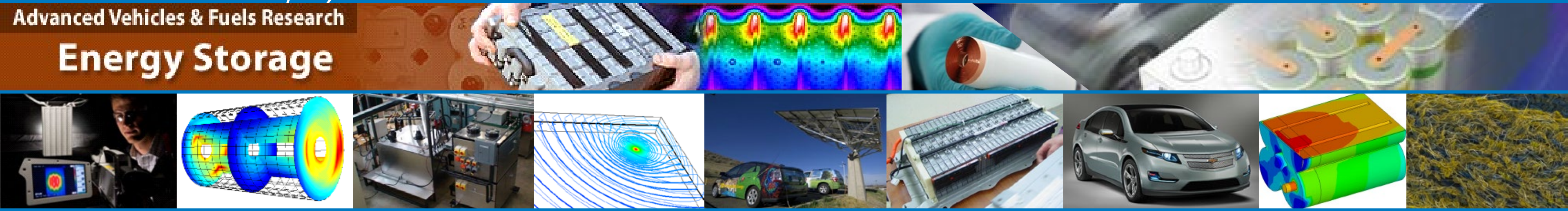
Model-Based Design and Integration of Large Li-ion Battery Systems



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11th Annual Knowledge Foundation's Lithium Battery Power 2015

Baltimore, MD November 17-19, 2015

NREL/PR-5400-65426

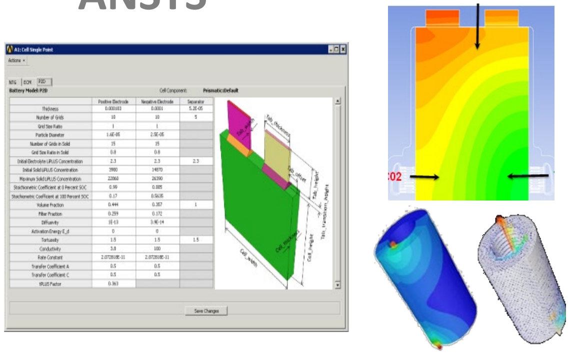
Outline

- **DOE's CAEBAT program**
- **Battery physics**
    - Performance
    - Degradation
    - (Safety – omitted here. See Dr. Gi-Heon Kim's separate presentation at Battery Safety this week)
- **Selected NREL modeling research**
- **Gaps and next efforts in model development**

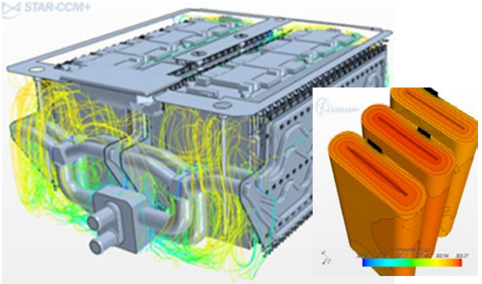
DOE’s CAEBAT Program

- Shorten time and cost for design of electric drive battery systems
- Integrate accomplishments of disparate battery modeling activities. Make them accessible as design tools for industry
- Led by Vehicle Technologies Office with support of US Army TARDEC
    - CAEBAT-1 (2010): Electrochemical-thermal (ECT)
    - CAEBAT-2 (2013): + computational efficiency, mechanical crush
    - CAEBAT-3 (2015): + microstructure
- Teams combining industry, national labs, universities
- Three commercially available toolsets with >60 licenses to date

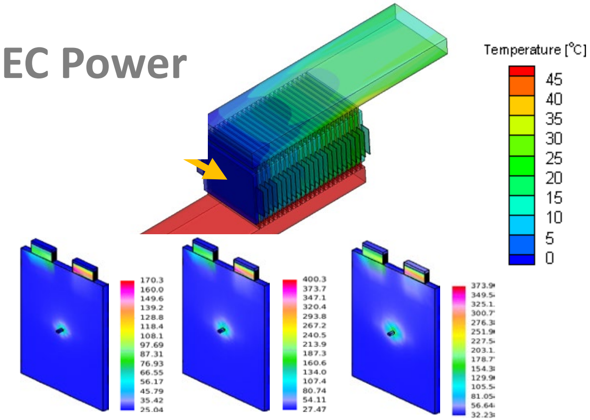
ANSYS



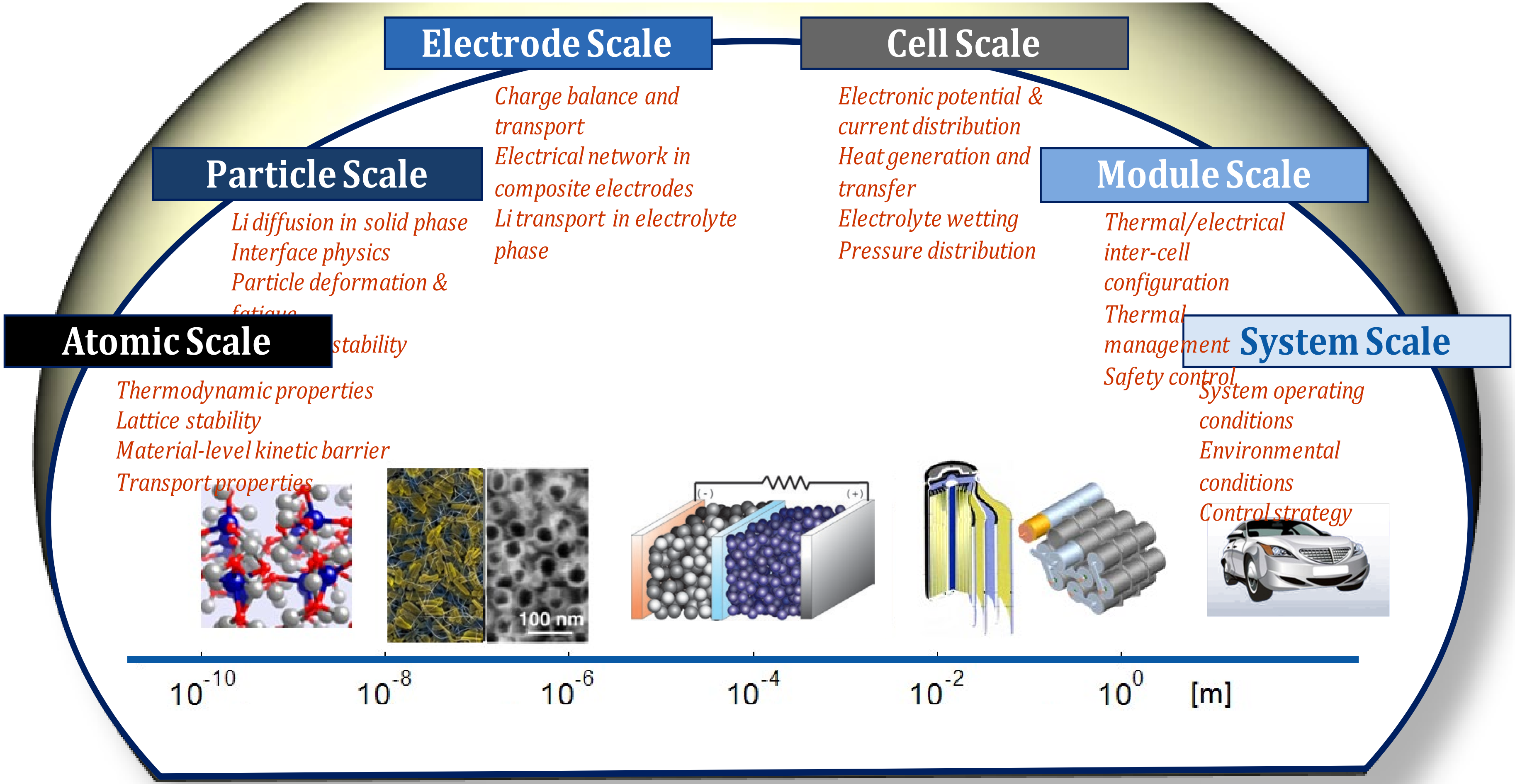
CD-Adapco



EC Power



Performance of Lithium-Ion Batteries Occurs Across Varied Length Scales



Atomic Scale

Thermodynamic properties
Lattice stability
Material-level kinetic barrier
Transport properties

Particle Scale

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

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

Module Scale

Thermal/electrical inter-cell configuration
Thermal management
Safety control

System Scale

System operating conditions
Environmental conditions
Control strategy

Practical computer-aided engineering (CAE) tools require fast, efficient frameworks and sub-models including reduced order models.

