Project ID #BAT339

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

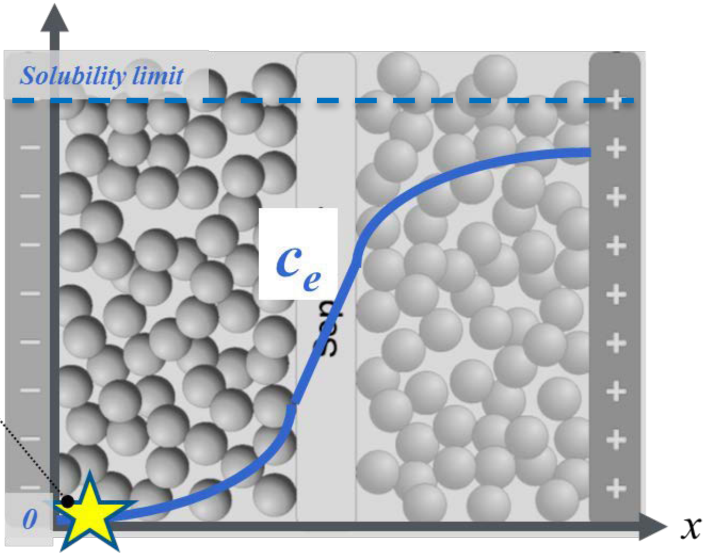
- Total project funding $1.1M
  - DOE share: 100%
  - Contractor share: 0
- Funding for FY 2018: $550k
- Funding for FY 2019: $550k

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)

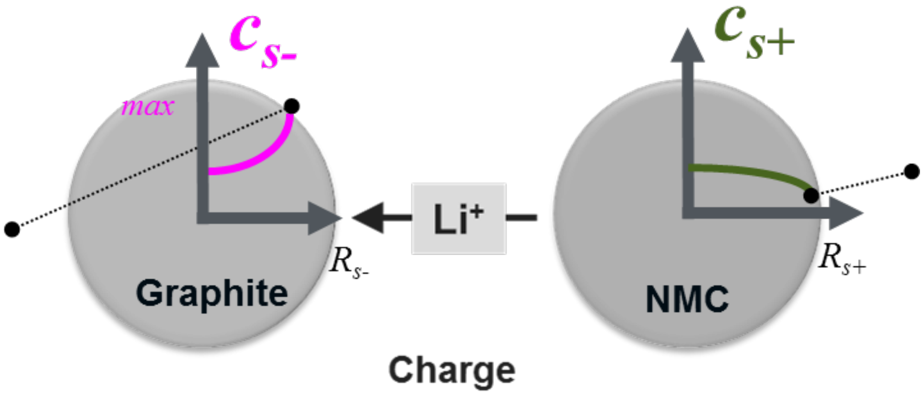
1) Li^+ depletion in electrolyte



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



3) Li depletion @ NMC surface

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

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

SOC: state of charge

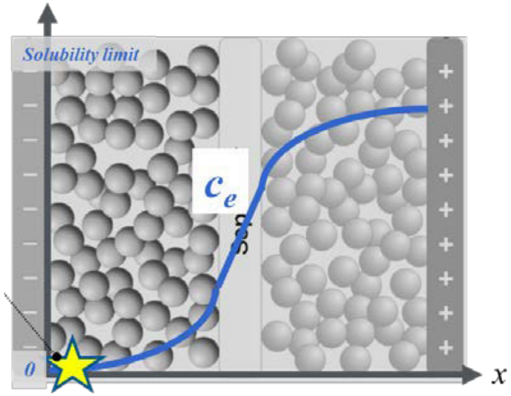
Relevance – Objectives

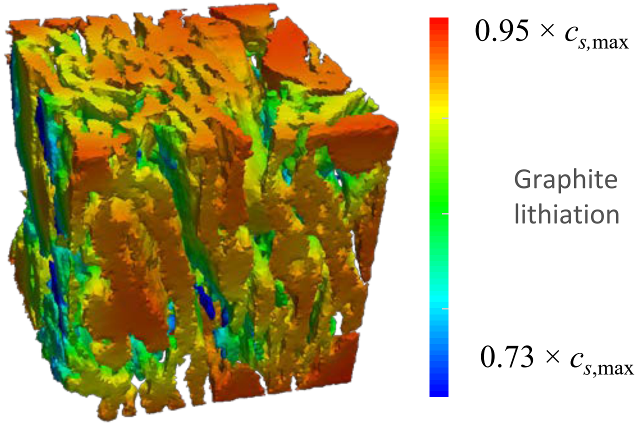
- Through modeling studies, quantify
  - Limits of today’s graphite-based electrode technologies for varying electrode designs (loadings, porosities, etc.)
  - Why some electrodes are better suited to XFC than others
    - Electrode tortuosity based on electrode morphology
  - Electrode and electrolyte 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

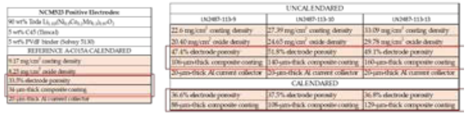
- **Electrochemical modeling tools for XFC**
  - Macro-homogeneous modeling
    - Guide electrode design and electrolyte requirements
  - Microstructure modeling
    - Effective properties determined via homogenization and geometric analysis (tortuosity, surface area, porosity, morphology)
    - 3D electrochemical 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)

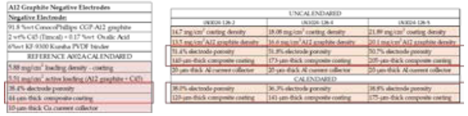
Cathodes



NCM523 Positive Electrodes
90 wt% Toda [illegible]
5 wt% C45 (Timcal)
5 wt% PVdF binder (Solvay 5130)
REFERENCE A-C015A CALENDARED
9.17 mg/cm² coating density
8.25 mg/cm² oxide density
33.5% electrode porosity
34-µm-thick composite coating
20-µm-thick Al current collector

UNCALENDARED		
[illegible]	[illegible]	[illegible]
22.6 mg/cm² coating density	27.39 mg/cm² coating density	33.09 mg/cm² coating density
20.40 mg/cm² oxide density	24.65 mg/cm² oxide density	29.78 mg/cm² oxide density
47.4% electrode porosity	51.8% electrode porosity	49.1% electrode porosity
106-µm-thick composite coating	140-µm-thick composite coating	160-µm-thick composite coating
20-µm-thick Al current collector	20-µm-thick Al current collector	20-µm-thick Al current collector
CALENDARED		
36.6% electrode porosity	37.5% electrode porosity	36.8% electrode porosity
88-µm-thick composite coating	108-µm-thick composite coating	129-µm-thick composite coating

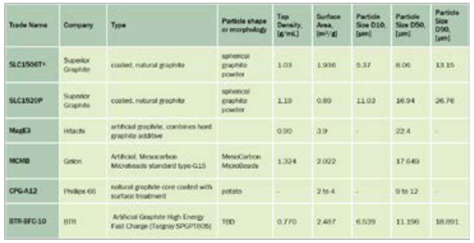
Anodes



A12 Graphite Negative Electrodes
Negative Electrode:
91.8 %wt ConocoPhillips CGP-A12 graphite
2 wt% C45 (Timcal) + 0.17 %wt Oxalic Acid
6%wt KF-9300 Kureha PVDF binder
REFERENCE A002A CALENDARED
5.88 mg/cm² loading density - coating
5.51 mg/cm² active loading (A12 graphite + C45)
38.4% electrode porosity
44-µm-thick composite coating
10-µm-thick Cu current collector

