



Multi-Dimensional Electrochemical- Thermal Coupled Model of Large Format Cylindrical Lithium Ion Cells

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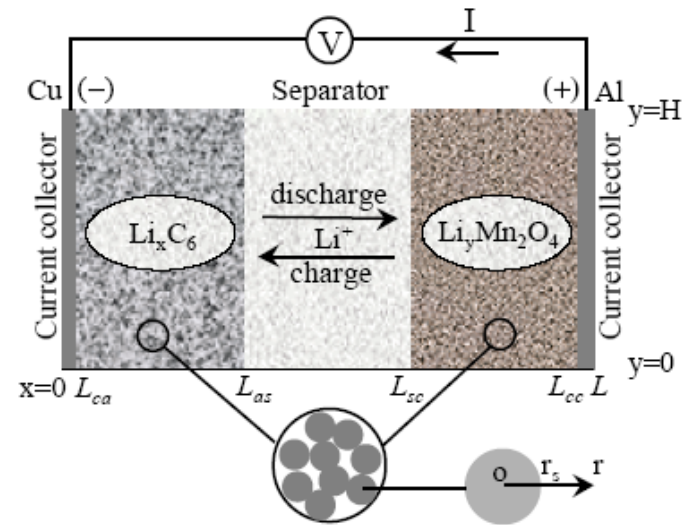
Why 3D Cell Model?

Physical Description of Lithium-Ion Cell

Chemical Kinetics

Heat & Mass Transport

Charge Conservation



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

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

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

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

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

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

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

Why 3D Cell Model?



Three dimensional features such as **thermal/electrical paths design** inside a cell, **form factors**, **dimensions** and **local boundary conditions** can have a significant impact on cell performance and life. (The impact would be more significant in large format cells due to size effect.)

Better understanding will give a chance for improving ...

- *Cell Design*
- *Cell Operation Strategy*
- *Cell Management*

Approach in Presented Study

Multi-Scale-Multi-Dimensional Model

- Difficulties in resolving thin layer structure in a computational grid
- ✓ Assumed negligible potential gradients along current collectors
- ✓ Focused on addressing temperature imbalance impact

Simulation Domain

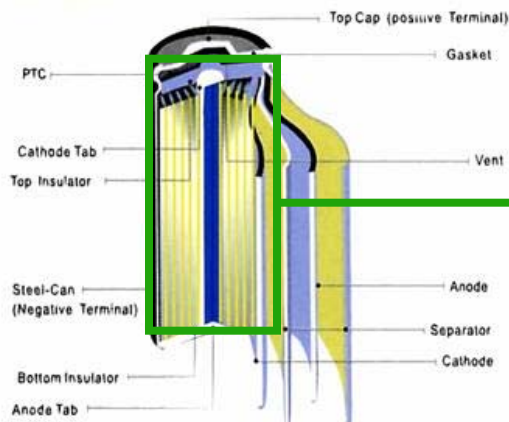
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Macro Grid

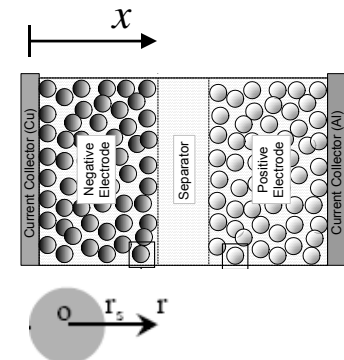
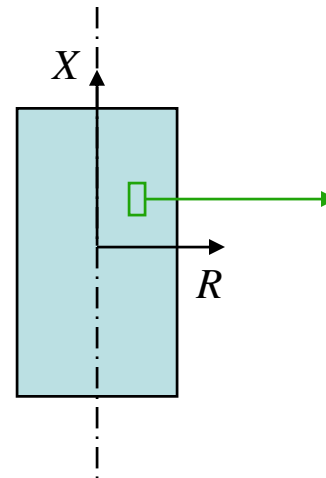
+

Micro Grid

(Grid for Sub-grid-scale Model)



Source: www.dimec.unisa.it

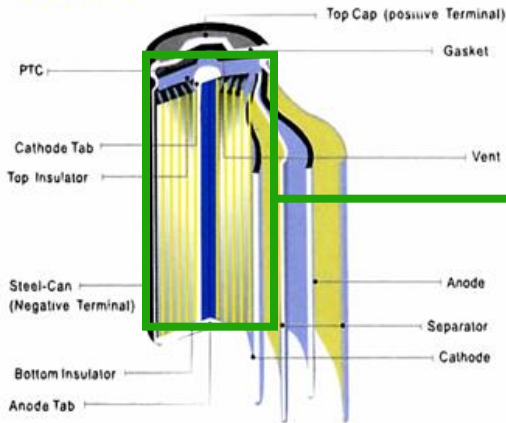


Assumptions

- Uniform V_o in (X,R) -domain, $V_o = V_o(t) = \phi_s(X, R, x=L, t) - \phi_s(X, R, x=0, t)$
- Uniform T in (x,r) -domain, $T = T(X, R, t)$

Solution Variables

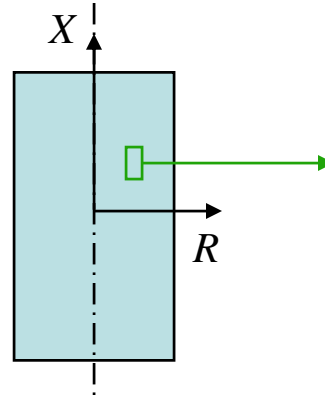
Detailed Structure



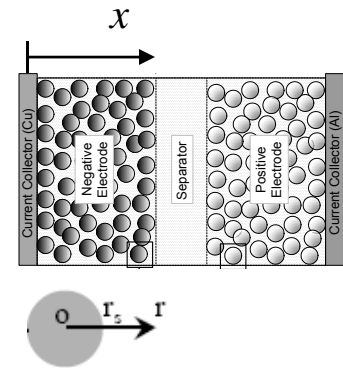
Source: www.dimec.unisa.it

NOTE
 Selection of “sub-grid electrochemical model” is independent to “macro-grid thermal model”.

