Non-Destructive Analysis of Lithium Ion Cells by Electrochemical Caolrimetry

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Outline

1. What is an “Electrochemical Calorimetry”
2. Attribution of Thermal Behavior
3. Non-Destructive Analysis of Cycled Cell
4. Conclusion

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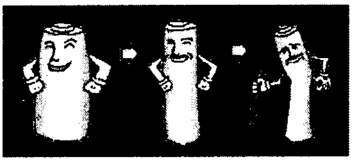
1. What is an "Electrochemical Calorimetry"?

- Merit of Electrochemical Calorimetry
- Schematic of Calorimeter
- Origin of Heat

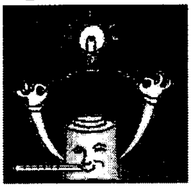
Typical Measurement Procedures of Lithium Ion Cells



- Electro(chemical)
  - Cycle performance test
  - Calendar life test
  - Peak power test
- Degradation Analysis
  - Destructive
    - XRD, NMR, GC/MS, TG/DTA
  - Non-destructive
    - EIS
    - Calorimetry

Merit of Electrochemical Calorimetry

- Simultaneous
  - Obtain & compare the electrochemical & thermal response
- Without special configuration of the cell
  - Commercialized (18650, prismatic), coin-type : OK
- Non-destructive
  - Apply to cells under cycling test
- Quantitative analysis of thermal properties
  - Database of the safety assessment



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Thermal Analysis of lithium ion cells & components

- Thermal stability of cells & components (abuse condition)
  - DSC : relative evaluation of thermal stability (components)
  - ARC : thermal stability of cells
- Electrochemical Calorimetry (normally operated condition)
  - Temperature measurement : easy & direct results
  - Calorimeter : High sensitivity, quantitative results

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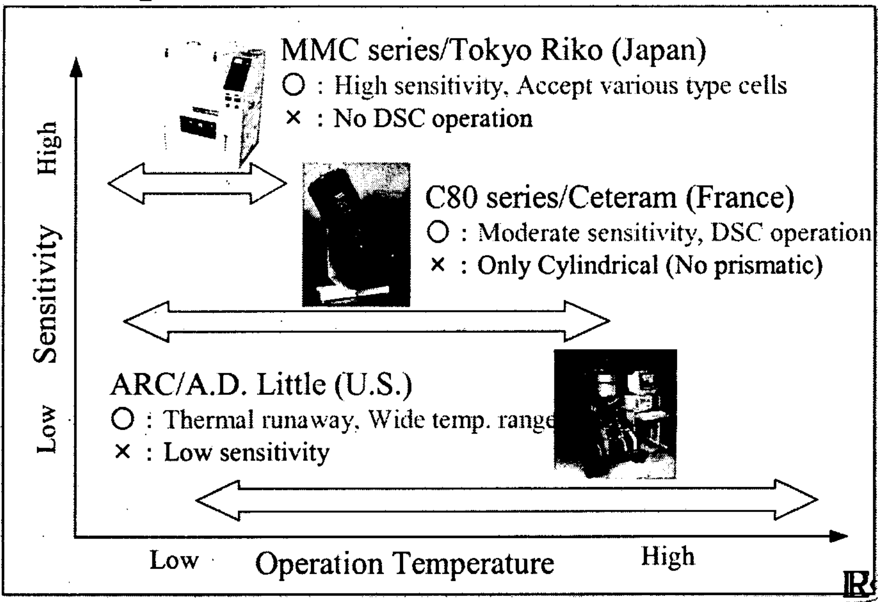
Comparison of Calorimeters



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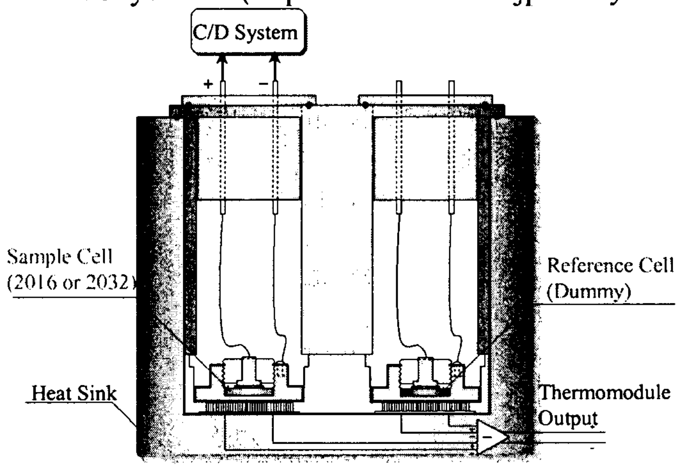
Schematic of Calorimeter