UNCALENDARED		
[illegible]	[illegible]	[illegible]
14.7 mg/cm² coating density	18.08 mg/cm² coating density	21.89 mg/cm² coating density
13.5 mg/cm² A12 graphite density	16.6 mg/cm² A12 graphite density	20.1 mg/cm² A12 graphite density
51.4% electrode porosity	51.9% electrode porosity	50.7% electrode porosity
145-µm-thick composite coating	173-µm-thick composite coating	205-µm-thick composite coating
20-µm-thick Al current collector	20-µm-thick Al current collector	20-µm-thick Al current collector
CALENDARED		
38.0% electrode porosity	36.3% electrode porosity	38.8% electrode porosity
120-µm-thick composite coating	141-µm-thick composite coating	175-µm-thick composite coating

+



Trade Name	Company	Type	Particle shape or morphology	Tap Density, [g/mL]	Surface Area, [m²/g]	Particle Size D10, [µm]	Particle Size D50, [µm]	Particle Size D90, [µm]
SLC1506T	Superior Graphite	coated, natural graphite	spherical graphite powder	1.03	1.936	5.37	8.06	13.15
SLC1520P	Superior Graphite	coated, natural graphite	spherical graphite powder	1.10	0.80	11.02	16.94	26.76
MagE3	Hitachi	artificial graphite, combines hard graphite additive		0.90	3.9	-	22.4	-
MCMB	Gelon	Artificial, Mesocarbon Microbeads standard type-G15	MesoCarbon MicroBeads	1.324	2.022		17.649	
CPG-A12	Phillips 66	natural graphite core coated with surface treatment	potato	-	2 to 4	-	9 to 12	-
BTR-BFC-10	BTR	Artificial Graphite High Energy Fast Charge (Tangray [illegible])	TBD	0.770	2.487	6.539	11.196	18.891

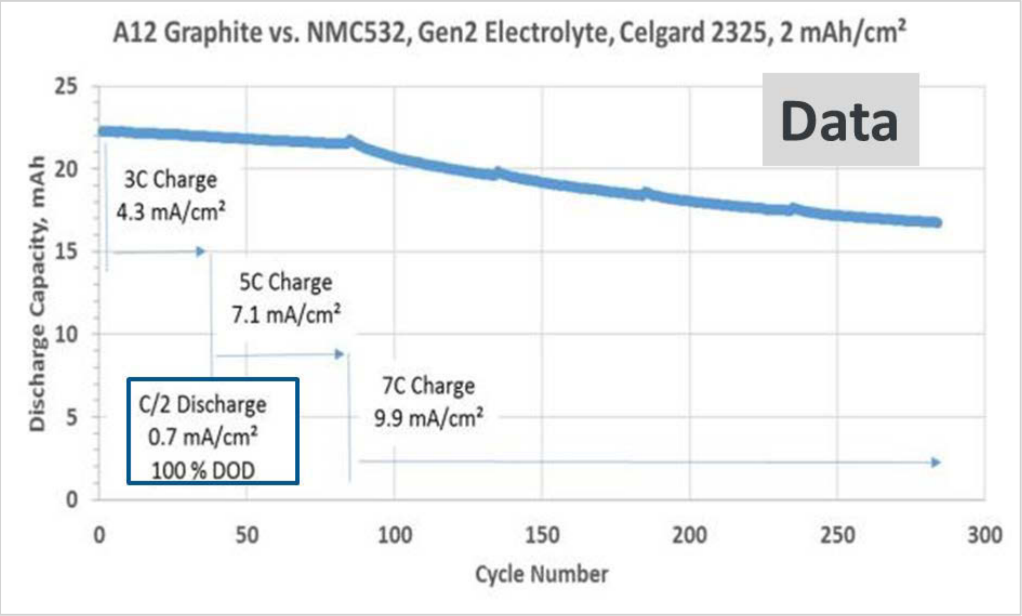
Ref: **ES030** Cell Analysis, Modeling, and Prototyping (CAMP) Research Activities

Milestones

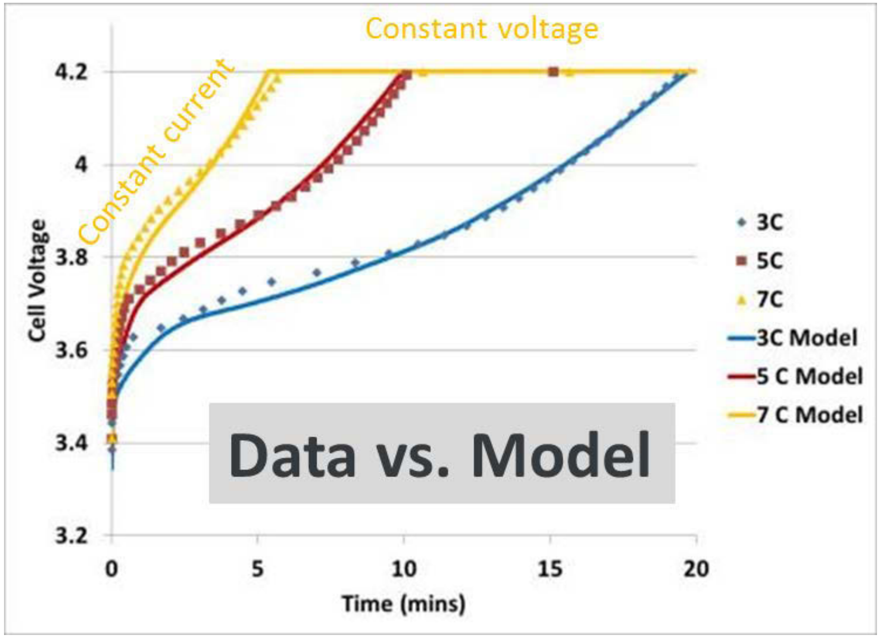
Remaining FY18 milestones	**Due (end of quarter)**	**Go/ No-go**	**Status**
M1. Use **macro model** to determine limits of **varying electrode designs** for accomplishing XFC	Q1	Yes	Complete
M2. Build **first case of microstructure models** for fast charge	Q2	No	Complete
M3. Report summarizing **measurement 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