Axisymmetric Thermal Model



Electrochemical Submodel (1D)



$$T(X, R, t)$$

$$V_o(t)$$

$$i(X, R, t)$$

$$SOC(X, R, t)$$

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

$$\phi_s(X, R, x, t)$$

$$\phi_e(X, R, x, t)$$

$$c_s(X, R, x, r, t)$$

$$c_e(X, R, x, t)$$

$$j_{Li}(X, R, x, t)$$

$$Q_i(X, R, x, t)$$

Analysis

MODEL COMBINATION 1

- ✓ *Macro Grid Model: Axisymmetric Thermal Model, Finite Volume Method*
- ✓ *Micro Grid Model: 1D FULL electrochemical Model, Finite Volume Method*

→ Moderate Discharge with a Large Format Cylindrical Cell

MODEL COMBINATION 2

- ✓ *Macro Grid Model: Axisymmetric Thermal Model, Finite Volume Method*
- ✓ *Micro Grid Model: **State Variable Model** [Ref\) K. Smith, Ph.D. dissertation, 2006](#)*

→ Performance Evaluation of a PHEV-type Large Format Cylindrical Cell

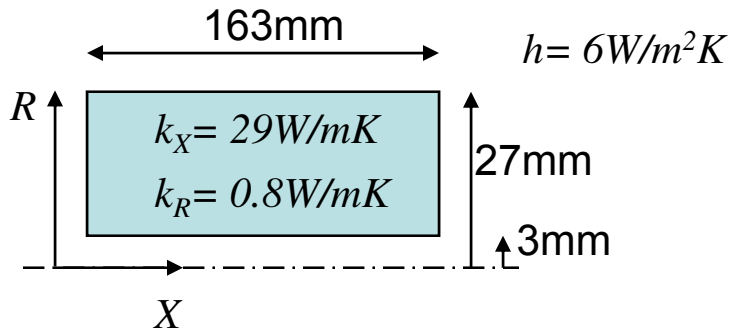
→ Form-factor (D/H) and cell size were examined for parameters

1. 150A Continuous Discharge, Moderate usage profile
2. 200A Geometric Cycle, Severe usage profile

MODEL COMBINATION 1

Axisymmetric Thermal Model

+ 1D FULL electrochemical Model



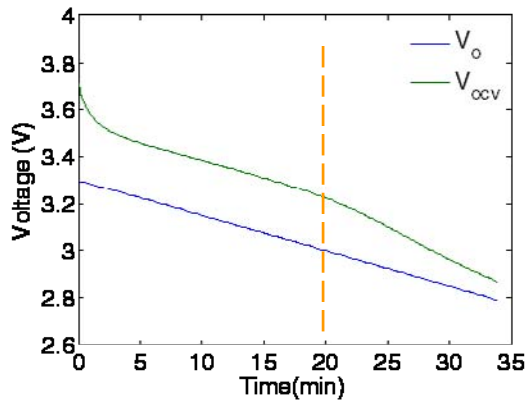
	X	R	x	r
Gird #	30	18	20	4

time step size: 1sec, time step #: 2040

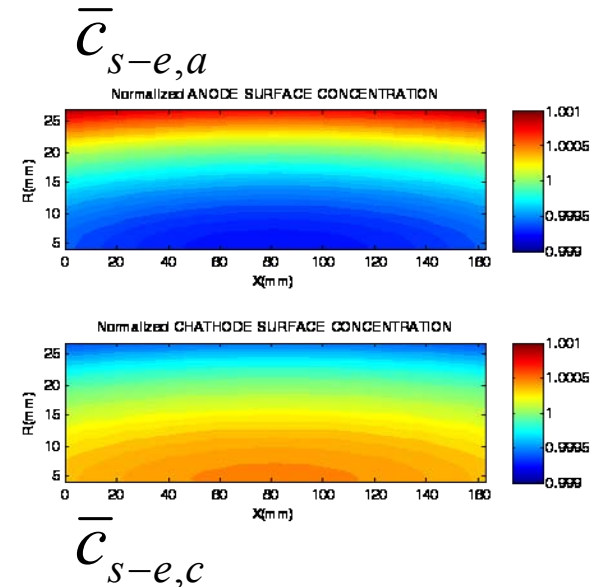
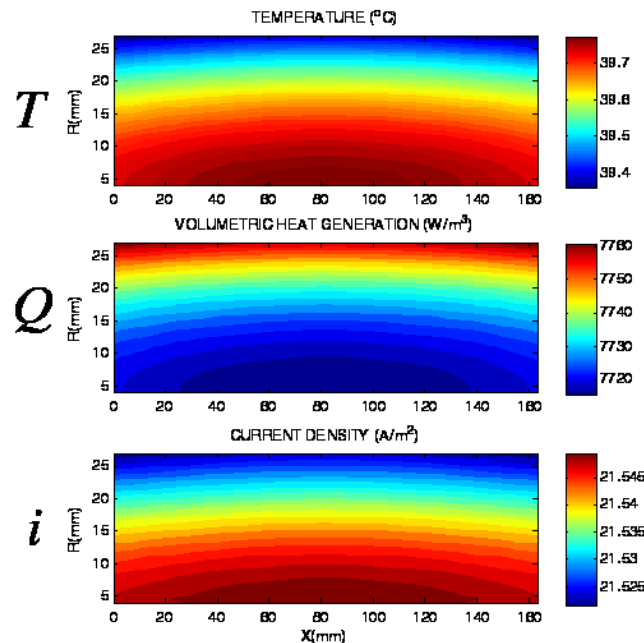
CPU time: 36 hours @ Windows/PC