Degradation Similarly Occurs Across Various Length Scales

Chemistry

- SEI growth
- Li plating
- Electrolyte decomposition
- Gas generation

Particle

- Surface fracture, active area growth
- Bulk fracture, damage of transport paths
- Phase evolution, voltage droop

Electrode

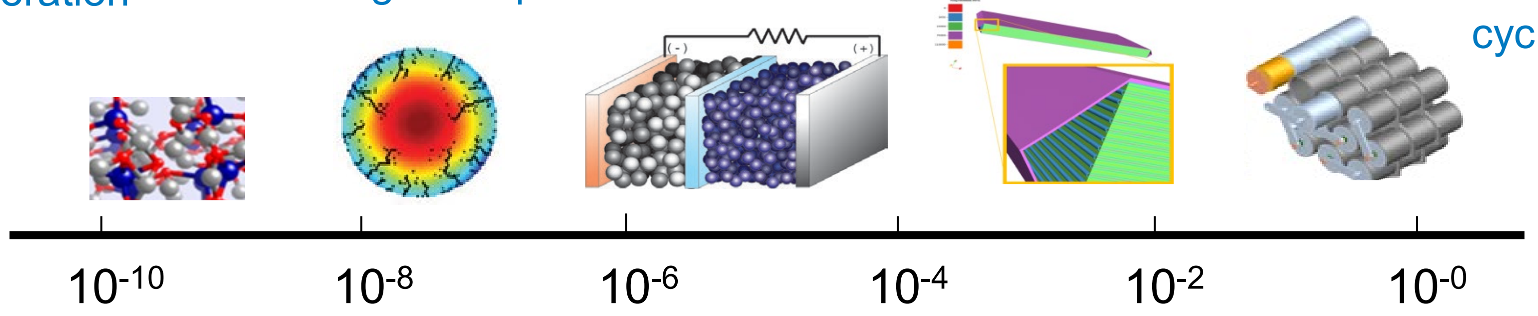
- Particle displacement, electrode creep, delamination, isolation
- Separator pore closure
- Salt precipitation
- Pore clogging

Cell

- 3D electrical, thermal, mechancial non-uniformity
- Tab effects
- Stack/wind

System

- Thermal & mechanical non-uniformity & boundary conditions
- Electrical duty-cycle



Not all degradation modes are fully understood. Life can be predicted, but only with sufficient cell aging test data.

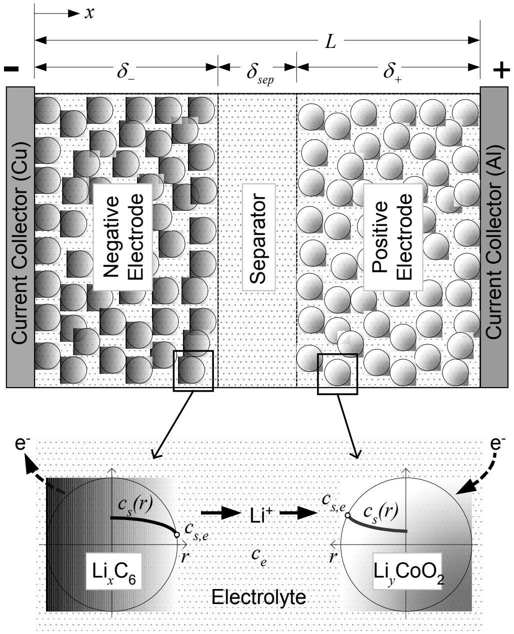
NREL Modeling & Research

- Fast electrochemical simulation
- Framework for efficient extension of electrochemistry to 3D cell & pack domains
- Chemical reaction modeling: SEI growth & Li plating
- Mixed material electrodes
- Mechanics:
    - Particle & electrode diffusion-induced damage
    - Cell-scale pressure management

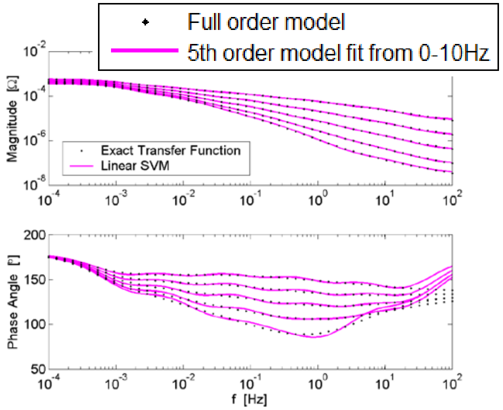
Fast Electrochemical Simulation

Frequency domain technique used to four PDEs governing electrochemical dynamics to a set of ~13 ODEs

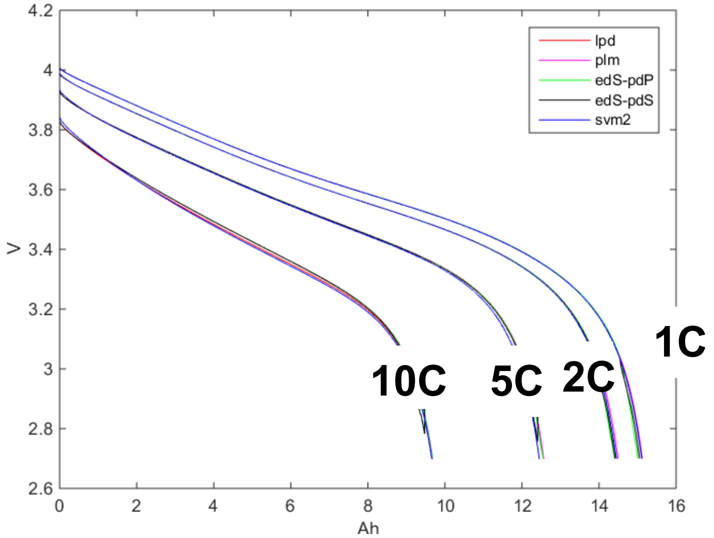
$$\dot{\mathbf{x}} = f(\mathbf{x}, u)$$
$$\mathbf{y} = h(\mathbf{x}, u)$$



- Previous[1]: Model reduction took 1-2 hours, only represented one battery design
- Accomplishment[2]: Single pre-calculated reduced model valid for all battery designs



100x faster than typical finite-volume models. Similar speed as circuit models, but also predicts electrochemical potentials & concentrations based on design parameters

