Battery Calorimetry of Li-Ion Cells to Prevent Thermal Runaway and Develop Safer Cells

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Motivation
Increase of safety and reliability of lithium-ion batteries for EV/HEV

→ For improving battery management system (BMS) and thermal management system (TMS) electrochemical and thermal behavior of the cells have to be thoroughly studied

Aim: Improvement of TMS and BMS by determination of quantitative data using battery calorimetry in combination with modelling and simulation

Feng et al., Energy Storage Materials 10 (2018) 246
Outline

- Short introduction to battery calorimetry
- Methods for the determination of total generated heat
- Safety tests
- Isoperibolic and adiabatic studies
Short institute presentation
Karlsruhe Institute of Technology (KIT)

1/10/2009 - Foundation of KIT

Merger of the University of Karlsruhe (TH) and the Forschungszentrum Karlsruhe GmbH

Data 2016

- Employees: 9,239
- Students: 25,892
- Professors: 365
- Budget: 851 Mio Euro
- Patents: 55
- Spin-offs: 21

Research – Teaching – Innovation

Campus South

Dr. C. Ziebert – AABC Europe, Mainz, 29.01.-01.02.2018
Possible conditions in an Accelerating Rate Calorimeter (ARC)

An ARC provides **isoperibolic** and **adiabatic** conditions.

Under isoperibolic conditions the environmental temperature is kept constant.

**Thermal resistance** $R_{th}$ defined

\[
T_C \text{ constant} \\
T_S(t) = T_{S_0} + \alpha \cdot t
\]

Under adiabatic conditions the heaters follow immediately any change of the bomb thermocouple thus preventing that the cell can transfer heat to the walls.

**Thermal resistance** $R_{th}$ very high

\[
T_C = T_C(t) = T_{C_0} + \alpha \cdot t
\]
At IAM-AWP: Europe`s Largest Battery Calorimetry Lab

Accelerating Rate Calorimeter (ARC)

Equipment: 6 ARC’s (THT); 2 Tian-Calvet calorimeters (C80, Alexys1000: Setaram); DSC (Netzsch), TGA+STA (TAG, Setsys, Setaram); IR camera (FLIR); 12 Temperature chambers; 10 Cyclers; EIS (Ref3000, Gamry)
Adiabatic and Isoperibolic Measurements

Adiabatic Measurements

Worst Case Conditions

→ Cell in a pack surrounded by other cells

Discharge parameter:
- method: constant current (CC)
- \( U_{\text{min}} = 3.0\,\text{V} \)
- \( I = 5\,\text{A} \rightarrow \text{C/8-rate} \)

Charge parameter:
- method: constant current, constant voltage (CCCV)
- \( U_{\text{max}} = 4.1\,\text{V} \)
- \( I = 5\,\text{A} \rightarrow \text{C/8-rate} \)
- \( I_{\text{min}} = 0.5\,\text{A} \)

→ after each electrochemical cycle the cell temperature increases further

\[ T_{\text{st}} = 23^\circ\text{C} \text{ (RT)} \]
Isoperibolic Measurements

Ideal conditions

→ Single cell

Discharge parameter:
- method: constant current (CC)
- \( U_{\text{min}} = 3.0 \text{V} \)
- \( I = 5 \text{A} \rightarrow C/8\)-rate

Charge parameter:
- method: constant current, constant voltage (CCCV)
- \( U_{\text{max}} = 4.1 \text{V} \)
- \( I = 5 \text{A} \rightarrow C/8\)-rate
- \( I_{\text{min}} = 0.5 \text{A} \)

→ after one electrochemical cycle the cell temperature reaches its initial value again

\[ \left( \frac{\delta E}{\delta T} \right) < 0 \]

temperature coefficient negative!
Methods for the determination of total generated heat

Heat generation of the cell during charging and discharging – Key data for thermal management and safety

Conversion of thermal data (temperature, temperature rate) to heat (Joule) and power (Watt) with the aim of understanding of heat release to determine heat removal requirements for thermal management.

To be measured:

- Cell effective specific heat capacity
- Heat transfer coefficient
- Reversible heat rate
- Irreversible heat rate
Measurement of effective specific heat capacity $c_p$

Control of the current applied to the heater mat to ensure a constant heating rate

$$c_p = \frac{\Delta Q}{m \cdot \Delta T_{ad}} = \frac{\int U \cdot I \, dt}{m \cdot \Delta T_{ad}}$$

$m$: Mass of the cell

$\Delta T_{ad}$: Temperature difference under adiabatic conditions

- e.g. at 30 °C: $c_p = 1.095 \, J/g \cdot K$
Measurement of heat transfer coefficient $h$ with heat flux sensors

**Working principle of heat flux sensor**

Tiny, serially connected semiconductor piles inside the sensor generate a voltage, which is proportional to the heat passing through the surface. The voltage is read out and depending on the sensor’s sensitivity the results are converted into the heat flux [2].