- Calorimeter : Twin, conductive (Calvet type)
  - Tokyo Riko (http://www2.ttcn.ne.jp/~tokyo-riko/)



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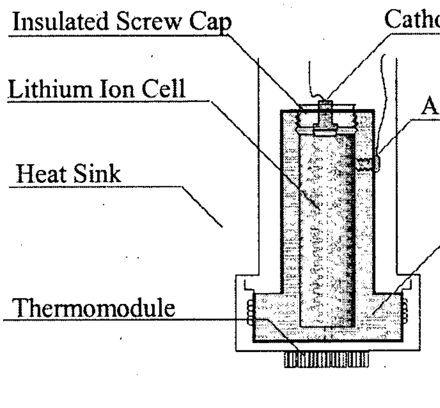
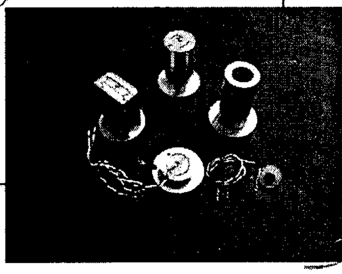
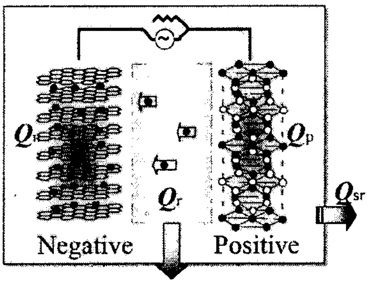
Cross section of Al vessel





Observed Heat Flow during Operation of Lithium Ion Cells

- Typical lithium ion cell
  - Cathode : $LiCoO_2$
  - Anode : Carbon
  - Electrolyte : Organic Solvent



- $Q_{tot}=Q_p+Q_n+Q_r+Q_{sr}$

Species of Heat	Reversibility	Current Proportion
Q_p : Reaction(Cathode)	Reversible	Linear
Q_n : Reaction(Anode)	Reversible	Linear
Q_r : Heat of Resistance	Irreversible	Quadratic
Q_{sr} : Side Reaction	Irreversible	------

- Commercialized Lithium Ion Cells
  - High reversibility & Low Impedance : Q_r, Q_{sr}→Negligible

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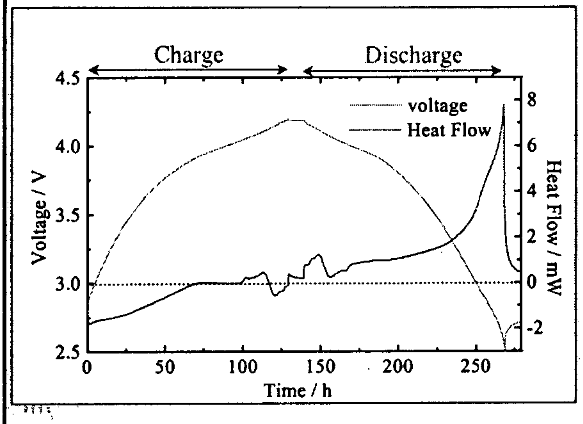
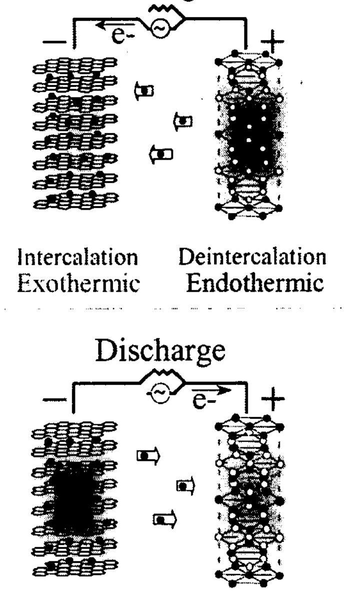
Typical Thermal Behavior





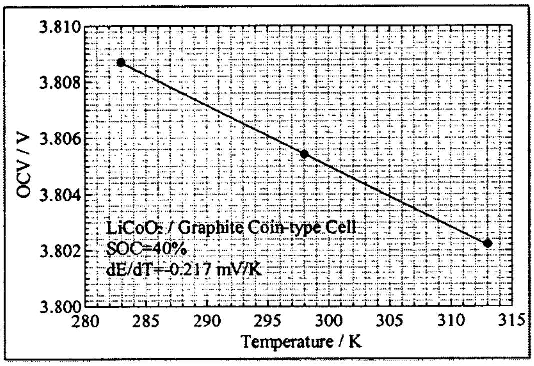
Cell : SONY 18650 (1250 mAh)
$LiCoO_2$ / Hard Carbon
4.2 / 2.5 V, 10 mA (C/100)

