NREL
NATIONAL RENEWABLE ENERGY LABORATORY

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Computational Design of Batteries from Materials to Systems

Kandler Smith, S. Santhanagopalan, Chuanbo Yang, Peter Graf,
Francois Usseglio-Viretta, Qibo Li, Donal Finegan, Ahmad Pesaran (*NREL*)
Koffi (Pierre) Yao, Daniel Abraham, Dennis Dees, Andy Jansen (*Argonne Nat. Lab.*)
Partha Mukherjee, Aashutosh Mistry, Ankit Verma (*Texas A&M Univ.*)
Josh Lamb (*Sandia National Laboratory*), Eric Darcy (*NASA*)

NREL/PR-5400-68770

Physics of Li-Ion Battery Systems in Different Length Scales

Electrode Scale

Charge balance and transport
Electrical network in composite electrodes
Li transport in electrolyte phase

Cell Scale

Electronic potential & current distribution
Heat generation and transfer
Electrolyte wetting
Pressure distribution

Particle Scale

Li diffusion in solid phase
Interface physics
Particle deformation & fatigue
Structural stability

Module Scale

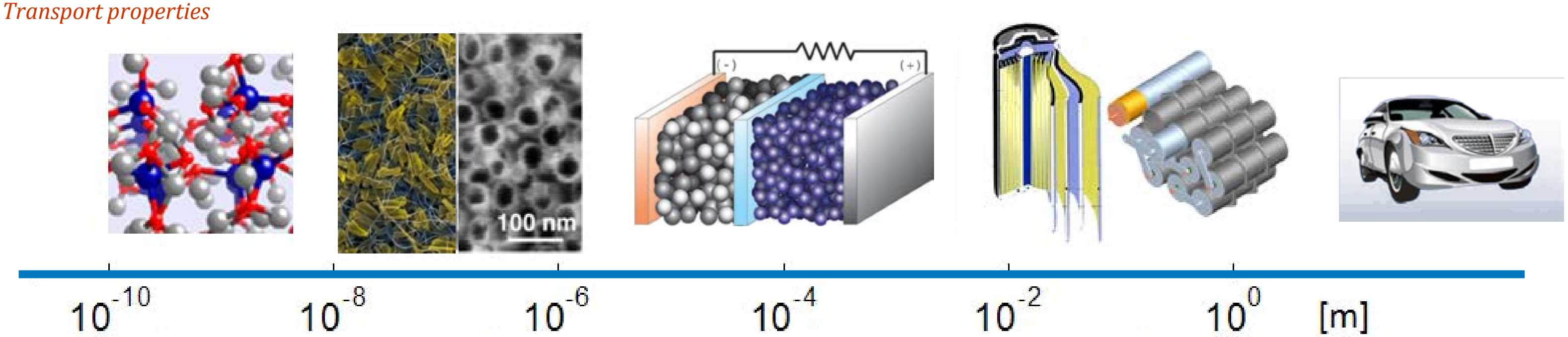
Thermal/electrical inter-cell configuration
Thermal management
Safety control

Atomic Scale

Thermodynamic properties
Lattice stability
Material-level kinetic barrier
Transport properties

System Scale

System operating conditions
Environmental conditions
Control strategy



Computational models offer pathway to advance next generation designs

DOE Computer-Aided Engineering of Batteries (CAEBAT) Program

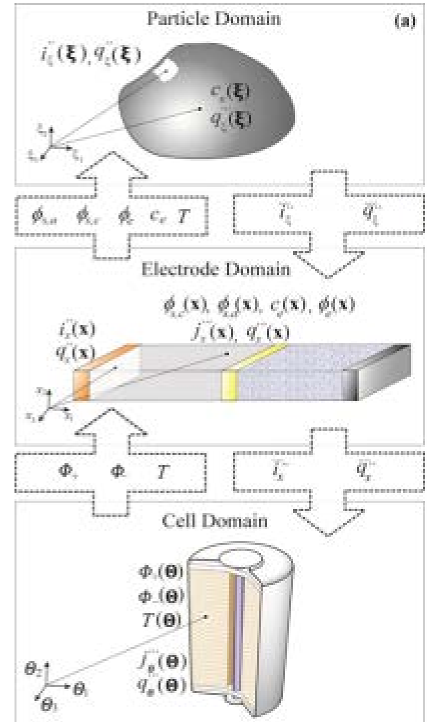
- **Goal**: Accelerate development of batteries for electric-drive vehicles
- **Successes**:
  - **Multiscale multidomain** model approach linking disparate length-scales (NREL)
  - Open architecture (ORNL)
  - Commercial software toolsets with 150+ users
- **Current priorities** based on feedback:
  - o Extend the models to include mechanical failure of cells and packaging components
  - o Increase computational efficiency
  - o Standardize identification of the model parameters
  - o Close gaps between materials R&D and CAEBAT modeling tools

MSMD

Multi-particle system

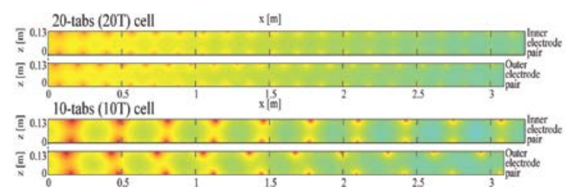
Electrochemical reaction / transport

+ 3D electron & heat transport

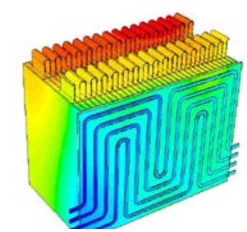


Examples

Preferential utilization in wound cell

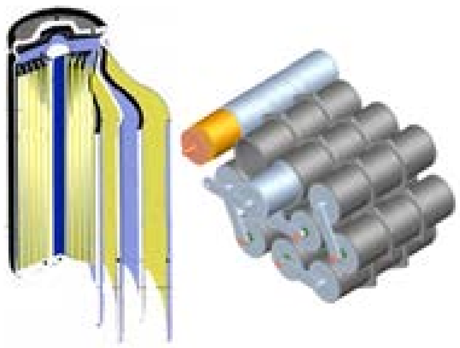


Thermal management design with commercial CAE tools

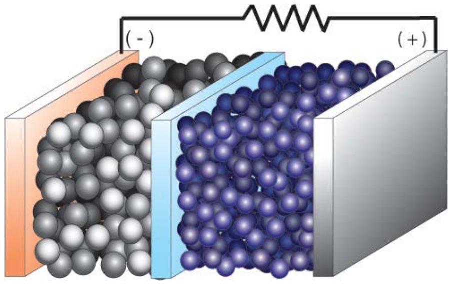


Outline

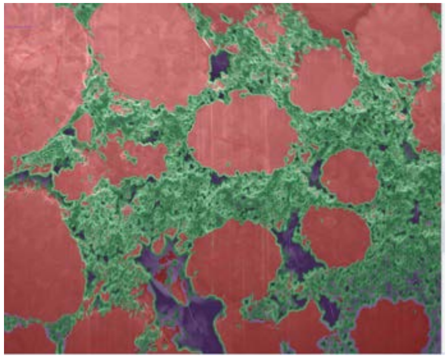
- Abuse
  - Internal short
  - Mechanical crush



- Electrode performance
  - Fast electrochemical simulation
  - Parameter identification

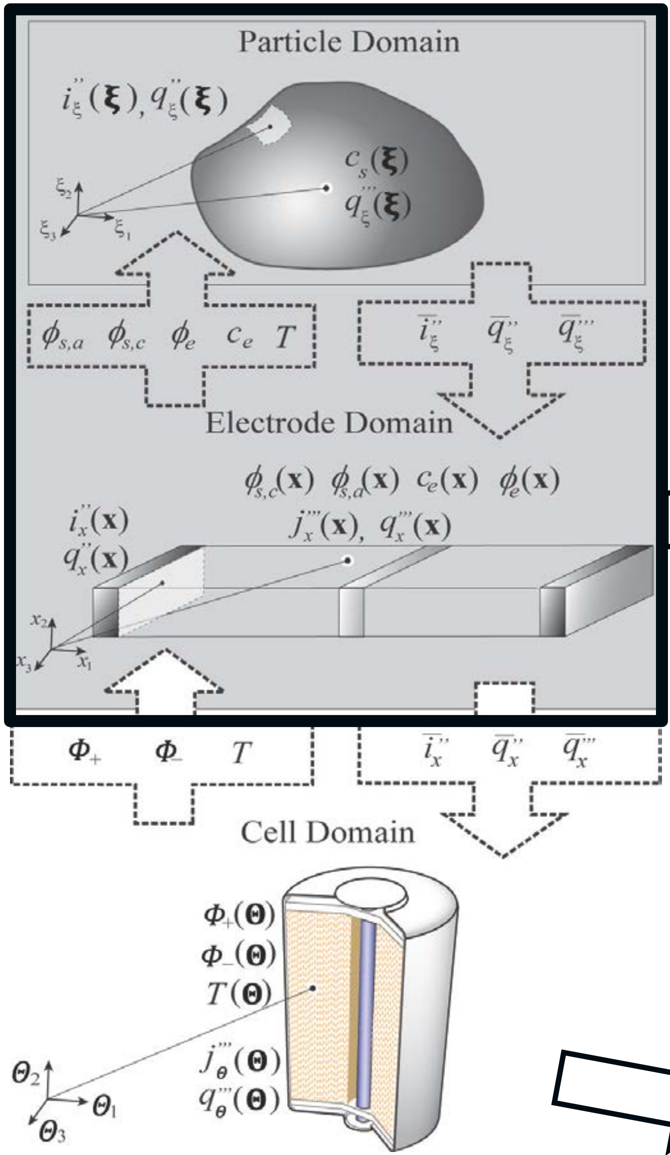


- Microstructure role
  - Electrode tortuosity & inhomogeneity
  - Carbon + binder phase



SEM image: Koffi Pierre Claver (ANL)

Safety Modeling Approach



NREL Electrode Domain Model Library

- Electrochemical State Variable Model (SVM)
- Abuse Reaction Kinetics Model (ARK)
- Internal Short Circuit Model (ISC)

NREL ARK Model*

$$
\begin{cases}
S = HW\dfrac{d\alpha}{dt} \\
\dfrac{d\alpha}{dt} = k(T)f(\alpha) \\
k(T) = Ae^{-\frac{Ea}{RT}} \\
f(\alpha) = \alpha^m(1-\alpha^n)(-\ln(1-\alpha))^p
\end{cases}
$$

S : volumetric reaction heat;
H : heat of reaction;
$d\alpha/dt$: reaction rate;
k(T) : temperature-dependent rate constant

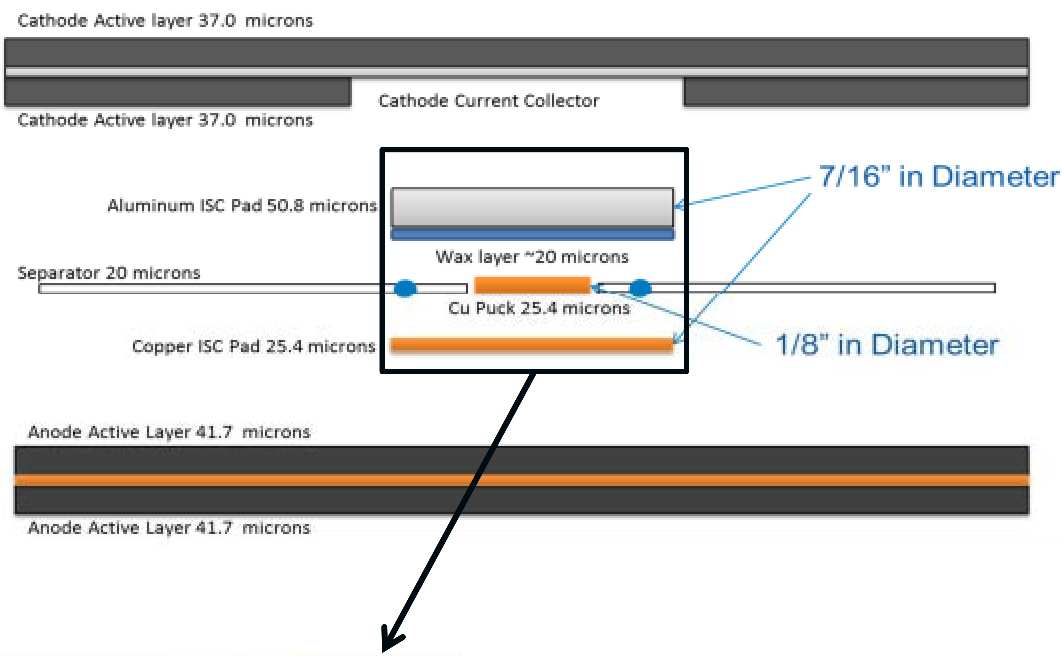
NREL ISC Model

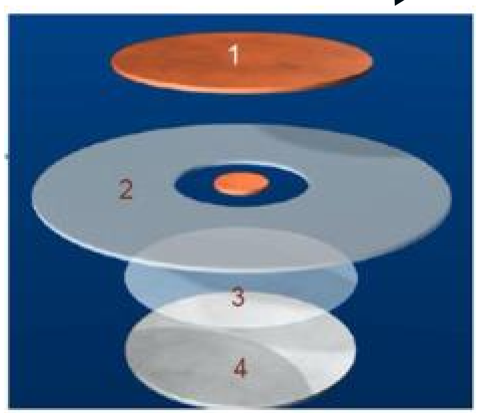
- 3D initial short circuit
- Cathode-anode short growth

