

Integrated Lithium-Ion Battery Model Encompassing Multi-Physics in Varied Scales: An Integrated Computer Simulation Tool for Design and Development of EDV Batteries



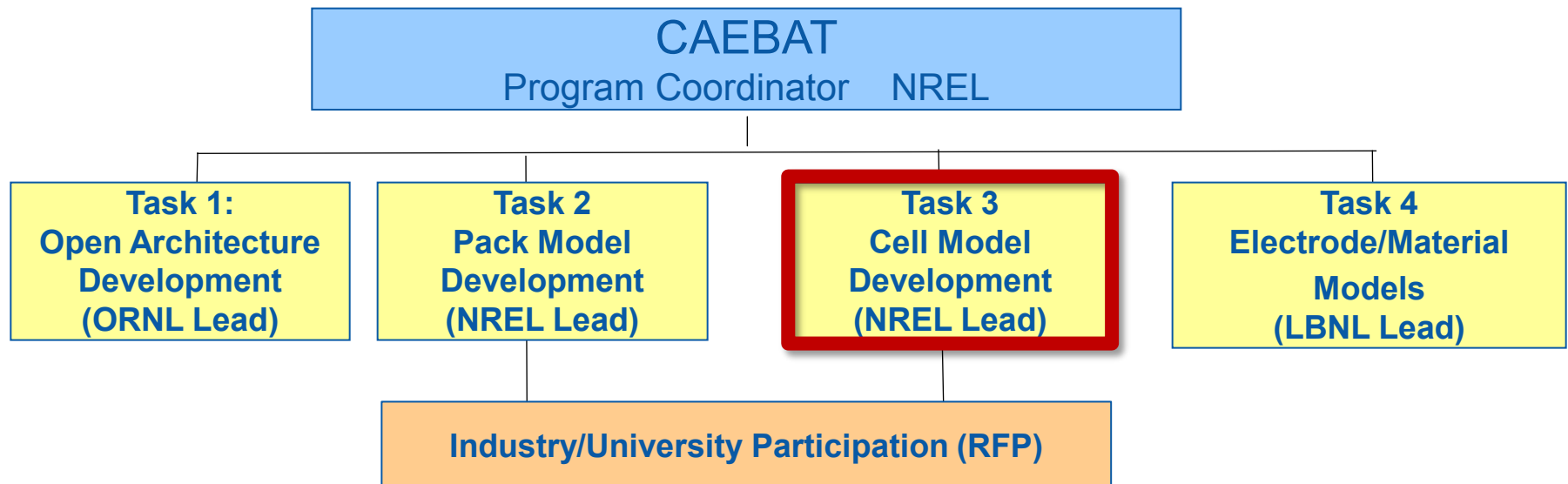
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Ahmad Pesaran**

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NREL/PR-5400-50248

DOE's CAEBAT Program

- To integrate the accomplishments of battery modeling activities in national lab programs and make them accessible as design tools for industry
- To shorten time and cost for design and development of EDV battery systems

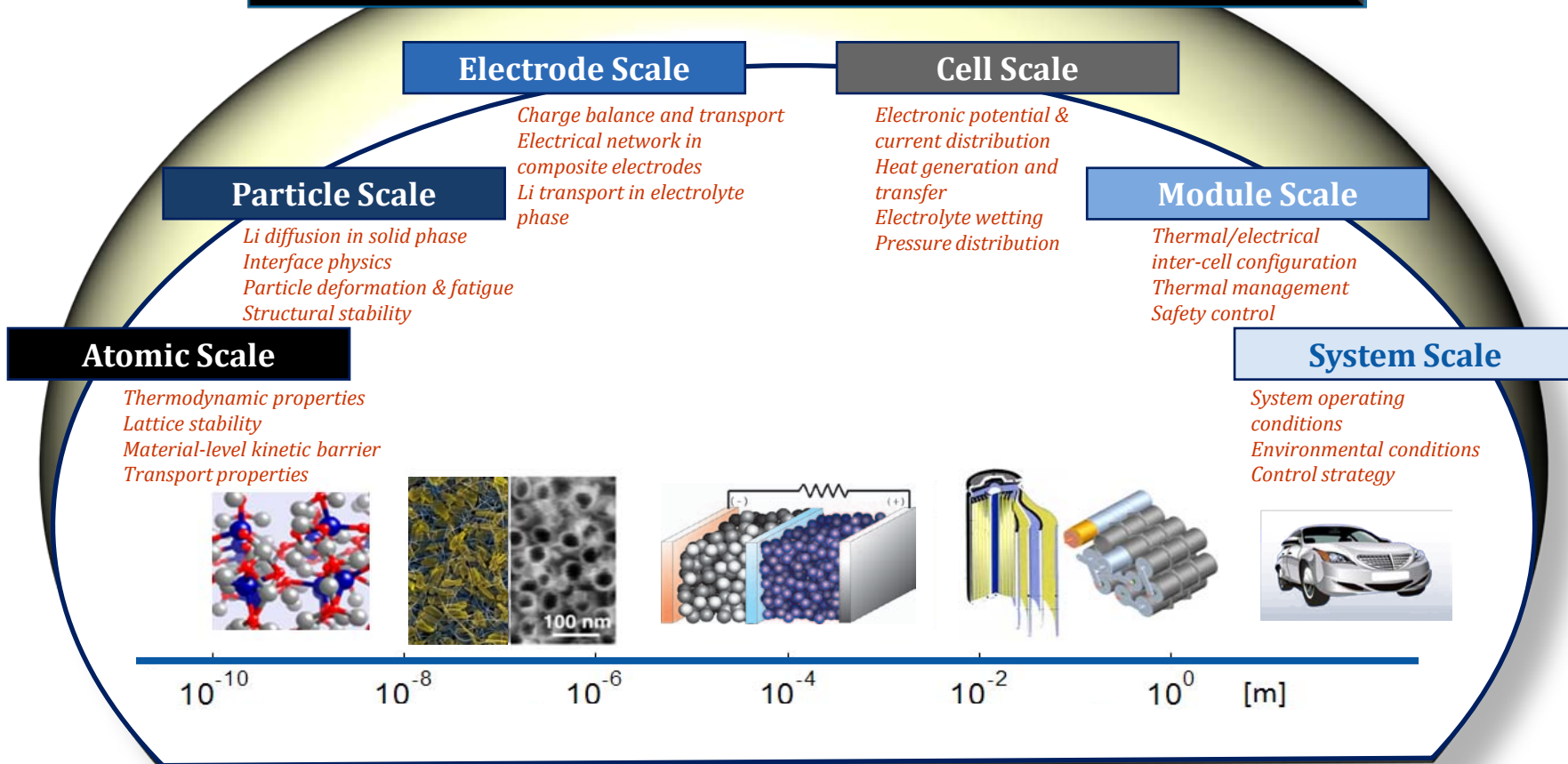


Contents

1. Introduction to *the NREL's MSMD* model
 - Multiphysics multiscale lithium battery model framework
2. Model application to large Li-ion battery *performance*
 - Stacked prismatic cell response simulation
 - Spiral wound cylindrical cell response simulation
3. Model application to large Li-ion battery *degradation*
 - Large tab-less cylindrical cell degradation simulation
4. Model application to large Li-ion battery *safety*
 - Multiphysics internal short circuit simulation
5. Summary

Performance, Durability and Safety

Physics of Li-Ion Battery Systems in Different Length Scales



Porous Electrode Performance Model

Charge Transfer Kinetics at Reaction Sites

$$j^{Li} = a_s i_o \left\{ \exp \left[\frac{\alpha_a F}{RT} \eta \right] - \exp \left[-\frac{\alpha_c F}{RT} \eta \right] \right\}$$

$$i_o = k(c_e)^{\alpha_a} (c_{s,max} - c_{s,e})^{\alpha_a} (c_{s,e})^{\alpha_c} \quad \eta = (\phi_s - \phi_e) - U$$

Species Conservation

$$\frac{\partial c_s}{\partial t} = \frac{D_s}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_s}{\partial r} \right)$$

$$\frac{d(\varepsilon_e c_e)}{dt} = \nabla \cdot (D_e^{eff} \nabla c_e) + \frac{1-t_+^o}{F} j^{Li} - \frac{\mathbf{i}_e \cdot \nabla t_+^o}{F}$$

Charge Conservation

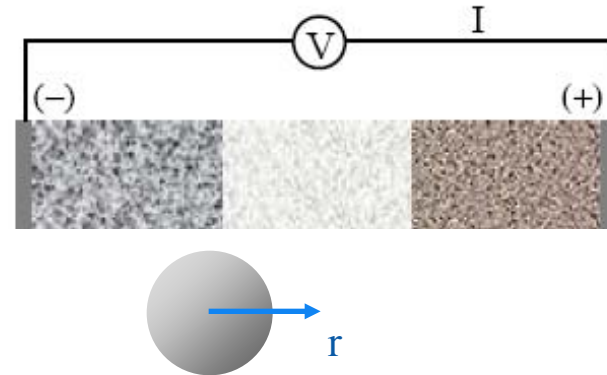
$$\nabla \cdot (\sigma^{eff} \nabla \phi_s) - j^{Li} = 0$$

$$\nabla \cdot (\kappa^{eff} \nabla \phi_e) + \nabla \cdot (\kappa_D^{eff} \nabla \ln c_e) + j^{Li} = 0$$

Energy Conservation

$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q'''$$

$$q''' = j^{Li} \left(\phi_s - \phi_e - U + T \frac{\partial U}{\partial T} \right) + \sigma^{eff} \nabla \phi_s \cdot \nabla \phi_s + \kappa^{eff} \nabla \phi_e \cdot \nabla \phi_e + \kappa_D^{eff} \nabla \ln c_e \cdot \nabla \phi_e$$

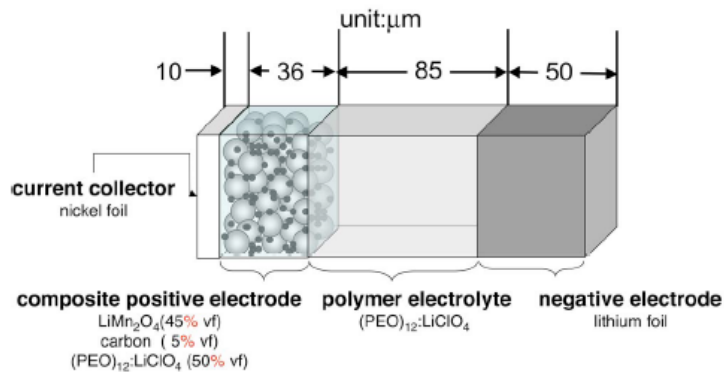


- Pioneered by Newman group (*Doyle, Fuller, and Newman 1993*)
- Captures *lithium diffusion dynamics and charge transfer kinetics*
- Predicts *current/voltage response* of a battery
- Provides design guide for thermodynamics, kinetics, and transport across electrodes

- Difficult to resolve *heat* and *electron current* transport in large cell systems

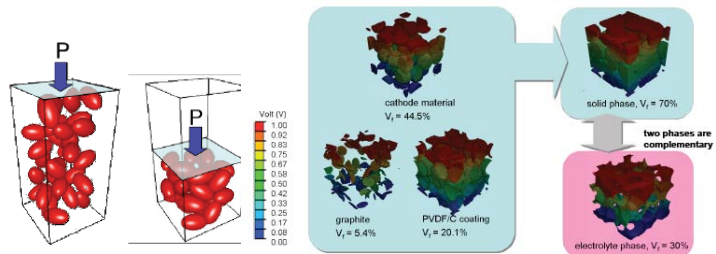
Mesoscale Modeling Approach

Wang and Sastry, JES, 2007



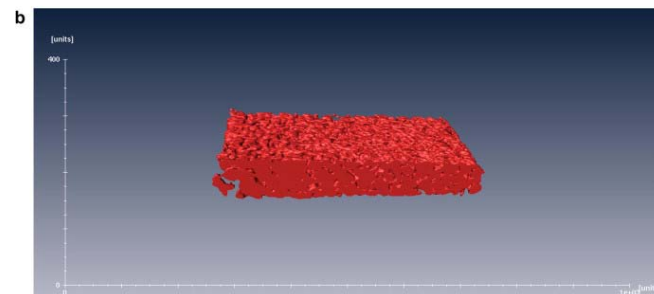
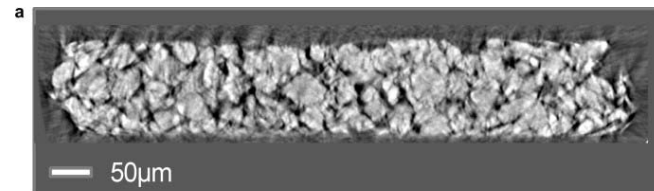
- Model addresses correlation of composition, morphology, and processing conditions by resolving mesoscale geometry
- Captures mesoscale geometry impact on transport properties of composite electrodes

- Computationally *expensive*



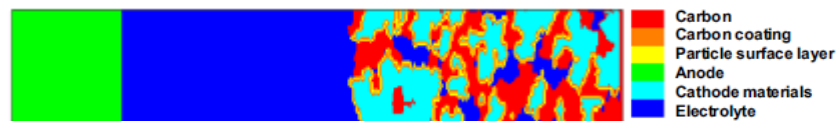
P.R. Shearing et. al, Electrochemistry Communication, 2010

X-Ray Tomography (Nano CT)



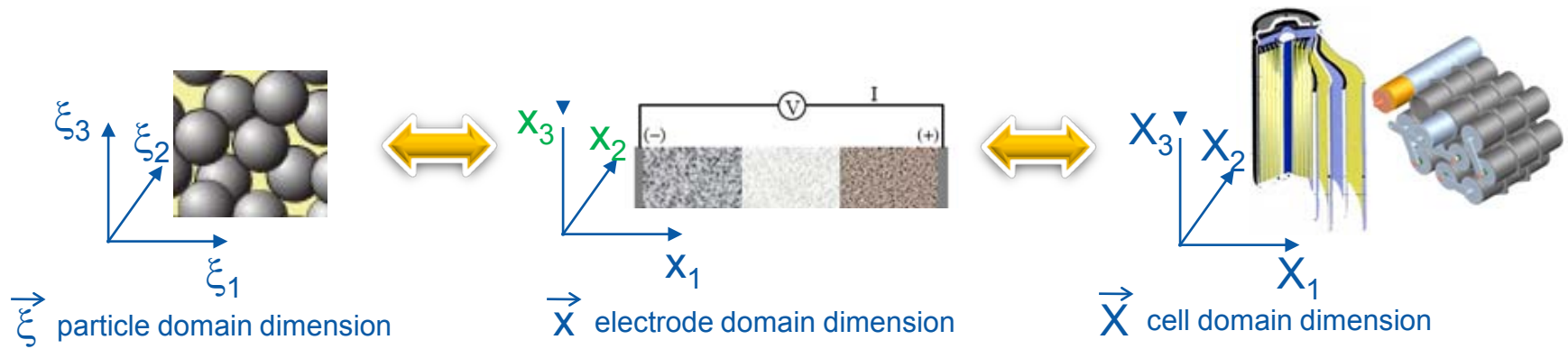
Liu and Siddique, 218th ECS, 2010

Micro-Structure Reconstruction



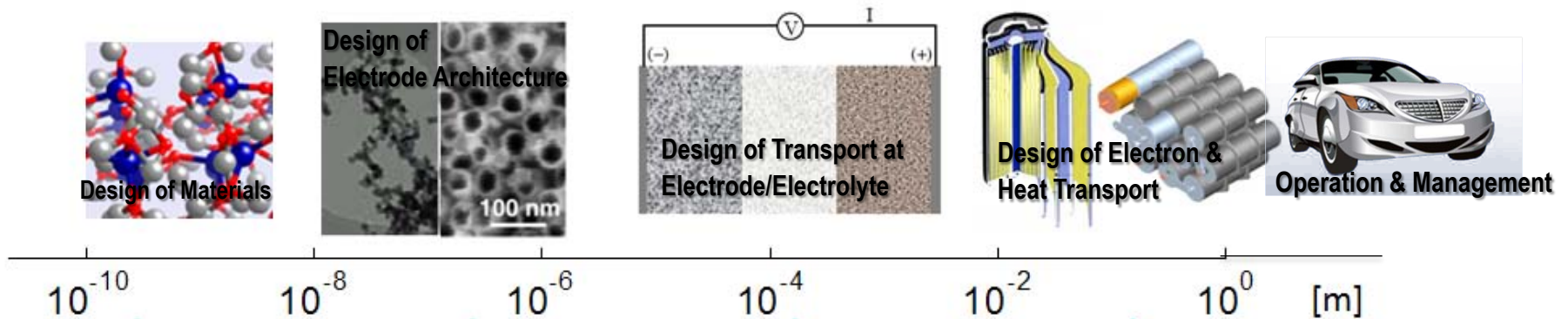
Computational domain generated by quasi-random reconstruction process

