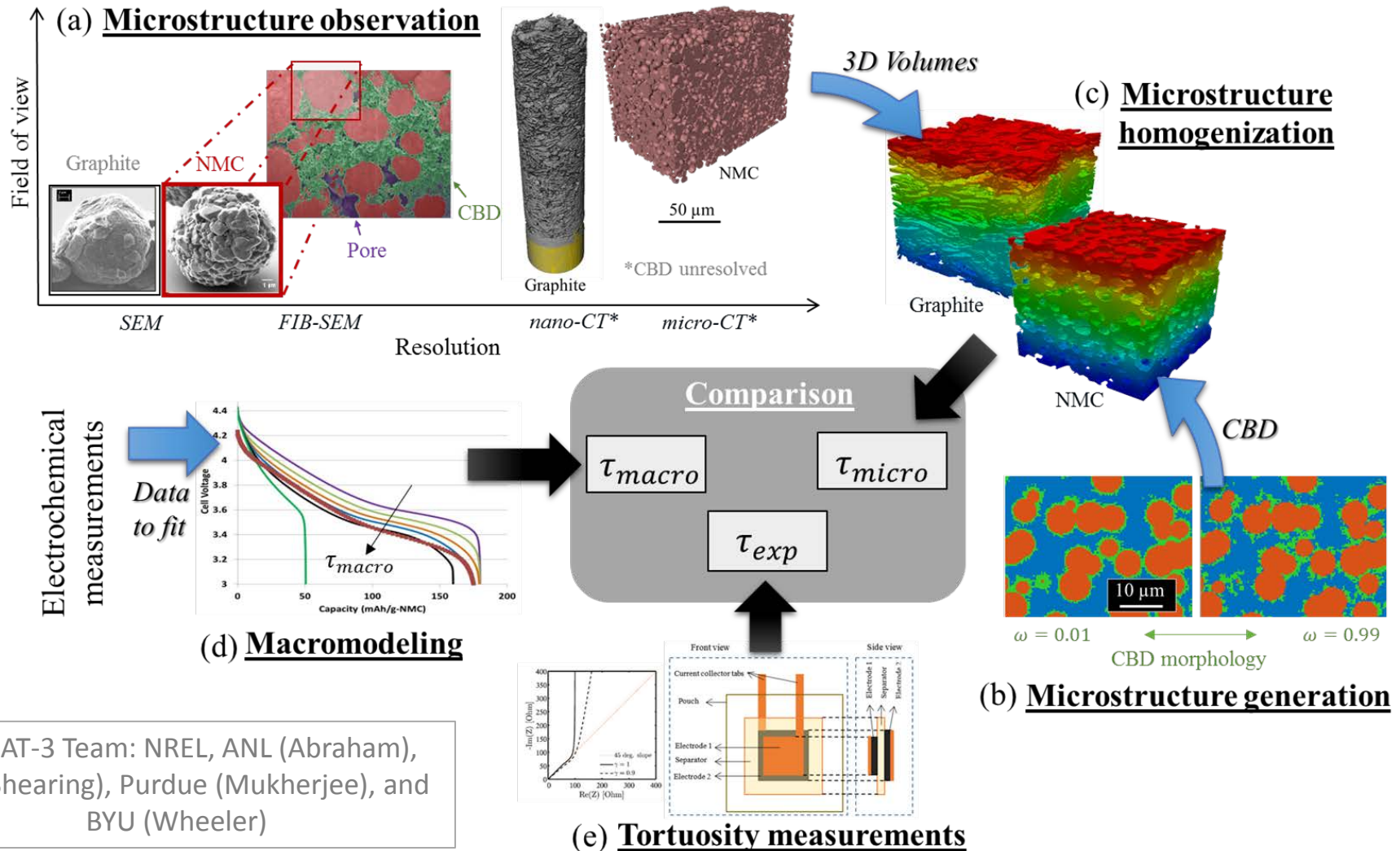
CAEBAT-3 Team: NREL, ANL (Abraham), UCL (Shearing), Purdue (Mukherjee), and BYU (Wheeler)

Francois L.E. Usseglio-Viretta et al. "Resolving the Discrepancy in Tortuosity Estimation for Li-ion Battery Electrodes …" submitted.

# First XFC Sample, SLC1506T, Imaged with X-ray Tomography, Tortuosity Calculated & Compared to CAEBAT Library. Additional XFC graphites underway.



