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

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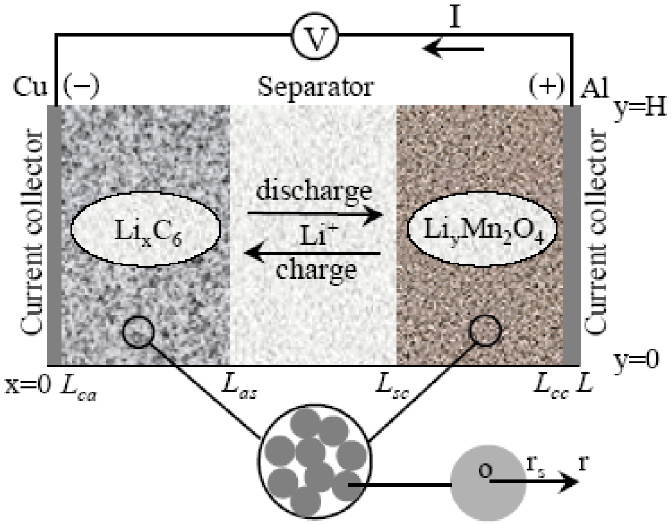
Why 3D Cell Model?

Physical Description of Lithium-Ion Cell

Chemical Kinetics

Heat & Mass Transport

Charge Conservation



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

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

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

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

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

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

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

Why 3D Cell Model?

Chemical Kinetics

Heat & Mass Transport

Charge Conservation

cell design features

Species Distribution
Temperature Distribution
Potential Distribution
…
→ Cell Performance

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 …

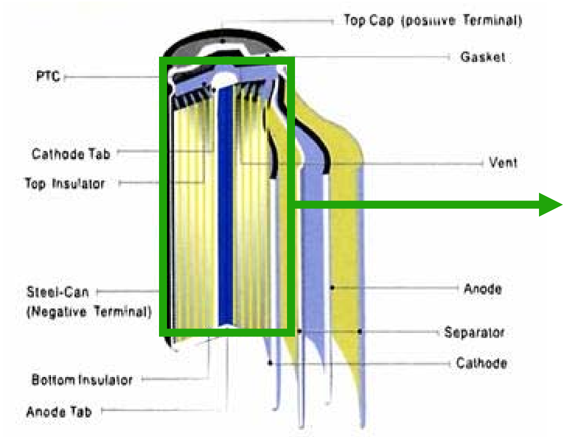
- *Cell Design*
- *Cell Operation Strategy*
- *Cell Management*

Approach in Presented Study

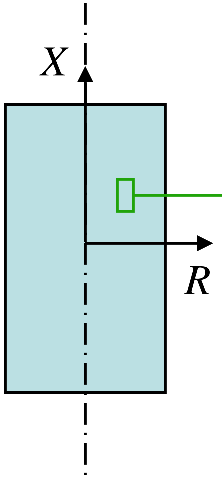
Multi-Scale-Multi-Dimensional Model

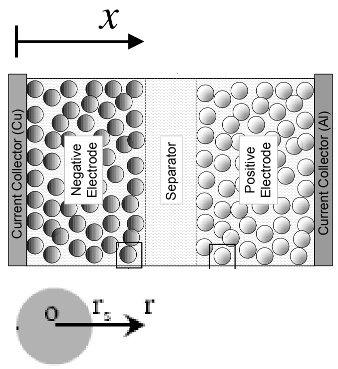
- Difficulties in resolving thin layer structure in a computational grid
- ✓ *Assumed negligible potential gradients along current collectors*
- ✓ *Focused on addressing temperature imbalance impact*

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



Source: www.dimec.unisa.it



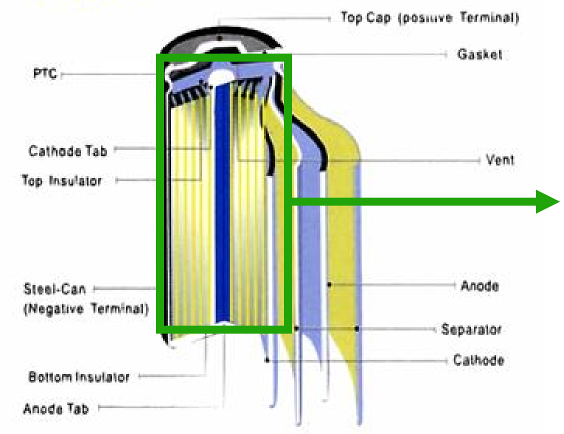


Assumptions

- *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 ≈ **Axisymmetric Thermal Model** + **Electrochemical Submodel (1D)**



