Overview of Microcalorimetry for Material Characterisation – Looking at Battery Behaviour.

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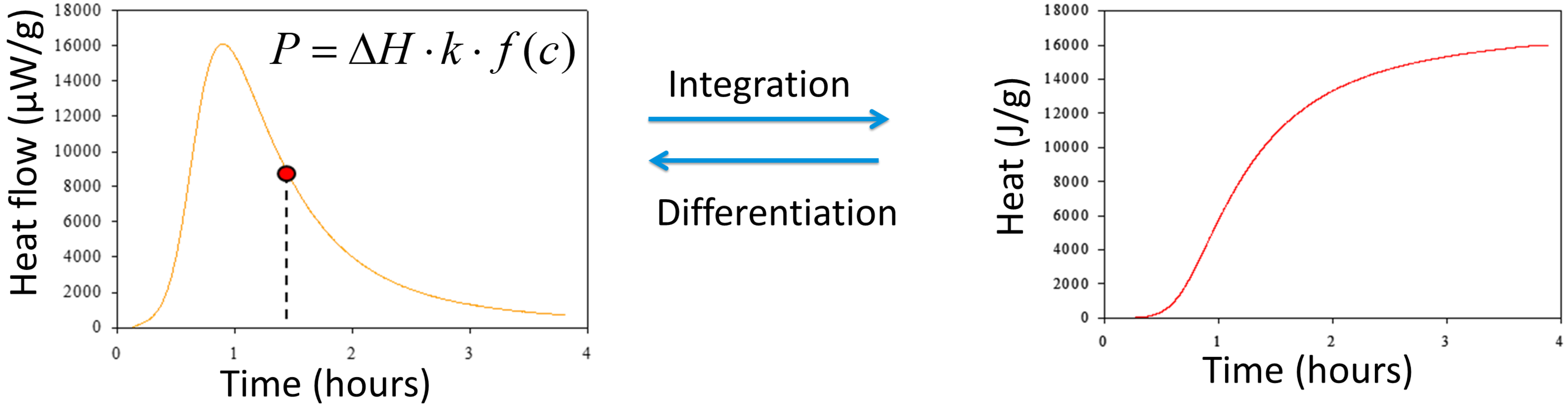
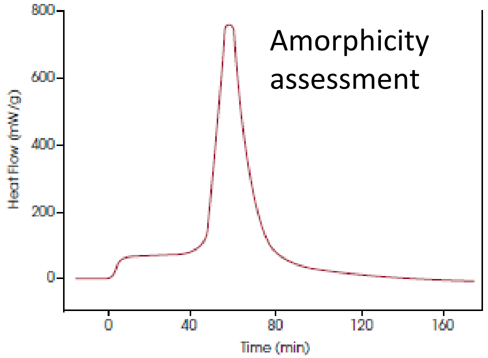
An isothermal microcalorimeter measures heat produced or consumed during a physical process or a chemical reaction in terms of heat flow at a constant temperature with microwatt sensitivity or better.

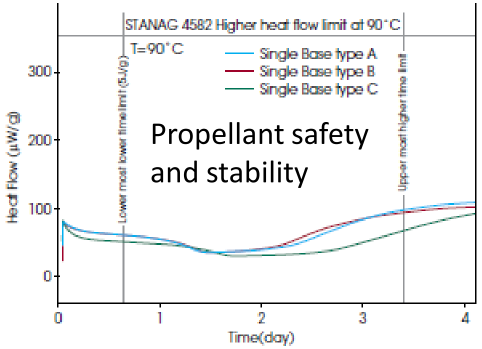
The heat production rate is directly related to the rate of reaction

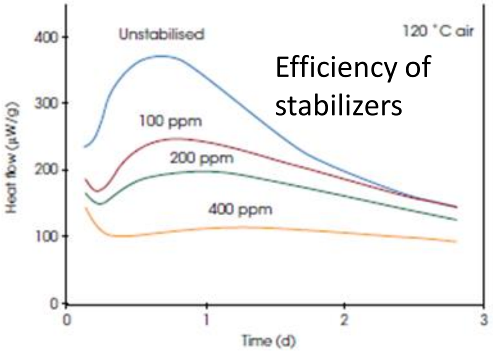
Total heat produced is related to the extent of the reaction

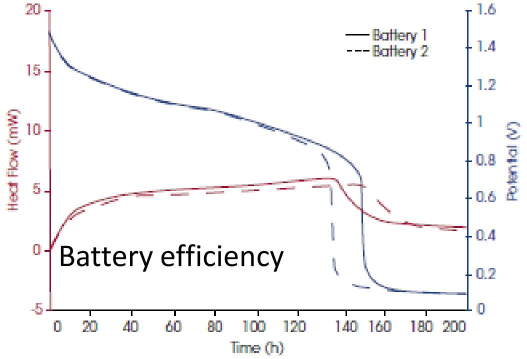


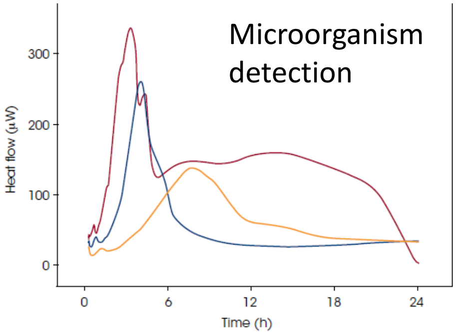
Isothermal calorimetry – a universal technique

