NREL National Renewable Energy Laboratory

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A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

Three-Dimensional Lithium-Ion Battery Model

Understanding Spatial Variations in Battery Physics to Improve Cell Design, Operational Strategy, and Management

ADVANCED
AUTOMOTIVE
BATTERIES

4th International Symposium on Large Lithium Ion Battery Technology and Application
Tampa, Florida
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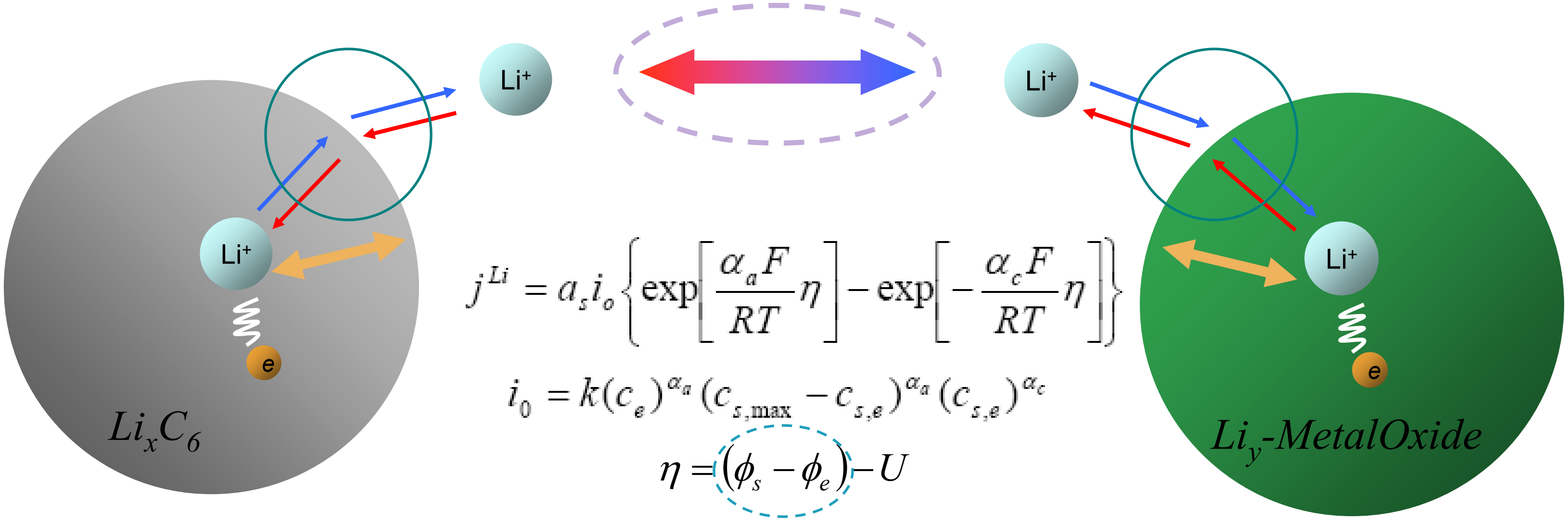
Multi-Scale Physics in Li-ion Battery



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

$$i_0 = k (c_e)^{\alpha_a} (c_{s,\max} - c_{s,e})^{\alpha_a} (c_{s,e})^{\alpha_c}$$

$$\eta = (\phi_s - \phi_e) - U$$

Electrochemical Kinetics

Solid-Phase Lithium Transport

Lithium Transport in Electrolyte

Charge Conservation/Transport

(Thermal) Energy Conservation

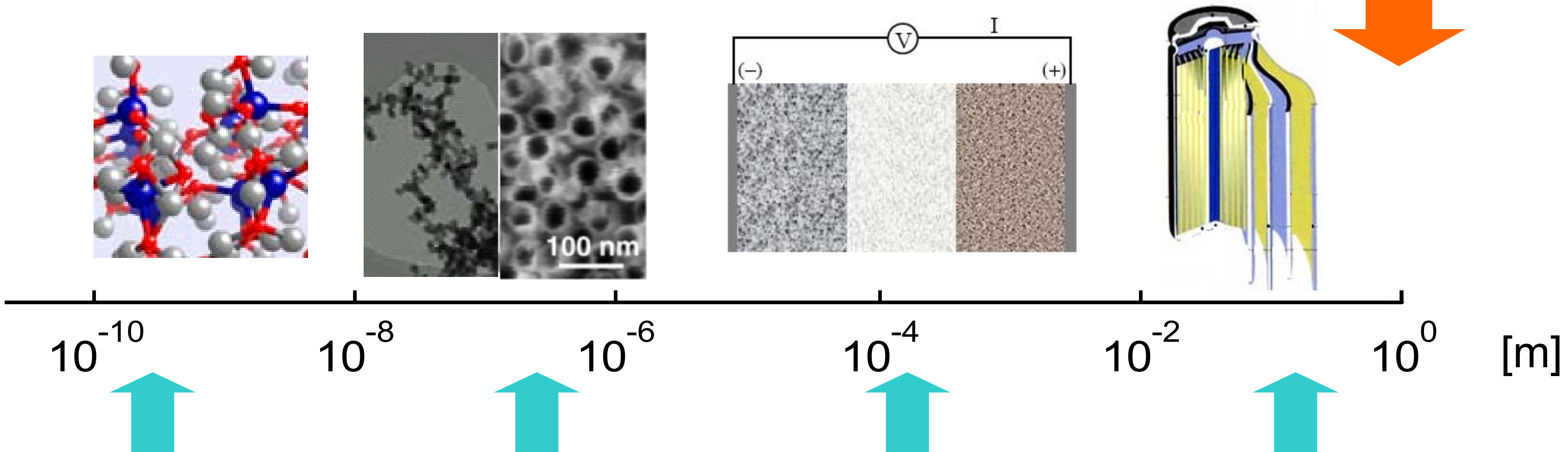
Basic battery physics occurs in a wide range of length & time scales

- *Kinetics*
- *Phase transition*
- *Ion transport*
- *Energy dissipation*
- *Heat transfer*

Requirements & Resolutions

*"**Requirements**" are usually defined in a macroscale domain and terms.*

Performance
Life
Cost
Safety



Design of Materials

- *Voltage*
- *Capacity*
- *Lattice stability*
- *Kinetic barrier*
- *Transport property*

Design of Electrode Architecture

- *Li transport path (local)*
- *Electrode surface area*
- *Deformation & fatigue*
- *Structural stability*
- *Interface physics*

Design of Electrodes Pairing and Lithium Transport

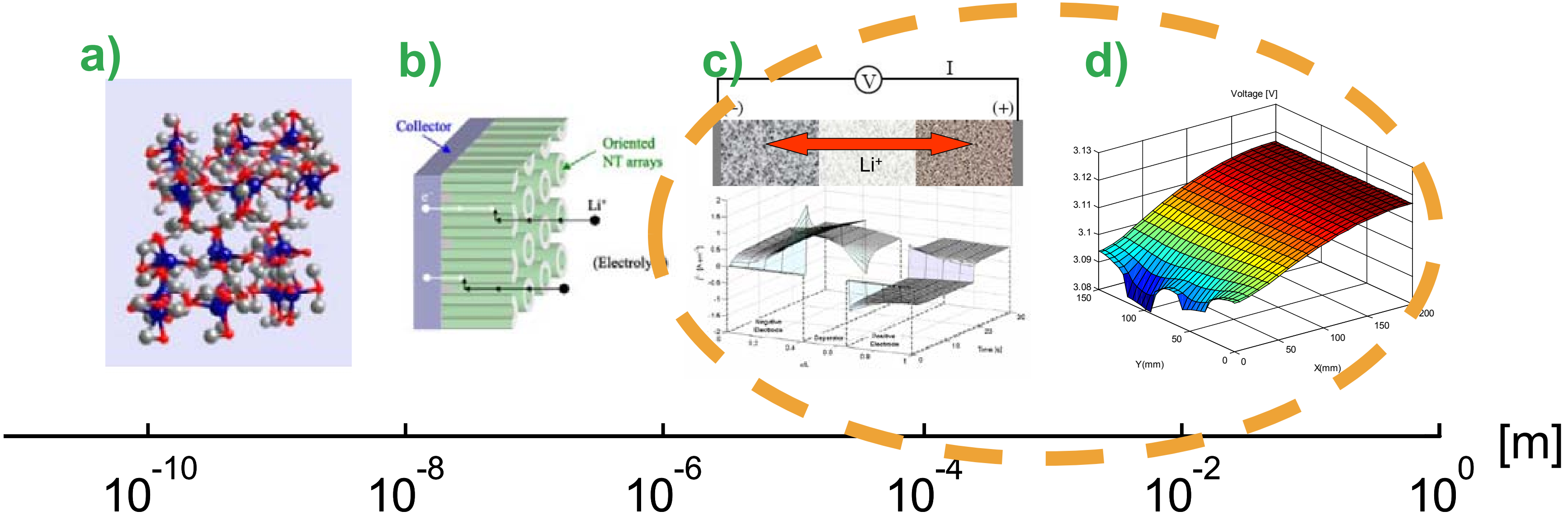
- *Electrodes selection*
- *Li transport*
- *Porosity, tortuosity*
- *Layer thicknesses*
- *Load conditions*

Design of Electronic Current & Heat Transport

- *Electric & thermal connections*
- *Dimensions, form factor*
- *Component shapes*

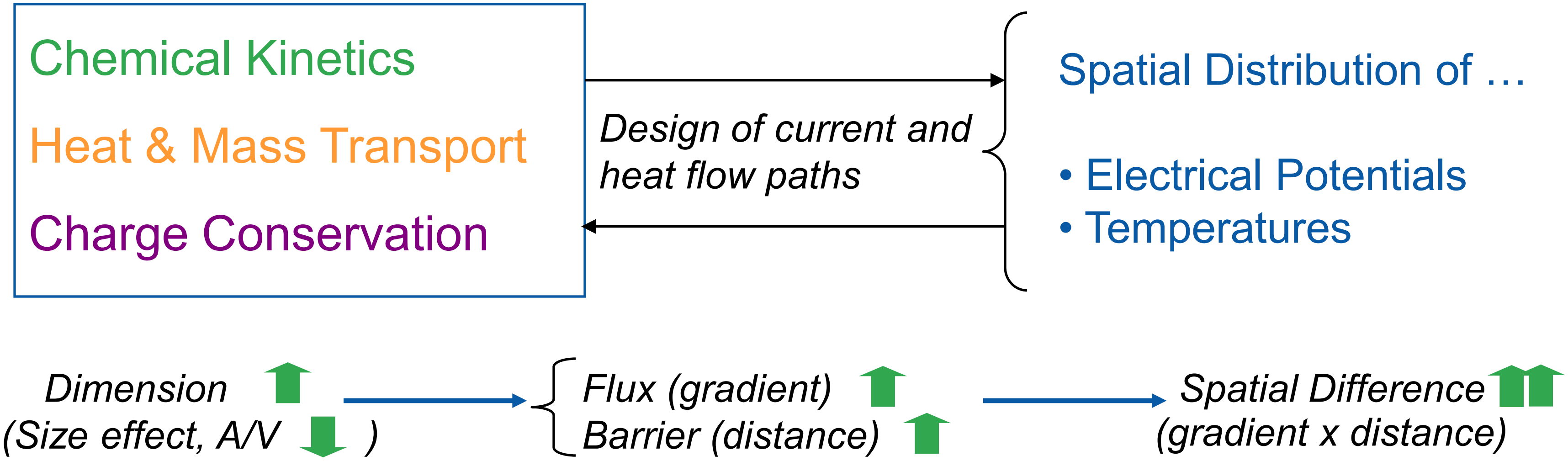
NREL's Li-ion Battery Model Activities

focusing on different length scale physics



a) Quantum mechanical and molecular dynamic modeling
b) Numerical modeling resolving architecture of electrode materials
c) Electrode-scale performance model
d) Cell-dimension 3D performance model

Why use a 3D model?