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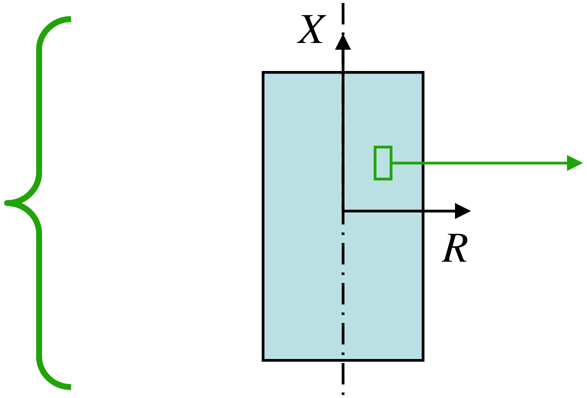
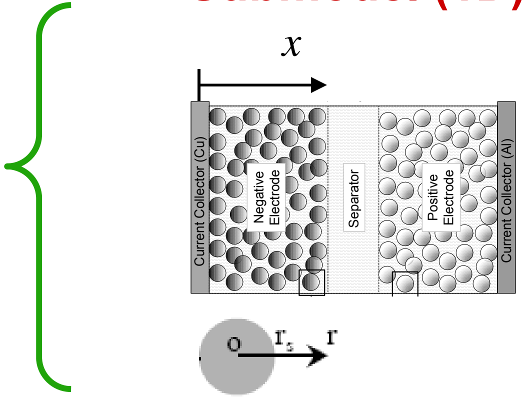




$$T(X,R,t)$$

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

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

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

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

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*

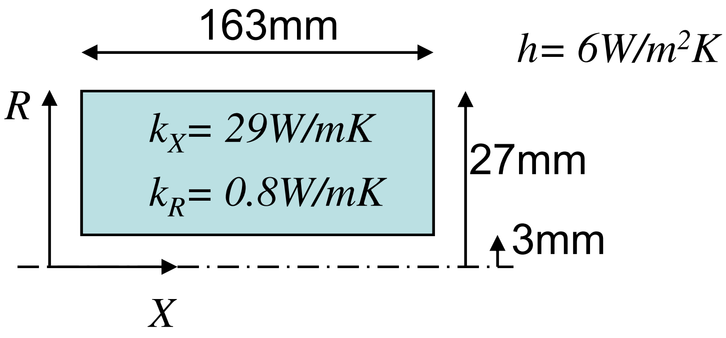
→ Performance Evaluation of a PHEV-type Large Format Cylindrical Cell

