Project ID #BAT299

Microstructure Characterization and Modeling for Improved Electrode Design

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National Renewable Energy Laboratory
June 20, 2018

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Koffi (Pierre) Yao, Daniel Abraham, Andy Jansen, **Argonne National Laboratory**
Aashutosh Mistry, Ankit Verma, Partha Mukherjee, **Purdue University**

Overview

This project was awarded in response to VTO FY15 Lab Call.

Timeline

- Project start date: Oct. 2015
- Project end date: Sept. 2018
- Percent complete: 75%

Budget

- Total project funding: $ 3.15M
  - DOE share: 100%
- Funding received in FY 2016: $1.05M

Funding received in FY 2017: $1.05M
Funding received in FY 2018: $ 600k

Barriers

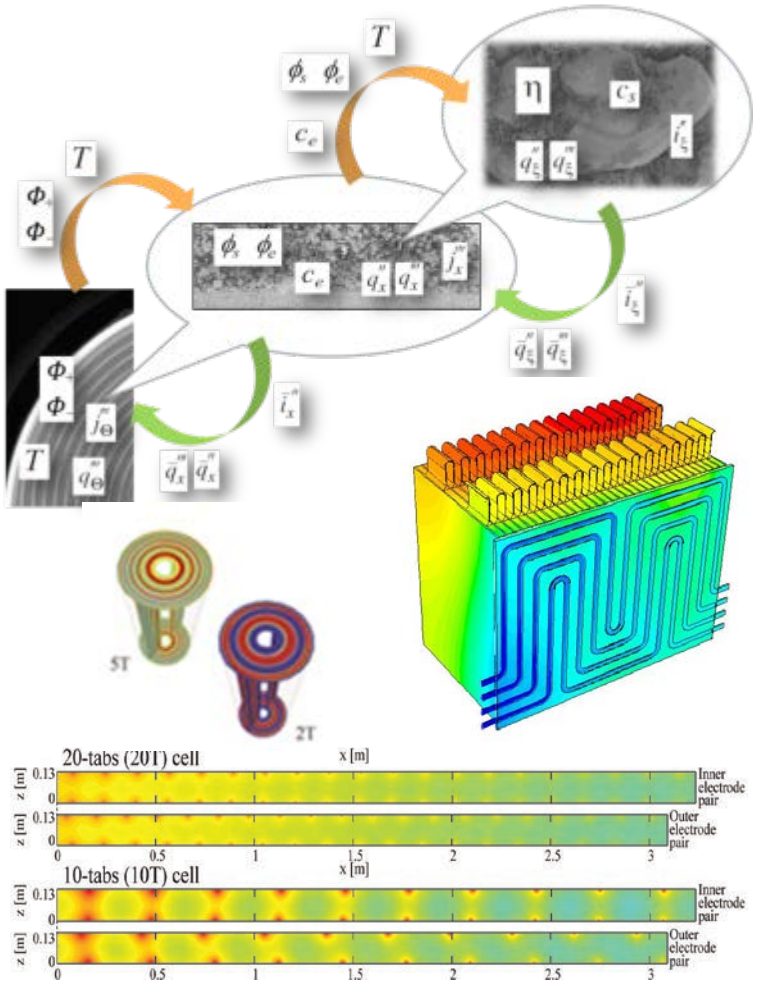
- Gaps between modeling tools and cell design process in the industry
- Lack of simulation models capturing the effect of electrode recipe, including inert components, on performance
- Low-cost, thick electrodes limited by tortuosity

Partners

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

Relevance

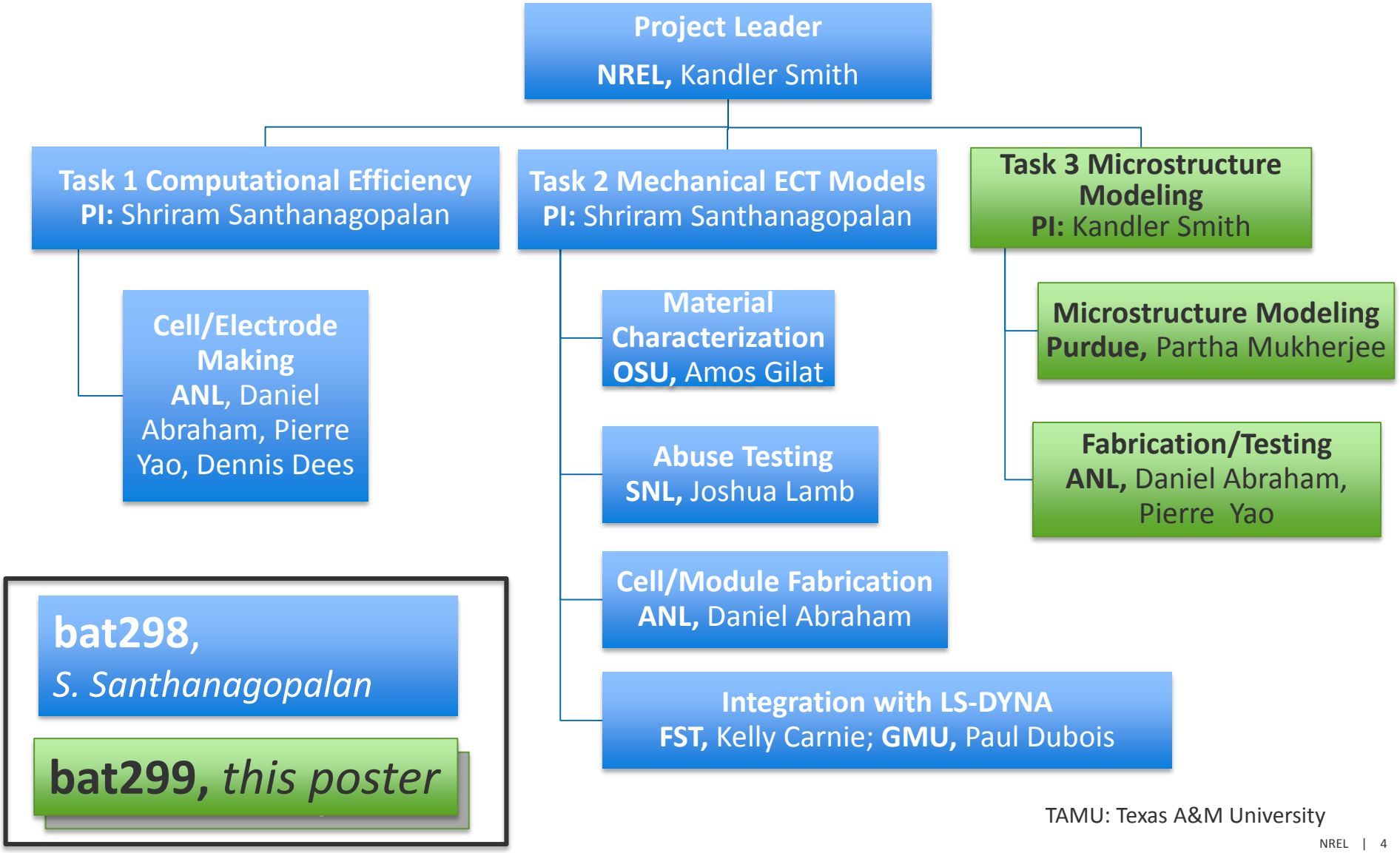
- VTO launched the Computer-Aided Engineering of Batteries (CAEBAT) project to develop validated modeling tools to accelerate development of batteries, in support of vehicle electrification R&D to reduce dependence on imported oil.
- Over 40 different end users from the community have adapted the Multi-Scale 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 helped us identify gaps.

Project Structure

Project Title: Computer-Aided Battery Engineering Consortium

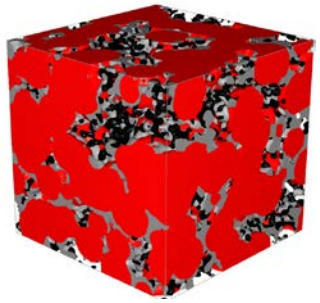


TAMU: Texas A&M University

Relevance – Objectives for March 2017 to March 2018

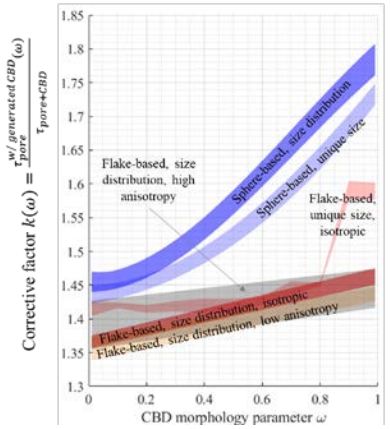
1) Electrode design through meso-scale modeling:

- Develop stochastic reconstructions of electrodes capturing electrochemical role of inert carbon-binder phases
- Apply meso-scale models to predict the impact of electrode recipe and design on performance



2) Microstructure characterization:

- Conduct electrochemical and imaging experiments to characterize and validate microstructure properties for a variety of electrode thicknesses, porosities and morphologies
- Perform homogenization calculations to determine effective properties (surface area, particle distribution, tortuosity)



3) 3D microstructure modeling:

- Perform 3D electrochemical physics simulation on detailed microstructure geometries

Task moved to DOE extreme fast charge program (xFC), BAT339

Impact: By making disruptive CAE design tools available on desktop computers 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

Milestones

	Milestone Name/Description	Deadline	Milestone Type	Status
Comp. Effic.	M 1.1 Draft summary documentation of GH-MSMD framework	8/31/2016	Qrt. Prog. Meas.	Done
	M 1.2 MSMD identification and simulation of graphite/NMC532 system	1/31/2017	Qrt. Prog. Meas.	Done
	M 1.3 Present at the DOE Annual Merit Review	6/30/2016	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
Mech. Abuse	M 2.1 Demonstrate simultaneous coupling in Mechanical-Electrochemical-Thermal (MECT) model that shows interaction of mechanical deformation with the thermal response of the cell under different strain-rates within 10% error against data	3/31/2016	Annual SMART (Go/No-Go)	Done
	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.	On track
	M 2.4 Report summarizing model validation for MECT simulations	9/30/2018	Qrt. Prog. Meas.	On track
Microstructure	M.3.1 Document microstructure model formulation and validation plan	12/31/2015	Qrt. Prog. Meas.	Done
	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

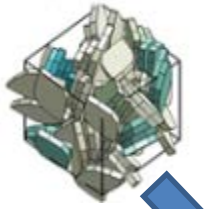
NMC: nickel manganese cobalt

Approach

PURDUE UNIVERSITY

Stochastic reconstruction & meso-scale physics

Validation of virtual 3D geometry



Argonne NATIONAL LABORATORY

Electrode fabrication, tomographic measurement, electrochemical response

Design inputs

- Chemistry
- Morphology
- Size distribution
- Binder
- Conductive additive
- Calendaring

Microstructure Model

NREL NATIONAL RENEWABLE ENERGY LABORATORY

- Geometry

- Physics

- High Performance Computing (HPC)

UCL

BYU

Electrochemical performance validated for multiple designs

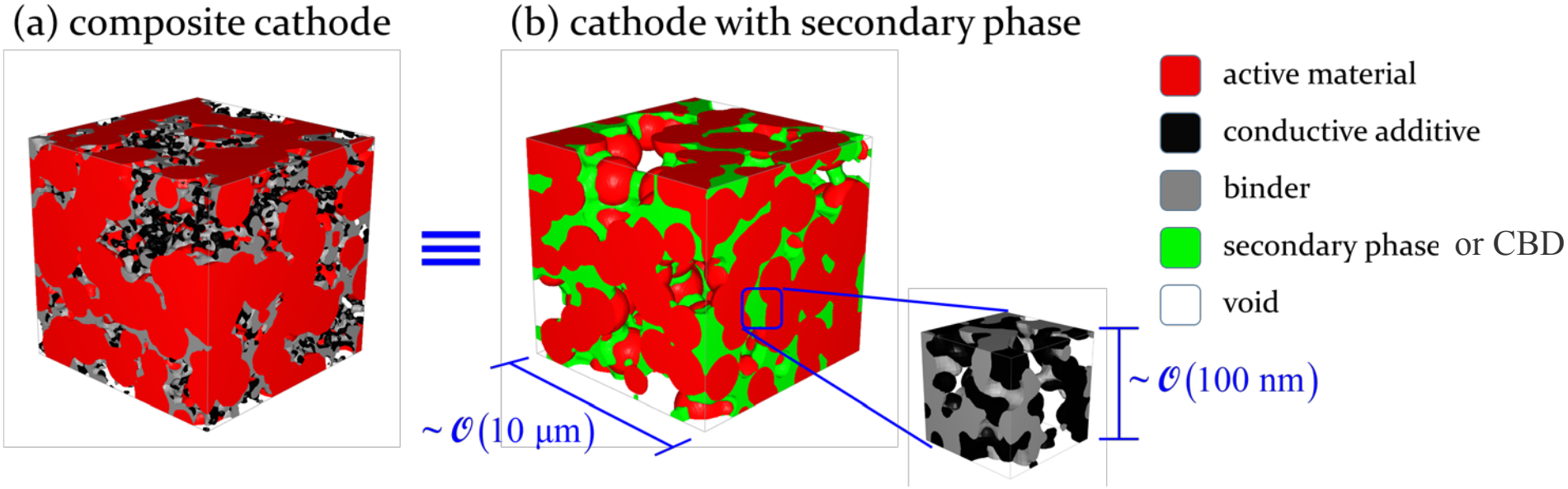
Homogenization

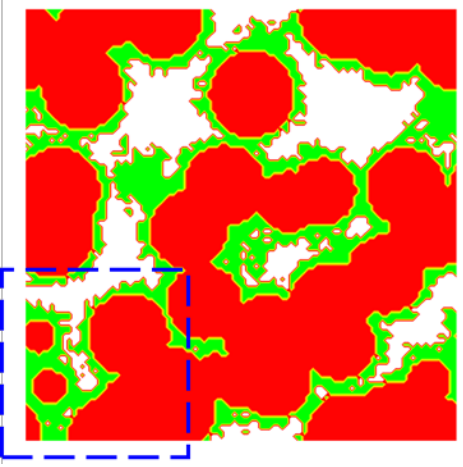
Linkage to CAEBAT macroscopic simulation toolsets

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

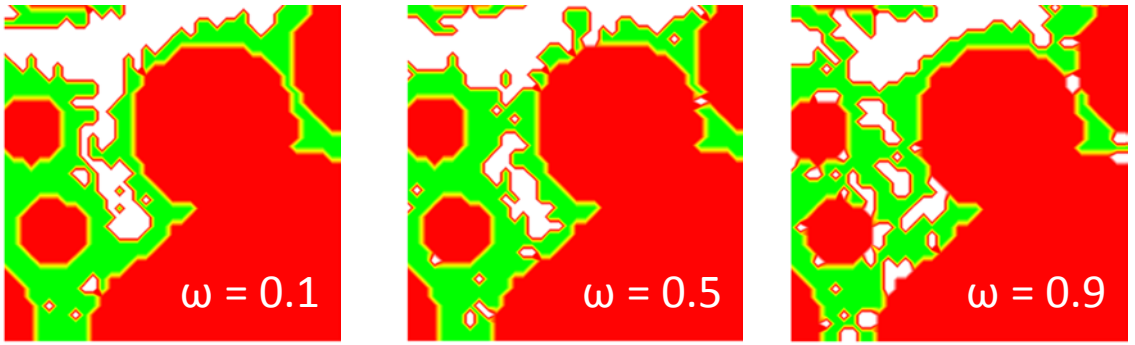
Meso-scale Modeling

Secondary Phase Stochastics in Composite Electrodes: Carbon + Binder Domain (CBD)





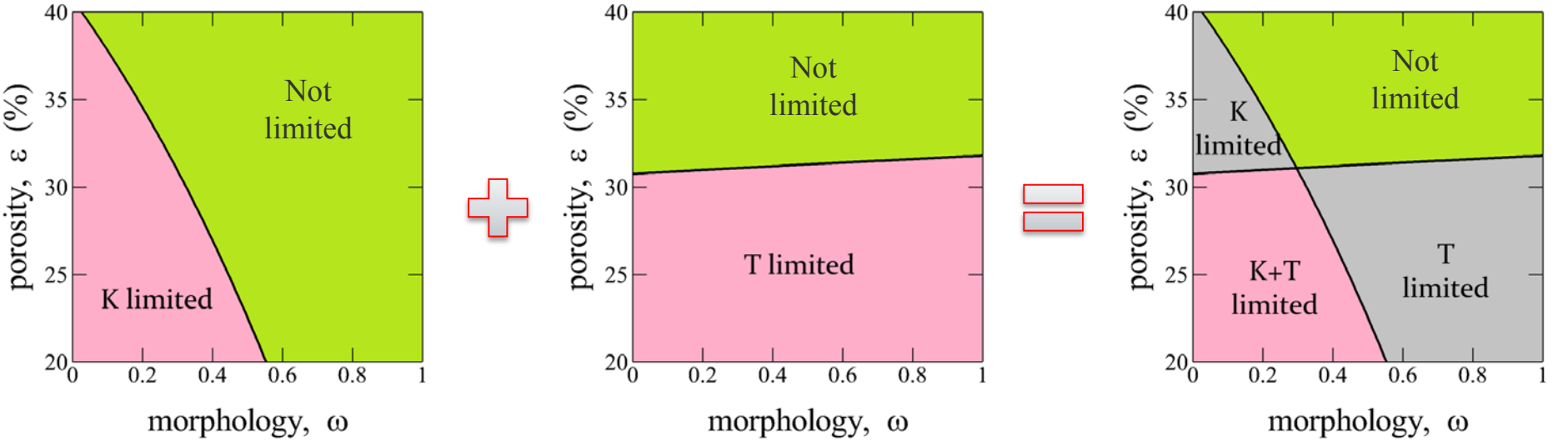
Secondary phase morphology (ω) alters microstructural arrangement and in turn affects kinetic and transport interactions