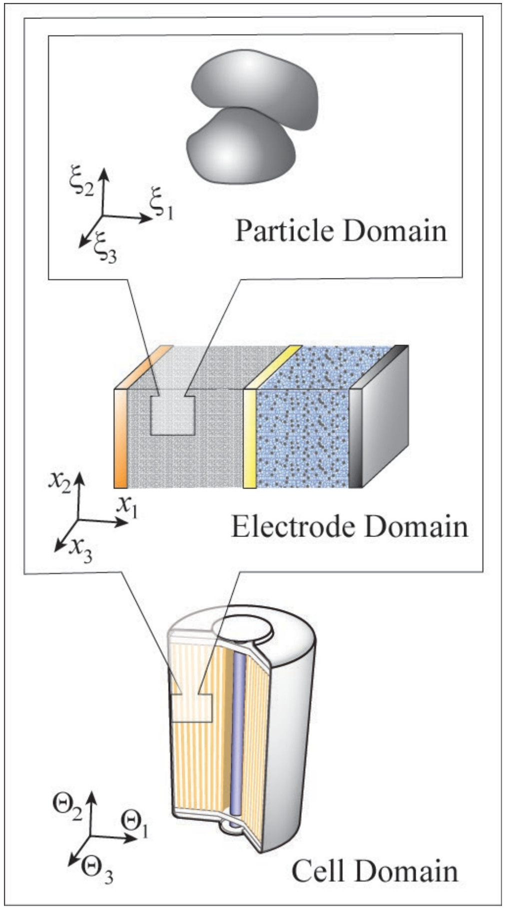


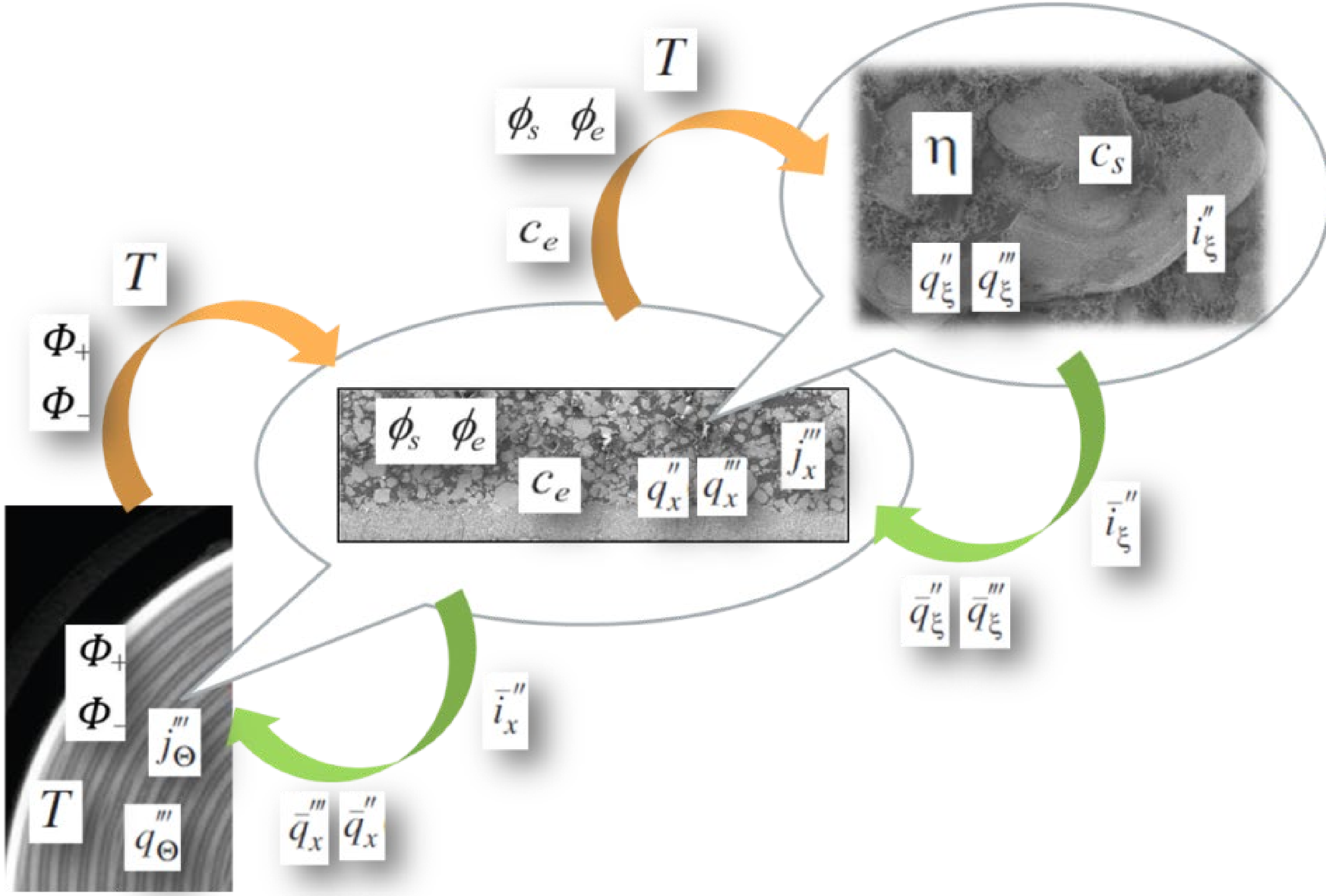
1. *K. Smith, C. Rahn, C.Y. Wang, "Control-oriented 1D electrochemical model of lithium ion battery," Energy Conv. & Mgmt., 48 (2007) 2565-2578.*
2. *M. Jun, K. Smith, P. Graf, "State-space Representation of Li-ion Battery Porous Electrode Impedance Model with Balanced Model Reduction." J. Power Sources, 2014.*

Extending Electrochemistry to Cell and Pack

NREL **M**ulti-**S**cale **M**ulti-**D**imensional (MSMD) Model

Modular architecture, linking interdisciplinary battery physics

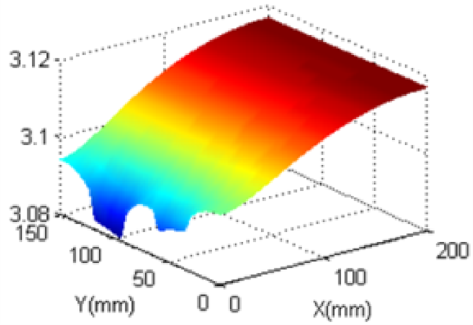


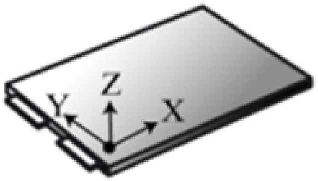


Kim et al., "Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales," *J. Electrochem. Soc.*, 2011, Vol. 158, No. 8, pp. A955–A969