→ 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

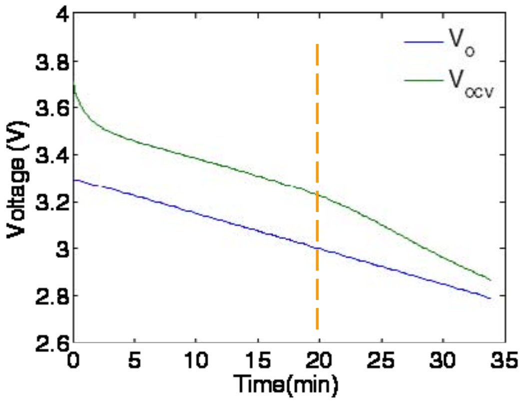
time step size: 1sec, time step #: 2040

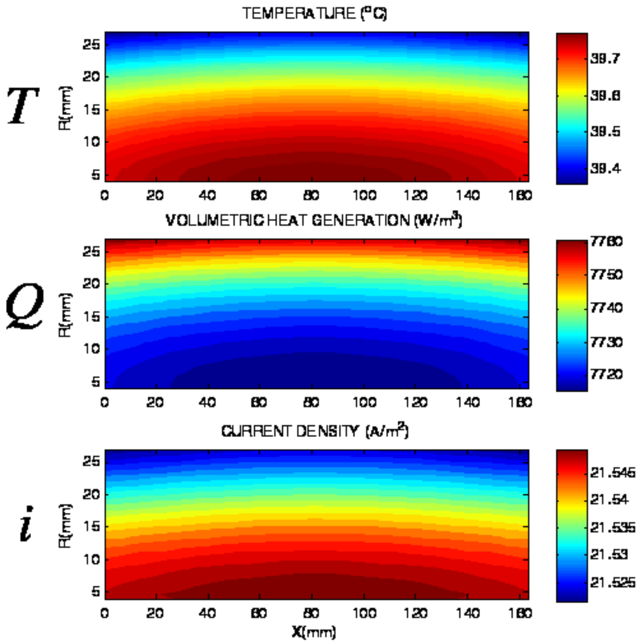
CPU time: 36 hours @ Windows/PC

~ 60 times slower than real time

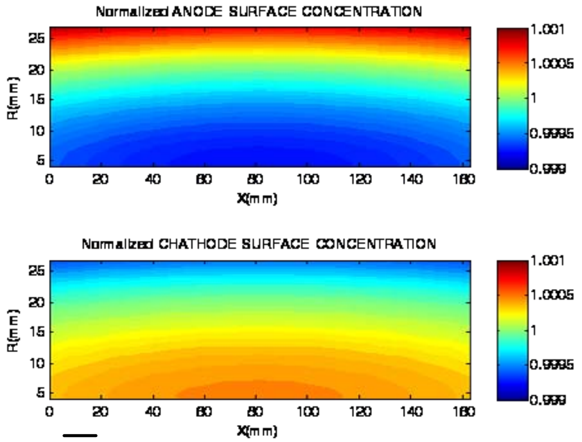
t= 20 min

Moderate Discharge





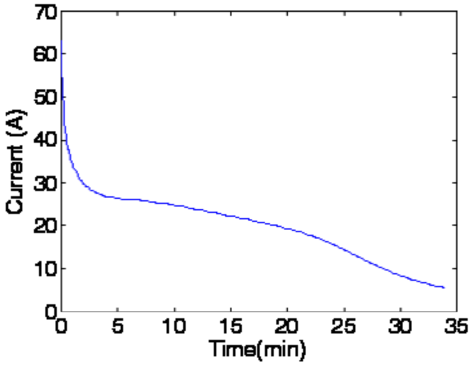
$\overline{c}_{s-e,a}$

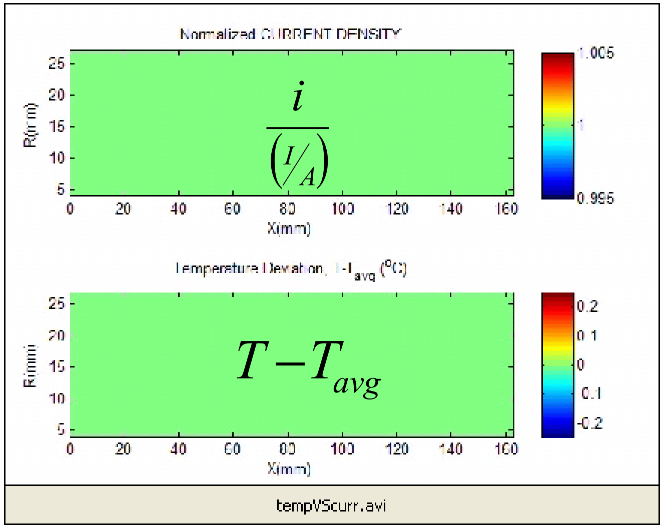


$\overline{c}_{s-e,c}$

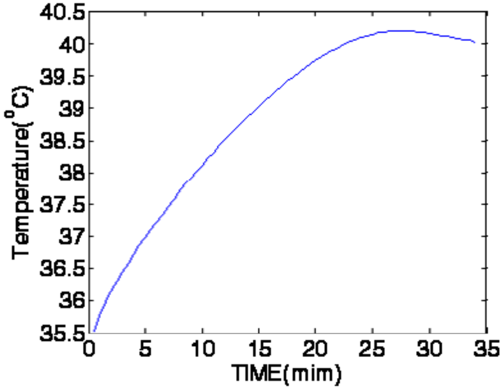
Current & Temperature Evolution

Cell Current



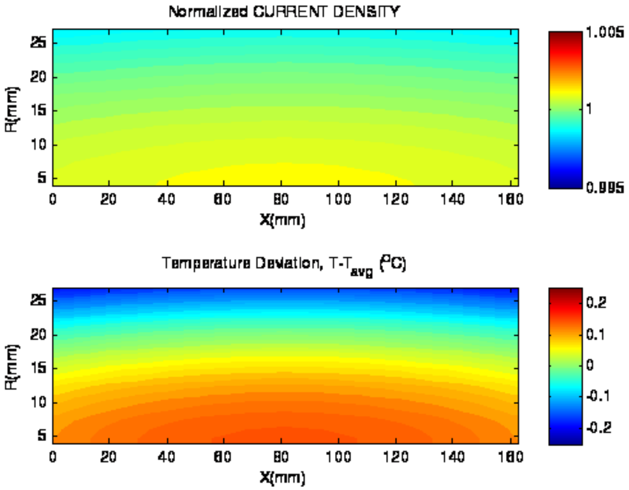


Avg Temperature



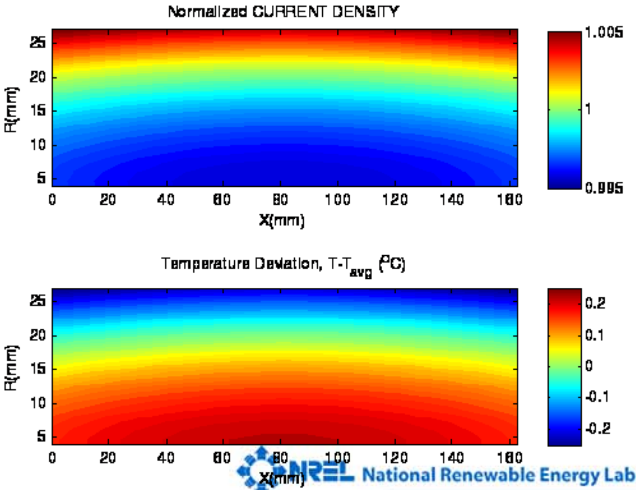
t= 15 min

t= 30 min



$$\frac{i}{(I/A)}$$

$$T - T_{avg}$$



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**

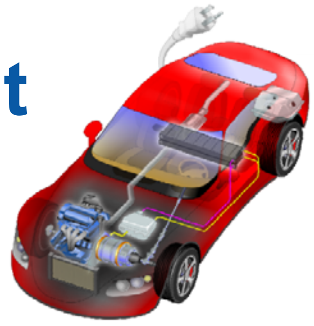
~10 hours to identify model from a single parameter set

- 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)