Chemical Kinetics

Heat & Mass Transport

Charge Conservation

Design of current and heat flow paths

Spatial Distribution of …

- Electrical Potentials
- Temperatures

Dimension ⬆ *(Size effect, A/V* ⬇ *)* → *Flux (gradient)* ⬆ *Barrier (distance)* ⬆ → *Spatial Difference* ⬆⬆ *(gradient x distance)*

→ Spatially Nonuniform Battery Physics

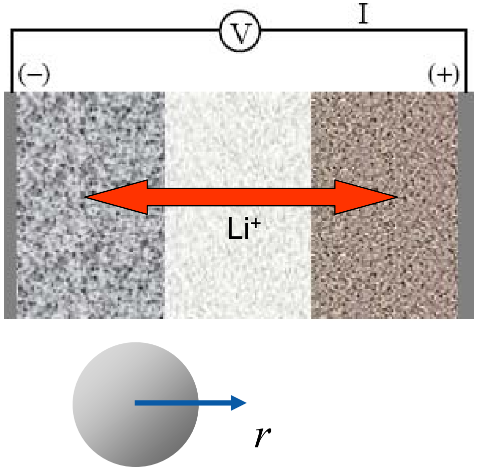
Enhanced understanding provides an opportunity for improving cell …

- *Design*
- *Operation Strategy*
- *Management*
- *Safety*

Electrode-Scale Model

(Doyle, Fuller, and Newman, 1993)

- *This model captures relevant solid-state and electrolyte diffusion dynamics and predicts the current/voltage response of a battery.*
- *Composite electrodes are modeled using porous electrode theory, meaning that the solid and electrolyte phases are treated as superimposed continua without regard to microstructure.*



NREL's Model

- *Finite-Volume Method*
- *Matlab Environment*

Chemical Kinetics

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

$$i_0 = k(c_e)^{\alpha_a}(c_{s,\max} - c_{s,e})^{\alpha_a}(c_{s,e})^{\alpha_c}$$

Heat & Mass Transport

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

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

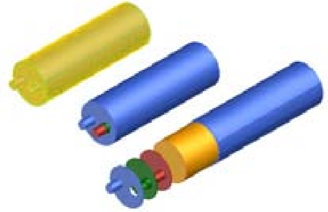
$$\rho c_p \frac{\partial T}{\partial t} = \nabla \cdot (k \nabla T) + q'''$$

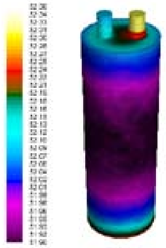
Charge Conservation

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

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

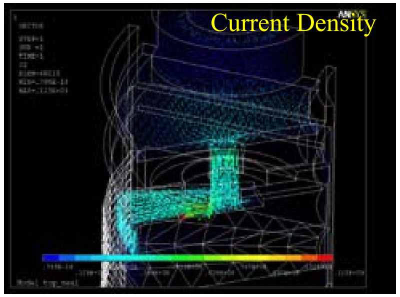
3D Battery Dimension Model

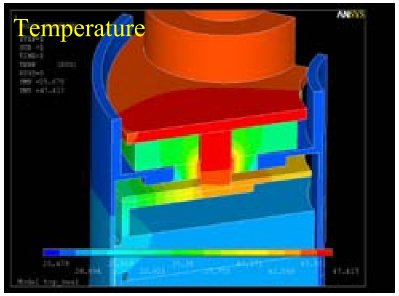


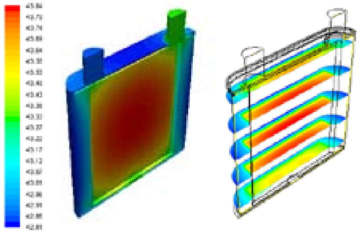


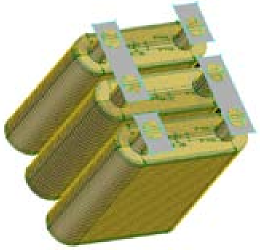
Addressing the effects of:

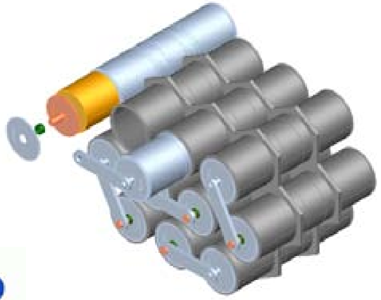
- Nonuniform distributions
- Thermal/electrical path design inside cells/batteries
- Localized phenomena
- Geometries; shape and dimensions of cell component

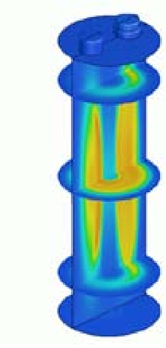


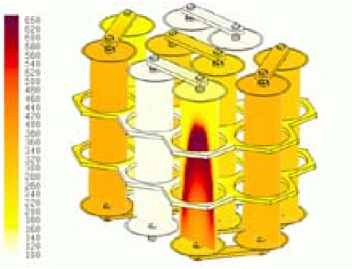










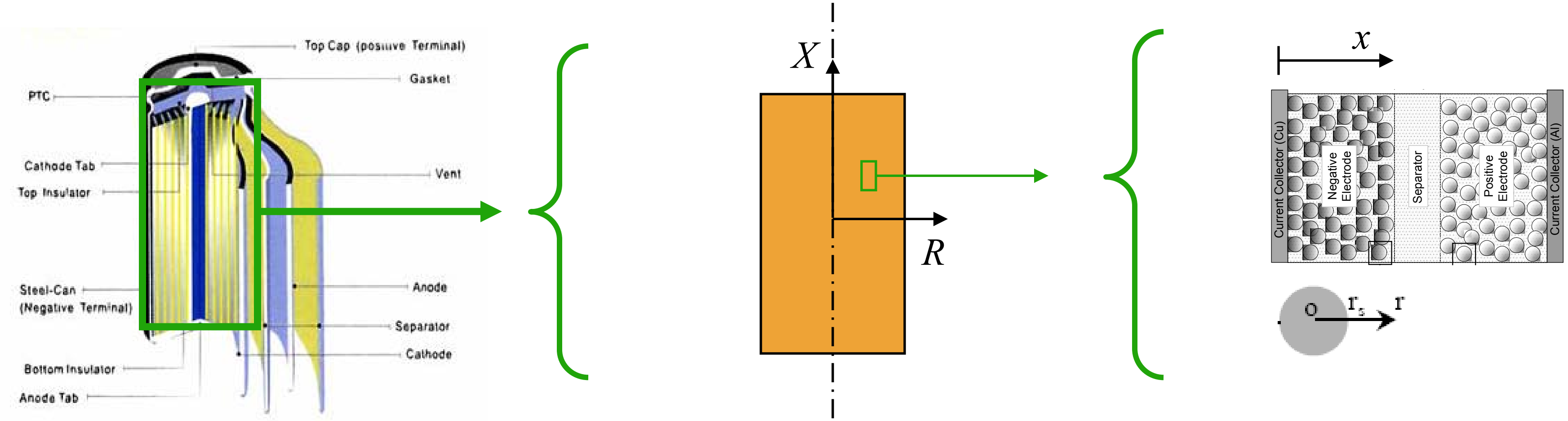


Approach in the Present Study:
Multi-Scale Multi-Dimensional (MSMD) Modeling

To Address ...

- Multi-scale physics from sub-micro-scale to battery-dimension-scales
- Difficulties in resolving microlayer structures in a computational grid

Simulation Domain = **Macro Grid** + **Micro Grid**
(Grid for Sub-grid-scale Model)



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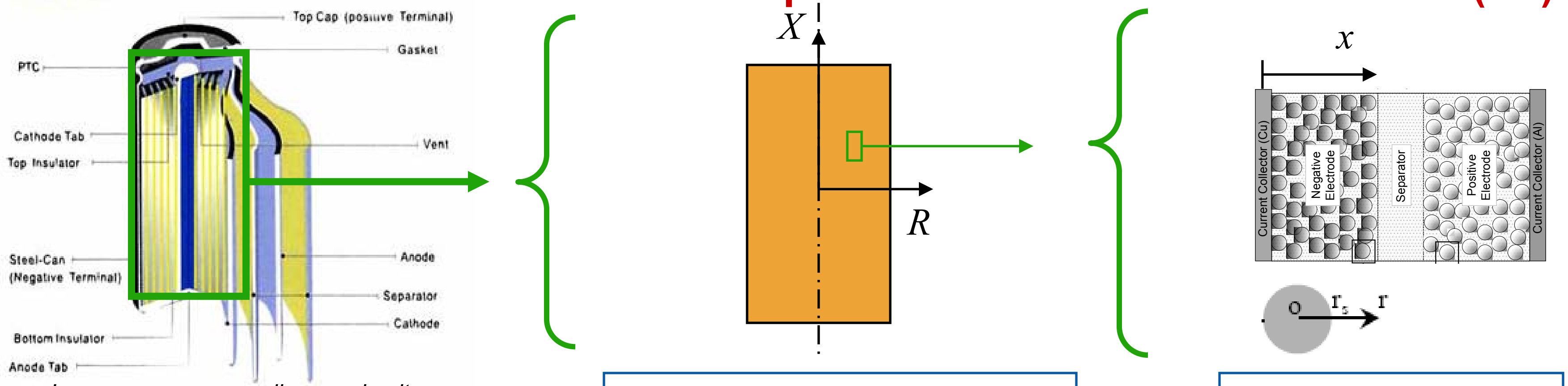
Solution Variables

Detailed Structure ≈ **Cell Dimension Transport Model** + **Electrode Scale Submodel (1D)**



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$$T(X,R,t)$$
$$V(X,R,t)$$
$$i(X,R,t)$$
$$SOC(X,R,t)$$
$$Q(X,R,t)=\int_x Q_i \frac{Adx}{V}$$

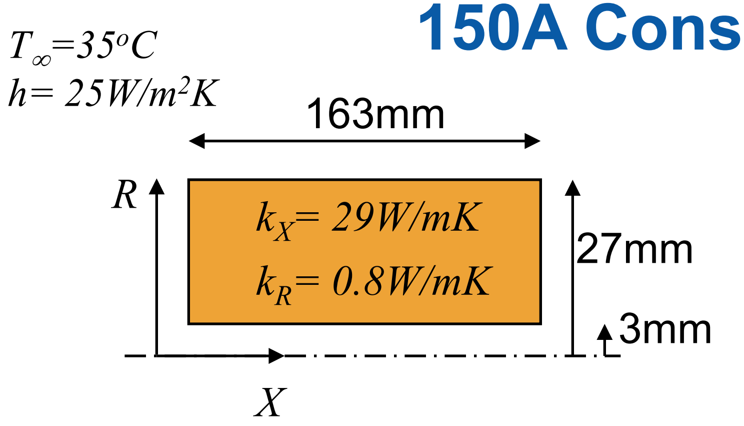
$$\phi_s(X,R,x,t)$$
$$\phi_e(X,R,x,t)$$
$$c_s(X,R,x,r,t)$$
$$c_e(X,R,x,t)$$
$$j_{Li}(X,R,x,t)$$
$$Q_i(X,R,x,t)$$

NOTE:
Selection of the "sub-grid electrochemical model" is independent of the "macro-grid model" selection.