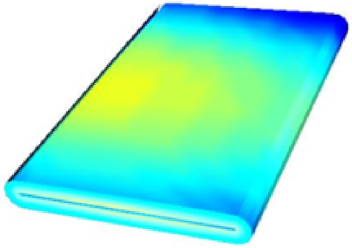
MSMD Realizations in Various Geometries

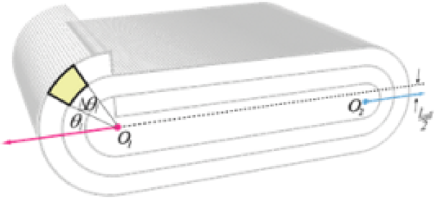
Stack Pouch



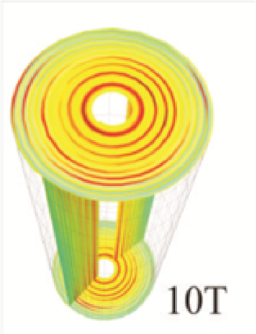


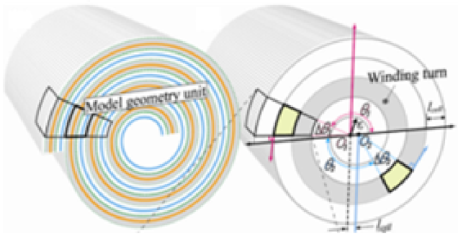
Wound Prismatic

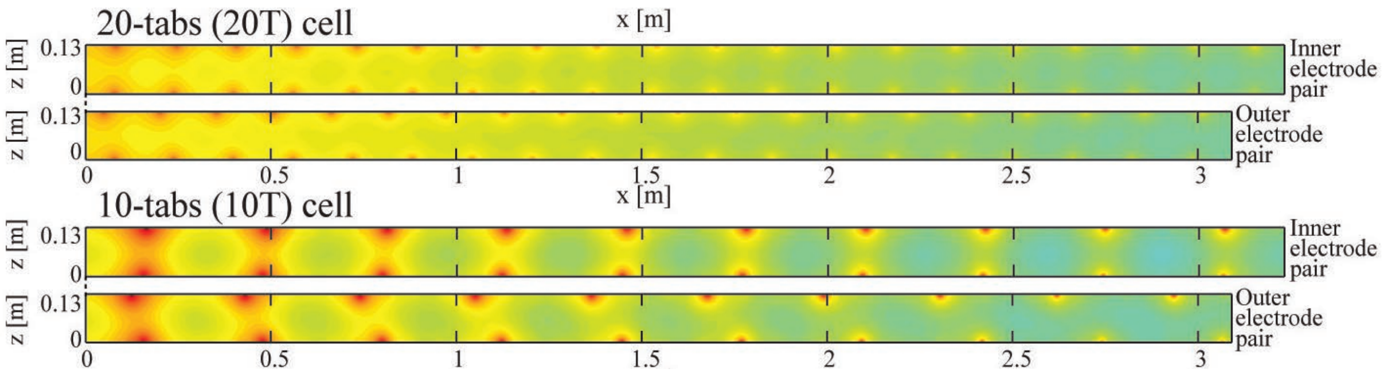




Wound Cylindrical

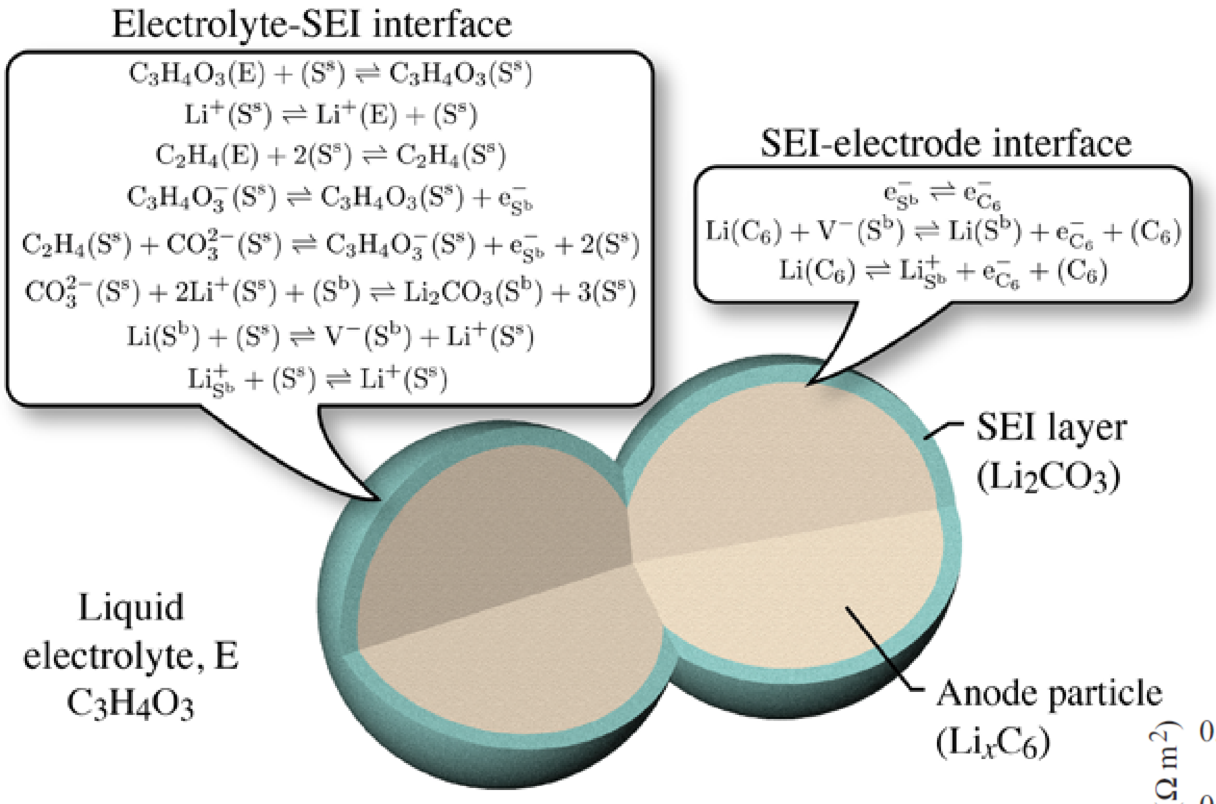






Kim et al., "Multi-Domain Modeling of Lithium-Ion Batteries Encompassing Multi-Physics in Varied Length Scales," *J. Electrochem. Soc.*, 2011, Vol. 158, No. 8, pp. A955–A969

Elementary Chemical Reactions w/ CSM



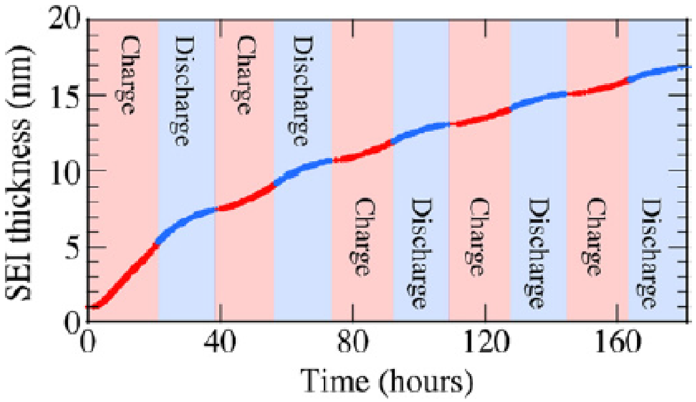
Electrolyte-SEI interface

$$\mathrm{C_3H_4O_3(E) + (S^s) \rightleftharpoons C_3H_4O_3(S^s)}$$
$$\mathrm{Li^+(S^s) \rightleftharpoons Li^+(E) + (S^s)}$$
$$\mathrm{C_2H_4(E) + 2(S^s) \rightleftharpoons C_2H_4(S^s)}$$
$$\mathrm{C_3H_4O_3^-(S^s) \rightleftharpoons C_3H_4O_3(S^s) + e^-_{S^b}}$$
$$\mathrm{C_2H_4(S^s) + CO_3^{2-}(S^s) \rightleftharpoons C_3H_4O_3^-(S^s) + e^-_{S^b} + 2(S^s)}$$
$$\mathrm{CO_3^{2-}(S^s) + 2Li^+(S^s) + (S^b) \rightleftharpoons Li_2CO_3(S^b) + 3(S^s)}$$
$$\mathrm{Li(S^b) + (S^s) \rightleftharpoons V^-(S^b) + Li^+(S^s)}$$
$$\mathrm{Li^+_{S^b} + (S^s) \rightleftharpoons Li^+(S^s)}$$

SEI-electrode interface

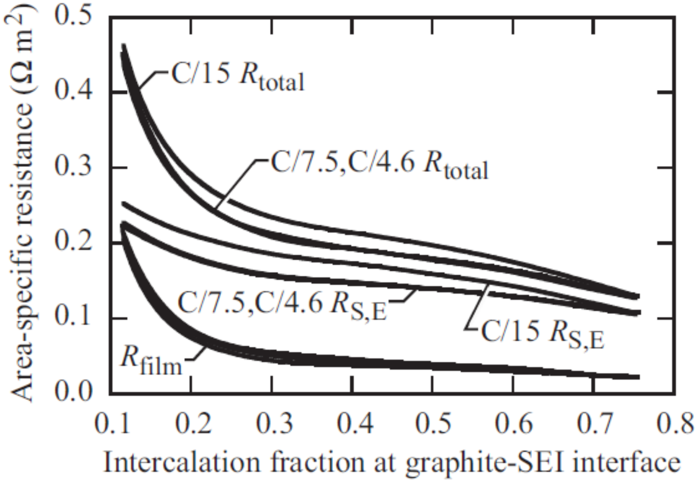
$$\mathrm{e^-_{S^b} \rightleftharpoons e^-_{C_6}}$$
$$\mathrm{Li(C_6) + V^-(S^b) \rightleftharpoons Li(S^b) + e^-_{C_6} + (C_6)}$$
$$\mathrm{Li(C_6) \rightleftharpoons Li^+_{S^b} + e^-_{C_6} + (C_6)}$$

A. Colclasure, K. Smith, R. Kee. (2011). “Modeling Detailed Chemistry and Transport for Solid-Electrolyte-Interface (SEI) Films in Li-ion Batteries,” Electrochemica Acta, 58(30), 33-43.



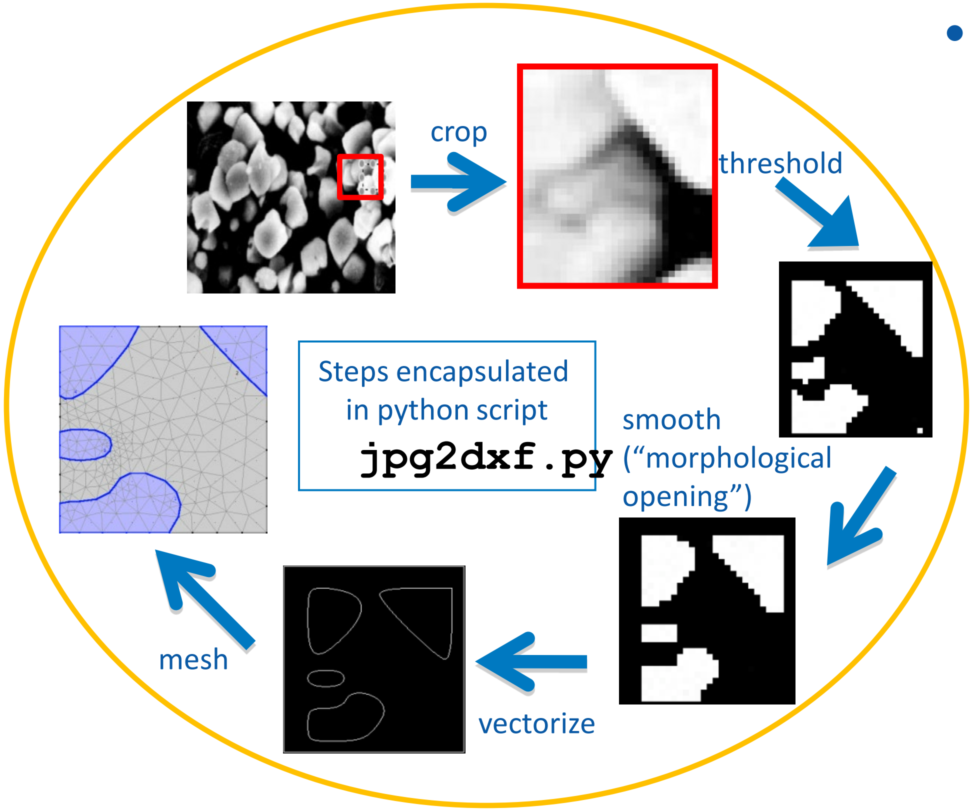
Validates square-root-of-time SEI growth models