~ 60 times slower than real time

Moderate Discharge

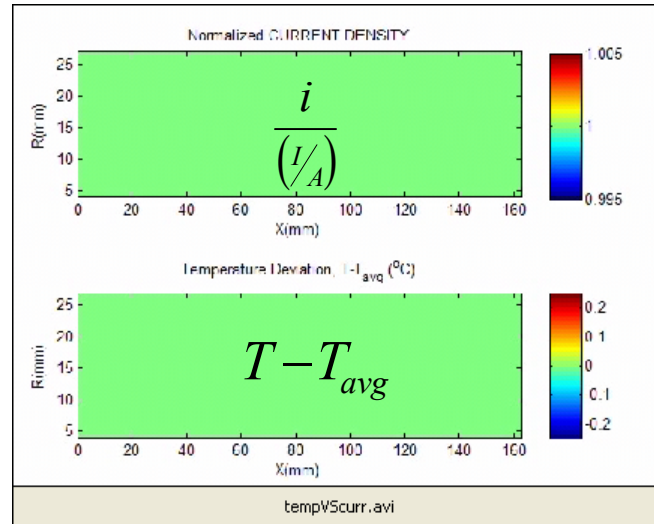
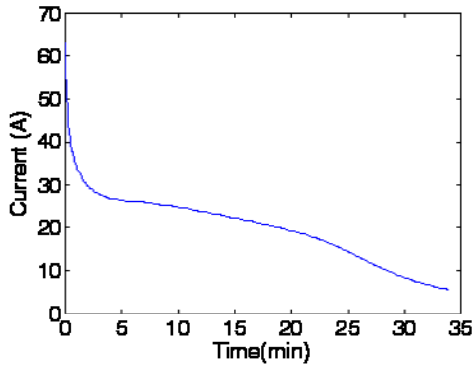


t = 20 min

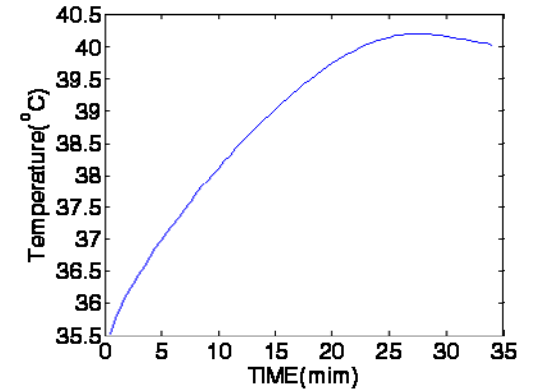


Current & Temperature Evolution

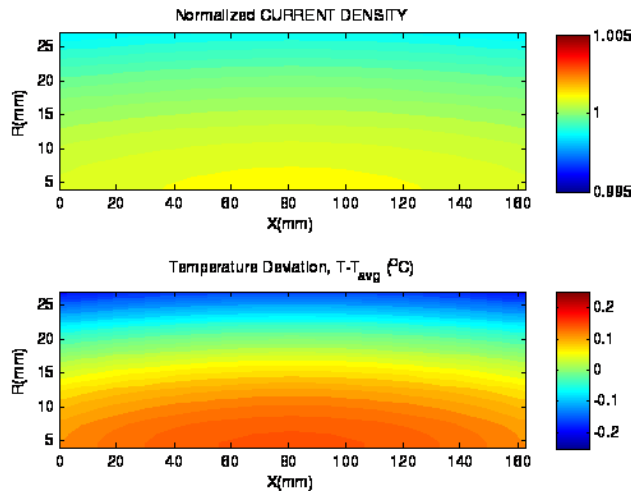
Cell Current



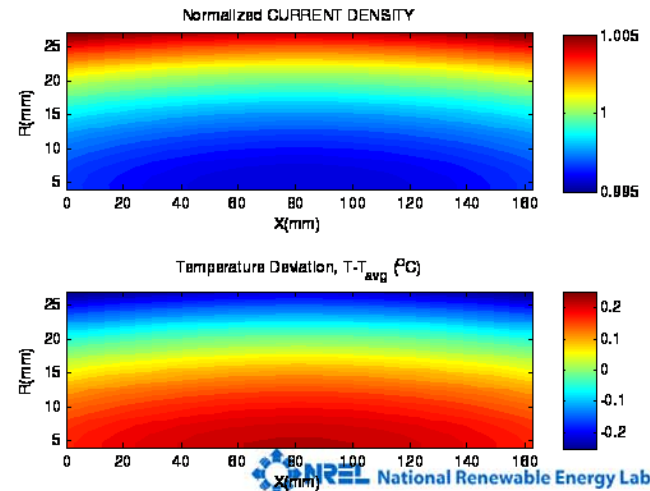
Avg Temperature



t= 15 min



t= 30 min



MODEL COMBINATION 2

Axisymmetric Thermal Model

+ State Variable Model (SVM)

SVM preferred due to its fast execution

- SVM Identification
 - Numerical “**curve fitting**” procedure in frequency domain
 - **Local-linearized models** (identified at each $T, \theta_{s,e-}, \theta_{s,e+}$)
 - Local models are assembled to form **global nonlinear model**

~10 hours to identify model from a single parameter set
- SVM Simulation
 - Micro-grid 1-D **Electrochemical model** has **explicit** solution
 - Macro-grid 2-D **Axisymmetric Thermal Model** typically converges in **2 iterations**
 - 9 minutes to simulate 150A discharge (940 sec simulation time, dt = 1 sec)

“MSMD model combination 2” runs ~1.75 faster than real time

Given continued issues in Li-ion thermal safety, there is a desire for a fast running thermal model incorporating realistic internal details of a cell.