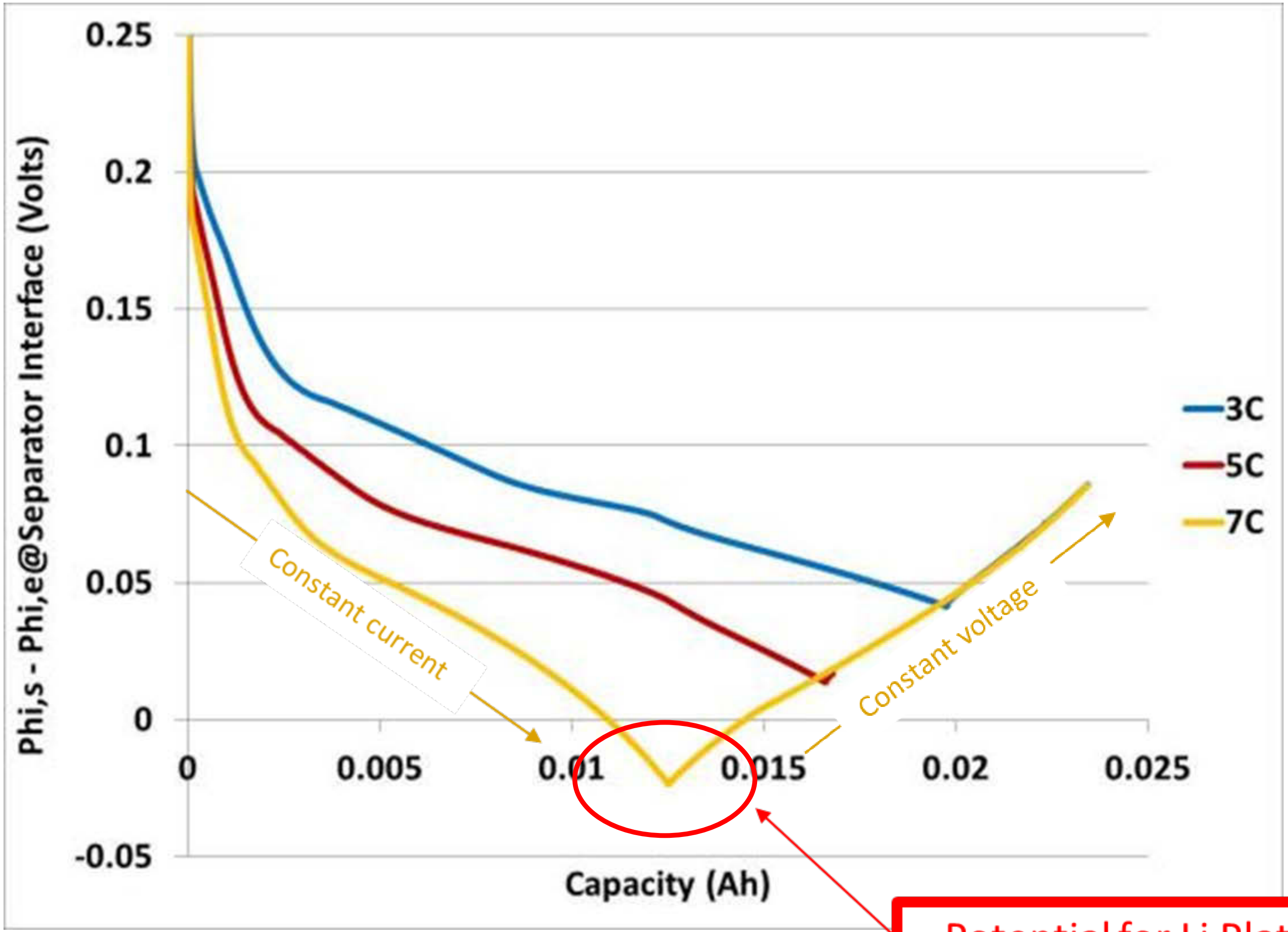


Data: Andy Jansen, Stephen Trask, and Bryant Polzin (ANL)
Model: Andrew Colclasure (NREL)



- 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



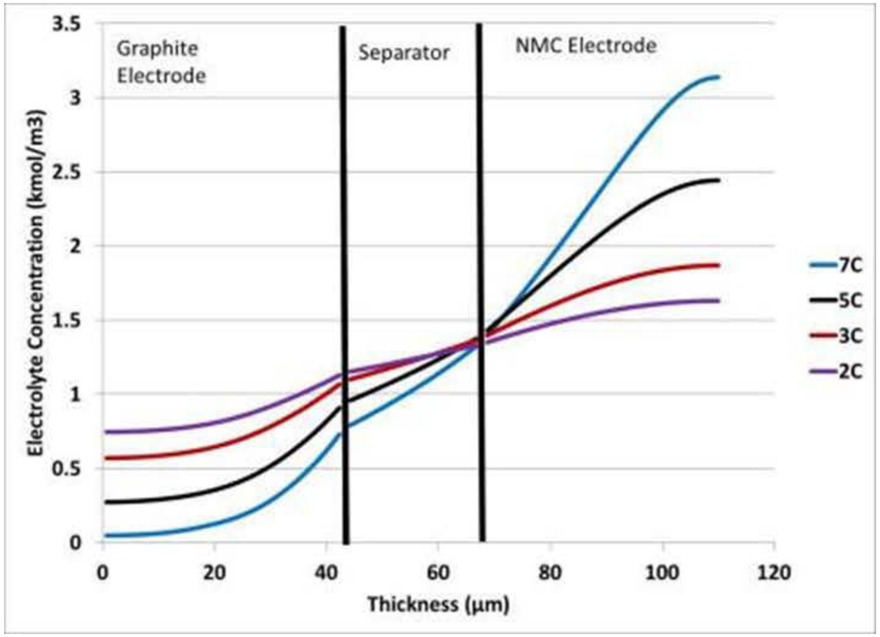
Potential for Li Plating

Electrolyte Li$^+$ Concentration Gradients at Transition from Constant Current to Constant Voltage Charge Step

Electrolyte transport severely limits charging rate at higher loadings

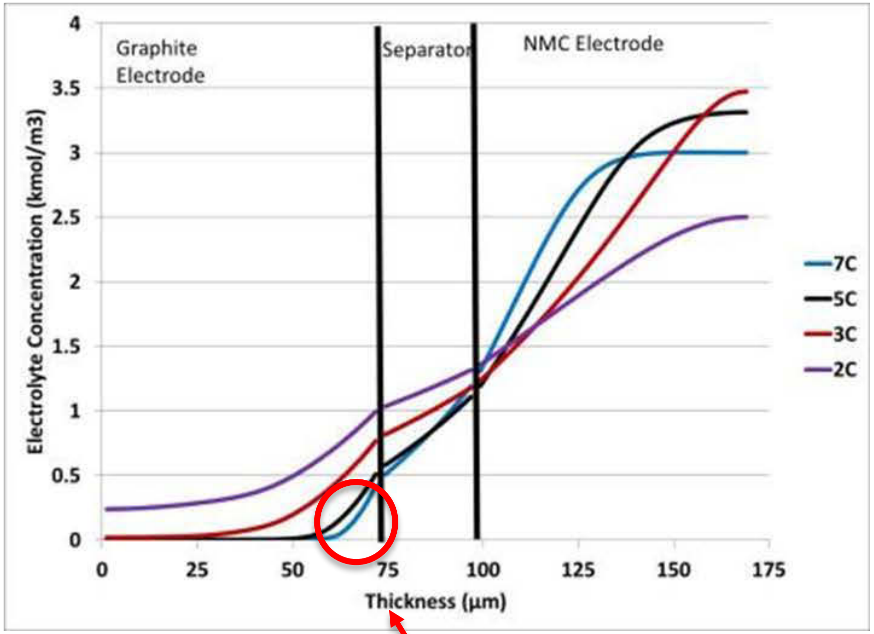
Low Electrode Loading

1.5 mAh/cm^2 cathode (42 µm)
1.84 mAh/cm^2 anode (43 µm)



Medium Electrode Loading

2.5 mAh/cm^2 cathode (71 µm)
3.07 mAh/cm^2 anode (87 µm)