Rate-dependent resistance



Elementary Chem. Reactions on Arbitrary Geometry

- Overcome limiting assumption of homogenization in most battery models (e.g. Li plating)



crop

threshold

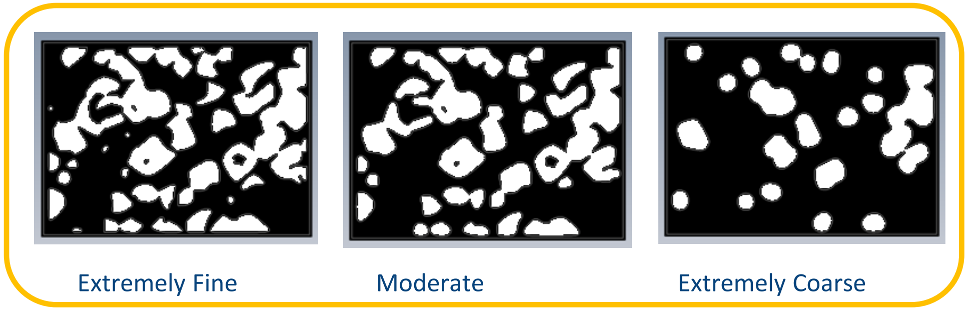
smooth (“morphological opening”)

vectorize

mesh

Steps encapsulated in python script `jpg2dxf.py`

Steps to convert an SEM image to a computational mesh

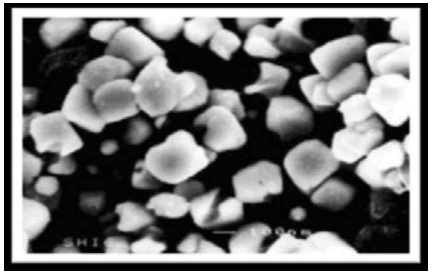


Extremely Fine

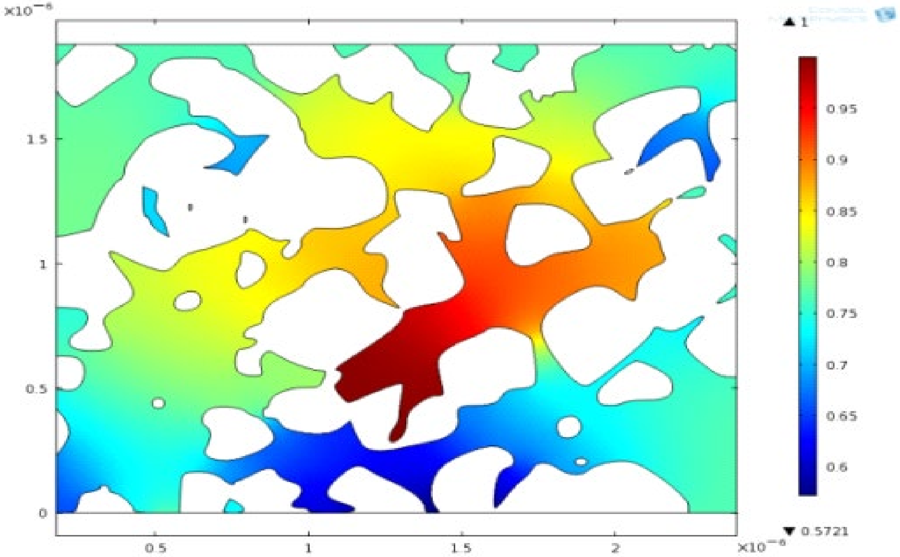
Moderate

Extremely Coarse

Study of surface-effects by varying geometry threshold value



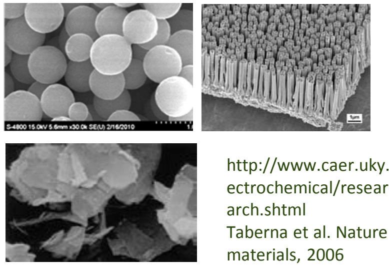
SEM image of an MCMB Anode



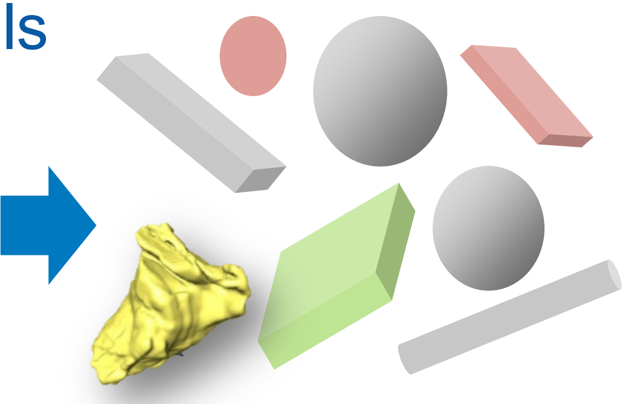
Electrolyte Distribution within the anode during charge

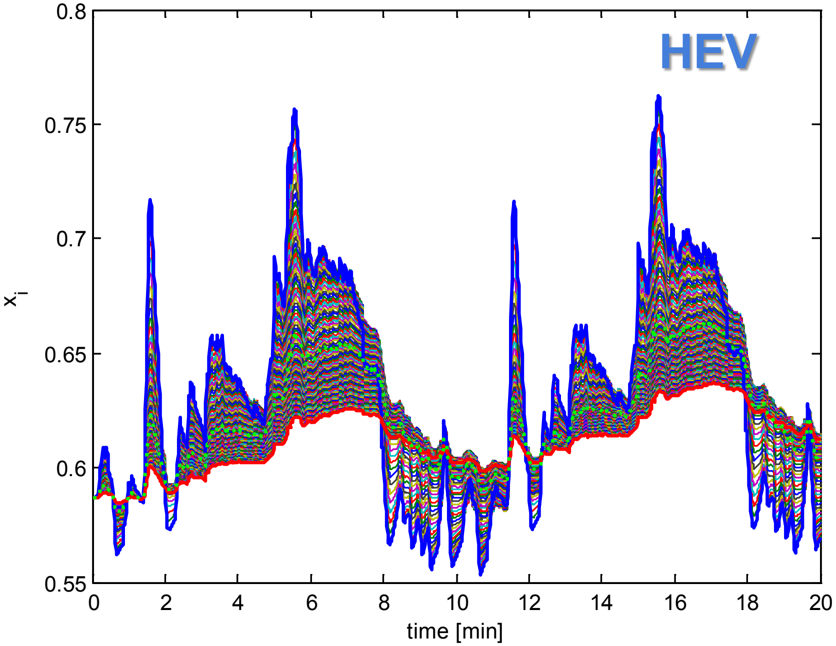
Modeling of Mixed Material Electrodes

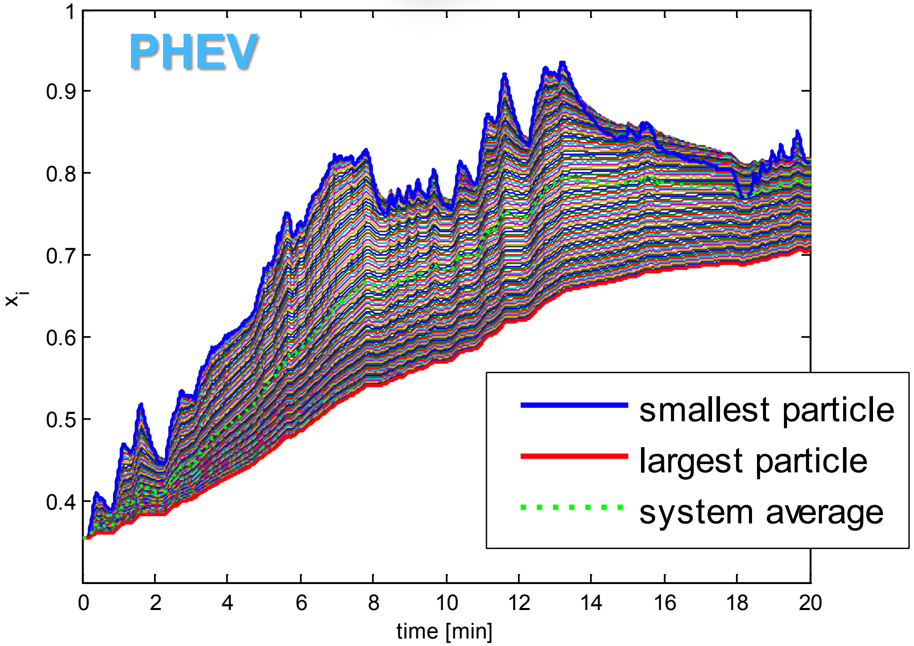
- Multiple chemistries, particle sizes, morphologies often blended for optimal power/energy/life characteristics
- MSMD Discrete-Diffusion Particle Models
  - Sphere
  - Rod
  - Flake
  - Arbitrary 3-D



