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ADVANCED AUTOMOTIVE BATTERIES
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International Battery Modeling Workshop

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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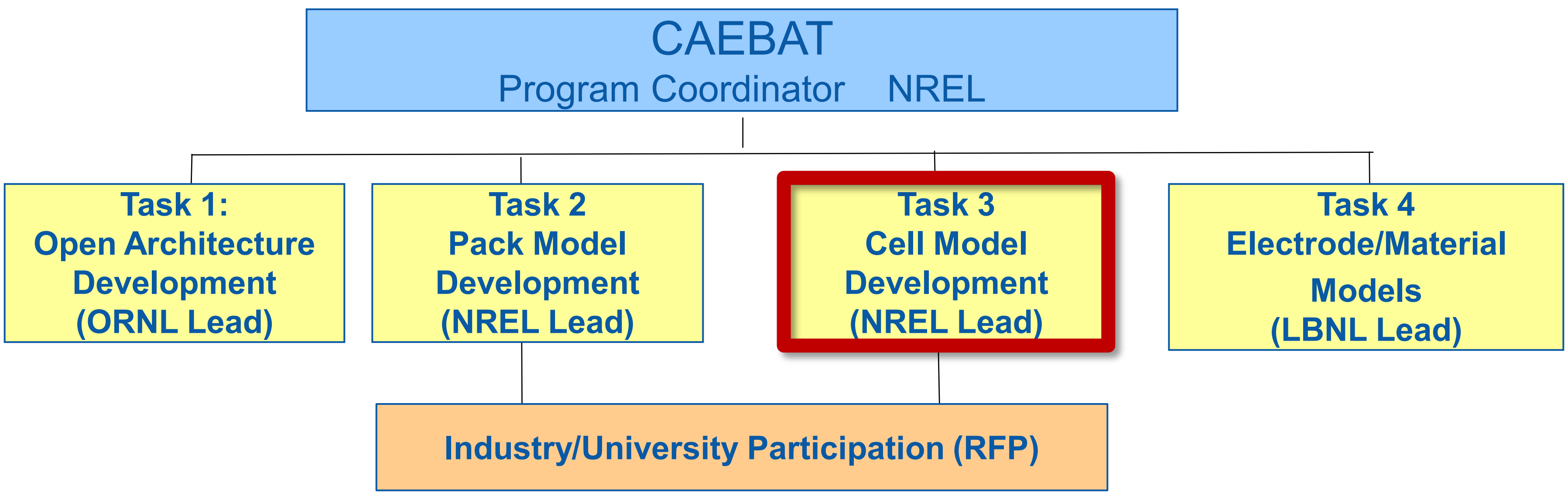
NREL/PR-5400-50248

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



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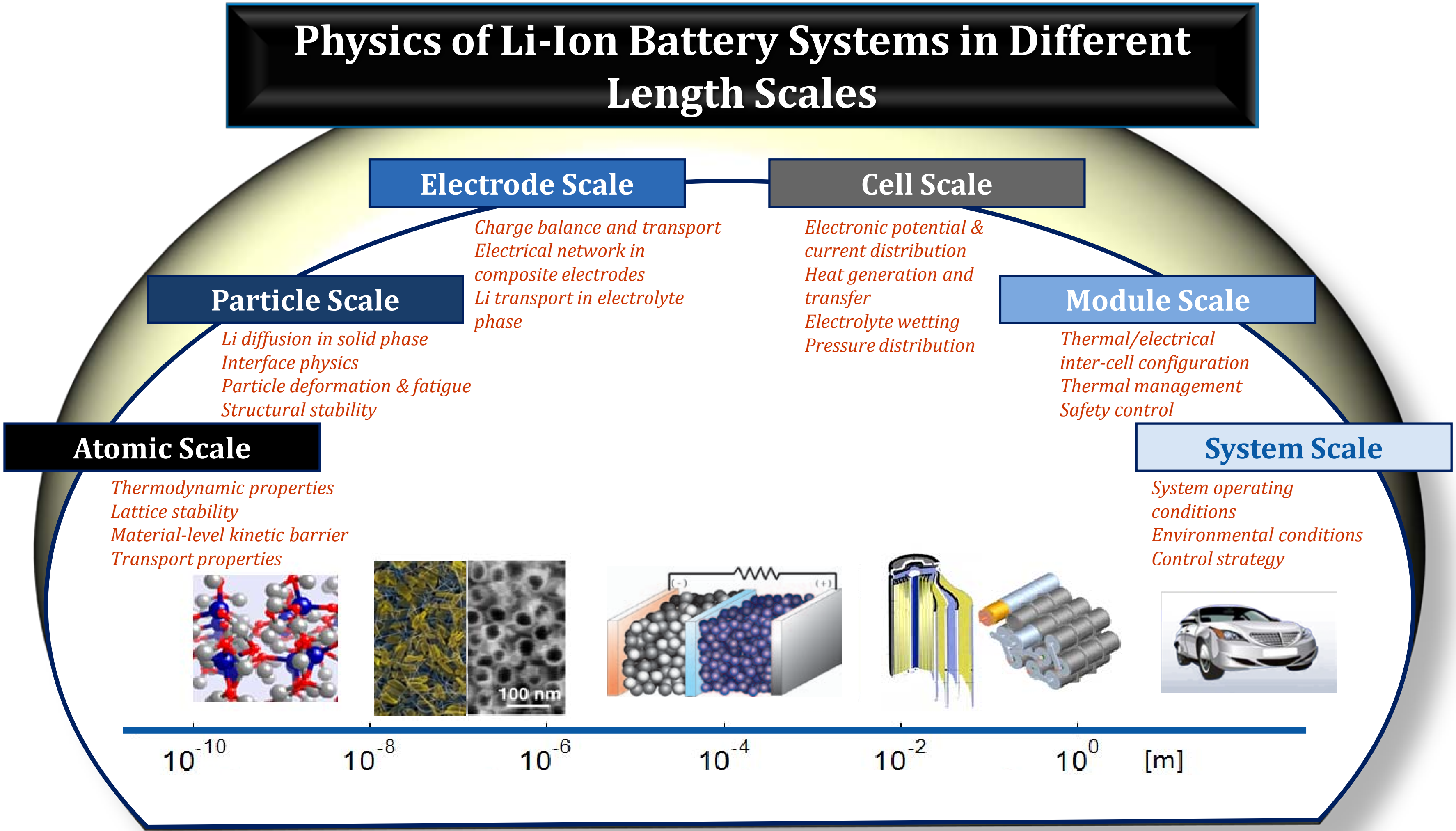
2. Model application to large Li-ion battery ***performance***
    - Stacked prismatic cell response simulation
    - Spiral wound cylindrical cell response simulation
3. Model application to large Li-ion battery ***degradation***
    - Large tab-less cylindrical cell degradation simulation
4. Model application to large Li-ion battery ***safety***
    - Multiphysics internal short circuit simulation
5. Summary

Performance, Durability and Safety



Porous Electrode Performance Model

Charge Transfer Kinetics at Reaction Sites

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

$$i_0 = k(c_e)^{\alpha_a}(c_{s,\max}-c_{s,e})^{\alpha_a}(c_{s,e})^{\alpha_c} \qquad \eta = (\phi_s-\phi_e)-U$$

Species Conservation

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

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

Charge Conservation

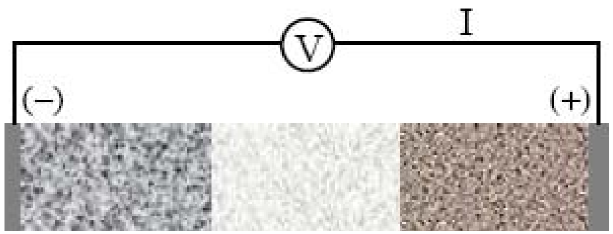
$$\nabla\cdot\left(\sigma^{eff}\nabla\phi_s\right) - j^{Li} = 0$$

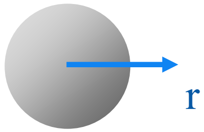
$$\nabla\cdot\left(\kappa^{eff}\nabla\phi_e\right)+\nabla\cdot\left(\kappa_D^{eff}\nabla\ln c_e\right)+j^{Li}=0$$

Energy Conservation

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

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



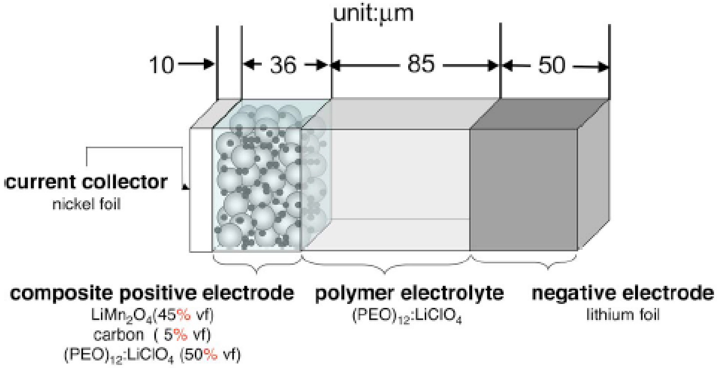


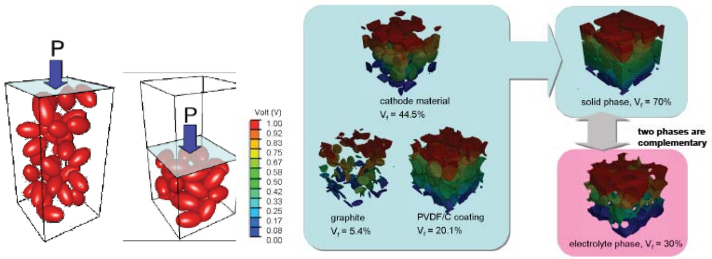
- Pioneered by Newman group (*Doyle, Fuller, and Newman 1993*)
- Captures *lithium diffusion dynamics* and *charge transfer kinetics*
- Predicts *current/voltage response* of a battery
- Provides design guide for thermodynamics, kinetics, and transport across electrodes

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

Mesoscale Modeling Approach

Wang and Sastry, JES, 2007



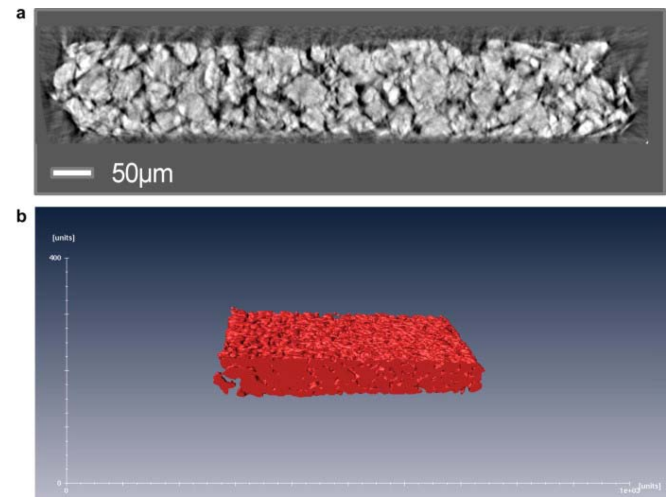


- Model addresses correlation of composition, morphology, and processing conditions by resolving mesoscale geometry
- Captures mesoscale geometry impact on transport properties of composite electrodes

- Computationally *expensive*

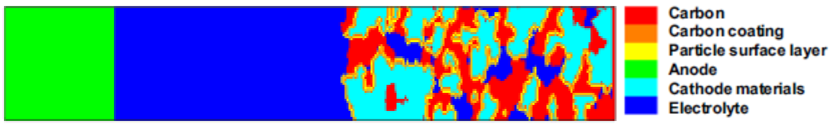
P.R. Shearinga et. al, Electrochemistry Communication, 2010

X-Ray Tomography (Nano CT)



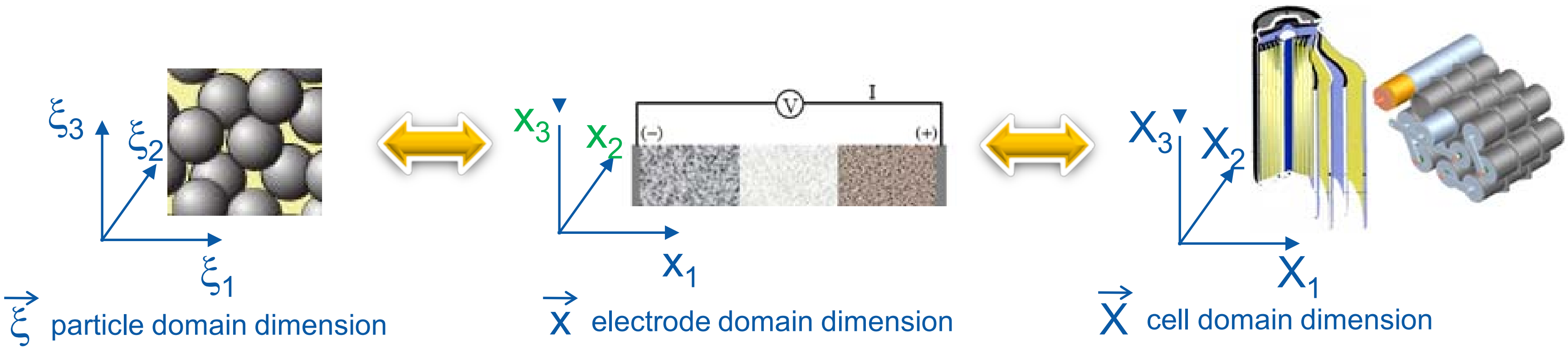
Liu and Siddique, 218th ECS , 2010

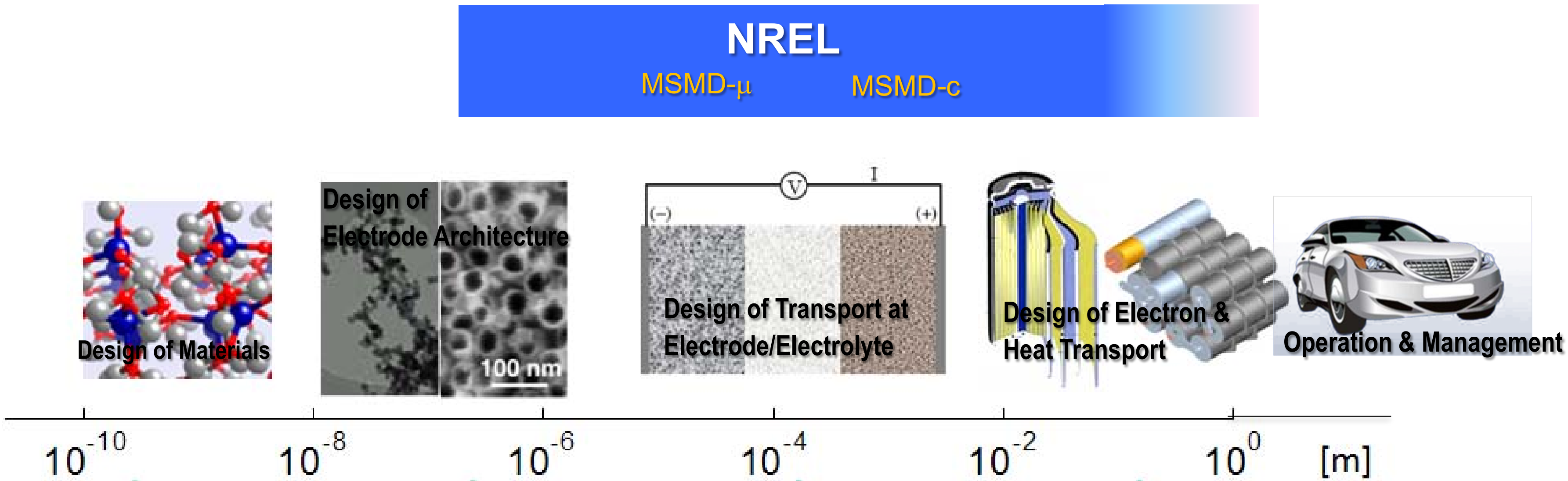
Micro-Structure Reconstruction



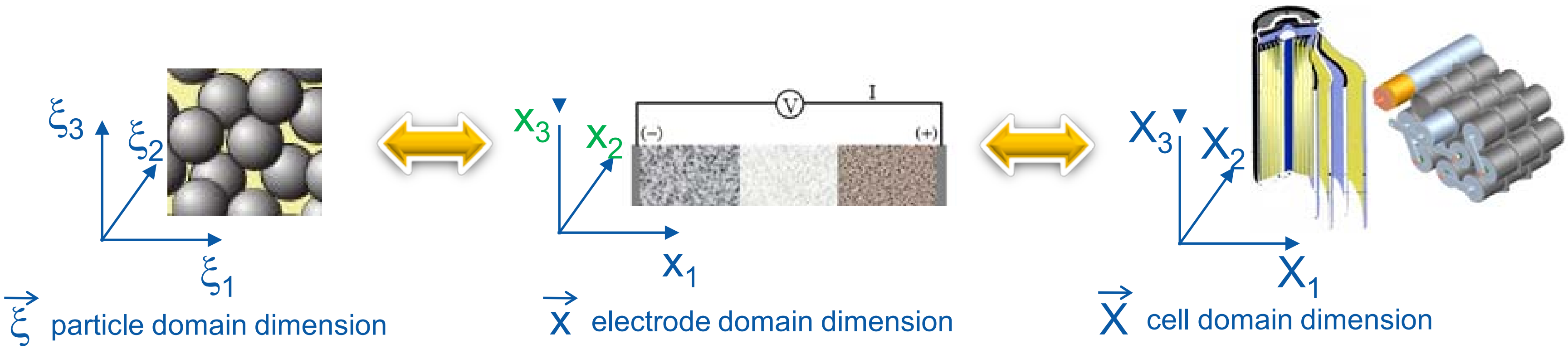
Computational domain generated by quasi-random reconstruction process