- ➤ **Microstrucure modeling**
- ➤ **Macroscopic modeling**
- ➤ **Experimental measurement**

**A12 graphite**

**Superior graphite SLC1506T**

Toda NMC532

Tortuosity, $\tau$

Porosity, $\varepsilon$



**Phillips A12 gr. (CAEBAT)**



**Superior SLC1506T gr. (XFC)**
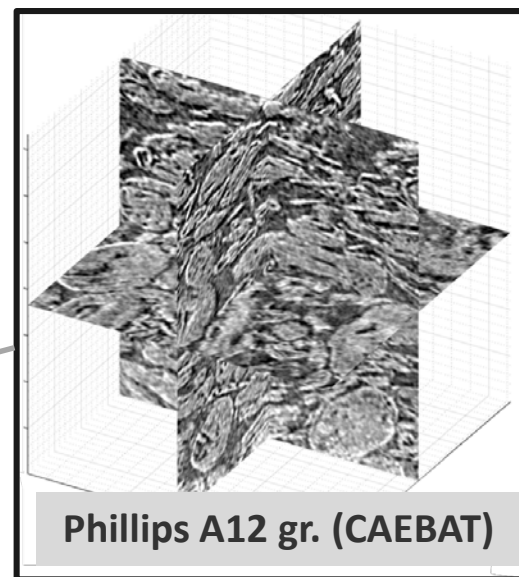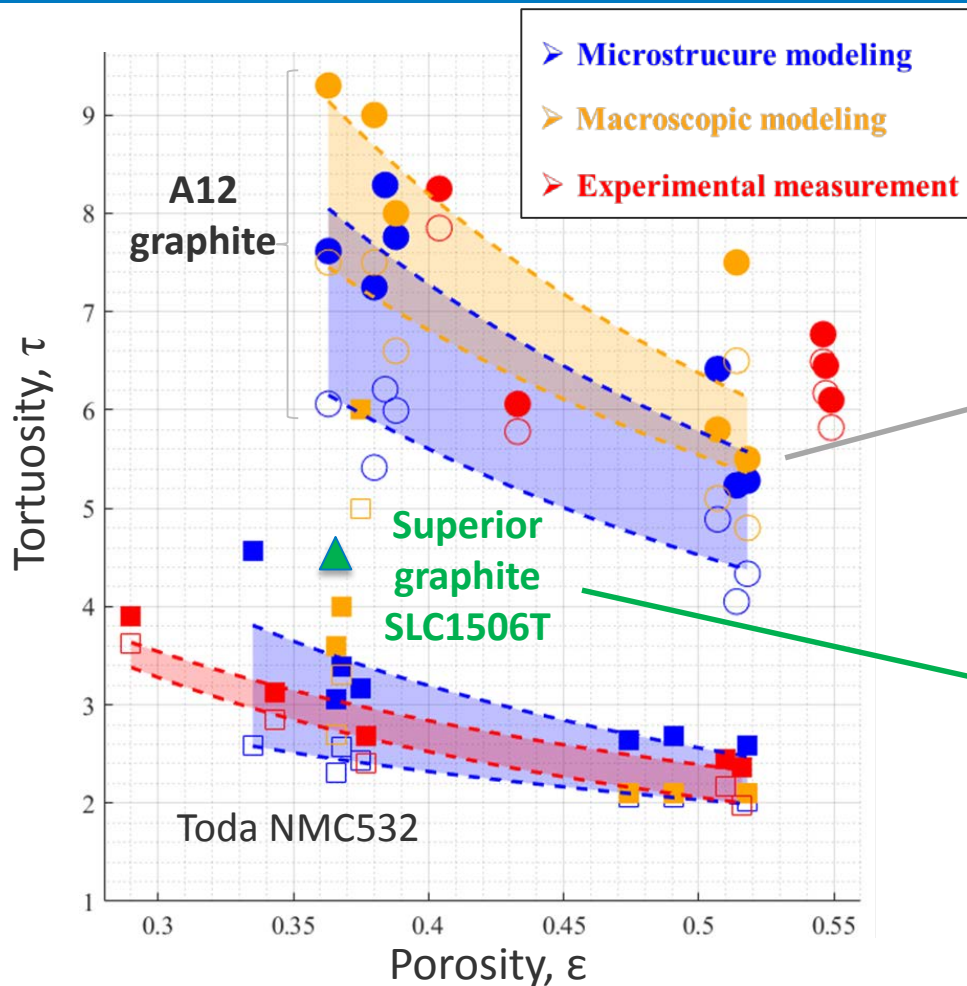
- A12 tortuosity ~7.6, SLC1506T tortuosity ~4.5
- Particle morphology and orientation play strong role