Large format high power batteries present challenging thermal requirements



- High energy *and* high power requirements
- Large format preferred to small cells
 - fewer interconnects
 - less monitoring & balancing circuitry
- Significant heating may be possible depending upon power profile
- Internal temperature imbalance expected to lead to:
 - Internal current imbalance
 - Increased time at temperature in localized regions (degradation)

APPENDIX A - USABC Goals for Advanced Batteries for PHEV's
Requirements of End of Life Energy Storage Systems for PHEVs

Characteristics at EOL (End of Life)		High Power/Energy Ratio Battery	High Energy/Power Ratio Battery
Reference Equivalent Electric Range	miles	10	40
Peak Pulse Discharge Power - 2 Sec / 10 Sec	kW	50 / 45	46 / 38
Peak Regen Pulse Power (10 sec)	kW	30	25
Available Energy for CD (Charge Depleting) Mode, 10 kW Rate	kWh	3.4	11.6
Available Energy for CS (Charge Sustaining) Mode	kWh	0.5	0.3
Minimum Round-trip Energy Efficiency (US ABC HEV Cycle)	%	90	90
Cold cranking power at -30°C, 2 sec - 3 Pulses	kW	7	7
CD Life / Discharge Throughput	Cycles/MWh	5,000 / 17	5,000 / 58
CS HEV Cycle Life, 50 Wh Profile	Cycles	300,000	300,000
Calendar Life, 35°C	year	15	15
Maximum System Weight	kg	60	120
Maximum System Volume	Liter	40	80
Maximum Operating Voltage	Vdc	400	400
Minimum Operating Voltage	Vdc	>0.55 x Vmax	>0.55 x Vmax
Maximum Self-discharge	Wh/day	50	50
System Recharge Rate at 30°C	kW	1.4 (120V/15A)	1.4 (120V/15A)
Unassisted Operating & Charging Temperature Range	°C	-30 to +52	-30 to +52
Survival Temperature Range	°C	-46 to +66	-46 to +66
Maximum System Production Price @ 100k units/yr	\$	\$1,700	\$3,400

- Traditional electrochemical model yield slow-running multi-dimensional electrochemical/thermal models

Electrode thickness, electrochemical model parameters chosen to represent PHEV-type cell



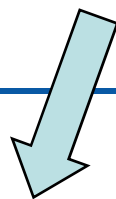
Johnson Controls/Saft



Valence Technologies



A123 Systems



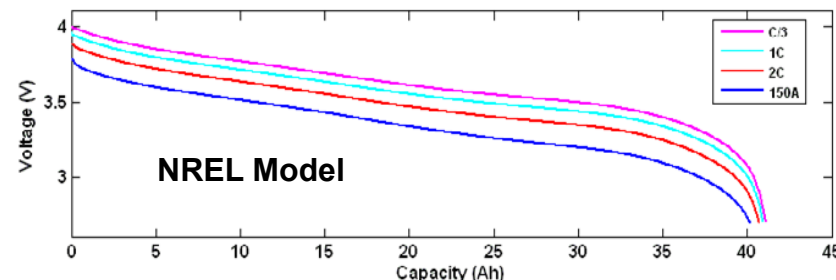
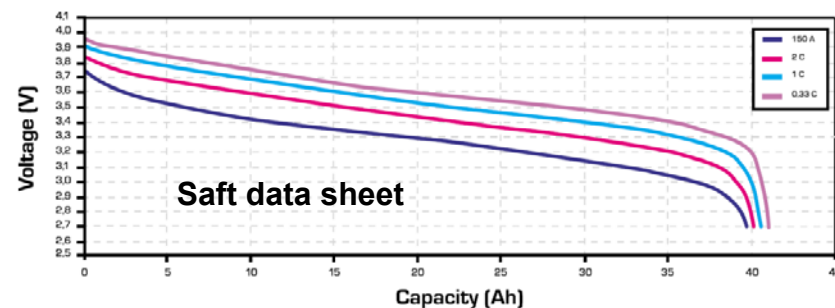
Saft VL41M

- Graphite-based anode
- Nickel oxide-based cathode



Nominal Capacity:	41 Ah
Nominal Voltage:	3.6 V
Mass:	1.07 kg
Power Density:	794 W/kg
Max. Continuous Current:	150A (3.7C)
Max. Peak Current:	300A (7.3 C)