NREL's Multi-Scale Multi-Dimensional Model Approach

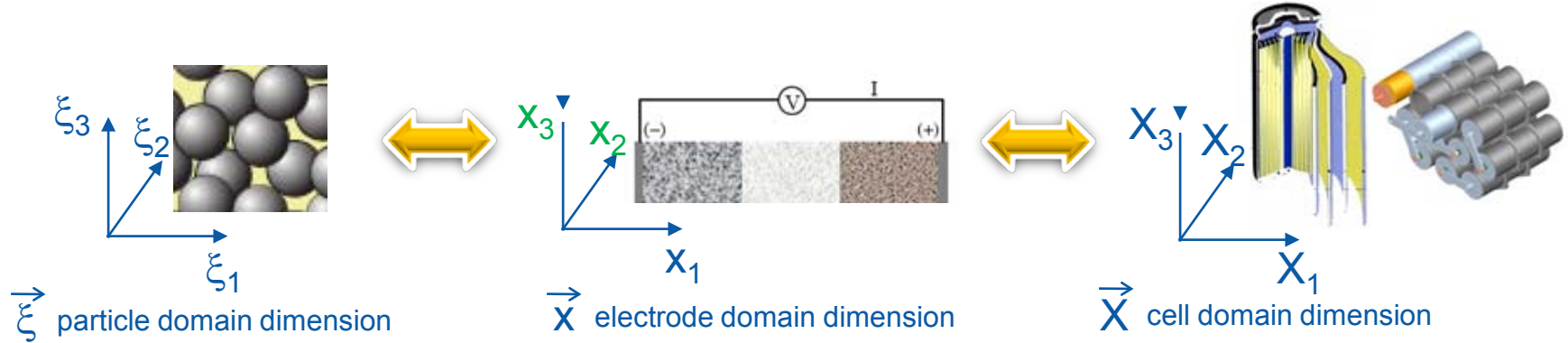


NREL

MSMD- μ MSMD-c



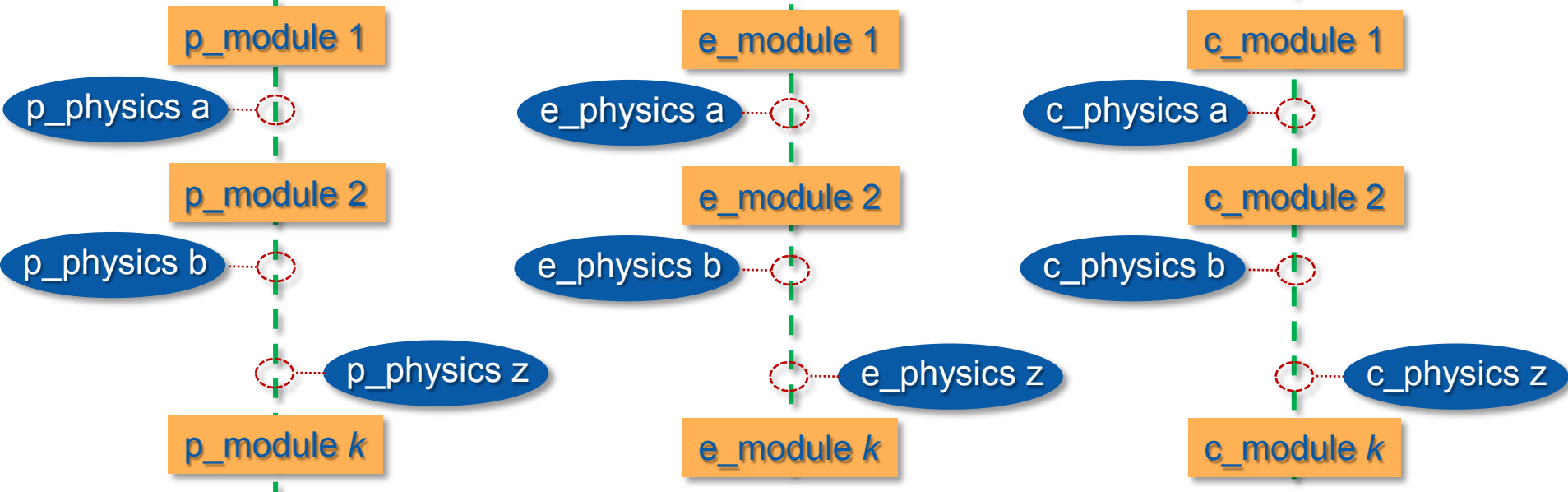
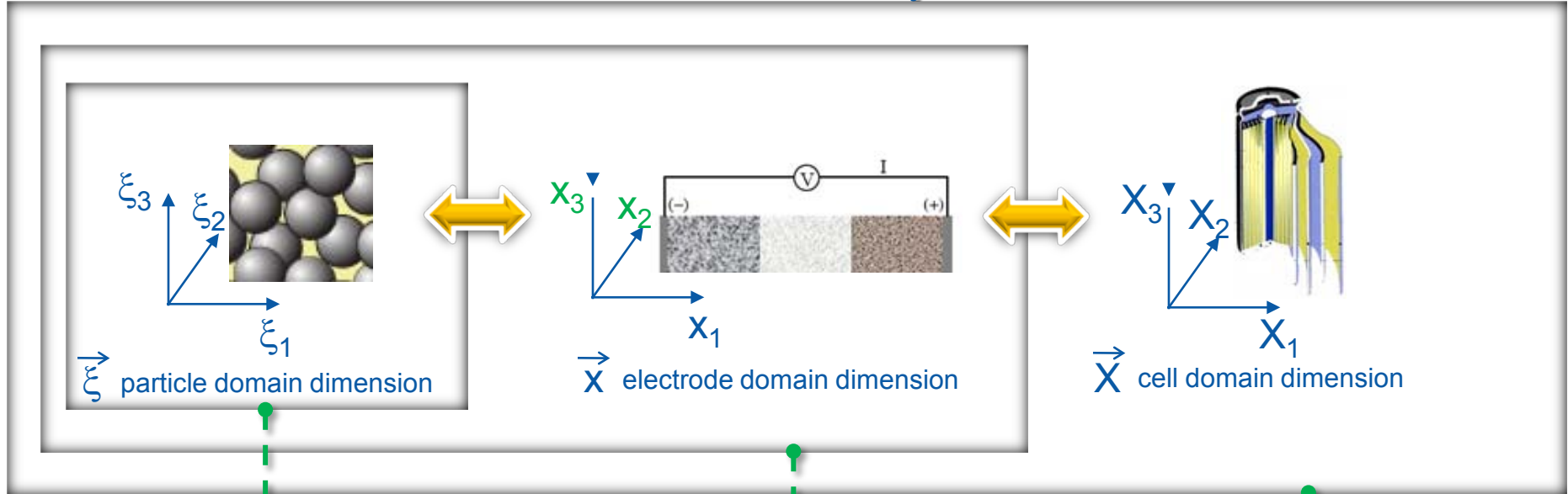
NREL's **Multi-Scale Multi-Dimensional Model Approach**



- Introduce **multiple computational domains** for corresponding length scale physics
- **Decouple geometries** between submodel domains
- **Couple physics** in two-way using predefined inter-domain information exchange
- Selectively resolve higher spatial resolution for smaller characteristic length scale physics
- Achieve high computational efficiency
- Provide flexible & expandable modularized framework

MSMD: Modularized Framework: *Flexible & Expandable*

The Model has Hierarchy Structure



Performance, Durability and Safety

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

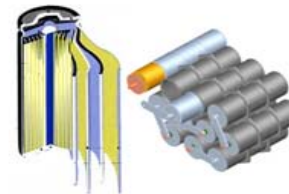
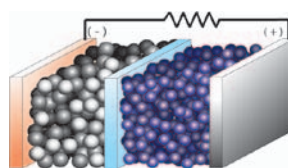
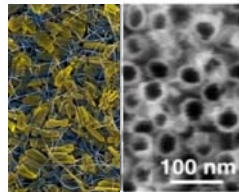
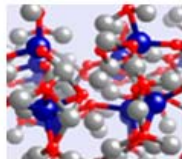
*Thermal/electrical inter-cell configuration
Thermal management
Safety control*

Atomic Scale

*Thermodynamic properties
Lattice stability
Material-level kinetic barrier
Transport properties*

System Scale

*System operating conditions
Environmental conditions
Control strategy*



10^{-10}

10^{-8}

10^{-6}

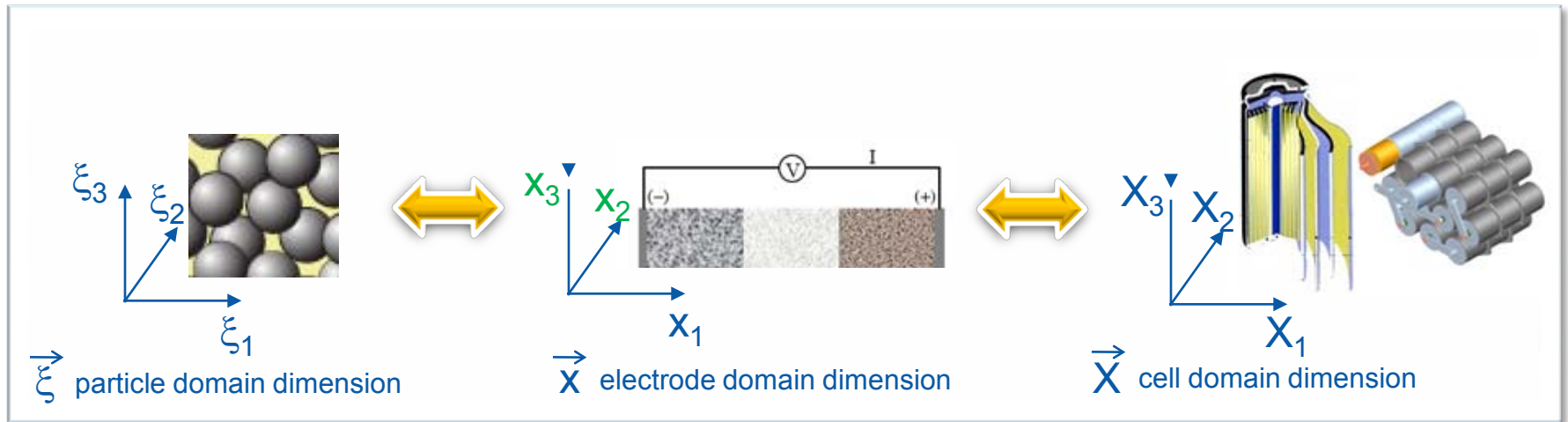
10^{-4}

10^{-2}

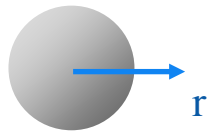
10^0

[m]

Model Prediction for a Large Stacked Prismatic Cell



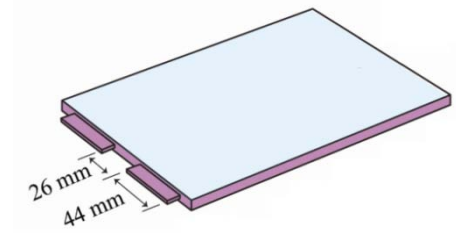
Sub-model Choice



1D spherical particle representation model



1D porous electrode model



3D SPPC model

Solution Method Choice

SVM

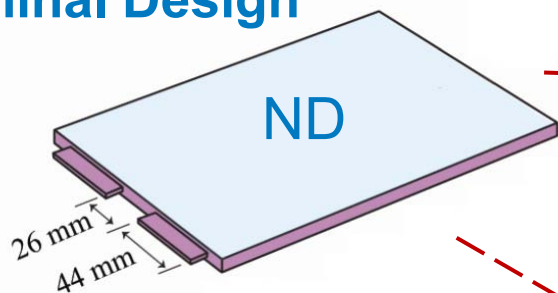
SVM

FVM

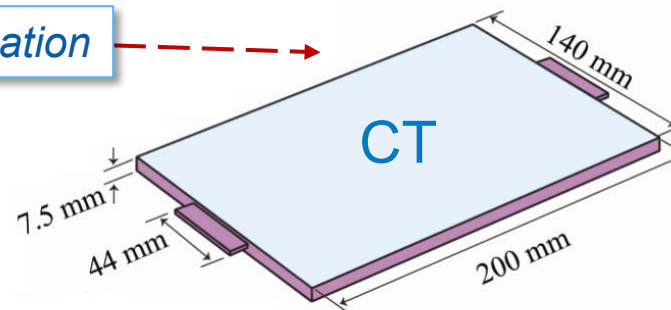
- ✓ Stacked prismatic design
- ✓ 200 x 140 x 7.5 mm³ form factor
- ✓ 20 Ah PHEV10 application
- ✓ Single side cooling 25W/m²K 25°C

Cell Design Evaluation

Nominal Design



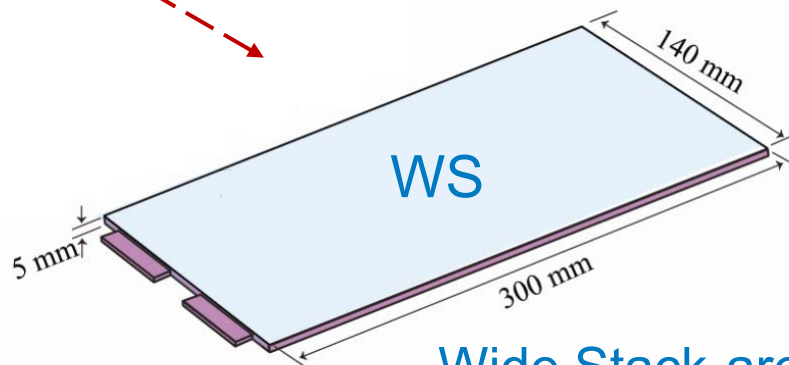
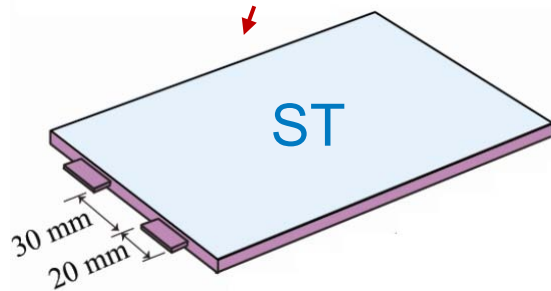
Counter Tab Design