Cell Domain Model: Single pair potential continuum (SPPC) electrothermal model in ANSYS® Fluent® MSMD-module

* Kim, G. , Pesaran, A. , and Spotnitz, R. , J. Power Sources, 170(2), pp. 476–489, 2007

Testing Using NREL's Internal Short Circuit (ISC) Device

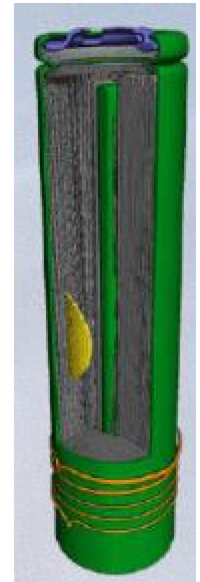




<u>Top to Bottom</u>

1. Copper Disc
2. Battery Separator
3. Phase Change Material (wax)
4. Aluminum Disc

Wax formulation used melts around 57°C



ISC device in 3rd wind of jellyroll

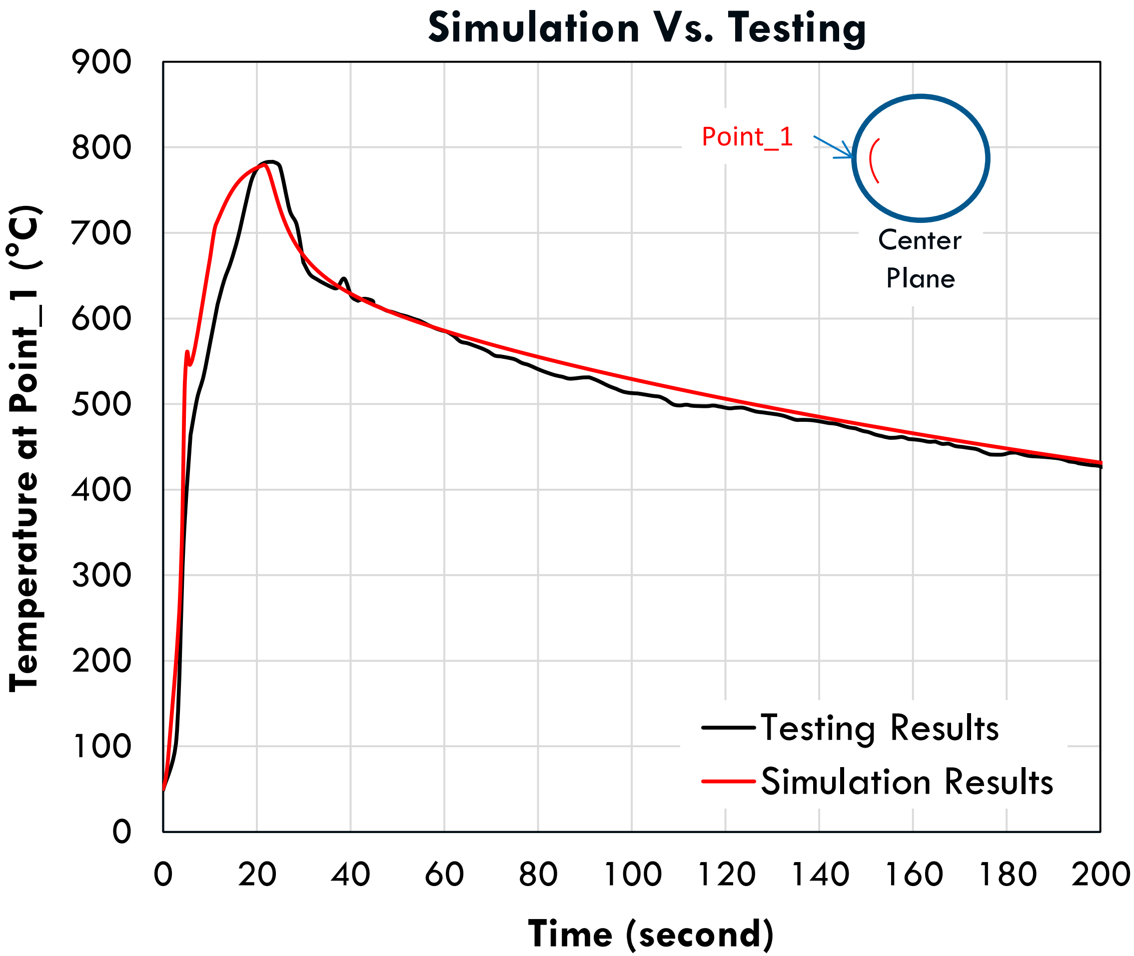
Tomography credits: University College of London

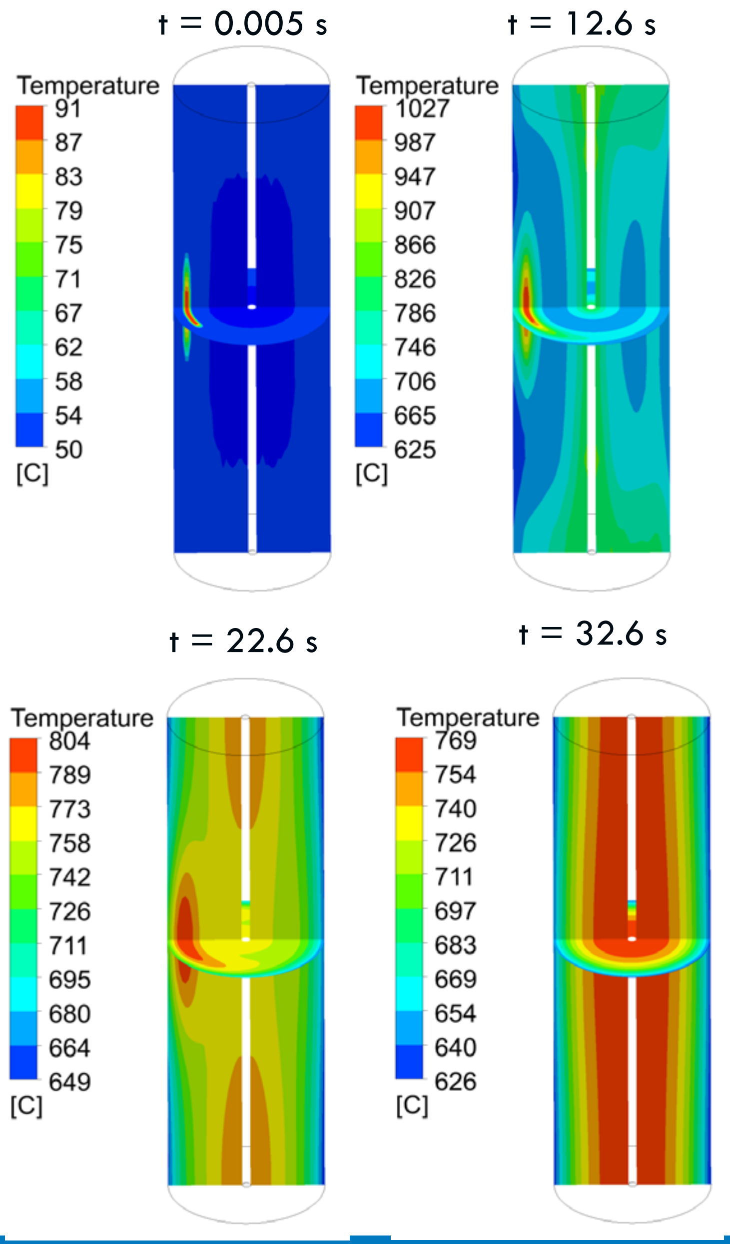
2010 Inventors:
NREL: Matthew Keyser, Dirk Long, and Ahmad Pesaran
NASA: Eric Darcy

US Patent # 9,142,829 awarded in 2015

2016 R&D100 Award Winner

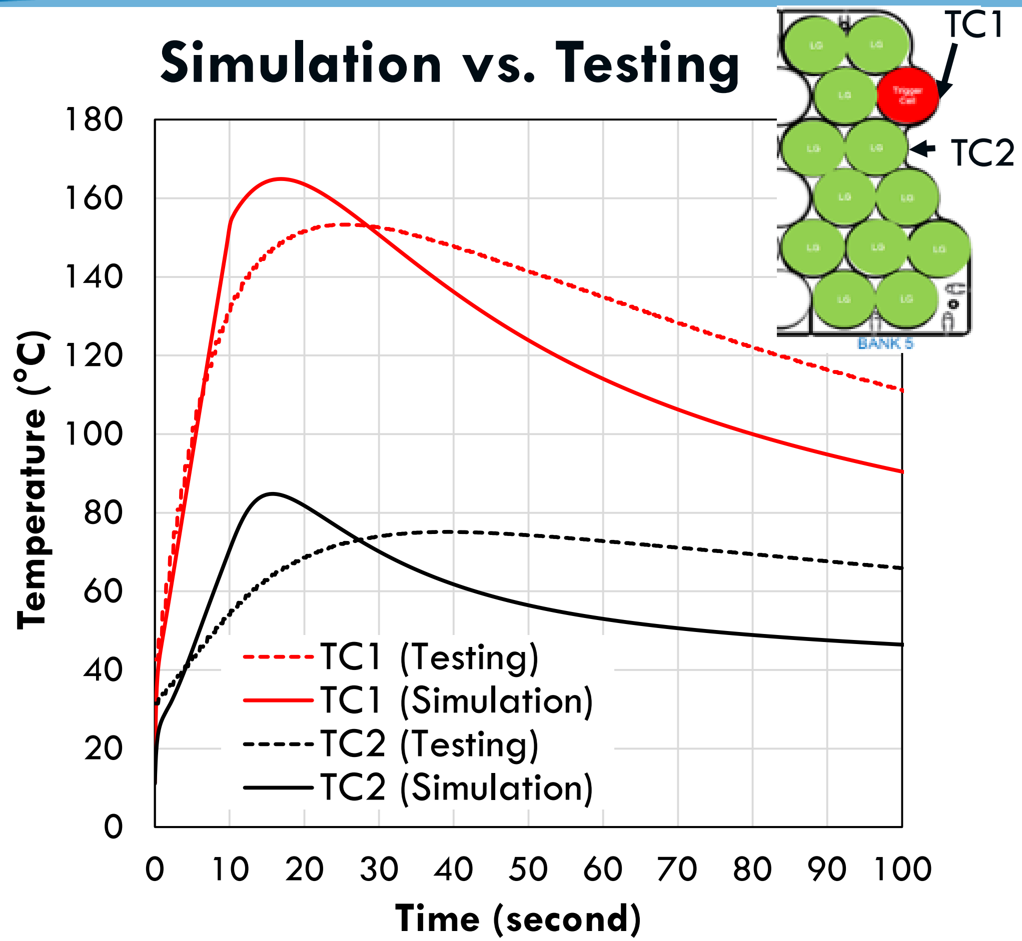
Validation of the 3D Simulation – 18650 Cell