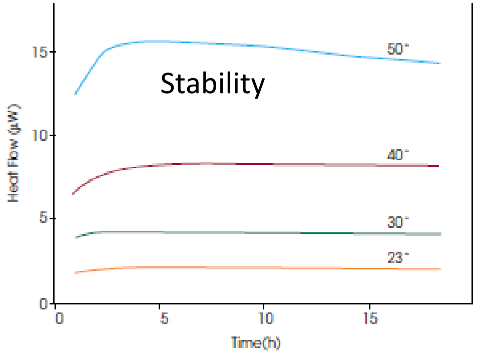


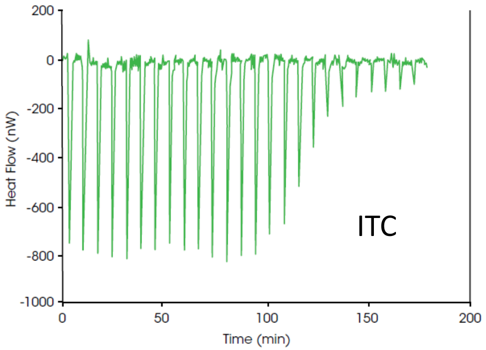


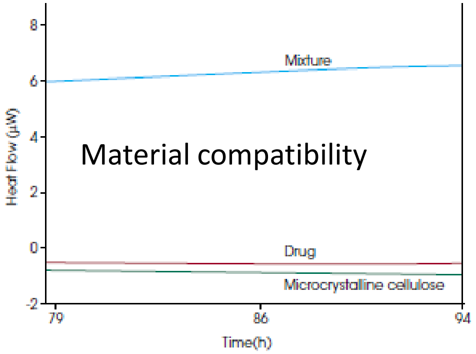


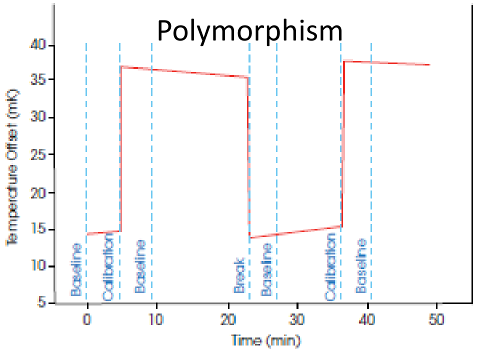








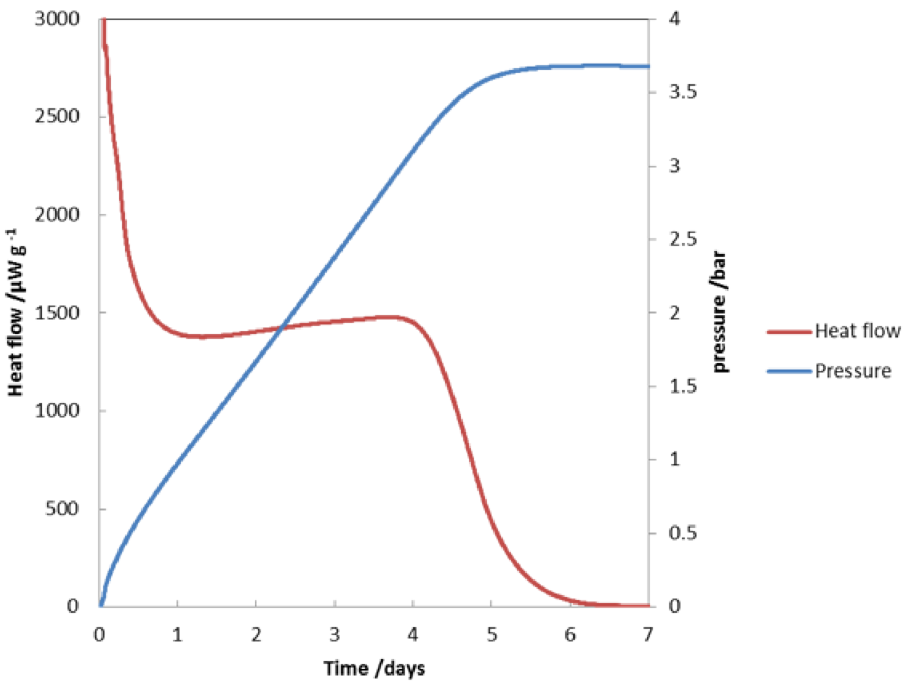




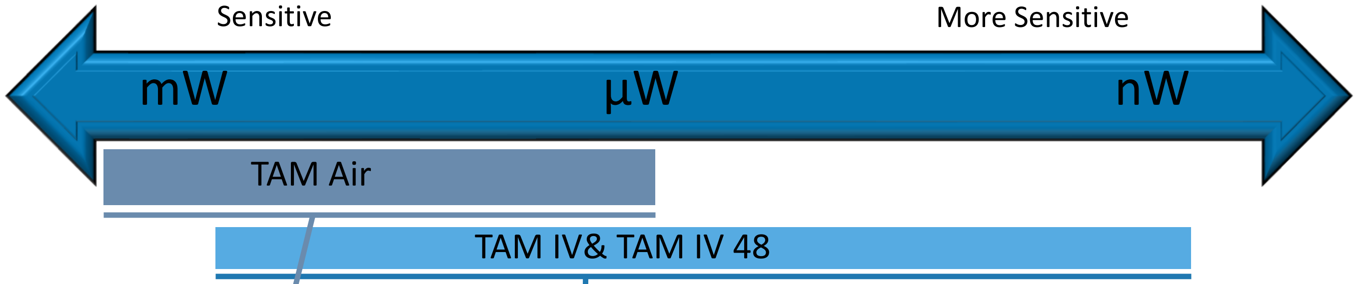
Isothermal calorimetry in material science