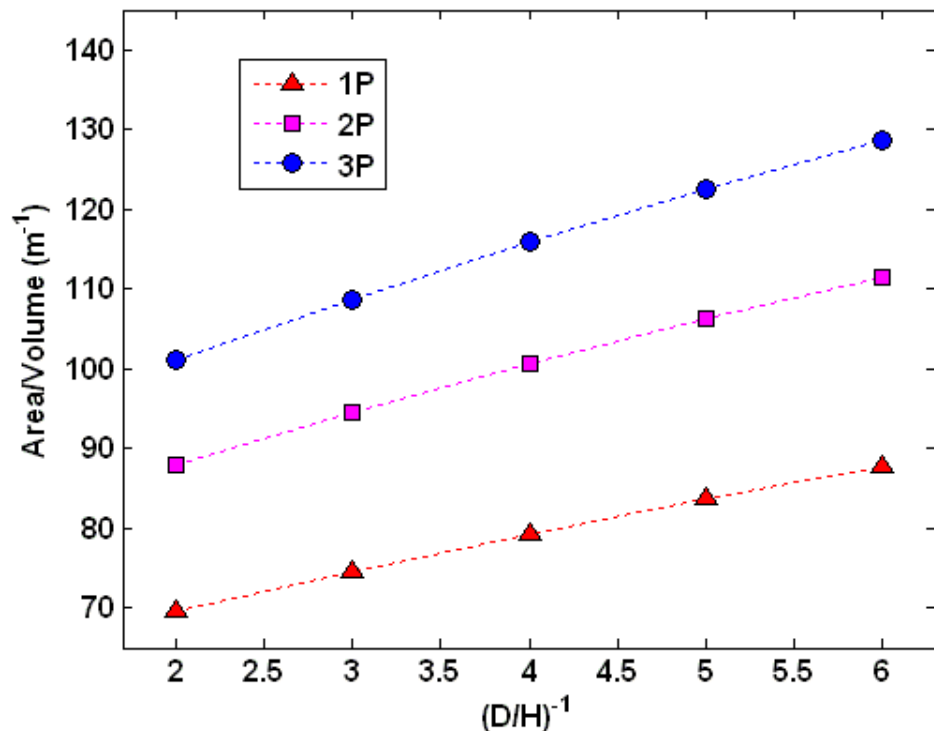
Source: www.saftbatteries.com



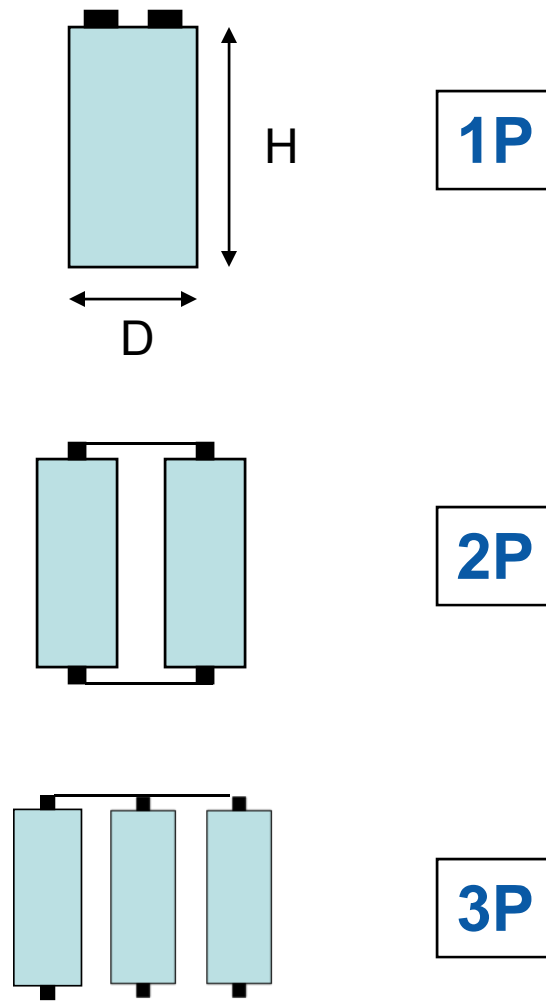
Cell design: What shape and size best meet thermal requirements?

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

- D/H ratio
- multiple cells in parallel (#P)



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

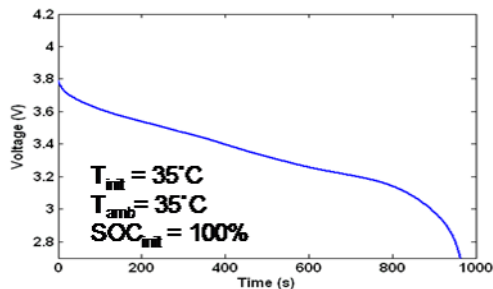


Usage profiles

Two cases explored in this presentation:

1 150A Max. Cont. Discharge

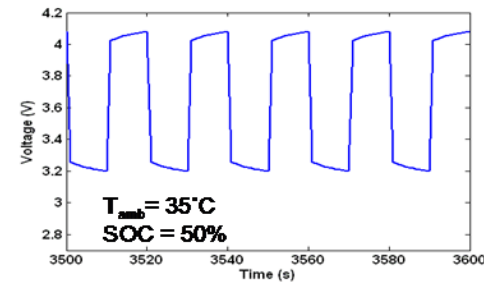
- Transient, Charge Depleting
- Air... Convection ($15 \text{ W/m}^2\text{K}$)



→ Moderate Thermal Condition

2 200A Geometric Cycle

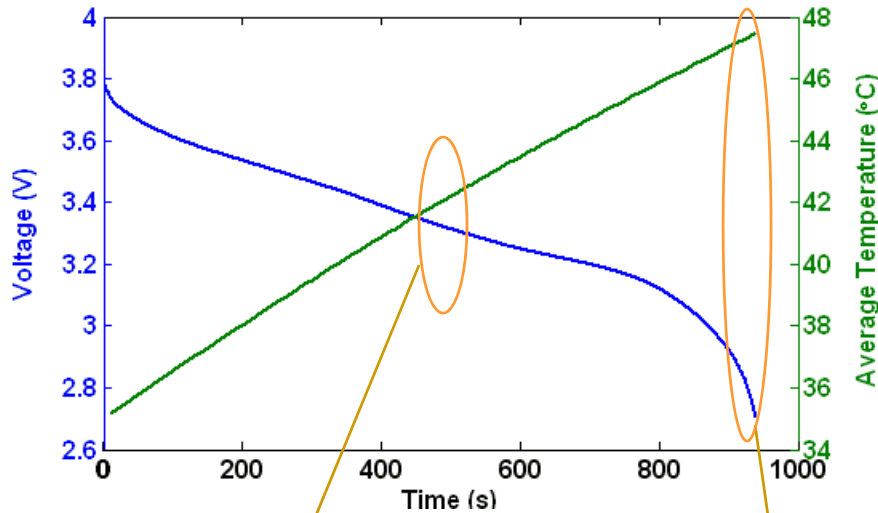
- Steady-State, Charge Sustaining
- Liquid Cooling ($150 \text{ W/m}^2\text{K}$)