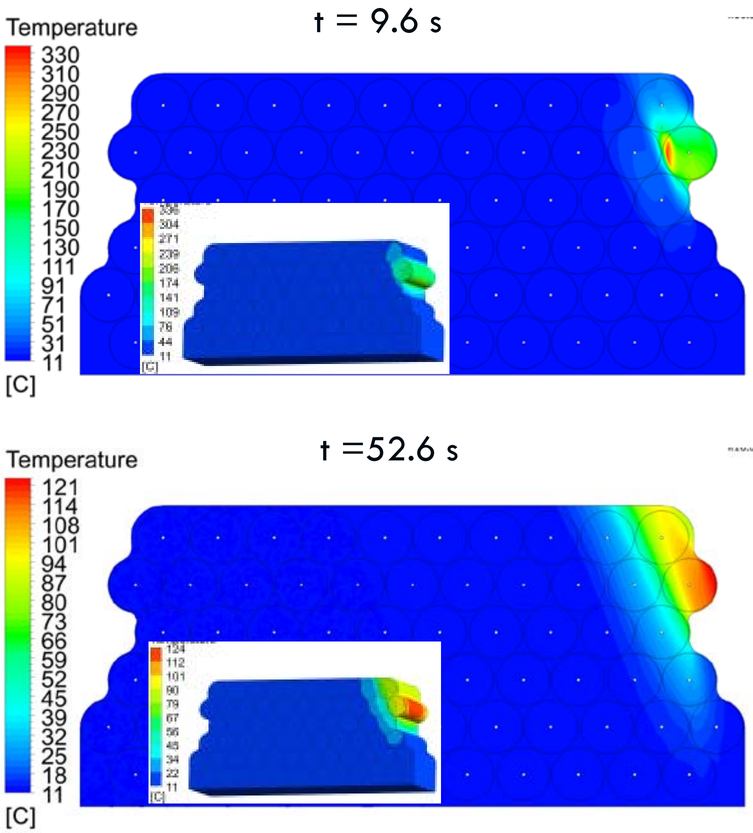




- Simulation result shows a good agreement with testing data
- ISC device is able to trigger thermal runaway of cell successfully
- Due to different thermal conductivity of cell, heat transfer rate along azimuthal and axial directions is faster than in the radial direction

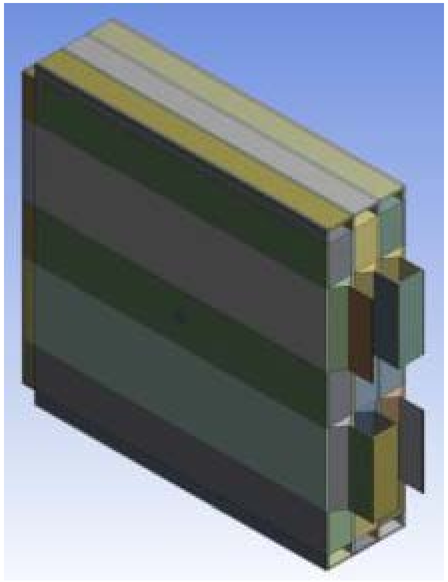
Validation of 3D Simulation – Module

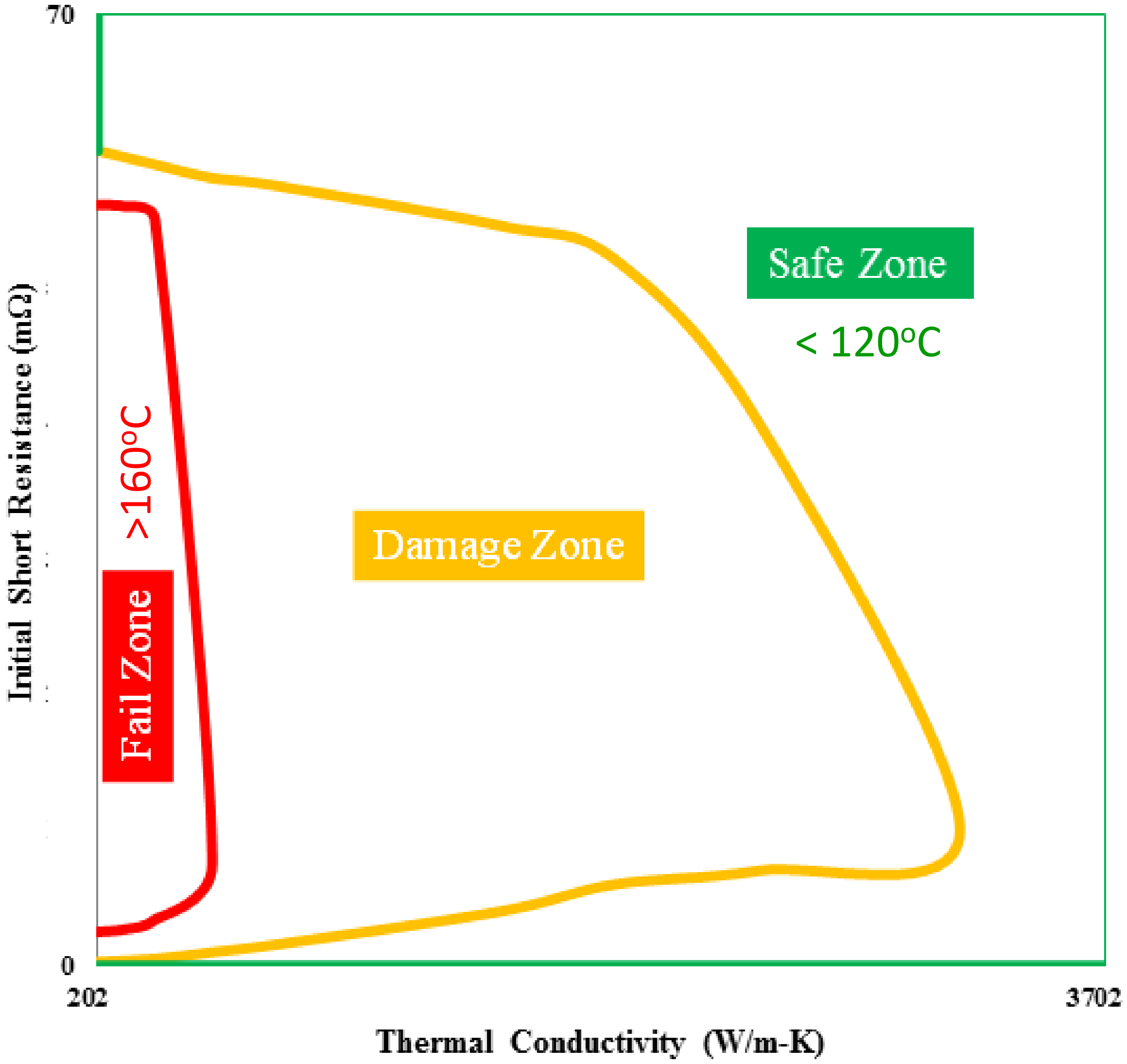




- Simulation results show the same trend as testing data, and the maximum temperature of simulation results at TC1 and TC2 is similar to the testing data
- There are two reasons that might affect the accuracy of simulation: complicated thermal conditions during testing and the location of thermocouples
- Thermal runaway models are generally accurate at predicting cell runaway (or not) and propagation

Heat Dissipation to Control Thermal Runaway





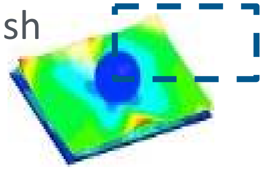
- 3S1P module
- 24-Ah LCO/graphite
- Shut-down separator
- Fin cooling
- Initial ISC in the middle cell

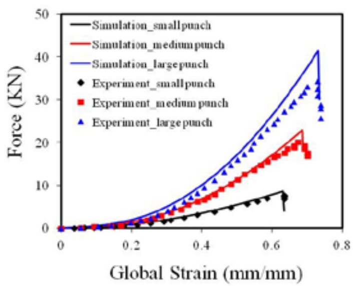
LCO = Lithium cobalt oxide

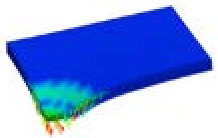
Mechanical Abuse Modeling Approach

<u>Objective:</u> Predict battery behavior during a crash event to optimize safety and weight reduction

Displacement under Crush





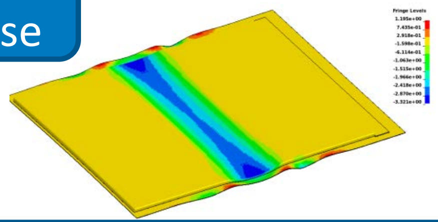


Current density under short-circuit

Step 1: Start with Component and Cell-Level Test Results as Input

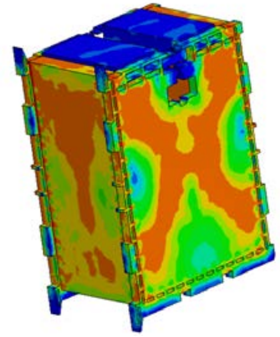
Step 2: Explicit Simulations Parameterize Material Response

Predicts cell temperatures to $\pm 10^{o}C$



Step 3: Simulate Cell-Level Response for Multiple Cases

Step 4: Scale to Module-Level



Step 5: Validate against Experimental Data

Goal: Identify localized failure modes and onset loads to within 30 MPa

Photo: Josh Lamb (SNL)

Sample Input:

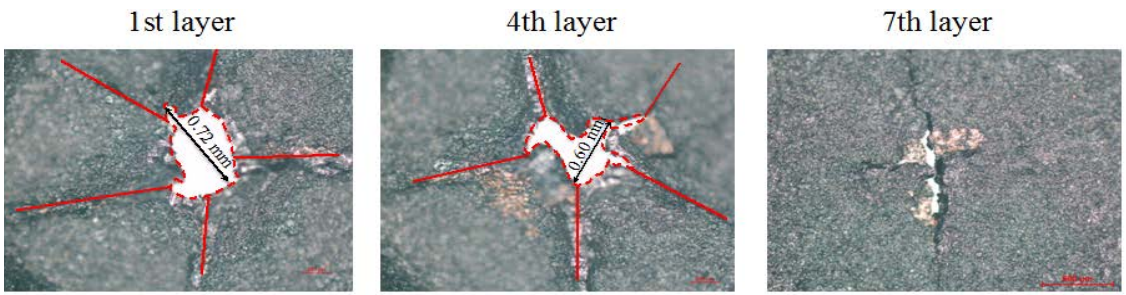
- Stress-strain curves for cell components (separator, current collector, etc.)
- Failure strengths for particles
- Mechanical data for cell packaging
- Temperature vs. C-rate for cell
- Abuse reaction data from calorimetry for specific chemistries

Sample Output:

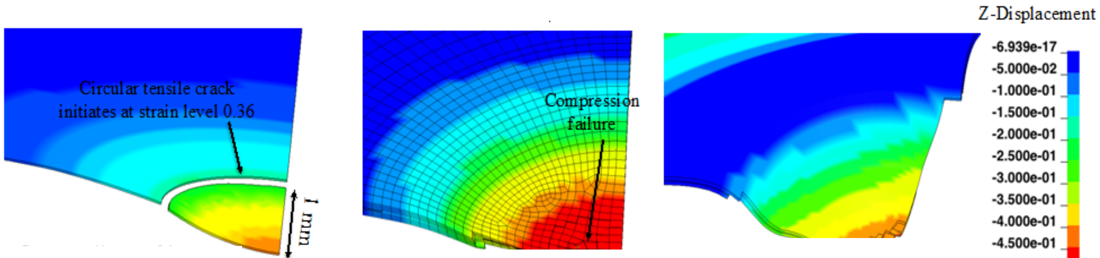
- Current distribution among the different cells within the module
- Localized heat generation rates far away from damage zone
- Stress distribution across multiple parts of the battery module

Mechanism of Failure Initiation following a Crush

Side-facing indenter



Sahraei et al. *Journal of Power Sources,* 2014.

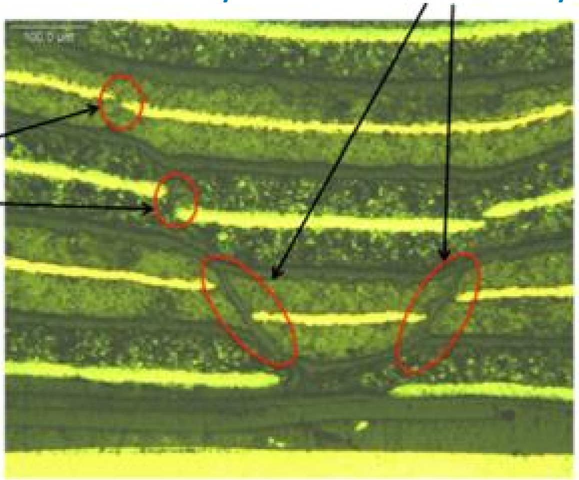


Copper foil Layer 1 | Anode Layer 4 | Cathode Layer 6

Failure of Copper Foil | **Cathode-Anode Short**

Shear failure of active material layers within a battery

Copper foil fails before separator ruptures



Wang, Shin et al., *Journal of Power Sources* 306, 2016, 424-430.