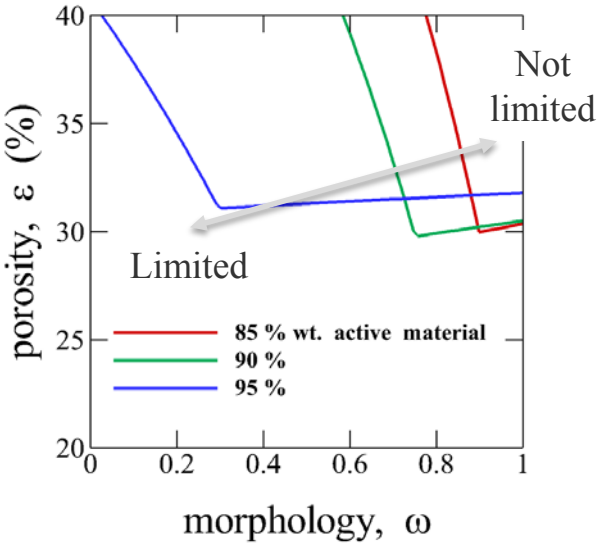
*Mistry, Smith and Mukherjee (2018) "Secondary Phase Stochastics in Li-ion Battery Cathodes," *ACS Appl. Mater. Interfaces* **10** (7), 6317

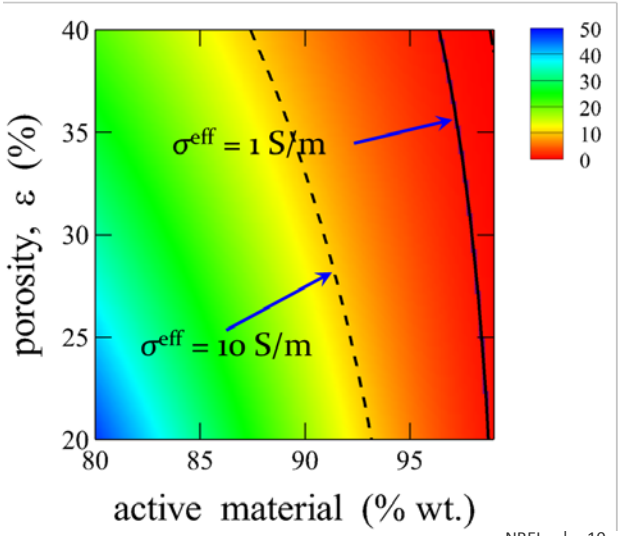
Microstructural Resistances versus Electrode Design

- Kinetic (K) and ion transport (T) limited regions for 95% wt. active material



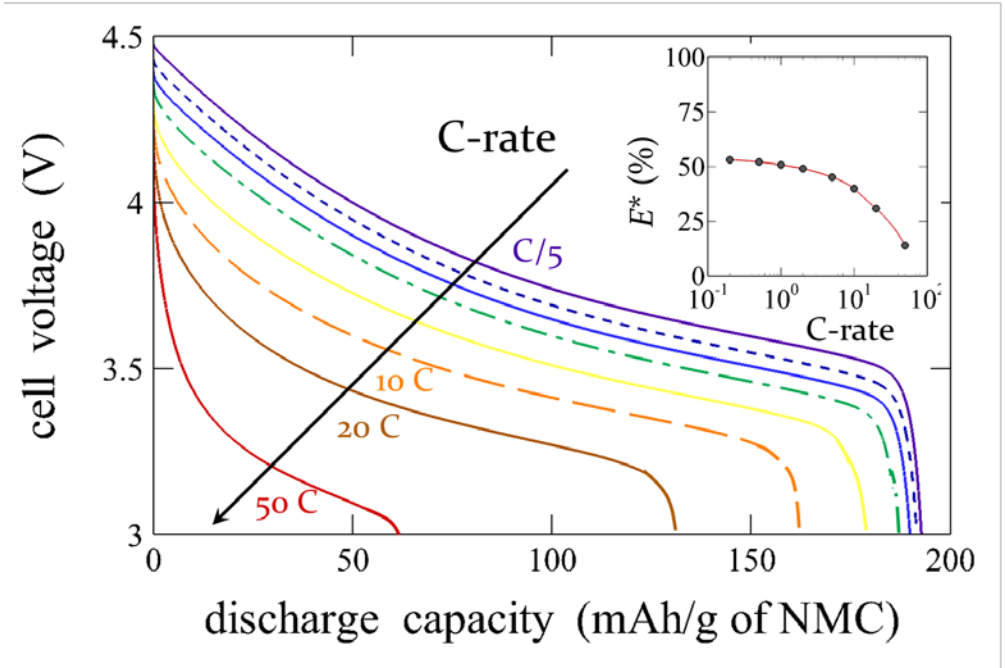
- Same, for 85%, 90%, and 95% wt. active material

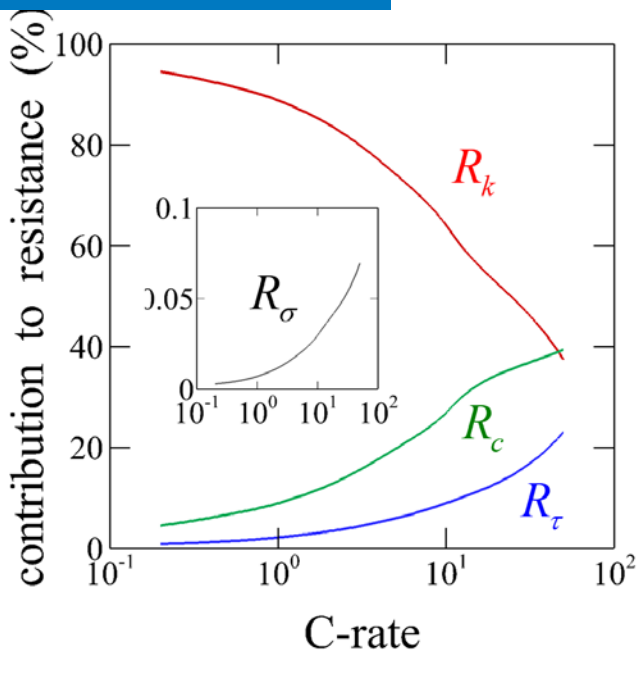




*Mistry, Smith and Mukherjee (2018) "Secondary Phase Stochastics in Li-ion Battery Cathodes," *ACS Appl. Mater. Interfaces* **10** (7), 6317

Components of Internal Resistance

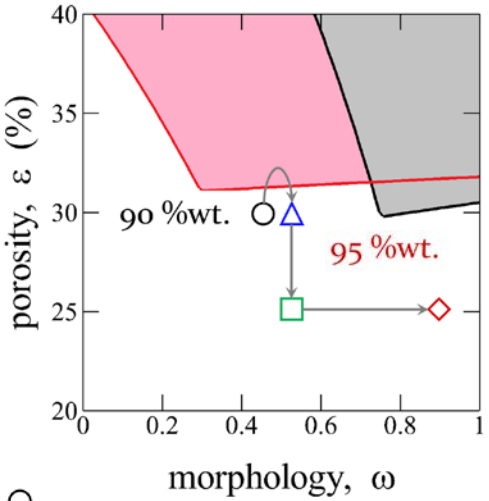


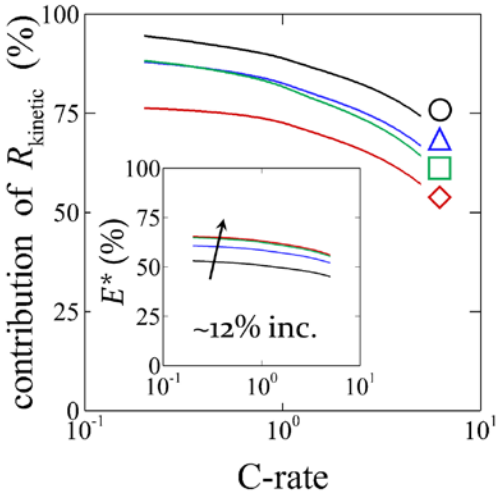


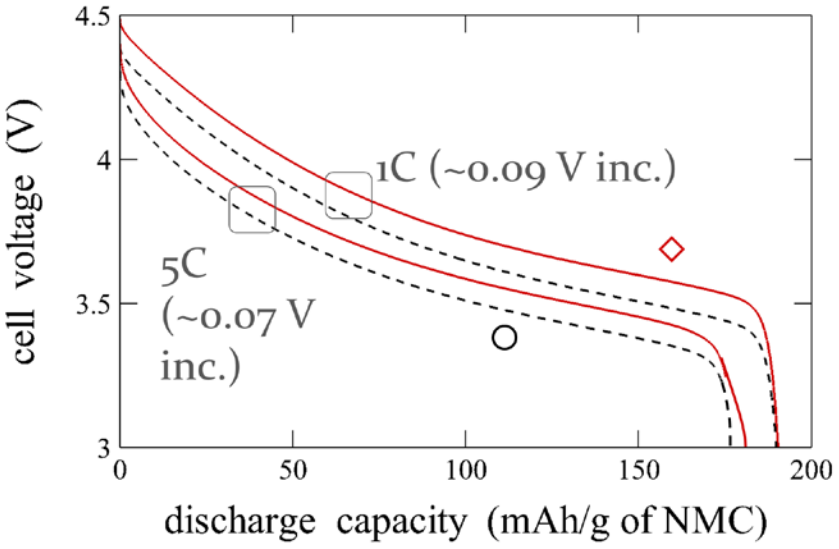
- Electrode: 30% porosity, 90% wt. active material (NMC333), ω = 0.5 and 25 µm thick
- Rate capability calculations are performed to identify contributions from different physicochemical process to total internal resistance:
  - R_k: kinetic resistance
  - R_c: concentration overpotential in active material resistance
  - R_τ: electrolyte transport resistance
  - R_σ: solid state conduction resistance
- This helps identify the dominant resistance mode(s).