Tab Location

Tab Size

Stack Area

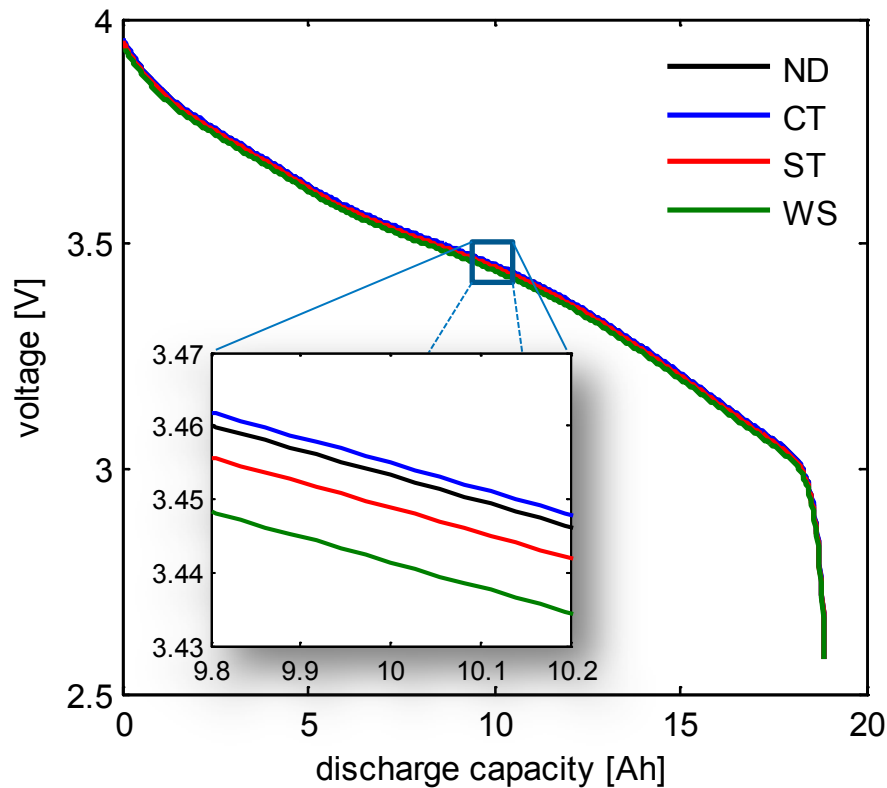
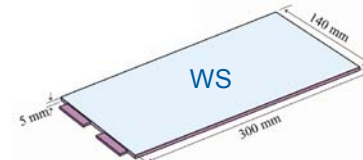
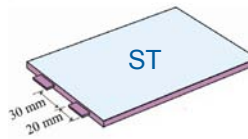
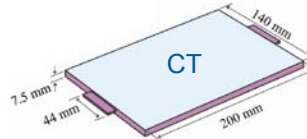
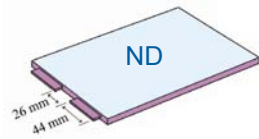


Small Tab Design

Wide Stack-area Design

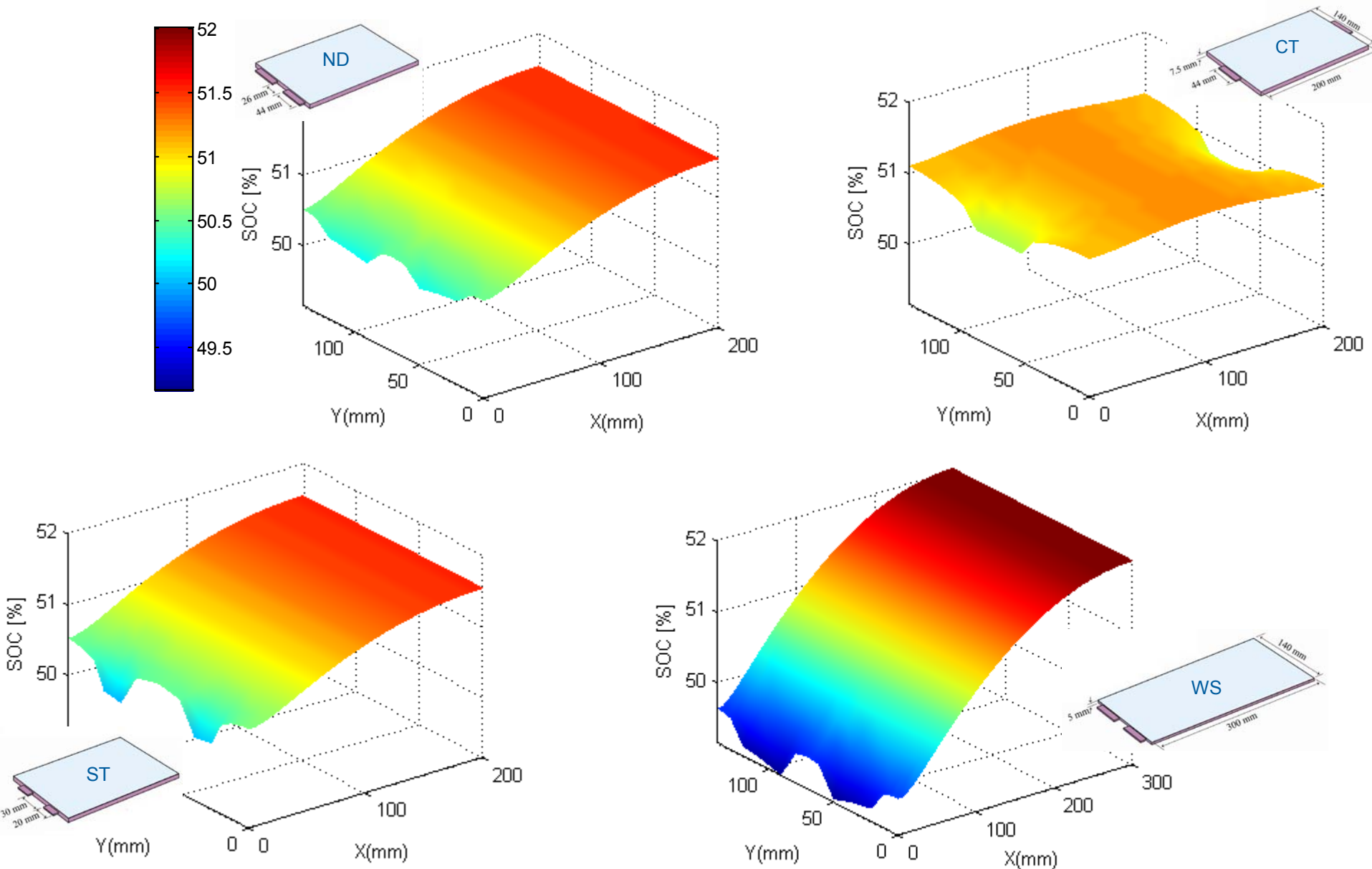
Case	Description	L_x [mm]	L_y [mm]	L_z [mm]	Tab width [mm]	Tab configuration
ND	Nominal design	200	140	7.5	44	Adjacent tabs
CT	Counter tab design	200	140	7.5	44	Counter tabs
ST	Small tab design	200	140	7.5	20	Adjacent tabs
WS	Wide stack-area design	300	140	5.0	44	Adjacent tabs

5C Discharge Voltage Response

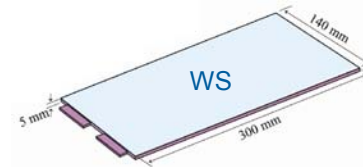
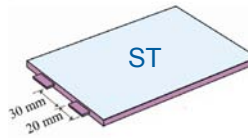
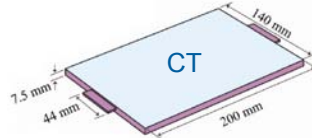
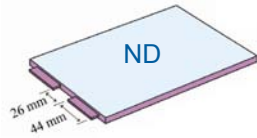


- Identical discharge capacity: 18.9 Ah at 5C
- Several mV difference in discharge voltage among the compared designs
- Tendency of a few millivolts voltage difference with design change cannot be easily confirmed by testing only

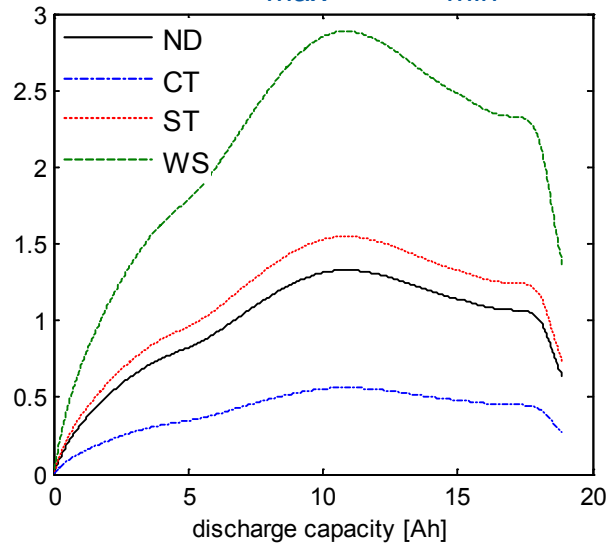
Cell Internal SOC Imbalance



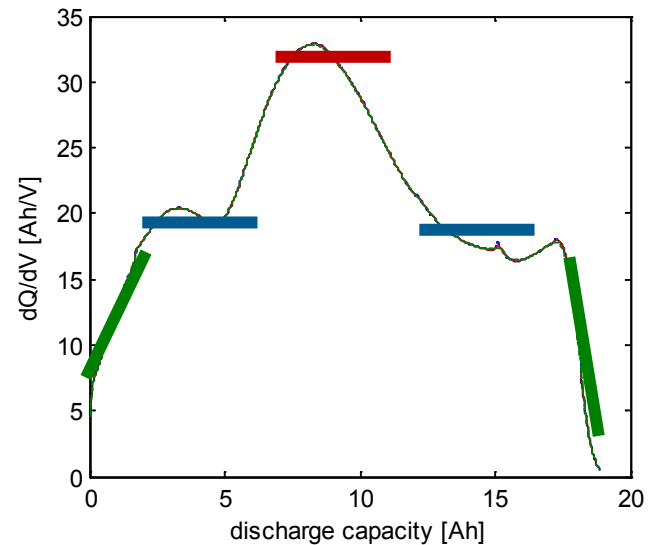
SOC Deviation during Discharge



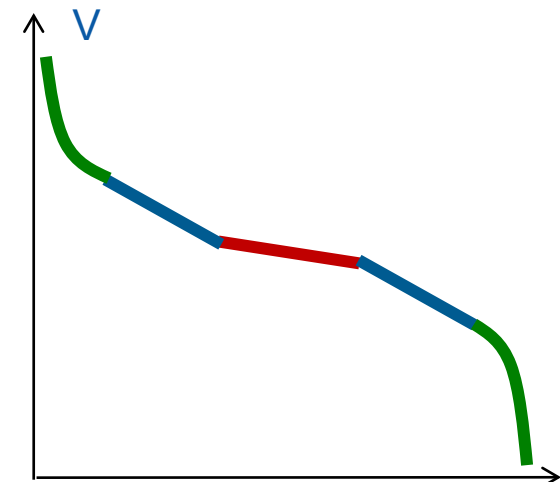
$\text{SOC}_{\max} - \text{SOC}_{\min}$



dQ/dV



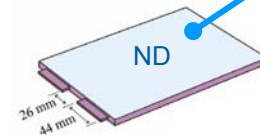
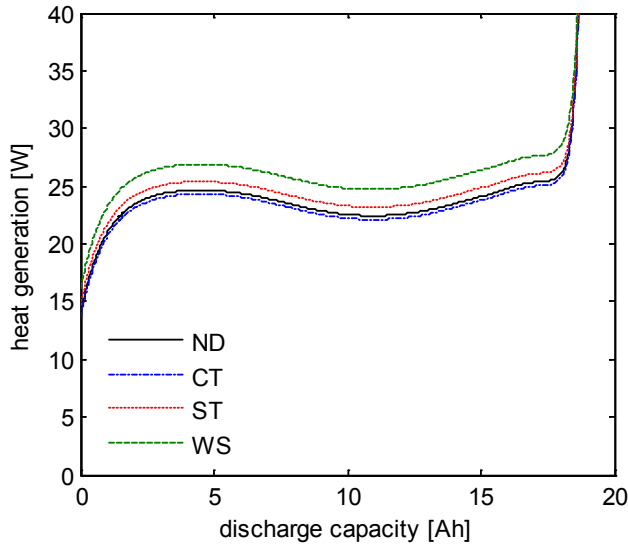
V



- Results imply that
 - ✓ Flat voltage slope would promote cell internal SOC imbalance
 - ✓ HEV cycling at “flat section” would cause larger internal imbalance
- Modifying thermodynamics vs Optimizing electrical/thermal configuration

Thermal Response during Discharge

Total Heat Generation



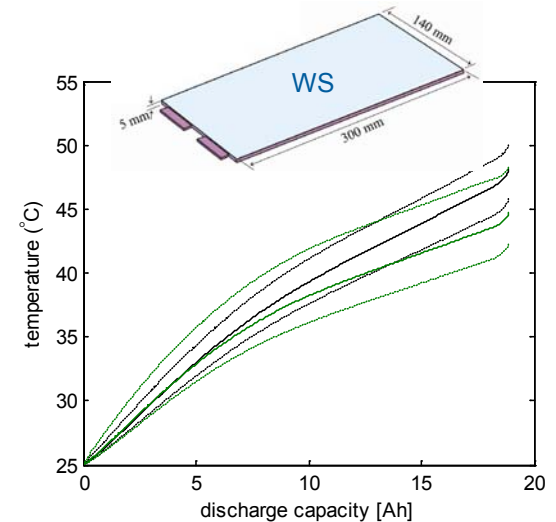
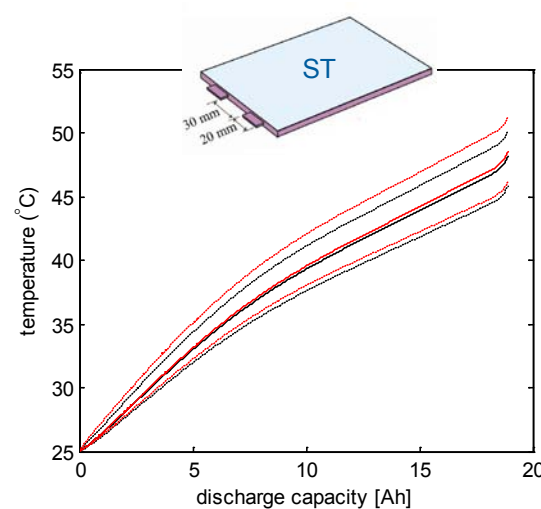
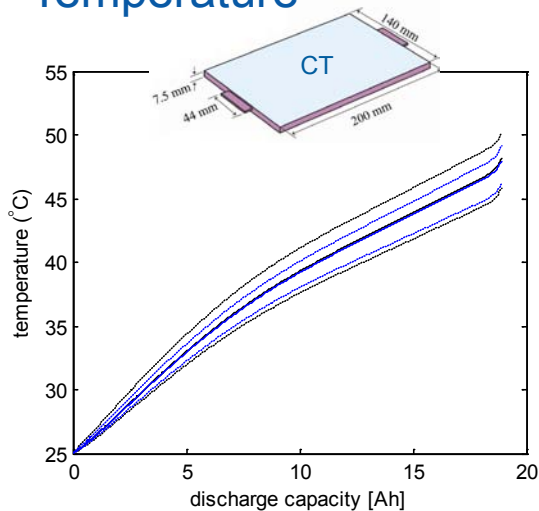
Single side cooling on top surface

✓ With $h = 25 \text{ W/m}^2\text{K}$

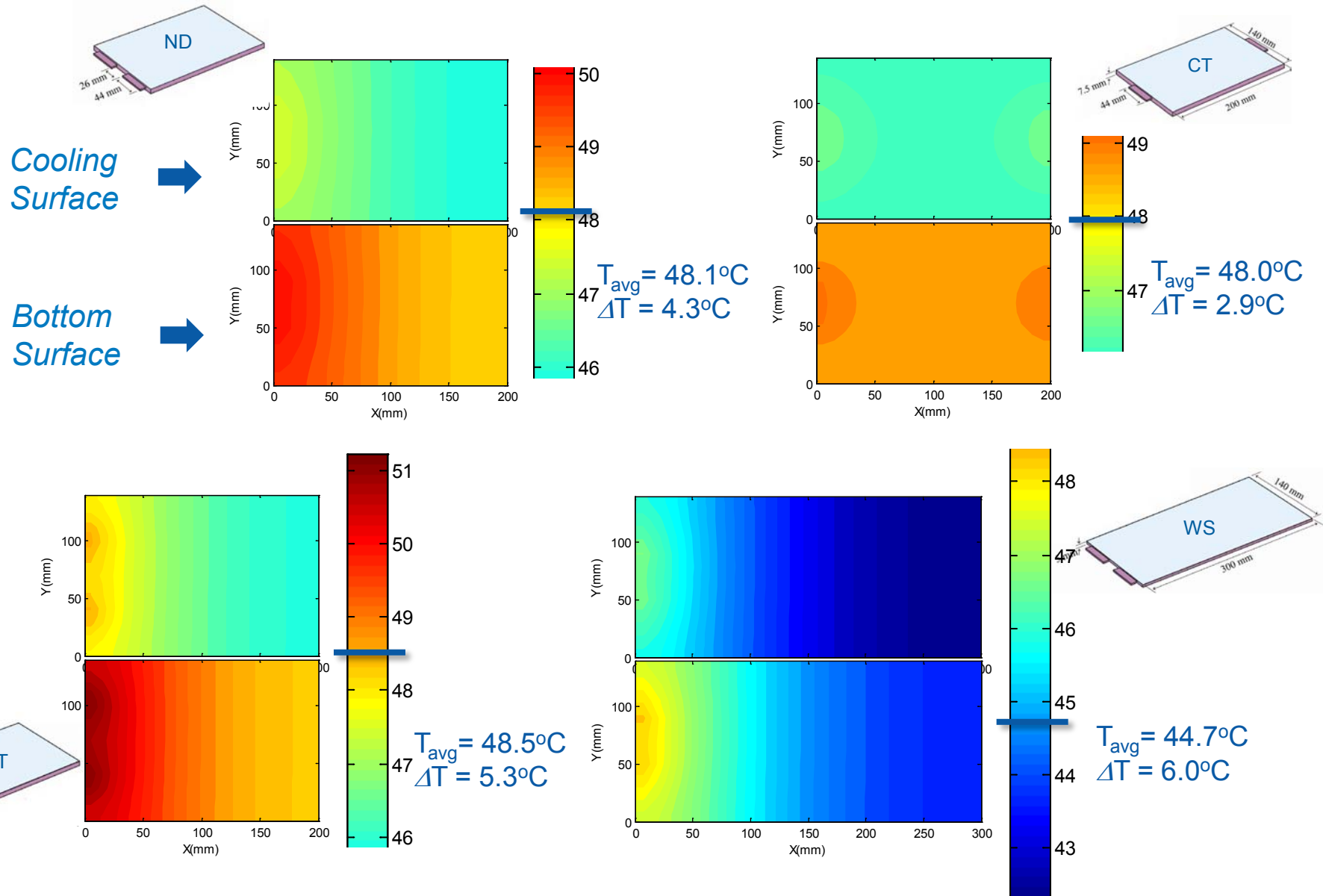
✓ At $T_{amb} = 25 \text{ }^\circ\text{C}$