NREL's Multi-Scale Multi-Dimensional Model Approach





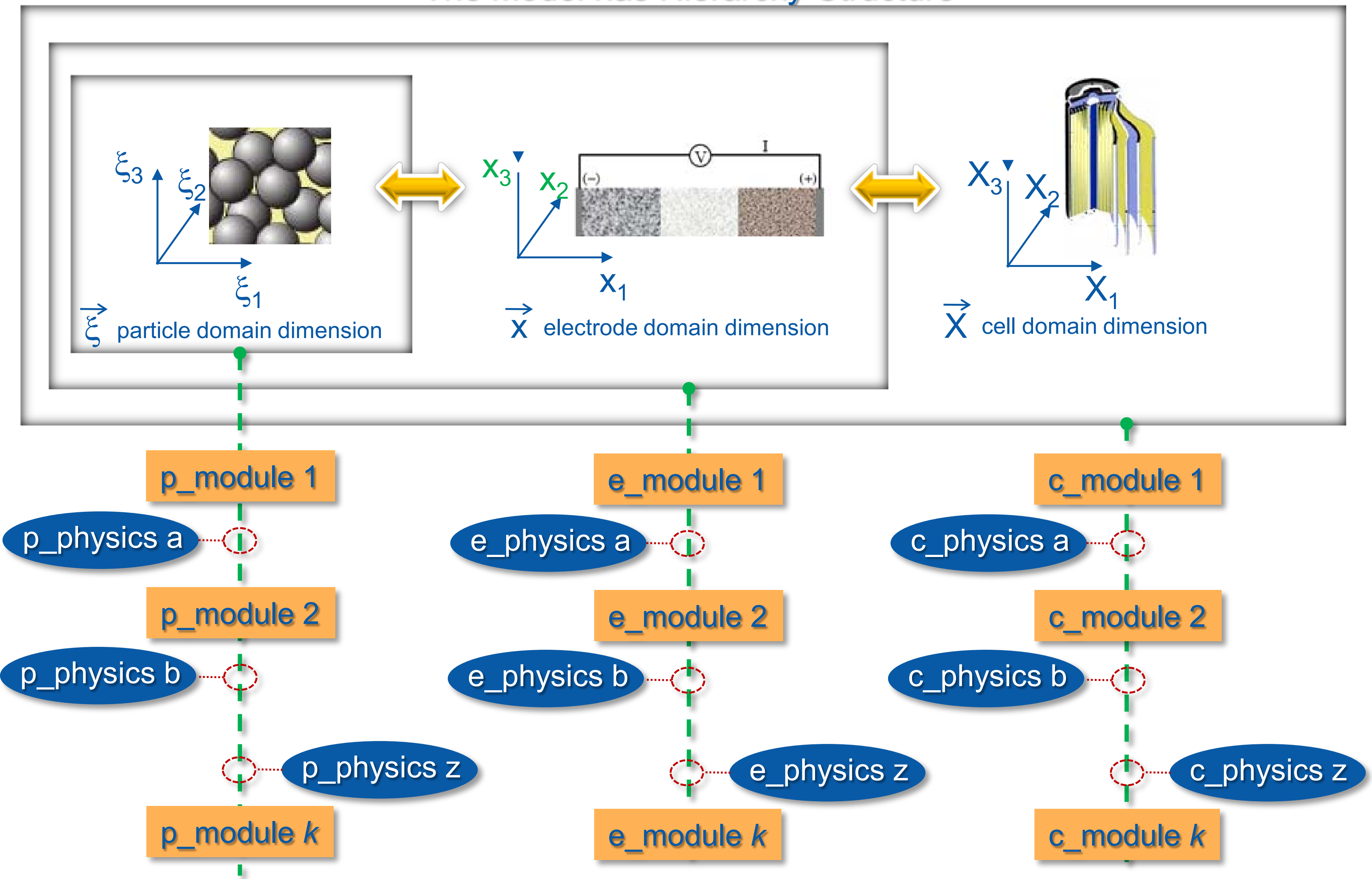
NREL's Multi-Scale Multi-Dimensional Model Approach



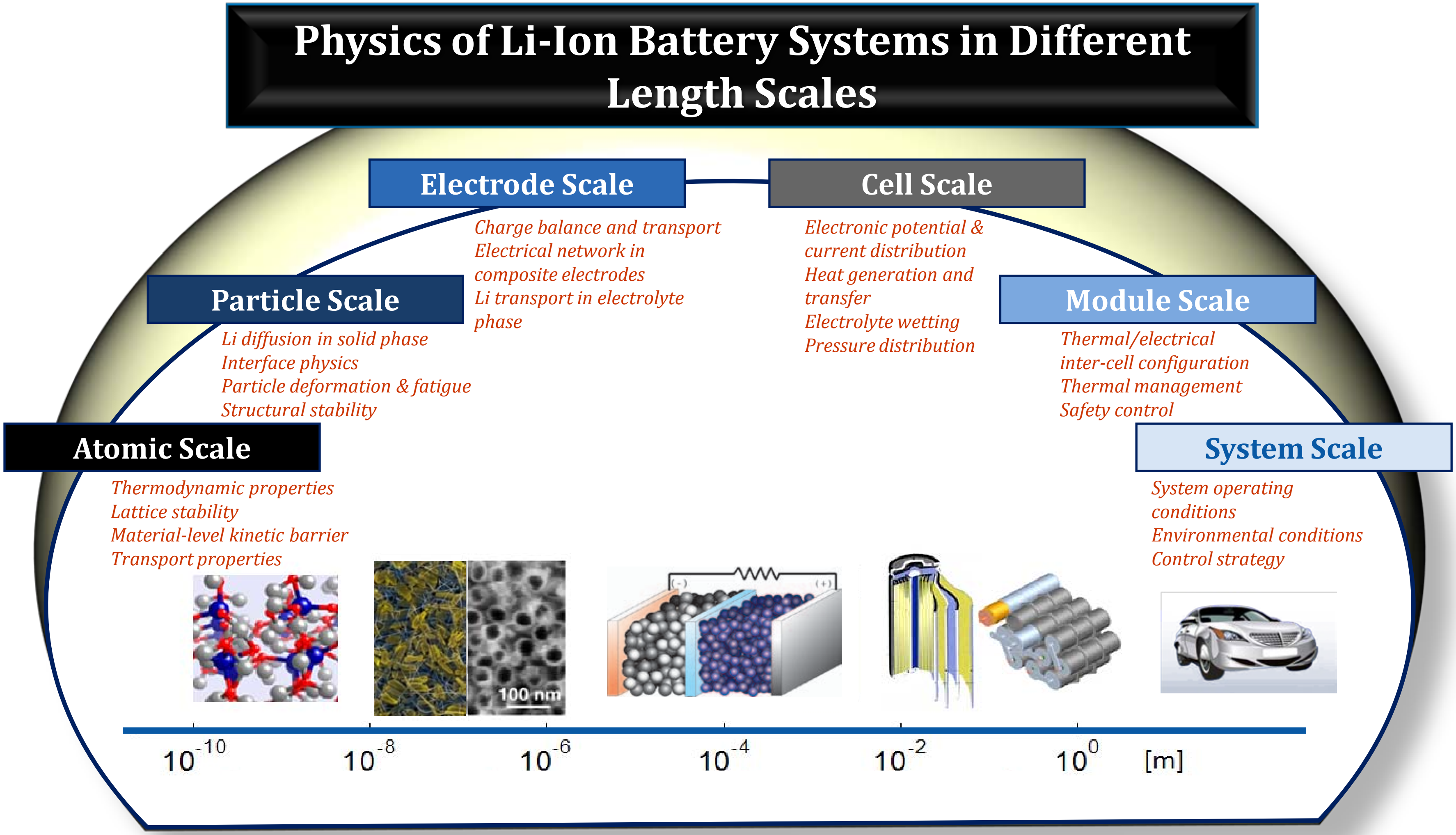
- Introduce multiple computational domains for corresponding length scale physics
- Decouple geometries between submodel domains
- Couple physics in two-way using predefined inter-domain information exchange
- Selectively resolve higher spatial resolution for smaller characteristic length scale physics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

MSDM: Modularized Framework: *Flexible & Expandable*

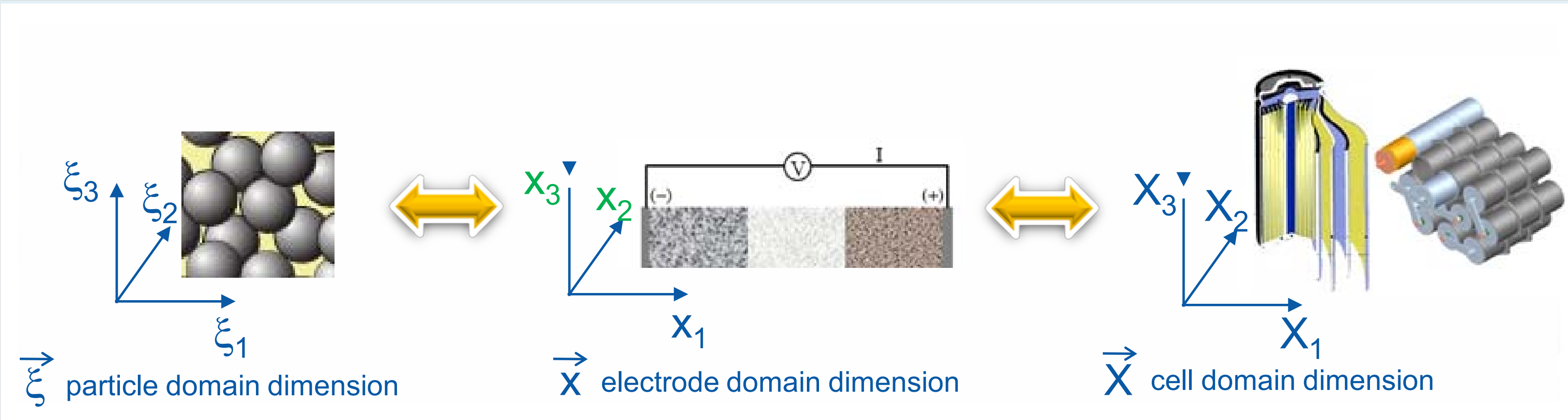
The Model has Hierarchy Structure



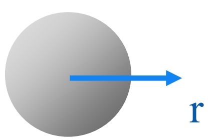
Performance, Durability and Safety



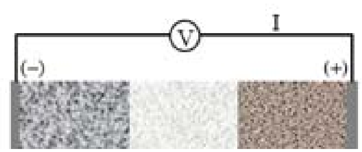
Model Prediction for a Large Stacked Prismatic Cell



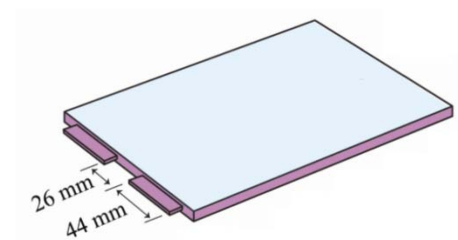
Sub-model Choice



1D spherical particle representation model



1D porous electrode model



3D SPPC model

Solution Method Choice

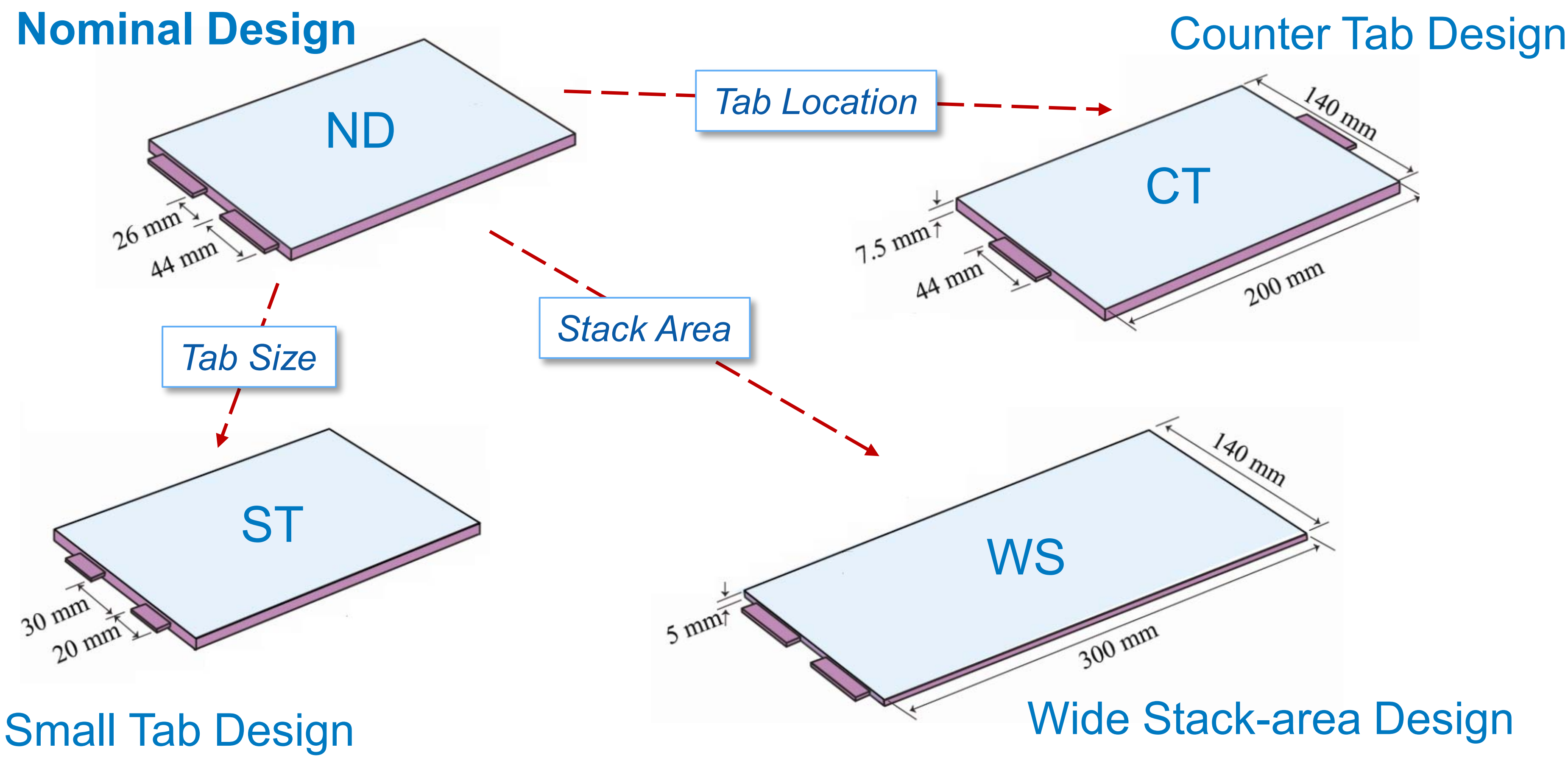
SVM

SVM

FVM

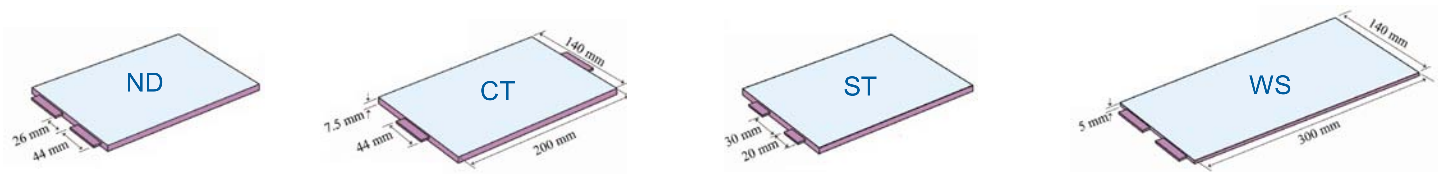
- ✓ *Stacked prismatic design*
- ✓ *200 x 140 x 7.5 mm^3 form factor*
- ✓ *20 Ah PHEV10 application*
- ✓ *Single side cooling 25W/m^2K 25^{o}C*