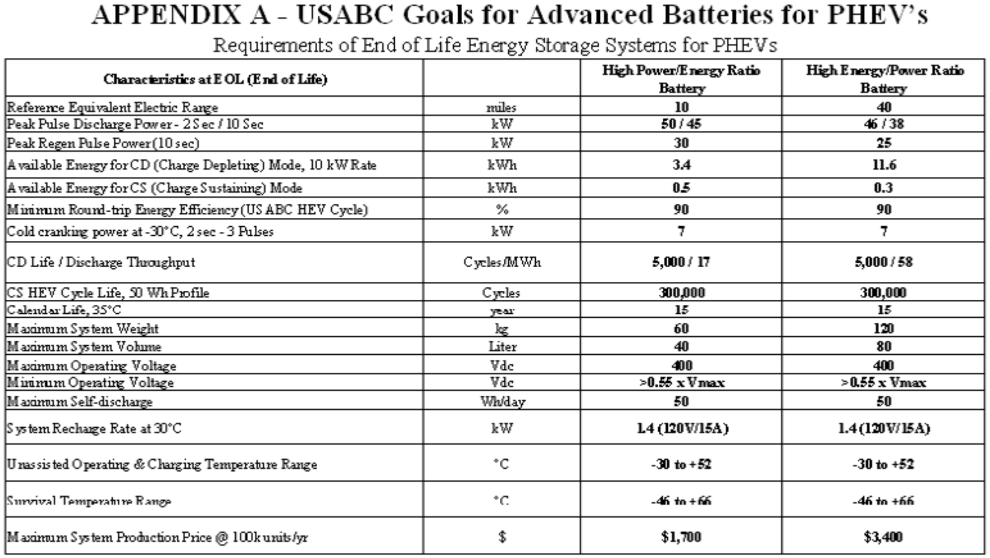
"MSMD model combination 2" runs ~1.75 faster than real time

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

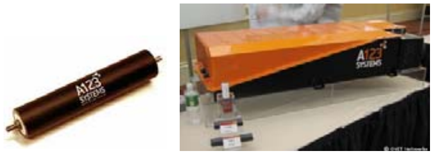
Characteristics at EOL (End of Life)		**High Power/Energy Ratio Battery**	**High Energy/Power Ratio Battery**
Reference Equivalent Electric Range	miles	**10**	**40**
Peak Pulse Discharge Power - 2 Sec / 10 Sec	kW	**50 / 45**	**46 / 38**
Peak Regen Pulse Power (10 sec)	kW	**30**	**25**
Available Energy 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 (USABC 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



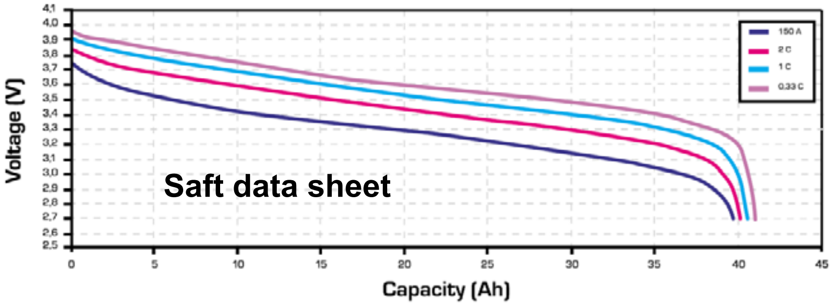
A123 Systems

Saft VL41M

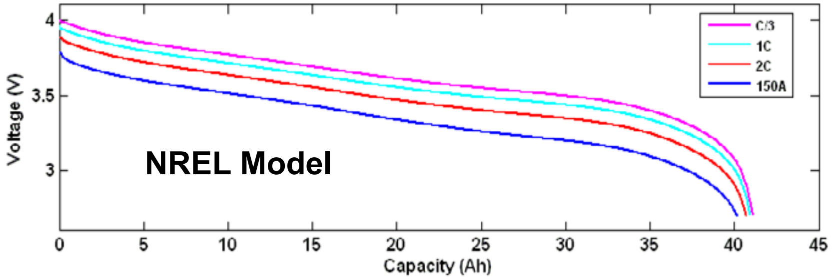
- Graphite-based anode
- Nickel oxide-based cathode