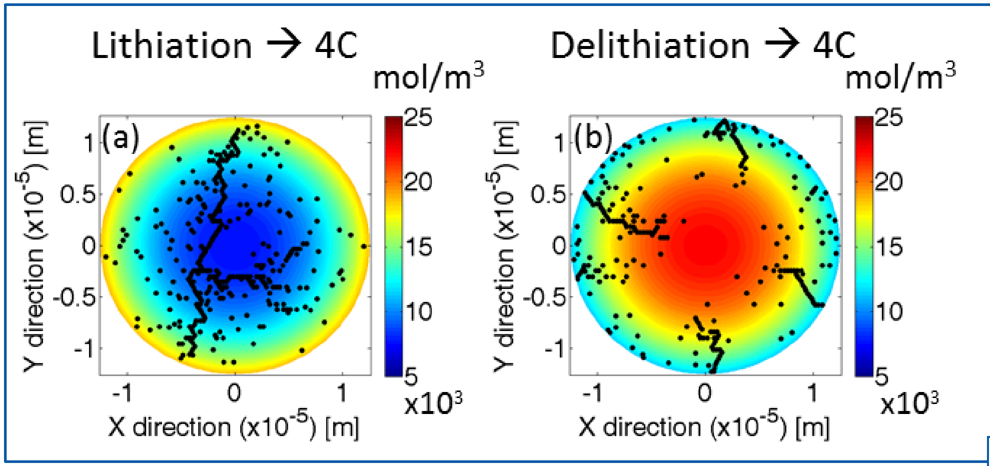
http://www.caer.uky.edu/electrochemical/research/research.shtml
Taberna et al. Nature materials, 2006







Particle-to-Electrode ECM Models w/ TAMU



- Concentration gradient drives particle fracture
- Inhibits diffusivity and performance

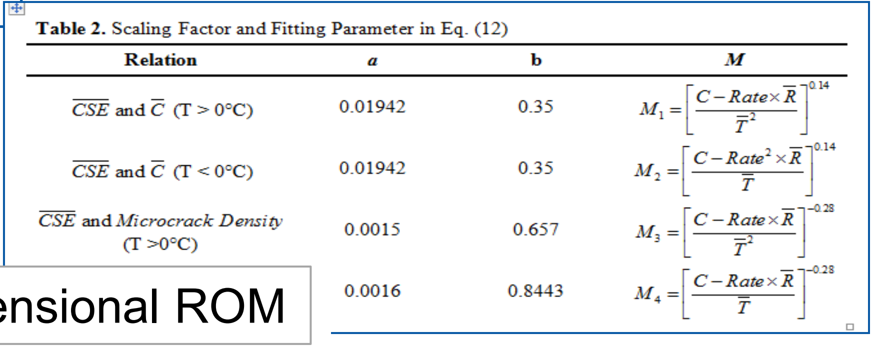
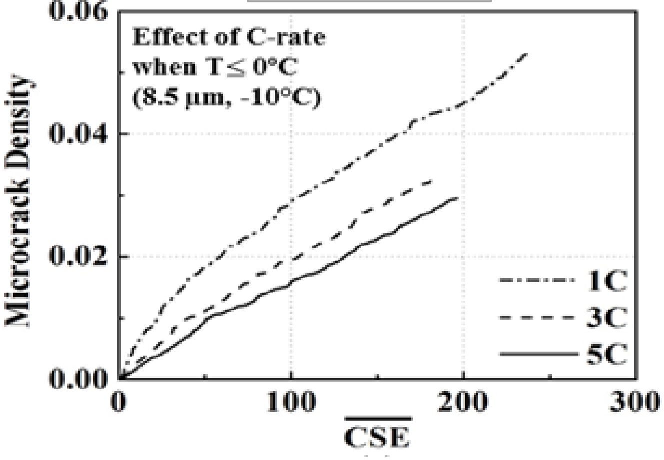


Table 2. Scaling Factor and Fitting Parameter in Eq. (12)

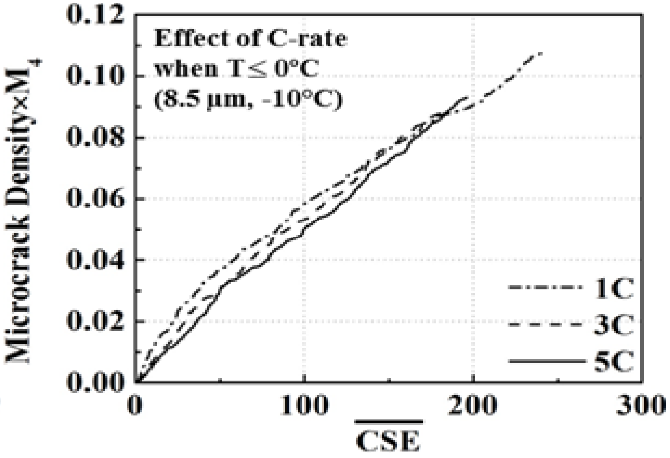
Relation	a	b	M
$\overline{CSE}$ and $\overline{C}$ (T > 0°C)	0.01942	0.35	$M_1 = \left[\frac{C-Rate\times\overline{R}}{\overline{T}^2}\right]^{0.14}$
$\overline{CSE}$ and $\overline{C}$ (T < 0°C)	0.01942	0.35	$M_2 = \left[\frac{C-Rate^2\times\overline{R}}{\overline{T}}\right]^{0.14}$
$\overline{CSE}$ and *Microcrack Density* (T >0°C)	0.0015	0.657	$M_3 = \left[\frac{C-Rate\times\overline{R}}{\overline{T}^2}\right]^{-0.28}$
	0.0016	0.8443	$M_4 = \left[\frac{C-Rate\times\overline{R}}{\overline{T}}\right]^{-0.28}$

- Order-reduced and integrated in electrode-scale models

Raw data



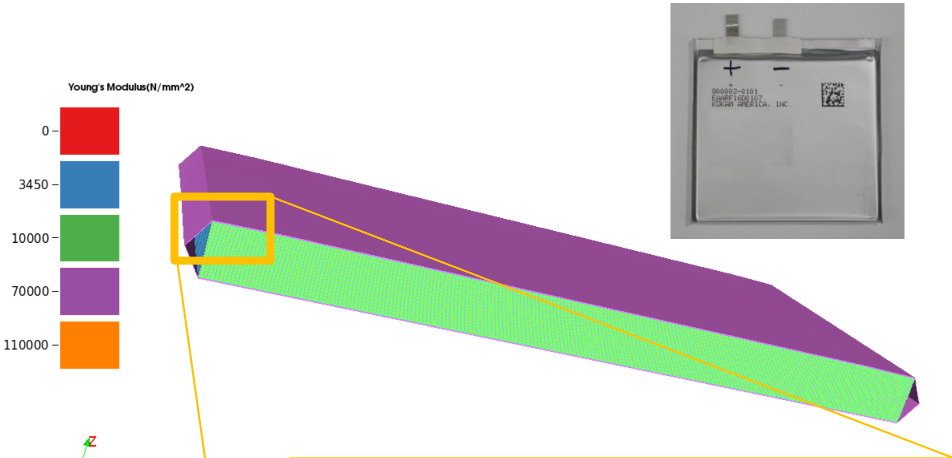
Non-dimensional ROM

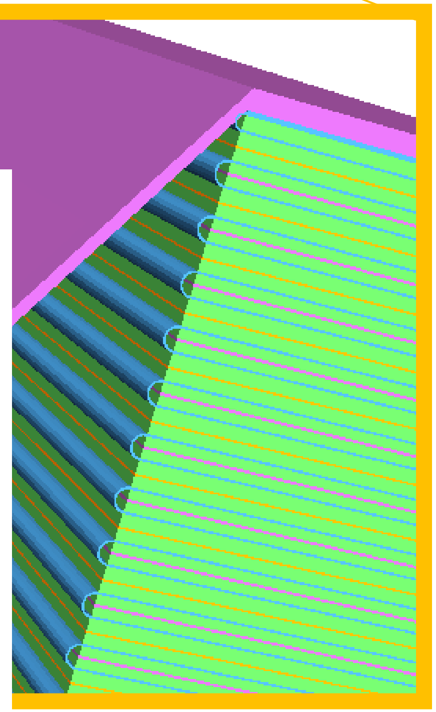


- P. Barai, K. Smith, C.-F. Chen, G.-H. Kim, P.P. Mukherjee, (2015) "Reduced Order Modeling of Mechanical Degradation Induced Performance Decay in Lithium-Ion Battery Porous Electrodes," J. Electrochem. Soc. 162 (9) A1751-A1771, http://dx.doi.org/10.1149/2.0241509jes.
- K. An, P. Barai, K. Smith, P.P. Mukherjee, (2014) "Probing the Thermal Implications in Mechanical Degradation of Lithium-Ion Battery Electrodes," J. Electrochem Soc. 161 (6) A1058-A1070, http://dx.doi.org/10.1149/2.069406jes.