Outcome:

- Comprehensive understanding of failure thresholds and propagation mechanism for each component within the cell
- Better explanation of test data results in recommendations for test-method development
- Light-weighting/right-sizing of cells without compromising safety

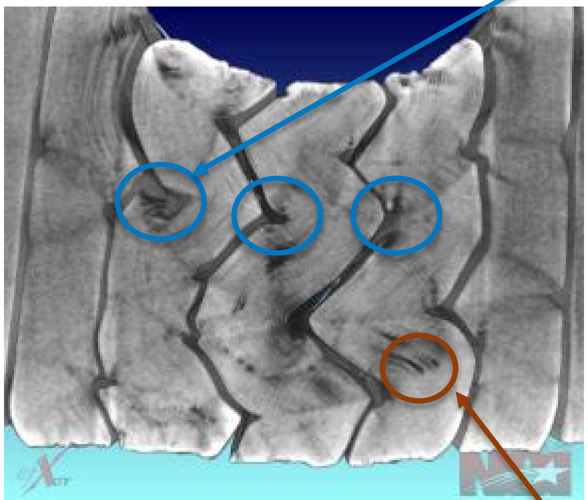
Multi-cell Crush Test and Simulation

Testing

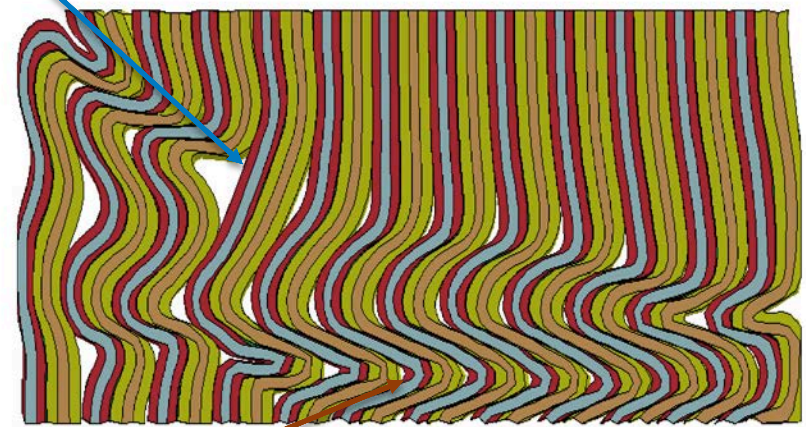
Bar crush of a 12-cell string

Josh Lamb, SNL

Compression from buckling



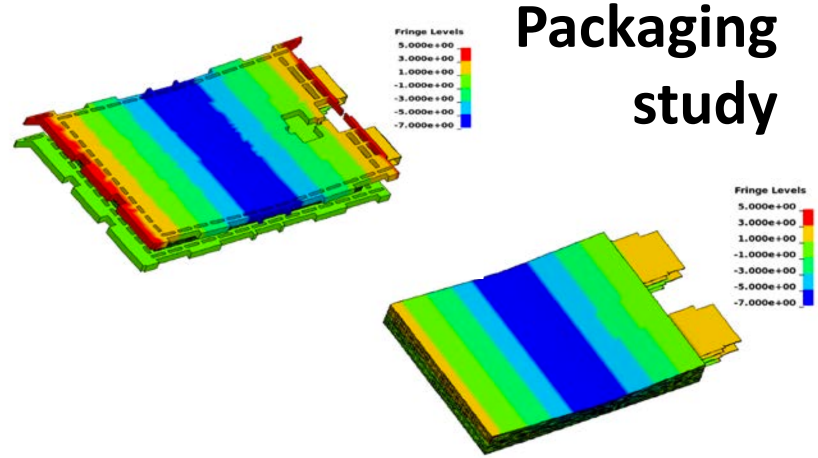
Initial validation



Separation of electrode layers

- Models capture qualitative features; numerical comparison of failure strains underway.
- The packaging can prevent deformation of the cells by as much as 50% under these crush test conditions.
- There is a significant scope to lightweight the pack, even after the safety threshold is met.

Packaging study



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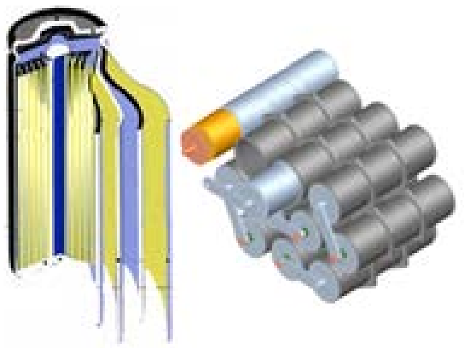
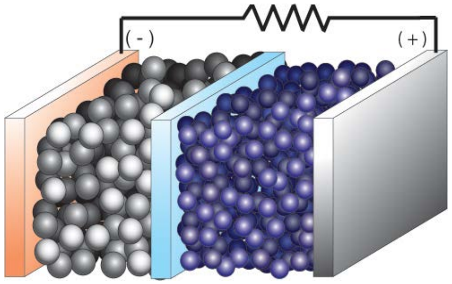
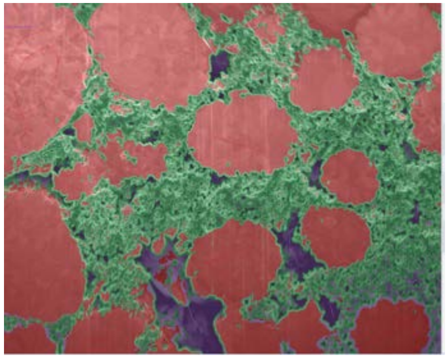
- Abuse
  - Internal short
  - Mechanical crush
- Electrode performance
  - Fast electrochemical simulation
  - Parameter identification (bottleneck)
- Microstructure role
  - Electrode tortuosity & inhomogeneity
  - Carbon + binder phase







SEM image: Koffi Pierre Claver (ANL)

Approach for Fast Electrochemical Simulation

Efficient and Extensible Quasi-Explicit Modular Nonlinear Multiscale Battery Model: GH-MSMD

Gi-Heon Kim, Kandler Smith,*,z Jake Lawrence-Simon, and Chuanbo Yang*

National Renewable Energy Laboratory, Golden, Colorado 80401, USA

Complex physics and long computation time hinder the adoption of computer aided engineering models in the design of large-format battery cells and systems. A modular, efficient battery simulation model—the multiscale multidomain (MSMD) model—was previously introduced to aid the scale-up of Li-ion material & electrode designs to complete cell and pack designs, capturing electrochemical interplay with 3-D electronic current pathways and thermal response. This paper enhances the computational efficiency of the MSMD model using a separation of time-scales principle to decompose model field variables. The decomposition

1) Nonlinear Multiscale Implicit Formulation

$$\phi = f(i; \boldsymbol{x}, \boldsymbol{p})$$

2) Timescale Separation & Variable Decomposition

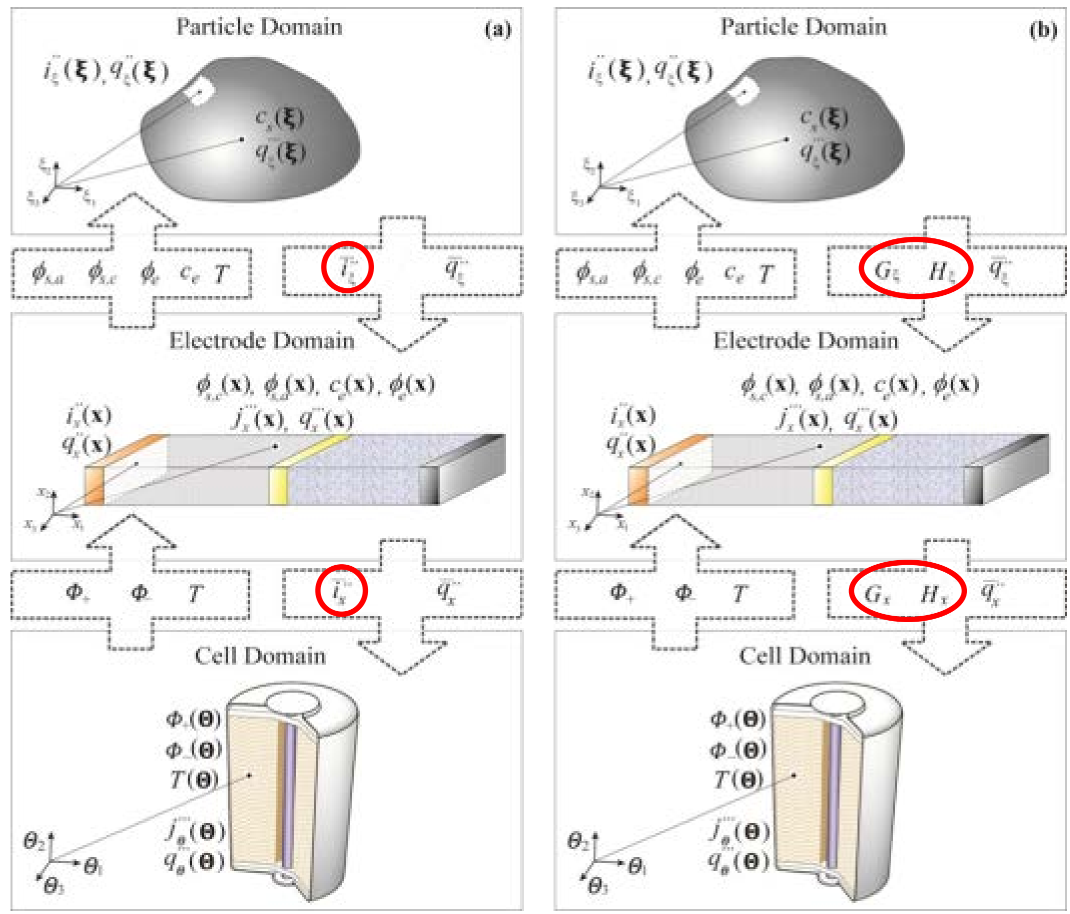
$$\phi = g(i; \boldsymbol{x}, \boldsymbol{p}) + h(i; \boldsymbol{x}, \boldsymbol{p})$$

3) Partial/Selective Linearization

$$G(i; \boldsymbol{x}, \boldsymbol{p}) = \frac{dg}{di}$$

$$\phi = G(i; \boldsymbol{x}, \boldsymbol{p})i + H(i; \boldsymbol{x}, \boldsymbol{p})$$