# Particle Elongation in Electrode In-plane Direction Strongly Correlates with Tortuosity

## Tortuosity vs. particle elongation



More tortuous

More spherical

Legend:
- □ NMC532, Toda-HE5050, UC
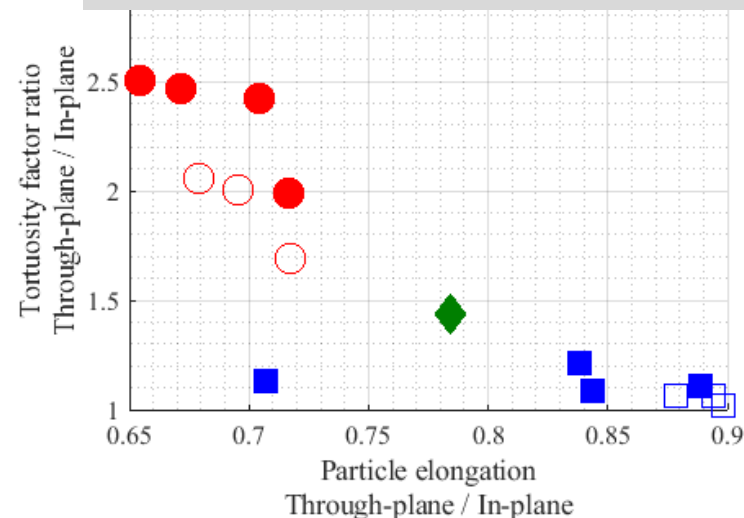- ■ NMC532, Toda-HE5050, C
- ○ Graphite, CPG-A12, UC
- ● Graphite, CPG-A12, C
- ◆ Graphite, Superior-SLC1506T

NMC Baseline 34 μm thick
High aspect-ratio & 2-3 particles
only along through-plane dimension
bias the anisotropy analysis

Y-axis: Through-plane Tortuosity factor
X-axis: Particle elongation: Through-plane / In-plane dimension
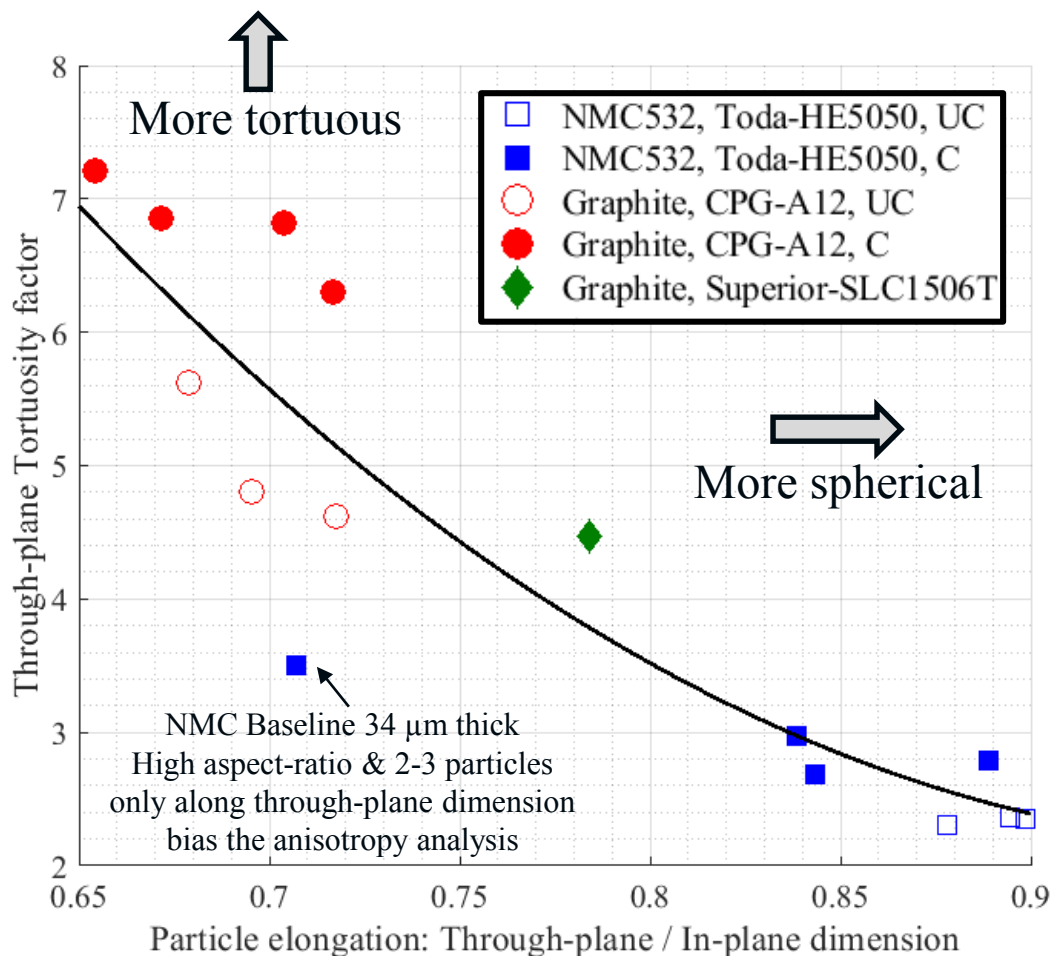
## Anisotropy vs. particle elongation