- Similar average temperatures: ND, CT, ST
- Smaller ΔT at CT
- Larger ΔT at ST
- Heat generation is highest with WS, but the EOD average T is lowest

Temperature

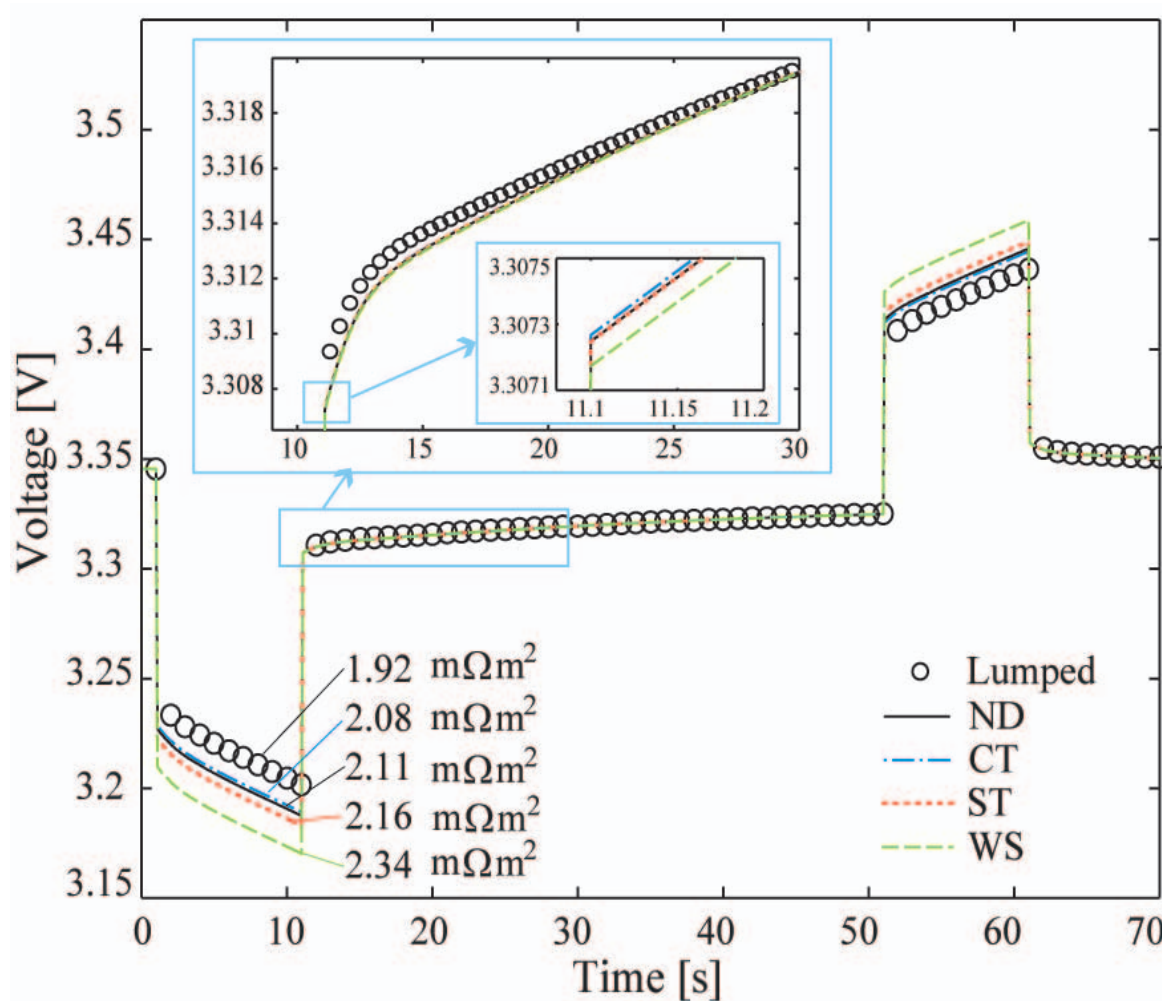


Temperature Imbalance at EOD



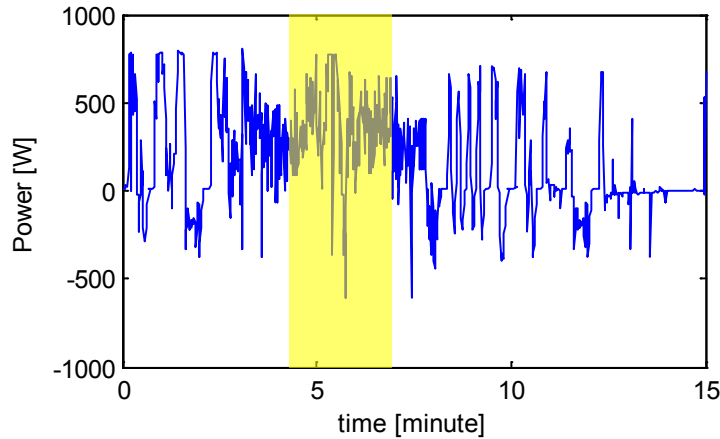
Pulse Power Response Comparison

- HPPC at 20% SOC at 25°C initial temperature



Vehicle Use Evaluation

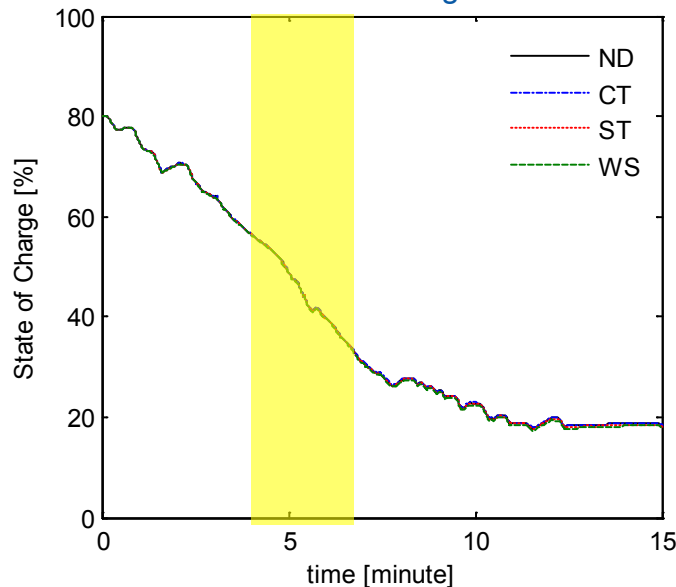
Battery Power per Cell



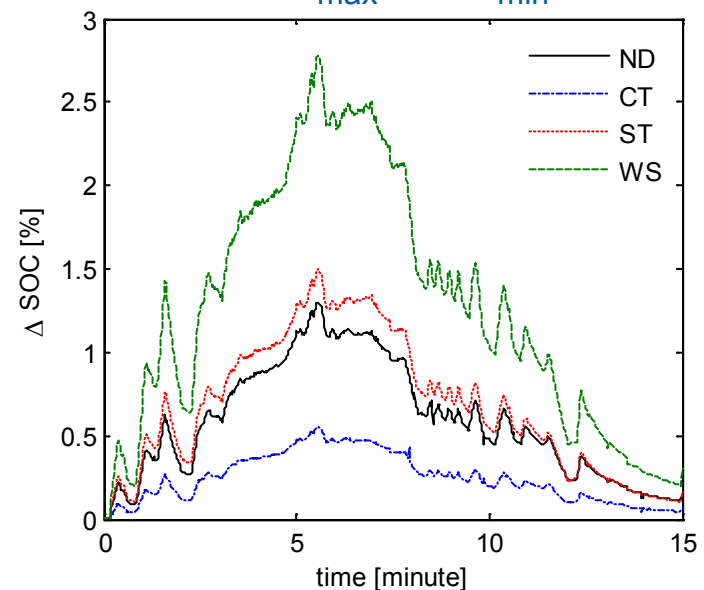
- PHEV10 mid-size sedan
- 15 minutes US06 Driving Profile
- Battery power from Vehicle simulation

Thermodynamics + Cell Design + System Control

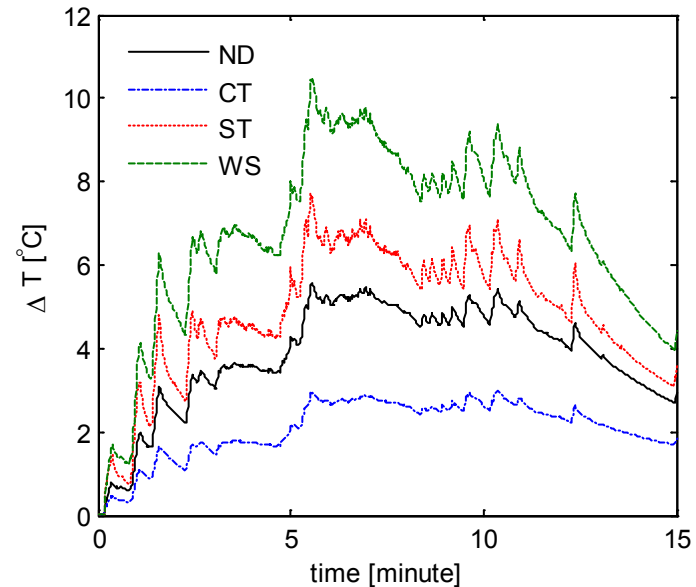
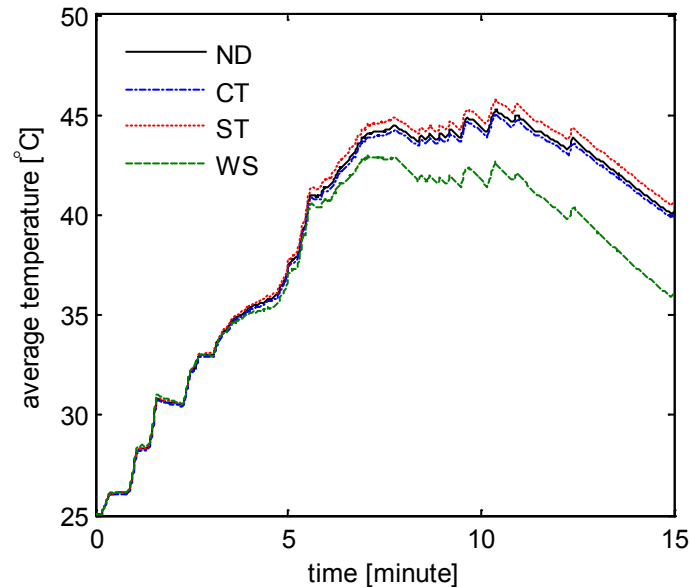
SOC_{avg}



SOC_{max}-SOC_{min}



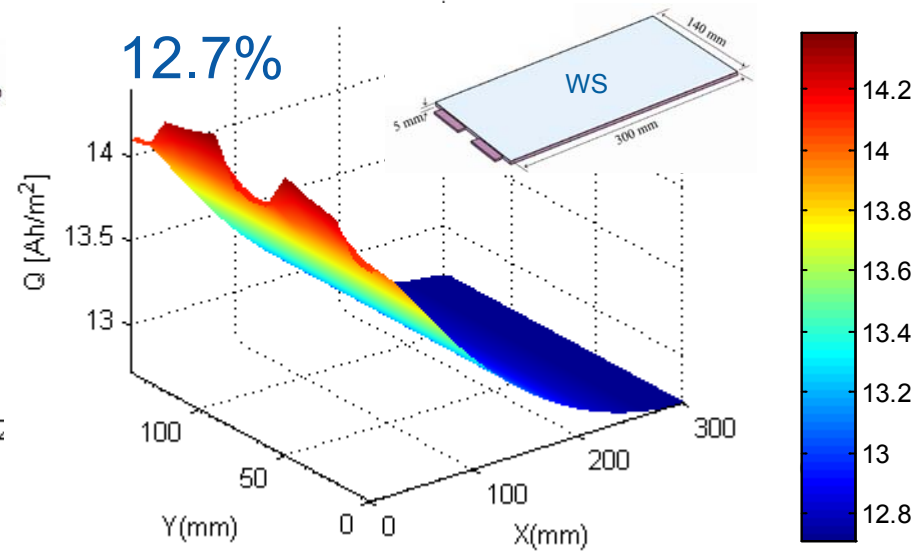
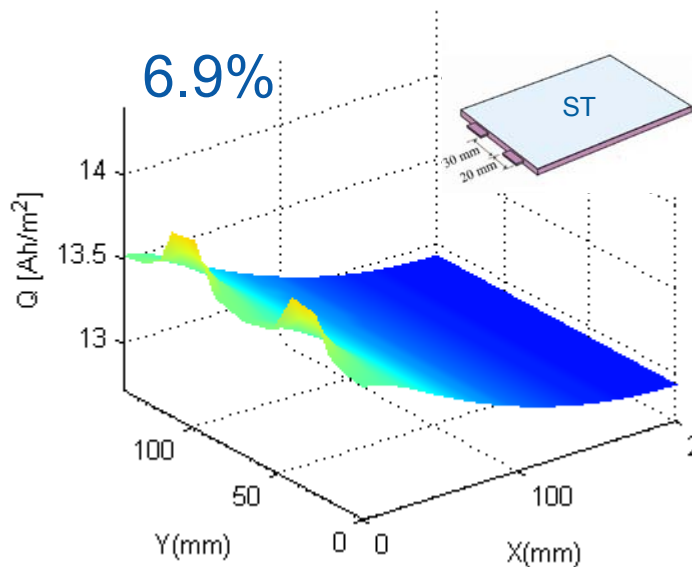
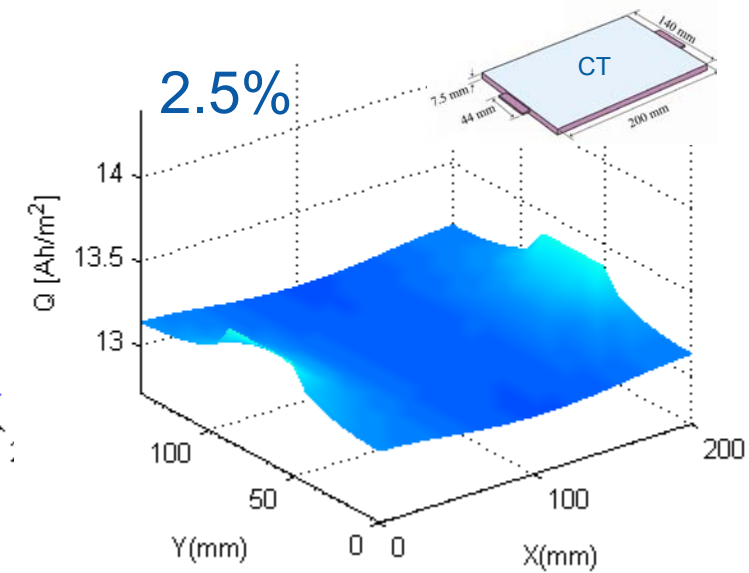
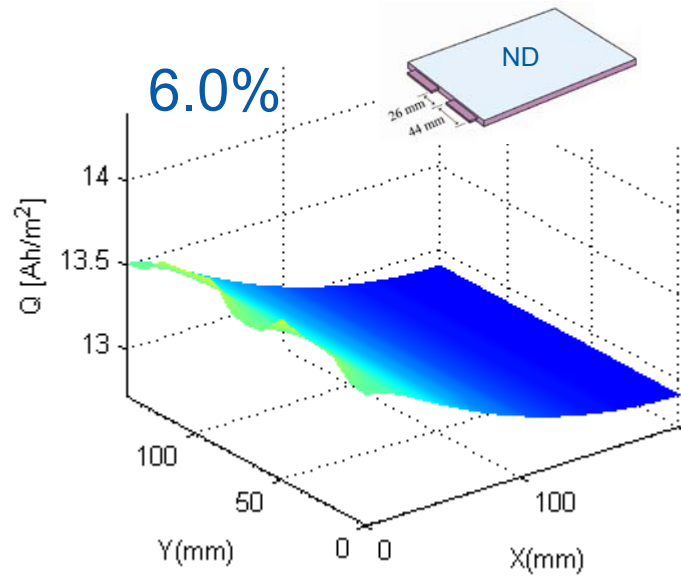
Thermal Response during Driving