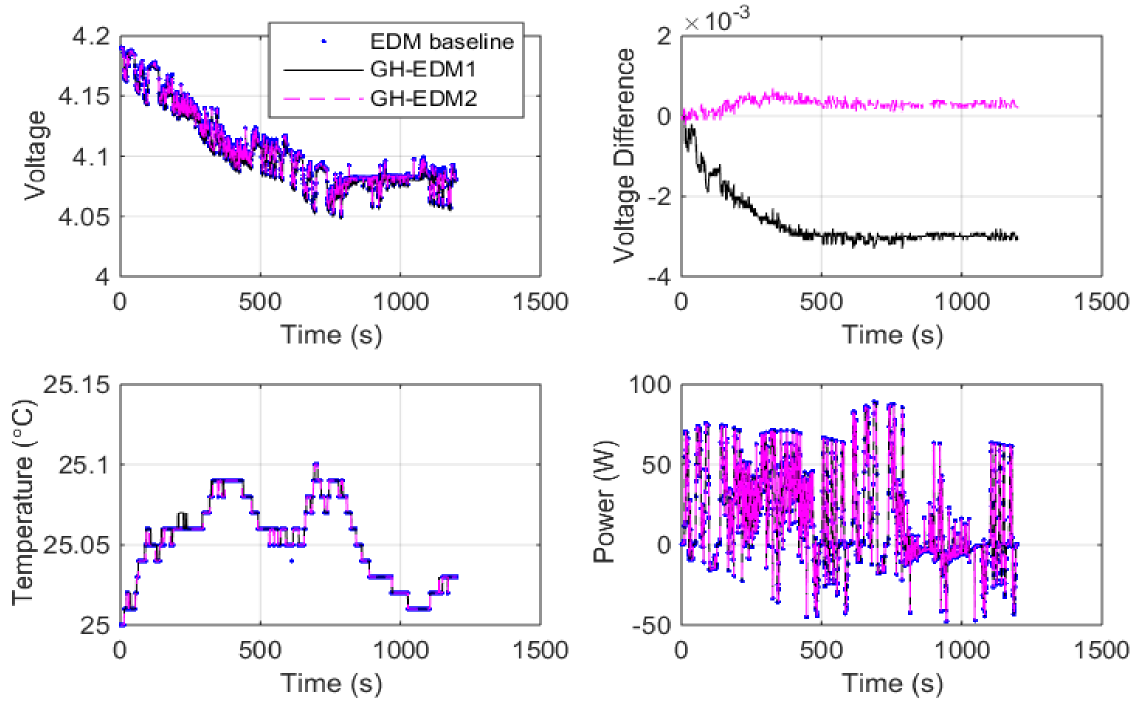
MSMD (Previous) **GH-MSMD (New)**



G.-H. Kim et al., *J. Electrochem. Soc.*, A1076-88, 2017

Example Speed-up of Electrode-domain Simulation

The selective G-H linearization approach drastically reduces computational burden



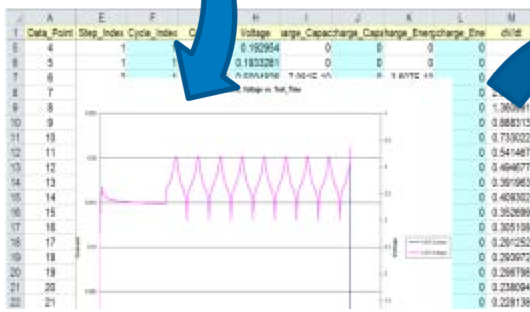
Simulation case		Computation time for Electrode Domain Models (EDM) in seconds		
Load Profile	Temperature (°C)	EDM baseline	GH-EDM1	GH-EDM2
1C	25	360.13	3.03	0.44
1C	0	816.21	3.50	0.47
Drive cycle	25	1205.92	7.06	0.83
Drive cycle	0	8786.45	45.00	1.27

Model Parameter Identification Workflow

Photo: Shriram Santhanagopalan

Experimental set up to cycle cells for collecting data

Pre-processing and filtering of raw data



Format data from native formats for battery cyclers

Setup baseline MSMD Inputs

$$\frac{\partial}{\partial x}\left(\ldots\right) + \frac{\partial}{\partial x}\left(\kappa_D^{eff}\frac{\partial}{\partial x}\ln c_e\right) + j_e^{Li} = 0$$

$$\kappa^{eff} = \kappa\varepsilon_e^{p}$$

$$\kappa_D^{eff} = \frac{2RT\kappa^{eff}}{F}(t_+^0 - 1)\left(1+\frac{d\ln f_\pm}{d\ln c_e}\right)$$

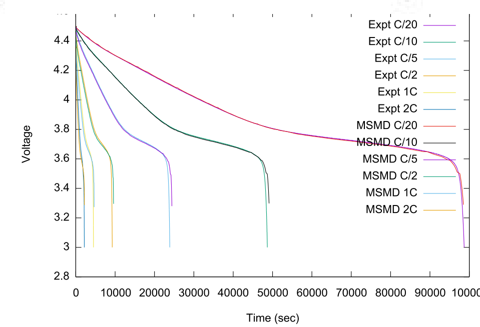
$$\frac{\partial(\varepsilon_e c_e)}{\partial t} = \frac{\partial}{\partial x}\left(D_e^{eff}\frac{dc_e}{dx}\right) + \frac{1-t_+^0}{F}j_e^{Li} - \frac{i_e\,\partial t_+^0}{F\,\partial x}$$

MSMD-Model

Fitting of model to data

C_{Li}^{max} = 4.905037e+04 ± 7.067772e+01 mol/m^3

D_s^{ref} = 4.392799e-15 ± 2.562774e-17 m^2/s



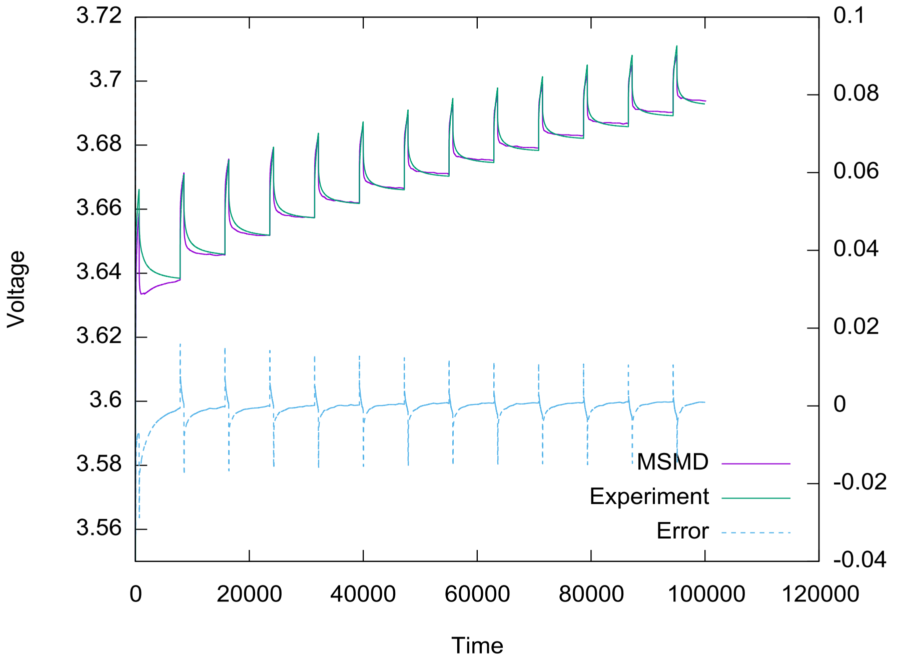
Calibrated Model and Parameters

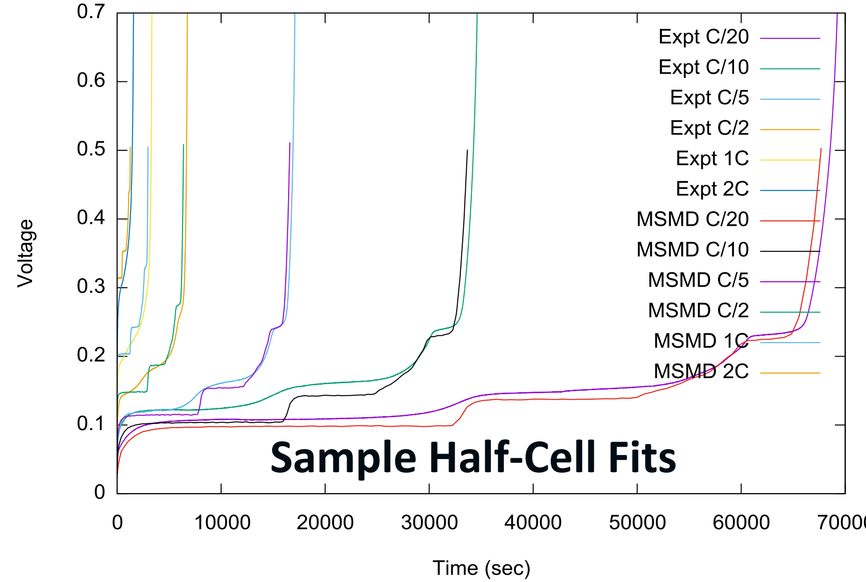
GUI: graphic user interface
OAS: open architecture software

- Python script parses data to meet model needs
- Parameter estimation based on Levenberg-Marquardt algorithm
- Workflow independent of model(s)/data set(s)
- Can use the same approach for multiple models and/or datasets – as long as the list of inputs and outputs are standardized (e.g., using the OAS)
- Process can be easily wrapped with a GUI as workflow stabilizes.

Parameter Identification Results

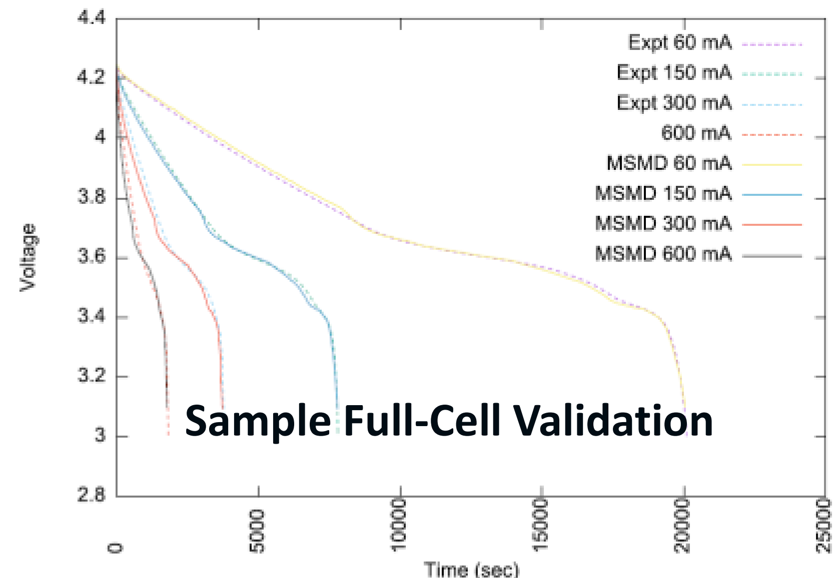
GITT: Model vs. Data





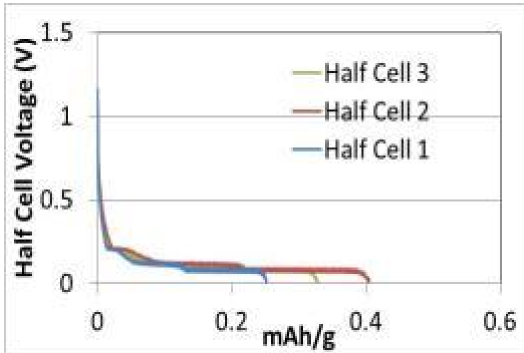
Examples of Parameters and Confidence Intervals

Parameter	Anode	Cathode
C_{Li}^{max} (mol/m^3)	2.9511e+04 ± 2.5377e+02	4.9050e+04 ± 7.0677e+01
D_s^{ref} (m^2/s)	3.015e-15 ± 2.469e-15	4.393e-15 ± 2.5634e-17



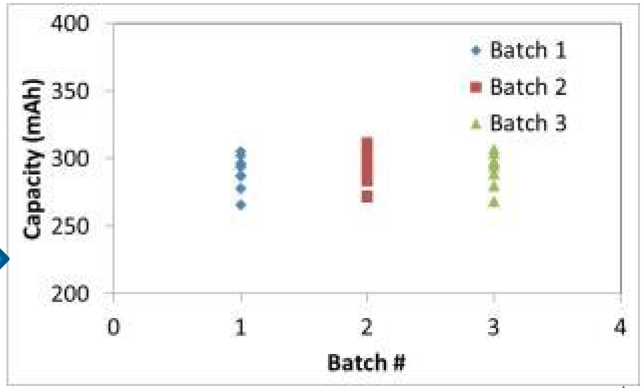
Automated procedure calibrates models with data from cyclers to a max. relative error < 5%

Underway: Analysis of Material/Data Quality



Determine what level of fidelity in calibration data is necessary by comparing against QC data/spec.

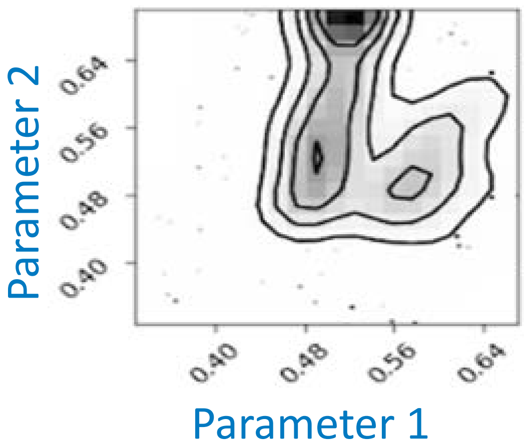
Distribution of cell-level metrics



Coin-cell dataset 1..N

Particle Domain fit for cells 1..N

Range of fitted Particle Domain parameters



Predict actual cell performance

Cell Domain fit + Confidence Intervals

Cell Domain fit with bounds on Particle Domain parameters

Closing the loop between lab-scale calibration data and production cell specs. will reduce development costs by directing improvements to processes that impact on cell quality the most.