Y-axis: Tortuosity factor ratio Through-plane / In-plane
X-axis: Particle elongation Through-plane / In-plane

- Ideally, elongated particles would be aligned in through-plane direction for fast Li$^+$ electrolyte transport
- Without control of particle alignment however, increasing sphericity is valuable approach to reduce the through-plane tortuosity as well as tortuosity anisotropy
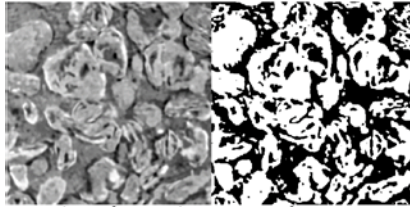
# Technical Accomplishment: 3D Microstructure Modeling of Heterogeneity
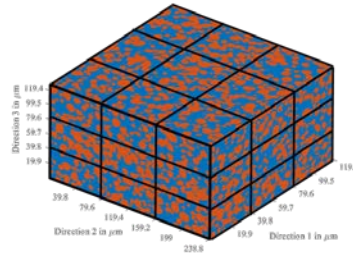
# 3D Microstructure Modeling*

**Geometry**

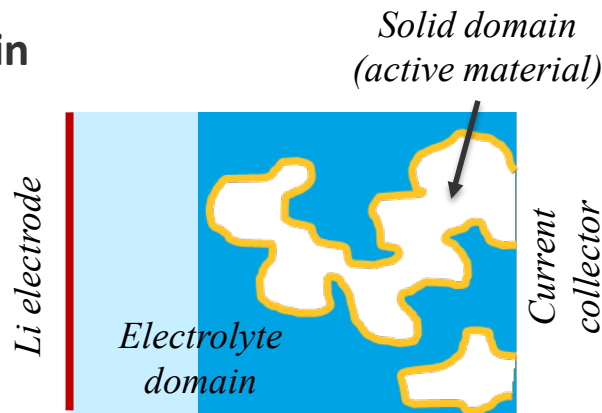- X-ray tomography & segmentation

*Grey-level*   *Segmented*



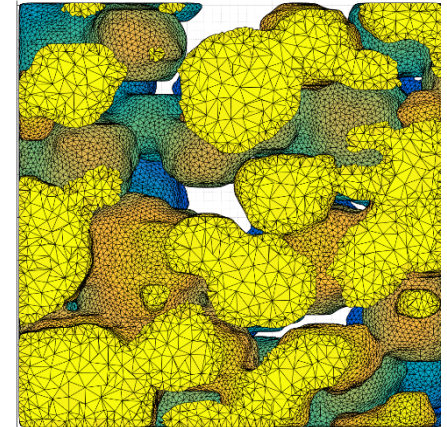**Representative volume analysis**

*Independent subdomains*



**Simulation domain and physics**

- Li & e⁻ conservation
- Charge transfer

*Li electrode*

*Electrolyte domain*

*Solid domain (active material)*

*Current collector*



**Meshing**

- Tetrahedral (iso2mesh)
- Density control
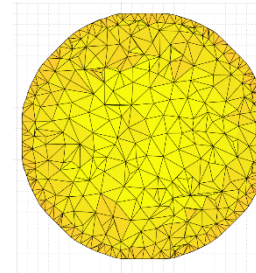


**Numerical implementation**

- FEniCS finite element package
- Implemented on high performance computer through message passing interface (MPI)



Photo: https://www.nrel.gov/hpc/peregrine-system.html

**Objective**: Establish a tool that predicts electrochemical heterogeneity induced by microstructure morphology. Heterogeneity increases probability of degradation.