Applications include:

- Stability
- Compatibility
- Curing
- Reaction kinetics
- Safety assessments
- Hydration and swelling
- Absorption
- Batteries
- Gas producing reactions



TAM – Thermal Activity Monitor



5 – 90 °C

Flexible
interchangeable calorimeter blocks depending on sample

Sample sizes
from 20 mL up to 125 mL

3 channel version
Large samples up to 125 mL

8 channel version
- Samples up to 20 mL
- Possibility to add and mix *in situ*

4 – 150 °C

Flexible
one system multiple possibilities

Modular
add functionality by choice of calorimeters, sample handling systems and accessories

Sample sizes
from less than 1 mL up to 125 mL

4 channel version
highest flexibility and sensitivity

48 channel version
highest throughput

TAM IV – a flexible multichannel microcalorimetric system

- 1 – 48 individual & independent calorimeters
- nW - mW sensitivity depending on calorimeter
- <1 ml to 20 ml and 125 ml sample sizes
- Sample handling system with possibilities to
  - Add and mix
  - Perfuse gas or liquid over a sample
  - Control and continously or stepwise change RH or gas/liquid composition
  - Measure pressure changes
  - Dissolve solid samples
  - Add additional probes for increased specificity
- One system – multiple possibilities

TAM IV – A Modular Microcalorimeter System

- The microcalorimeter system base is the TAM IV thermostat.
- Functionality and measuring capacity is obtained by adding:
  - Calorimeters
  - Sample handling systems (ampoules)
  - Auxiliary equipment

Why use TAM for battery testing?

- Only method that directly measures the occurrence of non-current producing reactions under load
- Very sensitive method to assess self-discharge, sometimes the only method
- Non-destructive
- Simple
- Continuous

Measured battery power

Battery under load

$$\frac{dq}{dt} = \frac{E^2}{R_{resistor}} + \frac{E^2}{R_{battery}} + parasitic\ reactions$$

Self-discharging battery

$$\frac{dq}{dt} = \frac{E^2}{R_{battery}} + parasitic\ reactions$$

Parasitic reactions are material compatibility issues,
side reactions not part of the battery chemistry

Battery applications

- Stability and shelf life
  - Self discharge will show heat production in an open circuit
- Life cycle
  - Variance of thermal performance during charge/discharge cycles
  - Evaluation of number of charge cycles possible
- Efficiency
  - How much of the total power generated is available for the external device?
  - Internal resistance
  - Depends on temperature, current draw, age, charge cycles etc.

Battery applications cont.d

- Performance
  - Depends on the discharge conditions such as the magnitude of the current, the allowable terminal voltage of the battery, temperature and other factors
- Quality control
  - For critical applications, e.g. pacemaker batteries, to make sure there are no unwanted processes and internal short circuits
- Development
  - New type of electrochemical components
  - Compatibility
  - Evaluation of individual battery components

Battery tests can be performed as function of

- Temperature
- Size & shape of battery
- Chemistry
- Current draw
- Age
- State of charge

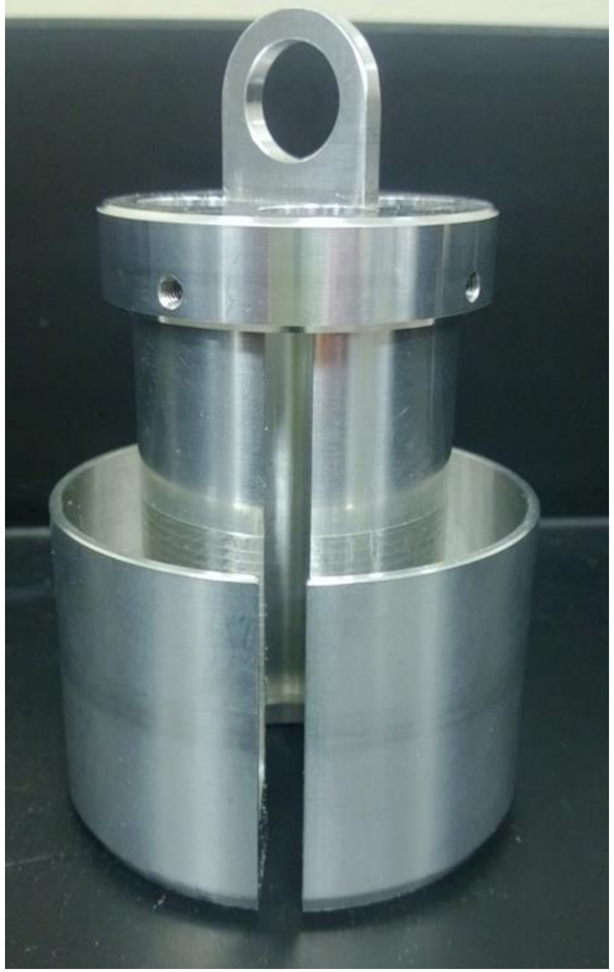
Calorimeters for battery testing

- Macrocalorimeter
  - Volume: 210 mL
    Sample size up to 61.2 mm diameter and 72 mm high
- 20 ml Micro or Mini/Multicalorimeter
  - For smaller batteries and where higher sensitivity is needed also the 20 ml calorimeters can be used.
- Battery measurements accessories
  - Insert for standard batteries
  - Lifters with wiring capabilities