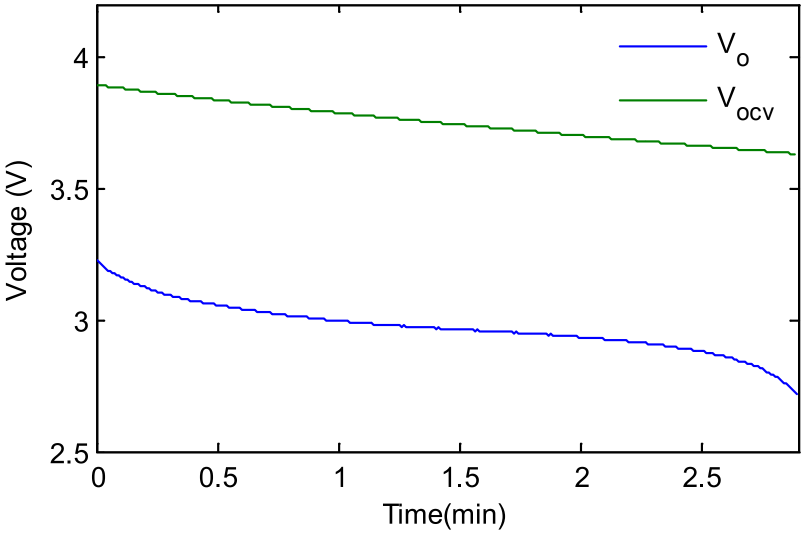
Model Combination

Axisymmetric FVM Model for Macro-Domain Model
+ 1D FVM Model for Electrochemistry Submodel

150A Constant Current Discharge



	X	R	x	r
Grid#	12	8	14	4



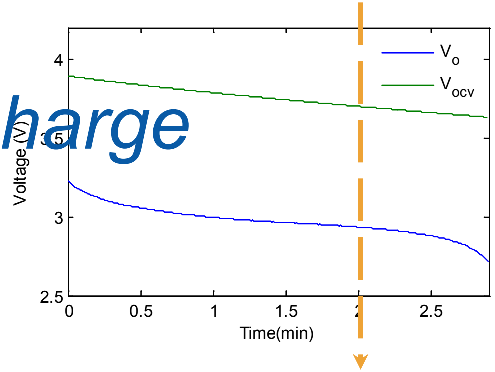
time step size: 0.5 sec, time step #: 360

Simulation time: 3 minutes

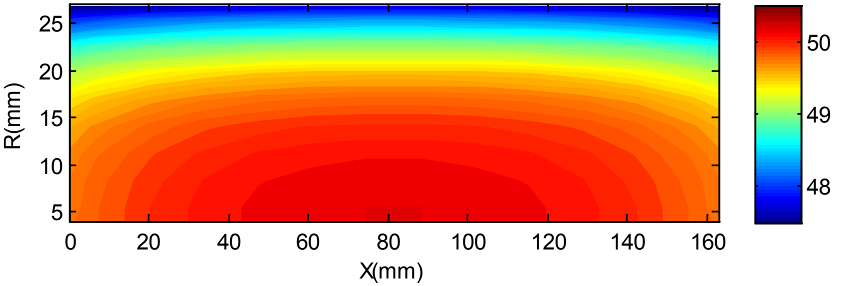
Computation time: 98 minutes (Windows/PC)

Simulation Results

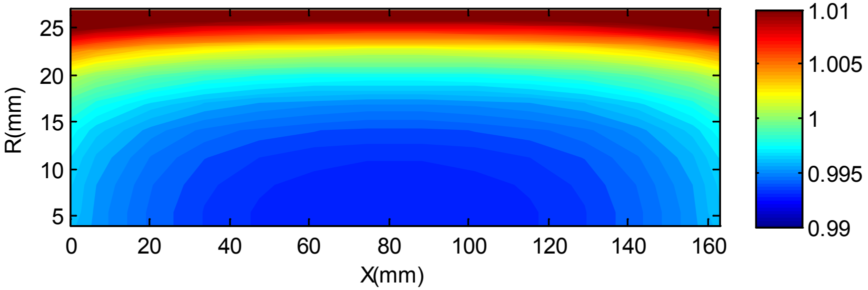
Snapshot 2 minutes after start of discharge



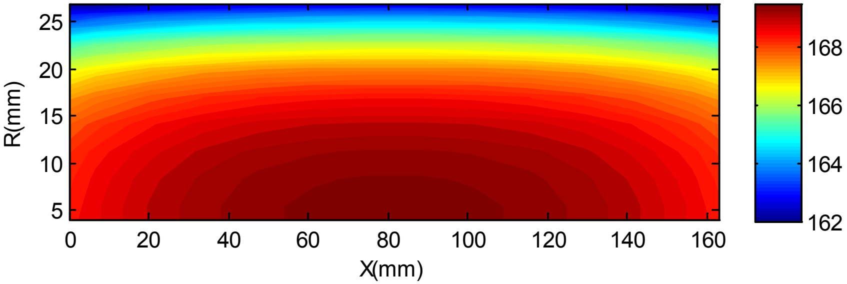
TEMPERATURE [^{o}C]



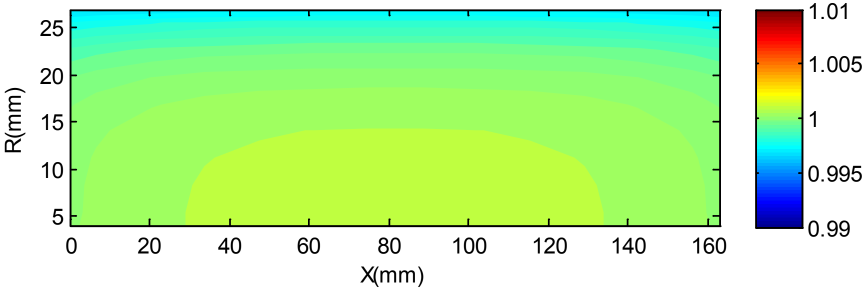
Normalized ANODE SURFACE CONCENTRATION



CURRENT PRODUCTION [A/m^2]



Normalized CHATHODE SURFACE CONCENTRATION



Another Combination Choice

Axisymmetric FVM Model for Macro-Domain Model
+ State Variable Model (SVM) for Submodel

MSMD model incorporating SVM Submodel runs ~1.75 faster than real time.

SVM is preferred because of its fast execution

- SVM, developed by Kandler Smith (NREL), quickly solves “Newman type” governing equations using numerical schemes for calculating load reduction.
- Dropping very fast battery responses (approx. 60 Hz or more) is one of the main calculation order reduction methods used in the model.
- SVM is **promising for use in on-board BMS reference model** because of its fast execution and capability to provide nonmeasurable electrochemical parameters and current and voltage responses with potentially better accuracy.

For details about the State Variable Model:
See the Poster Presentation by Kandler Smith (NREL) titled,
“Fast Running Electrochemistry-Based Models for Battery Design, Integration, and Control”

Analysis

Temperature Variation in a Cylindrical Cell

- *Uniform Potential Assumption*
- *Impact of Aspect Ratio*
- *Impact of Cell Size*

Temperature & Potential Variation in a Prismatic Cell

- *Impact of Tab Location and Size*

Analysis

Temperature Variation in a Cylindrical Cell

- *Uniform Potential Assumption*
- *Impact of Aspect Ratio*
- *Impact of Cell Size*

Temperature & Potential Variation in a Prismatic Cell

- *Impact of Tab Location and Size*

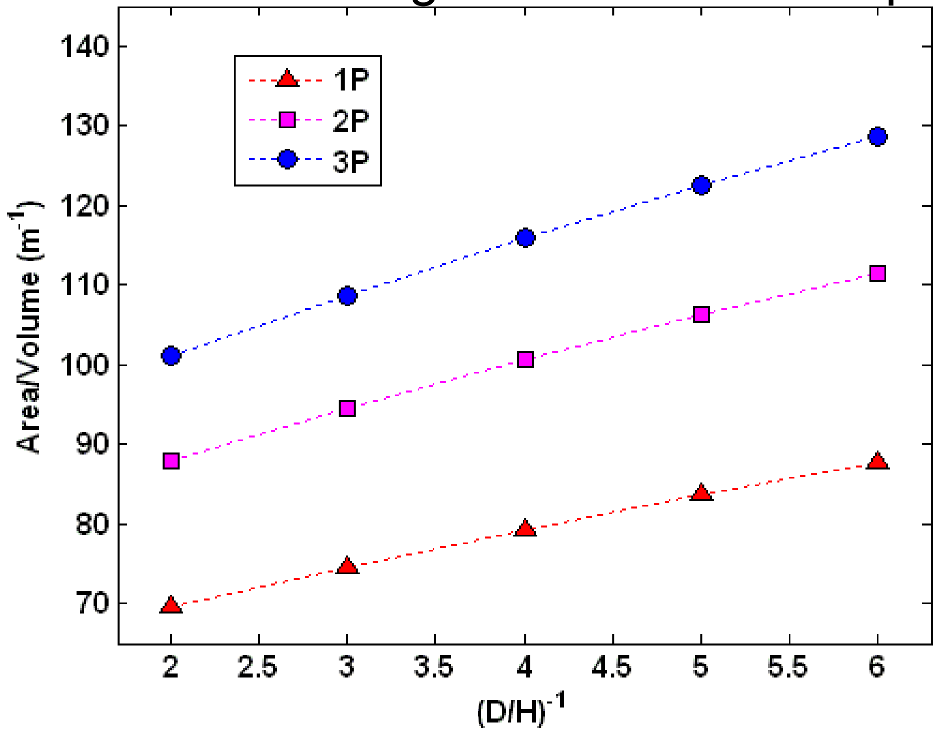
Considerations for Addressing Thermal Issues in PHEV-type Cells

- High energy *and* high power requirements
- Large format may be preferred to small cells
  - Fewer number of components
  - Fewer interconnects
  - Less monitoring & balancing circuitry
  - Less expensive
  - Less weight
- Significant heating may be possible, depending on power profile
- Internal temperature imbalance can lead to unexpected performance and life degradation

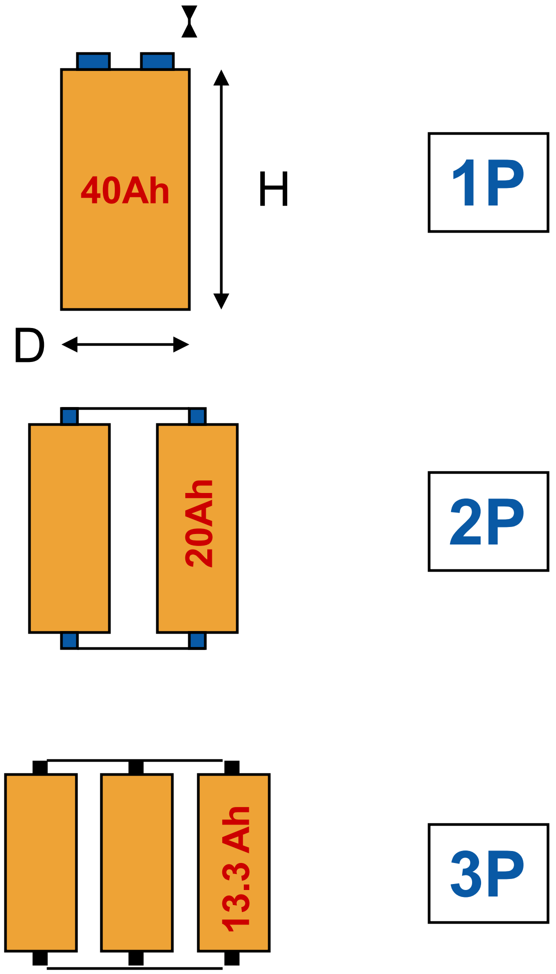
Analysis Parameters

For a fixed capacity (electrode volume), surface area for heat rejection can be increased via:

- Reducing D/H ratio
- Increasing number of cells in parallel (#P)



Surface area includes side, top & bottom of can. All cells assumed to have inactive inner mandrel with 8mm diameter.