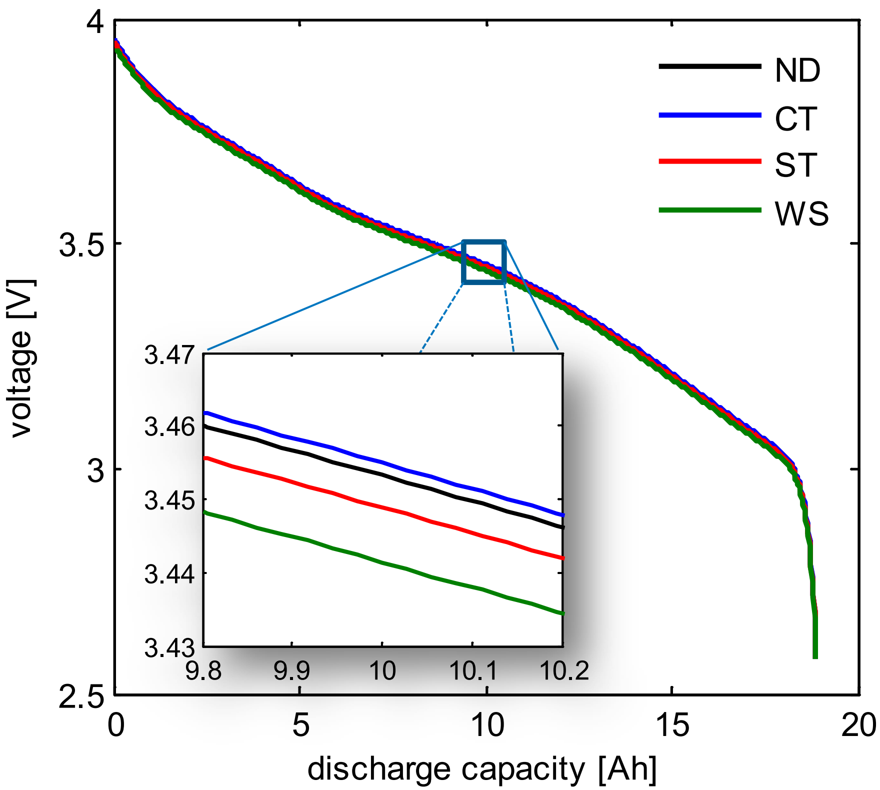
Cell Design Evaluation



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

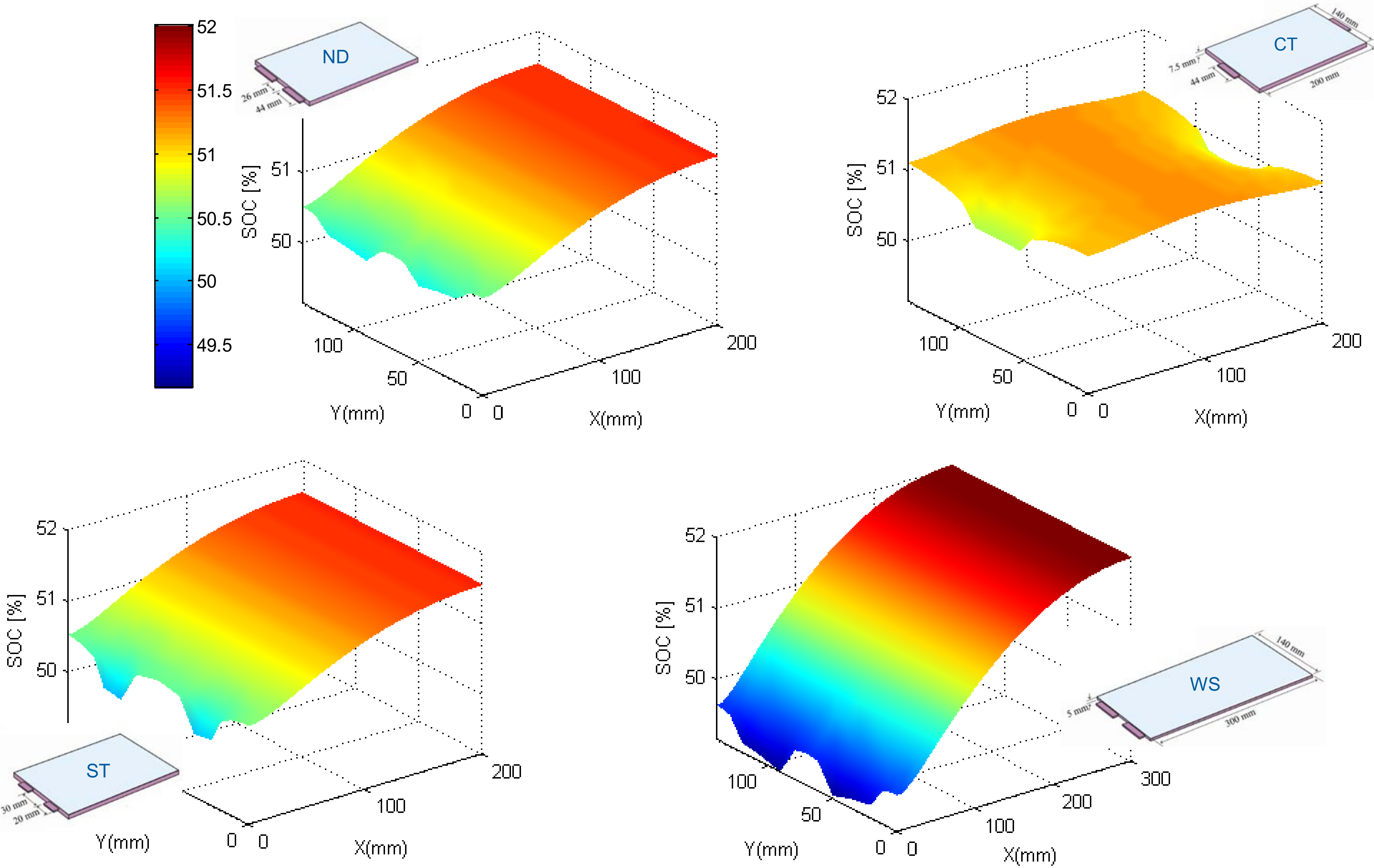
5C Discharge Voltage Response



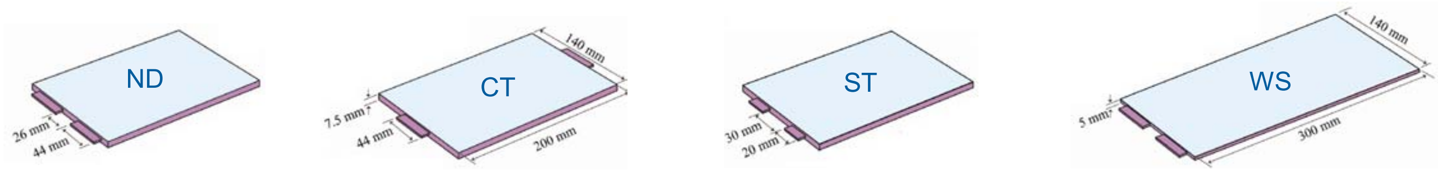


- Identical discharge capacity: 18.9 Ah at 5C
- Several mV difference in discharge voltage among the compared designs
- Tendency of a few millivolts voltage difference with design change cannot be easily confirmed by testing only

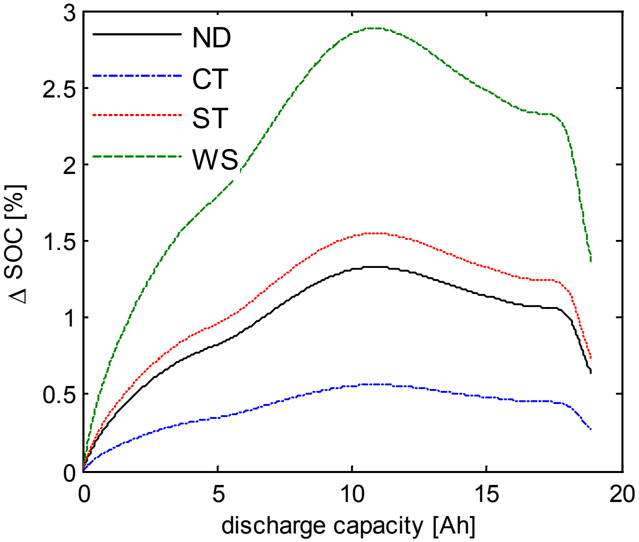
Cell Internal SOC Imbalance



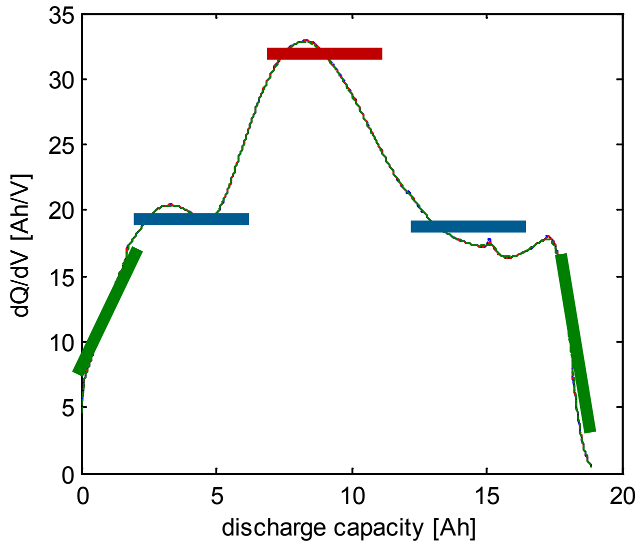
SOC Deviation during Discharge

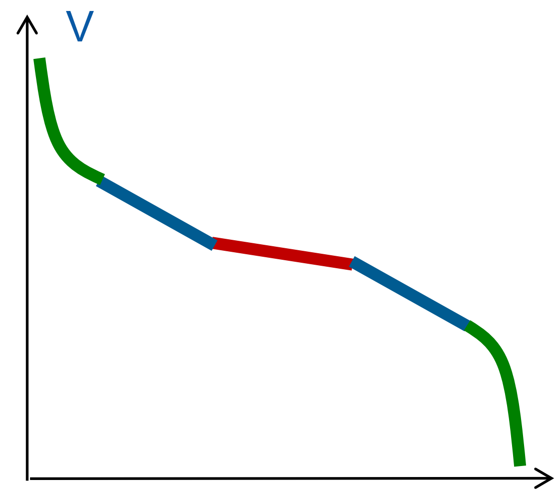


SOC_{max}-SOC_{min}



dQ/dV



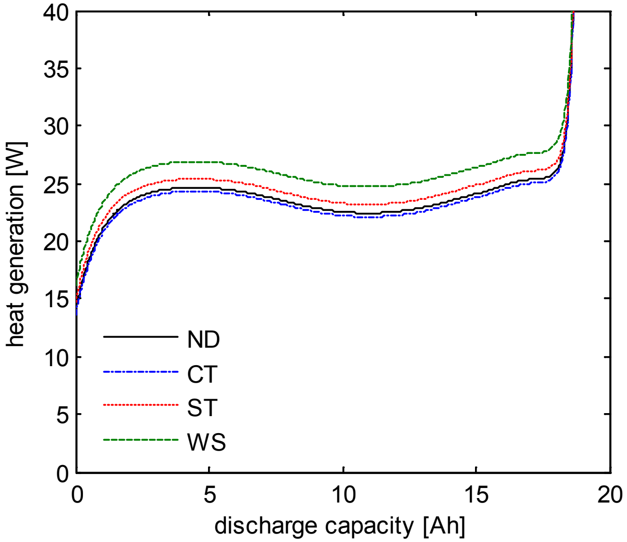


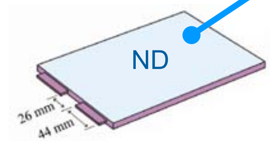
- Results imply that
  - ✓ Flat voltage slope would promote cell internal SOC imbalance
  - ✓ HEV cycling at “flat section” would cause larger internal imbalance

- Modifying thermodynamics vs Optimizing electrical/thermal configuration

Thermal Response during Discharge

Total Heat Generation



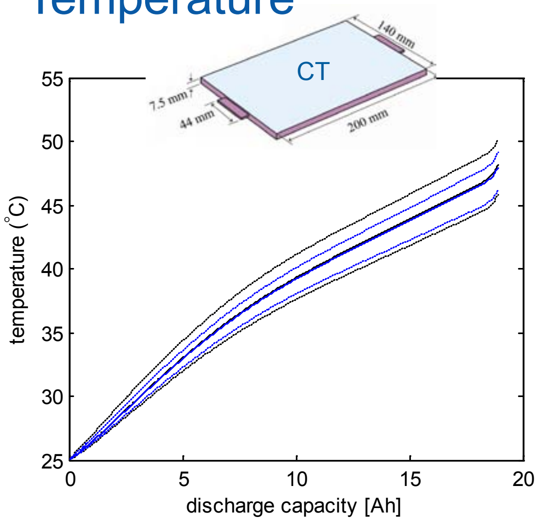


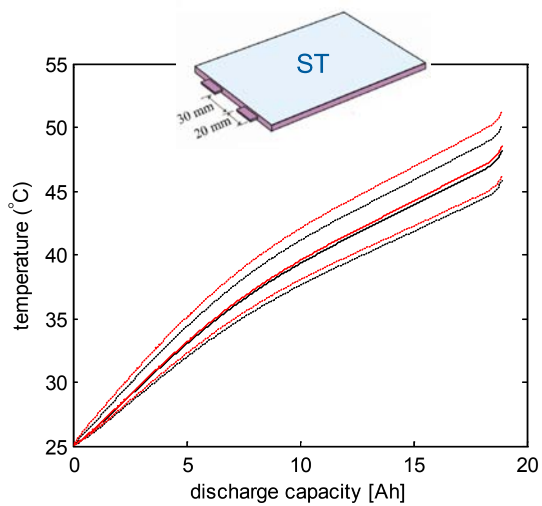
Single side cooling on top surface

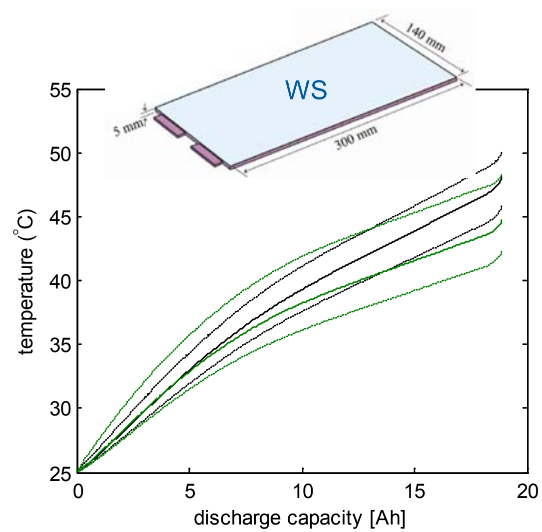
- ✓ With h = 25 W/m^{2}K
- ✓ At T_{amb}= 25 ^{o}C

