Using Battery Calorimetry for Improved Thermal Management and Thermal Runaway Prevention


Institute for Applied Materials – Applied Materials Physics (IAM-AWP)
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

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Outline

Isoperibolic and adiabatic studies

Short introduction to battery calorimetry

Safety Tests

Methods for determination of total generated heat
Short introduction to battery calorimetry

Possible conditions in an Accelerating Rate Calorimeter (ARC)

An ARC provides \textit{isoperibolic} and \textit{adiabatic} conditions

Under isoperibolic conditions the environmental temperature is kept constant.

\[ R_{th} \text{ defined} \]

\[ T_C \text{ constant} \]

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

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

\[ R_{th} \text{ very high} \]

\[ T_C(t) = T_{C_0} + \alpha \cdot t \]
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

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

Ideal conditions

→ Single cell

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

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 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

**Example:**

At $30^\circ C$, $c_p = 1.095 \, J/\, g \cdot K$
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**

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


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

1) Adiabatic Measurement

\[ \dot{Q}_g = mc_p \frac{dT}{dt} \]

2) Isoperibolic Measurement

\[ \dot{Q}_g = mc_p \frac{dT}{dt} + Ah \cdot (T_S - T_C) \]

3) Measurement of irreversible and reversible heat using potentiometric and CIT method

\[ \dot{Q}_g = -I(E_0 - E) - IT \frac{dE_0}{dT} \]

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


\[ Q_{\text{adia}} \]
\[ Q_{\text{iso}} \]
\[ Q_{\text{thermo}} \]

Discharge half cycles

T = 30 °C

E₀: Open circuit voltage (OCV), E: cell potential
Safety tests

a) Mechanical abuse: Nail penetration test

Comparison of different SOC

SOC 80

Thermal Runaway

SOC 70

No Thermal Runaway

Nail penetration test in the ARC on a 2.5 Ah pouch cell
b) Thermal Abuse: Heat-Wait-Seek (HWS) Method

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

Dr. C. Ziebert – Battery Show Europe 2018, Hannover, 15.-17.05.2018
Study of ageing effects of PHEV1 cells by thermal runaway tests

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KIT, IAM-AWP
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

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

Comparison of experimental and simulation results for 18650 cells

Thermal runaway including internal pressure evolution

Experiment (HWS)

Simulation (Ramp Heating)
The three-level strategy of reducing the hazard of thermal runaway

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

Level 2 – Cell:
Venting, CID, PTC

Level 3 – Pack
Passive propagation prevention

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http://www.hko.de/
Material qualification for passive propagation prevention

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

**Optimized Multilayer: HKO-Defensor ML 14**

- Extended time for propagation: 9 min
- Improved heat protection: temperature on top 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), ageing studies
  - Determination of the generated heat, Separation of heat in reversible and irreversible parts

Abuse conditions

- Thermal abuse: Heat-wait-seek test, ramp heating test, thermal propagation test
- External short circuit, nail penetration test
- Overcharge, deep discharge
  - Temperature measurement
  - External or internal pressure measurement
  - Gas collection, Post Mortem Analysis, Ageing studies

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

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