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



Saft data sheet

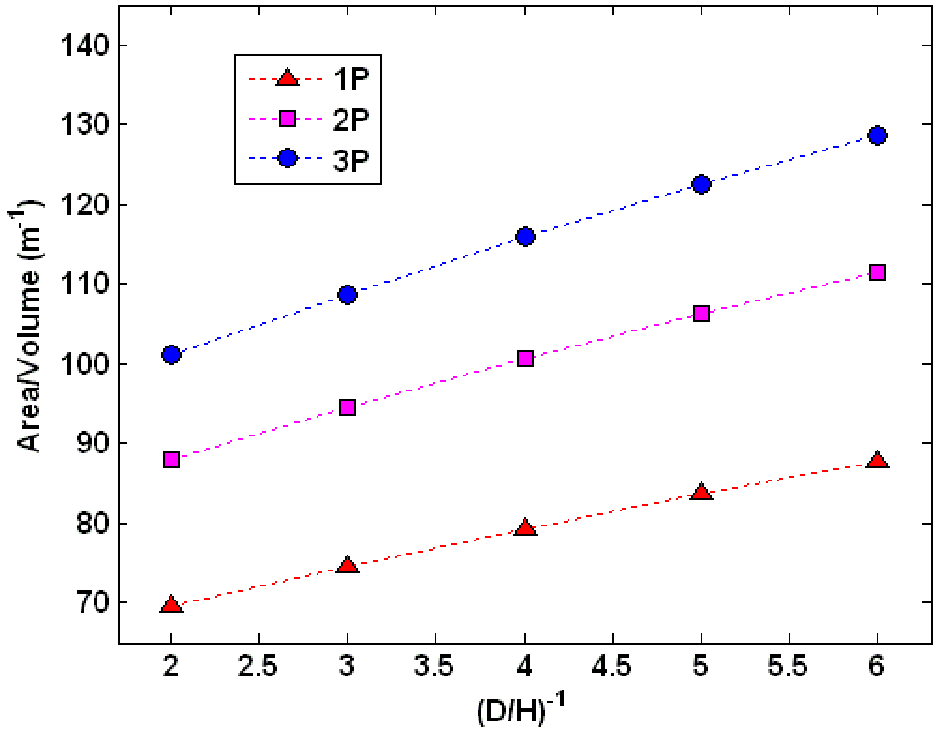


NREL Model

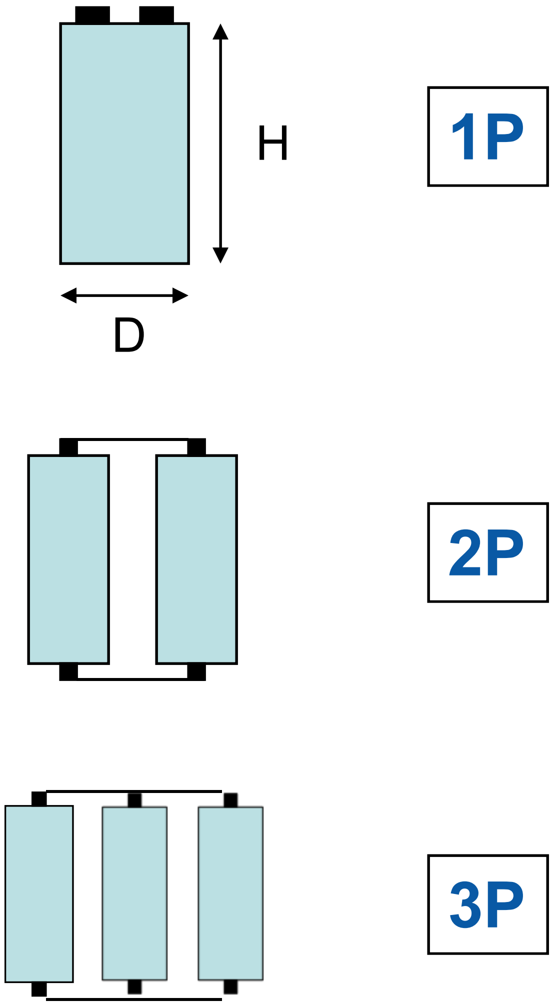
Cell design: What shape and size best meet thermal requirements?

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.*

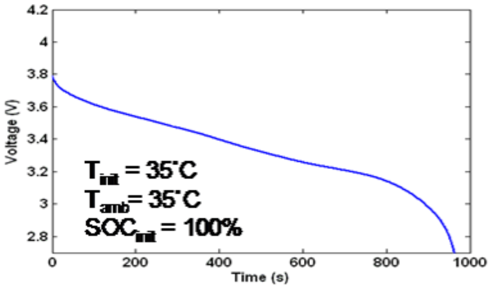


Usage profiles

Two cases explored in this presentation:

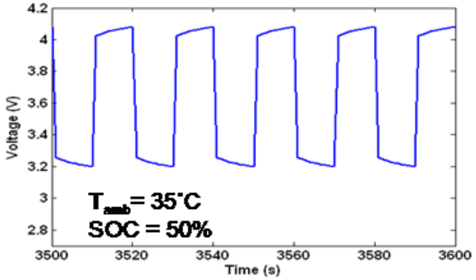
① **150A Max. Cont. Discharge**

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



② **200A Geometric Cycle**

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

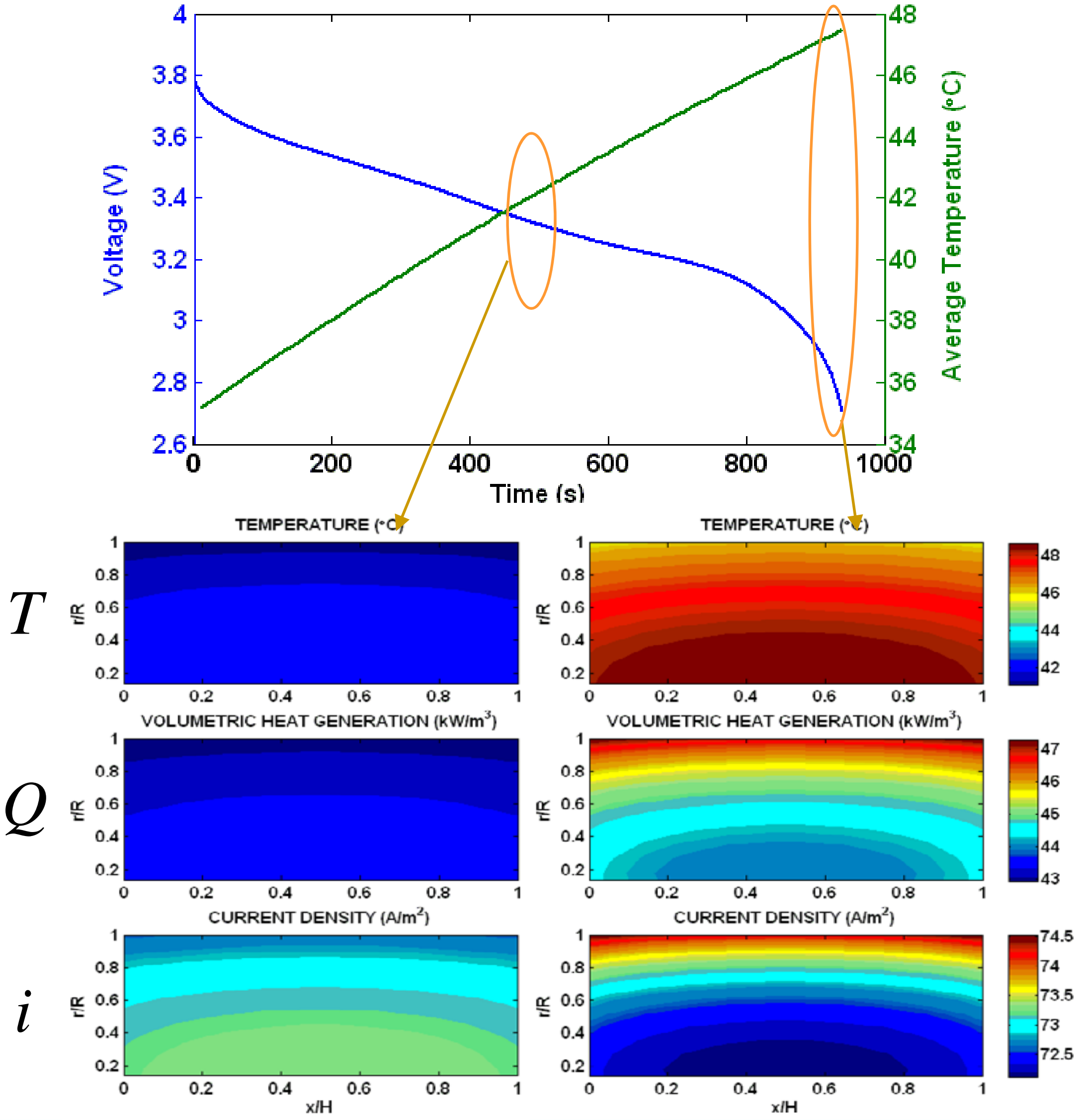


→ Moderate Thermal Condition

→ Severe Thermal Condition

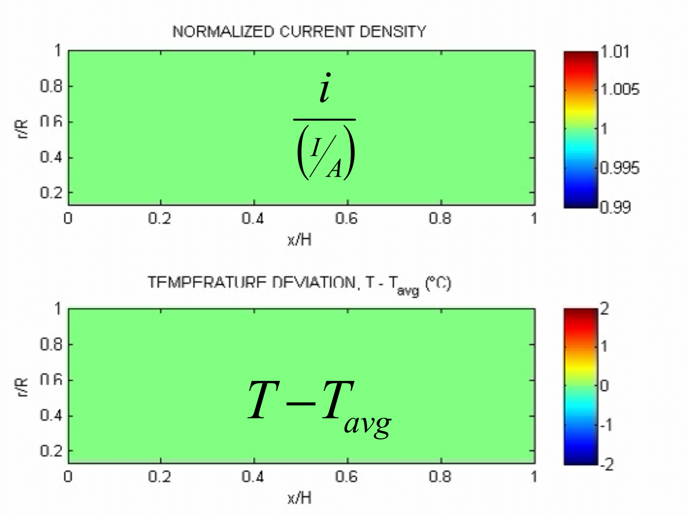
150A Discharge Case (Transient Results) :