- 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

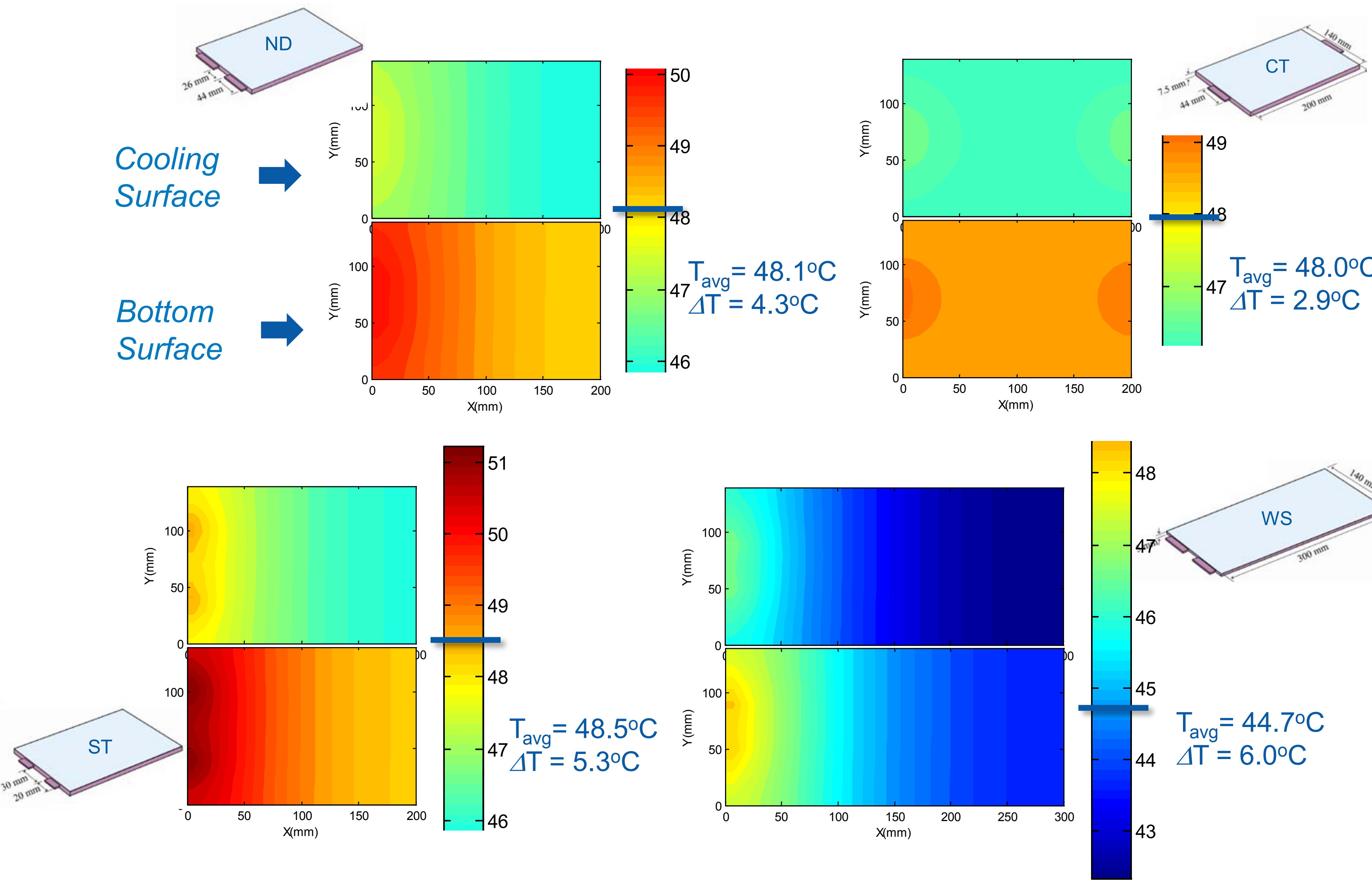
Temperature





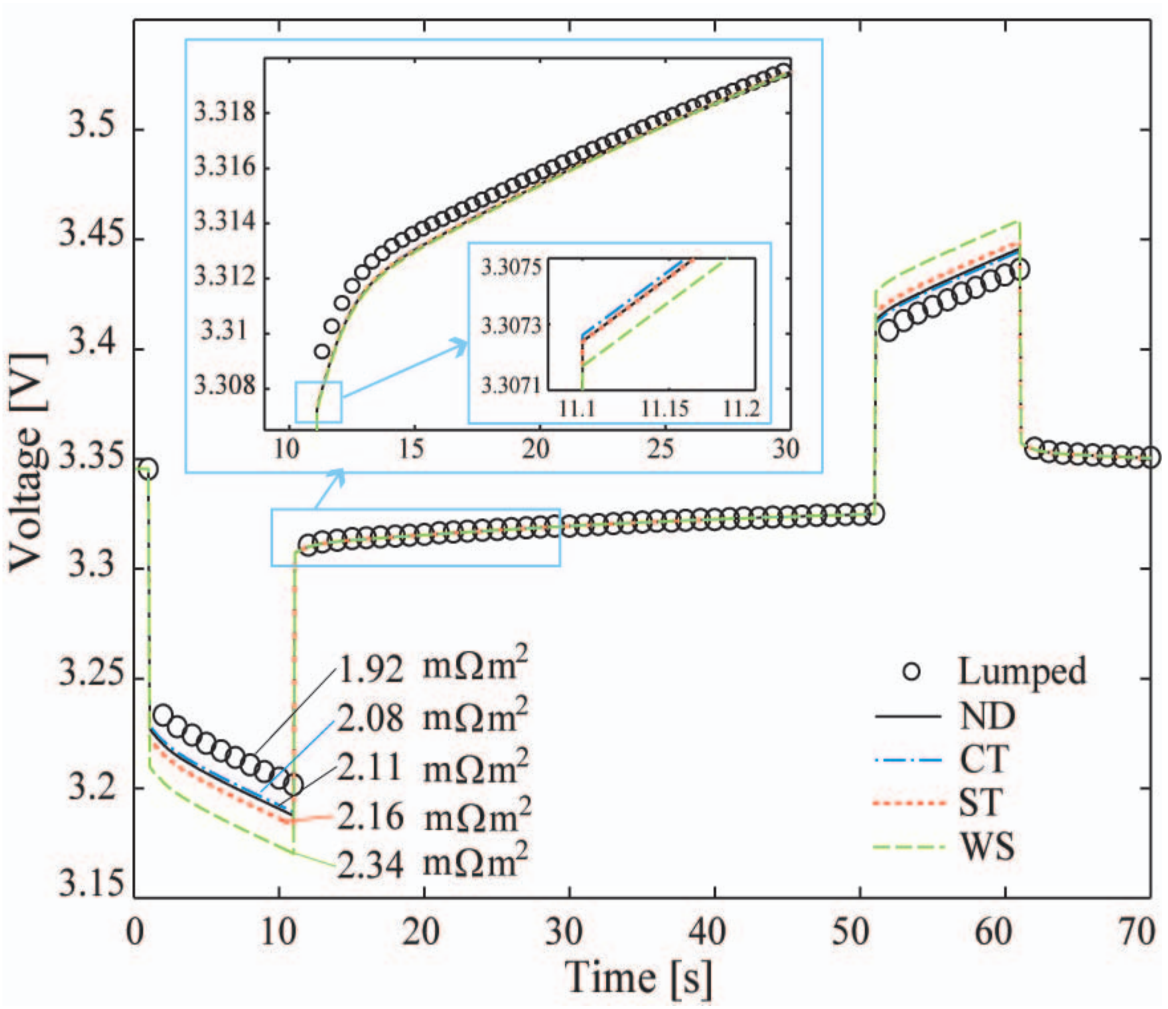


Temperature Imbalance at EOD

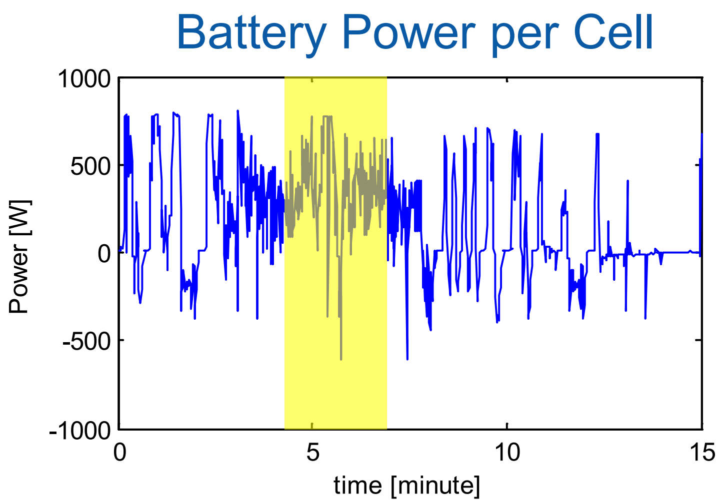


Pulse Power Response Comparison

- HPPC at 20% SOC at 25^{o}C initial temperature

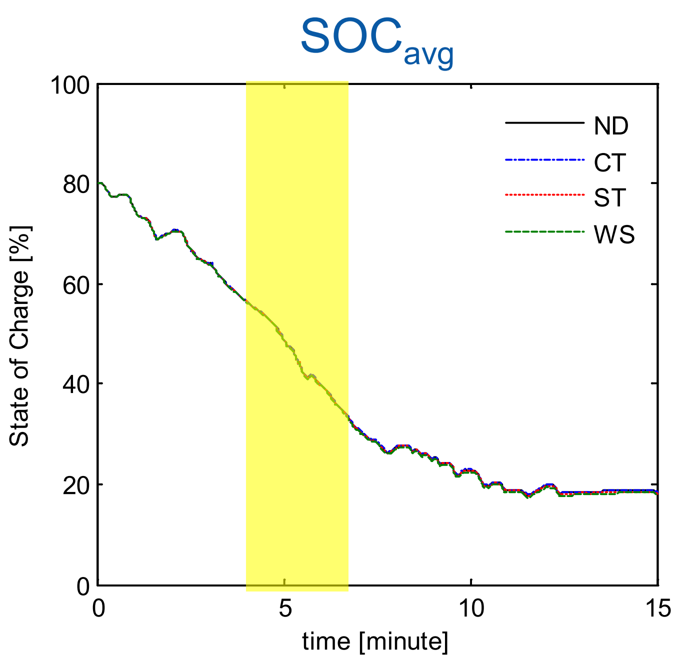


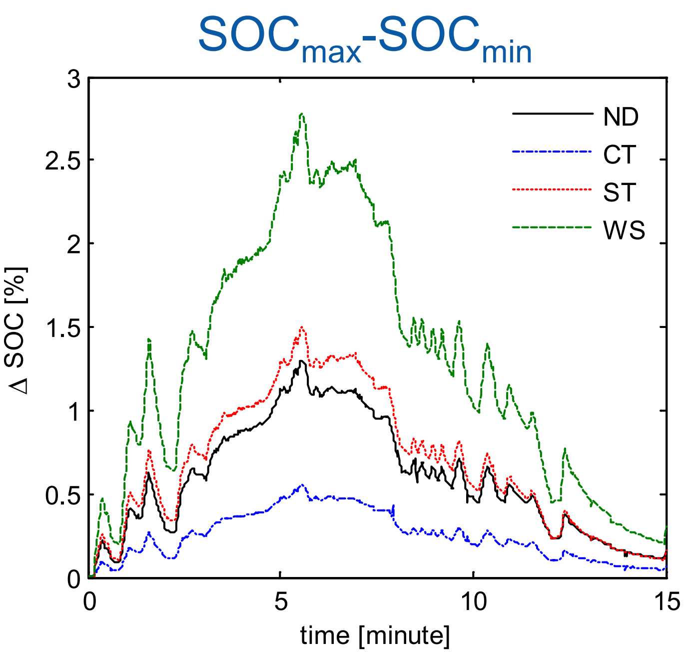
Vehicle Use Evaluation



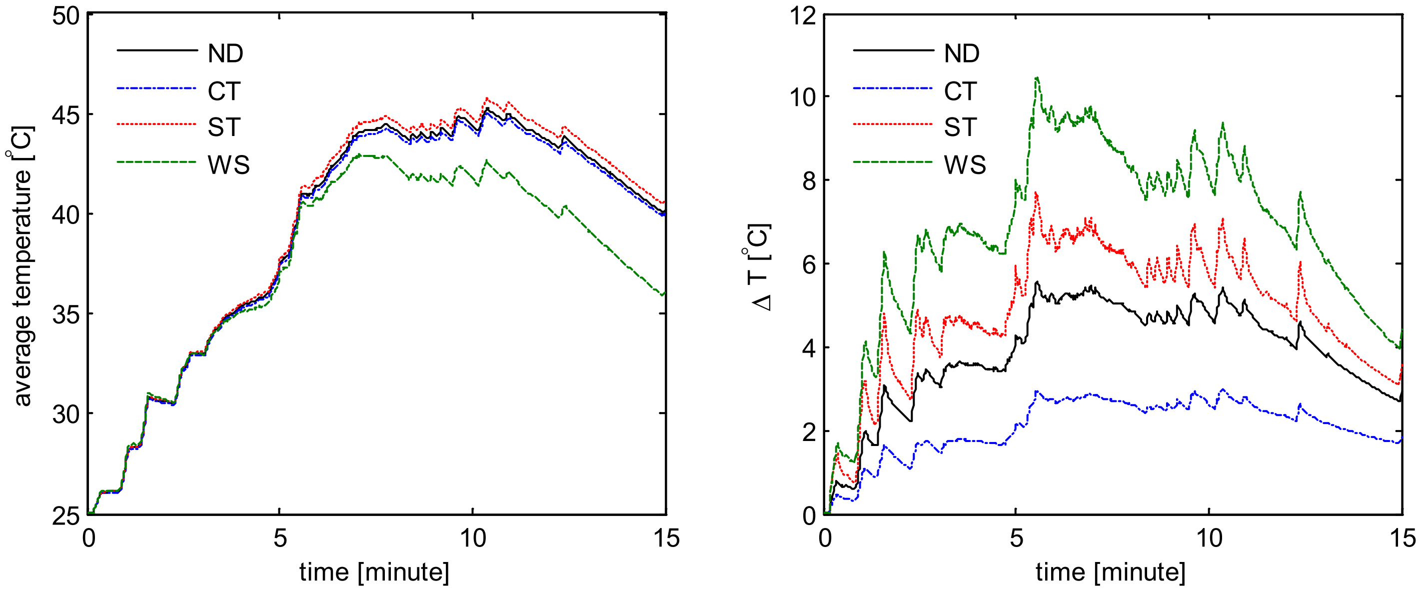
- PHEV10 mid-size sedan
- 15 minutes US06 Driving Profile
- Battery power from Vehicle simulation