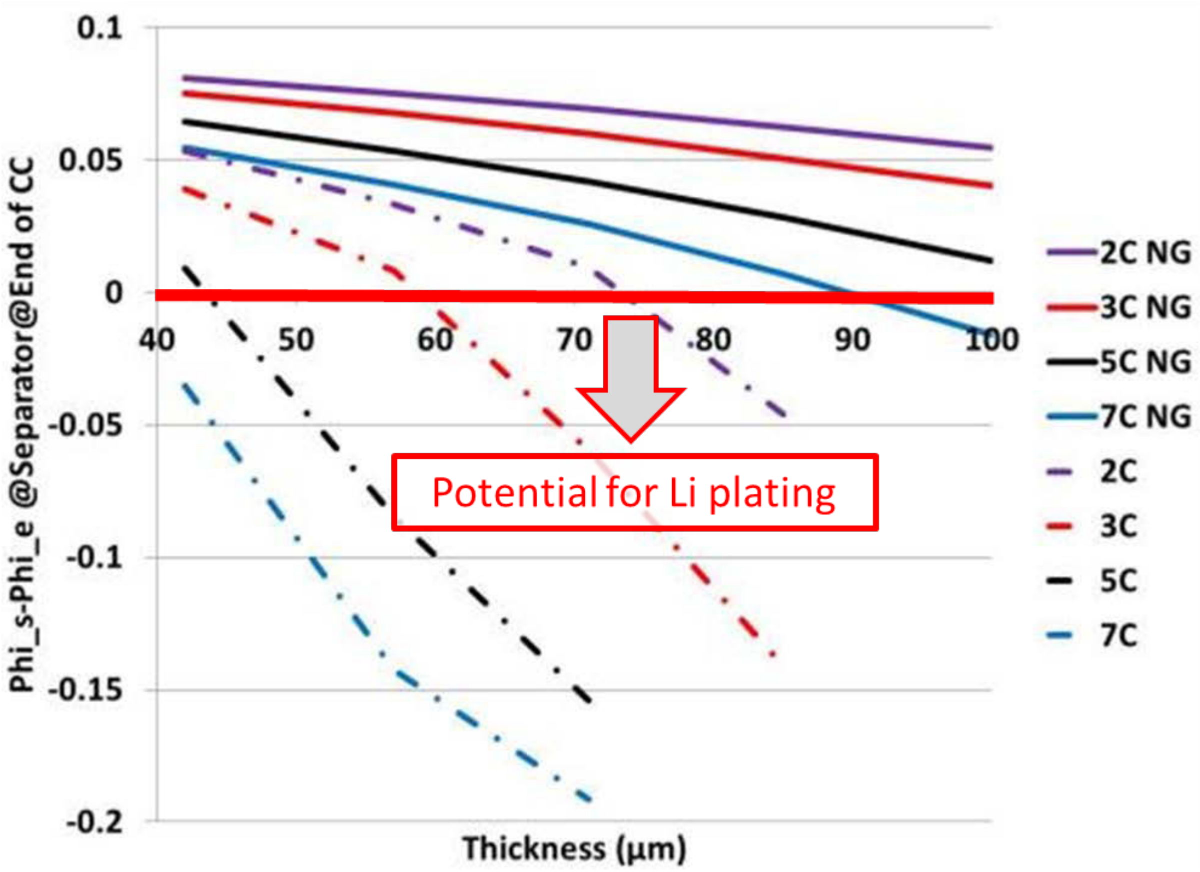


When electrolyte is depleted at the back of the electrode, only the front portion of the electrode remains active. Excessive local C-rates lead to Li plating near the separator.

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)

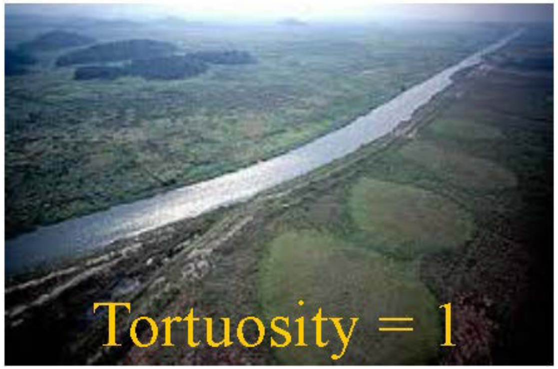


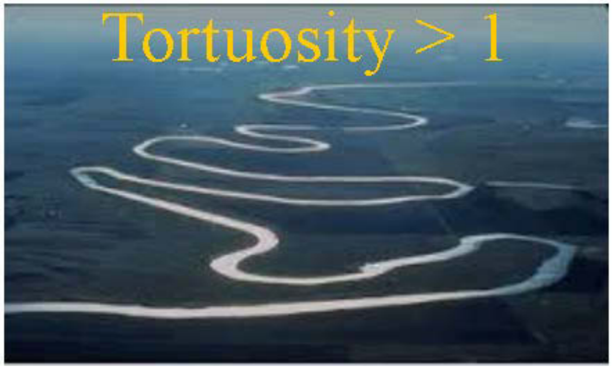
Potential for Li plating

Technical Accomplishment: Prediction of Microstructure Tortuosity

Calculation of Tortuosity from Microstructure

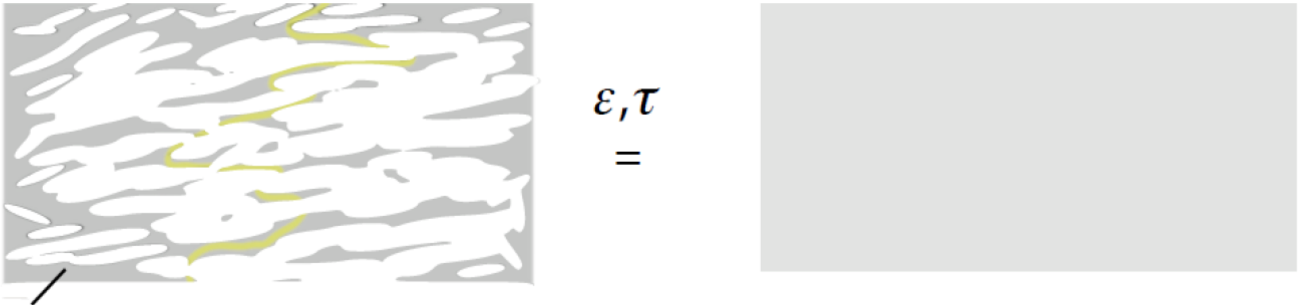
- What is tortuosity, τ?





- Homogenization calculation

Credit: Tommaso Magrini



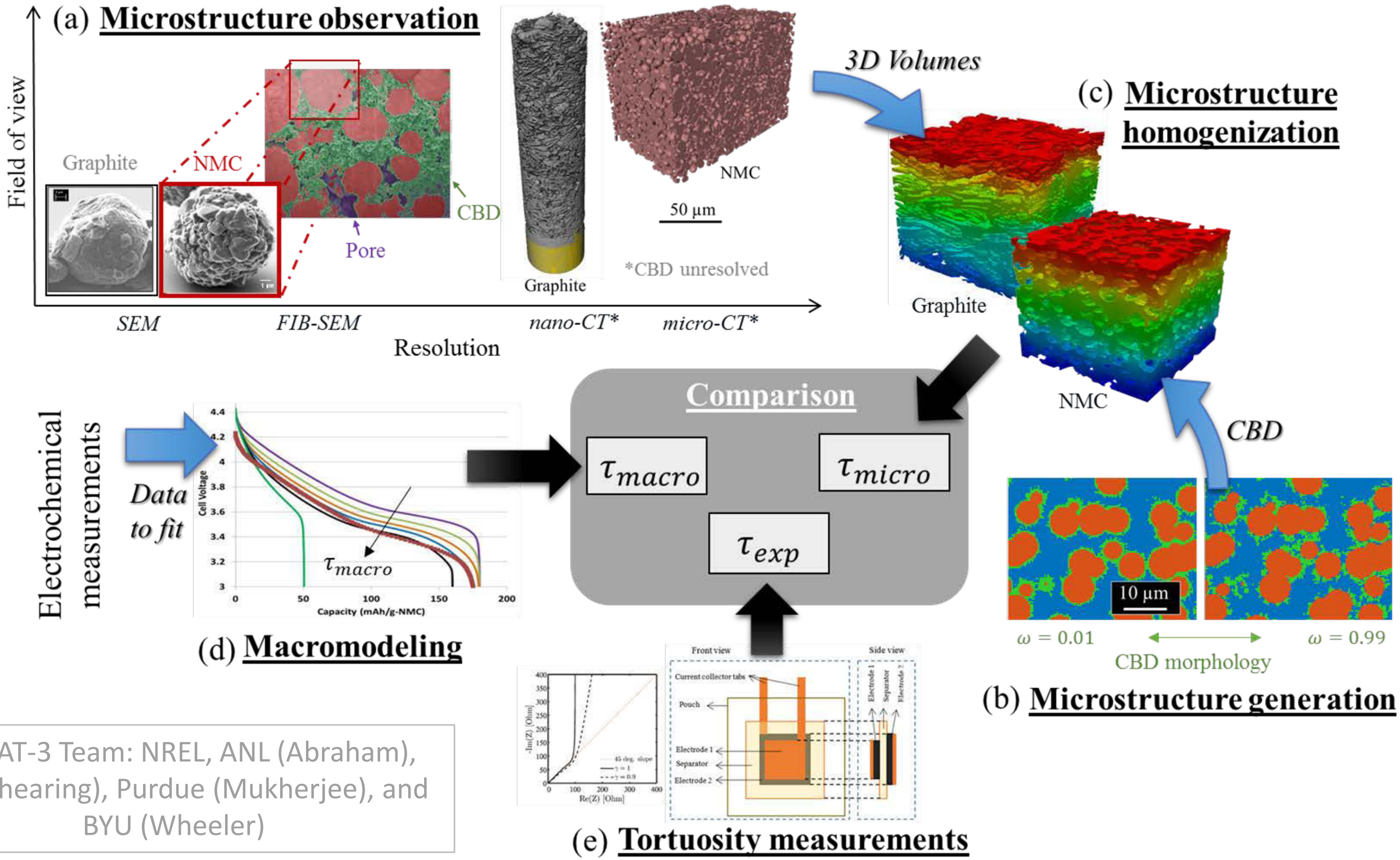
D_0 (bulk diffusion coefficient)

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.