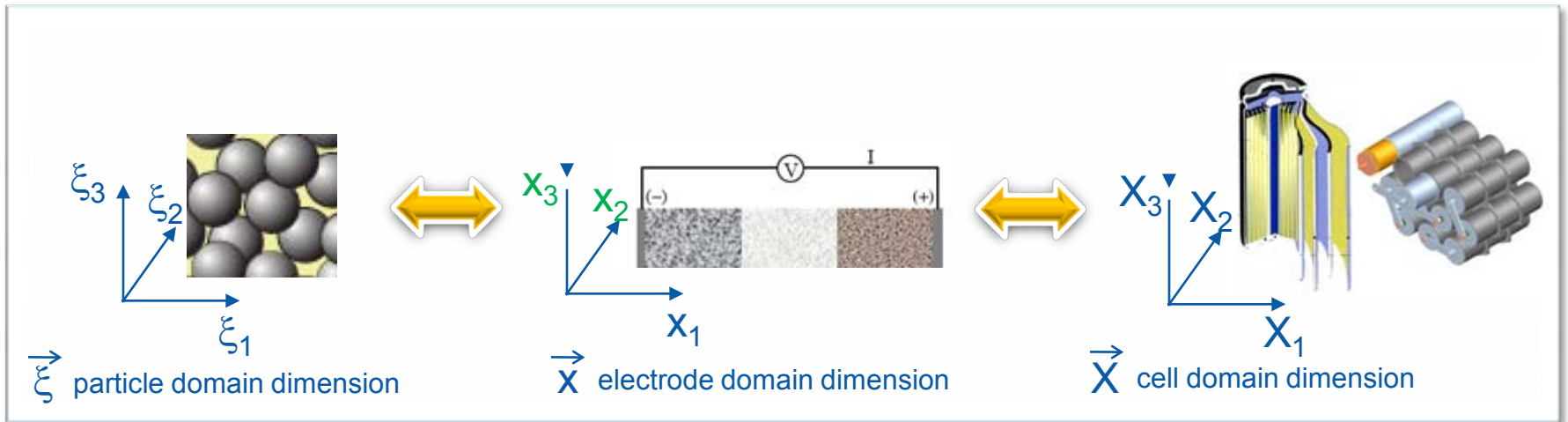
- Similar average temperatures: ND, CT, ST
- Smaller ΔT at CT
- Larger ΔT at ST
- WS: lower average T during CS mode drive, but significant ΔT

Cell Internal Kinetics Non-Uniformity

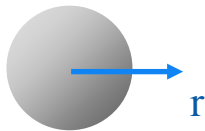
- Ah Throughput
- PHEV10
- 15min US06



Model Prediction for a **Spirally Wound Cylindrical Cell**



Sub-model Choice



1D spherical particle representation model



1D porous electrode model



3D SWC model

Solution Method Choice

SVM

SVM

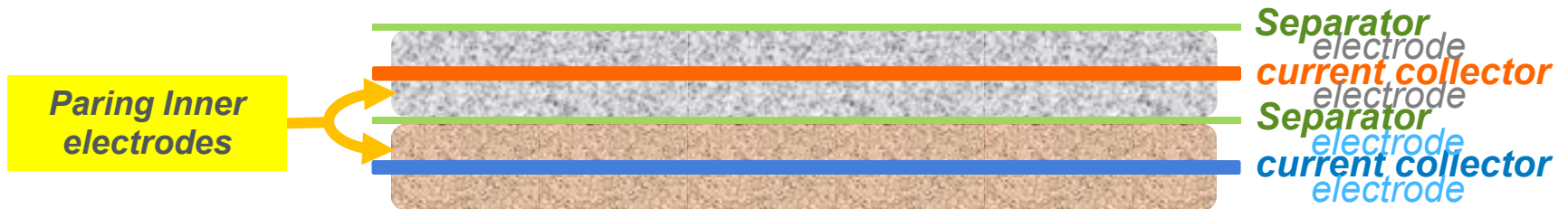
FVM

- ✓ Spirally wound cell design
- ✓ D40, H100 mm form factor
- ✓ 10 Ah PHEV10 application

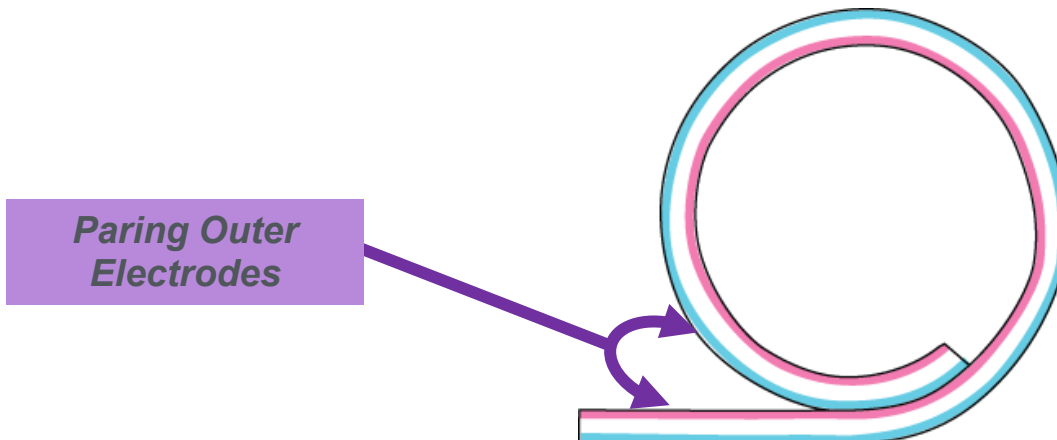
Spirally Wound Cell (SWC) Model

- Spirally Wound Cell :**
- One pair of **wide** current collector foils
 - Two pairs of **wide** electrode layers
 - Complex electrical configuration

Stacking process: Forming a pair between inner electrodes



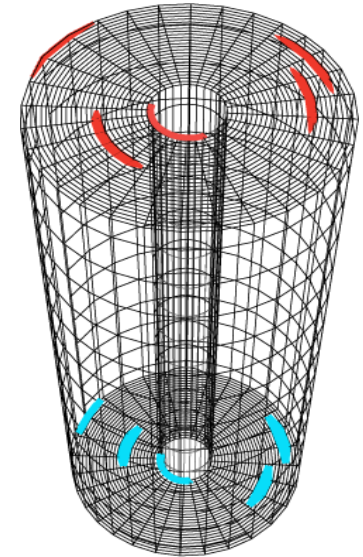
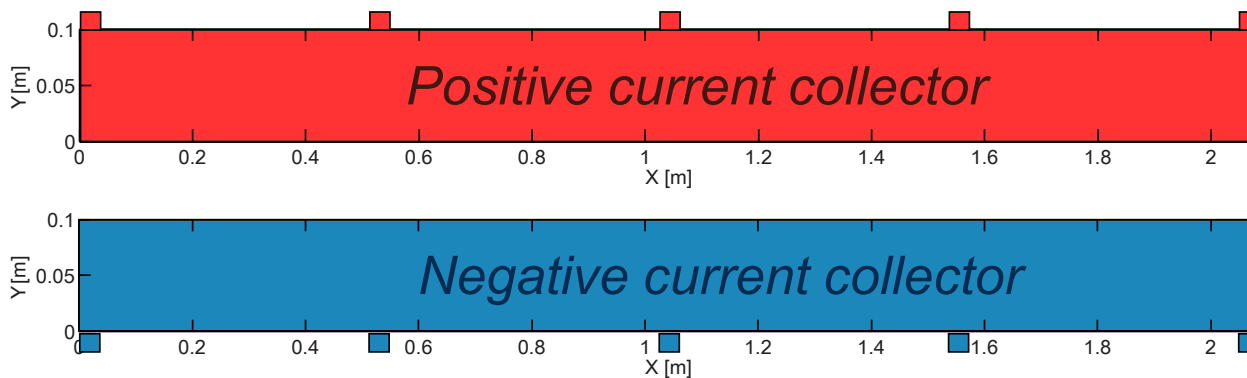
Winding process: Forming a second pair between outer electrodes



Model Case

- ✓ Diameter 40mm, inner diameter 8mm, height 100 mm form factor
- ✓ Positive tabs on the top side, negative tabs on the bottom side
- ✓ 10 Ah capacity

Tab locations for 5 tab case



Tab configuration of each electrode pairs

5C constant current discharge

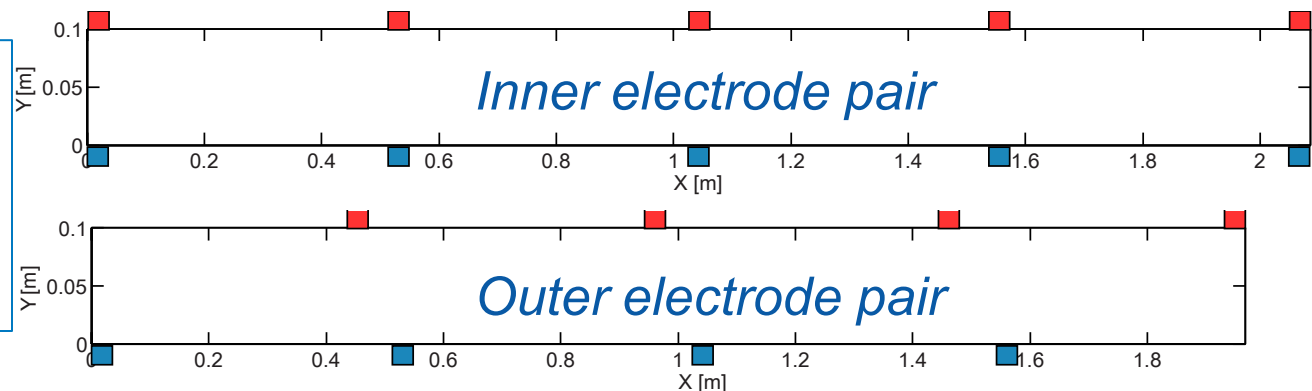
$\text{soc}_{ini} = 90\%$

Natural convection :

$h_{inf} = 5 \text{ W/m}^2\text{K}$

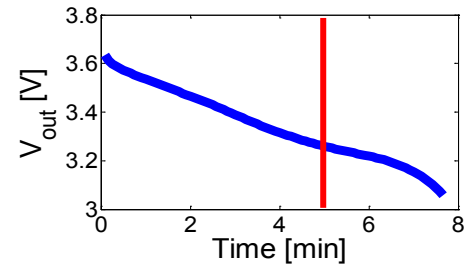
$T_{amb} = 25^\circ\text{C}$

$T_{ini} = 25^\circ\text{C}$



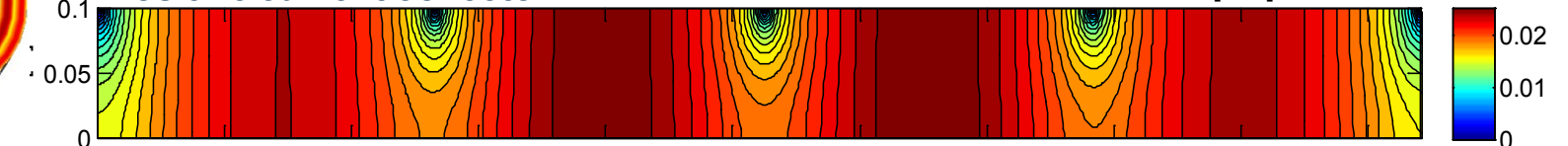
SWC Model Results

- 5 tabs in each current collector
- 5 min after 5C discharge

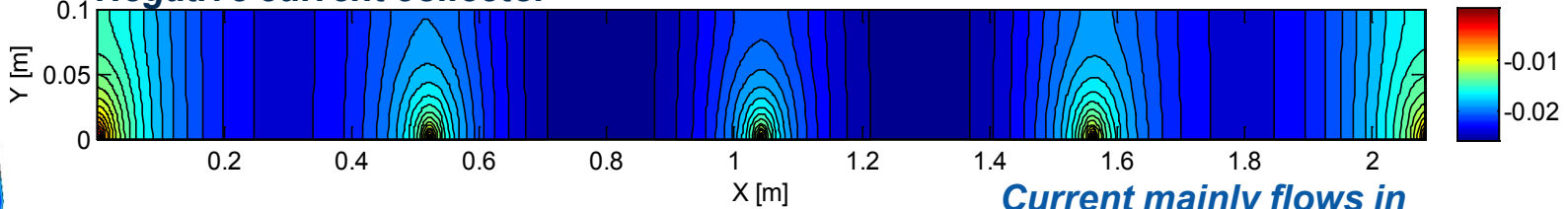


Electric potential

Positive current collector



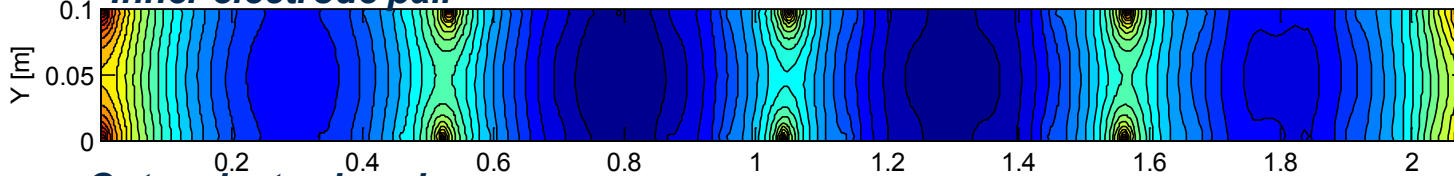
Negative current collector



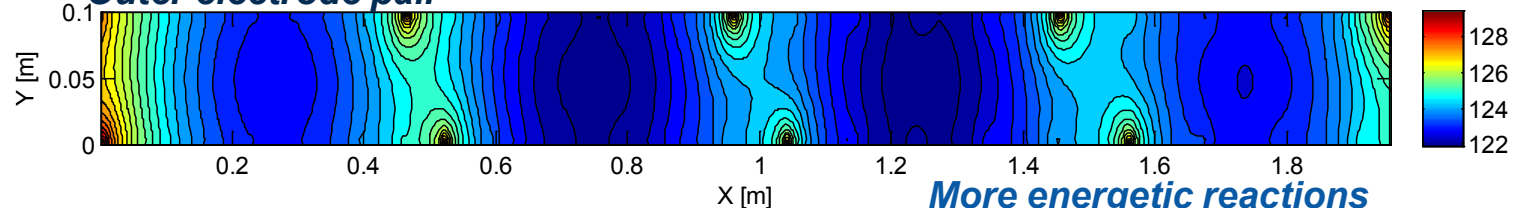
Current mainly flows in the winding direction