Example Microstructural Changes Resulting in Improved Performance at 1C and 5C rates

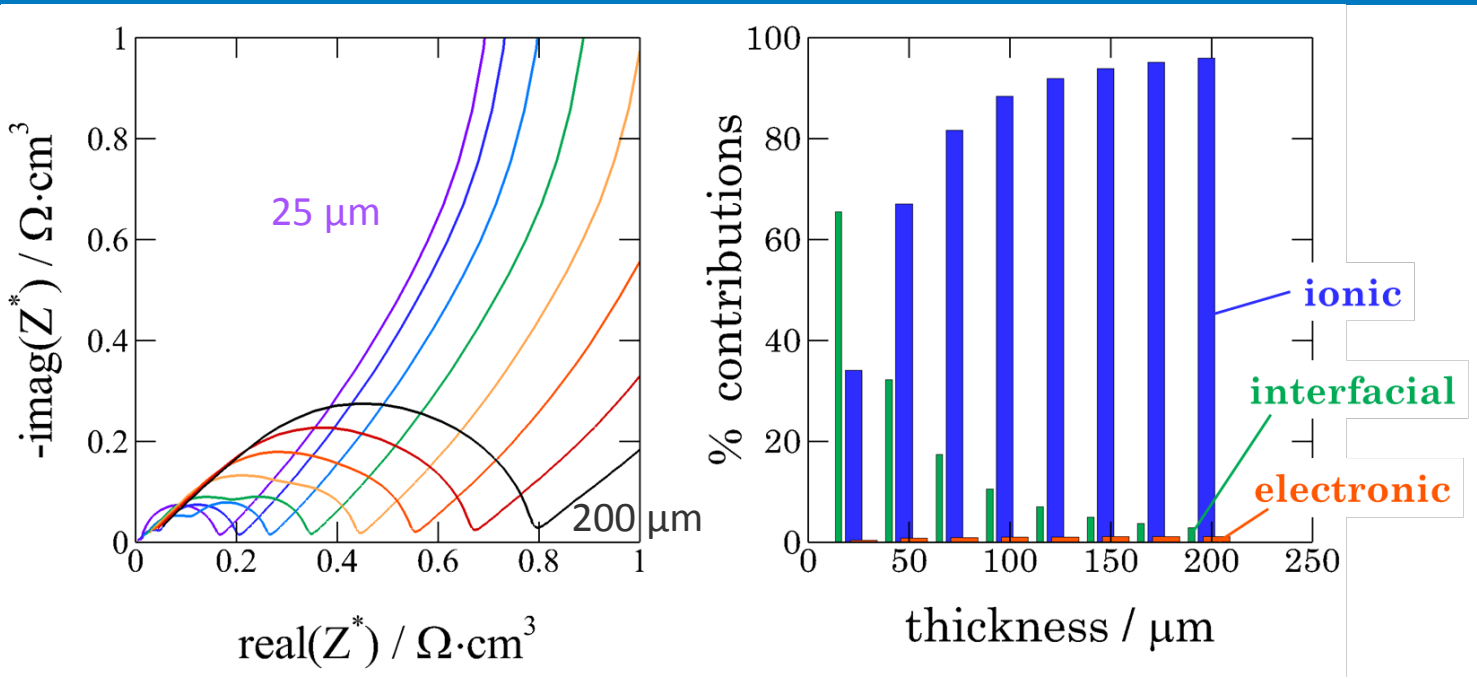
- Rate capability and internal resistance analysis identifies kinetic resistance as the most dominant cause of limitation.
- The microstructural resistance diagram is used to suggest changes in the electrode and in turn improve performance.
- Summary of changes:
  - Increase active material from 90% to 95% wt. (conductivity map ensures enough conduction even at 95%wt. active material)
  - Reduce porosity from 30% to 25% (electrolyte transport is not rate limiting; hence, porosity can be reduced to pack more active material without appreciable transport loss)
  - Improve morphology from 0.5 to 1.0 (higher secondary-phase morphology leads to greater active area and smaller kinetic resistance)







Resistive Mode Dependence on Electrode Thickness



- Dominant resistance mode changes as electrode thickness is increased.
- Here impedance analysis is carried out on electrodes with different thicknesses (without altering the structural arrangement) to understand the mutual coupling of these different rate-limiting effects. Electrode thickness is increased from 25 to 200 µm in 25-µm steps.
- For the same electrode microstructure, increasing the electrode thickness reduces the importance of interfacial (kinetic) effects, and ionic resistance is more rate limiting.

Microstructure Characterization

Leveraging Electrode Library from ANL-CAMP

- 14 graphite & NMC532 electrodes of varying thickness and porosity were manufactured and electrochemically characterized by ANL

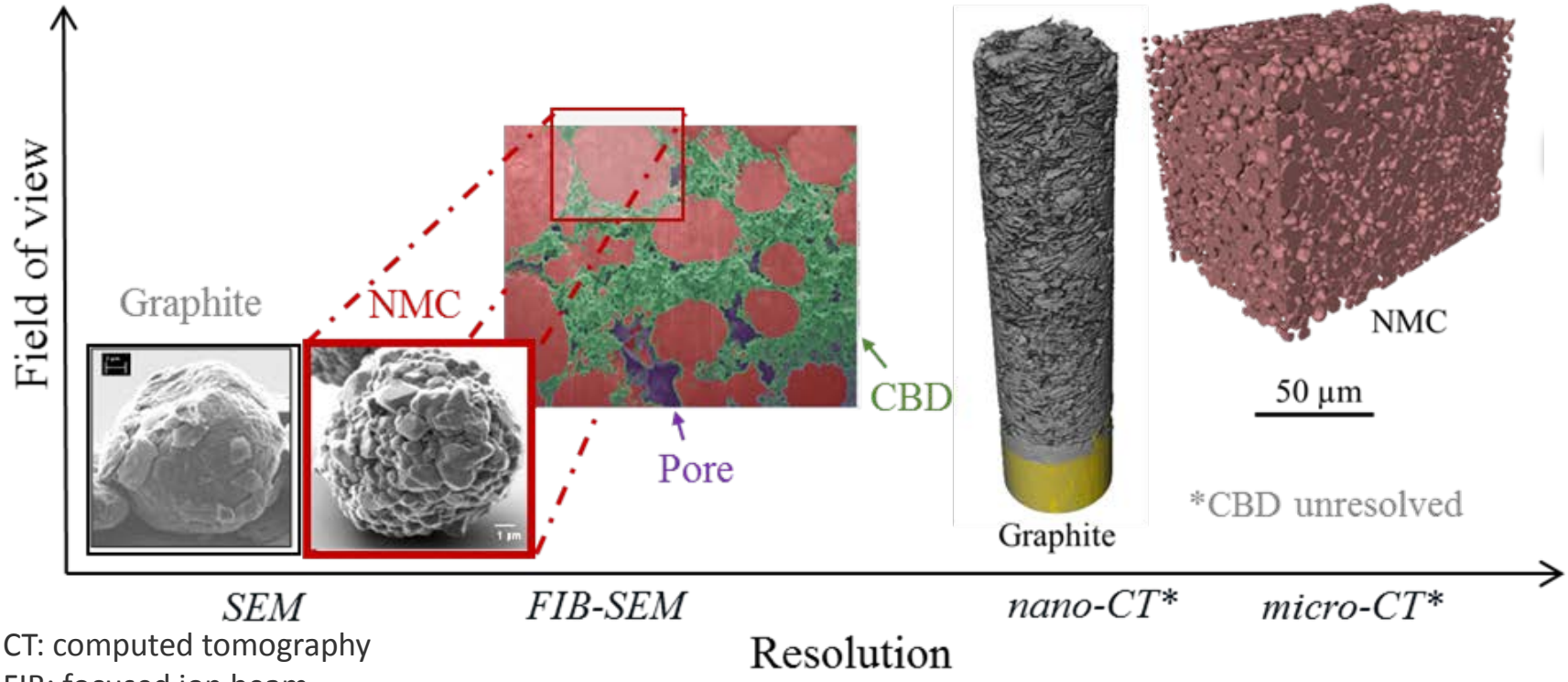
	Calendering	Name	Coating thickness [µm]	Volume fraction			Density [mg.cm^{-2}]		Loading [mAh.cm^{-2}]	Experimental C-rate[c] [mAh.g$_{active}^{-1}$]
				Pore	Active material	CBD	Coating	Active material	Active material	
NMC532	No	1-UNCAL	160	49.1	39.7	11.2	33.09	29.78	8.27	179
	Yes	1-CAL	129	36.8	49.3	13.9				178
	No	2-UNCAL	140	51.8	37.6	10.6	27.39	24.65	6.84	179
	Yes	2-CAL	108	37.5	48.8	13.7				180
	No	3-UNCAL	106	47.4	41.0	11.6	22.60	20.40	5.66	183
	Yes	3-CAL	88	36.6	49.5	13.9				182
	Yes	4-CAL	34	33.5	51.9	14.6	9.17	8.25	2.29	178
Graphite	No	5-UNCAL	205	50.7	44.6	4.7	21.89	20.1	7.48	336
	Yes	5-CAL	165	38.8	55.4	5.8				300
	No	6-UNCAL	173	51.8	43.6	4.6	18.08	16.6	6.17	330
	Yes	6-CAL	131	36.3	57.7	6.0				282
	No	7-UNCAL	140	51.4	44.0	4.6	14.70	13.5	5.02	351
	Yes	7-CAL	110	38.0	56.1	5.9				351
	Yes	8-CAL	44	38.4	55.8	5.8	5.88	5.51	2.05	363