Battery fixtures

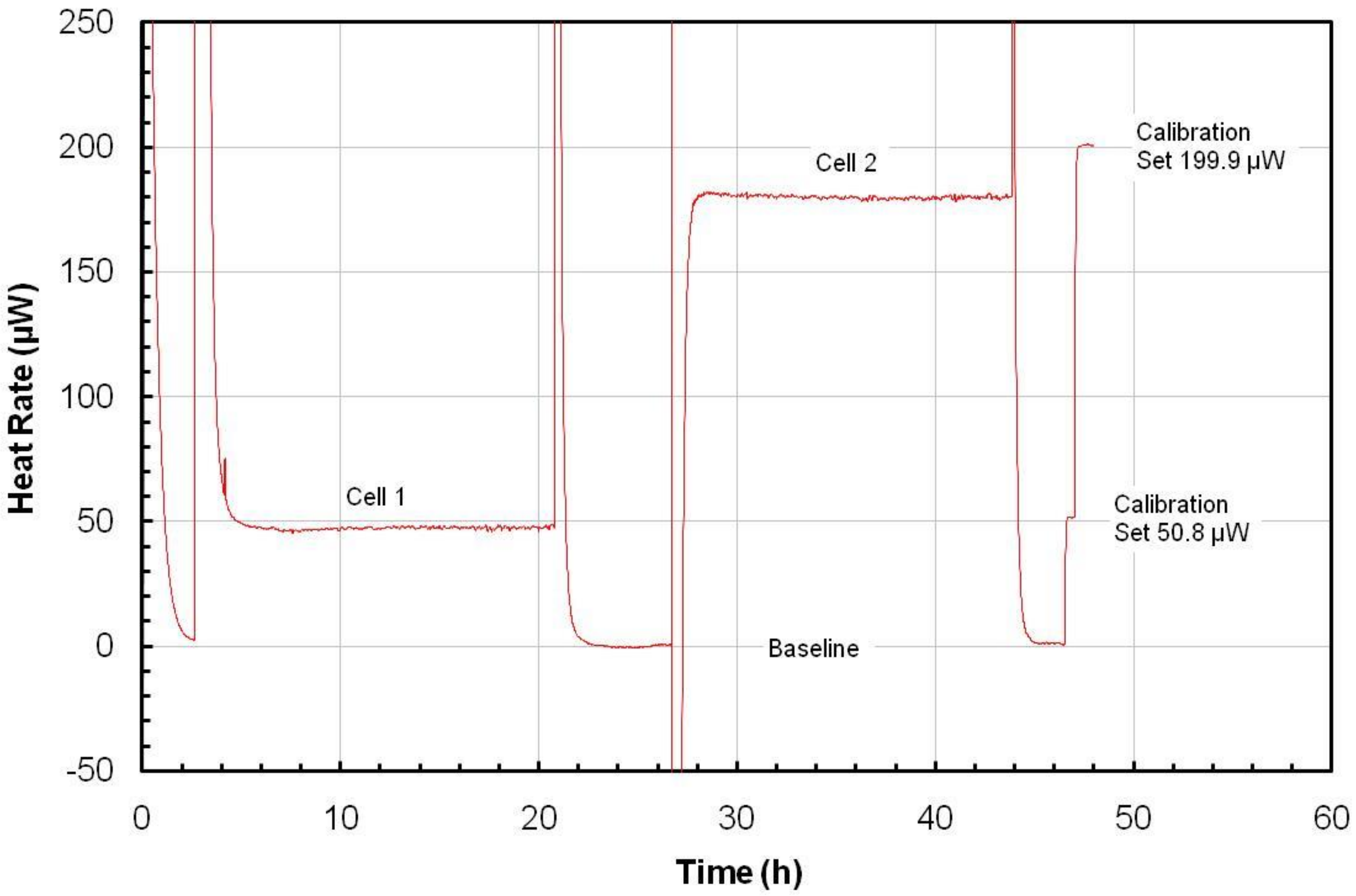
Purpose of fixture

- To optimise the thermal contact between the battery and the heat flow detector
- To make sure the position of the battery in the calorimeter is reproducible
- To facilitate the insertion of the battery into the calorimeter
- To avoid short-circuiting the battery and facilitate connections to the battery for load measurements
- Available for C- and D- cell batteries as well as 18650 batteries