Electrochemical reaction rate

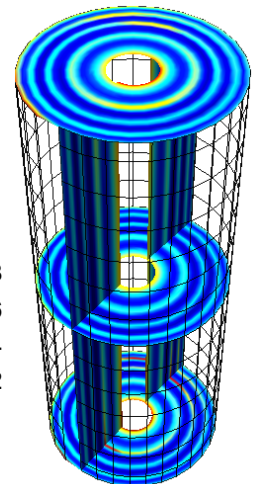
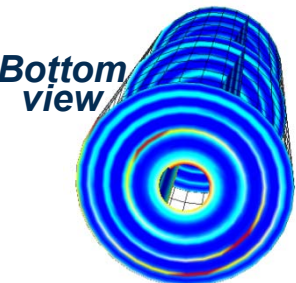
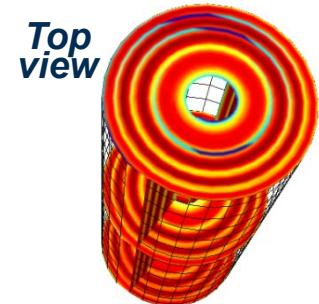
Inner electrode pair



Outer electrode pair

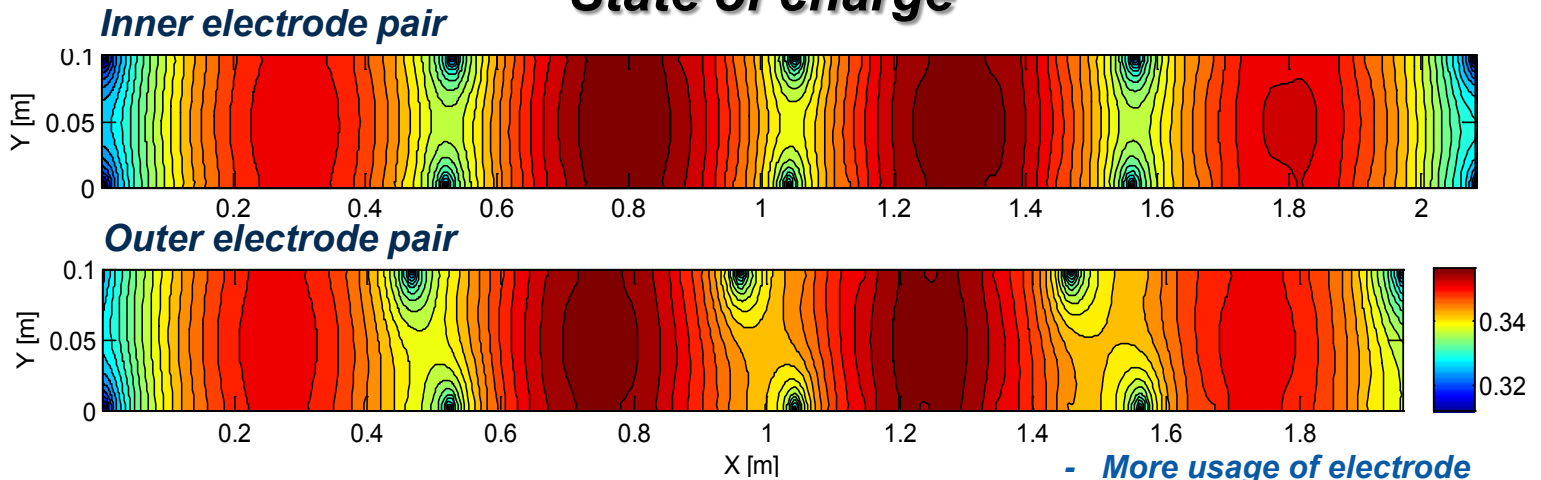
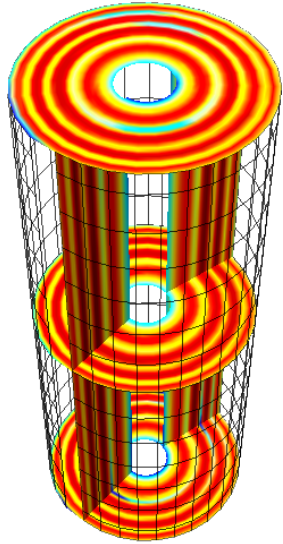


More energetic reactions near tabs



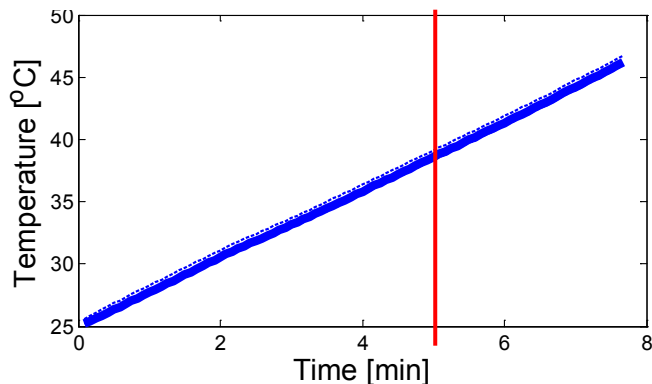
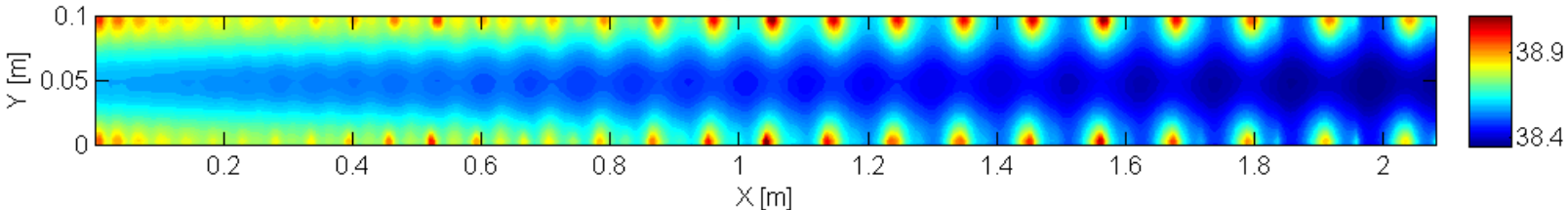
SWC Model Results

State of charge

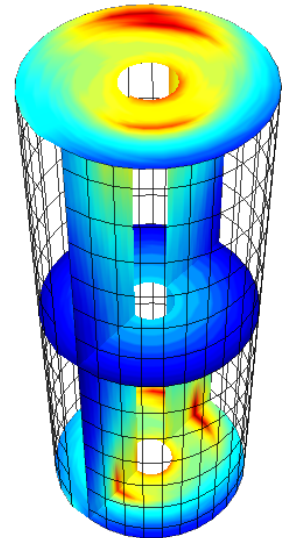


- More usage of electrode near tabs

Temperature

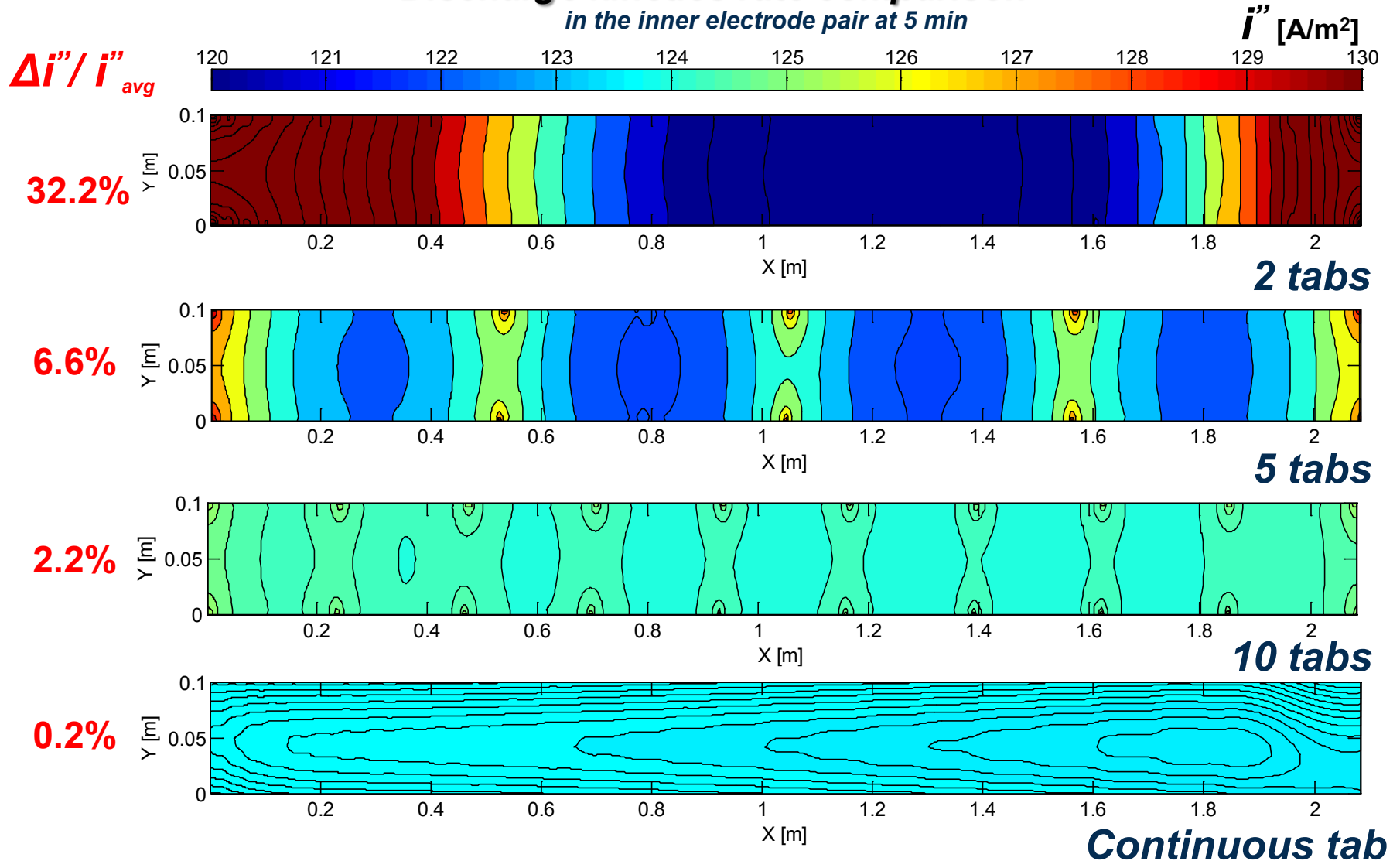


- High rate of discharge with a moderate heat transfer condition
- Heat generation dominates temperature distribution in the system
- Temperature difference in the system is relatively small