Thermodynamics + Cell Design + System Control





Thermal Response during Driving

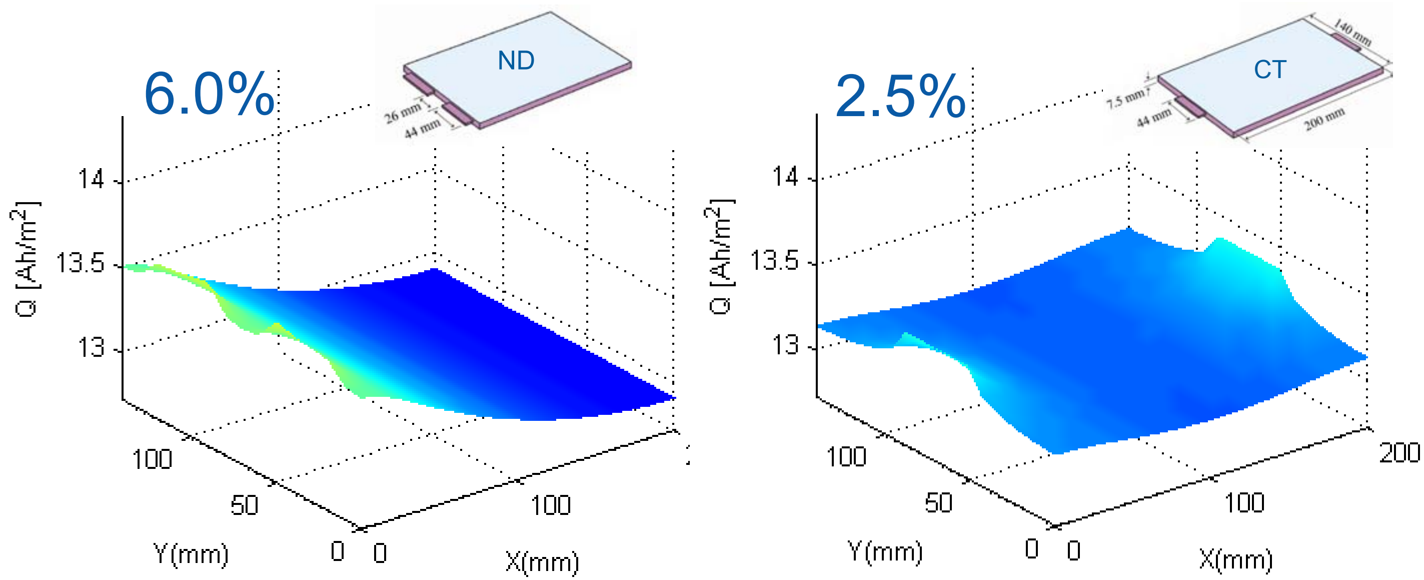


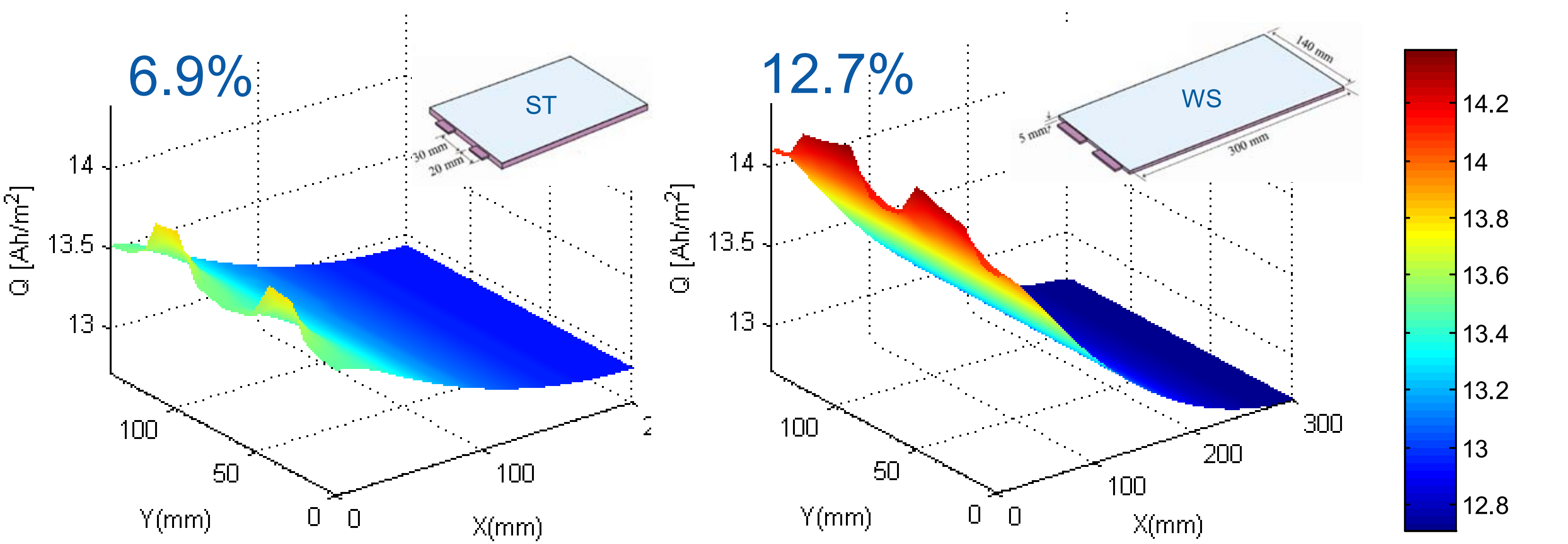
- Similar average temperatures: ND, CT, ST
- Smaller *ΔT* at CT
- Larger *ΔT* at ST
- WS: lower average *T* during CS mode drive, but significant *ΔT*

Cell Internal Kinetics Non-Uniformity

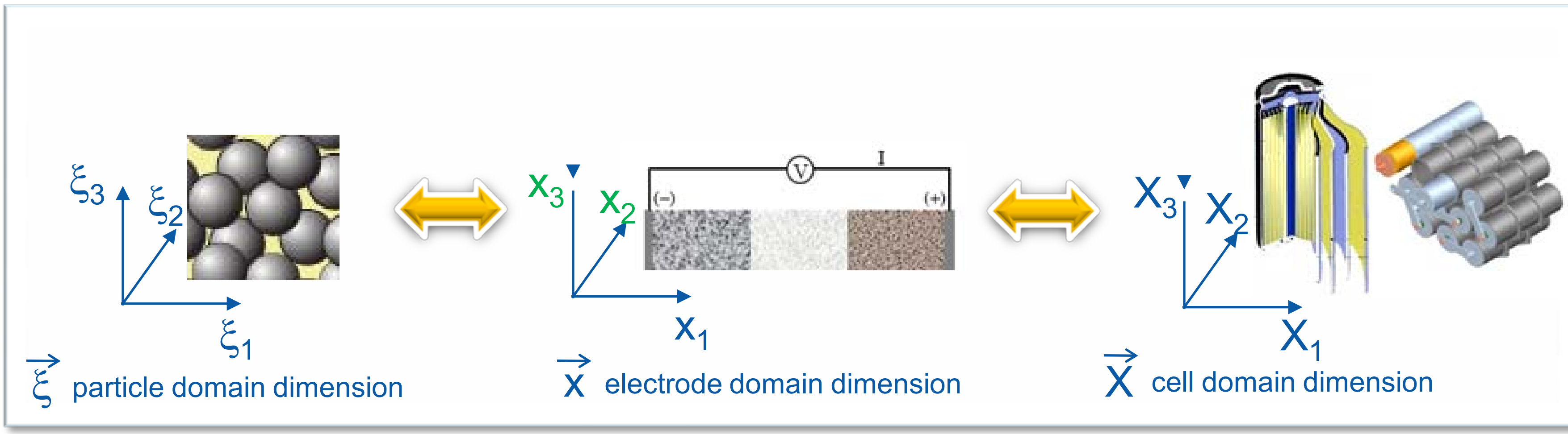
- Ah Throughput

- PHEV10
- 15min US06

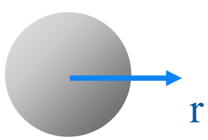




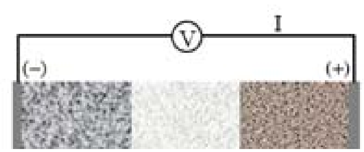
Model Prediction for a Spirally Wound Cylindrical Cell



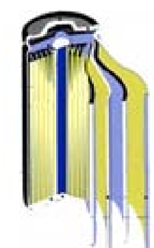
Sub-model Choice



1D spherical particle representation model



1D porous electrode model



3D SWC model

Solution Method Choice

SVM

SVM

FVM

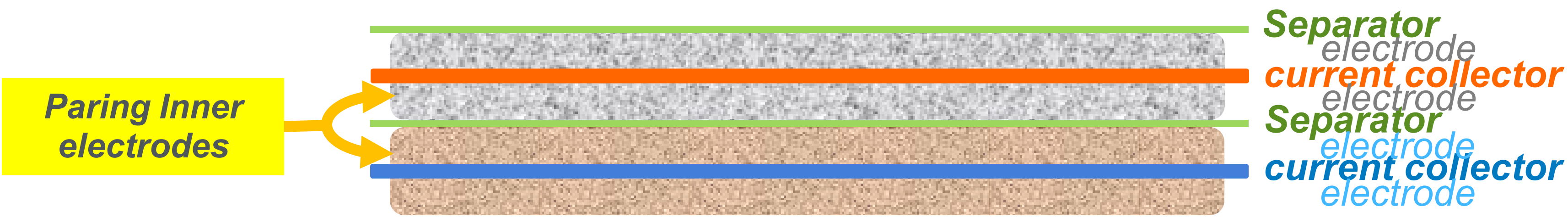
- ✓ *Spirally wound cell design*
- ✓ *D40, H100 mm form factor*
- ✓ *10 Ah PHEV10 application*

Spirally Wound Cell (SWC) Model

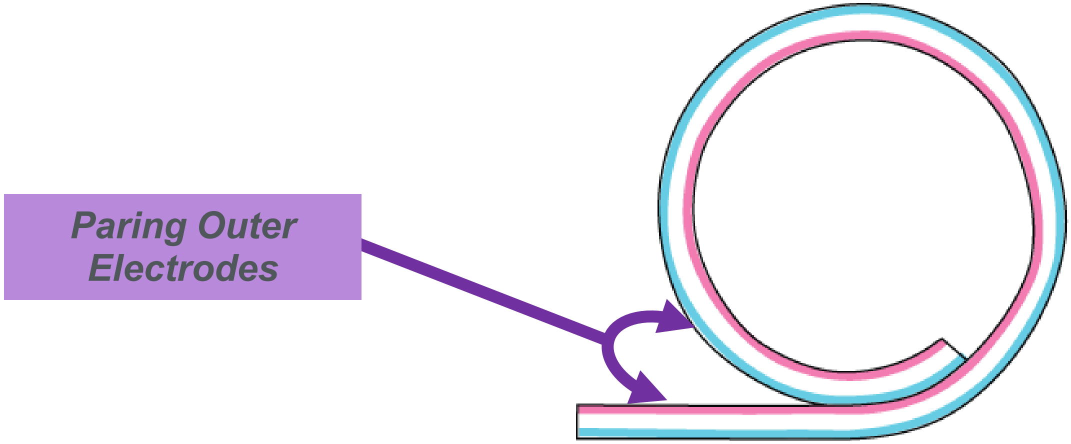
Spirally Wound Cell :

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

Stacking process: ***Forming a pair between inner electrodes***



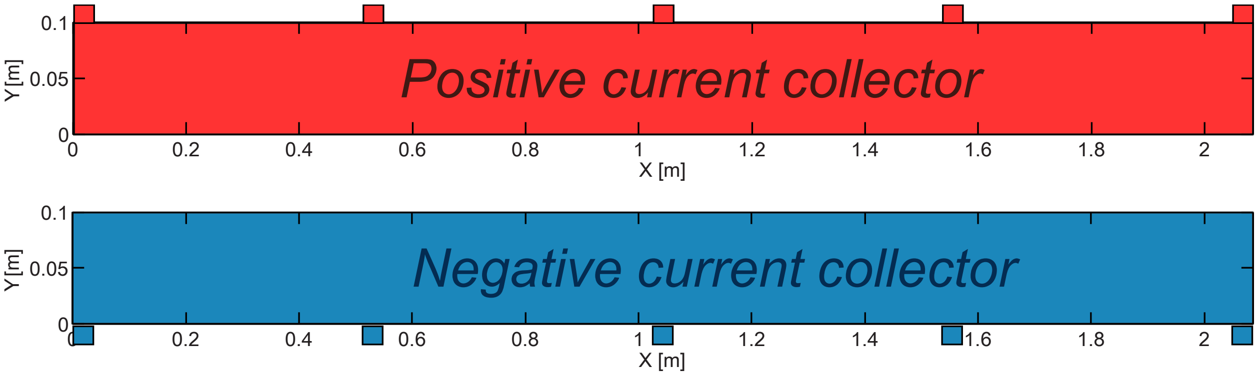
Winding process: ***Forming a second pair between outer electrodes***

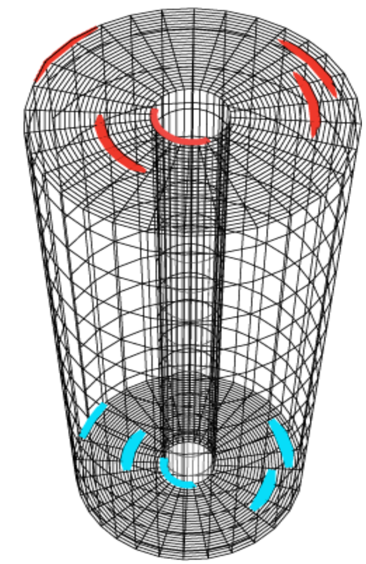


Model Case

- ✓ 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

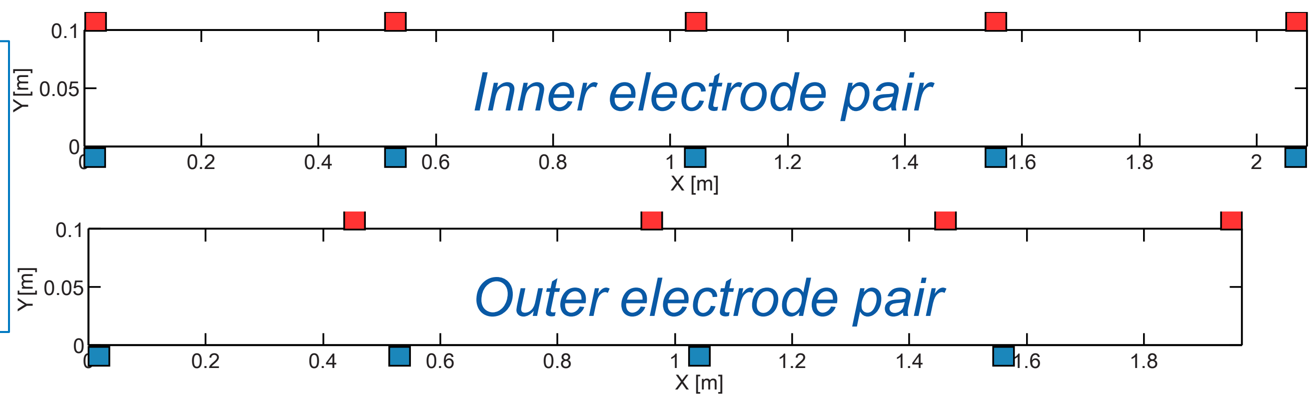
Tab locations for 5 tab case





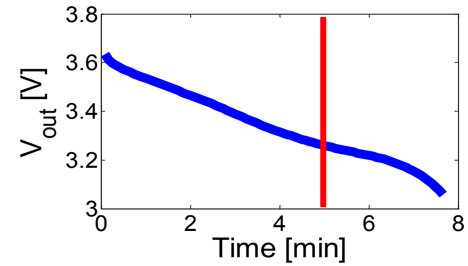
Tab configuration of each electrode pairs

5C constant current discharge
$soc_{ini} = 90\%$
Natural convection :
$h_{inf} = 5\ W/m^2K$
$T_{amb} = 25^oC$
$T_{ini} = 25^oC$

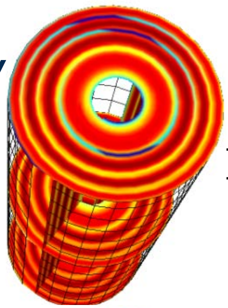


SWC Model Results

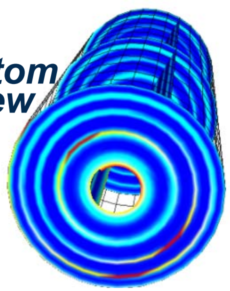
- *5 tabs in each current collector*
- *5 min after 5C discharge*