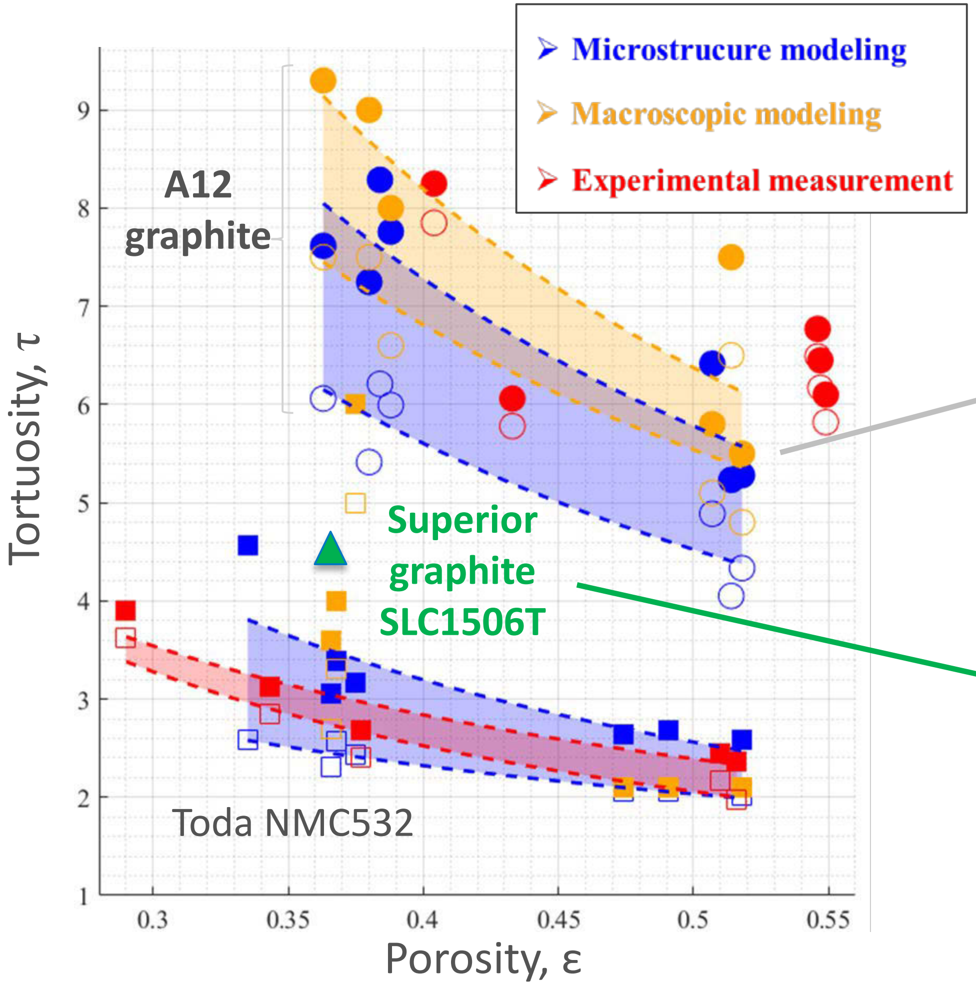
Background CAEBAT Project Work (Poster bat299) – Comparison of Three Microstructure Tortuosity Prediction Methods

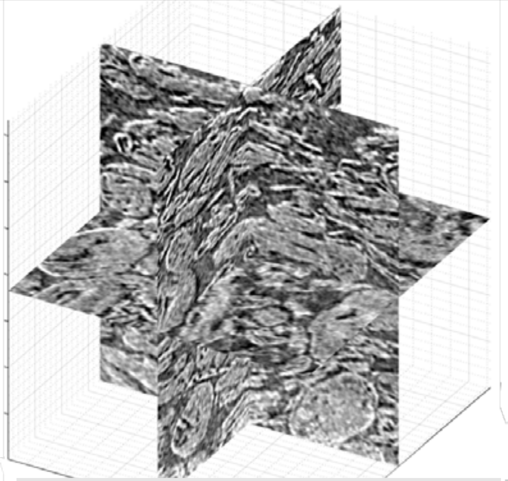


CAEBAT-3 Team: NREL, ANL (Abraham), UCL (Shearing), Purdue (Mukherjee), and BYU (Wheeler)

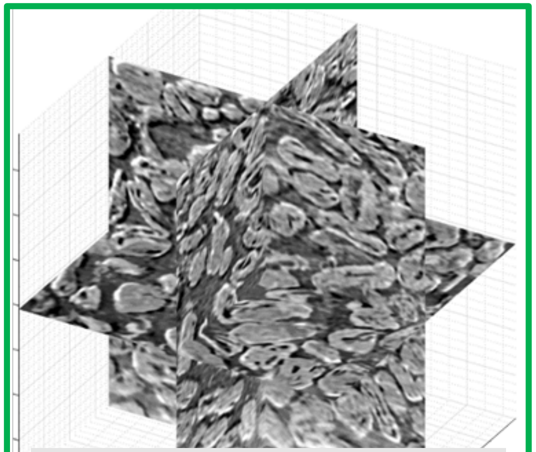
Francois L.E. Usseglio-Viretta et al. “Resolving the Discrepancy in Tortuosity Estimation for Li-ion Battery Electrodes …” submitted.