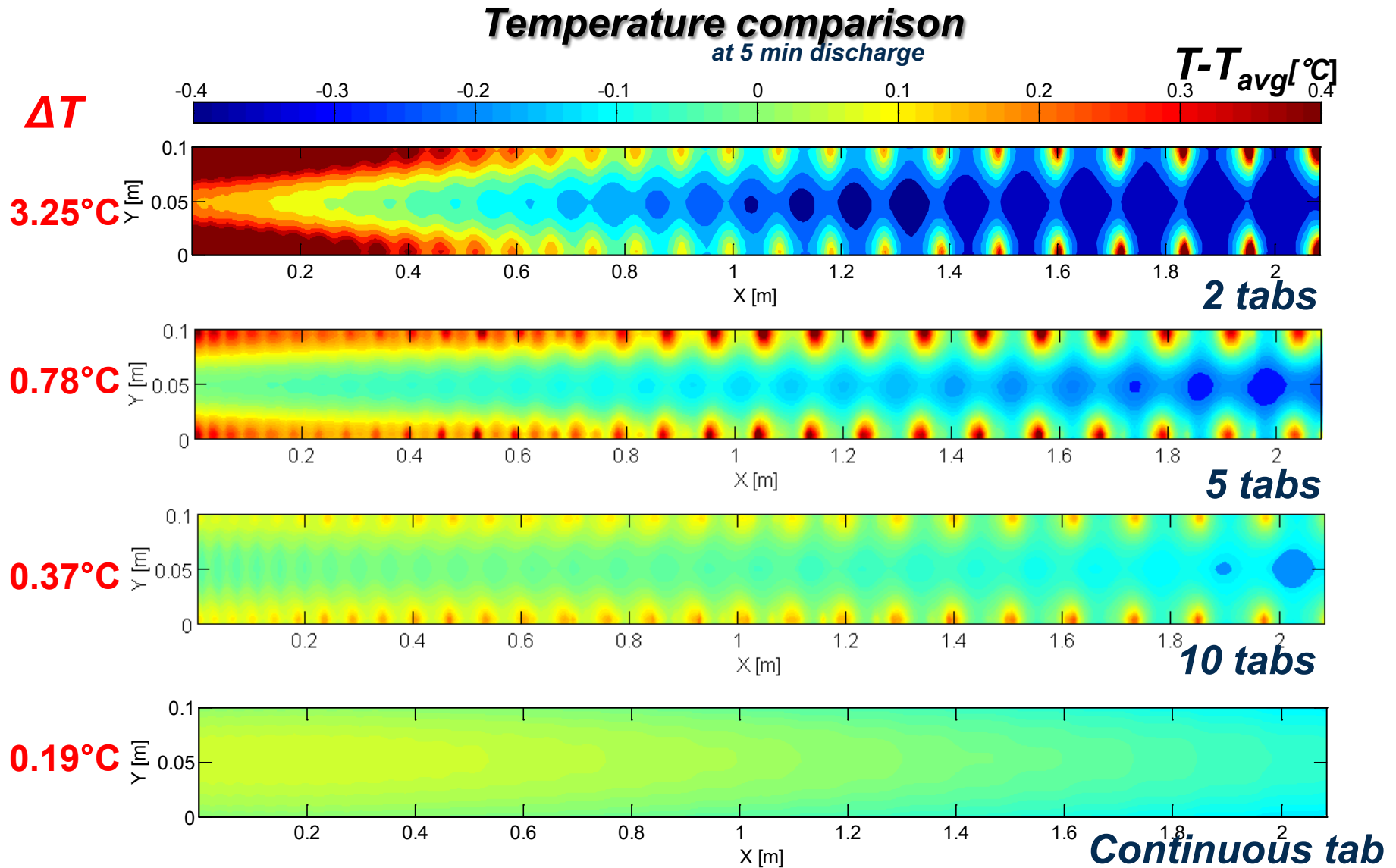


Impact of # of tabs - Discharge Kinetics

Discharge kinetics rate comparison in the inner electrode pair at 5 min

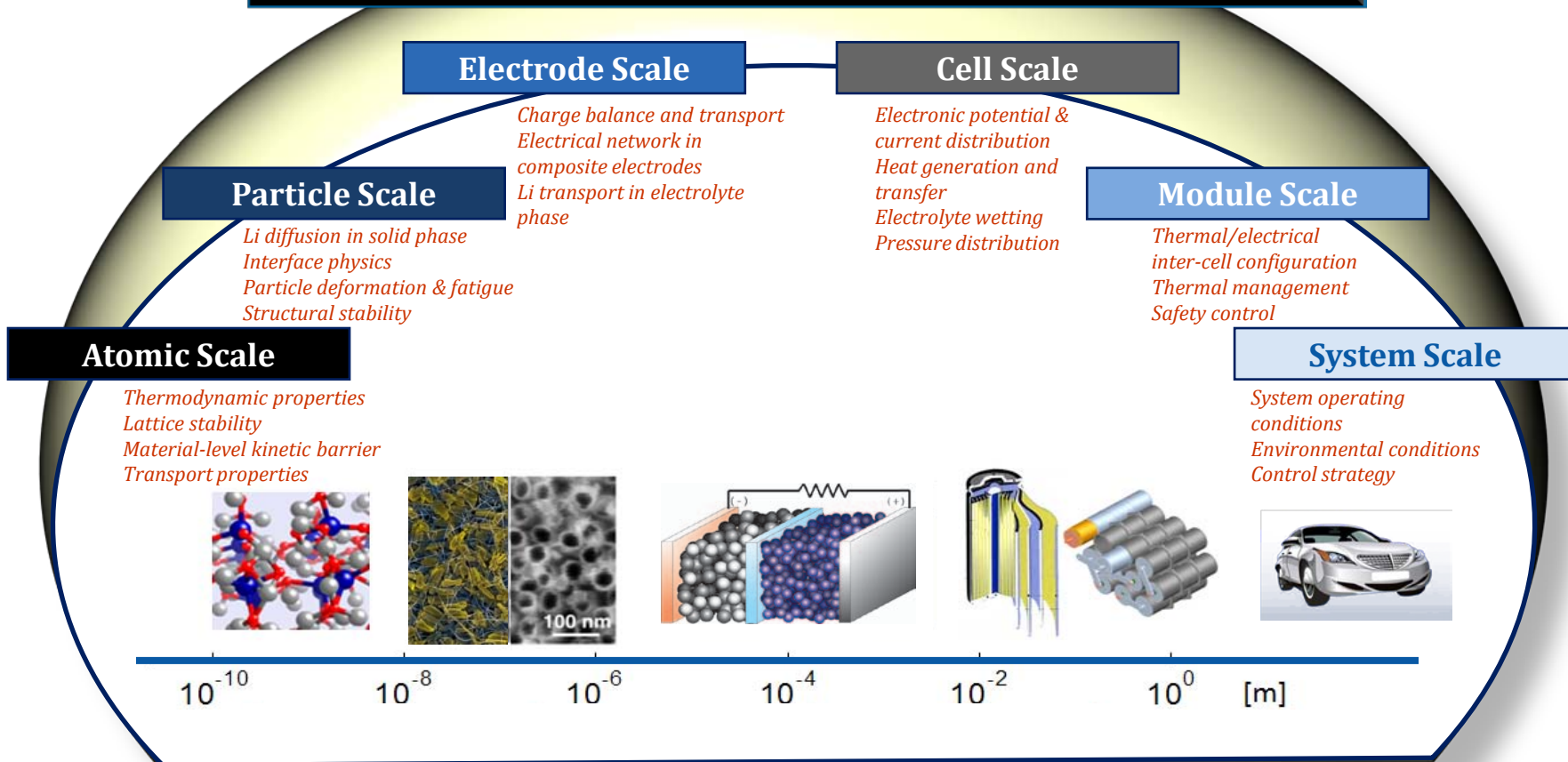


Impact of # of tabs - Temperature

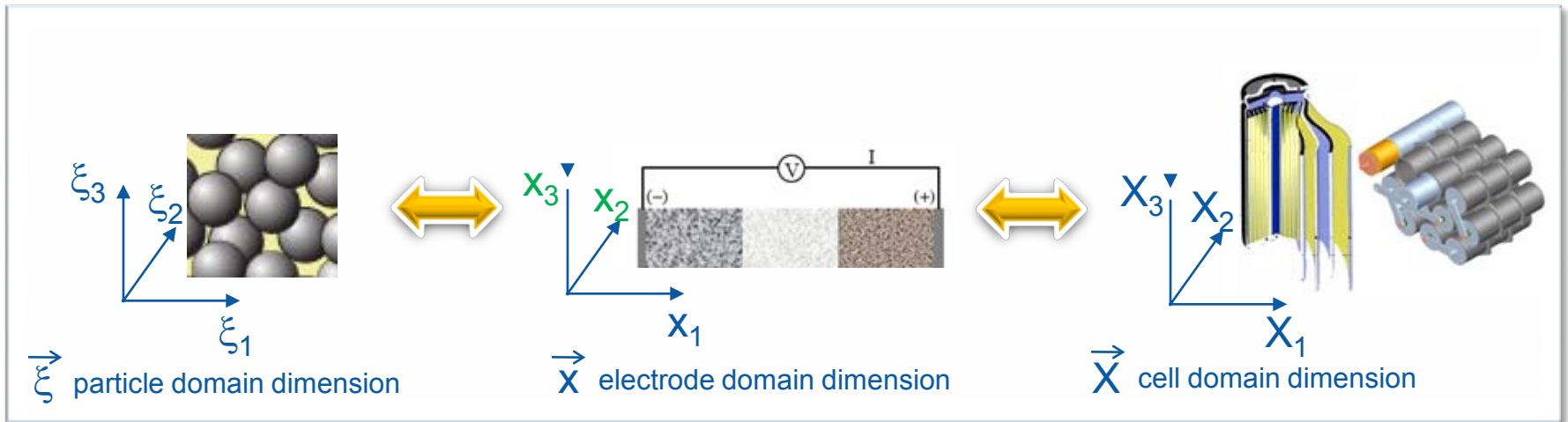


Performance, Durability and Safety

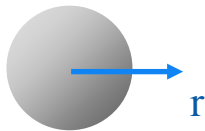
Physics of Li-Ion Battery Systems in Different Length Scales



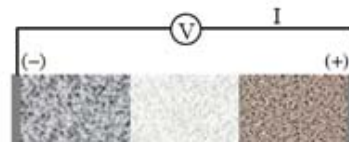
Model Prediction for Cylindrical Cell Degradation



Sub-model Choice



1D spherical particle representation model



1D porous electrode model
+ empirical life model



2D SPPC model

Solution Method Choice

SVM

SVM

FVM

- ✓ Spirally wound cell design
- ✓ D40, H100 mm form factor
- ✓ 10 Ah PHEV10 application

Life Modeling Approach

NCA datasets fit with empirical, yet physically justifiable formulas

Calendar fade

- SEI growth (partially suppressed by cycling)
- Loss of cyclable lithium
- $a_1, d_1 = f(\Delta DOD, T, V)$

Cycling fade

- active material structure degradation and mechanical fracture
- $a_2, e_1 = f(\Delta DOD, T, V)$

Resistance Growth

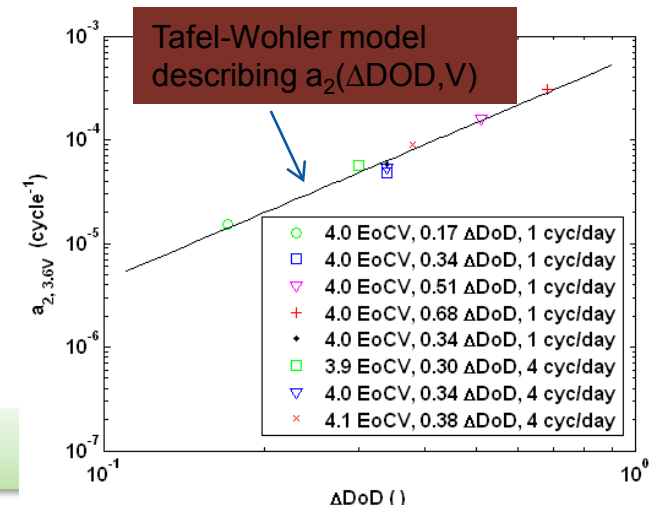
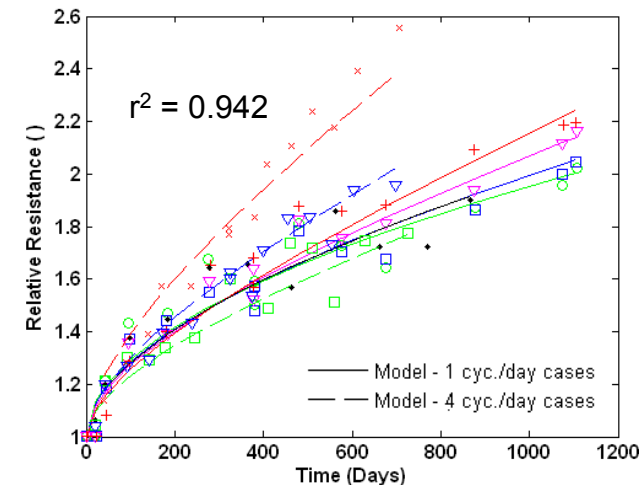
$$R = a_1 t^{1/2} + a_2 N$$

Relative Capacity

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

$$Q_{Li} = d_0 + d_1 t^{1/2}$$

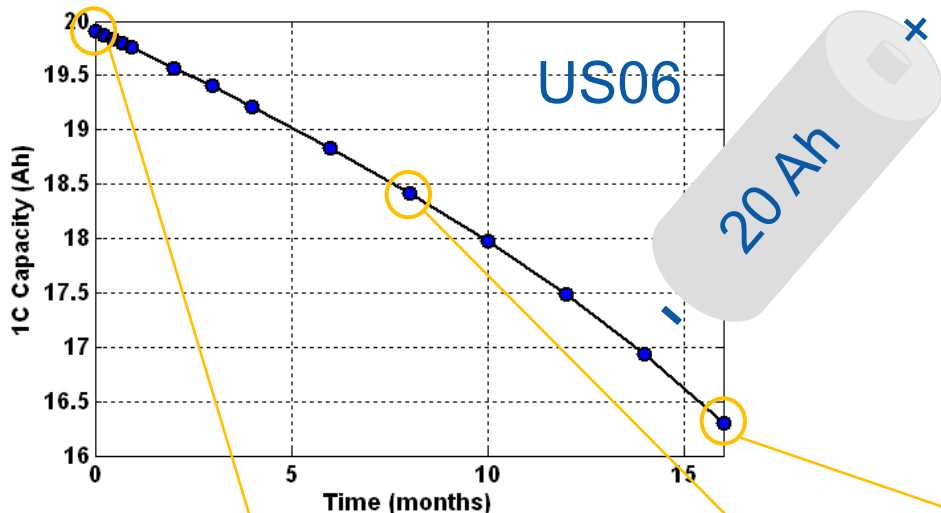
$$Q_{active} = e_0 + e_1 N$$



•Data shown above: J.C. Hall, IECEC, 2006.
•Model also fit to DOE/TLVT, Southern CA Edison & NASA data

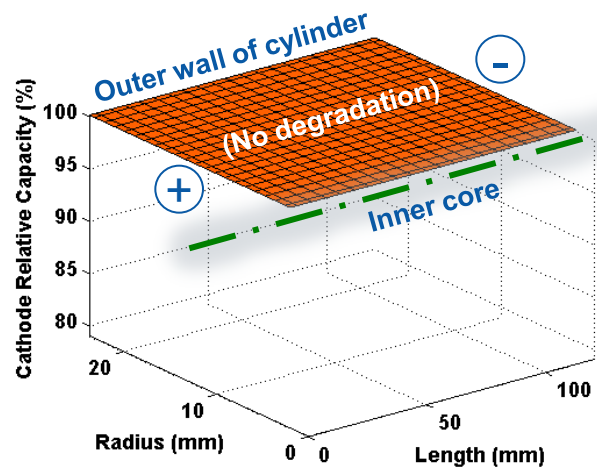
- Portability + Physical interpretation
- Applicable to complex real-world storage and cycling scenarios

US06 – Nonuniform Capacity Loss

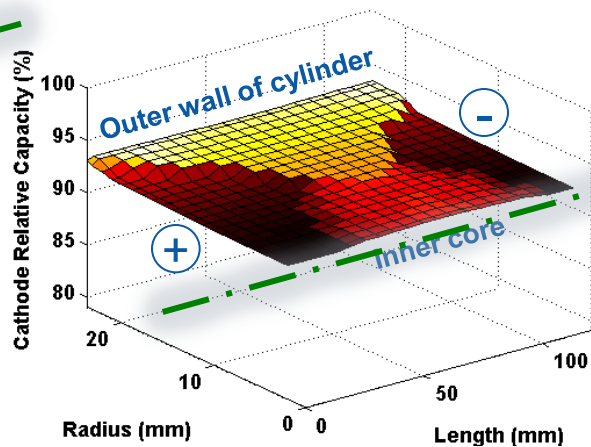


- Regions near terminals suffer most significant capacity loss
Large overpotential → Excessive cycling
- Inner core loses capacity faster than outer cylinder wall
High temperature → Material degradation

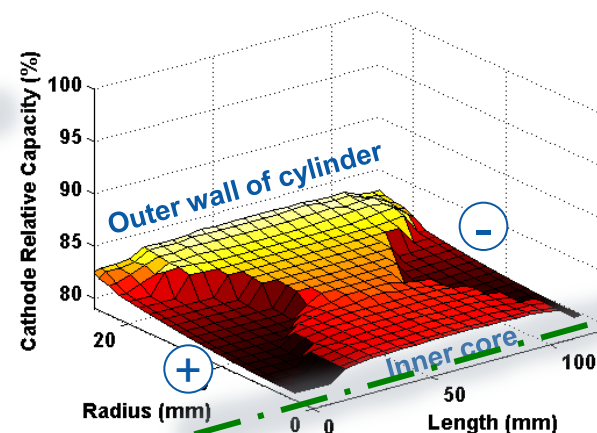
0 months:



8 months:



16 months:



US06 – Ah Imbalance (Nonuniform Cycling)

*Preferentially cycled regions shift early in life
Imbalance continually grows throughout life*

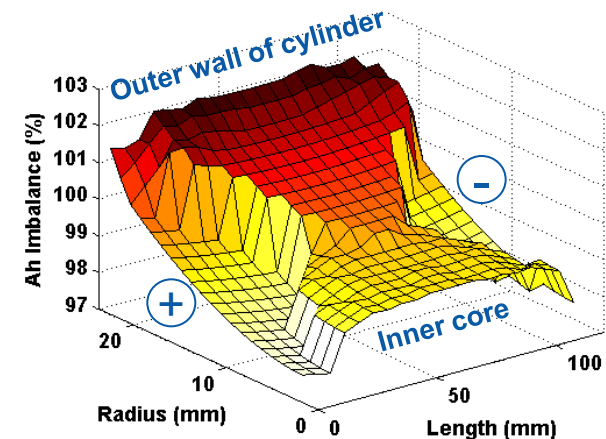
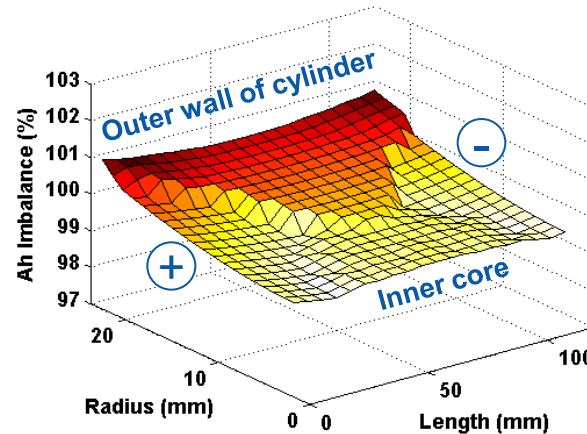
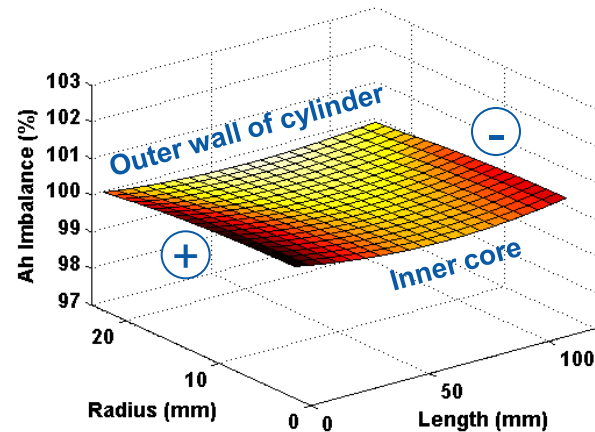
0 months:
0.7% Ah Imbalance