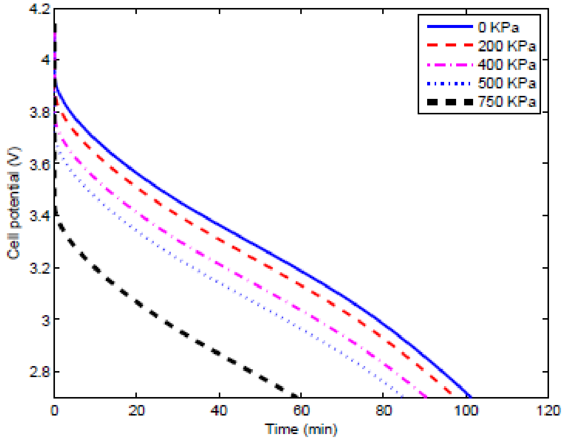
Cell Electrochemo-Mechanical Model w/ CU-B

Reza Behrou, Kurt Maute, Kandler Smith, "Numerical Simulation of Pressure Management Strategies for Lithium-ion Pouch Cells" U.S. National Congress on Theoretical & Applied Mechanics, June 15-20, 2014, East Lansing, MI.

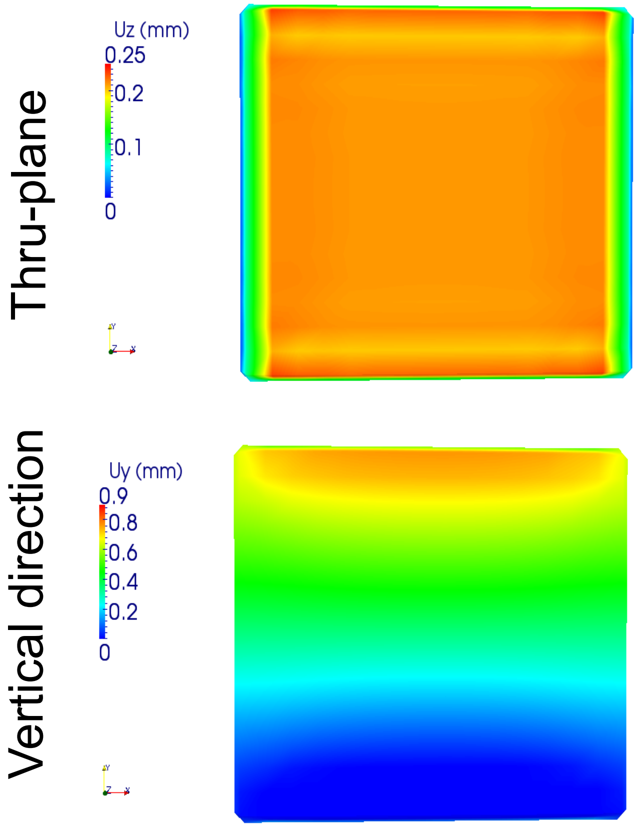




Impact of severe pressure on separator



Strain at end of full charge



Cell Resistance/Capacity Life Model

- Surrogate models for physical mechanisms regressed to aging test data
- Integrated in control algorithms and BLAST systems analysis model

- SEI growth & damage
- Particle fracture
- Electrode isolation
- Electrolyte decomposition
- Gas generation & delamination
- Li plating

Mechanism	Trajectory equation	State equation	Fitted parameter	Physics
Diffusion-controlled reaction	$x(t) = kt^{1/2}$	$\dot{x}(t) = \frac{k}{2}\left(\frac{k}{x(t)}\right)$	$k - rate$ $(p=1/2)$	(E)CT(M)
Kinetic-controlled reaction	$x(t) = kt$	$\dot{x}(t) = k$	$k - rate$ $(p=1)$	(E)CT
Mixed diffusion/ kinetic	$x(t) = kt^{p}$	$\dot{x}(t) = kp\left(\frac{k}{x(t)}\right)^{\left(\frac{1-p}{p}\right)}$	$k - rate$ $p - order,$ $0.4<z<1$	(E)CT(M)

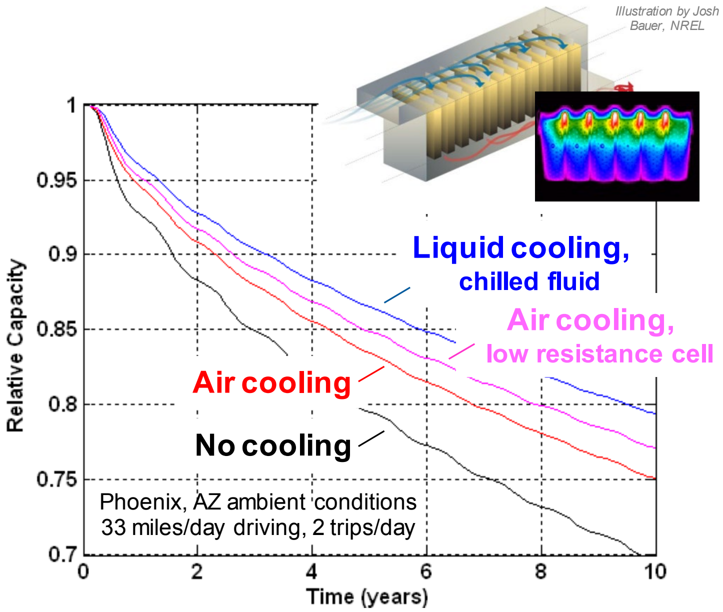
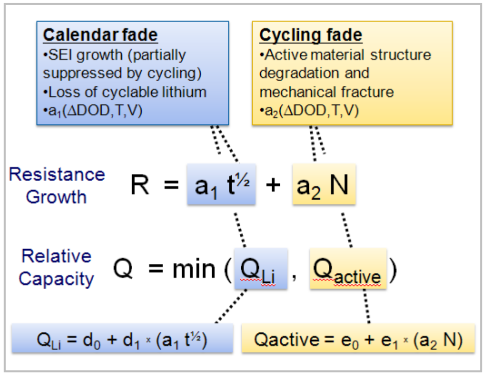


Illustration by Josh Bauer, NREL

Gr/NCA



Calendar fade
- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1(\Delta DOD,T,V)$

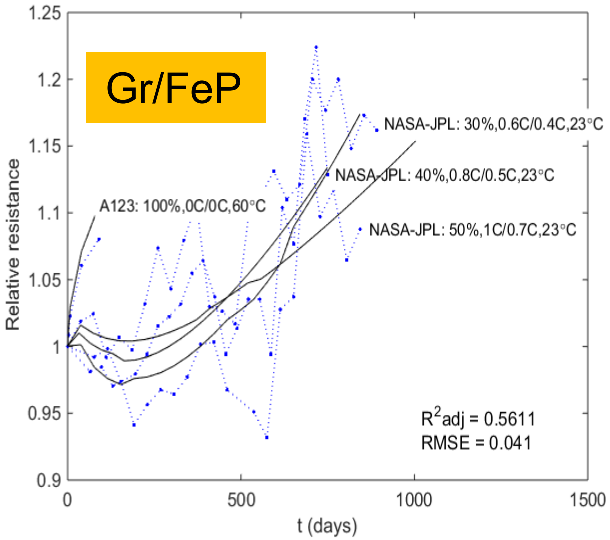
Cycling fade
- Active material structure degradation and mechanical fracture
- $a_2(\Delta DOD,T,V)$