**Sensitivity:**

$$S(T) = S_0 + (T - 22.5 \, ^\circ C) \cdot S_C$$

$$S_0 = 10.04 \frac{mV \cdot m^2}{W}$$

$$S_C = 0.0049 \cdot \frac{mV \cdot m^2}{W \cdot ^\circ C}$$

Room temperature sensitivity

Temperature correction factor

$$\Rightarrow h = \frac{\int U_{\text{sensor}}}{S(T)} \, dt / \int_0^t (T - T_C) \, dt$$


Comparison of the values for the generated heat determined by three different methods

1) Adiabatic Measurement
\[ \dot{Q}_g = m c_p \frac{dT}{dt} \]

2) Isoperibolic Measurement
\[ \dot{Q}_g = m c_p \frac{dT}{dt} + Ah \cdot (T_S - T_C) \]

3) Measurement of irreversible and reversible heat using potentiometric and CIT method
\[ \dot{Q}_g = -I(E_0 - E) - IT \frac{dE_0}{dT} \]

\( E_0 \): Open circuit voltage (OCV), \( E \): cell potential

Conclusion: good agreement between the values determined by the different methods

Influence of ageing phenomena on different modes of heat generation

Comparison between fresh 18650 cells and 3 cell groups (each consisting of 3 cells) after cyclic (G1) or calendaric (G2, G3) ageing for 30d: (a) Isoperibolic cycling (b) Adiabatic cycling in the ARC.

Conclusion: Recording of temperature profile can be used as a “fingerprint” for the SOH and as a fast and reliable method for the characterization of aging processes.
Safety tests

a) Thermal Abuse: Heat-Wait-Seek (HWS) Method

Exotherm

Heat

Wait

Cool

Idle

If T>T_f

dT/dt<onset

dT/dt>onset

Seek

end test

Example of a Heat-Wait-Seek step

**Thermal Runaway: 18650 cells with different cathode materials**

- **80<T<130°C:** low rate reaction, 0.02 - 0.05 °C/min: exothermic decomposition of the SEI
- **130<T<200°C:** medium rate reaction, 0.05 - 25 °C/min: solvent reaction, exothermic reaction between embedded Li ions and electrolyte ⇒ reduction of electrolyte at negative electrode
- **T > 200°C:** high rate reaction, higher than 25 °C/min: Exothermic reaction between active positive material and electrolyte at positive electrode ⇒ rapid generation of oxygen
Study of ageing effects of PHEV1 cells by thermal runaway tests
Development of internal pressure measurement methods for 18650 cells

Internal pressure could be used in BMS for early prediction of processes leading to thermal runaway

Electrochemical-Thermal Model: Lumped Matlab ODE model for ramp heating with venting

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a model for ramp heating with ODEs representing:

- the decomposition rates
- the energy balance
- the ideal gas flow equations
- the burst condition for the trigger pressure
- the partial ejection of the jelly roll

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KIT, IAM-AWP
Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

Experiment (HWS)

Simulation (Ramp Heating)
b) Mechanical abuse: Nail test

*Nail penetration test on pouch cells in the ARC*

Comparison of different SOC

Nail penetration test in the ARC on a 2.5 Ah pouch cell

SOC 80

SOC 70

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The three-level strategy of reducing the hazard of thermal runaway

Step 1 - BMS
Detection of mechanical, thermal, electrical abuse

Step 2 – Cell:
Venting, CID, PTC

Step 3 – Pack
Passive propagation prevention

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The three-level strategy of reducing the hazard of thermal runaway

Protective Material evaluation in battery calorimeters:

- Red: heater mat for thermal runaway initiation
- Gray: protective material for cell 4 and lid of battery box

- Extended time for thermal runaway propagation: 9 min
- Improved thermal protection: temperature outside of battery box < 80 °C during thermal runaway
Summary: Possible measurements with a battery calorimeter

Normal conditions of use

- Isoperibolic or adiabatic measurement
  - Measurement of temperature curve and temperature distribution during cycling (full cycles, or application-specific load profiles)
  - Determination of the generated heat, Separation of heat in reversible and irreversible parts

Abuse conditions

- Thermal abuse
- External short circuit, nail penetration test
- Overcharge, deep discharge
  - Temperature measurement
  - External or internal pressure measurement
  - Gas collection

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Important data for BMS, TMS and safety
Thank You For Your Kind Attention

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