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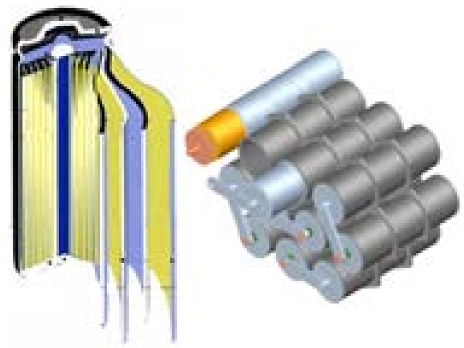
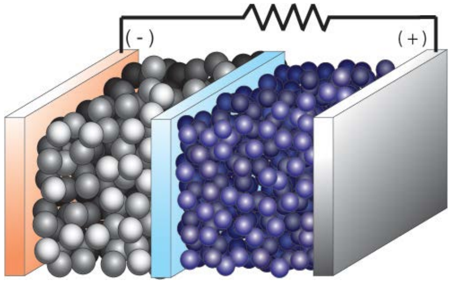
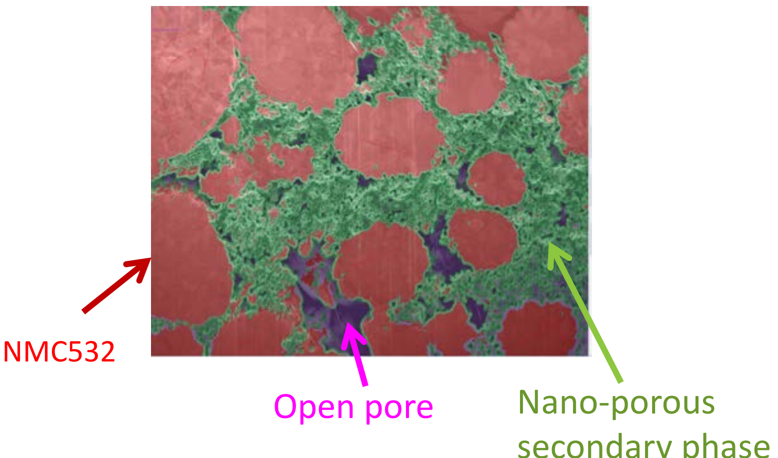


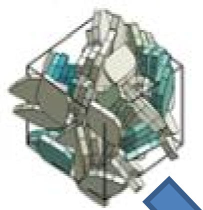




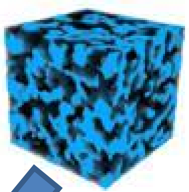
SEM image: Koffi Pierre Claver (ANL)

Enhancing Electrodes through Microstructure Modeling

Stochastic reconstruction & meso-scale physics



Validation of virtual 3D geometry



Cell Analysis, Modeling & Prototyping (CAMP) Facility

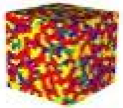
Electrode fabrication, tomographic measurement, electrochemical response

Design inputs

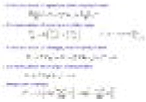
- Chemistry
- Morphology
- Size distribution
- Binder
- Conductive additive
- Calendaring

Microstructure Model

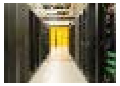
- Geometry



- Physics



- High Performance Computing (HPC)



Electrochemical performance validated for multiple electrode designs

Homogenization

Linkage to CAEBAT macroscopic simulation toolsets

Image credits:
Microstructure – Partha Mukherjee, TAMU
HPC – NREL image gallery
Coated electrode – hirano-tec.co.jp

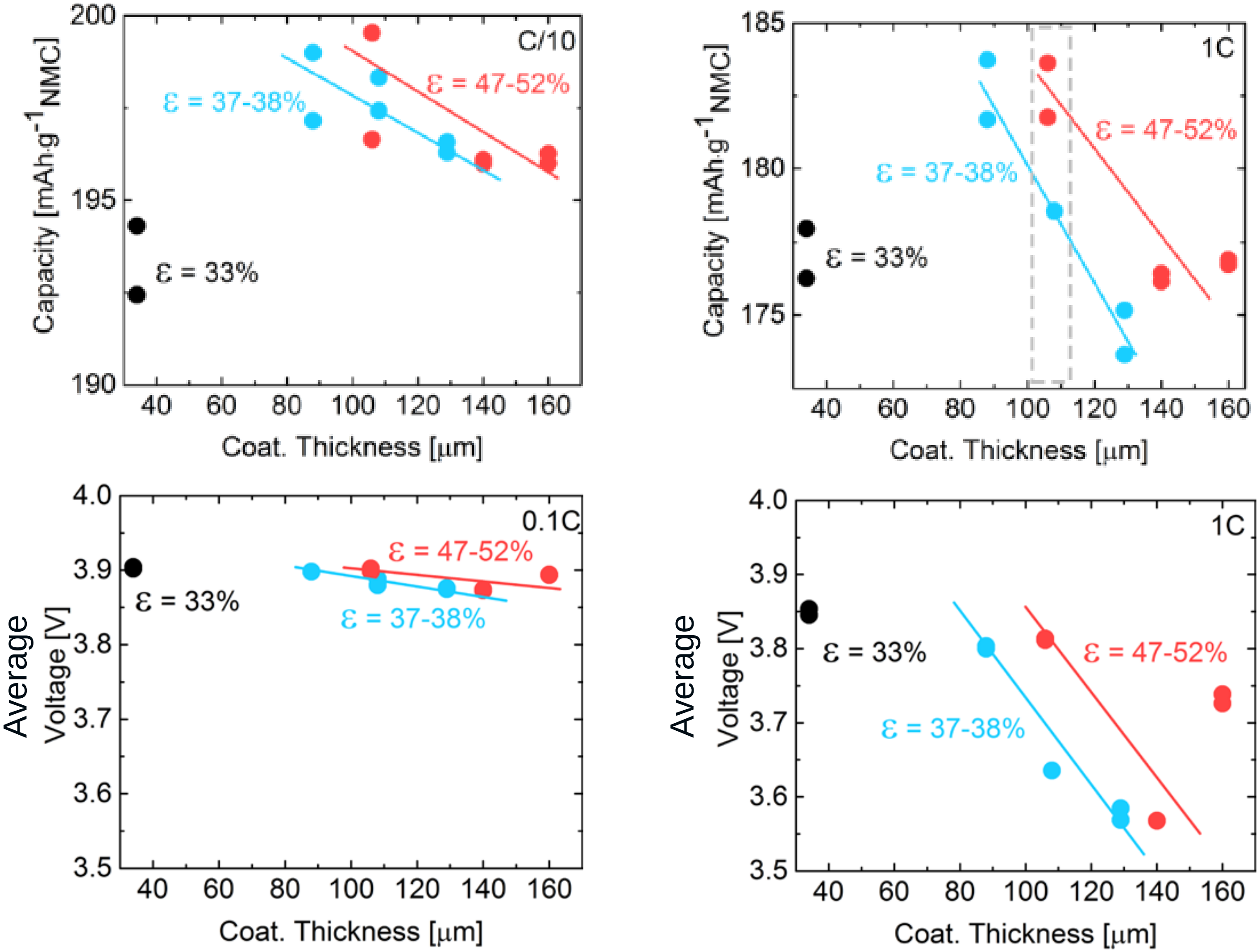
Electrochemical Characterization of Electrode Library

Argonne NATIONAL LABORATORY

- Comparison of seven NMC electrode designs vs. C-rate

Low rate discharge

High rate discharge

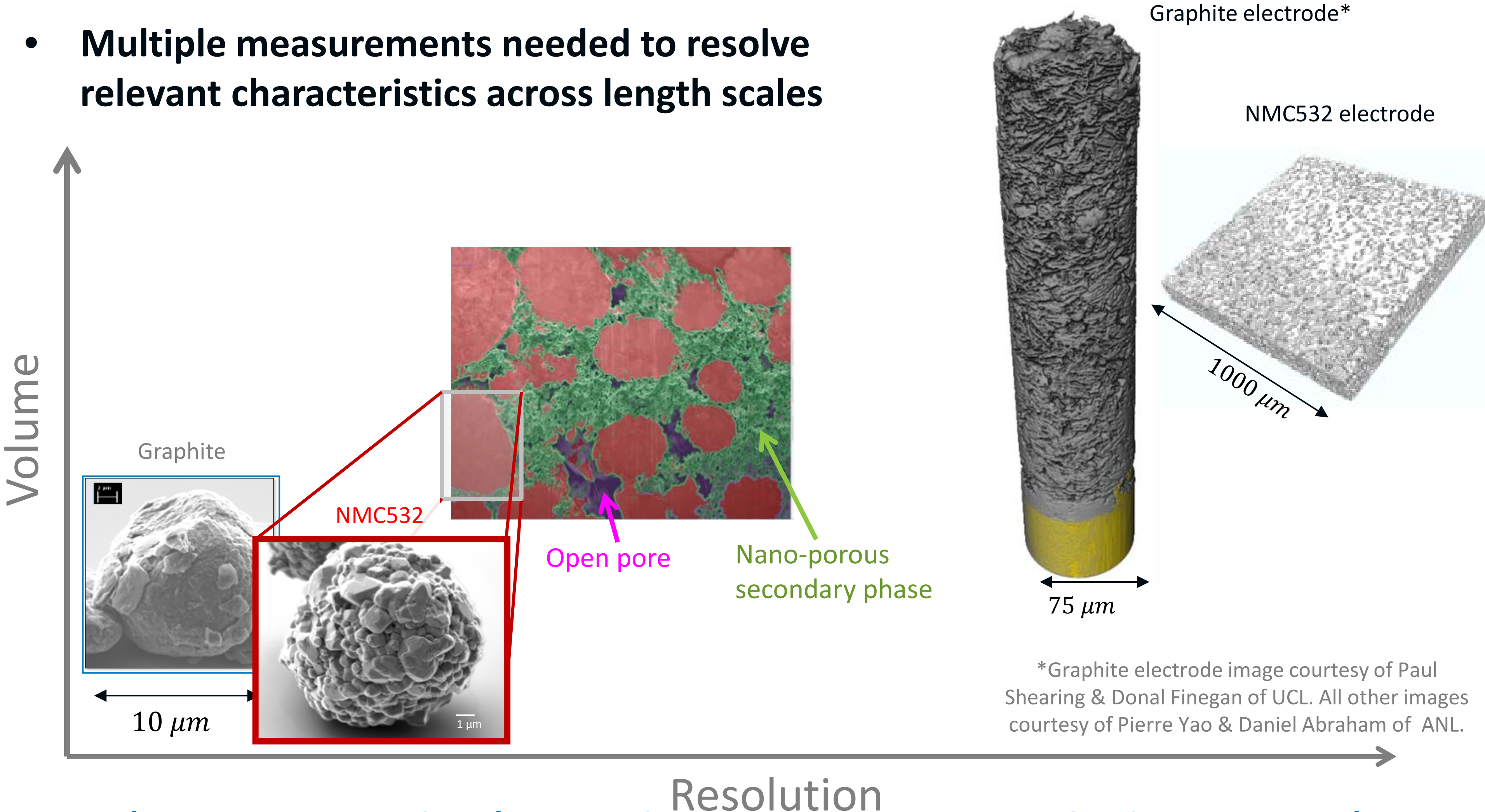


Capacity depends mainly on porosity due to electrolyte transport limitations

Average voltage drops due to ohmic and polarization losses

NMC: nickel manganese cobalt

- **Multiple measurements needed to resolve relevant characteristics across length scales**



*Graphite electrode image courtesy of Paul Shearing & Donal Finegan of UCL. All other images courtesy of Pierre Yao & Daniel Abraham of ANL.