- D/H = ¼
- h = 15 W/m^{2}K
- T_{amb} = 35°C



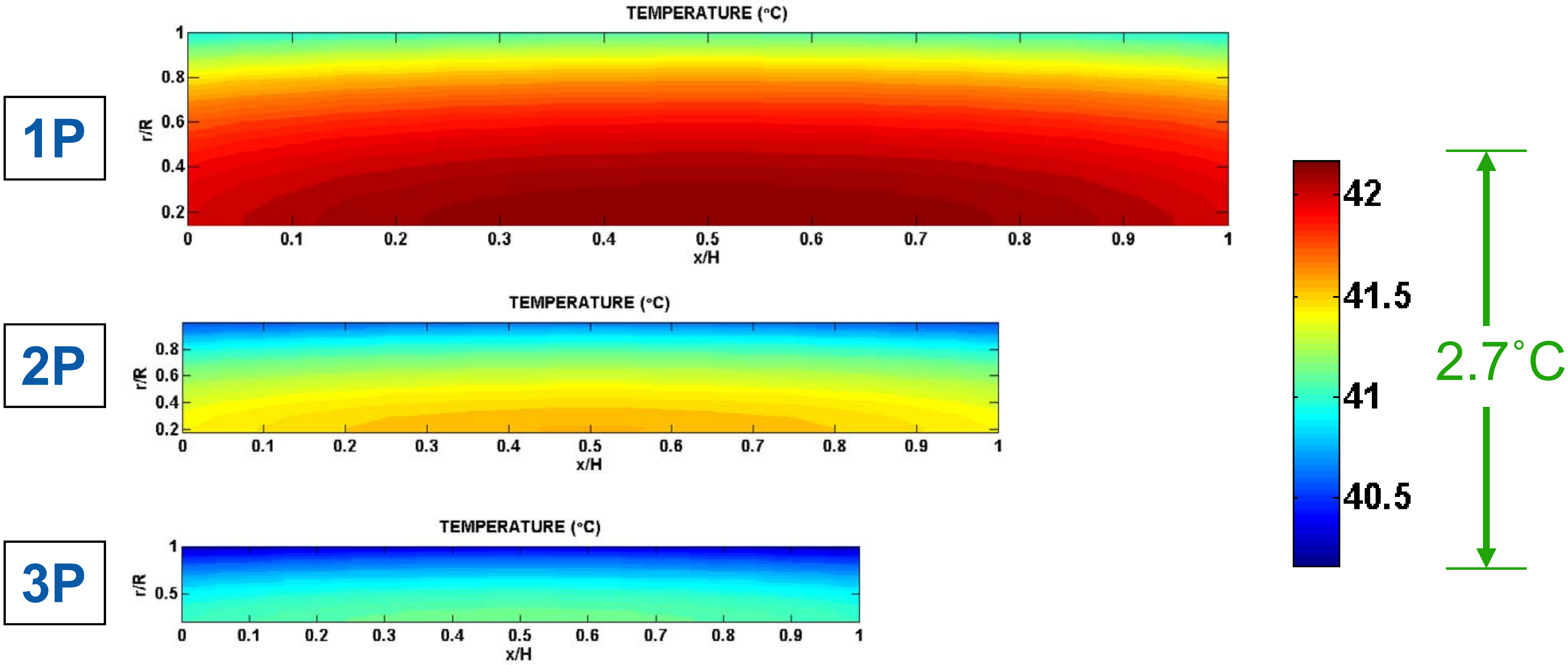
Movie of

- current imbalance
- temperature imbalance



150A Single Discharge (at End)