8 months:
1.7% Ah Imbalance



16 months:
4.8% Ah Imbalance

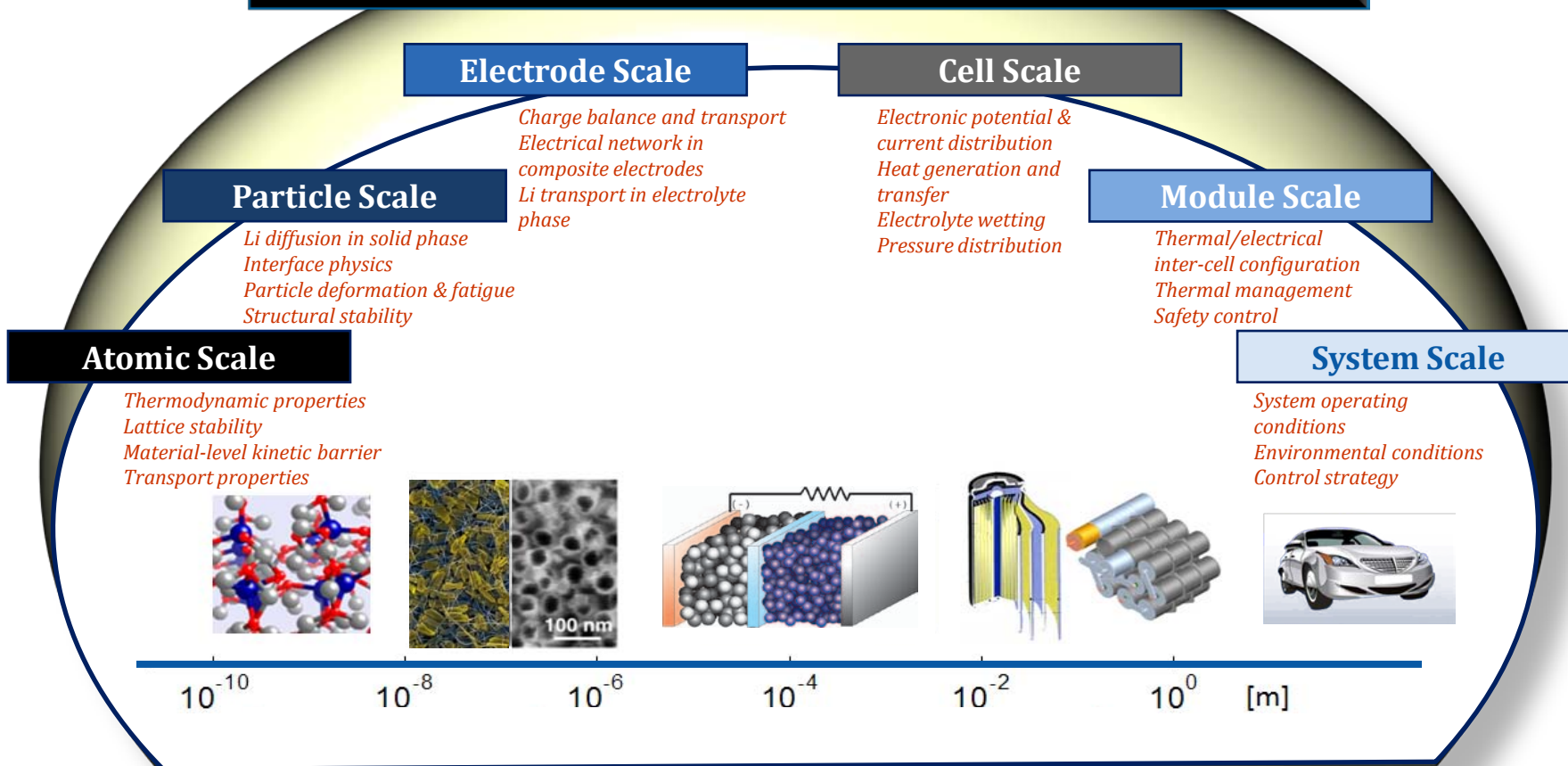


- Early in life, inner core and terminal areas are cycled the most

- Later in life, those same areas are most degraded and are cycled least

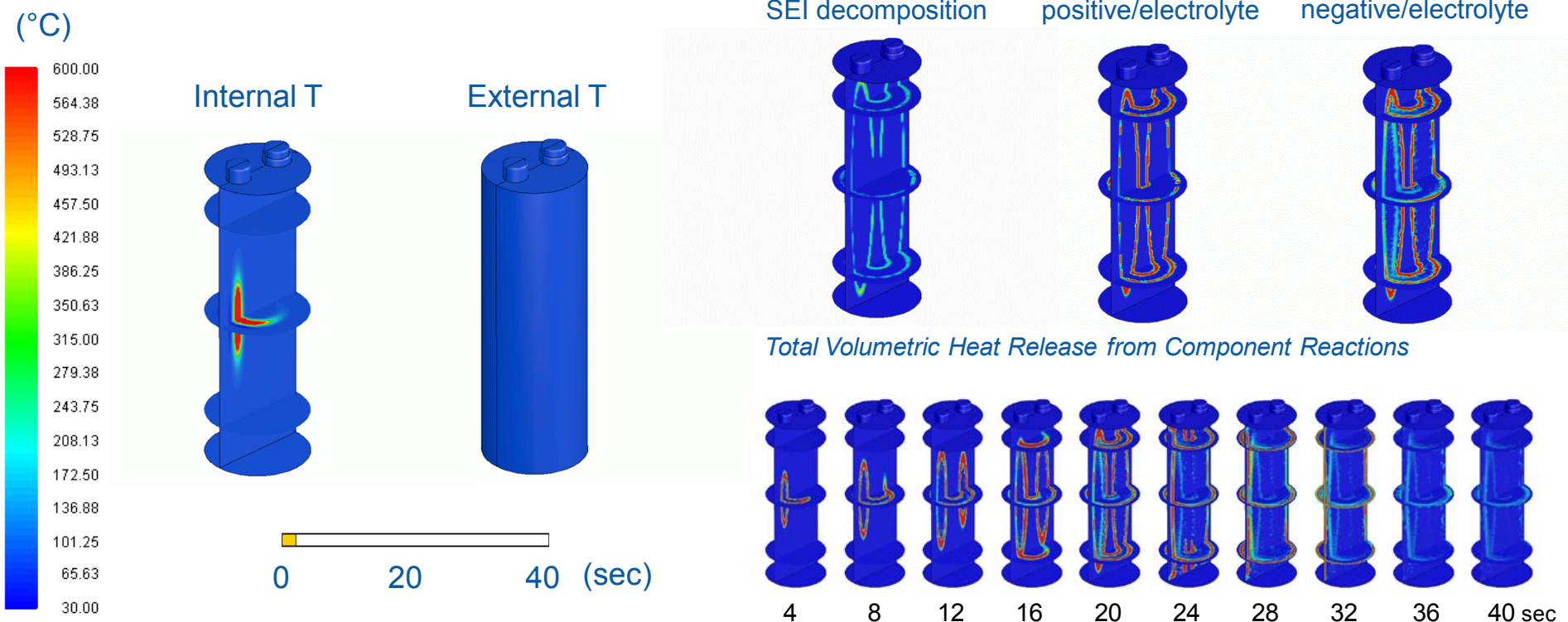
Performance, Durability and Safety

Physics of Li-Ion Battery Systems in Different Length Scales



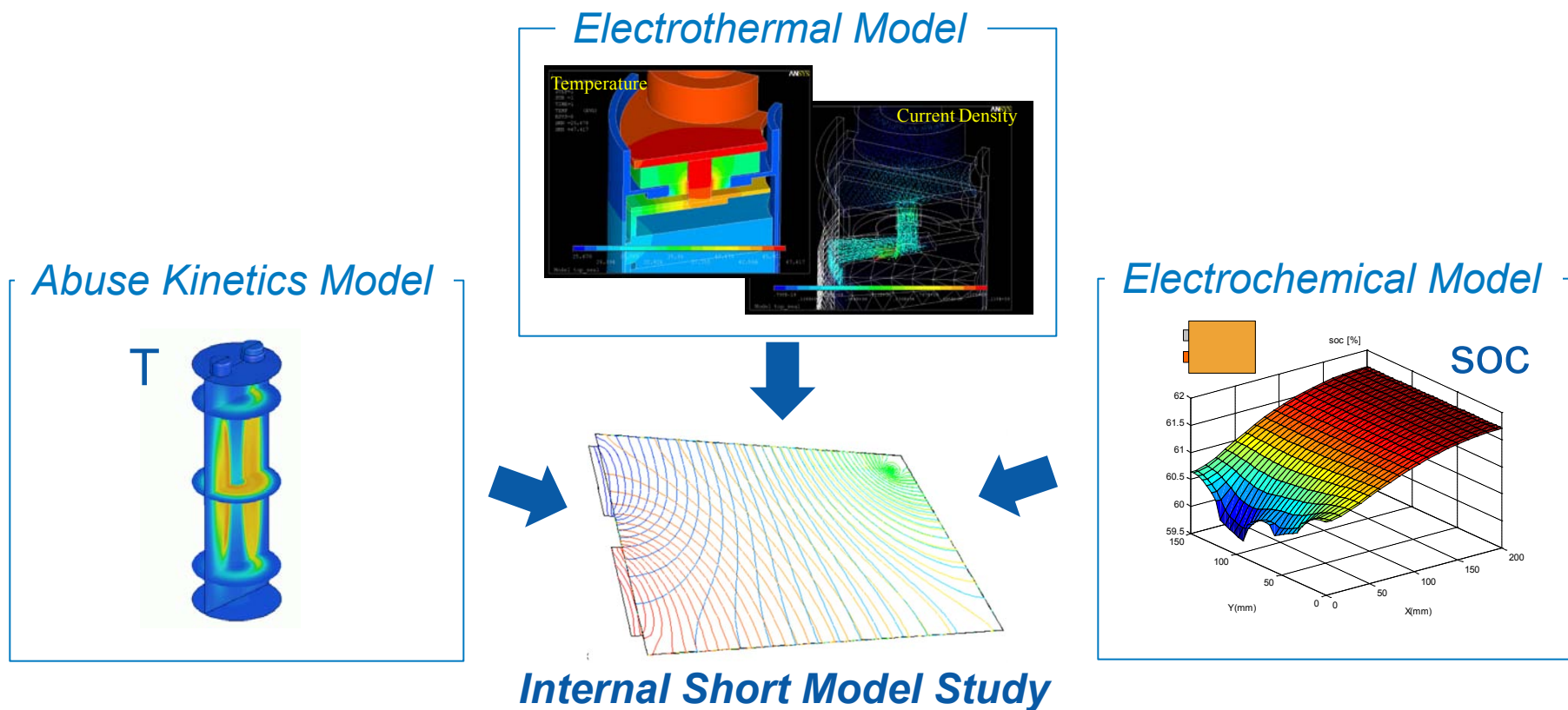
Modeling Thermal Runaway

- ✓ Constructed empirical reaction models using calorimetry data for component decompositions: approach practiced by J. Dahn's group
- ✓ Enhanced understanding of the interaction between heat transfer and exothermic abuse reaction propagation for a particular cell/module design
- ✓ Provided insight on how thermal characteristics and conditions can impact safety events of lithium-ion batteries



Multi-Physics ISC Model

- **Developed an integrated model** for multi-physics internal short circuit (ISC) of lithium-ion cells by linking and integrating NREL's unique electrochemical, electrothermal, and abuse reaction kinetics models
- Performed 3D multi-physics internal short simulation study to characterize an internal short and its evolution over time



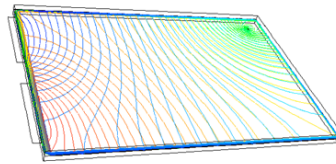
Shutdown Separator for Large Cells ?

Short Between Al & Cu Metal Foils

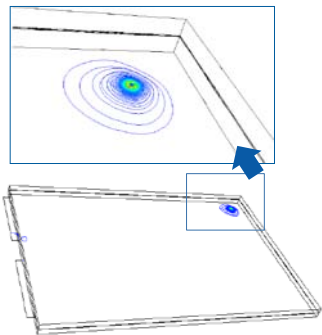
- Cell Capacity: 20 Ah

$$R_{\text{short}} \sim 10 \text{ m}\Omega$$

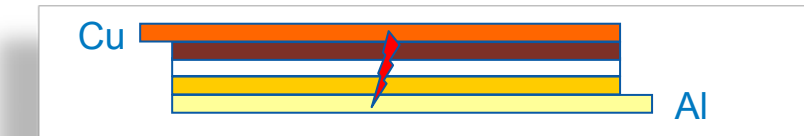
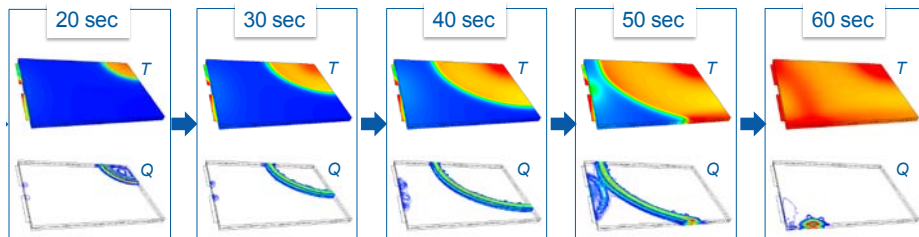
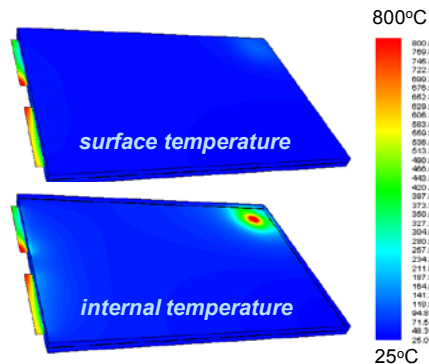
$$I_{\text{short}} \sim 300 \text{ A (15 C-rate)}$$



Joule Heat for Short



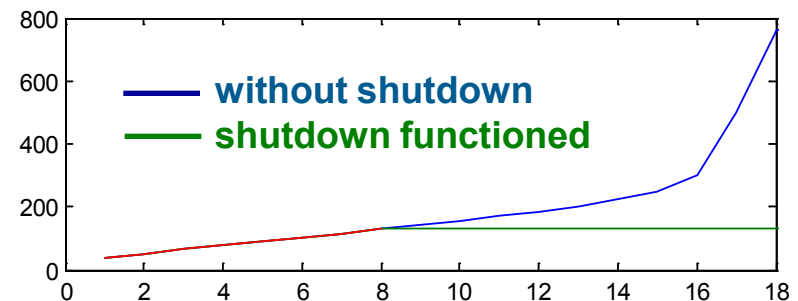
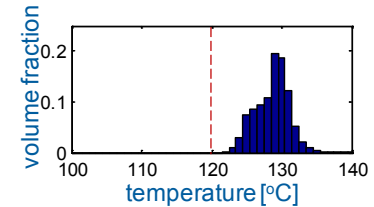
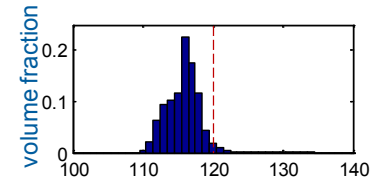
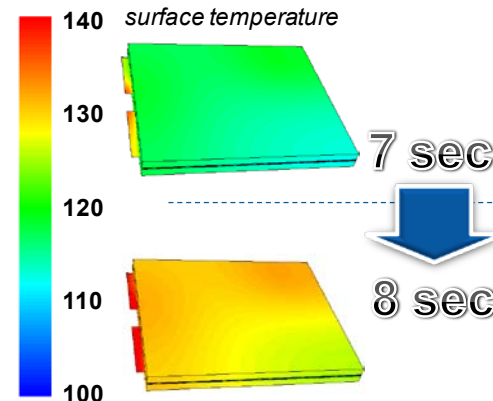
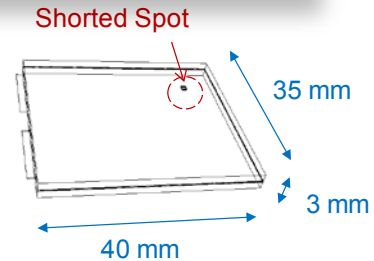
Temperature @10 sec after short



0.4 Ah

$$R_{\text{short}} \sim 7 \text{ m}\Omega$$

$$I_{\text{short}} \sim 34 \text{ A (85 C-rate)}$$



Summary

1. Introduction to *the NREL's MSMD* model
 - The MSMD model is a modularized multiphysics multiscale lithium battery model framework
2. Model application to large Li-ion battery *performance*
 - The model enhances understanding of interactions among varied scale physics beyond what's possible with experimentally measurable quantities only
 - Thermal/electrical design variation of a cell impacts internal battery kinetics
3. Model application to large Li-ion battery *degradation*
 - Internal imbalance of cell use grows continually throughout life
4. Model application to large Li-ion battery *safety*
 - Cell heating pattern is affected by cell characteristics (e.g. Ah, rate)

Acknowledgments

Vehicle Technology Program at DOE

- Dave Howell

CAEBAT operation at DOE

- Stephen Goguen, Brian Cunningham



Thank you for your attention!