Resistance Growth $R = a_1 t^{½} + a_2 N$

Relative Capacity $Q = \min(Q_{Li}, Q_{active})$

$Q_{Li} = d_0 + d_1 \times (a_1 t^{½})$

$Qactive = e_0 + e_1 \times (a_2 N)$



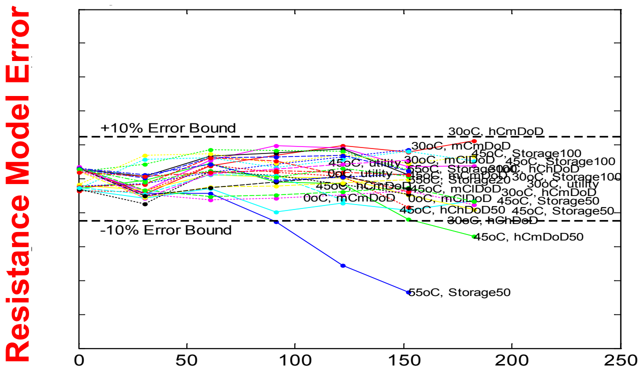
Life Model Validation at Pack Level

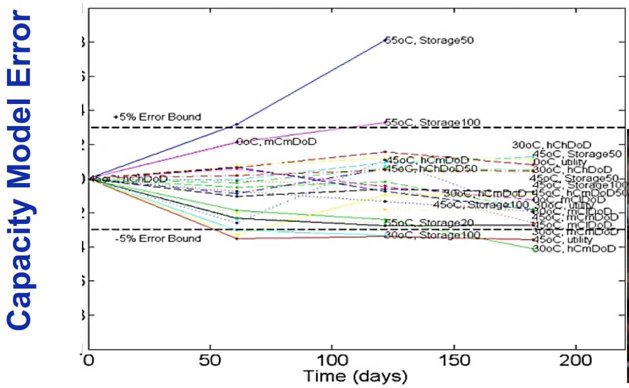
ARPA-E AMPED project led by Eaton Corporation (PI Dr. Chinmaya Patil)

- Demonstrating 30% smaller Eaton HEV battery with prognostic-based control
- Model accuracy maintained from cell-to-pack level (2-3% capacity, 7% resistance)

Cell Model Identification

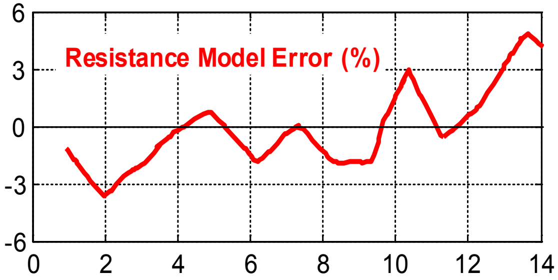
- 25 cells, 6 months
- Constant temperature & cycling

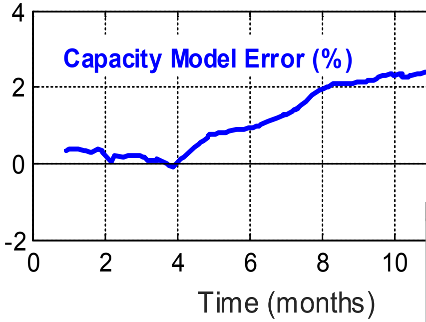


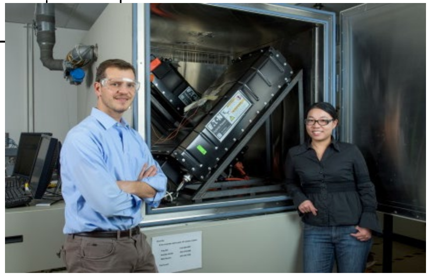


Pack Model Validation

- Cell model + temperature distribution
- 4-season temperature & variable cycling







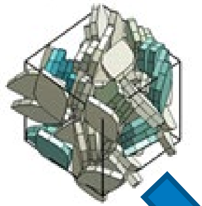
Filling the Gaps

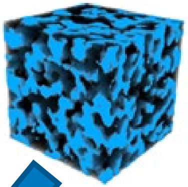
- Electrode microstructure simulation
- ECT parameter identification

3D Microstructure Model: Overcoming Limitations of Today's 1D Porous Electrode Models

- Enable virtual design of battery electrodes to shorten design cycle
- Create platform to explore new physics and geometries

Stochastic reconstruction
& meso-scale physics



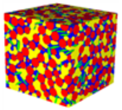


Electrode fabrication,
Tomography, electrochemical
testing

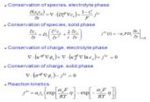
Electrode Design Inputs

Microstructure Model

- Geometry

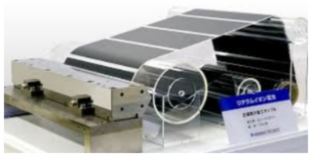


- Physics



- High Performance Computing

Validated electrochemical performance



Effective properties for upscaling

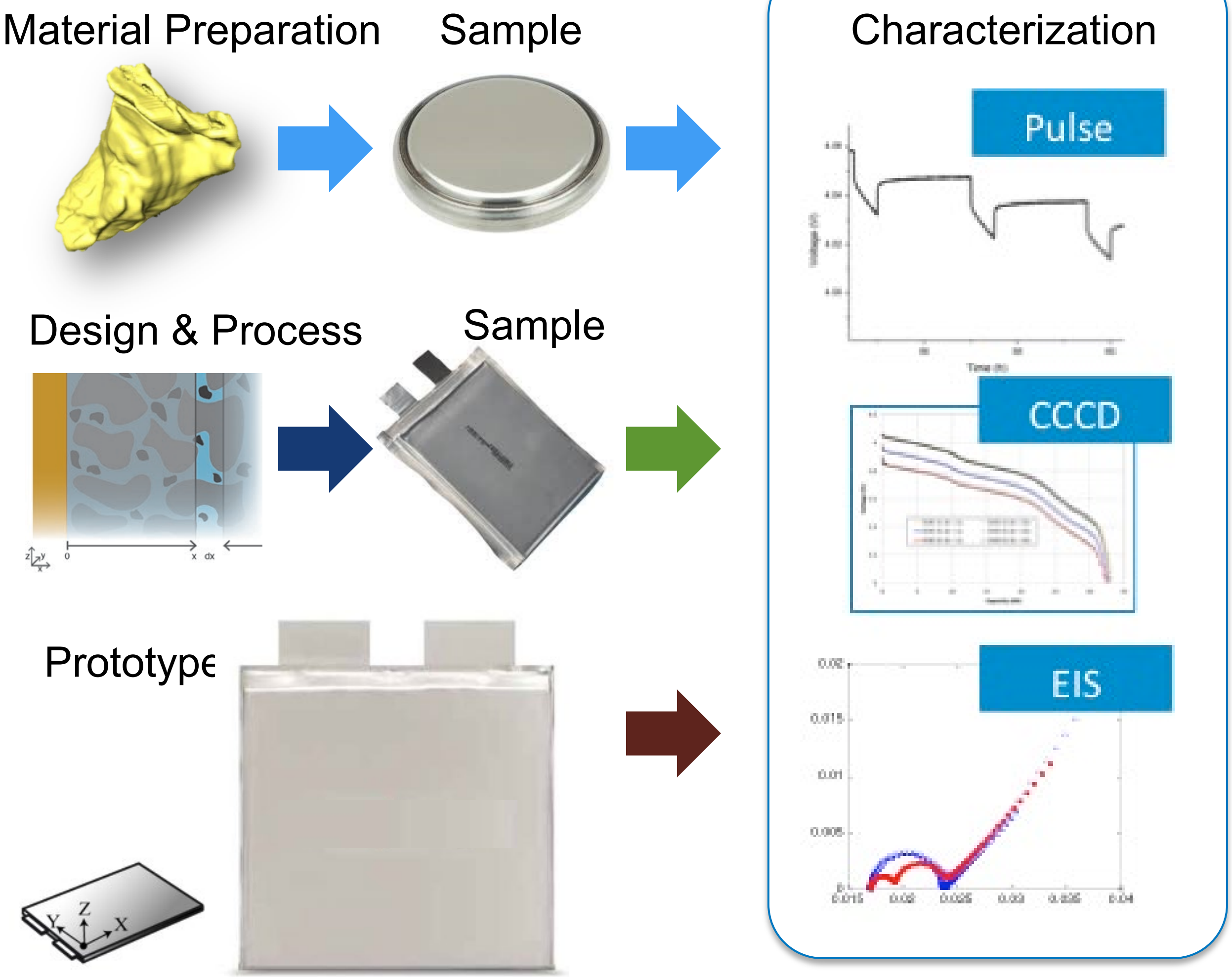
Parameter Identification using MSMD ECT Models

Electrochemical/thermal parameter identification is an intrinsically under-determined problem. NREL is developing sequential approach starting from smallest length scale with appropriate model at each length scale regressed to data.

- Thermodynamic properties
- Kinetics characteristics
- Ion transport characteristics
- Electrical characteristics
- Particle geometry/morphology

- Pore structure characteristics
- Transport limitation in electrolyte
- Ionic conductance
- Electronic conductance in matrices
- N-P balance
- Functional additive effects

- Thermal mass and conductance
- Electrode terminals and current collectors
- Performance evaluation
- Safety evaluation
- Life evaluation



Material Preparation

Sample

Design & Process

Sample

Prototype

Characterization

Pulse

CCCD

EIS

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