How to get ΔS

- Heat of reaction in the reversible secondary cell
  $\Rightarrow \Delta S$ during charge and discharge
- OCV dependence on Temperature
  $\Rightarrow dE/dT = \Delta S$

d*E*/d*T* measurement

1. SOC5% Shift (1 h)
2. Rest (>10 h)
3. 313 K (>3h) OCV
4. 298 K (>3h) OCV
5. 283 K (>3h) OCV (return to SOC5% Shift)



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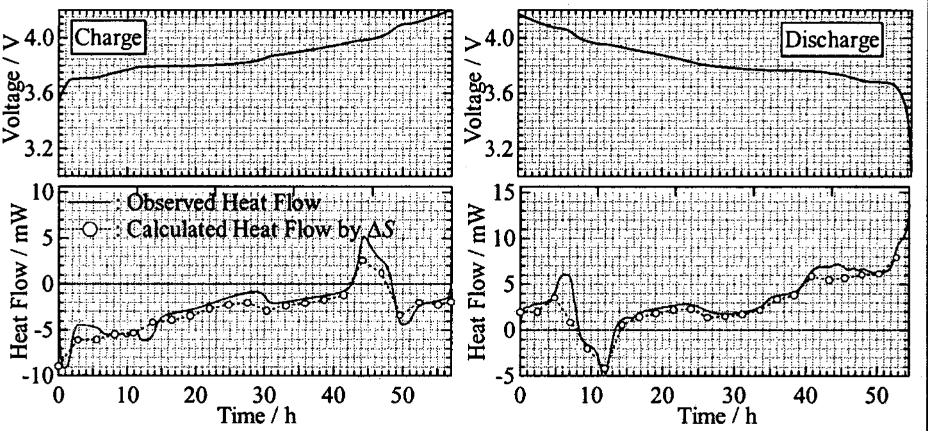
Thermal behavior of $LiCoO_2$/Graphite cell



ΔS (Observed heat flow)= ΔS (Calculated from dE/dT)

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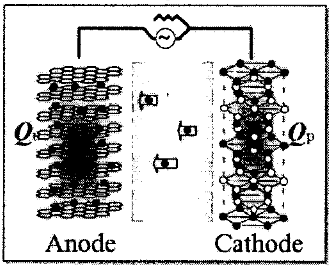
Observed heat during charge & discharge at low rate

□Commercialized cell

- □High reversibility
- □Low rate operation (C/50)
- ⇒Entropy change in electrodes ΔS



■ $Q_{tot}=Q_p+Q_n$

Species of Heat	Reversibility	Current Proportion
□ Q_p : Reaction (Cathode)	Reversible	Linear
□ Q_n : Reaction (Anode)	Reversible	Linear
□		
□		

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Summary 1 : Merit of Electrochemical Calorimetry

- Simultaneous & non-destructive measurement
- Obtain only heat of reactions on electrodes
  - At low rate operation
  - In the cell with high reversibility

2. Examples of Non-destructive Analysis

- Attribution of anode / cathode reaction
- Application to degradation analysis of electrodes
- Heat flow measurement vs. temperature measurement

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Heat of reaction on cathode or anode?

- Thermal behavior of lithium ion cells
  - contain cathode & anode information
- Separation of potential :
  - coin-type cell with Li reference electrode
  - Correlation between each potential & thermal behavior

- Separation of thermal behavior :
  - Coin-type cell with Li counter electrode
  - Thermal behavior of
    - $LiCoO_2$ / Li cell & Graphite / Li cell
  - Which is dominant ?

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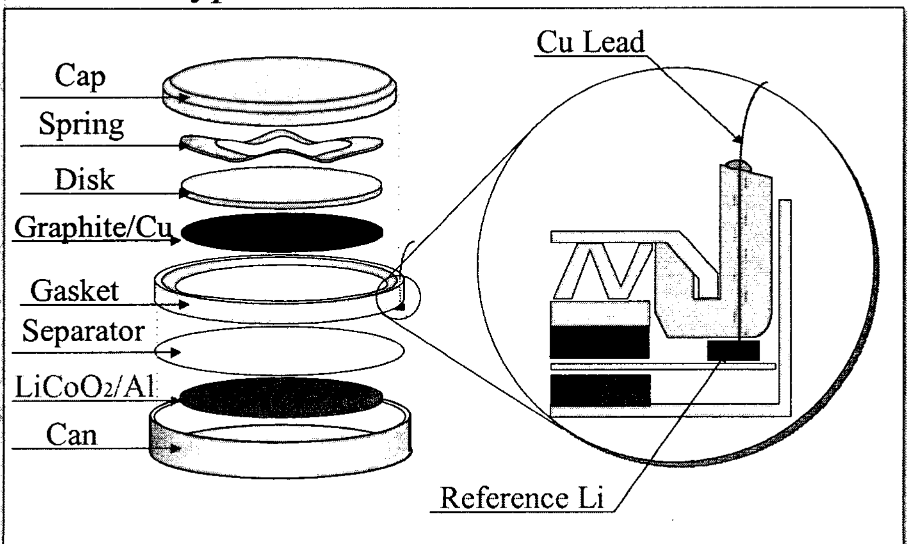
Separation of potential
-Coin-type cell with Li reference electrode-



Perfect "hand made" cell..