CAL: calendared, CBD: carbon/binder domain, UNCAL: uncalendared

Microstructure Imaging

- SEM imaging performed by ANL on select samples
- CT imaging performed by UCL (Paul Shearing) on entire library
  - Missing CBD phase numerically generated using Purdue University algorithm

CBD = carbon binder domain (inert phase)

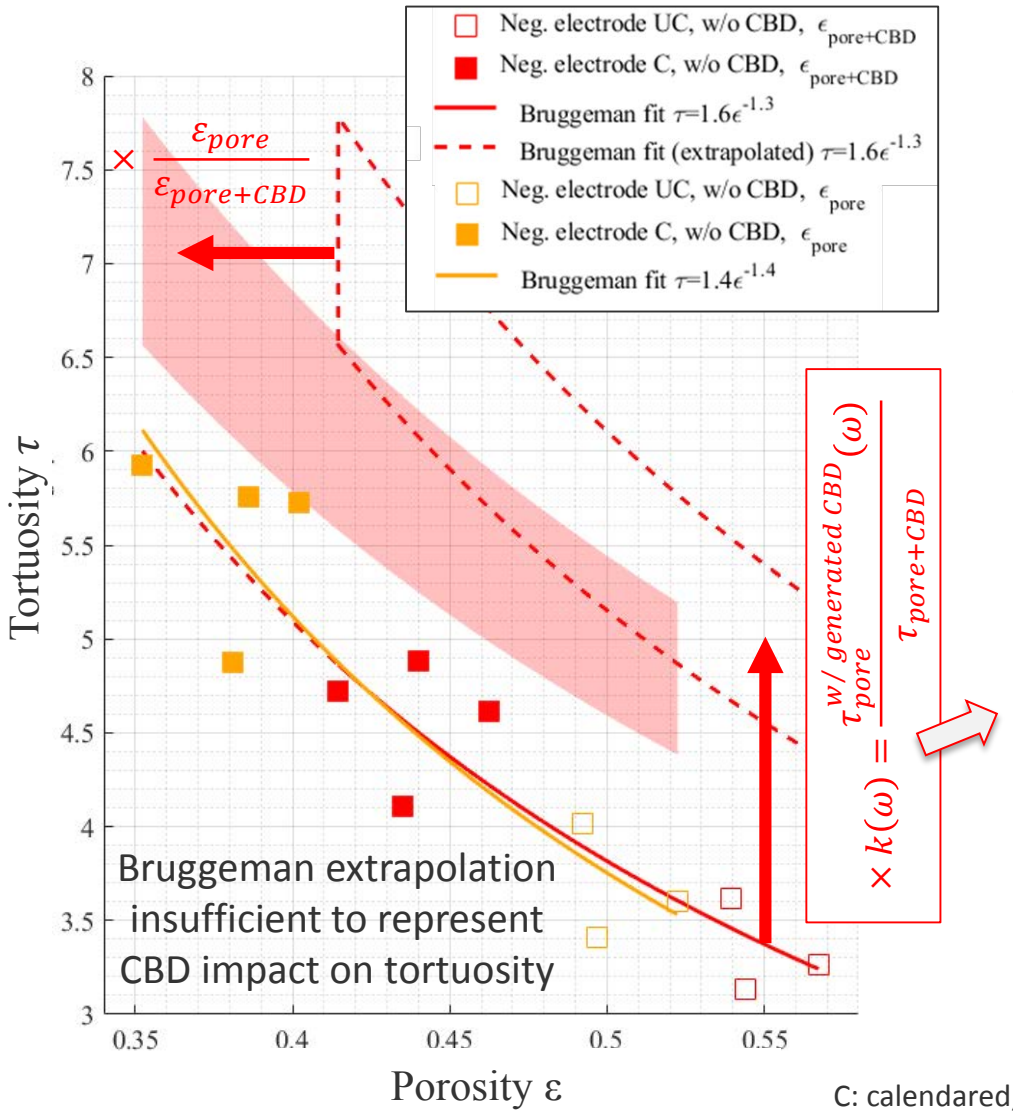


CT: computed tomography
FIB: focused ion beam
SEM: scanning electron microscope

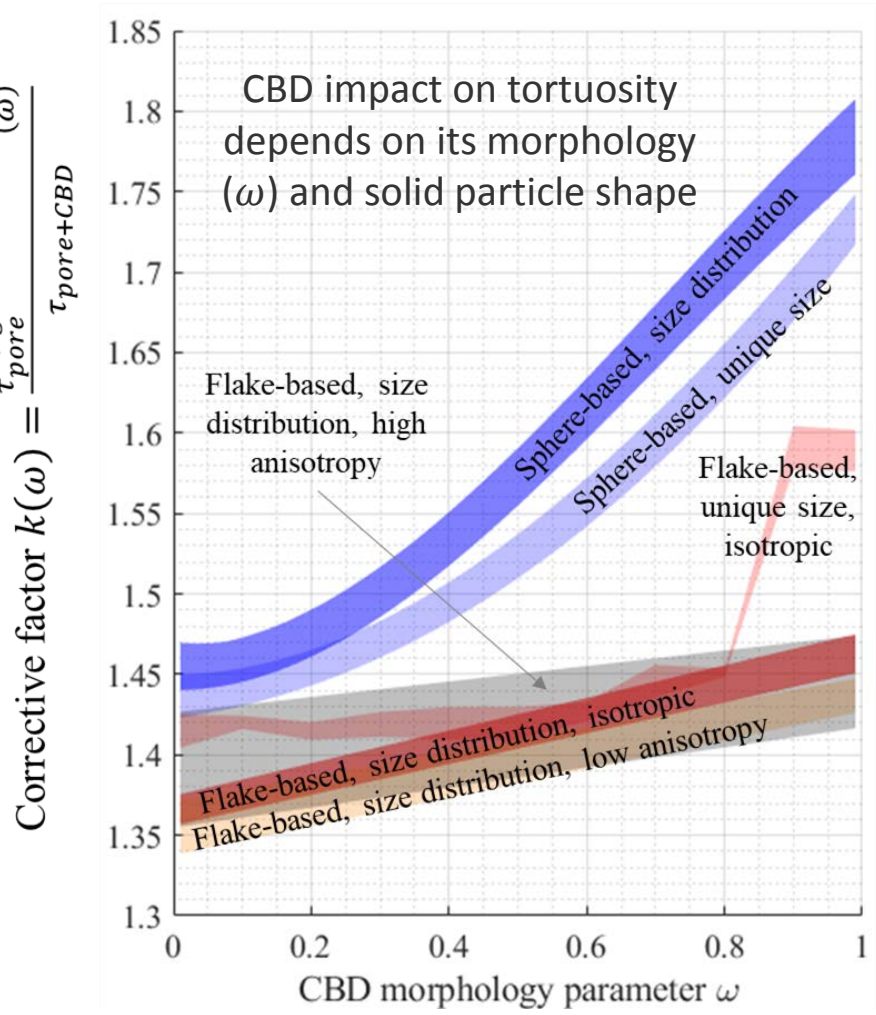
Corrective Factor Accounts for Additional Tortuosity Due to CBD

Tortuosity corrected for CBD

(actual graphite electrodes)