Top view

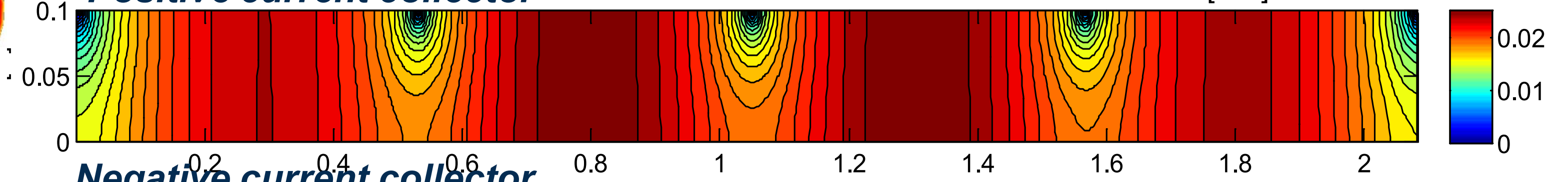


Bottom view

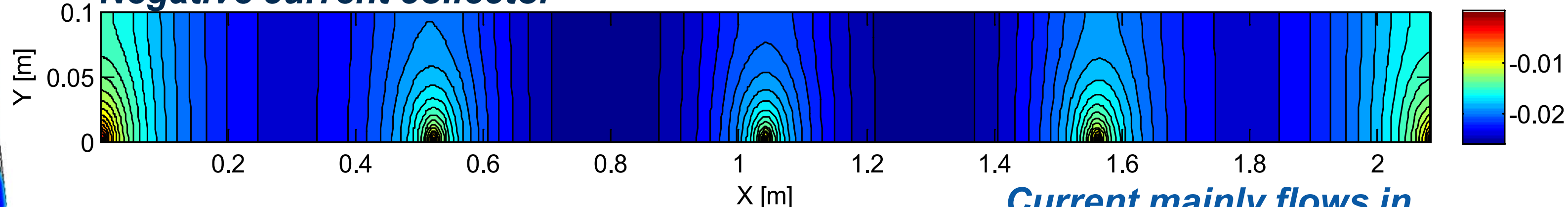


Electric potential

Positive current collector



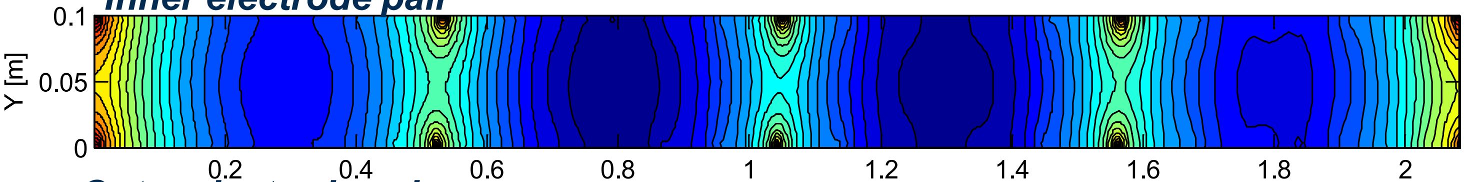
Negative current collector



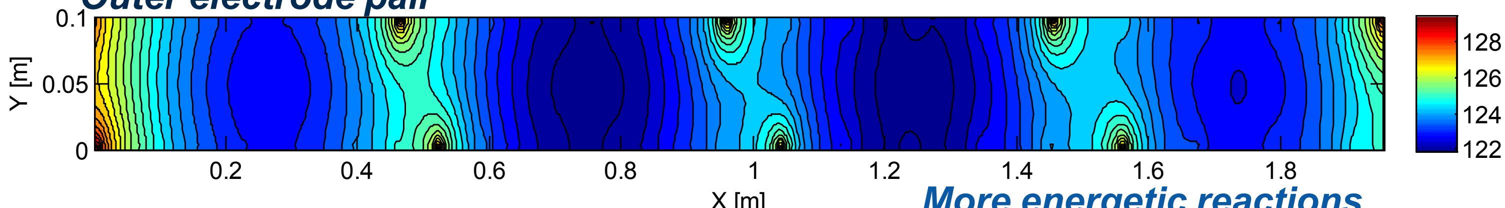
Current mainly flows in the winding direction

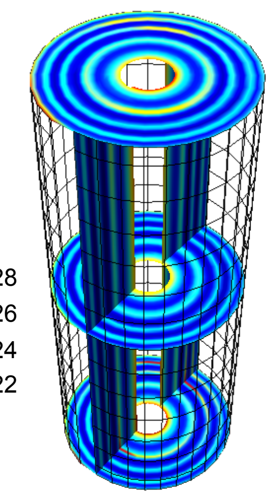
Electrochemical reaction rate

Inner electrode pair



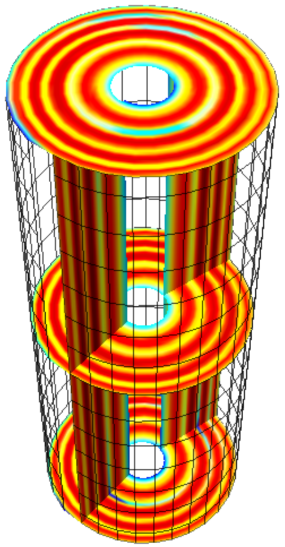
Outer electrode pair





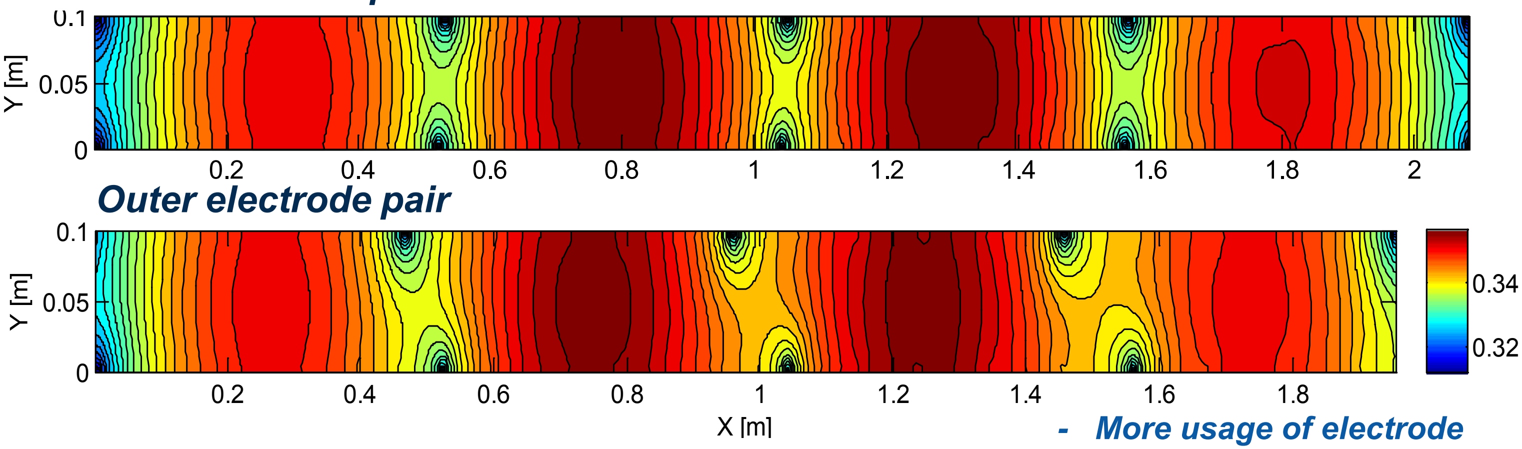
More energetic reactions near tabs

SWC Model Results



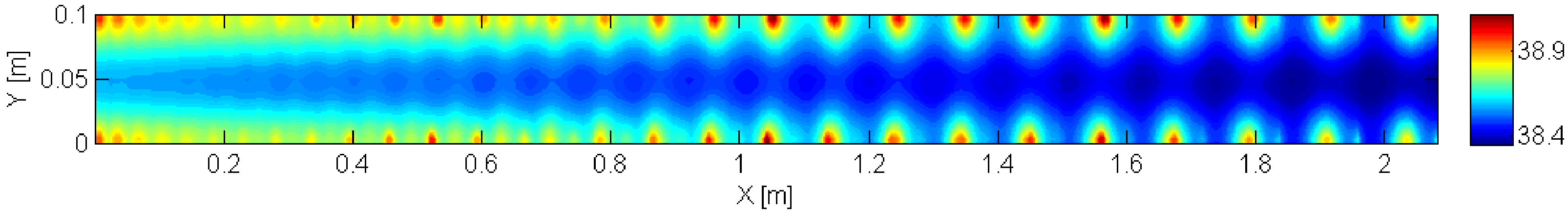
State of charge

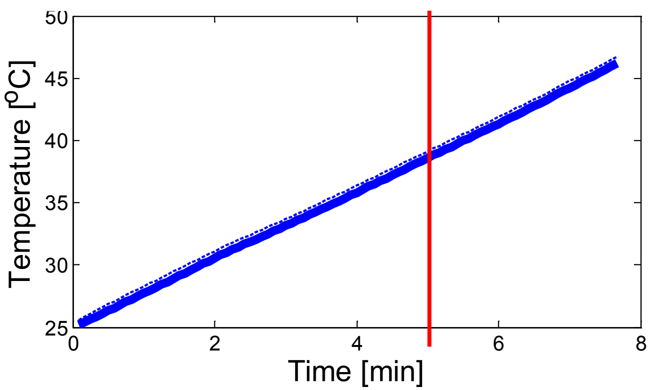
Inner electrode pair



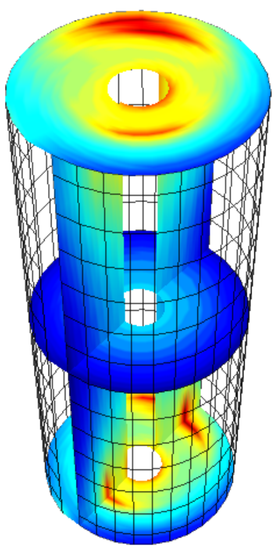
- More usage of electrode near tabs

Temperature

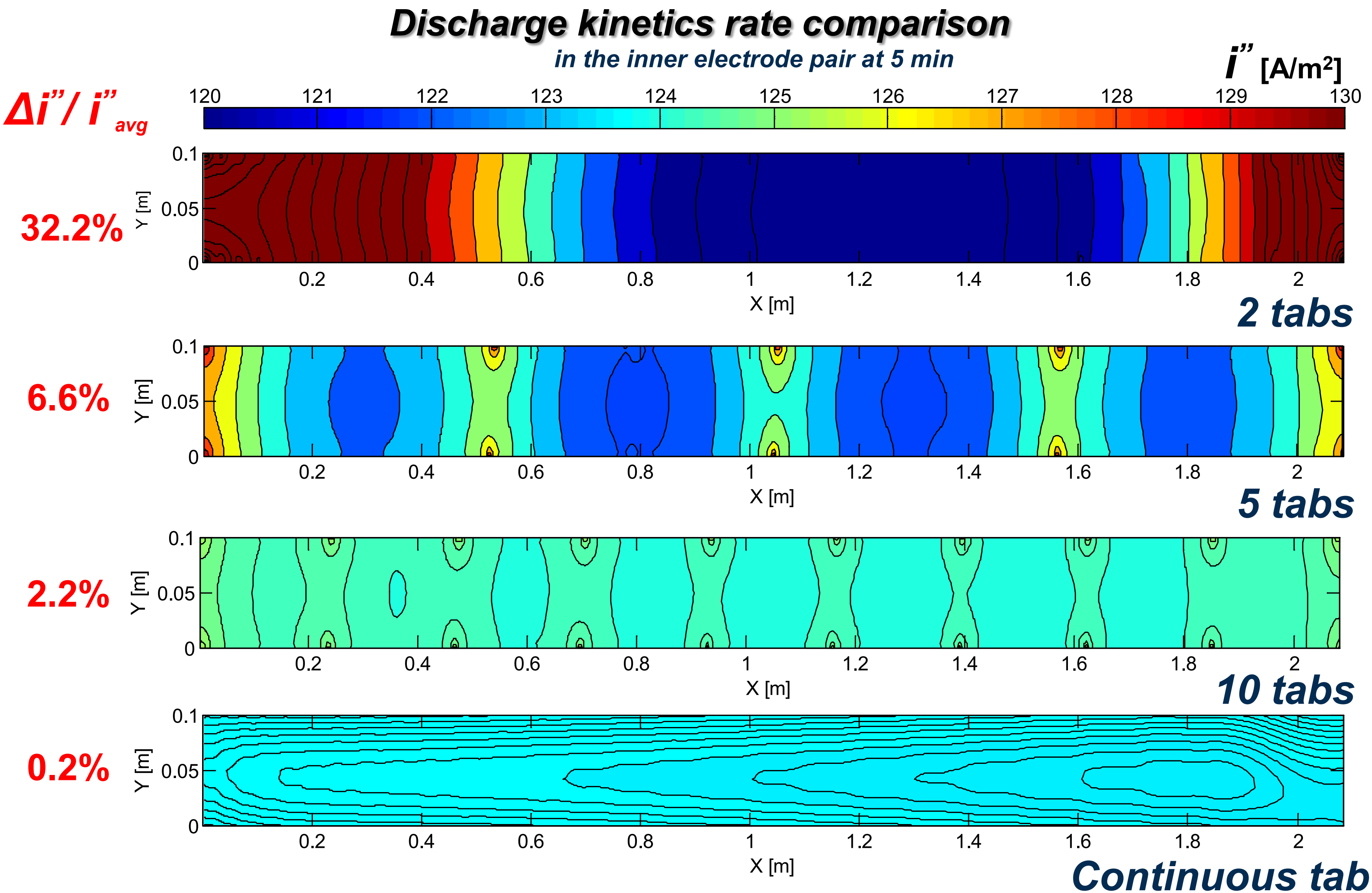




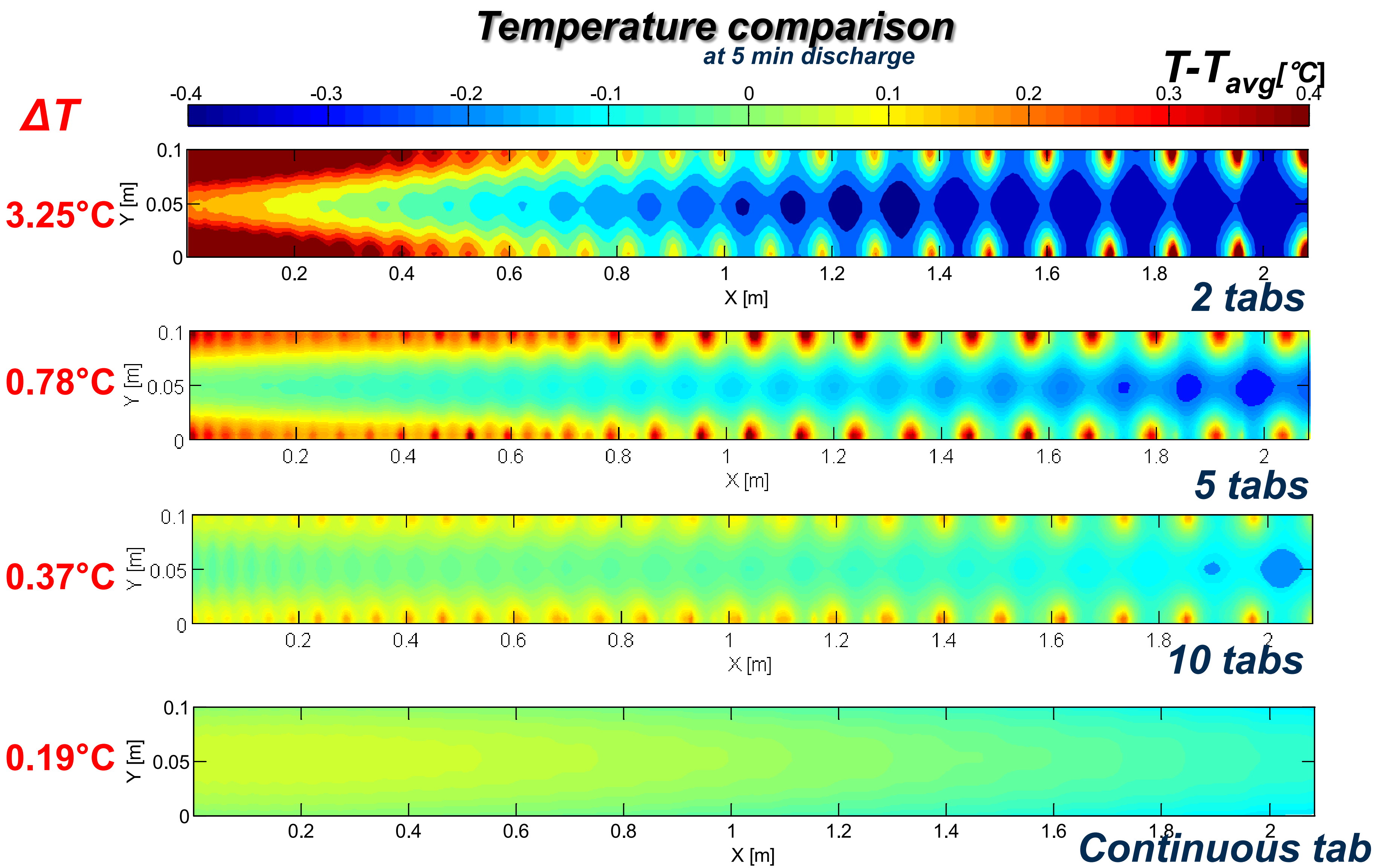
- ***High rate of discharge with a moderate heat transfer condition***
- ***Heat generation dominates temperature distribution in the system***
- ***Temperature difference in the system is relatively small***