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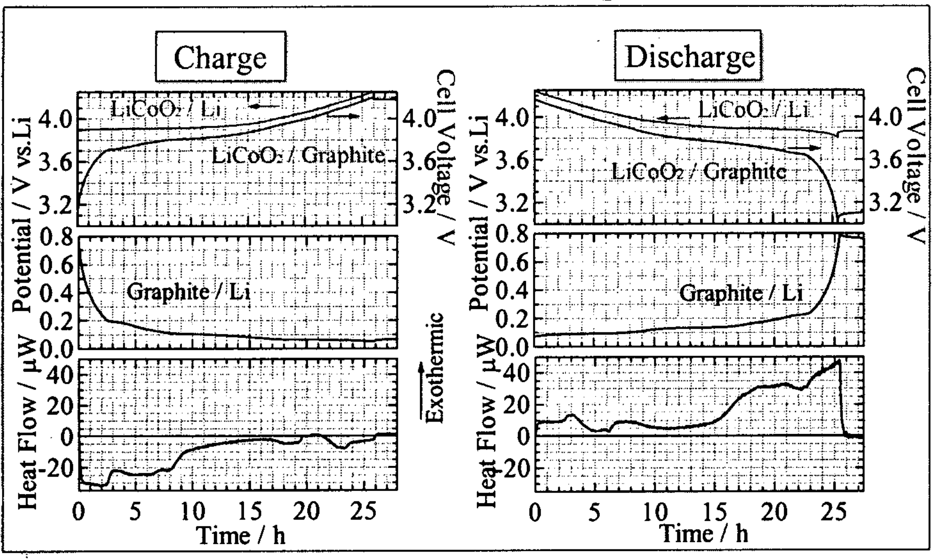
Separation of potential
-Heat flow & each electrode potentials-



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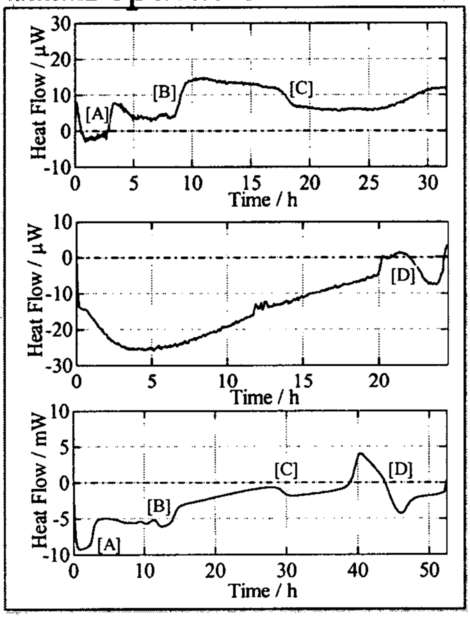
Separation of thermal behavior [Charge]



(a) Graphite/Li Coin-type
Exothermic
[A]:small endothermic

(b) $LiCoO_2$/Li Coin-type
Endothermic
[D]:small exothermic

(c) $LiCoO_2$/Graphite 18650-type
Endothermic
[D]:small exothremic

∴Heat of reaction on $LiCoO_2$ is dominant!

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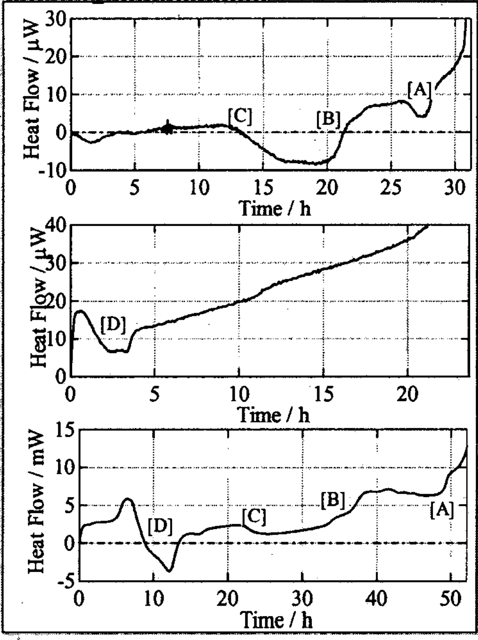
Separation of thermal behavior [Discharge]