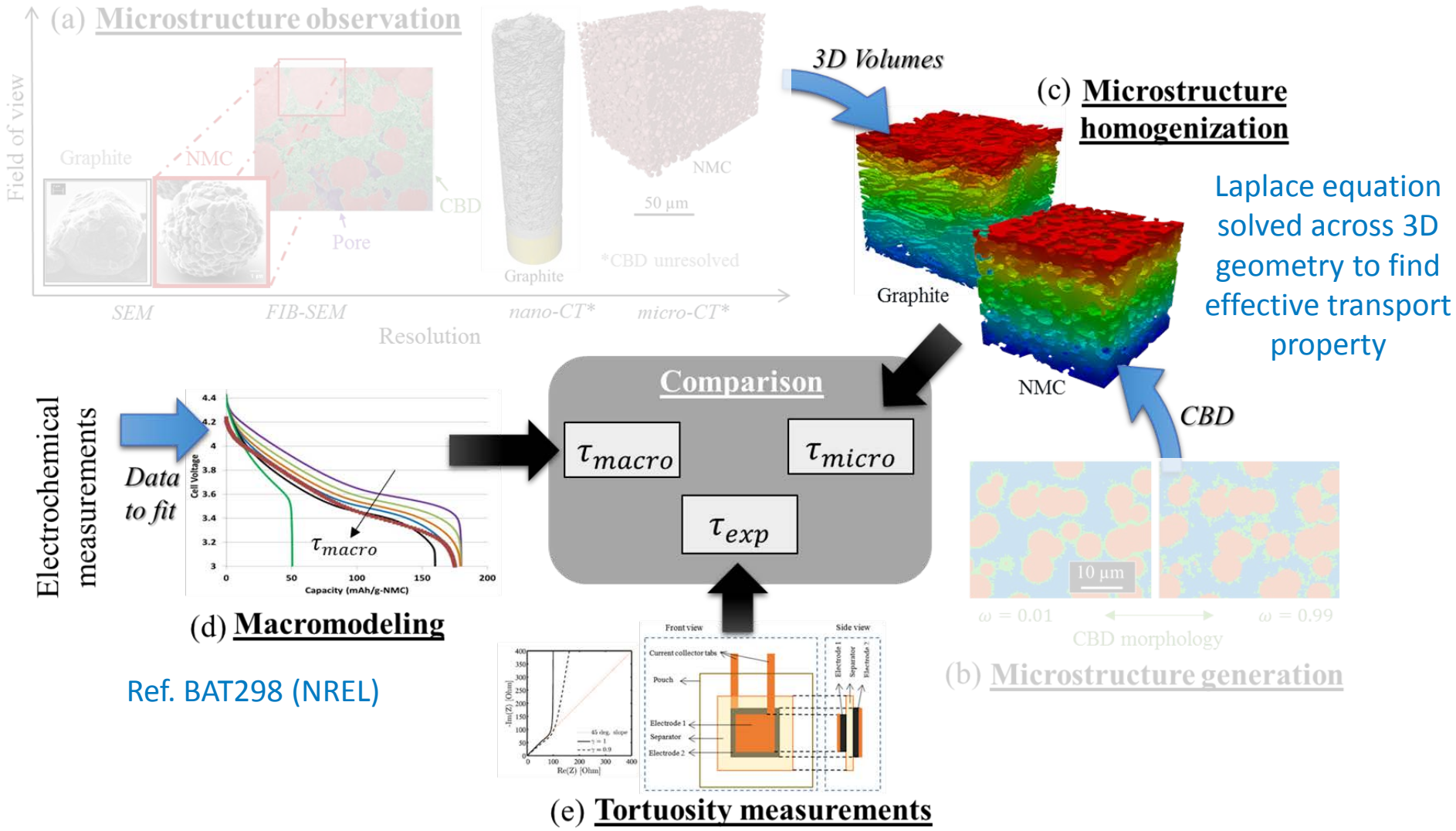


Corrective factor for other particle morphologies



C: calendared, UC: uncalendared

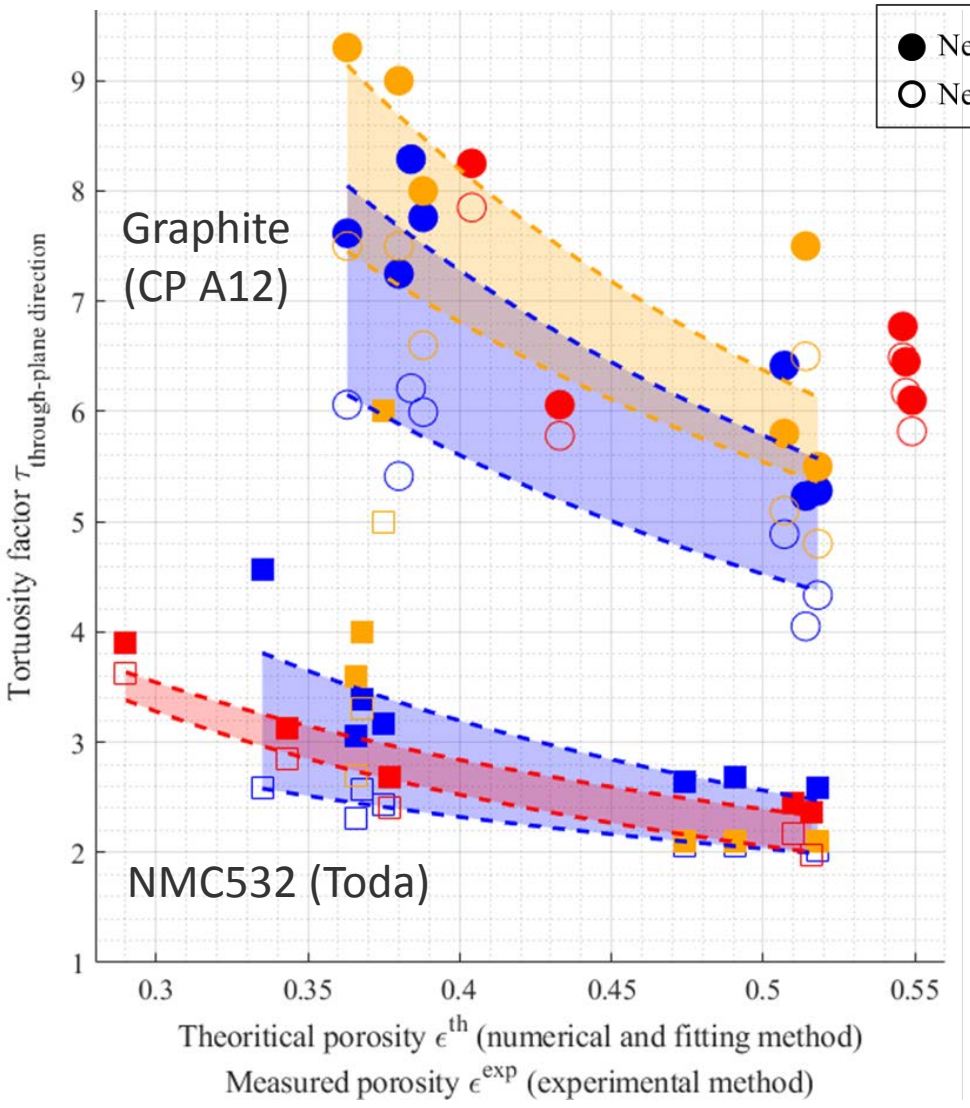
Tortuosity via Microstructure Homogenization Validated with Two Independent Methods



Ref. BAT298 (NREL)

N.A. Zacharias, D.R. Wheeler et al. "Direct measurements of effective ionic transport in porous Li-ion electrodes," *J. Electrochem. Soc.* **160**, A306-A311 (2013).

Comparison of Three Tortuosity Prediction Methods



- Microstrucure modeling
- Macroscopic modeling
- Experimental measurement

- 14 ANL-CAMP electrodes of varying thickness and porosity
- Validates microstructure homo-genization approach with CBD phase
  - CBD morphology tends towards web-like structure, ω → 1
- Higher tortuosity leads to higher variability in both measurements and model predictions
- Quasi-spherical NMC particles have much lower tortuosity than graphite platelets aligned with electrode

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

Remaining Challenges and Barriers

- Obtain 3D images of CBD with sufficient field of view and resolution to validate morphology, incl. surface coverage and nano porosity
- Enhance stochastic reconstruction of CBD to capture mechanics
- Develop quantitative models coupling particle-to-electrode electrochemistry with mechanics
- Develop appropriate identification and validation experiments

Future Work

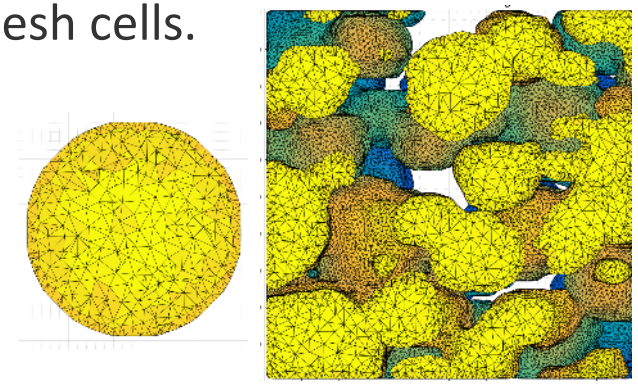
- Enhance models as described above, including particle, carbon-binder, and electrode mechanics/degradation mechanisms. Validate.
- Apply models to electrode design studies for new materials, 3D architectures and applications, e.g., fast charge

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

Responses to Previous Year Reviewers' Comments

- Comment: All major principles are well modeled, however there are some ambiguities around electrodes that expand and the impact of electrolyte. How to characterize binder strength and failure mechanisms?