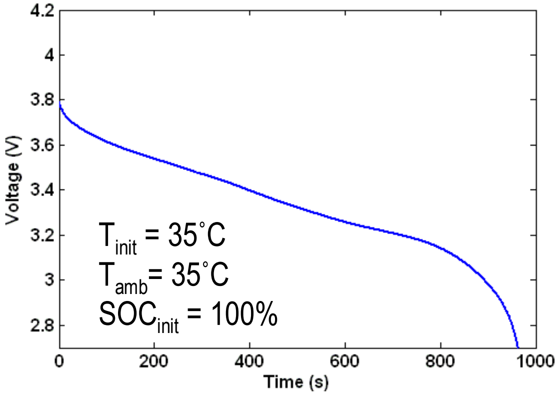


Two Usage Profiles

The two cases explored in this presentation:

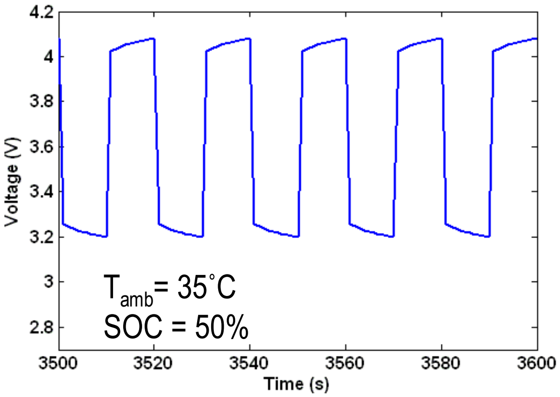
① **150A Max. Cont. Discharge**

- Transient, Charge Depleting
- Air Convection (15 W/m^{2}K)



② **200A Geometric Cycle**

- Steady-State, Charge Sustaining
- Liquid Cooling (150 W/m^{2}K)



→ Moderate Thermal Condition

→ Severe Thermal Condition

Results: 150 A Continuous Discharge

Transient Results

D/H = ¼

h = 15 W/m²K

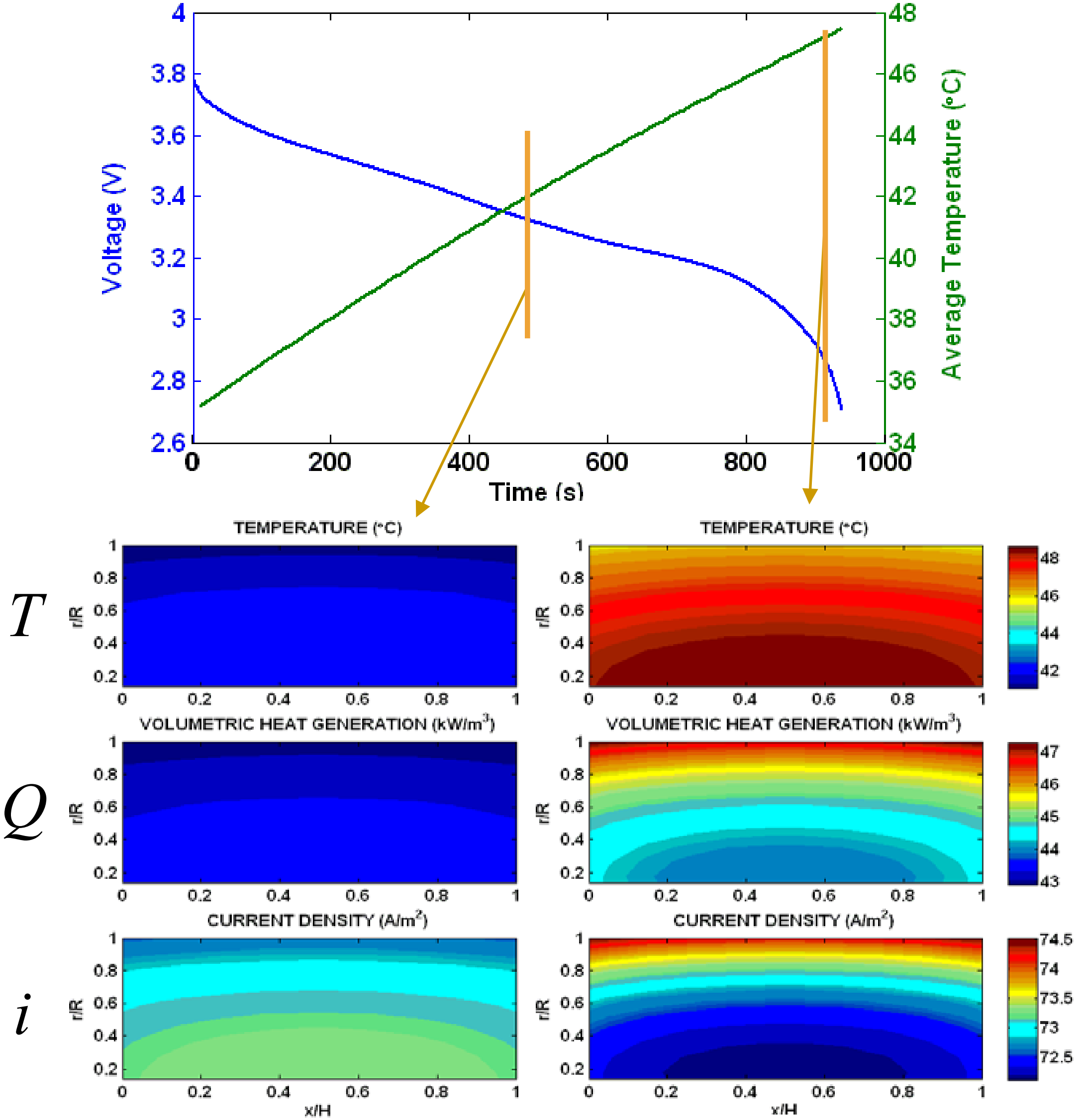
T_{amb} = 35°C

After 500 seconds of discharge:

- Cell center is slightly warmer than exterior
- Preferential reaction current at cell center

Near the end of discharge:

- Cell center depleted/saturated
- Preferential reaction current at cell exterior



150 A Single Discharge (at End)

D/H = ¼

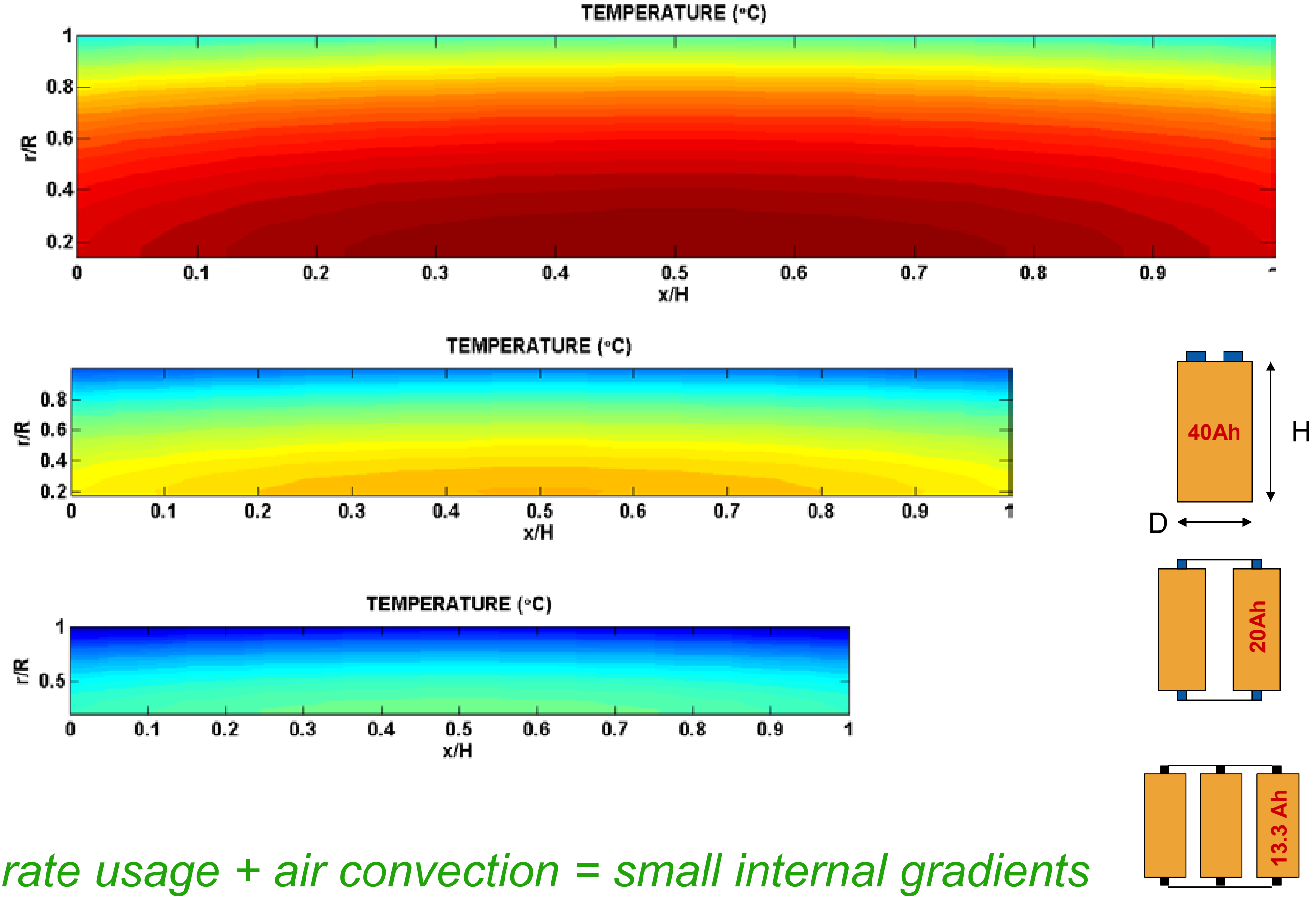
h = 15 W/m^2K

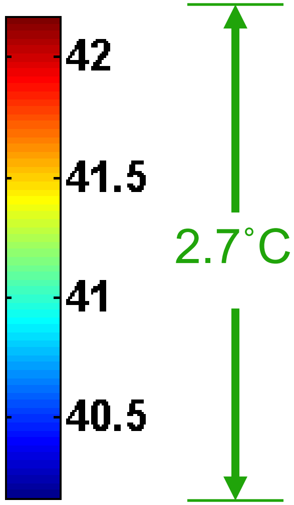
T_{amb} = 35 C

1P

2P

3P

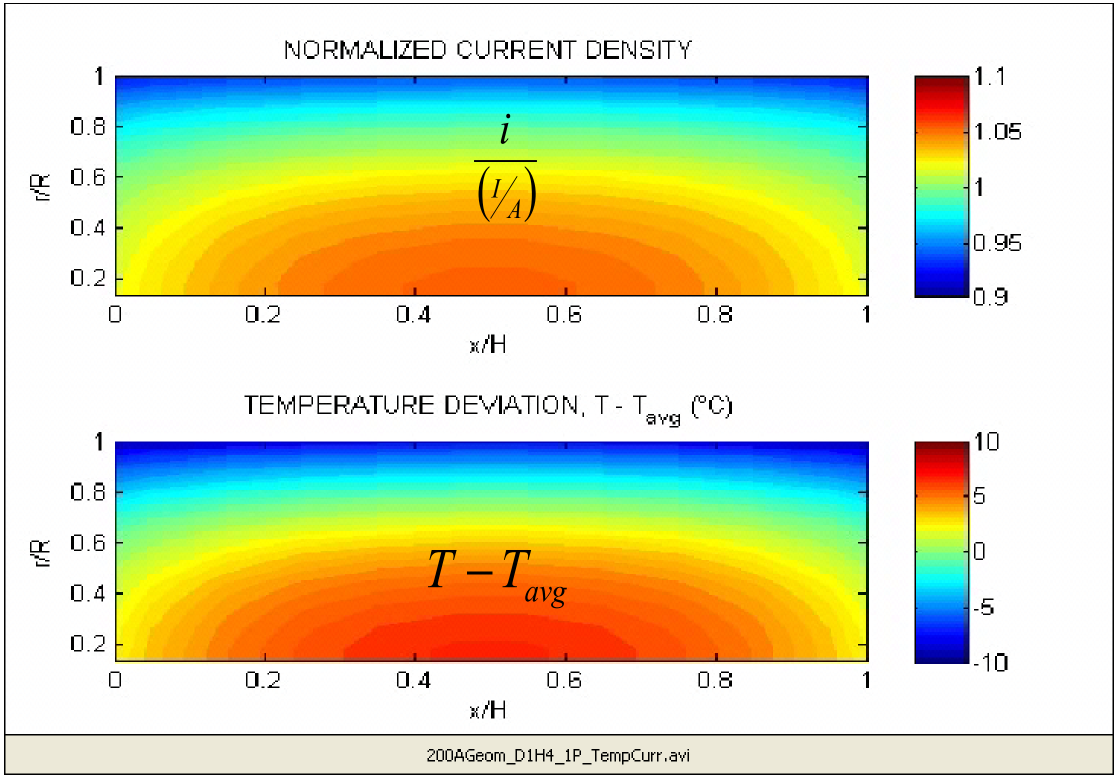




Moderate usage + air convection = small internal gradients

200 A Geometric Cycling

At Steady State



~16% difference in local current production

$\Delta T = \sim 17\ ^{o}C$

D/H = ¼

h = 150 W/m^2K

T_{amb} = 35°C

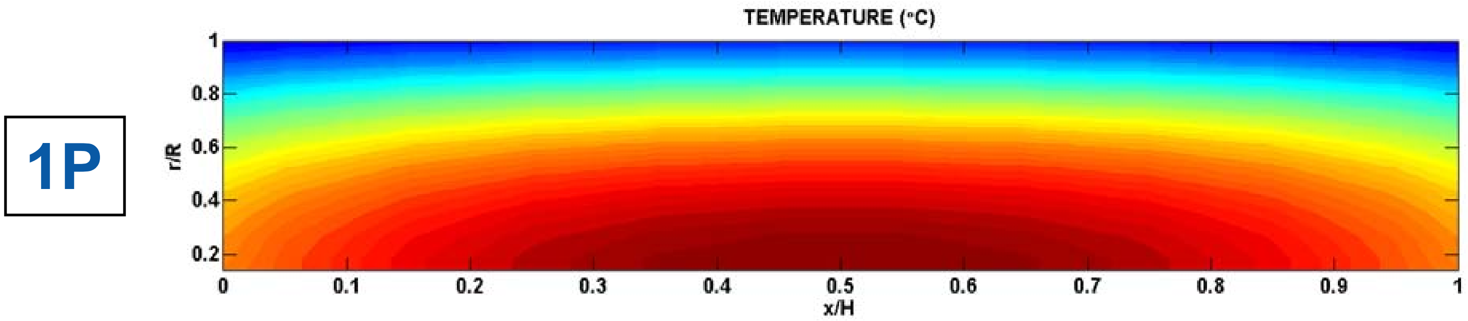
1P size cell (40 Ah)