(d) Graphite/Li Coin-type
[C] →[B] : Endothremic

[B]→[A] : Exothremic

(e) $LiCoO_2$/Li Coin-type
Exothermic only

(f) $LiCoO_2$/Graphite 18650-type
Exothermic
[D]:small endothermic

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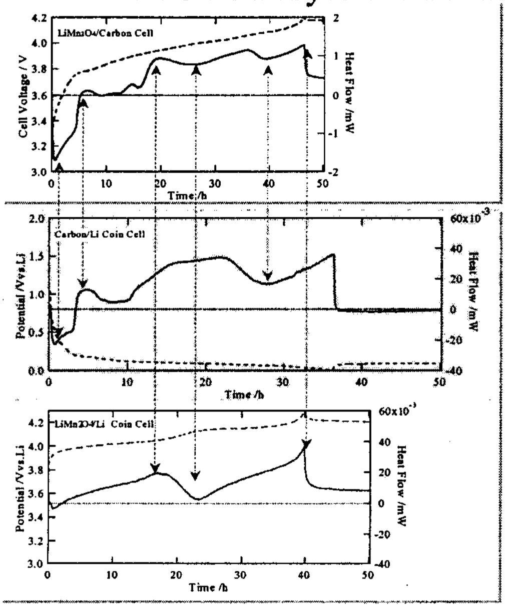
Attribution of thermal behavior $LiMn_2O_4$/Carbon system in charge



$LiMn_2O_4$/Carbon

Carbon/Li

$LiMn_2O_4$/Li

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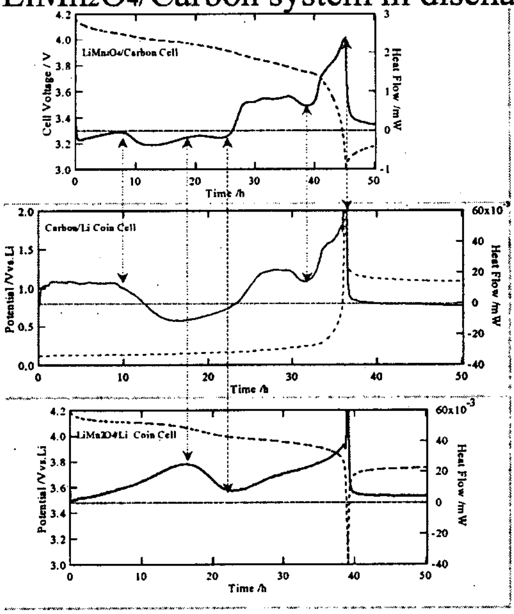
Attribution of thermal behavior
$LiMn_2O_4$/Carbon system in discharge

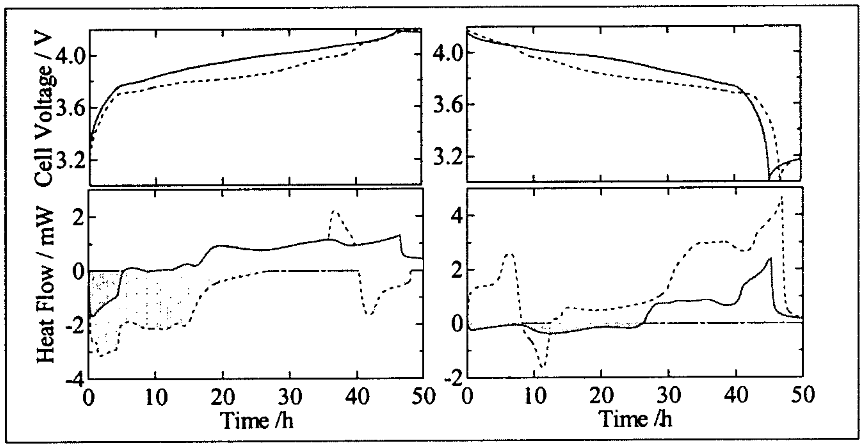


$LiMn_2O_4$/Carbon

Carbon/Li

$LiMn_2O_4$/Li

Comparison of thermal behavior
$LiCoO_2$/Graphite vs. $LiMn_2O_4$/Graphite



Larger endo / exothermic profile : $LiCoO_2$/Graphite system

Comparison of each electrodes

	Charge			Discharge		
SOC/%	0	50	100	0	50	100
Graphite	↓	↑	↑	↓	↓	↑
$LiCoO_2$	↓	↓	↓	↑	↑	↑
Lithium Ion ($LiCoO_2$/Graphite)	↓	↓	↓	↑	↑	↑
$LiMn_2O_4$	↓	—	↑	↓	—	↑
Lithium Ion ($LiMn_2O_4$/Graphite)	↓	↑	↑	↓	↓	↑

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Non-destructive degradation analysis of lithium ion cells

- Characteristic thermal profiles (cathode & anode) selection
- Comparison thermal behaviors between cycled & fresh cells
- Which is dominant degradation?