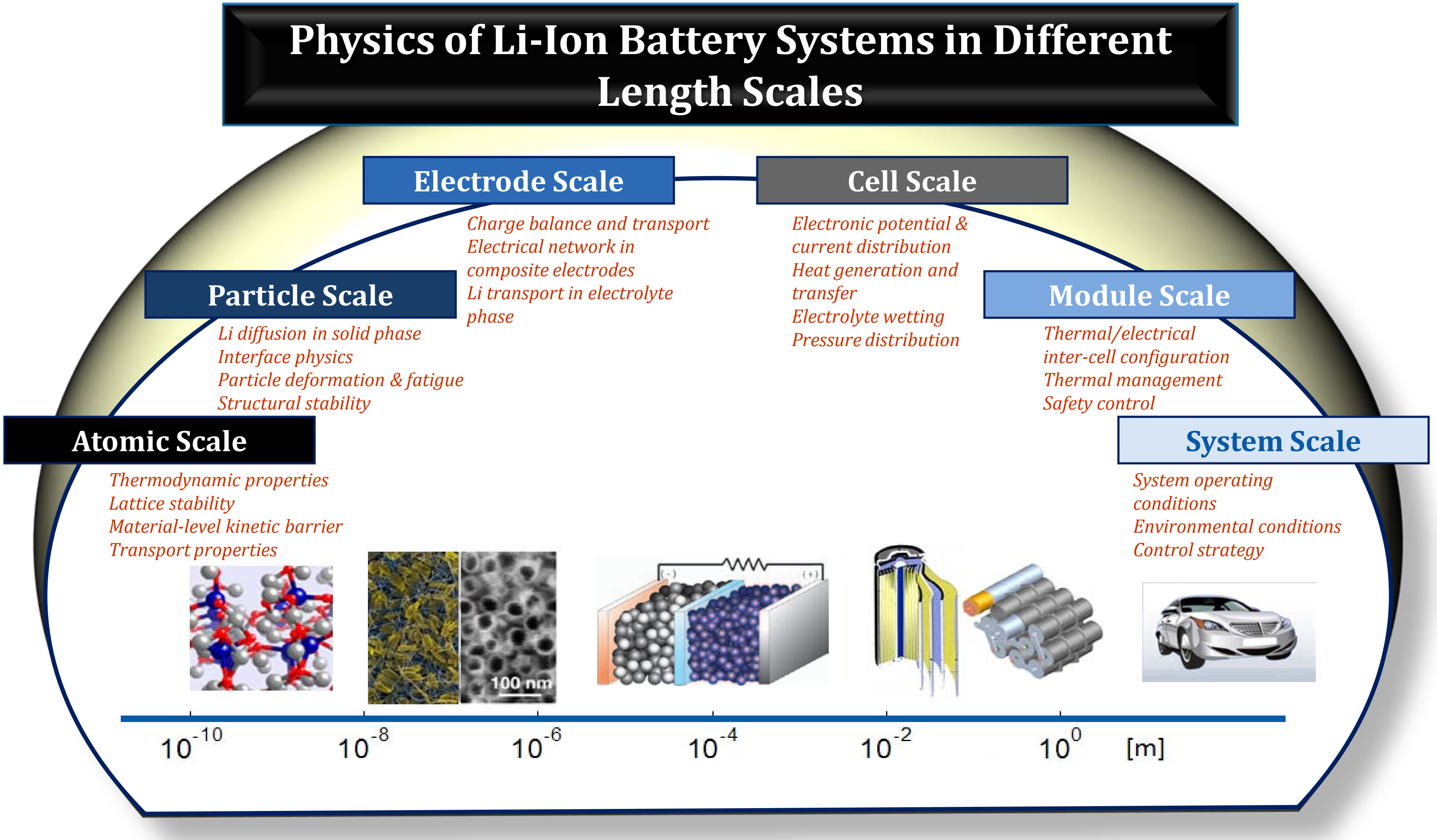
Impact of # of tabs - Discharge Kinetics



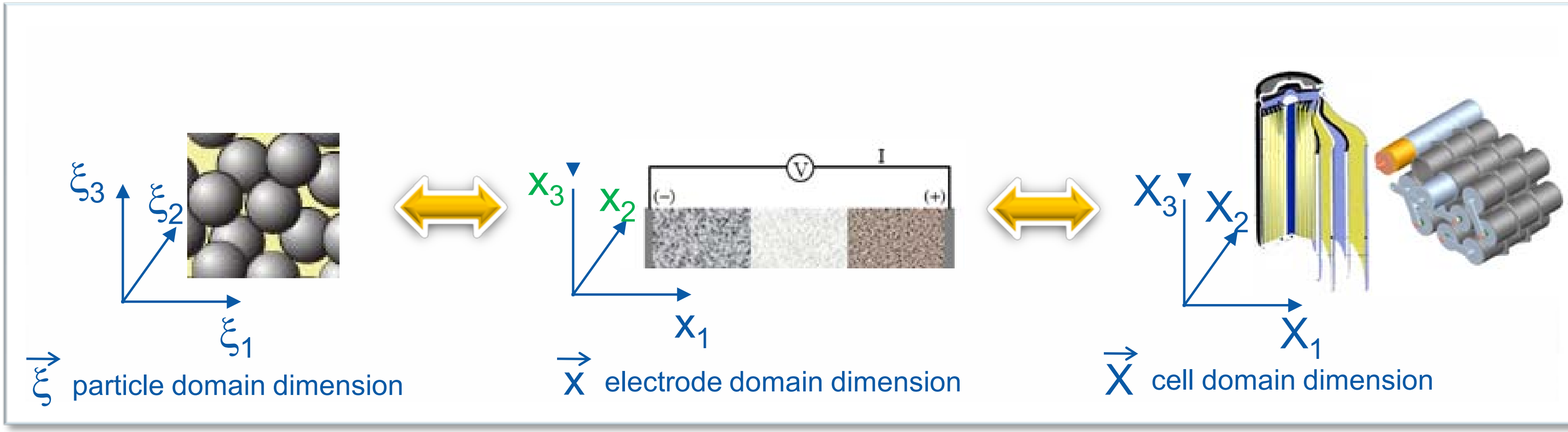
Impact of # of tabs - Temperature



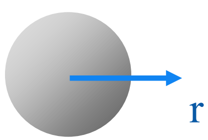
Performance, Durability and Safety



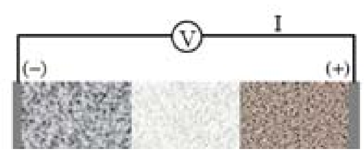
Model Prediction for Cylindrical Cell Degradation



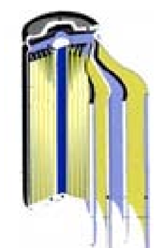
Sub-model Choice



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(ΔDOD,T,V)

Cycling fade
- active material structure degradation and mechanical fracture
- a_2, e_1 = f(ΔDOD,T,V)

Resistance Growth

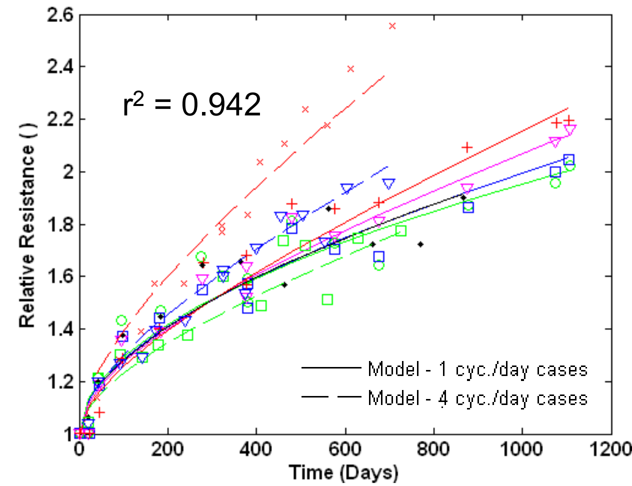
$$R = a_1 t^{1/2} + a_2 N$$

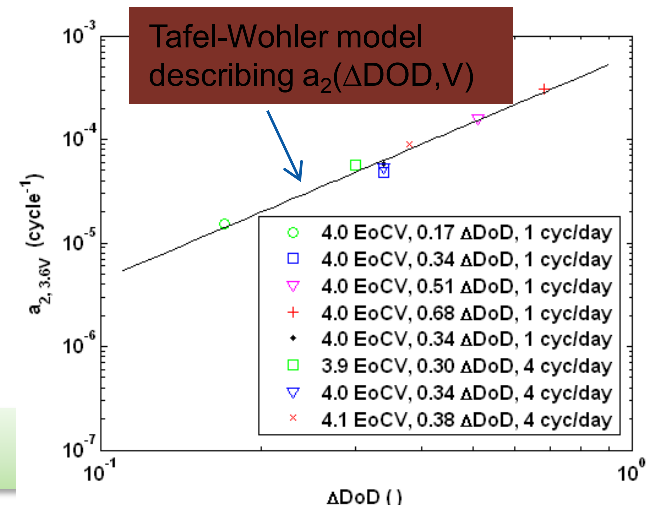
Relative Capacity

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

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

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

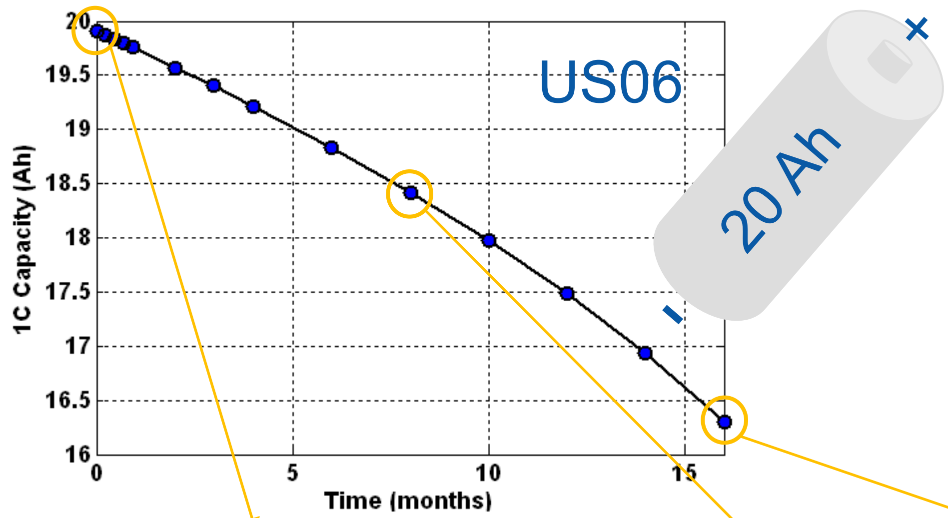




•Data shown above: J.C. Hall, IECEC, 2006.
•Model also fit to DOE/TLVT, Southern CA Edison & NASA data

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

US06 – Nonuniform Capacity Loss

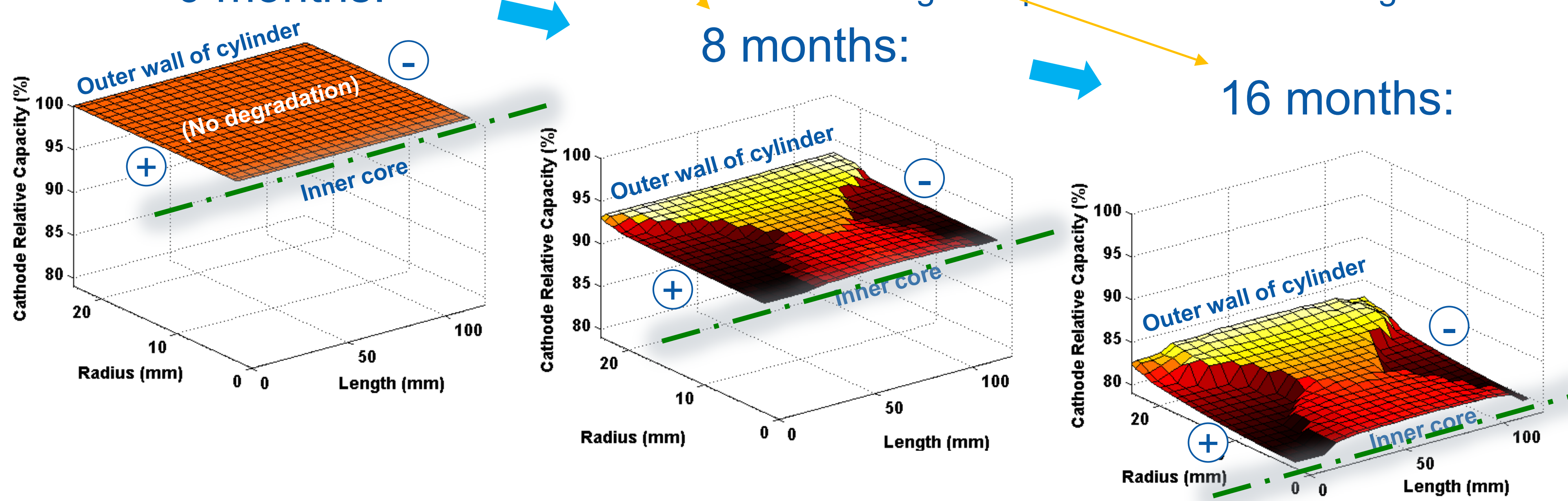


- Regions near terminals suffer most significant capacity loss

  Large overpotential → Excessive cycling

- Inner core loses capacity faster than outer cylinder wall

  High temperature → Material degradation

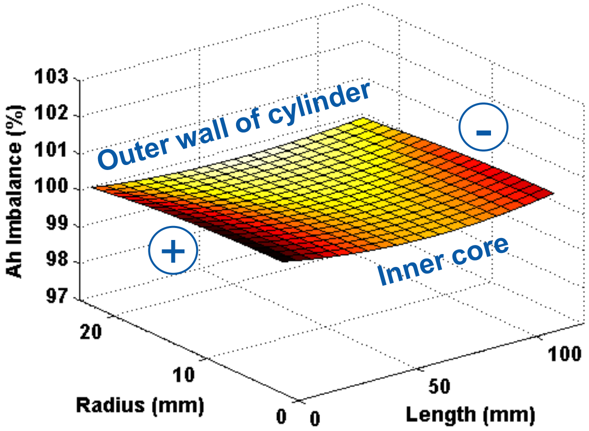


US06 – Ah Imbalance (Nonuniform Cycling)

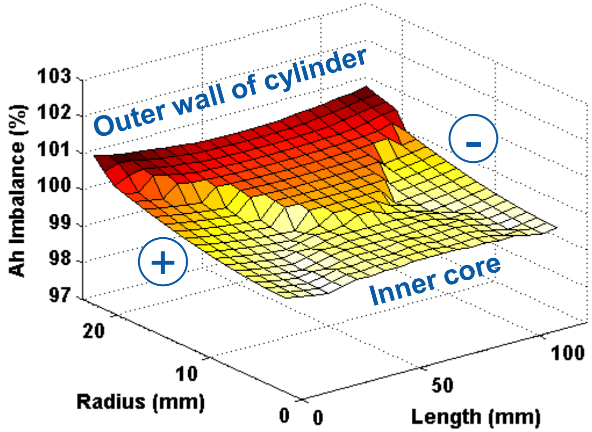
Preferentially cycled regions shift early in life