Focused Ion Beam – Scanning Electron Microscopy

- Particle surface & morphology
- Secondary phase (conductive additive + binder)

Nano- & Micro-Tomography

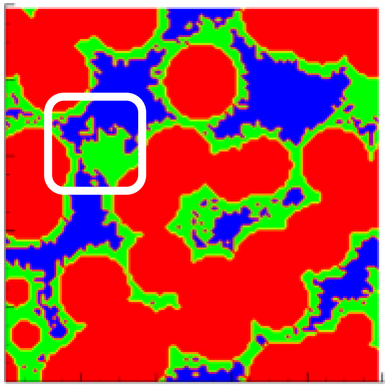
- Ionic & electronic tortuous paths

(lacks secondary phase, however)

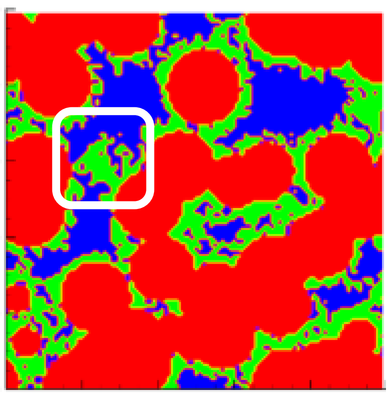
Meso-scale Modeling of Conductive/Binder Phase

- Numerical algorithm stochastically generates conductive/binder phase taking on different morphologies

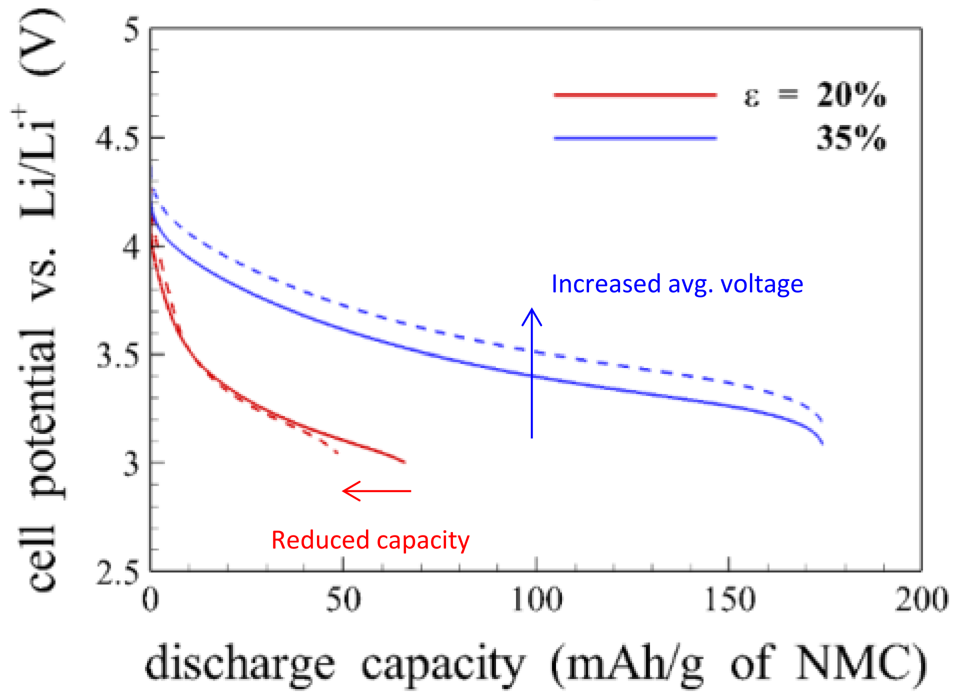
A) Film-like deposits (solid lines)



B) Finger-like deposits (dashed lines)



5C discharge

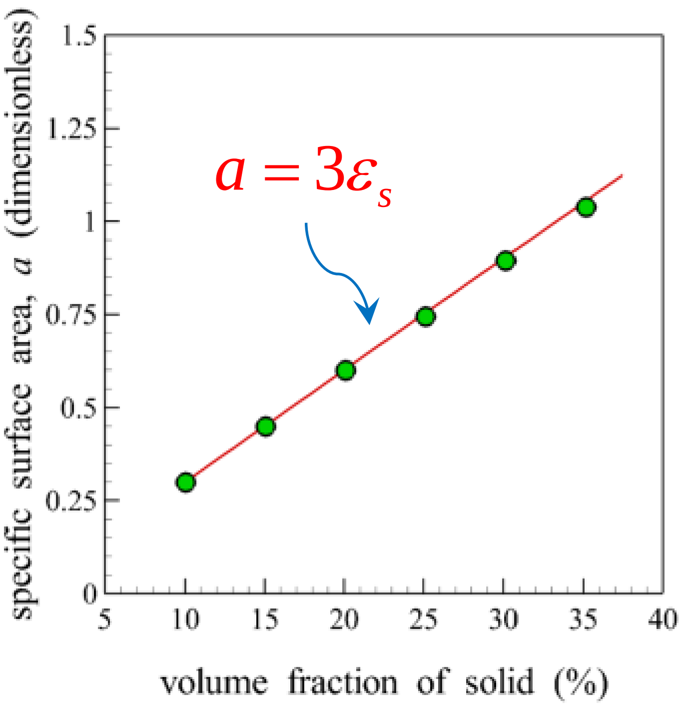


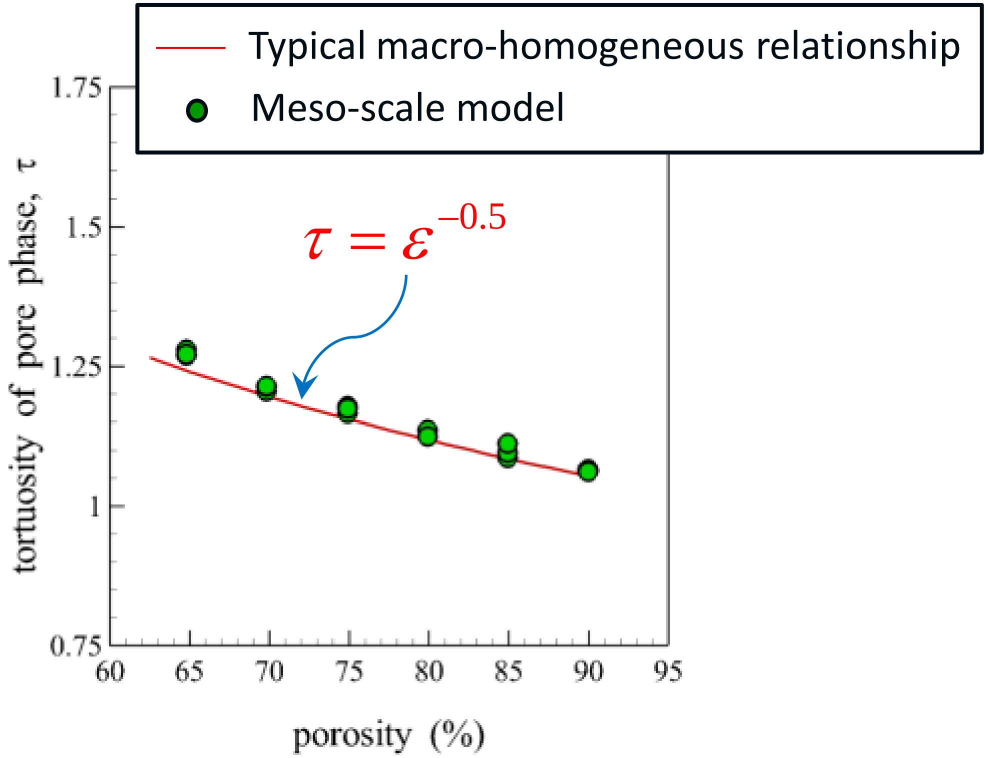
Finger-like deposits improve electronic conductivity but introduce additional tortuosity for electrolyte-phase transport

Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Meso-scale Modeling of Effective Electrode Properties (1/2)

- Microstructure property relations used in today's macro-homogeneous models hold well in the limit of low solid volume fraction / high porosity…





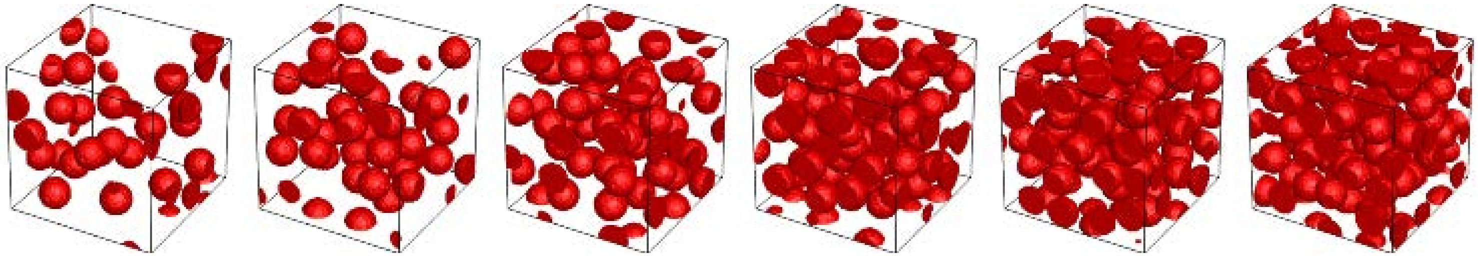
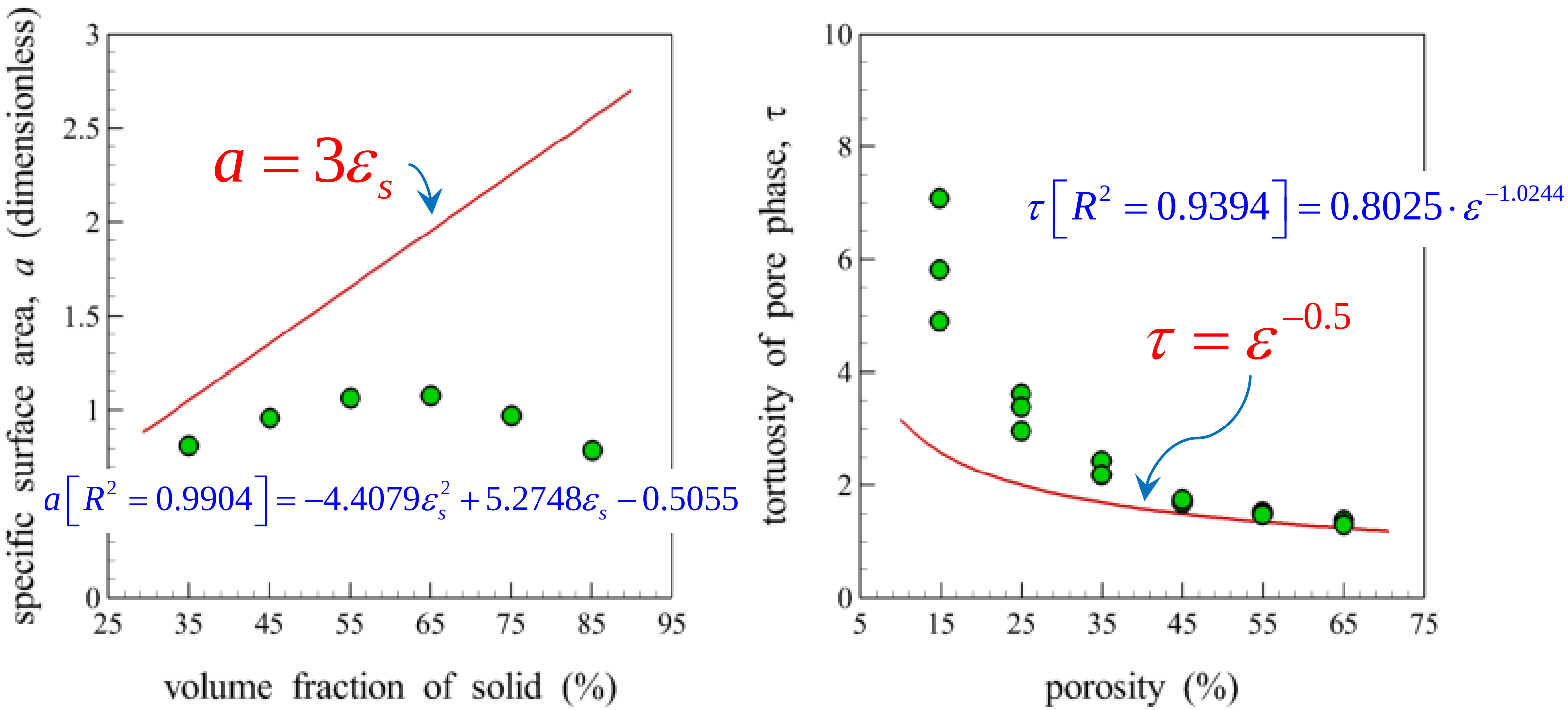


Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Meso-scale Modeling of Effective Electrode Properties (2/2)

- … but lose validity for dense electrodes
- Meso-scale models were used to develop more accurate property relations for dense electrodes across entire electrode design space. To be validated and extended to non-spherical geometries



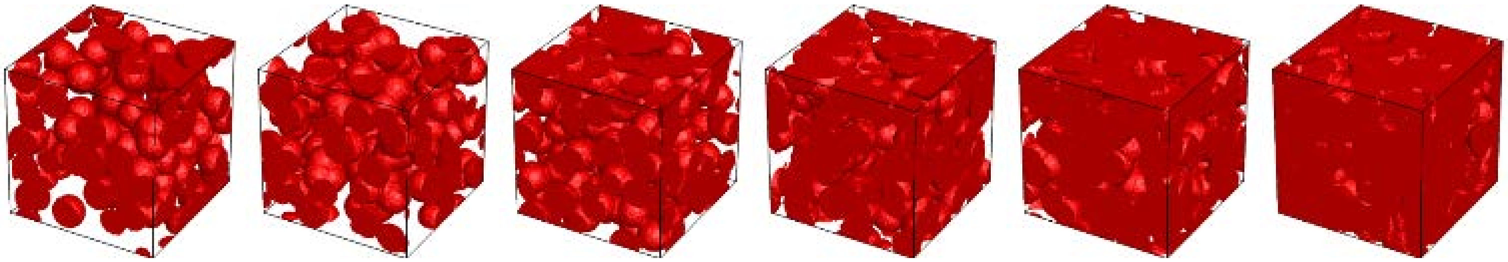
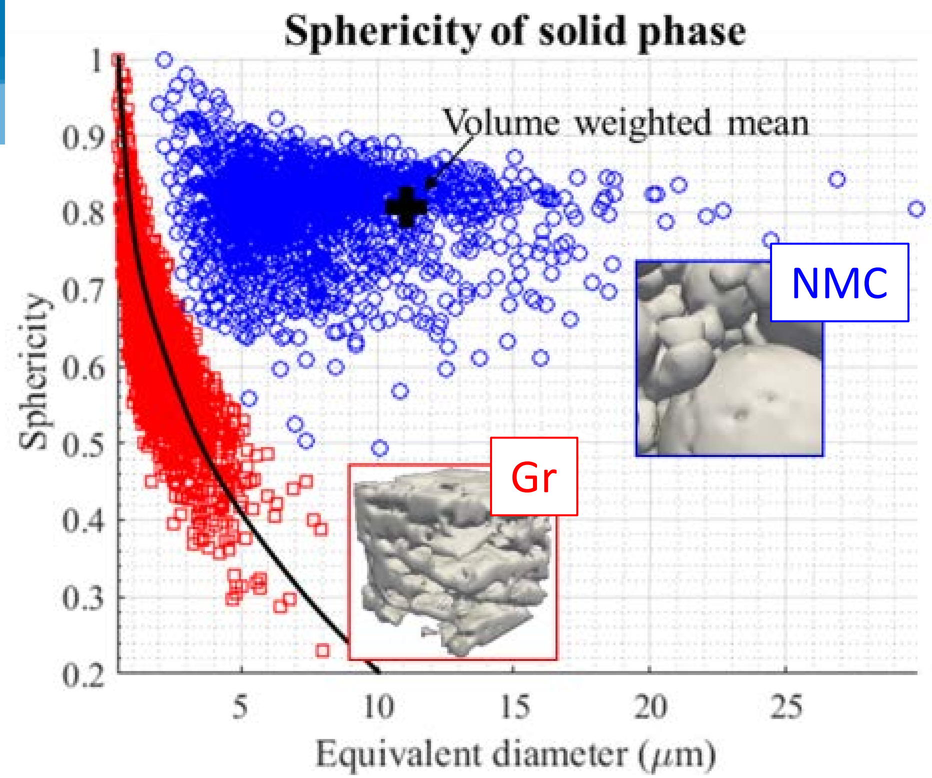
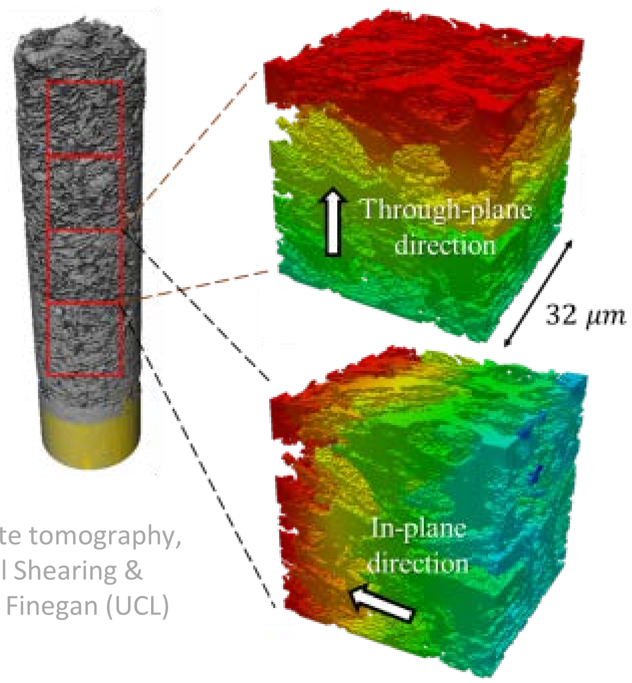


Figure credit: Aashutosh Mistry and Partha Mukherjee, TAMU

Microstructure Analysis

- Particle size and morphology of calendared electrodes
  - Clear differences between graphite and NCM morphologies
  - Calendaring slightly elongates and re-aligns of particles





Graphite tomography, Paul Shearing & Donal Finegan (UCL)

- Tortuosity* via homogenization calculation

*Micro-pore, neglects conductor + binder phase for now

Direction	Negative, cal.	Positive, uncal.	Positive, cal.
Through-plane	3.8	1.4	1.6
In-plane	1.8	1.4	1.5

Summary and Future Work

- Safety models able to represent and predict thermal runaway propagation in a battery module
  - Model-based design cost-effective and repeatable
  - ISC device preferred to other test methods (nail, pinch, etc.)
  - Mechanical abuse/crash validation underway
- Addressing bottlenecks for adoption of electrochemical models into battery CAE design process
  - Parameter identification
    - Enabled by fast running models
    - Optimizing experiments and test articles
  - Addressing heterogeneity in electrode microstructure
  - Prediction of effective properties for electrode models
    - Thick electrode, fast charge optimization

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www.nrel.gov/transportation/energystorage/

Publications and Presentations

- Z. Wu, C. Zhang, L. Cao, and S. Santhanagopalan, "Effect of Aging on Mechanical Properties of Lithium-Ion Battery Components," *J. Electrochem. Soc.,* submitted 2017.
- S. Santhanagopalan, L. Cao, J. Hartig, and Z. Wu, "Characterizing Battery Safety on Aged Cells," invited presentation at the 231st Meeting of the Electrochemical Society, New Orleans, LA (2017).
- G-H. Kim, K. Smith, J. Lawrence-Simon, and C. Yang, "Efficient and Extensible Quasi-Explicit Modular Nonlinear Multiscale Battery Model: GH-MSMD," *J. Electrochem. Soc.,* A1076-1088 (2017).
- C. Zhang, J. Xu, L. Cao, Z. Wu and S. Santhanagopalan, "Constitutive Behavior and Progressive Mechanical Failure of Electrodes in Lithium-ion Batteries," *J. Power Sources*, accepted 2017.
- C. Zhang, S. Santhanagopalan, and A. Pesaran, "Simultaneously Coupled Mechanical-Electrochemical-Thermal Simulation of Lithium-Ion Cells," *ECS Trans.,* 72(24), p. 9-19, (2016).
- C. Zhang, S. Santhanagopalan, and A. Pesaran, "Coupled Analysis of Failure Propagation in Li-Ion Batteries," 12th World Congress on Computational Mechanics, Seoul, Korea (2016).
- K. Gruchalla, M. Stock, N. Brunhart-Lupo, C. Zhang, and S. Santhanagopalan, "Interpretation of Simultaneous Mechanical-Electrical-Thermal Failure in a Lithium-Ion Battery Module," finalist at the Super Computing 2016 Visualization Competition, Salt Lake City UT (2016).
- S. Santhanagopalan, C. Zhang, M.A. Sprague, and A. Pesaran, "A Representative-Sandwich Model for Simultaneously Coupled Mechanical-Electrical-Thermal Simulation of Lithium-ion Battery Cell under Quasi-Static Indentation Tests," *J. Power Sources*, 298, p. 102-113 (2016).
- A. Pesaran, "Computer Aided Battery Engineering Consortium," presented at the VTO Annual Merit Review, Washington, D.C. (2016).
- L. Cao, C. Zhang, S. Santhanagopalan, and A. Pesaran, "Effect of Aging on Mechanical Properties of Li-Ion Cell Components," presented at the 229th Meeting of the Electrochemical Soc., San Diego CA (2016).

Publications and Presentations, cont.

- A. Mistry, D. Juarez-Robles, M. Stein IV, K. Smith, P.P. Mukherjee, "Analysis of Long-Range Interaction in Lithium-Ion Battery Electrodes," *J. Echem. Energy Conversion and Storage,* Vol. 13 (3) 2016.
- G-H. Kim, K. Smith, J. Lawrence-Simon, and C. Yang, "Efficient and Extensible Quasi-Explicit Modular Nonlinear Multiscale Battery Model: GH-MSMD," *J. Electrochem. Soc.*, A1076-1088, 2017.
- Daniel Abraham, "Revealing Aging Mechanisms in Lithium-Ion Cells," International Battery Seminar and Exhibit 2017, Fort Lauderdale, FL; March 20-23, 2017.
- François Usseglio-Viretta, Kandler Smith, "Quantitative Microstructure Characterization of a NMC Electrode," 231st Echem. Soc. Mtg., New Orleans, LA, May 28–June 1, 2017.
- P. P. Mukherjee, "Virtual Electrode Engineering: From Mesoscale Underpinnings to System Characteristics," 17th Annual Advanced Automotive Battery Conference (AABC), June 19-22, San Francisco, CA (2017).
- P. P. Mukherjee and A. Mistry, "Mesoscale Implications in Li-Ion Battery Safety," International Battery Safety Workshop, Albuquerque, NM, May 9-10 (2017).
- A. Mistry and P. P. Mukherjee, "Mesoscale Probing of Transport-Interface Interaction in Lithium-ion Battery Electrodes," TMS 2017 146th Annual Meeting and Exhibition, San Diego, CA (1st Mar 2017).
- P. P. Mukherjee, "Mesoscale Electrode Physics in Energy Storage," *School on Multiscale Computational Modeling of Materials for Energy Applications*, International Center for Theoretical Physics, Trieste, Italy, July 12 (2016).
- P. P. Mukherjee, "Mesoscale Electrode Physics in Lithium-Ion Batteries," Indo-US Workshop on Recent Advances in Multiscale, Multiphysics Phenomena in Li-Ion Batteries, June 17 (2016).
- A. Mistry, A. Verma, R. Mukherjee and P. P. Mukherjee, "Image-based Reconstruction and Statistical Characterization of the Li-ion Battery Electrode Microstructure," 229th Meeting of Electrochemical Society, San Diego, CA (29th May – 2nd Jun 2016).
- A. Mistry, A. Verma, D. Juarez-Robles and P. P. Mukherjee, "How Electrode Processing Affects Li-ion Battery Performance?", Material Challenges in Alternative and Renewable Energy 2016, Clearwater, FL, Apr 17-21, 2016.
- A. Mistry, et al., "Li-ion Battery Electrode Microstructure – A Mesoscale Perspective," *in preparation*.
- A. Mistry et al., "Secondary Phase Stochastics in Li-ion Battery Electrodes," *in preparation*.
- François Usseglio-Viretta et al., "Non-parametric Discrete Particle Algorithm and Application to Microstructure of Li-ion Battery Electrodes," *in preparation*.