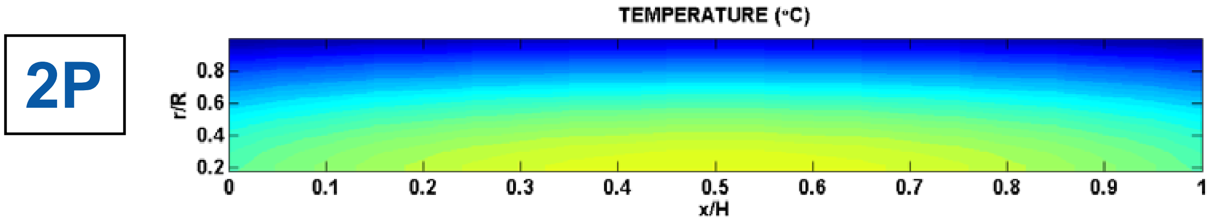
200 A Geometric Cycle (Steady-State)

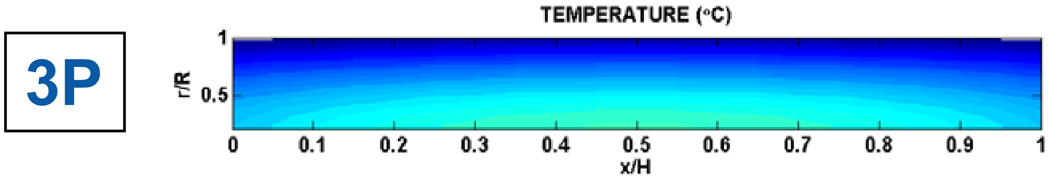
D/H = ¼

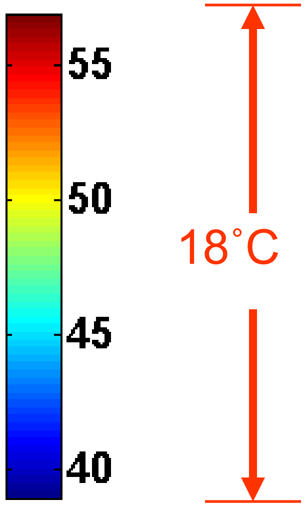
h = 150 W/m²K

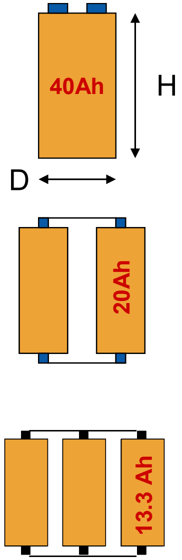
T_{amb} = 35 C











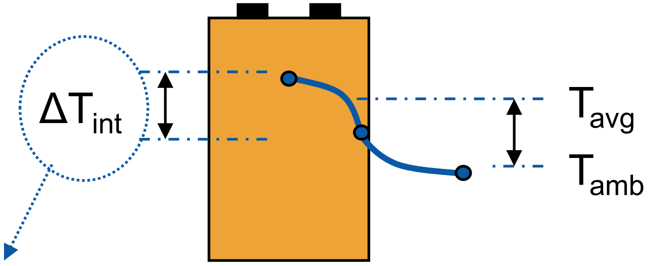
Severe usage + liquid cooling = large internal gradients

200 A Geometric Cycle (Steady-State)

Internal Temperature Difference

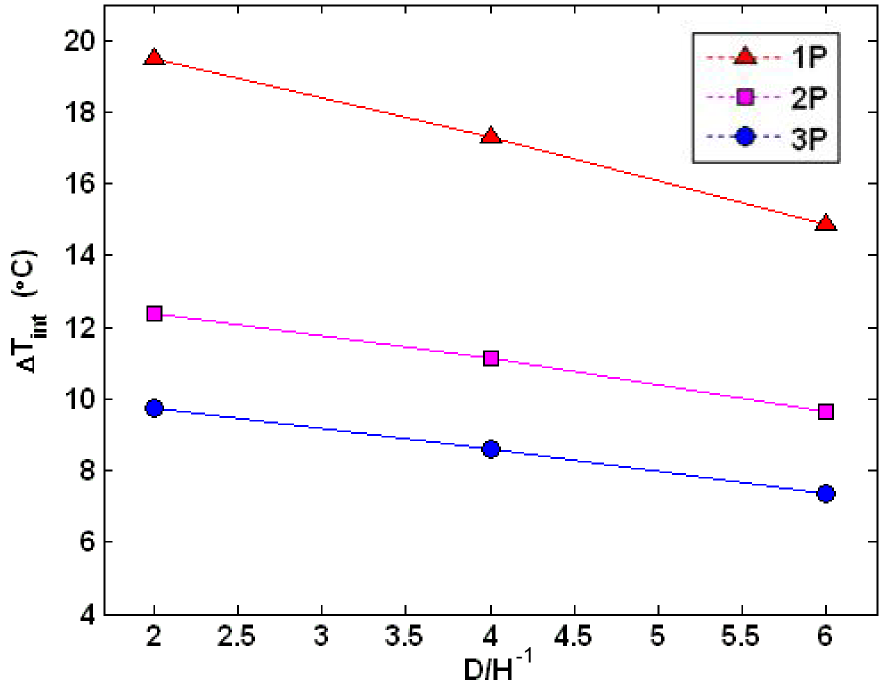
D/H ratio ~4.5˚C ↕

2P ~6.0˚C, 3P ~9.0˚C ↓



h = 150 W/m²K

T_{amb} = 35°C



- *Under severe usage, low D/H and/or >1P designs significantly reduce thermal stress*
- *Larger diameter leads to higher internal gradient*

- *Multidimensional electrochemical cell model quantified the impacts of D/H aspect ratio and cell size on the internal temperature difference.*

Analysis

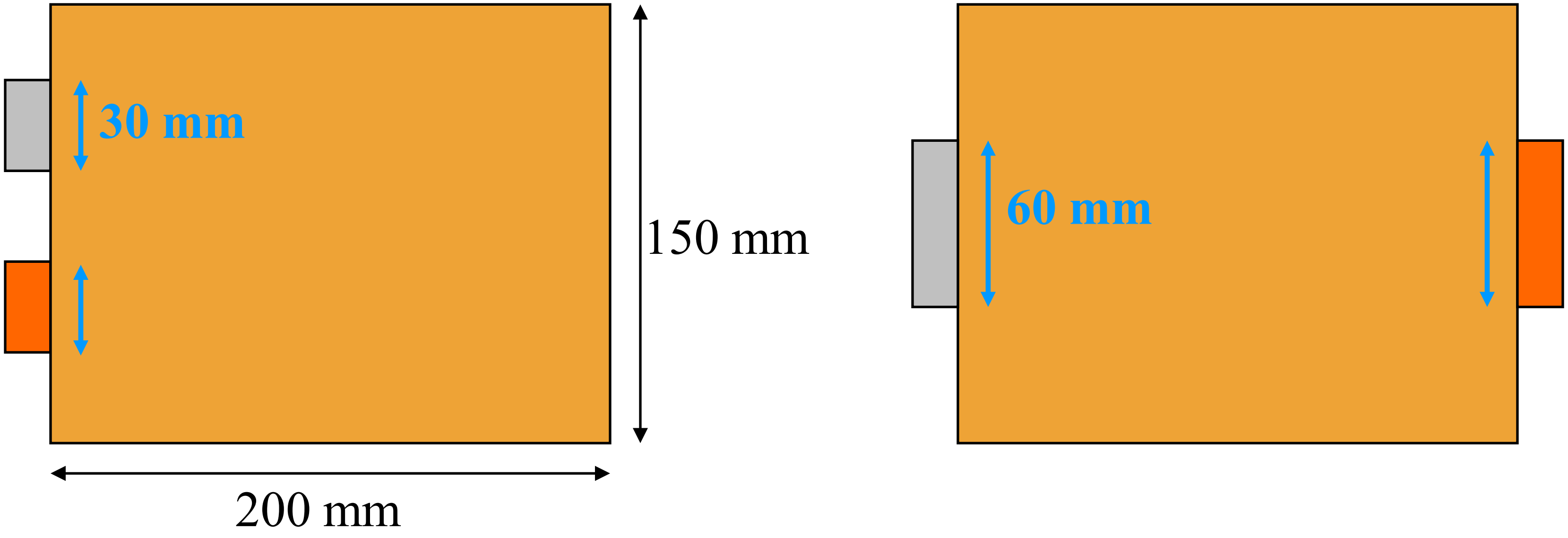
Temperature Variation in a Cylindrical Cell

- *Uniform Potential Assumption*
- *Impact of Aspect Ratio*
- *Impact of Cell Size*

Temperature & Potential Variation in a Prismatic Cell

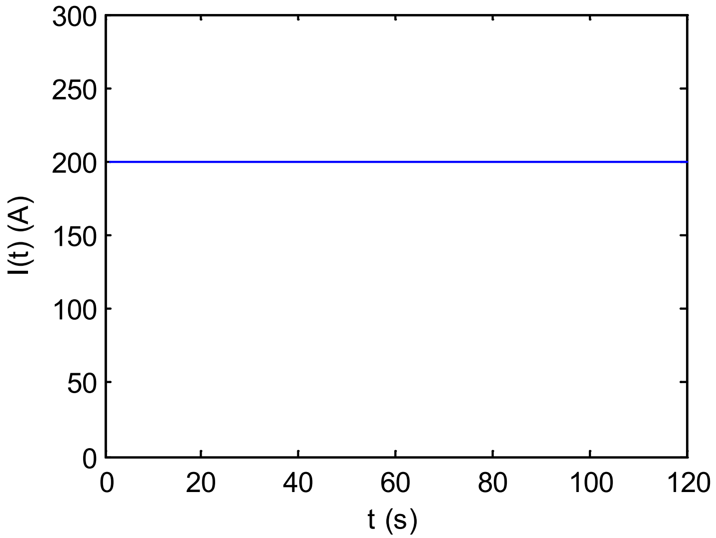
- *Impact of Tab Location and Size*

Impact of Tab Location & Size

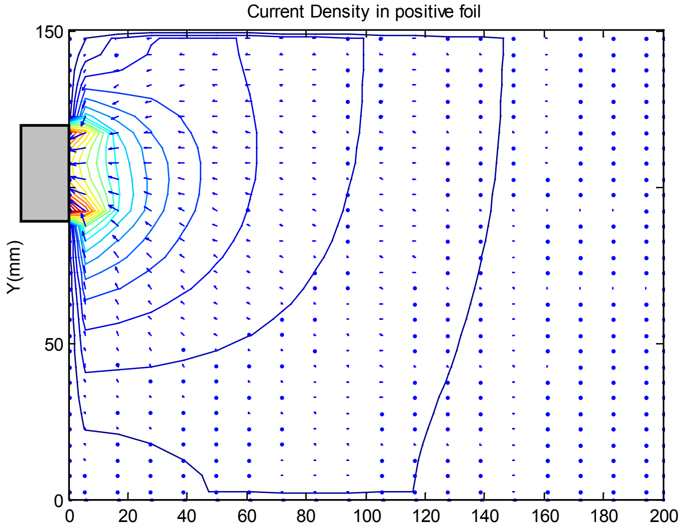


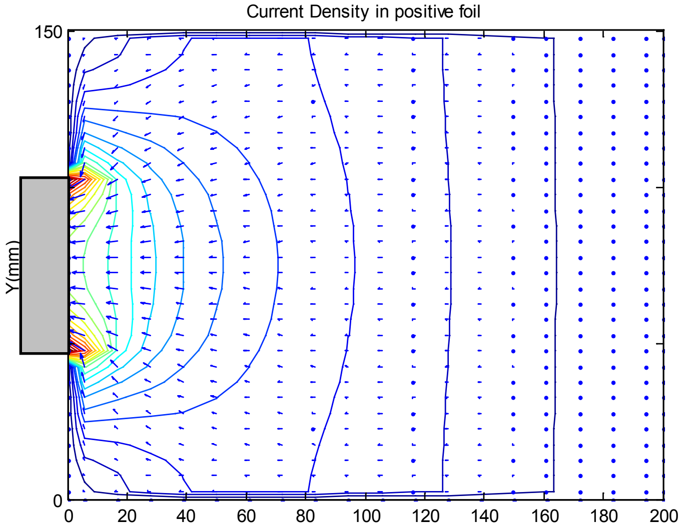
- Thickness: 12 mm
- 40 Ah
- 2-minute discharge, 200 A
- 200A geometric cycle