*Initiated under CAEBAT in FY17. Activity transferred to XFC program in FY18.

# Example 1: NMC Spherical Particles Packed in Series
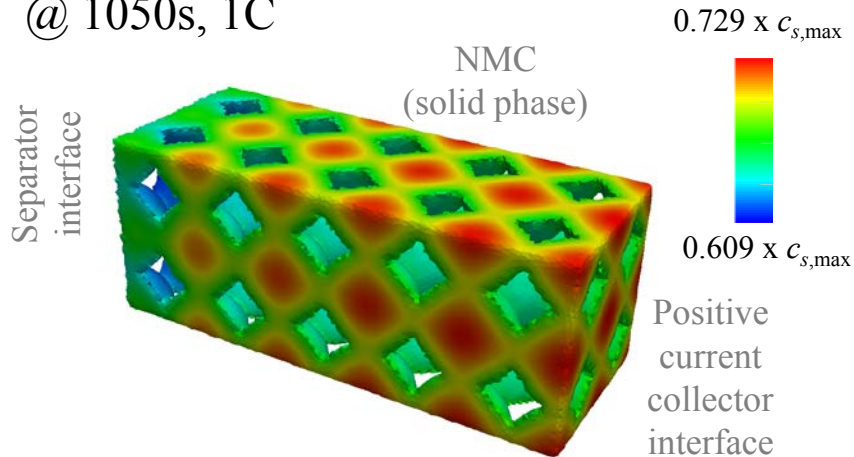
## Solid-phase concentration
@ 1050s, 1C

NMC
(solid phase)

$0.729 \times c_{s,\text{max}}$

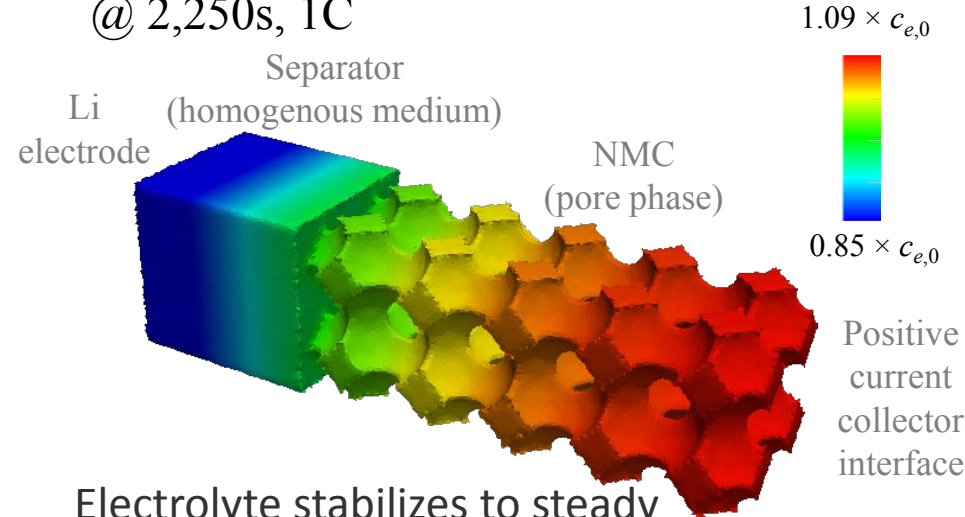$0.609 \times c_{s,\text{max}}$
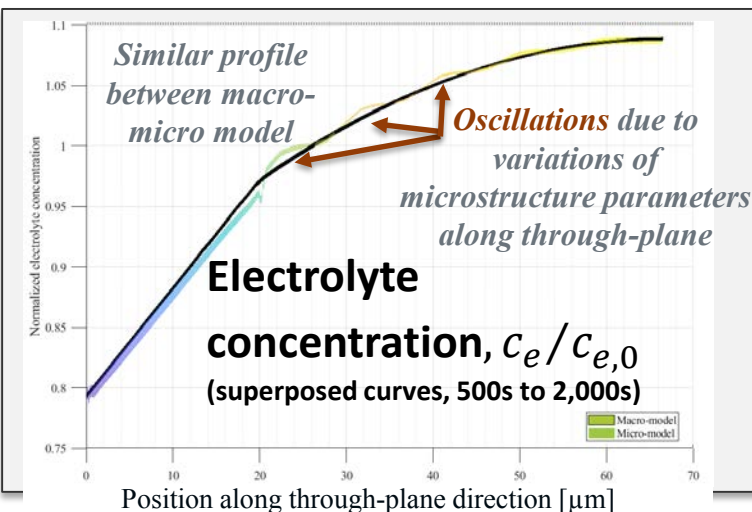
Separator interface