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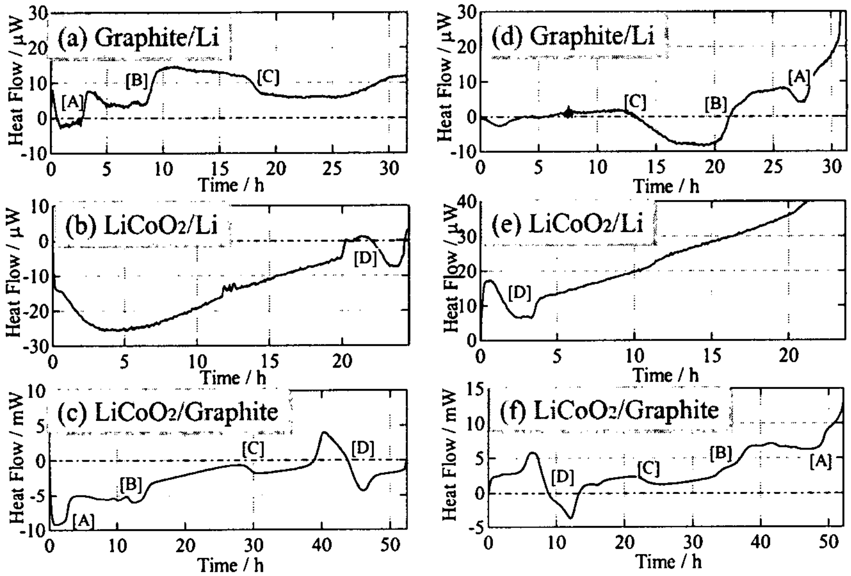
Attribution of thermal behavior



Charge

Discharge

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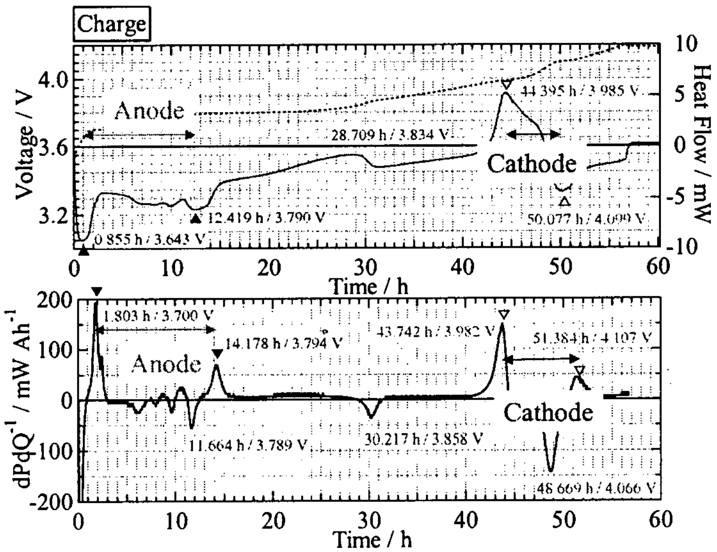
Estimation of capacities (anode / cathode) from attributed thermal behavior



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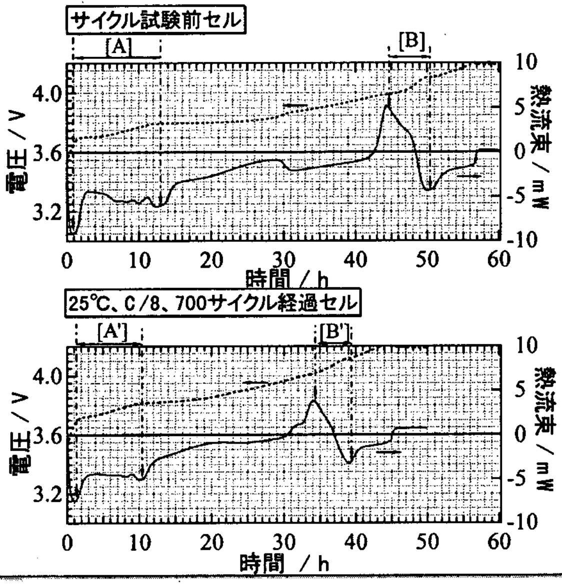
Degradation Analysis (25°C,C/8,700cyc)