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





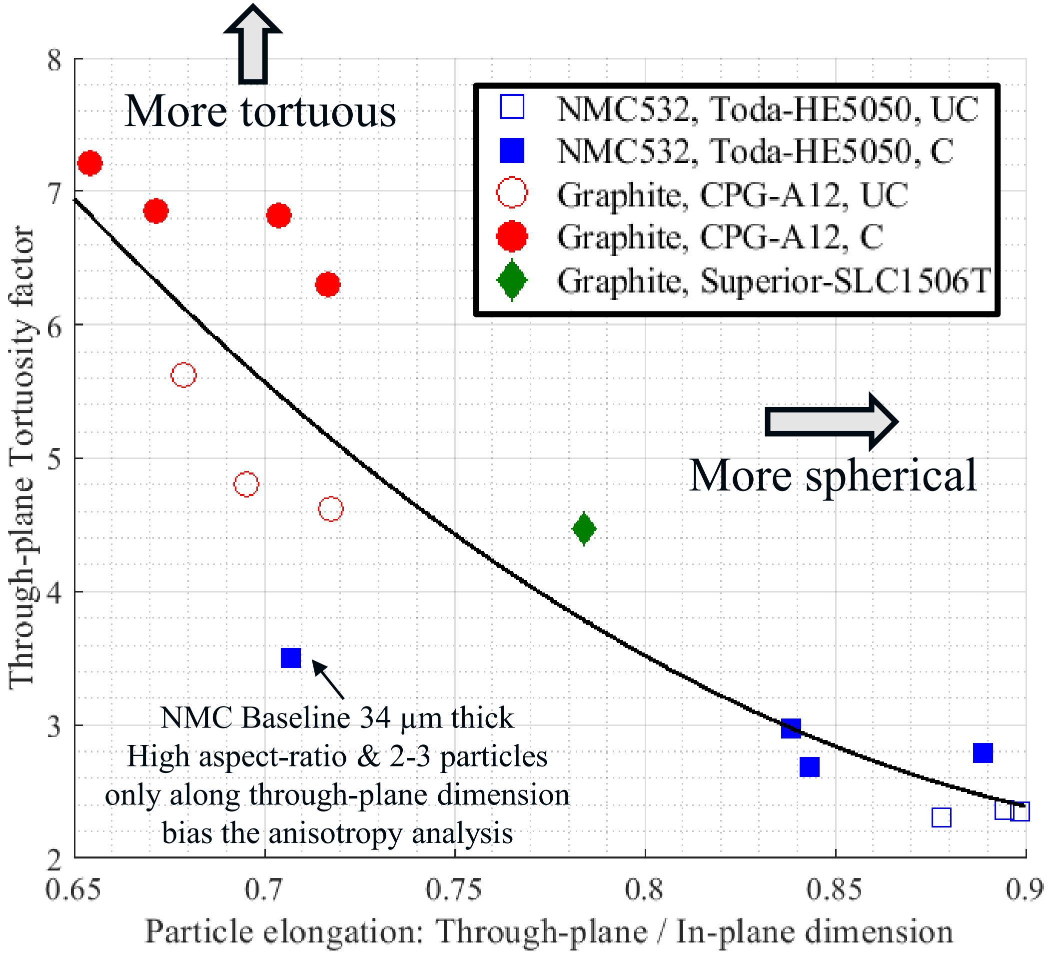
Phillips A12 gr. (CAEBAT)



Superior SLC1506T gr. (XFC)

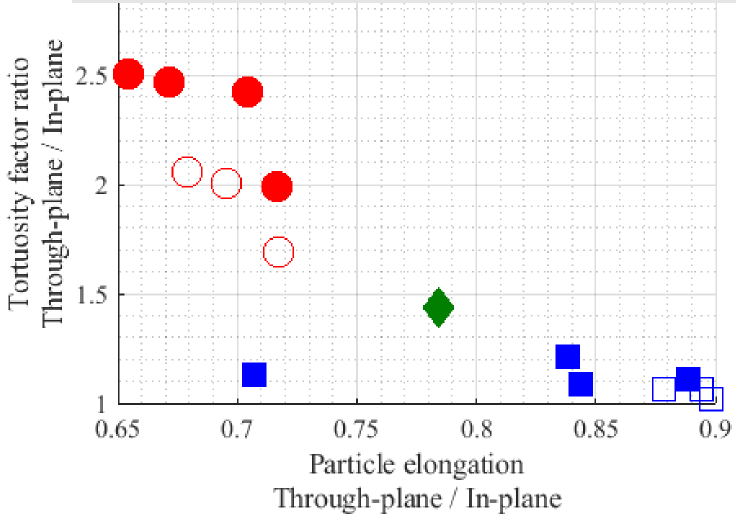
- A12 tortuosity ~7.6, SLC1506T tortuosity ~4.5
- Particle morphology and orientation play strong role

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



Tortuosity vs. particle elongation

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



Anisotropy vs. particle elongation

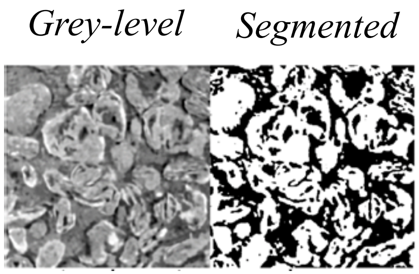
- Ideally, elongated particles would be aligned in through-plane direction for fast Li^+ electrolyte transport
- Without control of particle alignment however, increasing sphericity is valuable approach to reduce the through-plane tortuosity as well as tortuosity anisotropy

Technical Accomplishment: 3D Microstructure Modeling of Heterogeneity

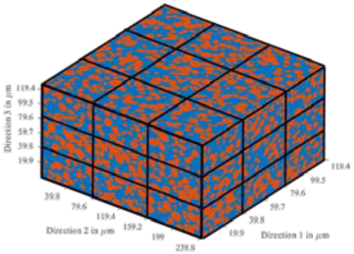
3D Microstructure Modeling*

Geometry

- X-ray tomography & segmentation

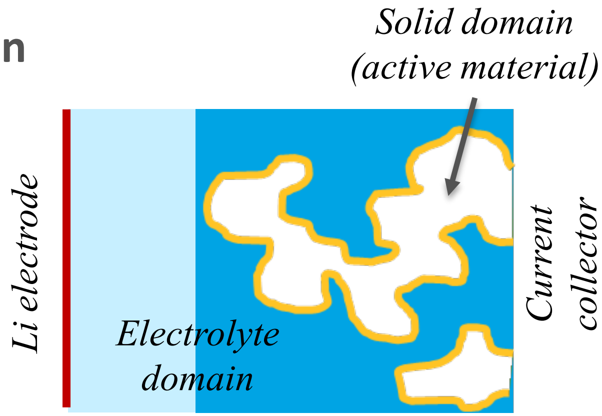


Representative volume analysis



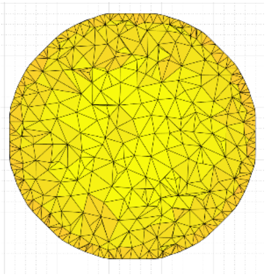
Simulation domain and physics

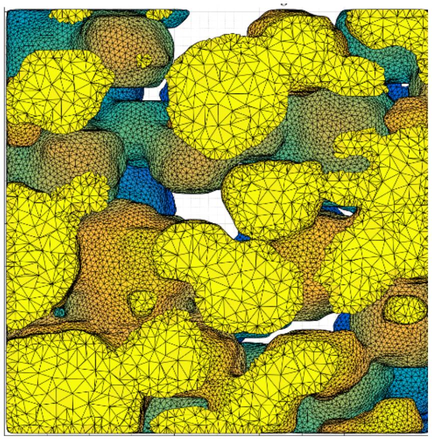
- Li & e$^-$ conservation
- Charge transfer



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

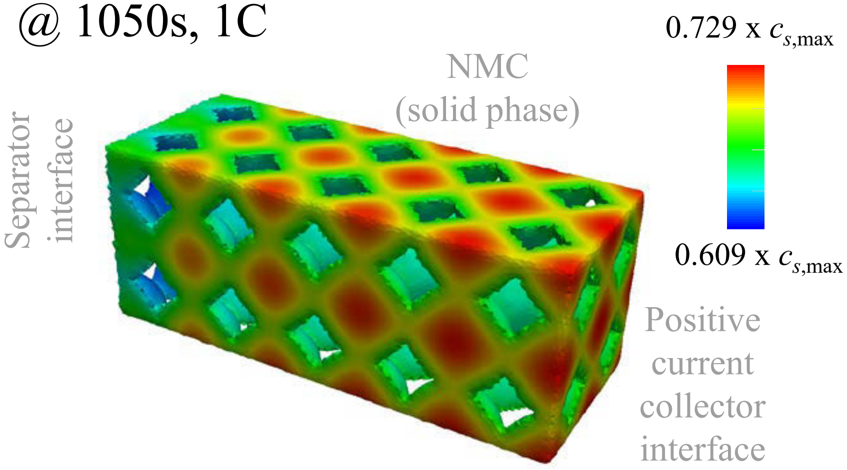
Objective: Establish a tool that predicts electrochemical heterogeneity induced by microstructure morphology. Heterogeneity increases probability of degradation.