Positive current collector interface

Preferential use of active material close to separator and particle surfaces

## Electrolyte-phase concentration
@ 2,250s, 1C

Separator
(homogenous medium)

Li electrode

NMC
(pore phase)

$1.09 \times c_{e,0}$

$0.85 \times c_{e,0}$

Positive current collector interface

Electrolyte stabilizes to steady state in first ~300 seconds

---

*Similar profile between macro-micro model*

*Oscillations due to variations of microstructure parameters along through-plane*

**Electrolyte concentration,** $c_e/c_{e,0}$
**(superposed curves, 500s to 2,000s)**

Macro-model
Micro-model

Position along through-plane direction [$\mu$m]

Normalized electrolyte concentration

### Micro vs. macro model comparison

**Overpotential,**
$$\eta = \phi_s - \phi_e - U$$

@ 500s, 1C

Overpotential $\eta$ [V]

Position along electrode thickness ($\mu$m)

*Similar change of slope*

@ 1,500s, 1C

Overpotential $\eta$ [V]

Position along electrode thickness ($\mu$m)

- Multi-modal feature where large particle lags behind small platelets

Local morphology controls the local concentration distribution
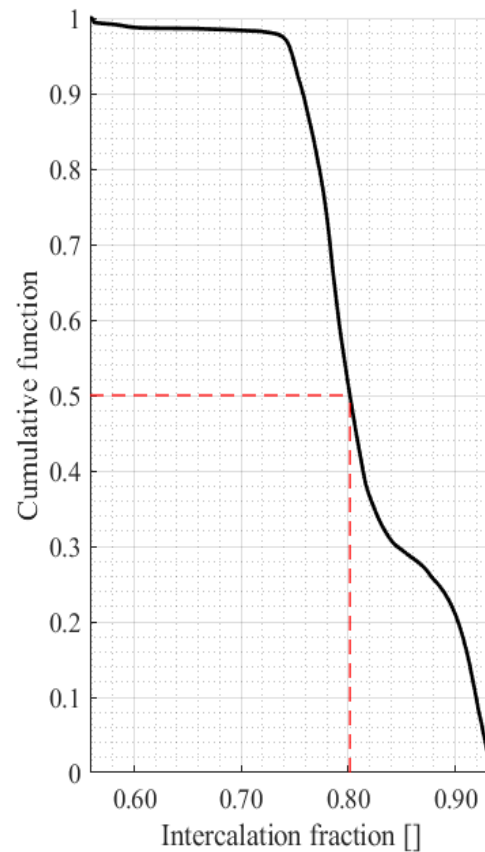