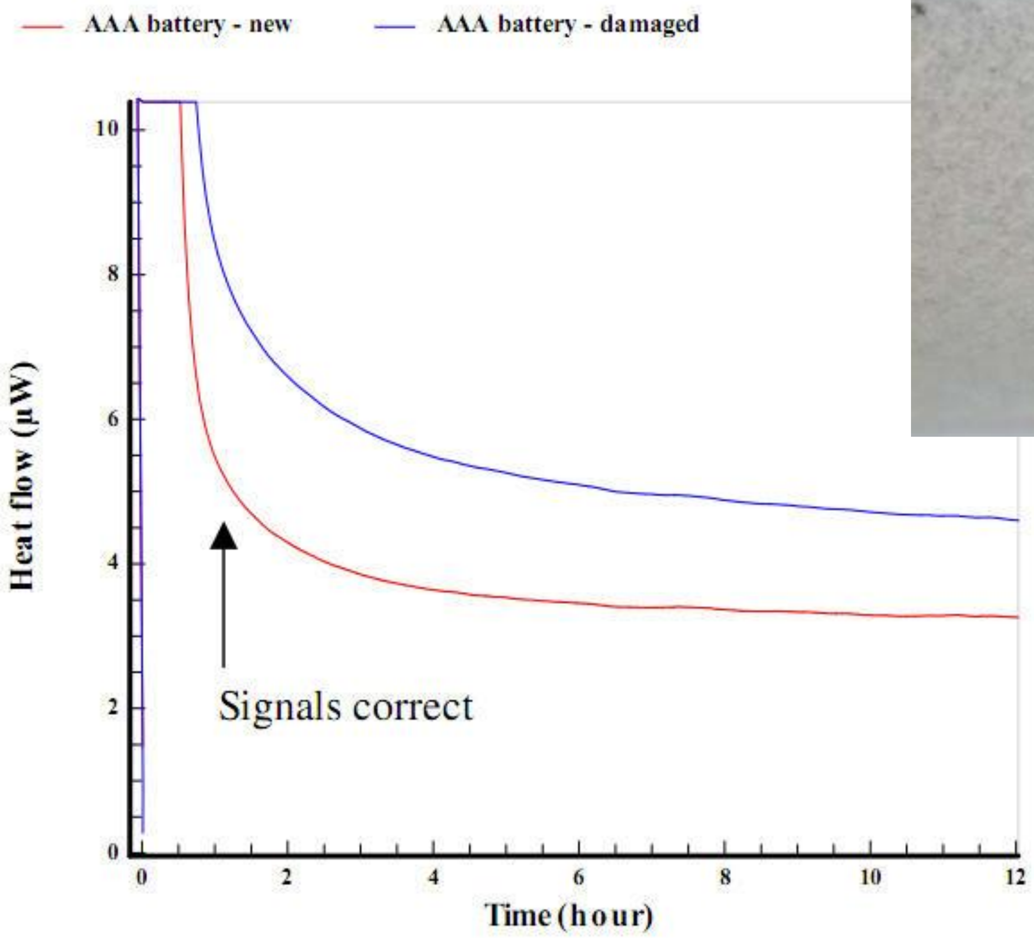


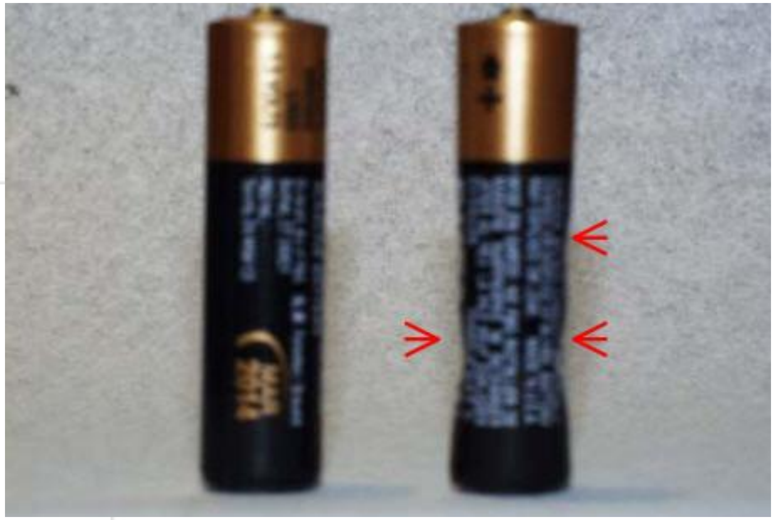
Open circuit discharge

Example on two different batteries and calibrations



Damaged batteries





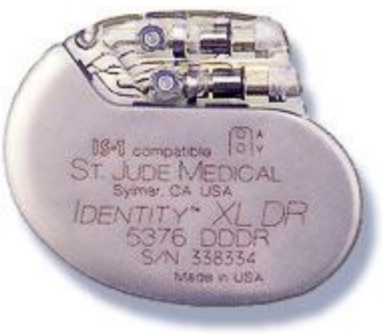
Tests for short-circuited batteries

- Internally short-circuited battery

	Open circuit voltage (V)	Load voltage (V)	Heat output (µW)
Good cell	2.8	2.75	25
Shorted cell	< 2.5	< 2.0	150 - 200

