How battery calorimeters can help in advancing thermal management and safety of cells and packs


KIT, Institute for Applied Materials – Applied Materials Physics
The Group Batteries – Calorimetry and Safety

Dr. Carlos Ziebert
Group leader Batteries – Calorimetry and Safety

E-Mail: Carlos.Ziebert@kit.edu

Data 2022

Employees: 15
Running LIB projects: 4
HELIOS, POLiS, BatgasMod, AnaLiBa
Industry cooperation: 8
Motivation: Increase of safety and reliability of LIB

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 of thermal properties using calorimeters.

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

- Heat generation under normal use
- Heat generation under abuse
- Thermal propagation
- Short introduction to battery calorimetry
At IAM-AWP: Europe`s Largest Calorimeter Center

Equipment: 7 Accelerating rate calorimeters (ARC); 2 Tian-Calvet calorimeters; 5 DSC; IR camera; 13 Temperature chambers (23l - 400 l; -40°C to 180°C); 11 Cyclers (210 channels, 0.01-800 A); EIS; 2 GC/MS
How can calorimetry help in battery research?

Research for improving performance parameters
- Higher energy or power density
- Smaller heat release during operation
- Faster charging rates
- Increased cycle life and thermal life

Research for improving safety parameters
- Higher safe operating temperature
- Better resistance to thermal/mechanical/electrical abuse
- Less energy release during decomposition

Differential scanning calorimeters
- Tian-Calvet calorimeters
- Small ARC
- Medium-size ARC
- Large-size ARC

Components
- 1 - 80 mAh
- 3 - 5 Ah
- 5 - 40 Ah
- 40 - 75 Ah

Cell Size and Capacity

Pressure measurement in ARC
Nail penetration test in ARC
Possible conditions in an ARC

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

- **Isoperibolic conditions**: The environmental temperature is kept constant.
  \[ R_{th} \text{ defined} \]
  \[ T_c \text{ constant} \]
  \[ T_s(t) = T_{s0} + \alpha \cdot t \]

- **Adiabatic conditions**: The heaters follow immediately any change of the bomb thermocouple thus preventing the cell from transferring heat to the walls.
  \[ R_{th} \text{ very high} \]
  \[ T_c = T_c(t) \]
  \[ = T_{c0} + \alpha \cdot t \]
Overview

- Heat generation under normal use
- Short introduction to battery calorimetry
- Thermal propagation
- Heat generation under abuse
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

\( \frac{\delta E}{\delta T} < 0 \) temperature coefficient negative!
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

40 Ah pouch cell

$T_{\text{st}} = 23^\circ\text{C (RT)}$
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:

- Effective specific heat capacity
- Heat transfer coefficient
- Reversible heat rate and irreversible heat rate
Effective specific heat capacity $c_p$

![Graph showing effective specific heat capacity $c_p$ vs. temperature in °C.](image)

- At 30 °C, $c_p = 1.095 \text{ J/g} \cdot \text{K}$

**Important input data for simulation**

**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
**Heat transfer coefficient**

**Working principle of heat flux sensor (hfs)**

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.

\[ \int \frac{U_{sensor}}{S(T)} \, dt \]

\[ \Rightarrow h = \frac{\int_{0}^{t} \frac{U_{sensor}}{S(T)} \, dt}{\int_{0}^{t} (T - T_C) \, dt} \]

Sensitivity:

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

\[ S_0 = 10.04 \, \frac{mV \cdot m^2}{W} \]

\[ S_C = 0.0049 \, \frac{mV \cdot m^2}{W \cdot ^\circ C} \]

**Room temperature sensitivity**

**Temperature correction factor**

https://www.greenteg.com/faq-heat-flux-sensing/
Comparison of values for generated heat

1) Adiabatic Measurement

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

2) Isothermal Measurement

\[ \dot{Q}_{gen} = mc_p \frac{dT}{dt} + Ah \cdot (T_s - T_C) \]