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

Example 1: NMC Spherical Particles Packed in Series

Solid-phase concentration

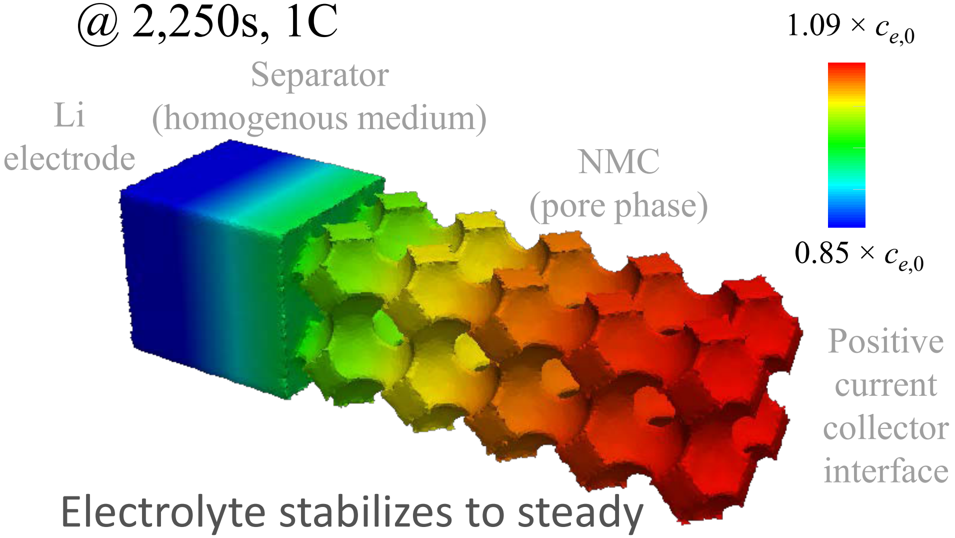
@ 1050s, 1C



Preferential use of active material close to separator and particle surfaces

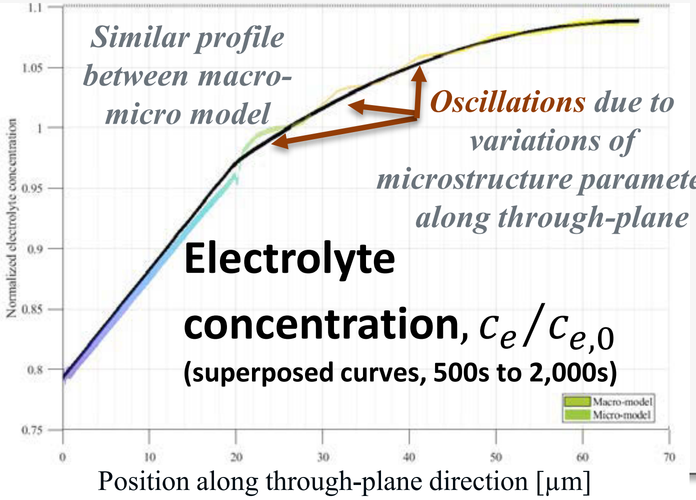
Electrolyte-phase concentration

@ 2,250s, 1C



Electrolyte stabilizes to steady state in first ~300 seconds

Micro vs. macro model comparison

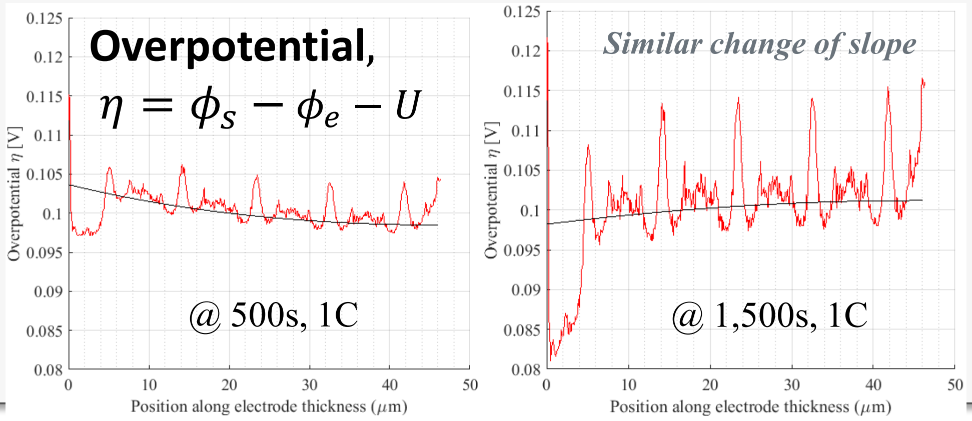


Similar profile between macro-micro model

Oscillations due to variations of microstructure parameters along through-plane

Electrolyte concentration, $c_e/c_{e,0}$

(superposed curves, 500s to 2,000s)