→ Severe Thermal Condition

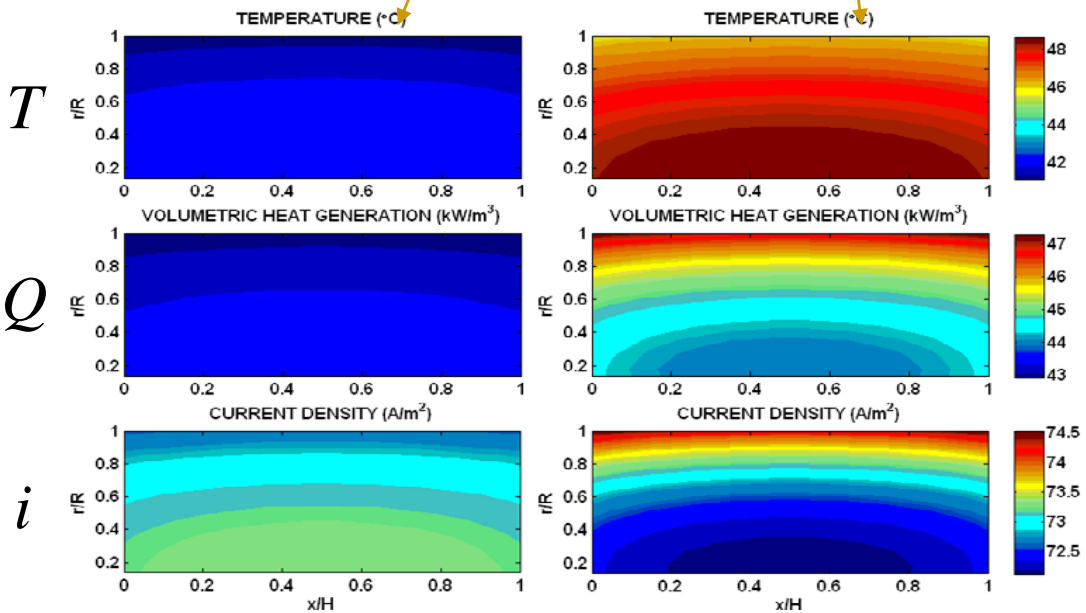
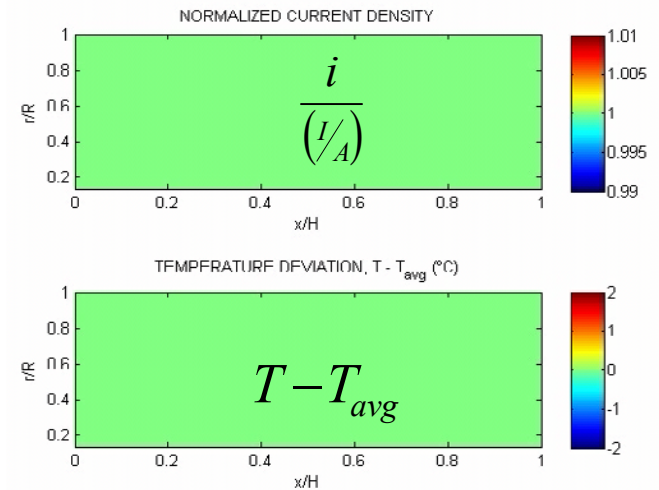
150A Discharge Case (Transient Results)

- $D/H = 1/4$
- $h = 15 \text{ W/m}^2\text{K}$
- $T_{\text{amb}} = 35^\circ\text{C}$



Movie of

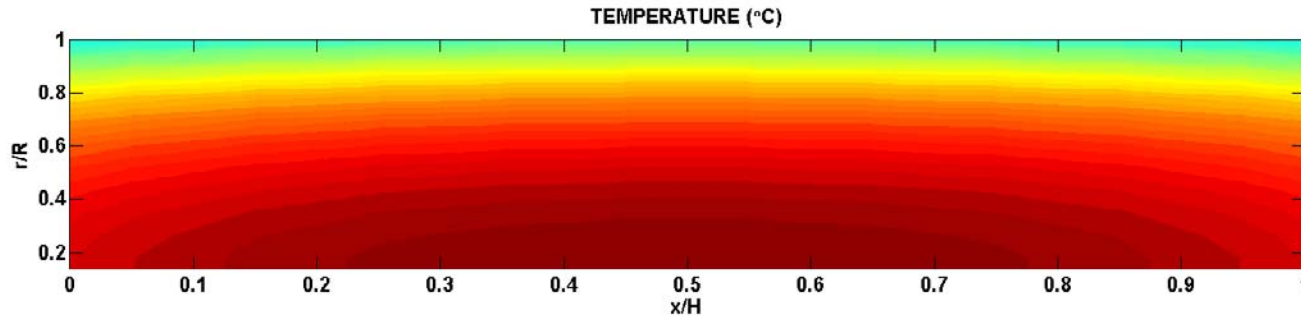
- current imbalance
- temperature imbalance



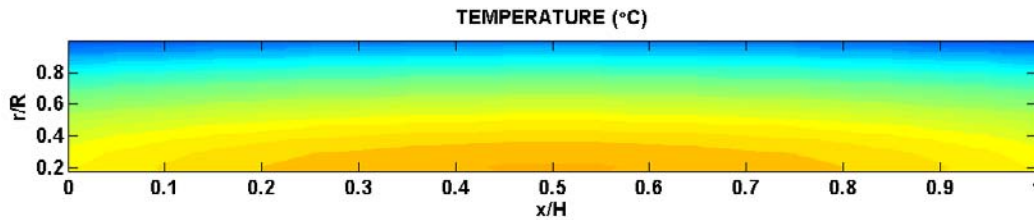
150A Single Discharge (at End)