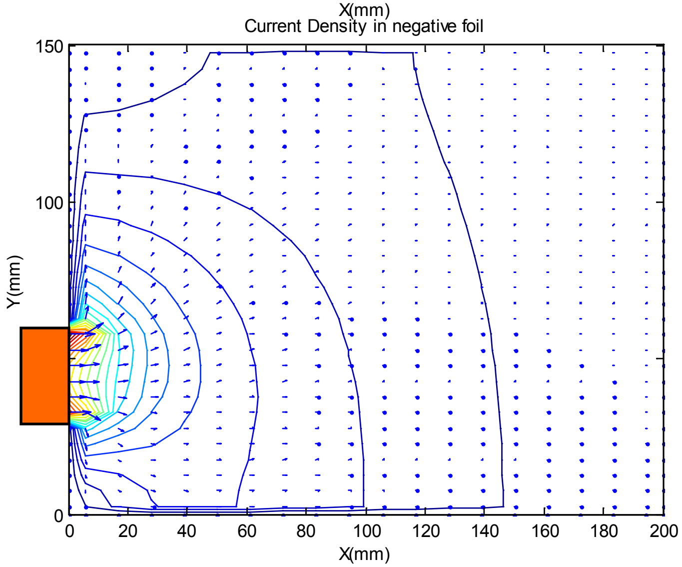
200A Discharge for 2 minutes

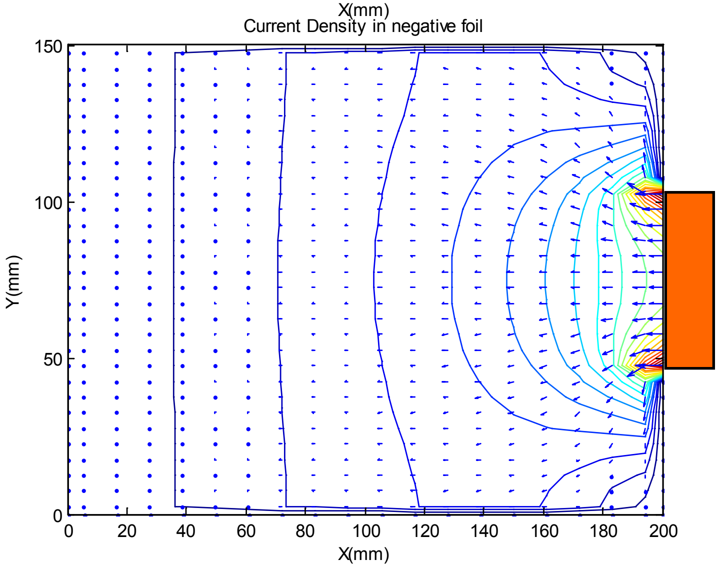


Current Field – *2-min 200 A discharge*


Current Density in positive foil

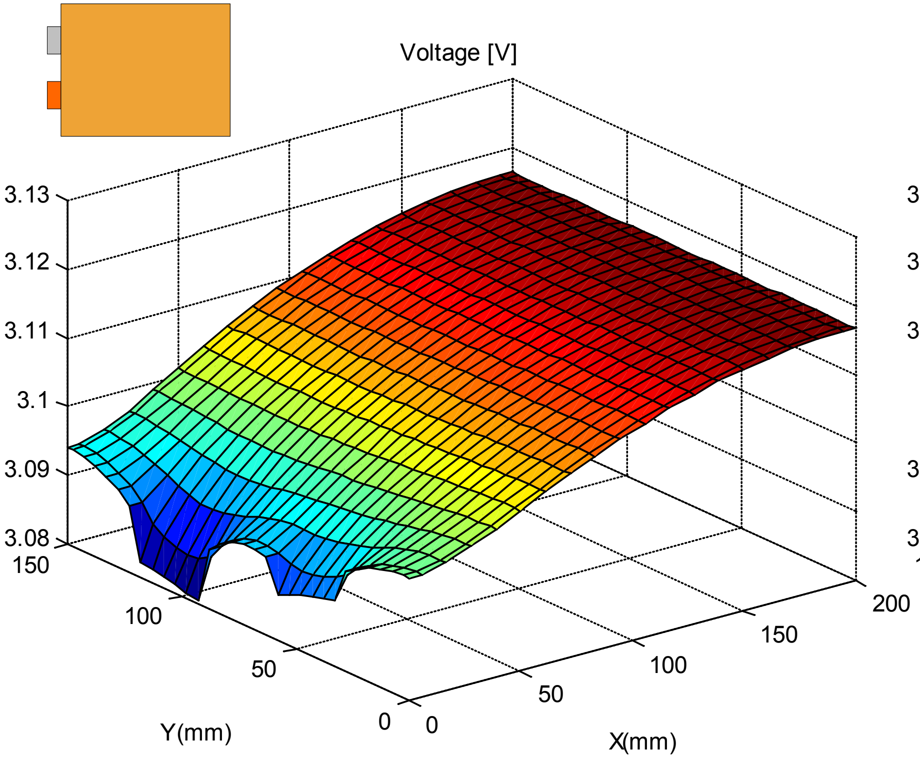

Current Density in positive foil


Current Density in negative foil

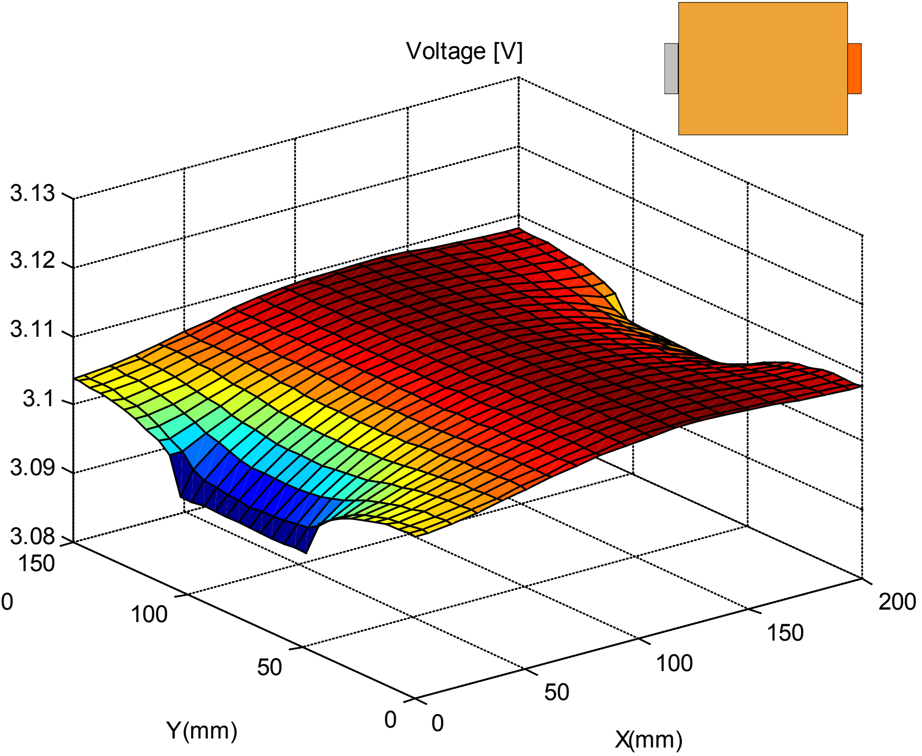

Current Density in negative foil

Voltage across Current Collector Foils

– *2-min 200 A discharge*

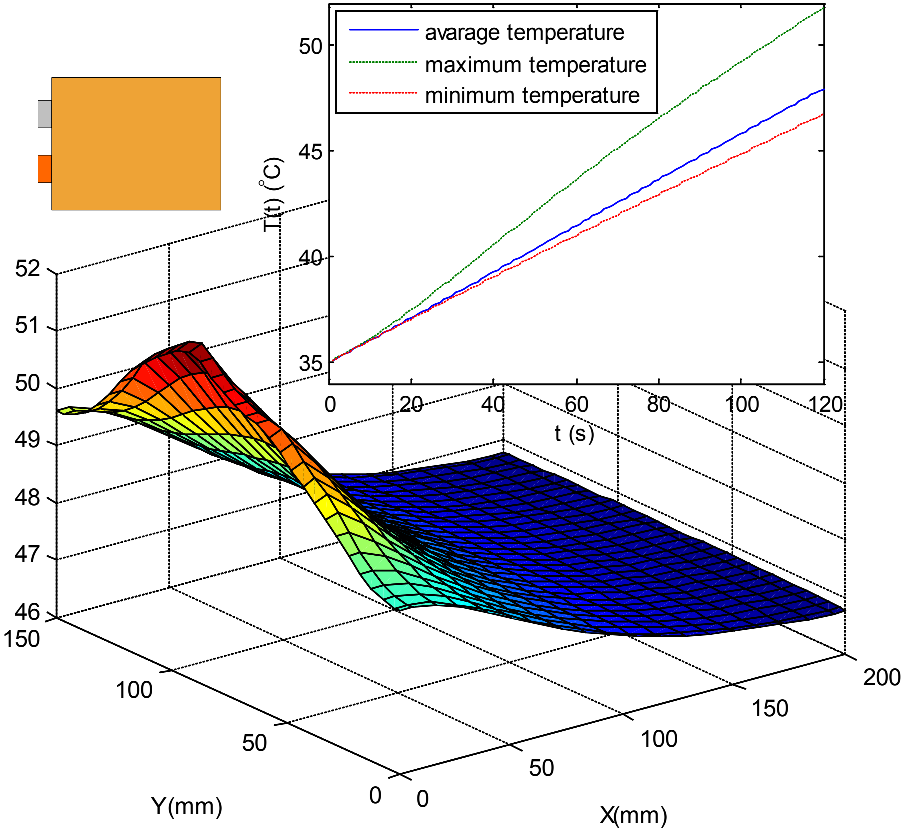


V_{max}-V_{min}= 0.0364 V

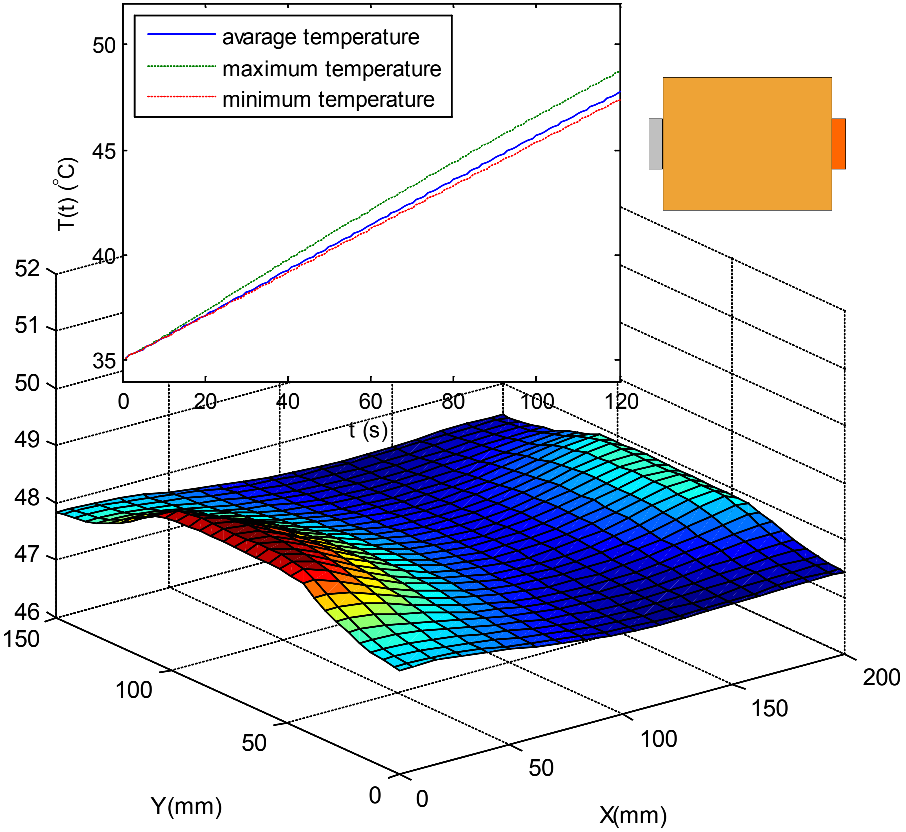


V_{max}-V_{min} = 0.0154 V

Temperature – *2-min 200 A discharge*

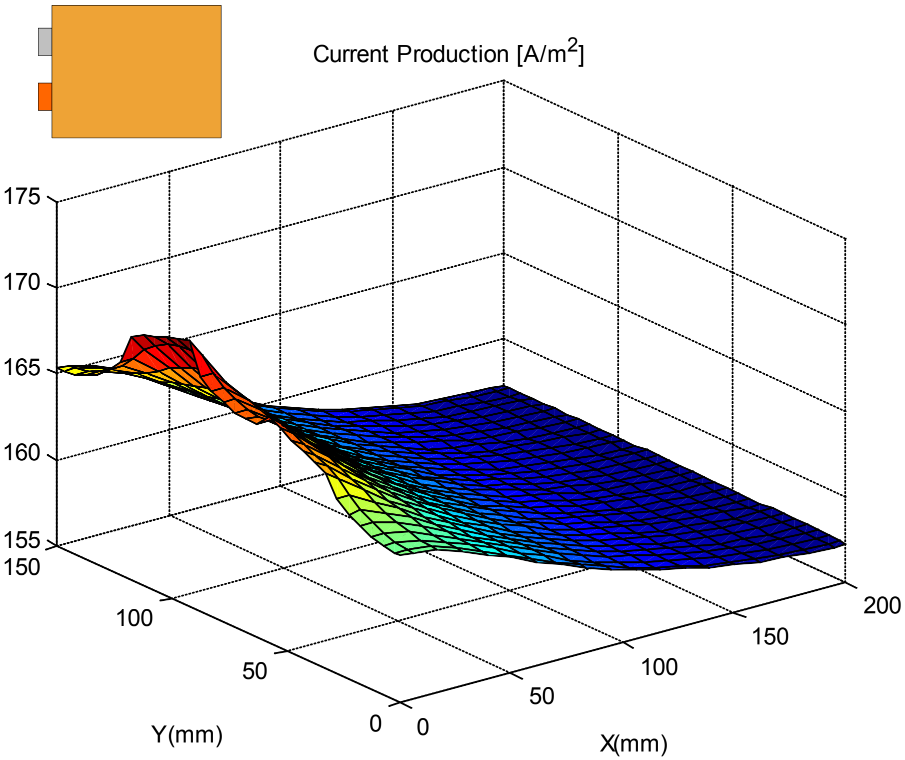


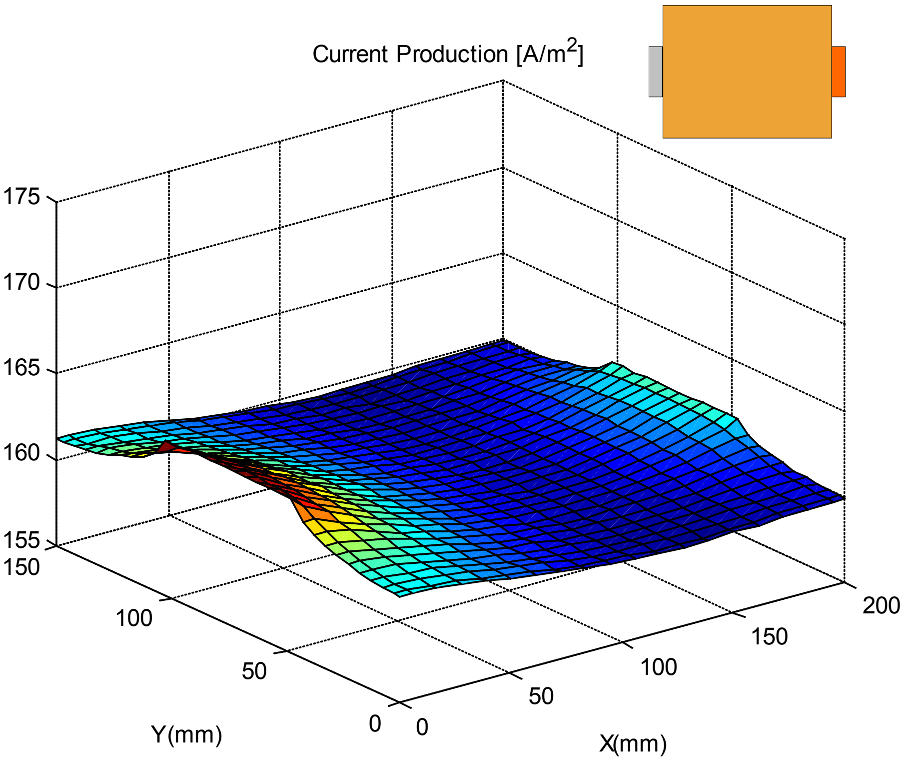
T_{max}-$T_{min} = 5.03^{o}C$



T_{max}-$T_{min} = 1.35^{o}C$

Current Production – *2-min 200 A discharge*

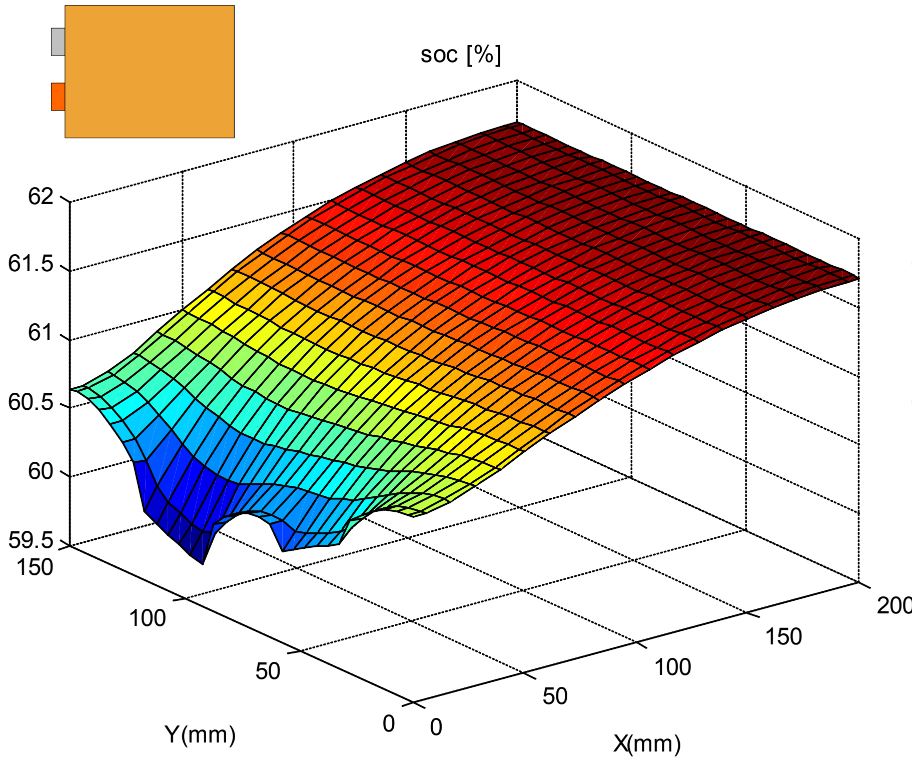