3) Measurement of irreversible and reversible heat

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

E<sub>0</sub>: Open circuit voltage (OCV), E: cell potential

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


40 Ah pouch cell

Discharge half cycles

T = 30 °C

Total heat generated Q<sub>g</sub> in kJ

<table>
<thead>
<tr>
<th>discharge rate</th>
<th>Q&lt;sub&gt;adia&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;iso&lt;/sub&gt;</th>
<th>Q&lt;sub&gt;thermo&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/8</td>
<td>2</td>
<td>4</td>
<td>6</td>
</tr>
<tr>
<td>C/4</td>
<td>4</td>
<td>8</td>
<td>12</td>
</tr>
<tr>
<td>C/2</td>
<td>8</td>
<td>16</td>
<td>24</td>
</tr>
<tr>
<td>C/1</td>
<td>16</td>
<td>32</td>
<td>48</td>
</tr>
</tbody>
</table>

14.07.2022  C. Ziebert – Battery Experts Forum 2022
Overview

Heat generation under normal use

Short introduction to battery calorimetry

Thermal propagation

Heat generation under abuse
Thermal abuse: Heat-Wait-Seek (HWS) Method in ARC

Example of a Heat-Wait-Seek step

Comparison of 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
Activation energies and reaction heats

**Activation energy:**

\[
\ln\left(\frac{dT}{dt}\right) \approx \ln(\Delta T_{ad} \cdot A) - \frac{E_a}{k_B \cdot T}
\]

\(E_a\): Activation energy, \(A\): pre-exponential factor
\(k_B\): Boltzmann constant = 8.62e\(^{-5}\) eV \(
\cdot\) K\(^{-1}\)

**Cathode Material**

<table>
<thead>
<tr>
<th>Cathode Material</th>
<th>LiMn(_2)O(_4) (LMO)</th>
<th>LiFePO(_4) (LFP)</th>
<th>Li(Ni(<em>{0.33})Mn(</em>{0.33})Co(_{0.33}))O(_2) (NMC)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Onset temperature</strong></td>
<td>91</td>
<td>90</td>
<td>91</td>
</tr>
<tr>
<td><strong>of self-heating in °C</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>(T_{max}) in °C</strong></td>
<td>303</td>
<td>259</td>
<td>731</td>
</tr>
<tr>
<td><strong>((dT/dt)_{max}) in °C/min</strong></td>
<td>1429</td>
<td>3</td>
<td>7577</td>
</tr>
<tr>
<td><strong>(c_p) at 60°C SOC100 in J/g(\cdot)K</strong></td>
<td>0.83</td>
<td>1.19</td>
<td>0.95</td>
</tr>
<tr>
<td><strong>(E_a) in eV</strong></td>
<td>1.07</td>
<td>0.56</td>
<td>1.37</td>
</tr>
<tr>
<td><strong>Reaction heat in J/g</strong></td>
<td>180</td>
<td>184</td>
<td>597</td>
</tr>
</tbody>
</table>


Reaction heat:

\[
\frac{\Delta H}{m} = c_p \cdot \Delta T_{ad}
\]

**Important input data for simulation**

\(\Delta T_{ad}\): adiabatic temperature rise
Comparison of 21700 cells with different cathode materials and SOC

- NCA and NMC cells behave comparably
- NCA HP cells behave differently
- NCA and NCA HP cells behave comparably
- NMC cells behave differently

LFP cells shifted to higher temperatures

SOC 100

SOC 60
Onset and CID triggering temperature

- NCA and NMC (on the right also NCA HP): higher SOC results in lower temperature
- NMC: lower temperature than NCA, NCA HP and LFP cells
- LFP: significantly higher temperatures, no clear SOC influence

=> data has higher variation, therefore more experiments have been conducted
Venting and start of thermal runaway / highest rate (LFP) temperature

- NMC, NCA, NCA HP: clear influence of SOC, temperatures close to each other
- NMC: slightly earlier than NCA cells (for cooling)
- LFP: significantly higher temperatures, influence of SOC unclear
  but step between CID triggering and venting is much smaller as well as the self heat rates => harder to detect
HELIOS (High-performance modular packs for sustainable urban electromobility Services)

The HELIOS project aims at developing and integrating innovative materials, designs, technologies and processes to create a new concept of smart, modular and scalable battery pack for a wide range of electric vehicles used in urban electromobility services, from mid-size full-electric vehicles to electric buses, with improved performance, energy density, safety and Levelized Cost of Storage (LCoS).