- $D/H = 1/4$
- $h = 15 \text{ W/m}^2\text{K}$
- $T_{\text{amb}} = 35^\circ\text{C}$

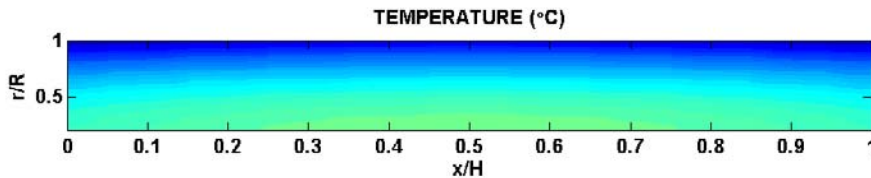
1P



2P



3P

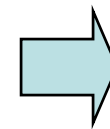
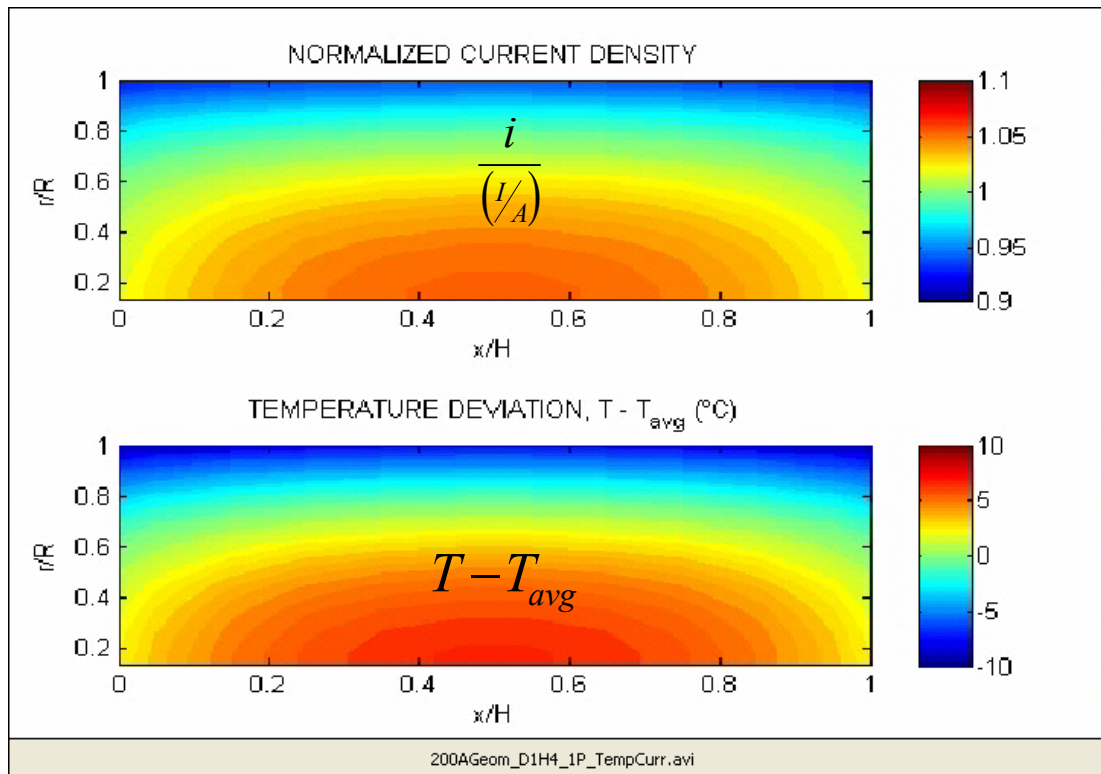


Moderate usage + Air convection = small internal gradients

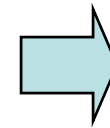
200A Geometric Cycling

- $D/H = 1/4$
 $h = 150 \text{ W/m}^2\text{K}$
 $T_{\text{amb}} = 35^\circ\text{C}$

At Steady State



~20% difference in local current production

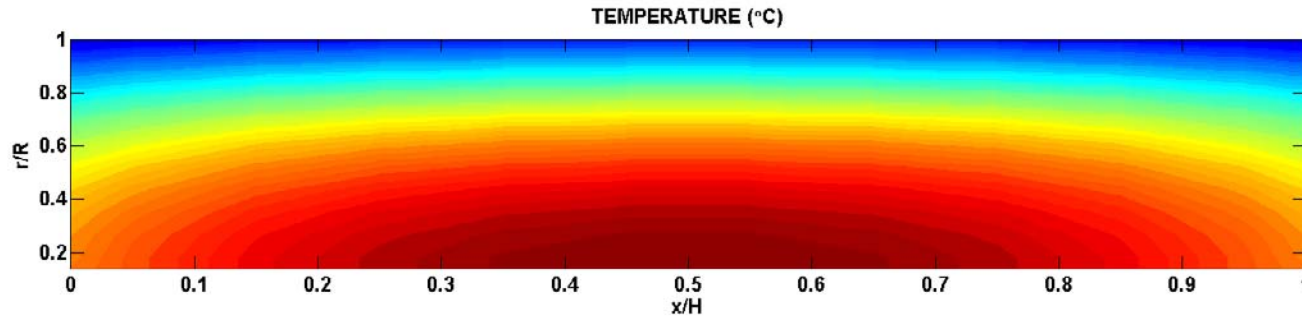


$\Delta T = \sim 18^\circ\text{C}$

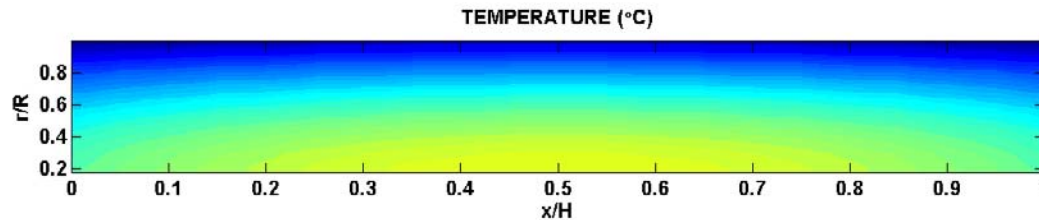
200A Geometric Cycle (Steady-State)