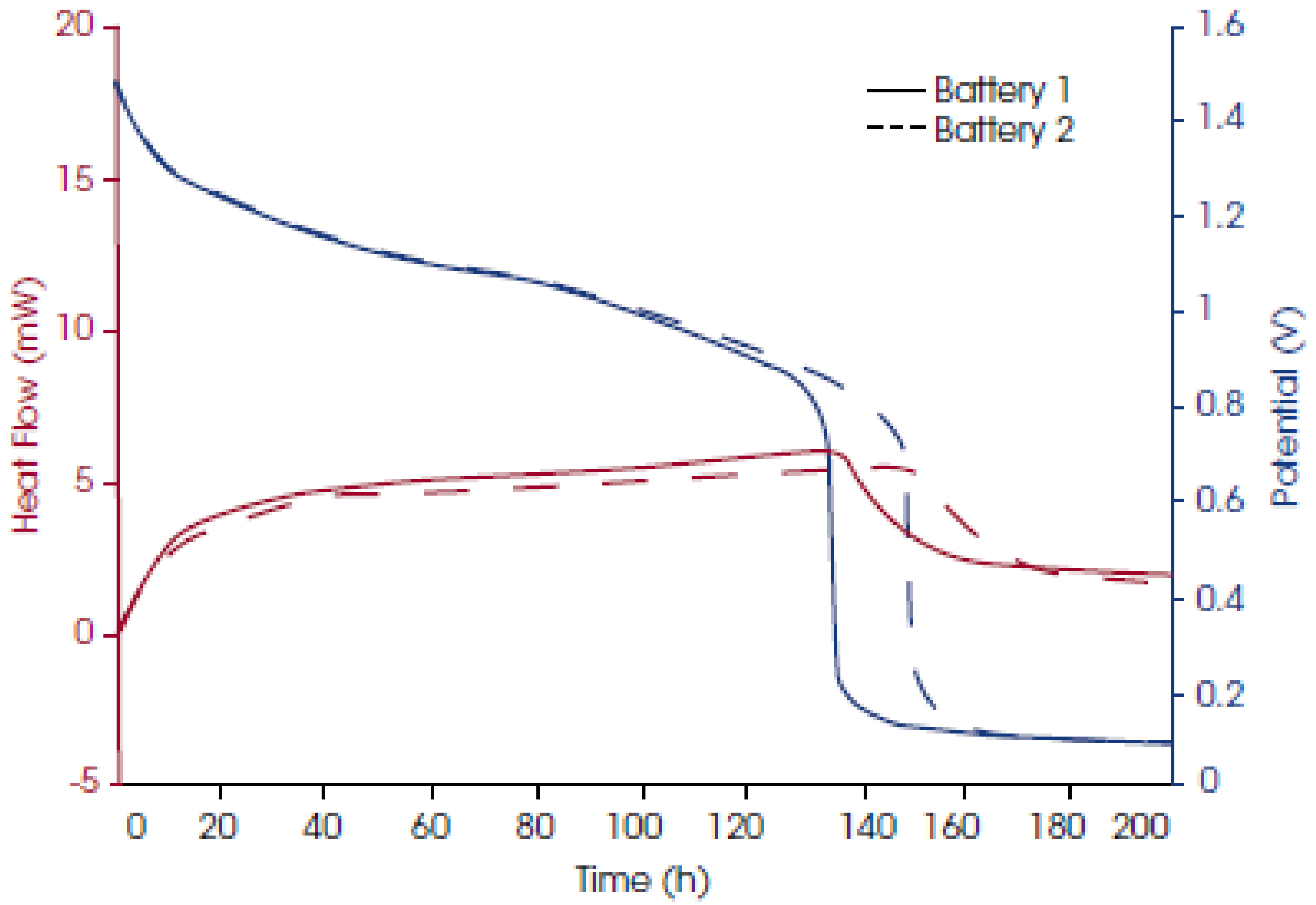
- Pacemaker batteries
  - Tested with a well defined circuit in the calorimeter