Electrode Peak		Retention
Total		79%
Anode	[A']/[A]	78%
Cathode	[B']/[B]	88%

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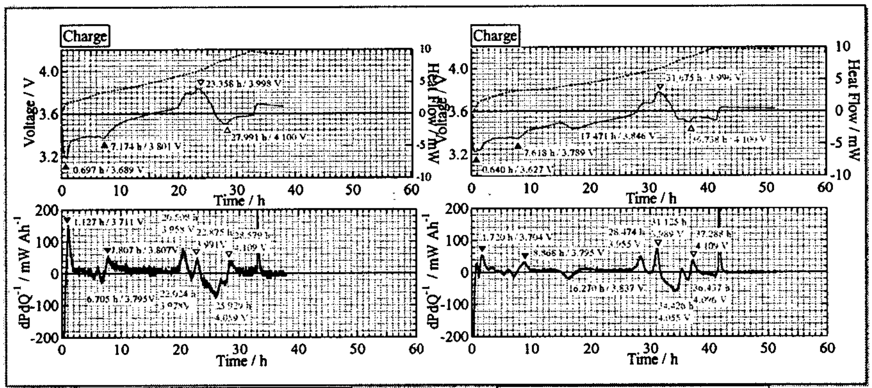
Thermal behaviors of cycled cells



40°C, C/2, 1100cyc

50°C, C/1, 2200cyc

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Retention of each electrode materials obtained from electrochemical calorimetry

Condition	25°C, C/8	40°C, C/2	50°C, C/1
Cycle Number	700 cyc	1100 cyc	2000 cyc
Retention of Cell*	**79 %**	**58 %**	**73 %**
Cathode(thermal peak)	88 %	82 %	88 %
Cathode(differential peak)	97 %	81 %	90 %
Anode(thermal peak)	**78 %**	**56 %**	**60 %**
Anode(differential peak)	**74 %**	**54 %**	**58 %**

* : vs. capacity of fresh cell at C/50 condition

Degradation of anode is dominant !

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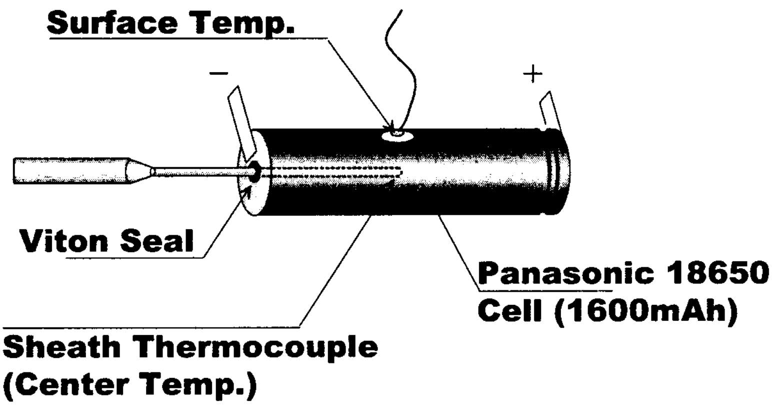
Comparison between internal temperature & thermal behavior

- Direct measurement of surface and center temp. during C/D
- Correlation of result obtained from calorimetry



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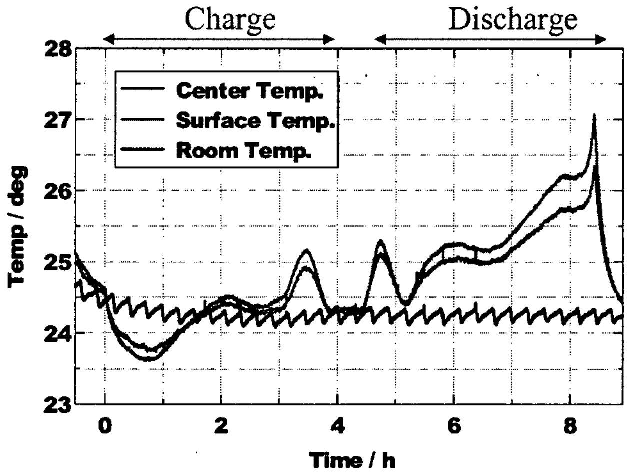
Surface & center temp. variation under operation



Condition : 4.2 / 3.0 V, 400 mA (C/4)