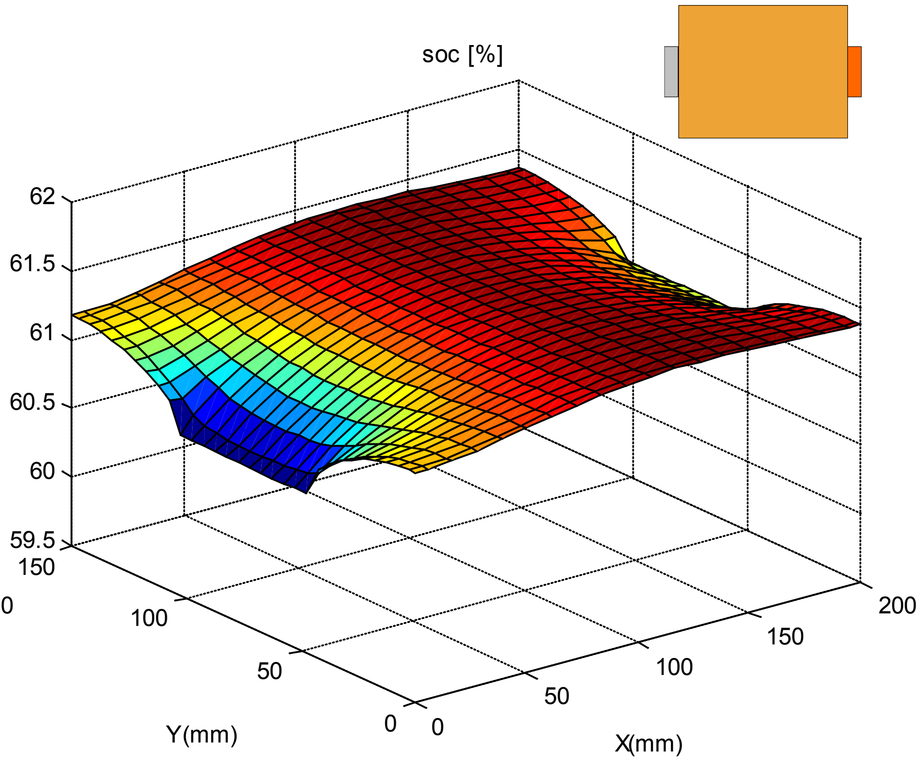
$i_{max}-i_{min} = 13.2\ A/m^2$

$i_{max}-i_{min} = 4.54\ A/m^2$

SOC – *2-min 200 A discharge*

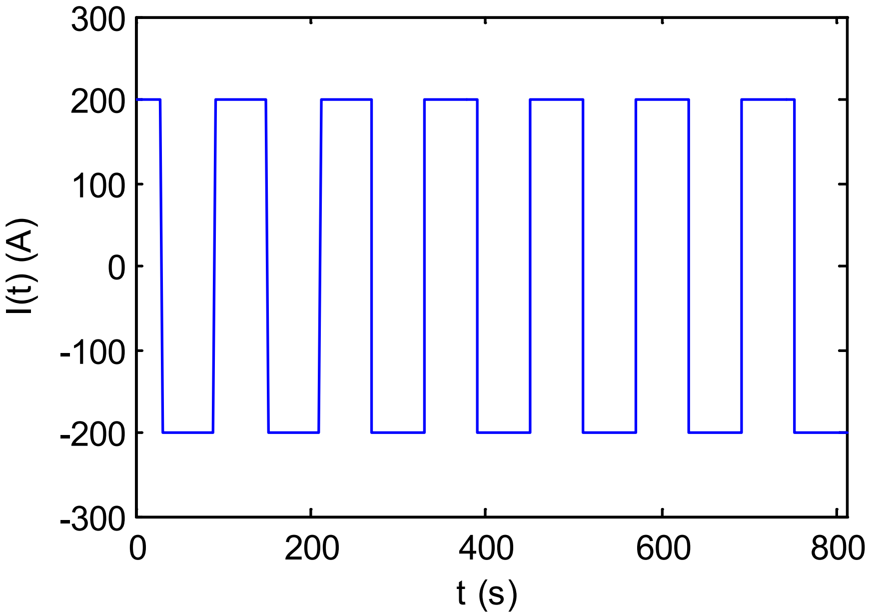


$SOC_{max}-SOC_{min} = 1.91\%$

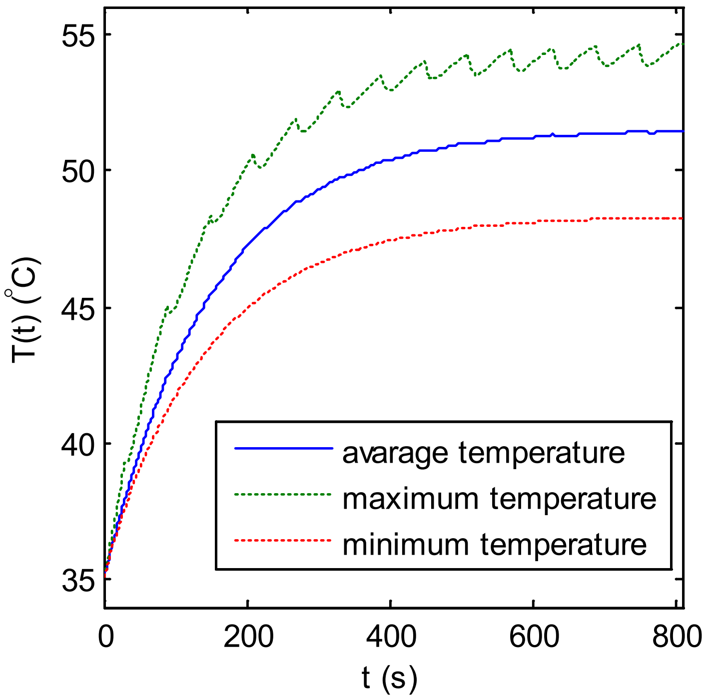


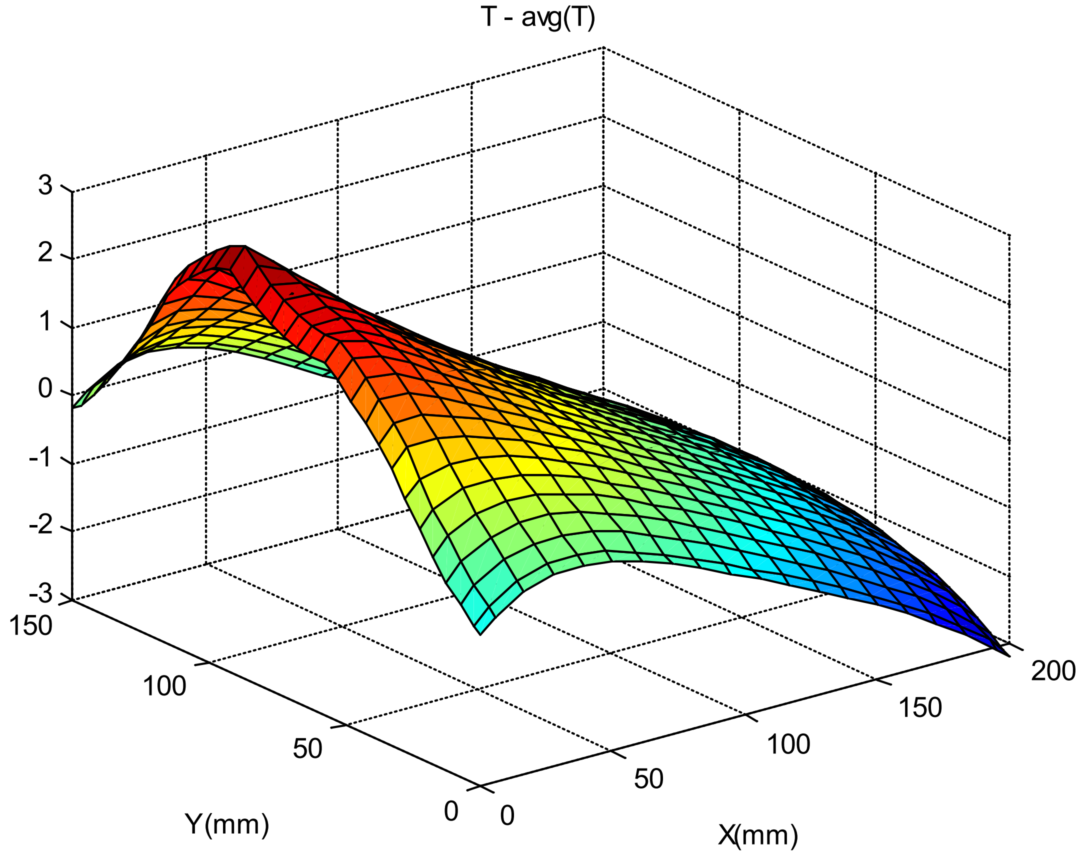
$SOC_{max}-SOC_{min} = 0.76\%$

200A Geometric Cycling

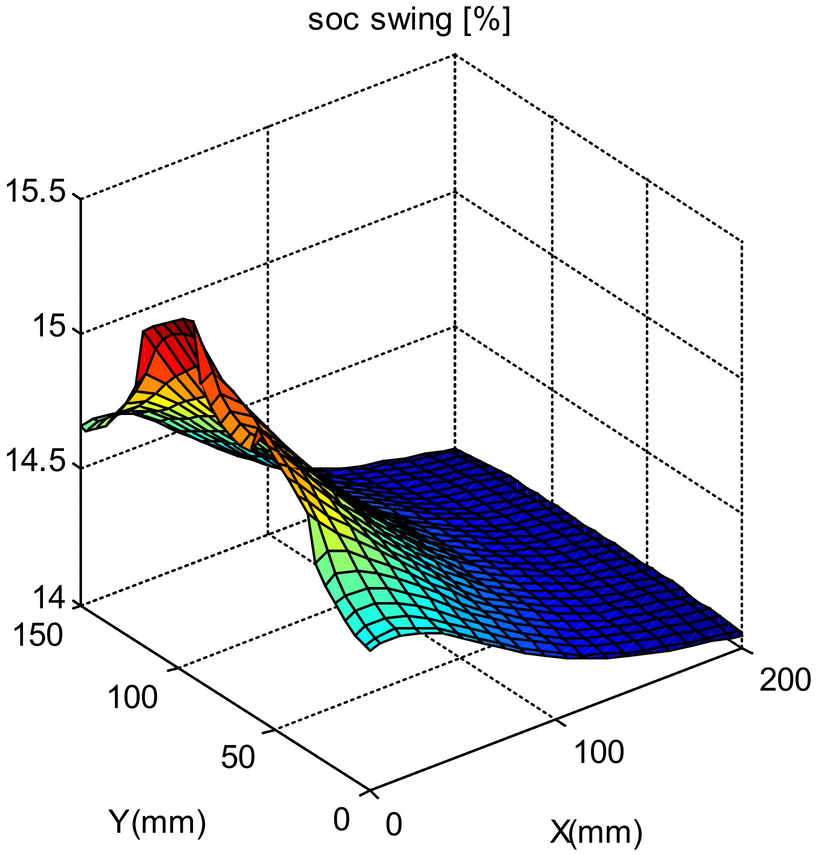


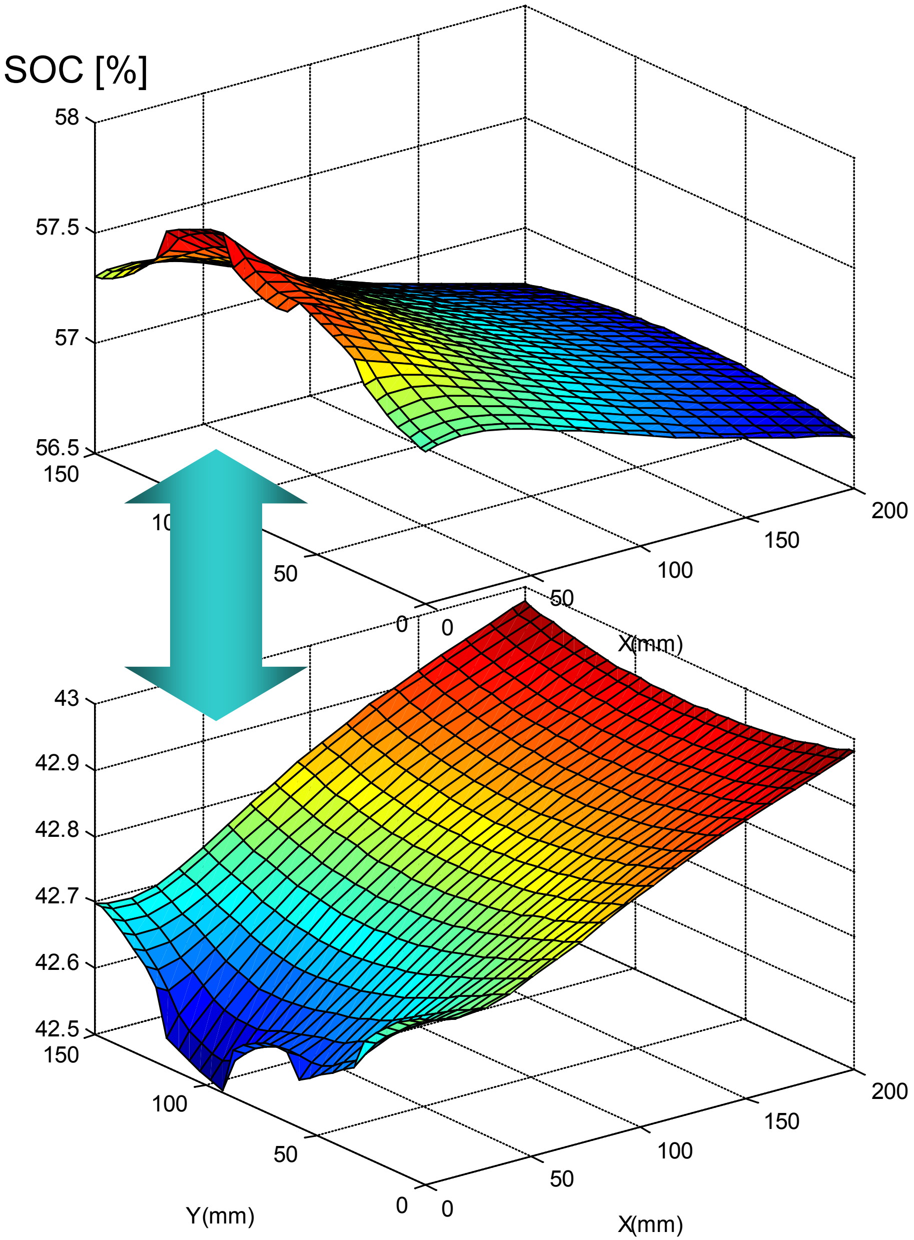
Temperature Variation





SOC swing


soc swing [%]
15.5
15
14.5
14
150
100
50
0
Y(mm)
0
100
200
X(mm)


SOC [%]
58
57.5
57
56.5
150
10
50
0
0
50
100
150
200
X(mm)
43
42.9
42.8
42.7
42.6
42.5
150
100
50
0
Y(mm)
0
50
100
150
200
X(mm)

Summary

- Nonuniform battery physics, which is more probable in large-format cells, can cause unexpected performance and life degradations in lithium-ion batteries.
- A three-dimensional cell performance model was developed by integrating an electrode-scale submodel using a multiscale modeling scheme.
- The developed tool will be used to provide better understanding and help answer engineering questions about improving *cell design*, *cell operational strategy*, *cell management*, and *cell safety*.

- Engineering Questions to be addressed in *future works* include …

What is the optimum form-factor and size of a cell?
Where are good locations for tabs or current collectors?
How different are measured parameters from their non-measurable internal values?
Where is the effective place for cooling? What should the heat-rejection rate be?
How does the design of thermal and electrical paths impact under current-related safety events, such as internal/external short and overcharge?

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