  Response: Modeling mechanical stress, strain, and damage have been outside project scope so far; however we intend to add these physics pending future modeling resources.
- Comment: Reviewer would like to see more details on direct numerical simulation (DNS), its justification, and whether PI expects mixing rather than diffuse flows.
- Response: Convection of electrolyte is not expected to be significant in porous electrodes and is hence neglected. Diffusion is considered. To avoid confusion with turbulence problems, we will use the term "3D microstructure model" instead of "DNS".
- Comment: The team should be able to use a non-structured mesh to better resolve shape and actually save on number of mesh cells.
- Response: Thank you for this comment. We have reviewed and now adopted an unstructured mesh (iso2mesh) for the 3D microstructure model, indeed reducing the number of mesh cells.



Collaboration and Coordination with Other Institutions

Category	Institution	Role
National Laboratories	Argonne National Lab	Electrode/cell prototyping and characterization
Universities	Purdue University (sub to NREL CAEBAT project)	Stochastic reconstruction for microstructure studies Mesoscale electrode modeling
	University College of London (informal collaboration)	Nano and micro X-ray computed tomography
	Brigham Young University (informal collaboration)	Tortuosity measurement

Summary

- Developed stochastic algorithm to generate carbon-binder geometry on active material
- Quantified impact of carbon-binder inert phase on electrodes of varying recipe
  - Sufficient carbon-binder weight fraction required for electronic conductivity
    - Generally does not limit performance
  - Kinetic resistance dominated by carbon-binder morphology + how much blocks active surface
    - Dominant factor for electrodes <40 µm thick (hybrid electric vehicle batteries)
  - Ionic resistance dominated by electrode thickness and tortuosity
    - Dominant factor for electrodes >40 µm thick (EV batteries)
- Characterized 14 NMC532 and graphite electrodes from ANL-CAMP with varying porosity and thickness
  - Performed nano- and micro-CT imaging as well as electrochemical rate testing
- Completed study resolving many previous differences observed between various methods for tortuosity estimation
  - Corrective factor accounts for additional tortuosity due to carbon-binder
  - Carbon-binder increases electrode tortuosity by 30%–80% (greater values for spherical particle morphologies with size distribution, less for platelet morphologies and/or unique size distr.)
    - Significant part of this increase is not accounted by Bruggeman correlation (nearly half)
  - For porosities ranging from 0.50 to 0.35, observed overall electrode tortuosities of
    - 5.5-8.0 for Conoco Philips A12 graphite (elongated particles with aspect ratio ~ 0.69)
    - 2.2-3.6 for Toda NMC532 (quasi-spherical morphology with aspect ratio ~ 0.87)
  - Macro-homogeneous modeling and direct measurement of tortuosity confirm these values

Acknowledgements

- We appreciate support and funding provided by Vehicle Technologies Office at the U.S. Department of Energy
  - Brian Cunningham
  - Samuel Gillard
  - David Howell

Thank You

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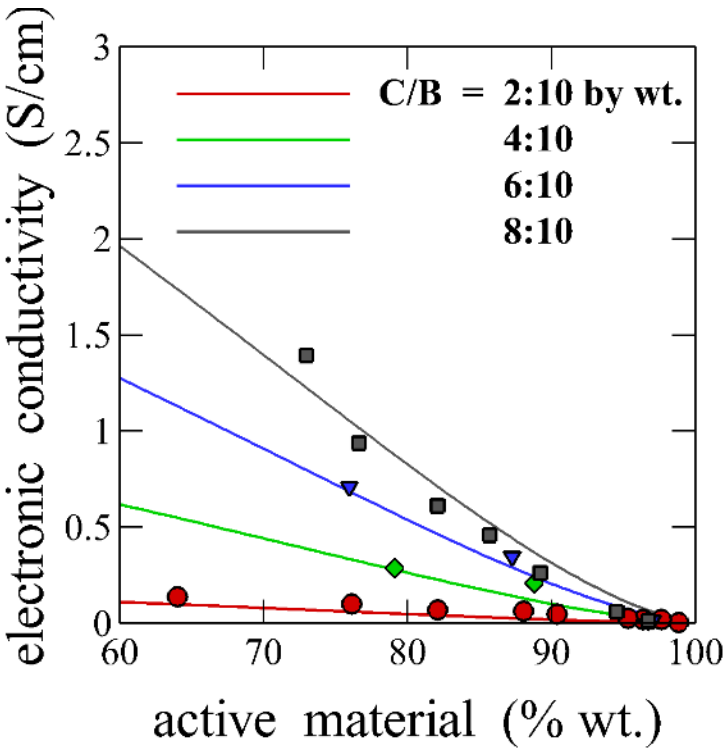
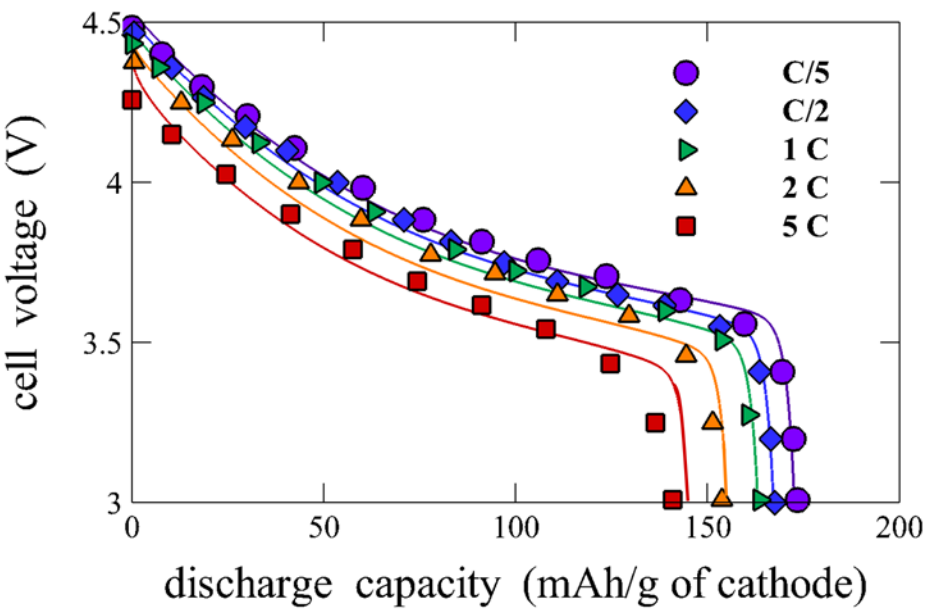
Technical Back-Up Slides

Meso-scale Model Validation at Different Length Scales: Electronic Conductivity and Rate Capability