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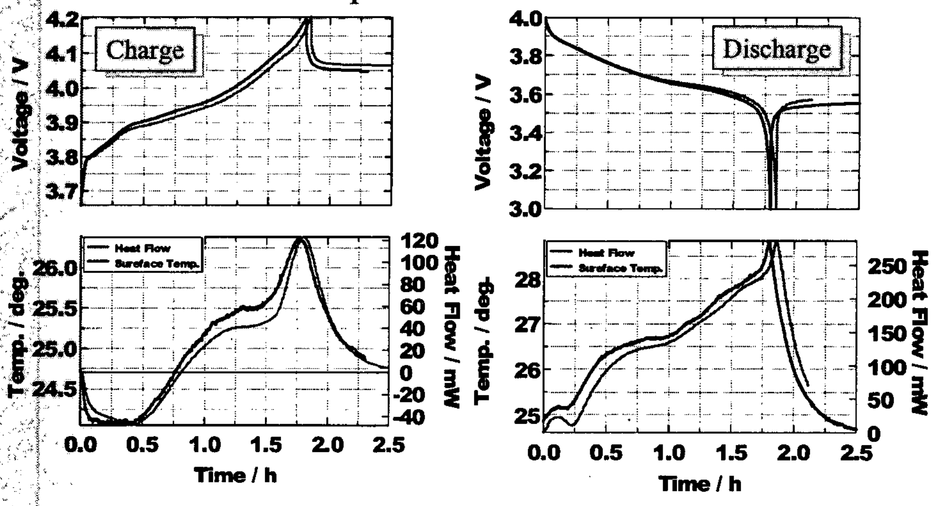
Surface Temp. vs. Thermal behaviors



Condition : 4.2 / 3.0 V, 800 mA (C/2)

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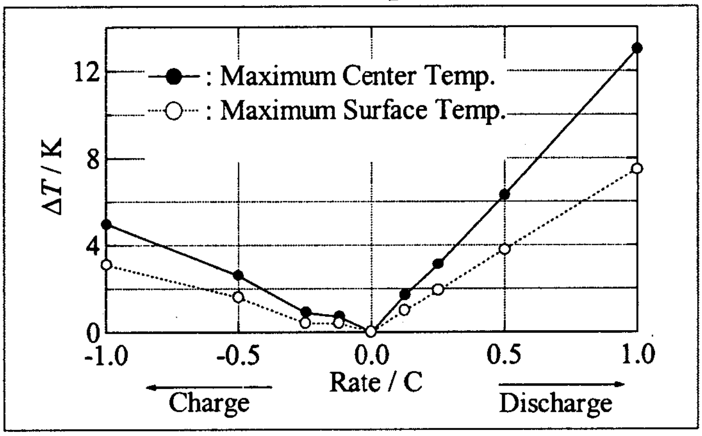
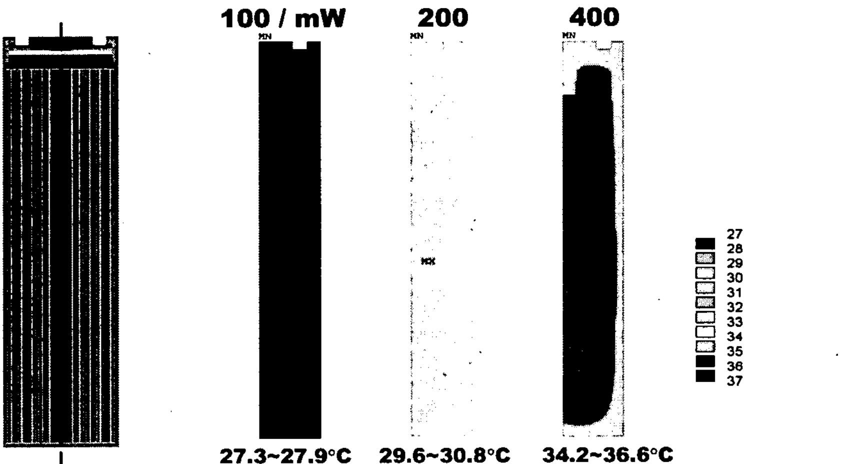
Surface & center temp. under various rate



Correlation between heat flow & Temperature
Surface temp.(end of discharge 1h ave.) : 60 mW/K
Center temp.(max.) : 30 mW/K

Simulation result of 18650 cell

H = 10 W/m²•K



Surface & center temp. : good correlation between experimental results

Summary 2 : Non-destructive analysis by electrochemical calorimetry

- Separation / Attribution of heat of electrode reactions :
  - Separation : by using Li counter electrode
  - $LiCoO_2$/Graphite system : heat of cathode reaction is dominant.
- Degradation estimation by non-destructive analysis
  - Capacity retention of cathode / anode : comparable
- Direct measurement of internal temperature
  - Good correlation between heat flow & surface / center temp.

Conclusion

- Electrochemical Calorimetry:
  - Apply from coin-type to 18650 cell
  - Powerful tool for the non-destructive analysis
- Thermal response from electrodes contains
  - Entropy change of Li^+ (not detectable by XRD)
  - Phase transition, change of stage structure
  - Degradation reactions
  - Lots of unknown reactions…

References

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