Overpotential,

$$\eta = \phi_s - \phi_e - U$$

@ 500s, 1C

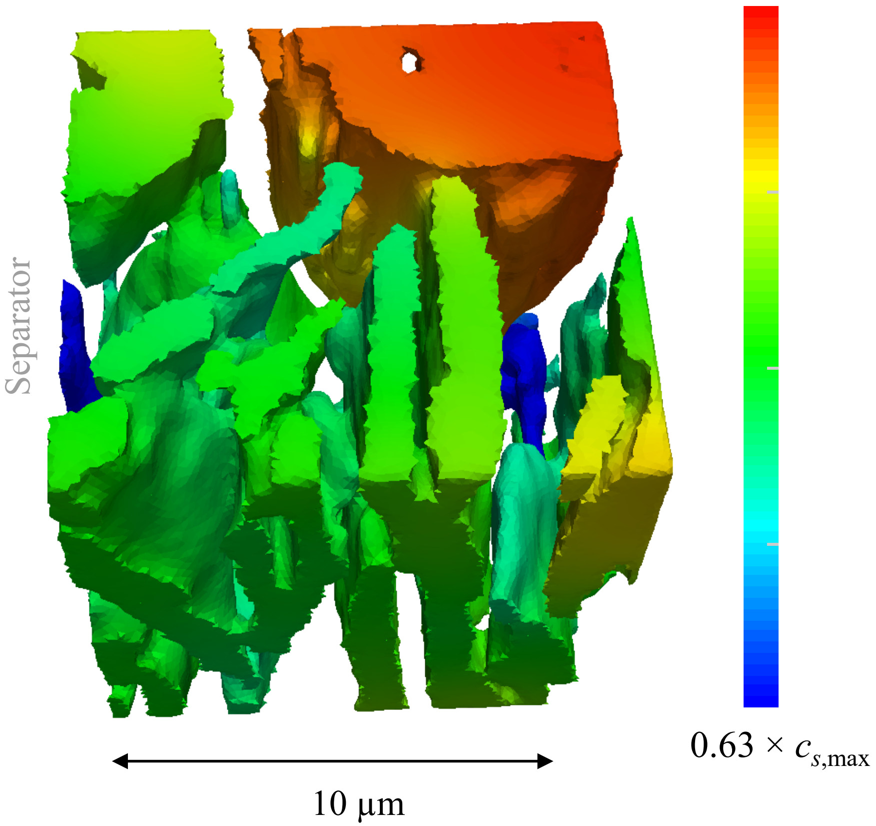
Similar change of slope

@ 1,500s, 1C

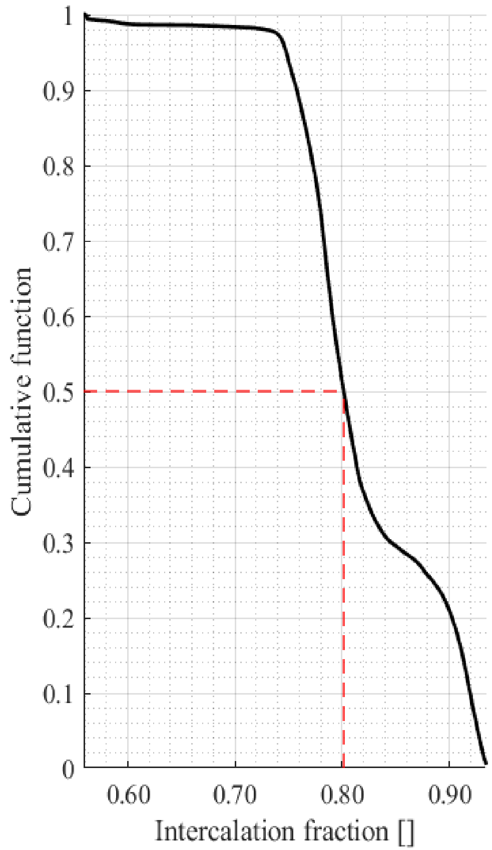
Example 2: Graphite Actual Geometry

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

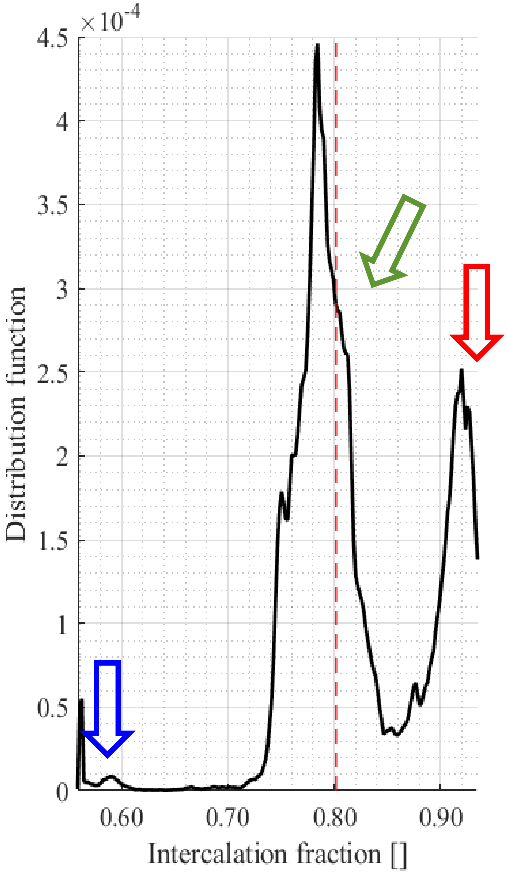
Local morphology controls the local concentration distribution



Cumulative function



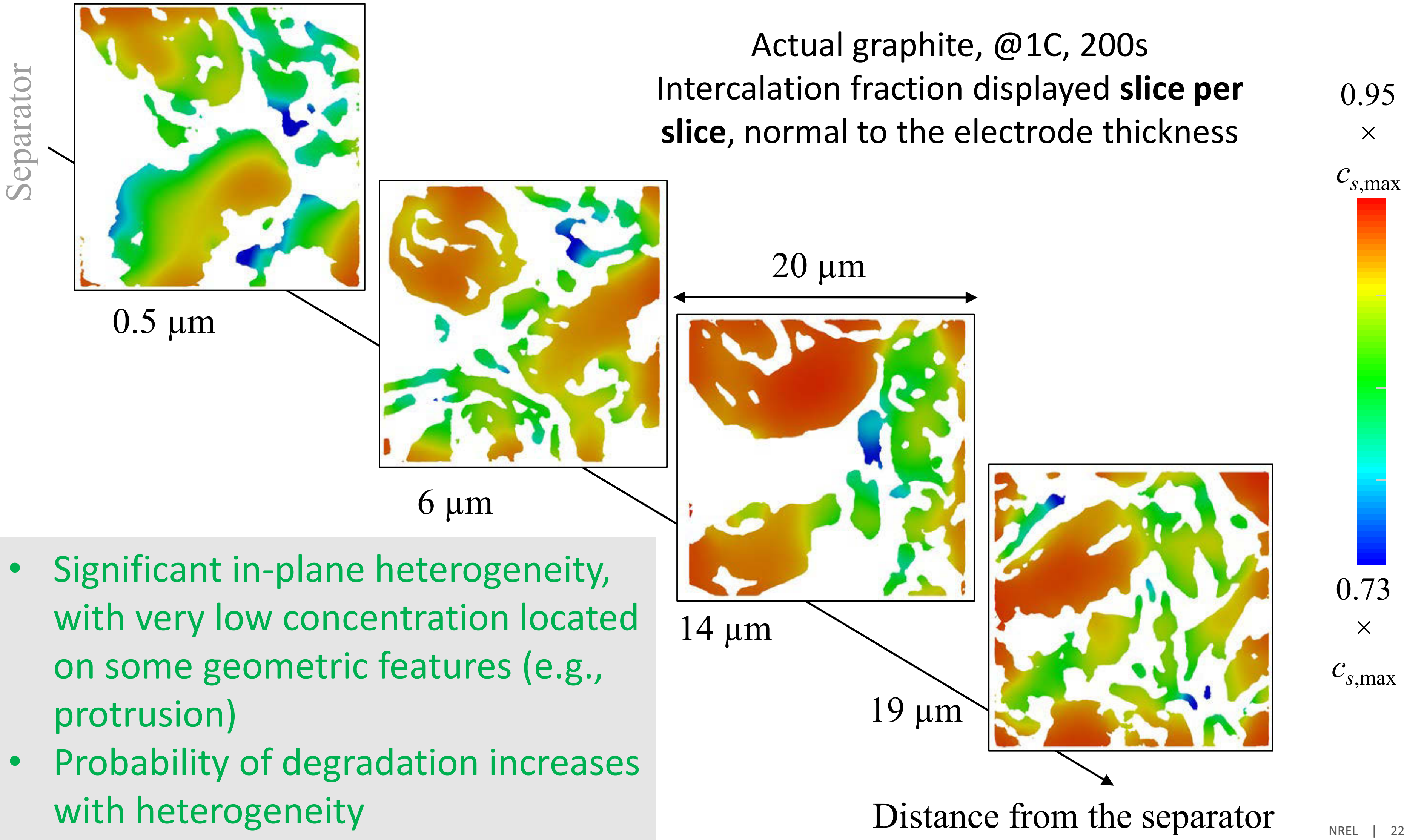
Distribution function



Time = 472s, mean intercalation fraction = 0.82

Example 2: Graphite Actual Geometry

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



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

- 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 μm^3	30 x 30 x 30 μm^3
– Goal:	30 x 30 x thickness μm^3	40 x 40 x thickness μm^3

Responses to Previous Year Reviewers' Comments

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

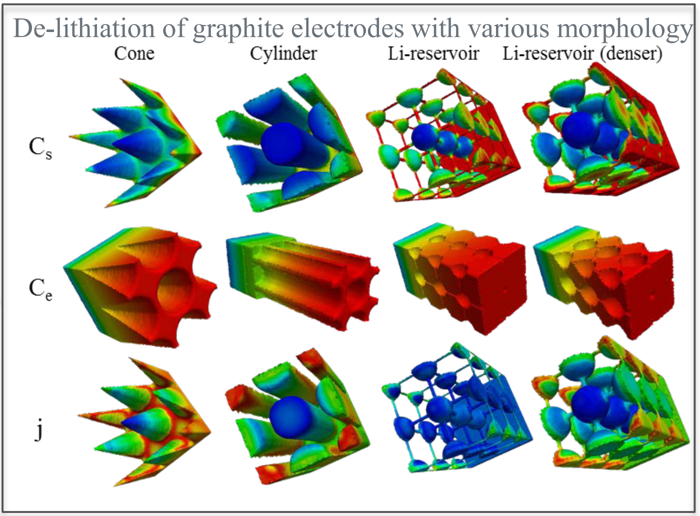
Acknowledgements

- 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

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, τ, 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 → $\tau = 7$
    - Superior SLC1506T aspect ratio of 0.78 → $\tau = 4.5$
    - Toda NCM523 aspect ratio of 0.85 → $\tau = 3$

- 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

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