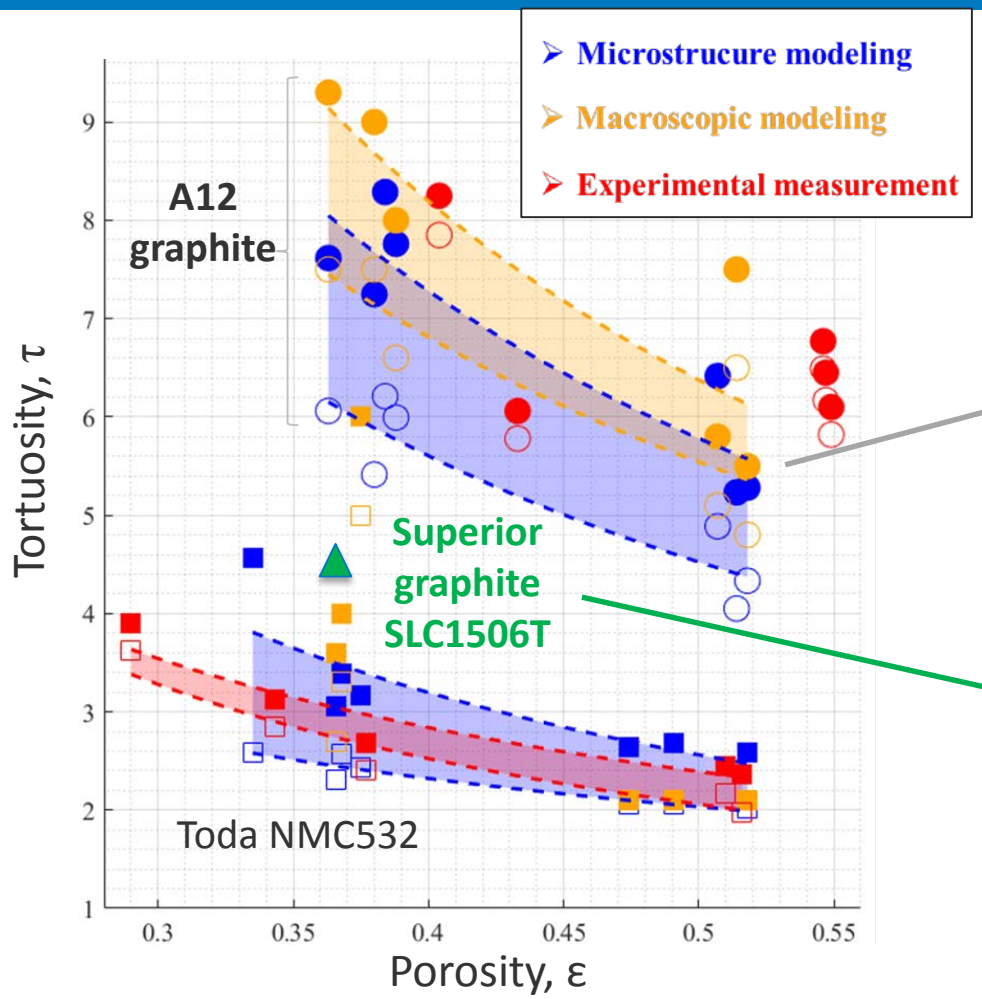


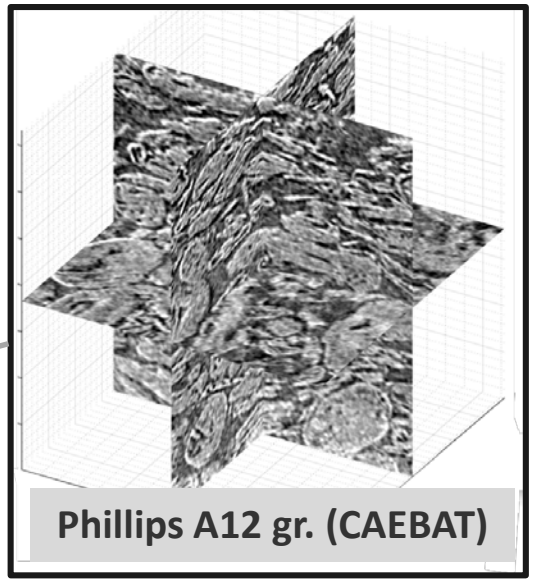


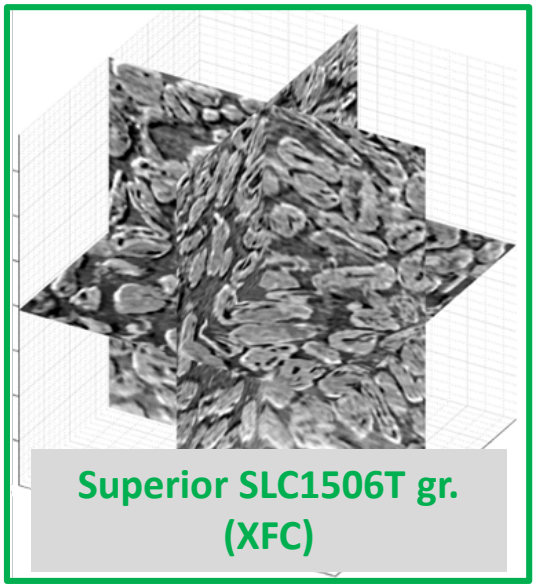
- Microstructures are validated against electronic conductivity data from Liu et al. (2012) *J. Electrochem. Soc.* **159** (3), A214
- Microstructure information is scaled up to porous electrode description (accounting for active area, tortuosity, conductivity etc.), and validated against experimental tests from H. Zheng et al. (2012) *Electrochimica Acta* **71**, 258

*Mistry, Smith and Mukherjee (2018) *ACS Appl. Mater. Interfaces* **10** (7), 6317

CAEBAT Method is Being Applied to Additional Graphite Electrodes Under xFC Project (BAT339). First Additional Graphite Shown



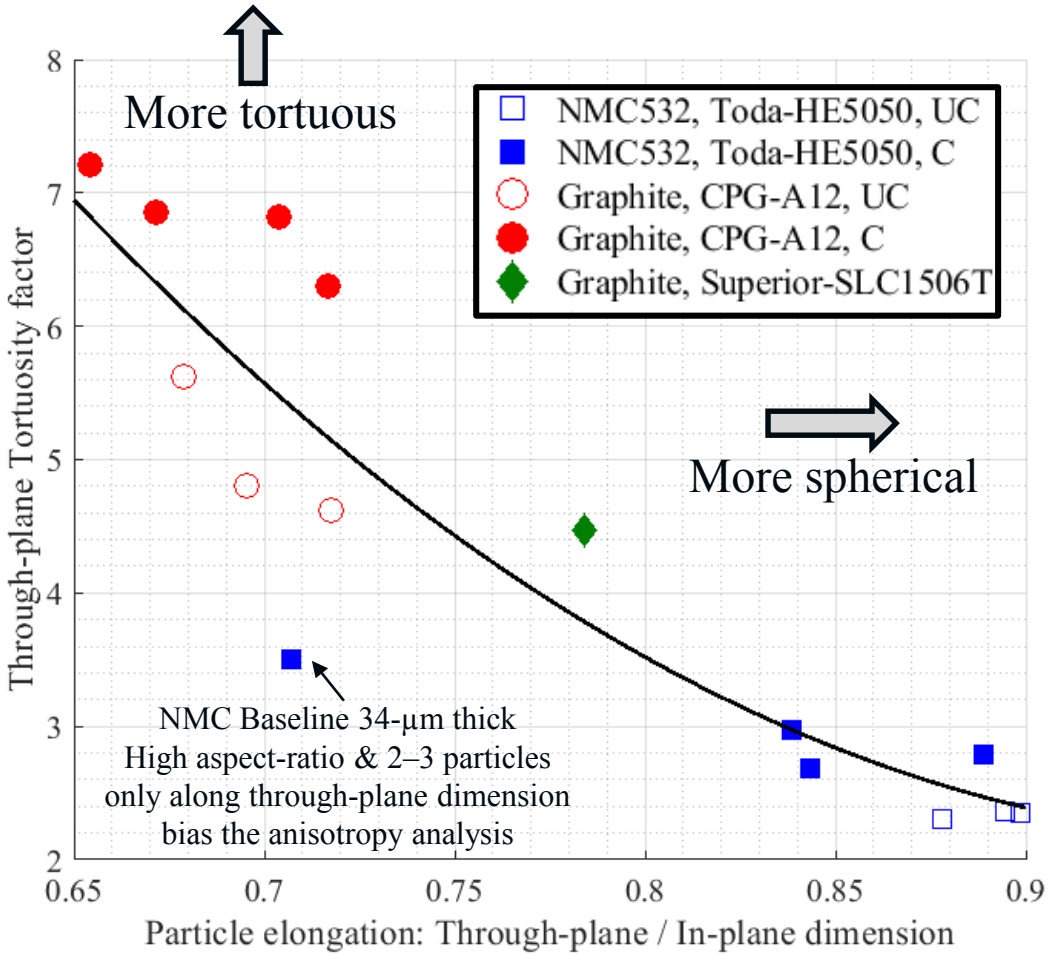




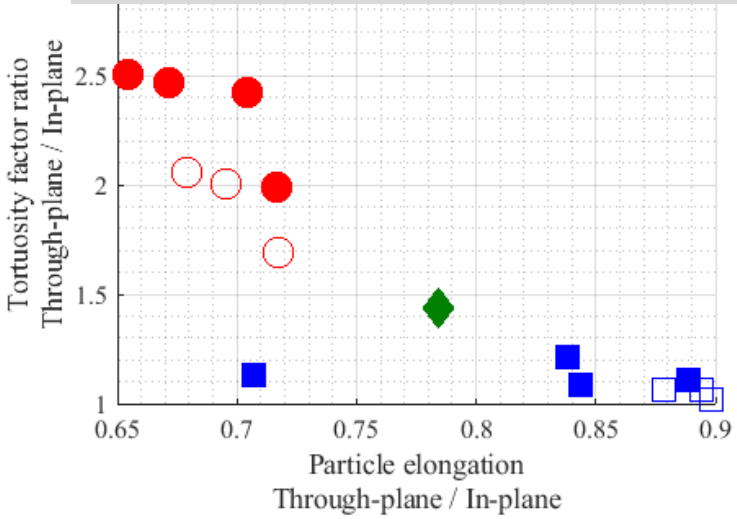
- A12 tortuosity ~7.6, SLC1506T tortuosity ~4.5
- Particle morphology and orientation play strong role

Particle Elongation in Electrode In-plane Direction Explains Widely Varying Tortuosities of Different Materials

Tortuosity vs. particle elongation



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