    Good batteries < 20 µW
    Bad batteries > 70 µW

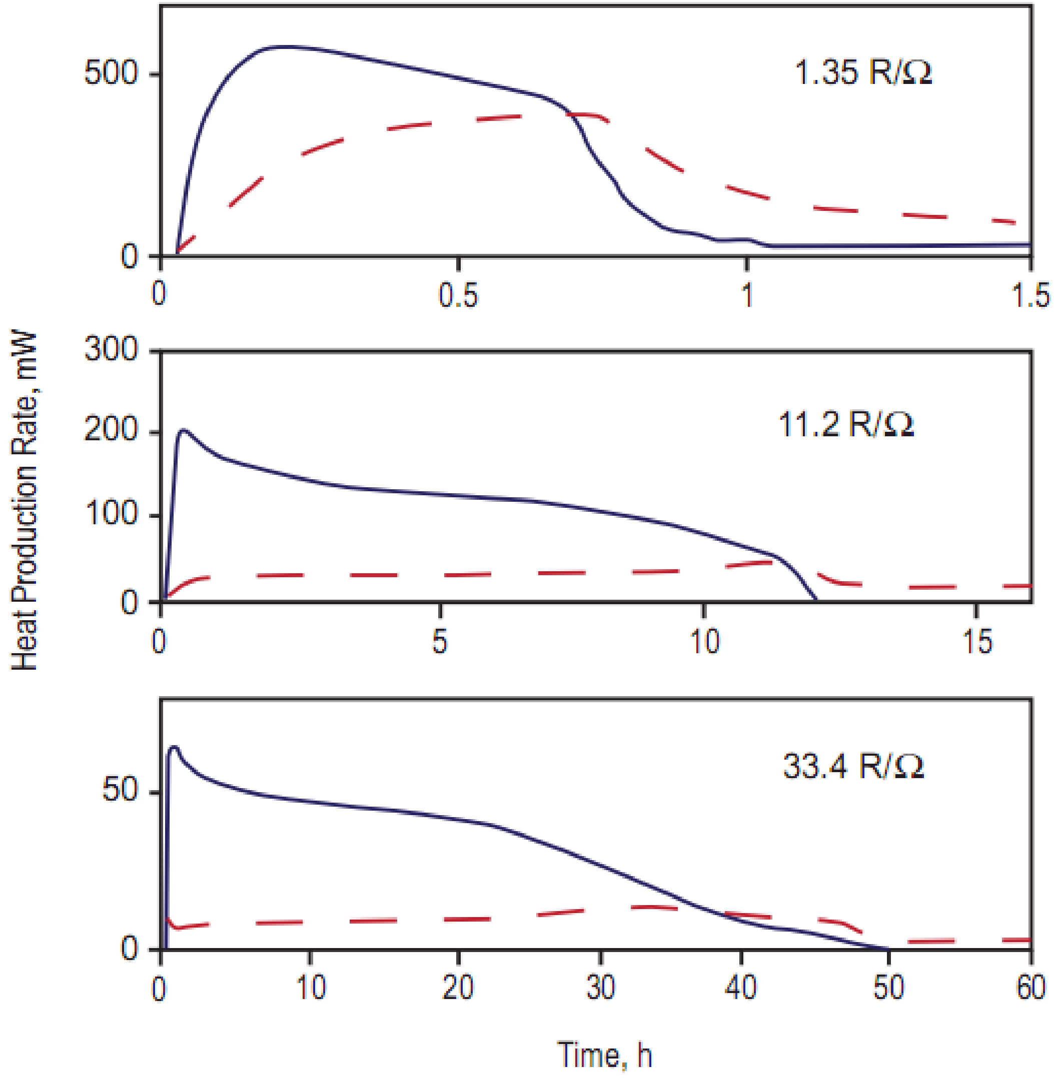


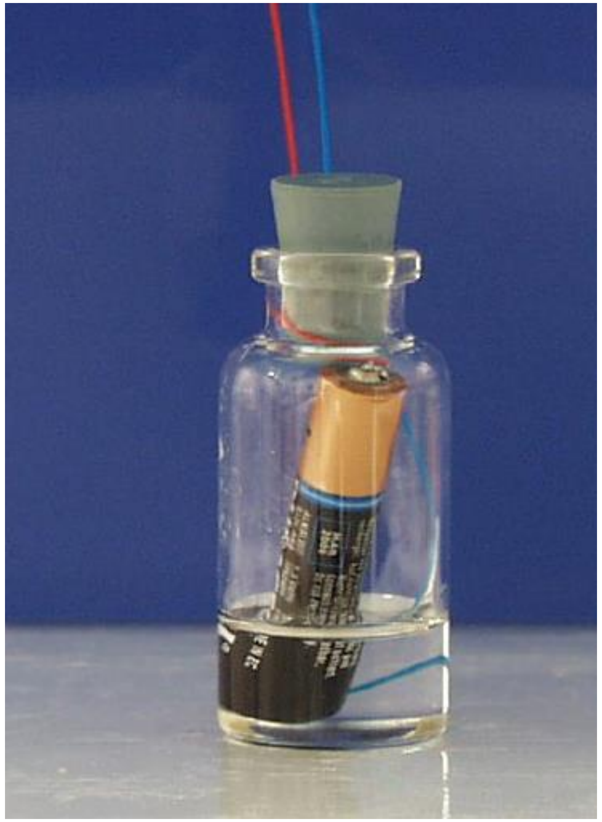
Charge - Discharge

Heat flow and voltage measurements

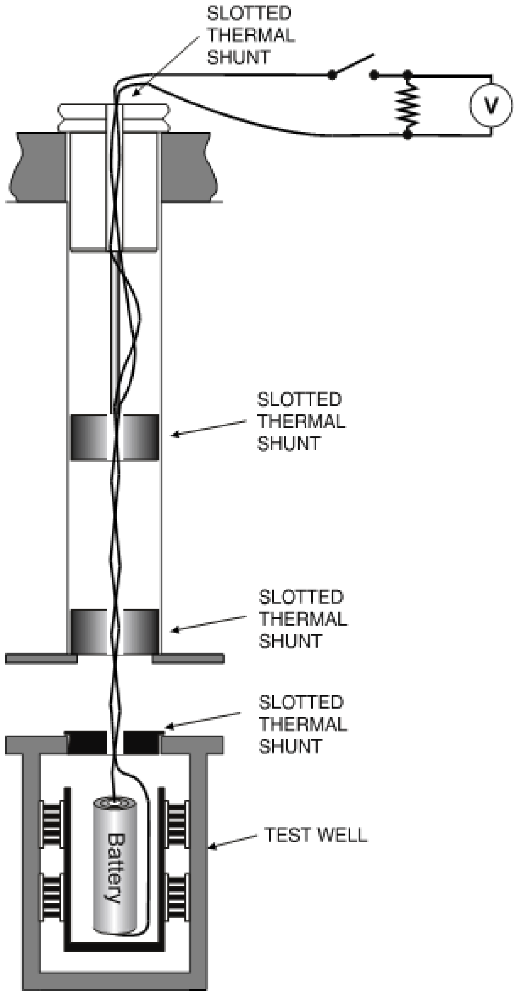


Battery under load





Battery with load in the calorimeter



Experimental setup

A set 18650 batteries had metal tabs spot-welded to each terminal of each battery.