- $D/H = 1/4$
- $h = 150 \text{ W/m}^2\text{K}$
- $T_{\text{amb}} = 35^\circ\text{C}$

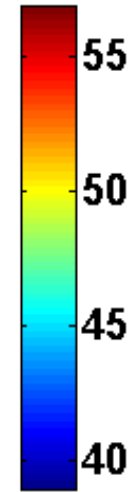
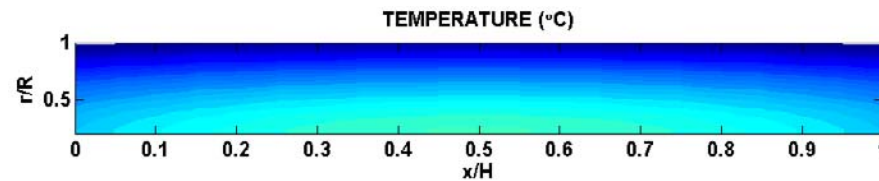
1P



2P



3P



18°C

This vertical double-headed arrow indicates a temperature difference of 18°C, spanning from the 40°C mark to the 58°C mark on the color scale.

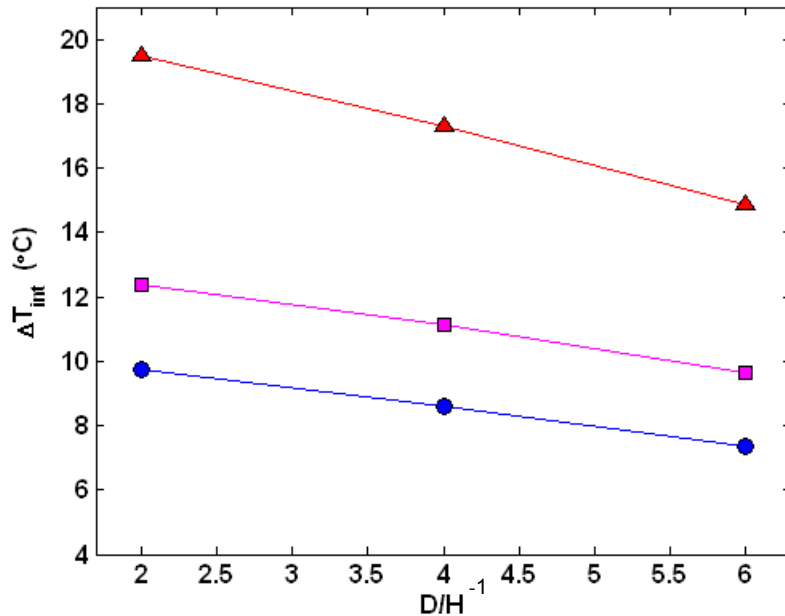
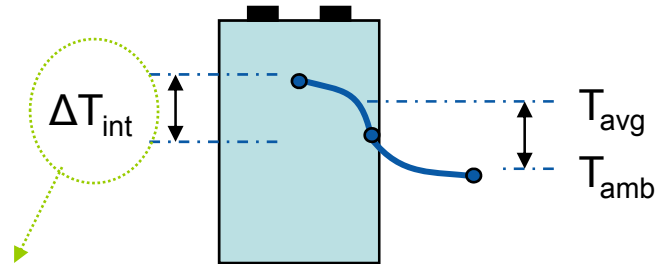
Severe usage + liquid cooling = large internal gradients

200A Geometric Cycle (Steady-State)

- $h = 150 \text{ W/m}^2\text{K}$
- $T_{\text{amb}} = 35^\circ\text{C}$

Internal Temperature Difference

- D/H ratio $\sim 4.5^\circ\text{C}$ \downarrow
- 2P $\sim 6.0^\circ\text{C}$, 3P $\sim 9.0^\circ\text{C}$ \downarrow



- *Under severe usage, low D/H and/or >1P designs significantly reduce thermal stress*
- *The impacts of D/H aspect ratio and cell size on the internal temperature difference were quantified using multi-dimensional electrochemical cell model*

Conclusions

Multi-Dimensional Cell model (MSMD model) was Developed

e.g.) Modeling Approach: Axisymmetric Thermal Model + SVM

- Runs ~1.75 faster than real time
- Practical engineering tool for applications such as:
 - Cell design
 - Determination of safe operating limits

The Model Capability was Demonstrated

e.g.) Numerical investigation of 41 Ah cell

- Under moderate usage
 - Internal temperature difference is very small ($< 3^{\circ}\text{C}$).
- Under severe usage,
 - Large internal temperature imbalance ($>20^{\circ}\text{C}$) leads to significant reaction current imbalance ($\pm 10\%$).
 - Proper choice of aspect ratio and cell size can greatly reduce thermal stress.
 - Large convection (such as liquid cooling) lowers average temperature, but causes greater internal imbalance.

Future Work

- Explore thermal imbalance at low temperatures including possible impact on operating limits
- Extend to 3-D
- Include detailed internal structure of actual cells (current paths, ...)
 - External shorts
- Develop modeling tools for safe cell design
 - Internal shorts & defects

Acknowledgements

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