$0.95 \times c_{s,\max}$

$0.63 \times c_{s,\max}$

Separator

10 μm
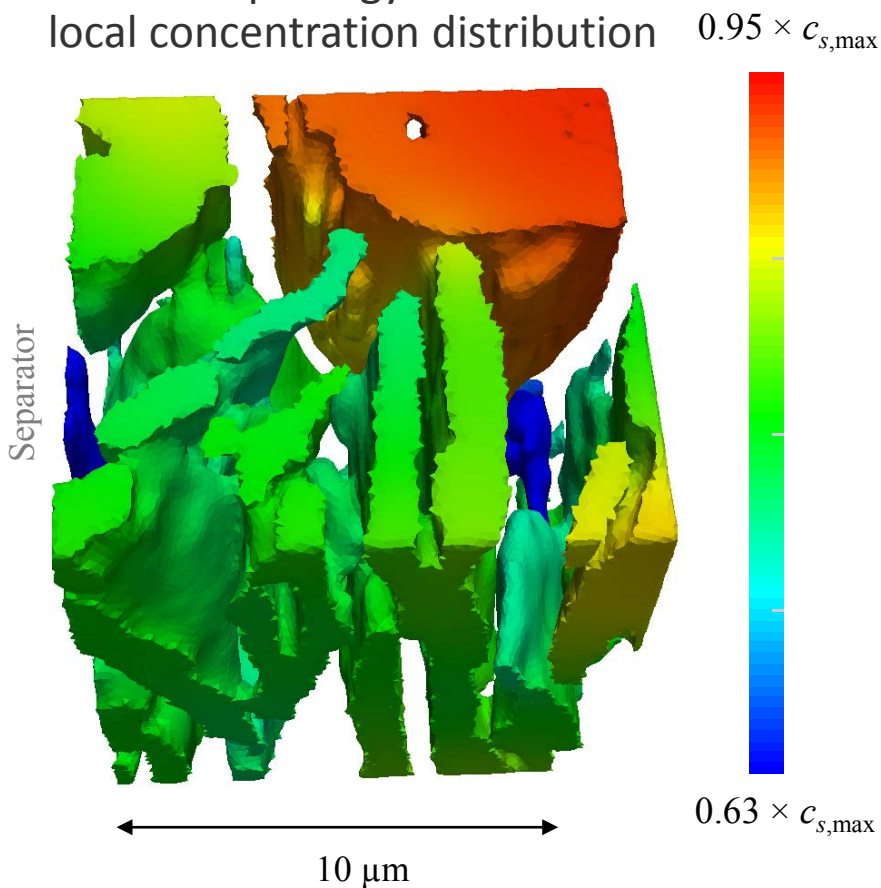
Cumulative function



Distribution function
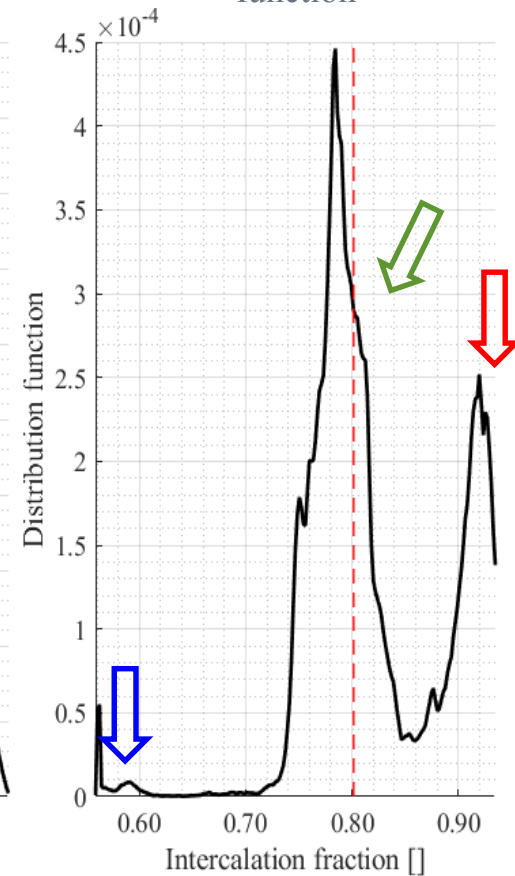


Time = 472s, mean intercalation fraction = 0.82

# Example 2: Graphite Actual Geometry

In-plane heterogeneities (**none of which is captured by macro model**)



Separator

0.5 μm

6 μm

14 μm

19 μm

Actual graphite, @1C, 200s
Intercalation fraction displayed **slice per slice**, normal to the electrode thickness

20 μm

$0.95 \times c_{s,max}$

$0.73 \times c_{s,max}$

Distance from the separator

- Significant in-plane heterogeneity, with very low concentration located on some geometric features (e.g., protrusion)
- Probability of degradation increases with heterogeneity

# Collaboration and Coordination with Other Institutions

| Category | Institution | Role |
|---|---|---|
| National Laboratories | Argonne National Lab | Electrode/cell prototyping, characterization, graphite transport modeling, post-test analysis |
| | Idaho National Lab | Charge protocols, aging studies, Li plating diagnostics |
| Universities | Purdue University (sub to NREL under CAEBAT project) | Stochastic reconstruction for microstructure studies |
| | University College of London (informal collaboration) | Nano and micro X-ray computed tomography |
| | Brigham Young University (informal collaboration) | Tortuosity measurement |

# Remaining Challenges and Barriers

## XFC

- Achieving electrode and electrolyte systems capable of XFC

- System challenges
  - Cell, pack and thermal management design
  - Safety, control. Avoiding lithium plating
  - Infrastructure

## Modeling

- Enhance description of transport and interfacial physics in both micro/macro models + carbon-binder domain representation in the micromodel

- Determine importance (or not) of electrode-level heterogeneity by coupling with degradation mechanisms
  - Lithium plating
  - Mechanical stress

- Efficient scale-up of microstructure simulations (~10x)

|          | Graphite | NMC |
|----------|----------|-----|
| Present: | 20 x 20 x 20 $\mu m^3$ | 30 x 30 x 30 $\mu m^3$ |
| Goal: | 30 x 30 x thickness $\mu m^3$ | 40 x 40 x thickness $\mu m^3$ |