HELIOS WP Overview

- Start date: 01-01-2021
- Funding source: EC
- Funding: appr. 10 million Euro
- Partners: 18 from 8 countries

https://www.helios-h2020project.eu/project
HELIOS (High-performance modular packs for sustainable urban electromobility Services)

**HELIOS main building blocks**

- Circular design of battery packs
  - Battery testing & Modelling
  - Hybrid thermal management system
  - Advanced materials for housing and insulation

- VESTEL
  - 150-380 kW charger

- Multilevel converters
  - SOCs and SOH
  - Control Unit
  - Cell Balancing
  - Wiring & connections

- PHM, predictive maintenance
  - Graphical User Interface
  - Decision Support System
  - Data acquisition and storage

- IoT platform
  - Smart parking tool
  - CO2 traceability

- Fleet management platform
  - Exemplary safety test on large pouch cell

- Digital Twin
  - V2G
  - LCA, LCC tools
  - New BM, products and services

- Exemplary safety test on large pouch cell

**Sileo S12 e-bus produced by Bozankaya**
Internal pressure measurements on 18650 cells

Pressure line (Ø 1.5 mm)

1.6 Ah 18650 cell

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

Gas collection after ARC Abuse-Tests

- Collection option for gases through the Swagelok system
- Measurement of various parameters (two temperatures, pressure in the canister, voltage of the cell)
- Coupling to GC-MS Perkin-Elmer Clarus 690 Arnel 4019
Gas analysis after 0.5 overcharge test of 14 Ah prismatic cell

- Cell shows venting after 165 min and goes into thermal runaway after 170 min
- Data determined:
  - Maximum temperature: 534 °C
  - Maximum pressure: 12.5 bar
  - Evolved gas volume: 60 l (at 25 °C, 1013 mbar)
Overview

Heat generation under normal use

Short introduction to battery calorimetry

Heat generation under abuse

Thermal propagation
Thermal propagation

Passive Defense
- Early Warning
  - Abuse
    - M: Crush
    - E: Penetr.
    - T: Overchar.
    - O: Overdisch.
    - H: Overheat

Intrinsic Safety
- Thermal Runaway
  - Step 2 – Cell
    - Venting, CID, PTC

Extend Time for Escaping
- Propagation
  - Step 3 – Pack
    - Passive propagation prevention

Adapted from: Feng et al., Energy Storage Materials 10 (2018) 246
Thermal propagation tests on small pack level

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

Material qualification for propagation prevention

Optimized Multilayer:
- Extended time for propagation: 9 min
- Improved heat protection: temperature on top of battery box < 80 °C during thermal runaway
Summary: Possible calorimetric measurements

Normal use conditions
- Isoperibolic or adiabatic measurements
  - 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
- Electrical abuse: External short circuit, Overcharge, Deep discharge
- Mechanical abuse: Nail penetration test
  - Temperature measurement
  - External or internal pressure measurement
  - Gas collection and analysis, Post Mortem Analysis, Ageing studies

Important data for BMS, TMS and safety systems

14.07.2022
Thank you for your attention!

Contact data

Prof. Dr. Hans Jürgen Seifert
Tel.: +49 721 608-23895
hans.seifert@kit.edu

Dr. Carlos Ziebert
Tel.: +49 721 608-229195
carlos.ziebert@kit.edu

Karlsruhe Institute of Technology (KIT)
Institute for Applied Materials –
Applied Materials Physics (IAM-AWP)
Hermann-von-Helmholtz-Platz 1
Building 681
76344 Eggenstein-Leopoldshafen

https://www.iam.kit.edu/awp/169.php

Acknowledgement

This project has received funding from the European Union’s Horizon 2020 research and innovation programme under grant agreement No 963646. This document reflects the view of its author only. The funding agency is not responsible for any use that may be made of the information it contains.