- D/H = ¼
- h = 15 W/m^2K
- T_{amb} = 35°C

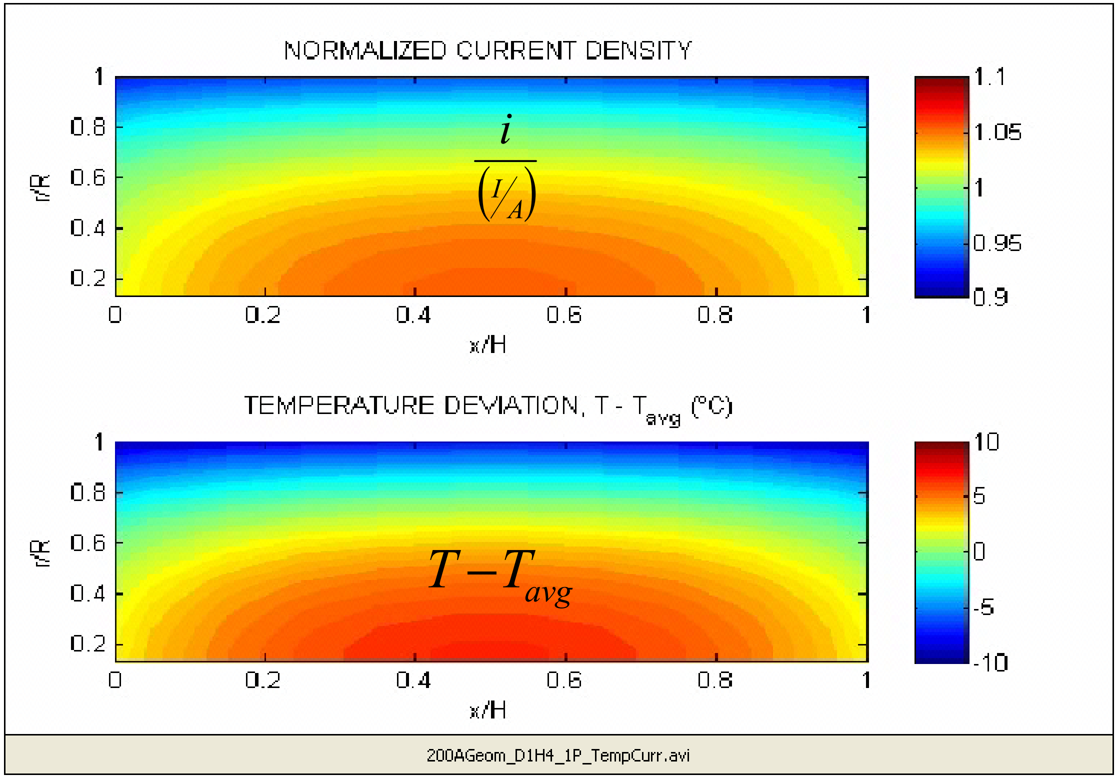


Moderate usage + Air convection = small internal gradients

200A Geometric Cycling

- D/H = ¼
  h = 150 W/m²K
  T_{amb} = 35°C

At Steady State

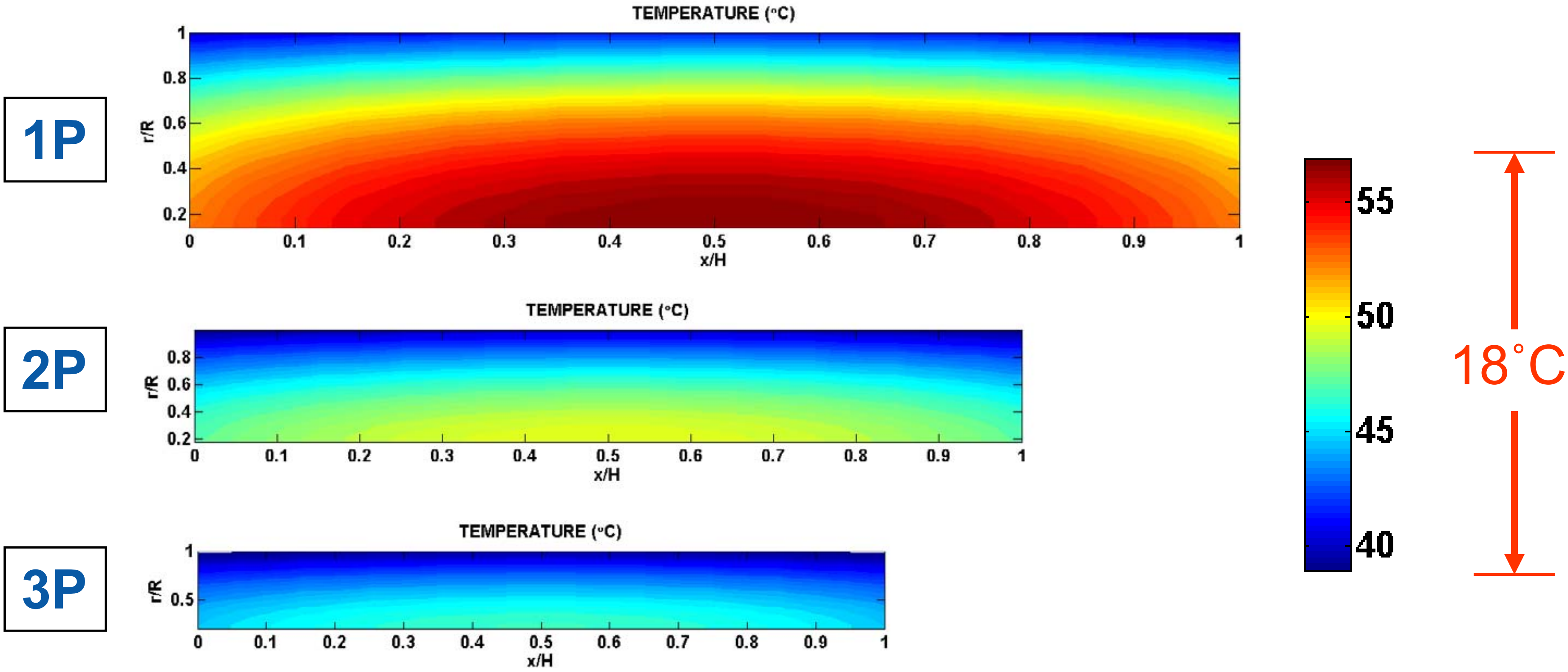


~20% difference in local current production

ΔT = ~18 °C

200A Geometric Cycle (Steady-State)

- D/H = ¼
- h = 150 W/m²K
- T_{amb} = 35°C



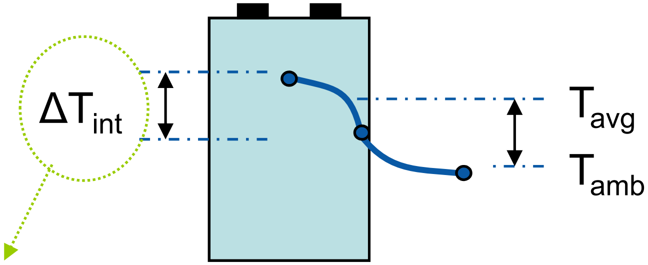
Severe usage + liquid cooling = large internal gradients

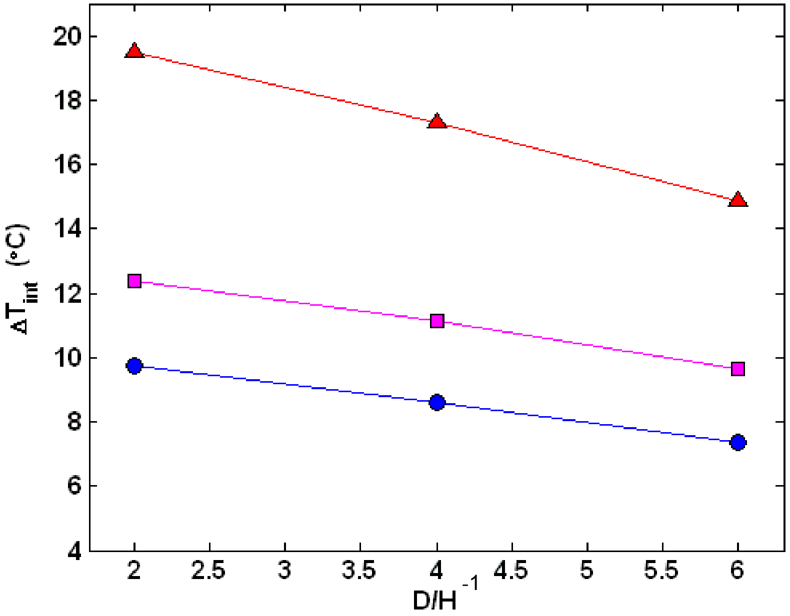
200A Geometric Cycle (Steady-State)

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

Internal Temperature Difference

- D/H ratio ~4.5˚C ↕
- 2P ~6.0˚C, 3P ~9.0˚C ↓





- *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 (< 3ºC).
- Under severe usage,
  - Large internal temperature imbalance (>20ºC) leads to significant reaction current imbalance (±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

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