# Responses to Previous Year Reviewers' Comments

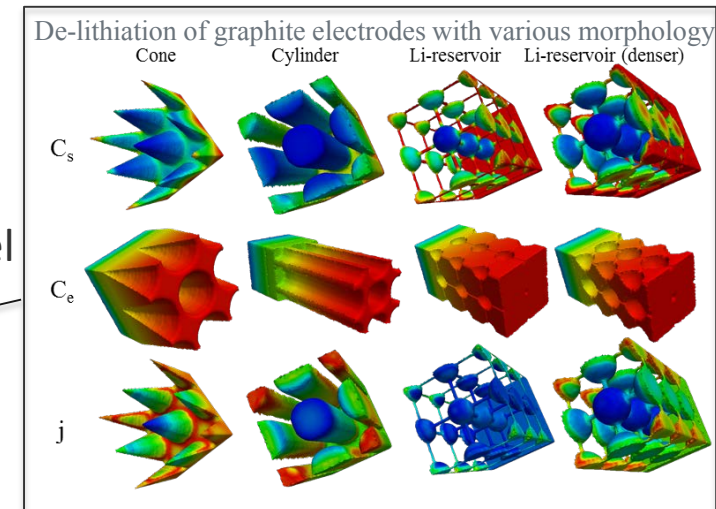- This project began in FY18 and, hence was not reviewed last year.

# Acknowledgements

- Support for this work from Battery R&D, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Samm Gillard, Steven Boyd, and David Howell

# Proposed Future Research

| Remaining FY18 milestones | Due (end of quarter) | Go/No-go | Status |
|---|---|---|---|
| M3. Report summarizing **measurement of electrochemical parameters** for graphitic electrodes and **impact on cell-level performance** | Q3 | No | On track |
| M4. Comparison of **model predictions** against **test data** | Q4 | No | On track |

- XFC electrode-level studies
  - Continue **graphite microstructure characterization** as samples become available (FY18)
  - Adopt **multi-phase graphite transport** model under investigation by ANL (FY18)
  - **Evaluate fast charge protocols** using models (FY18)
  - Validate **Li plating** onset conditions based on ANL, INL, NREL experiments (FY19)
- Perform macro and micro calorimetry at NREL on ANL half cells and full cells (FY18-19)
  - Determine heat removal requirements
  - Probe calorimetry for onset of lithium plating
- Future extensions (FY19+)
  - Couple microstructure heterogeneity with degradation
    - Predict onset of lithium plating
    - Mechanical stress
  - Numerical scaling studies with microstructure model
  - Optimize/test various 3D electrode architectures with microstructure model
  - 3D cell, pack and thermal management design

De-lithiation of graphite electrodes with various morphology
Cone  Cylinder  Li-reservoir  Li-reservoir (denser)
$C_s$
$C_e$
j

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

# Summary

- Multi-lab team working to characterize graphite electrodes and better understand transport and lithium plating phenomena on fast charge
- Leveraged and enhanced CAEBAT micro/macro models to aid XFC electrode-level studies
- 3D microstructure model was demonstrated and validated with macro model
  - Extensible platform for 3D architecture and physics research
  - In-plane heterogeneity, not captured by macro models, important for degradation analysis

- Quantified impact of different graphite and NMC morphologies:
  - 35% variation in tortuosity, $\tau$, between two graphites characterized thus far
    - Helps quantify reason for electrochemical performance difference measured by ANL-CAMP
  - In absence of through-plane alignment, spherical particles better. At porosity, $\varepsilon \approx 0.35$
    - CPG-A12 aspect ratio of 0.65 $\rightarrow$ $\tau$ = 7
    - Superior SLC1506T aspect ratio of 0.78 $\rightarrow$ $\tau$ = 4.5
    - Toda NCM523 aspect ratio of 0.85 $\rightarrow$ $\tau$ = 3

- Established preliminary electrode/electrolyte requirements
  - With present electrolytes, electrodes must have <45μm thickness to avoid Li plating at 6C
  - Requirements for 10-minute fast charge of BEV200+ with >85μm electrode
    - Electrolytes with enhanced transport (1.5x conductivity, 3.0x diffusivity, transference num. increased by 0.1)
    - Low electrode tortuosity (graphite same as NMC, reduced from 6.0 to 2.85)
  - Increasing electrode porosity increases fast charge capability at expense of 1C energy density

# Thank You

**www.nrel.gov**

Publication Number

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