Imbalance continually grows throughout life

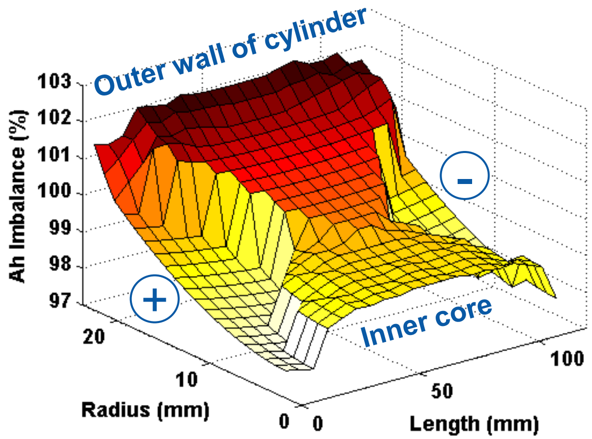
0 months:
0.7% Ah Imbalance



8 months:
1.7% Ah Imbalance



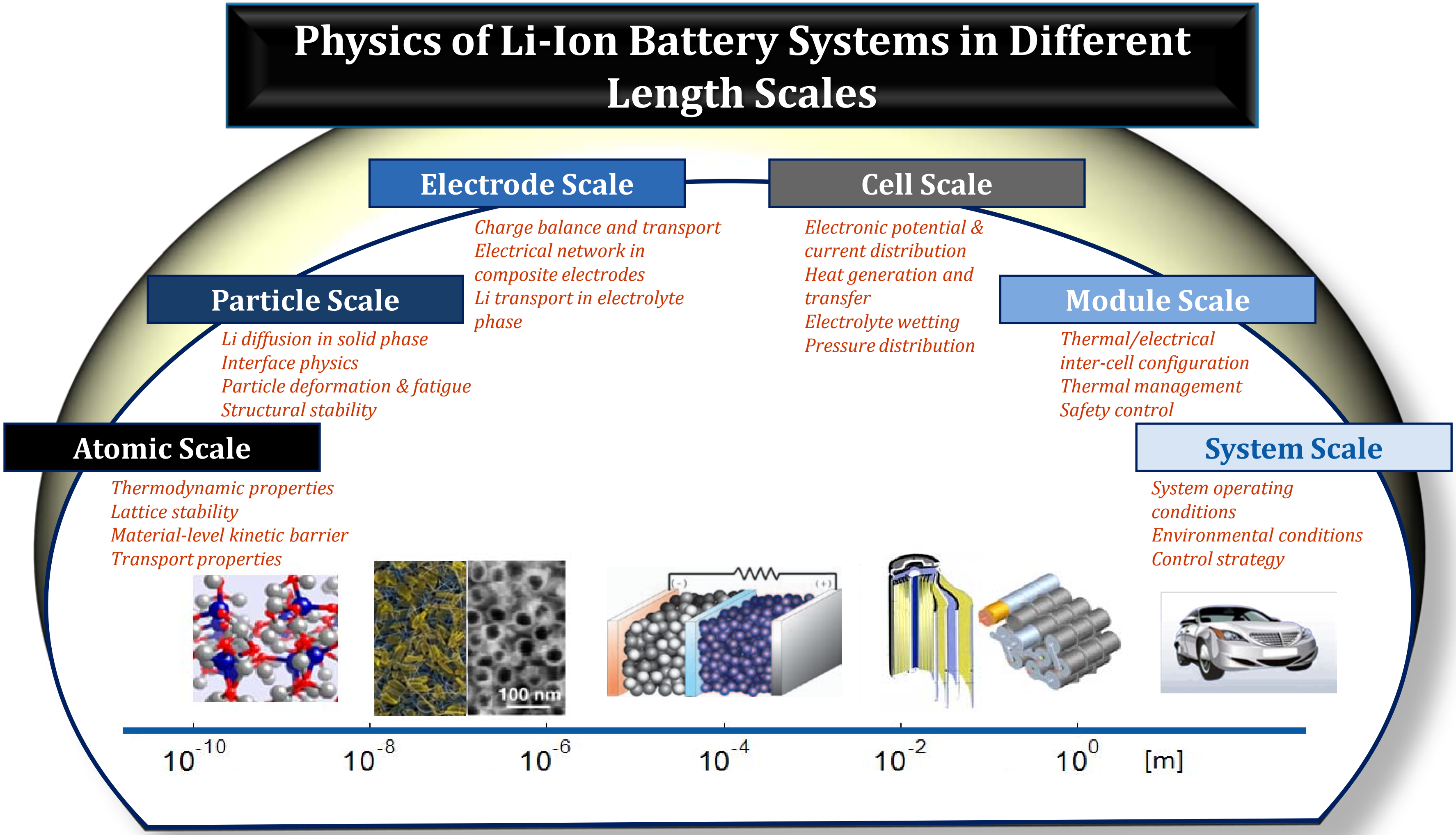
16 months:
4.8% Ah Imbalance



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

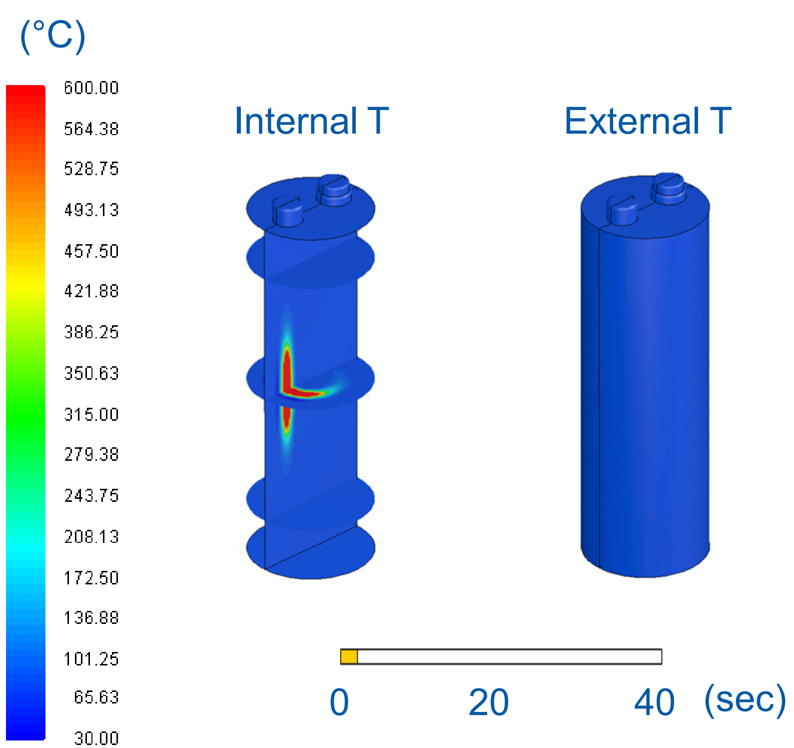
- Later in life, those same areas are most degraded and are cycled least

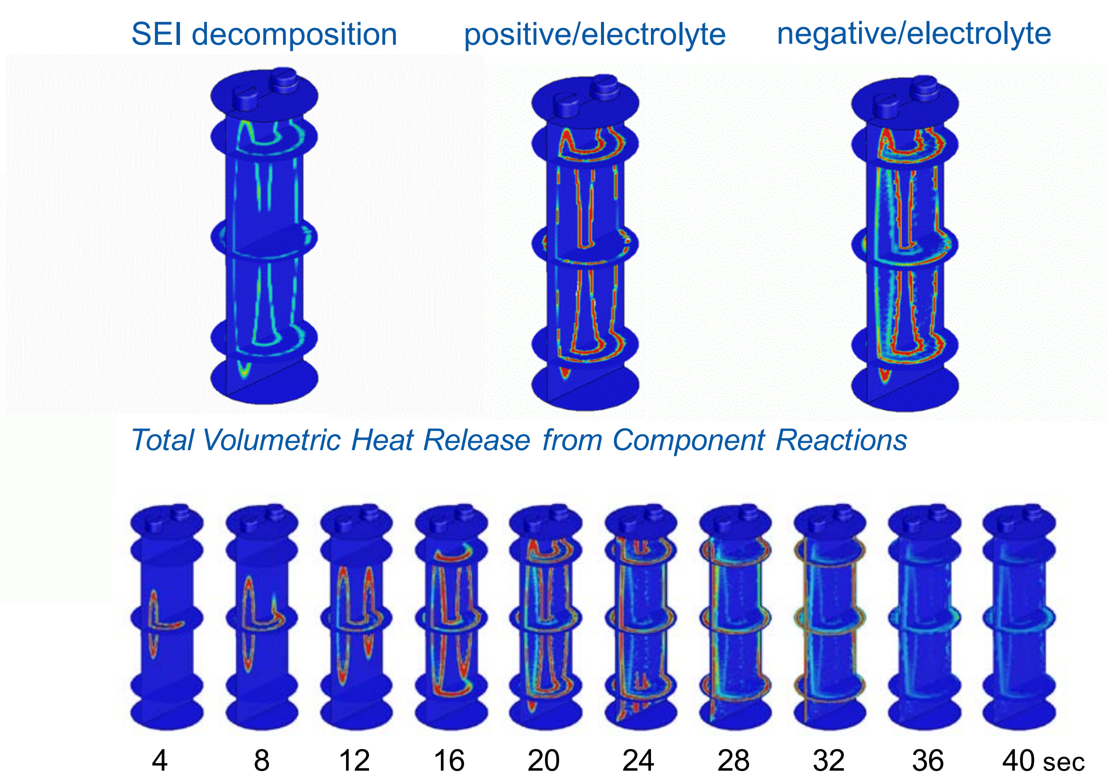
Performance, Durability and Safety



Modeling Thermal Runaway

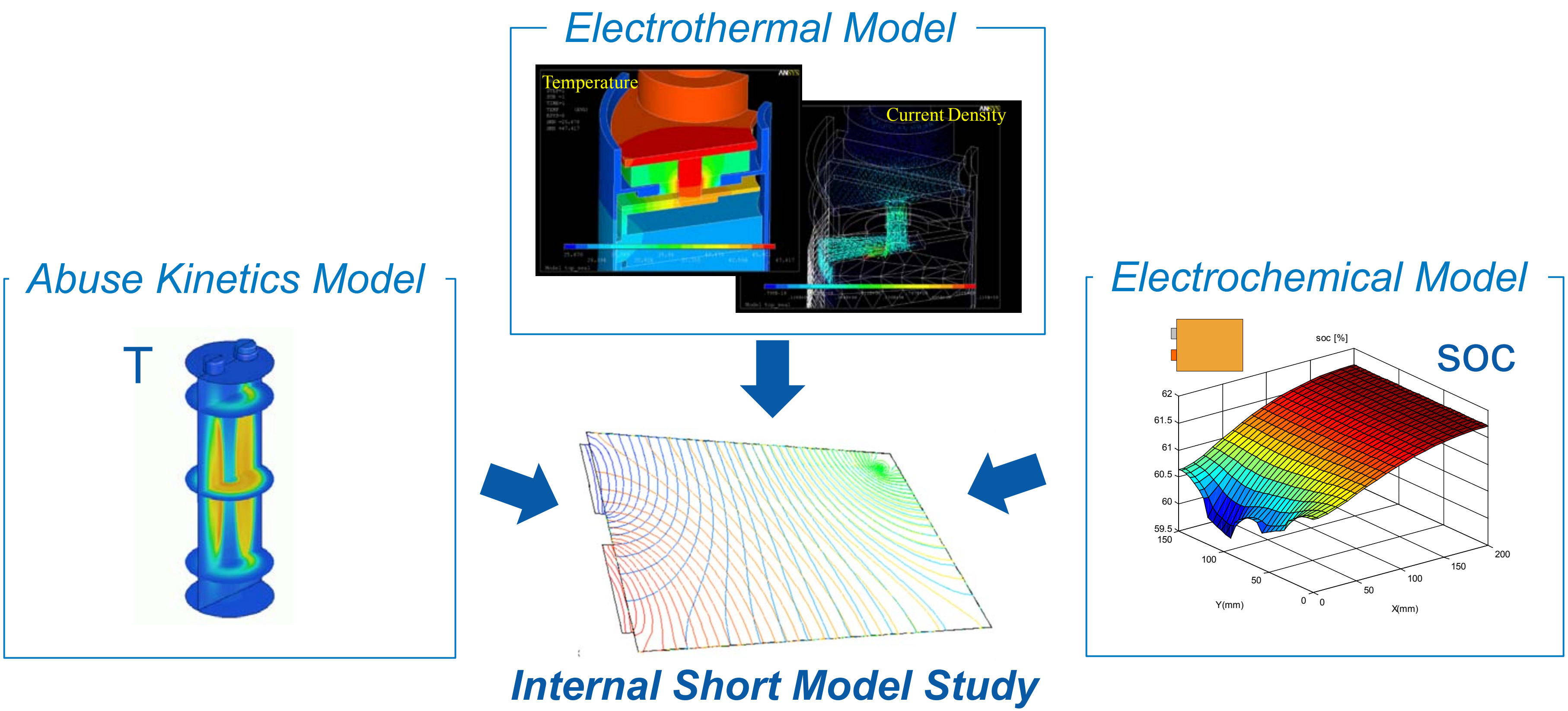
- ✓ Constructed empirical reaction models using calorimetry data for component decompositions: approach practiced by J. Dahn's group
- ✓ Enhanced understanding of the interaction between heat transfer and exothermic abuse reaction propagation for a particular cell/module design
- ✓ Provided insight on 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

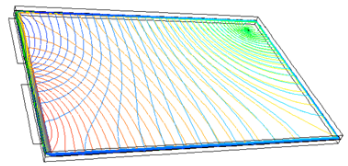


Shutdown Separator for Large Cells ?

Short Between Al & Cu Metal Foils

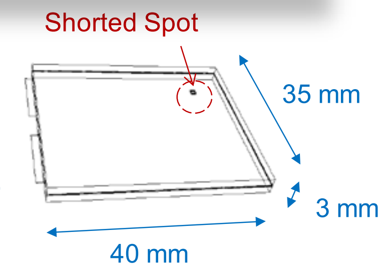
- Cell Capacity: 20 Ah

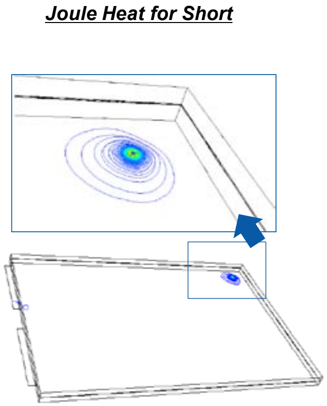
R_{short} ~ 10 mΩ
I_{short} ~ 300 A (15 C-rate)

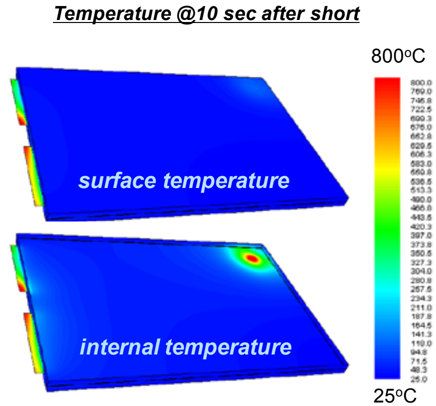


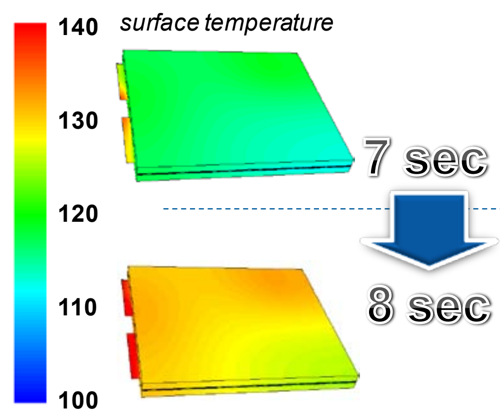
0.4 Ah

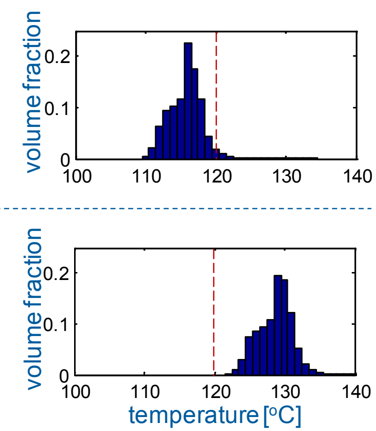
R_{short} ~ 7 mΩ
I_{short} ~ 34 A (85 C-rate)

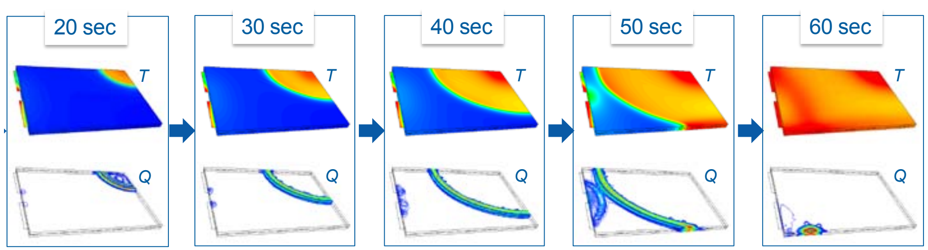


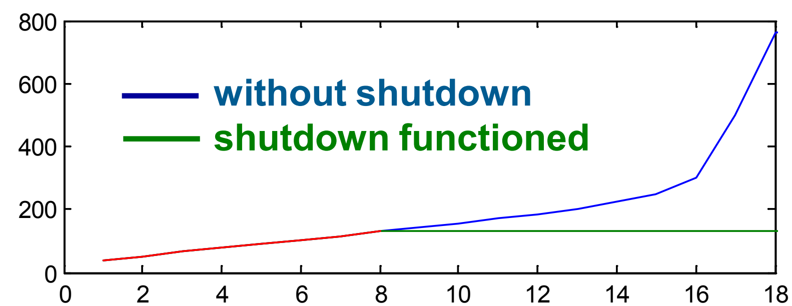












Summary

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!