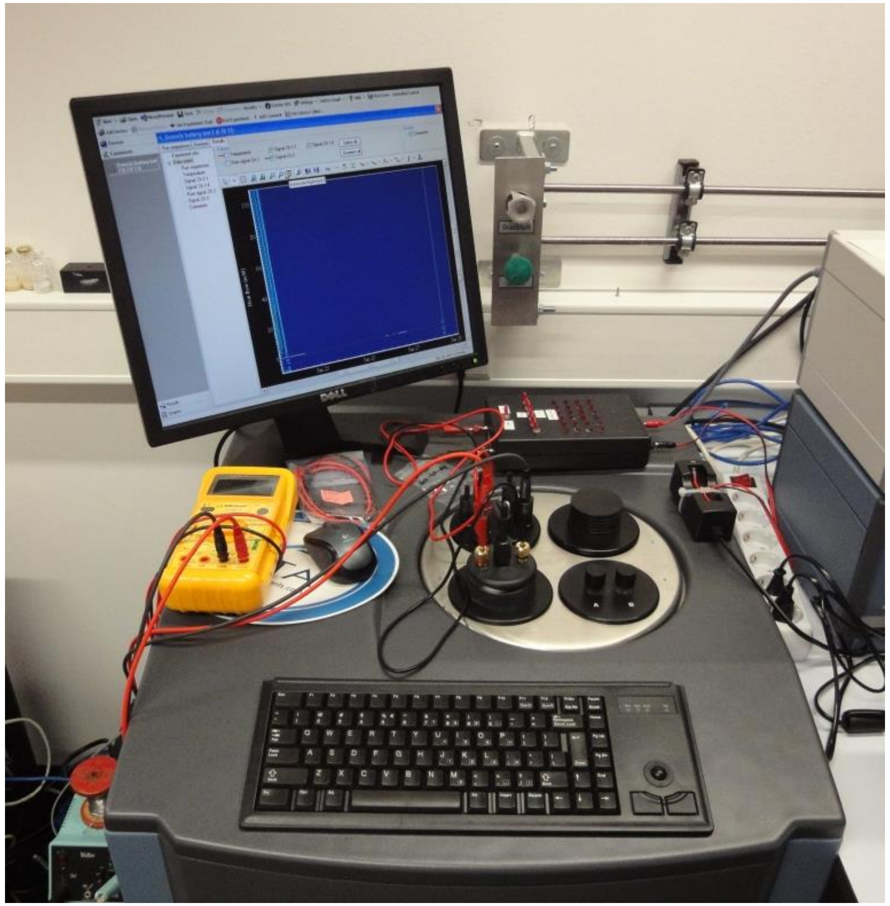
Two wires were soldered to each tab – a black set to the negative side and a red set to the positive side.

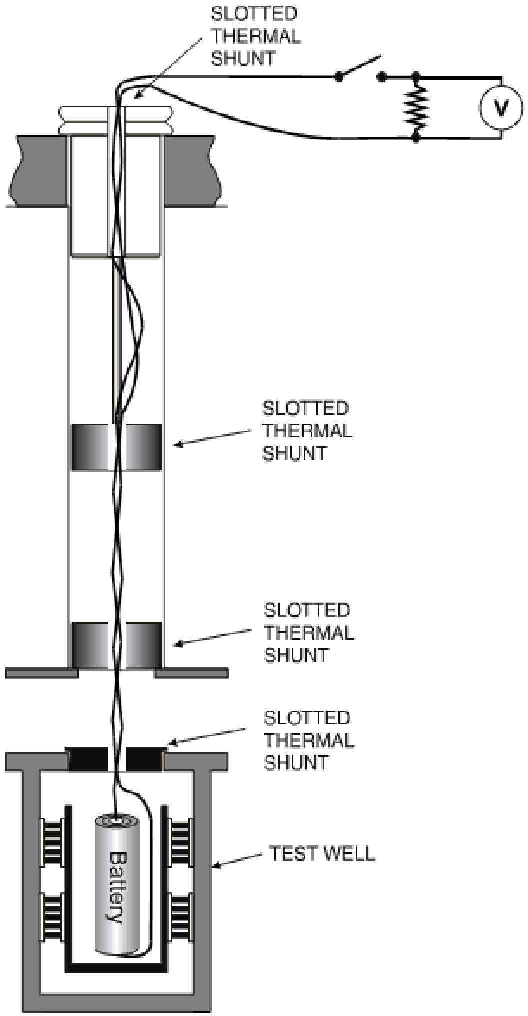
The ends were then covered with capton tape to electrically insulate the terminals

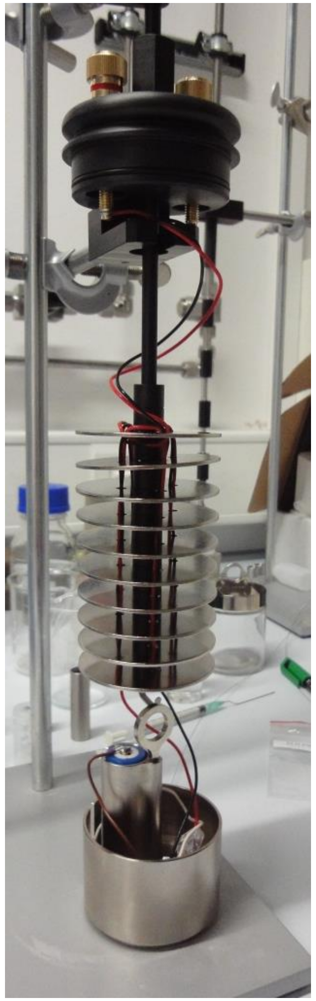
The batteries were placed inside adapters and the wires through the holes in the shunts, then the adapters were placed inside the TAM.

A battery tester was connected to one set of wires, while the other set were connected to a voltage measurement device.

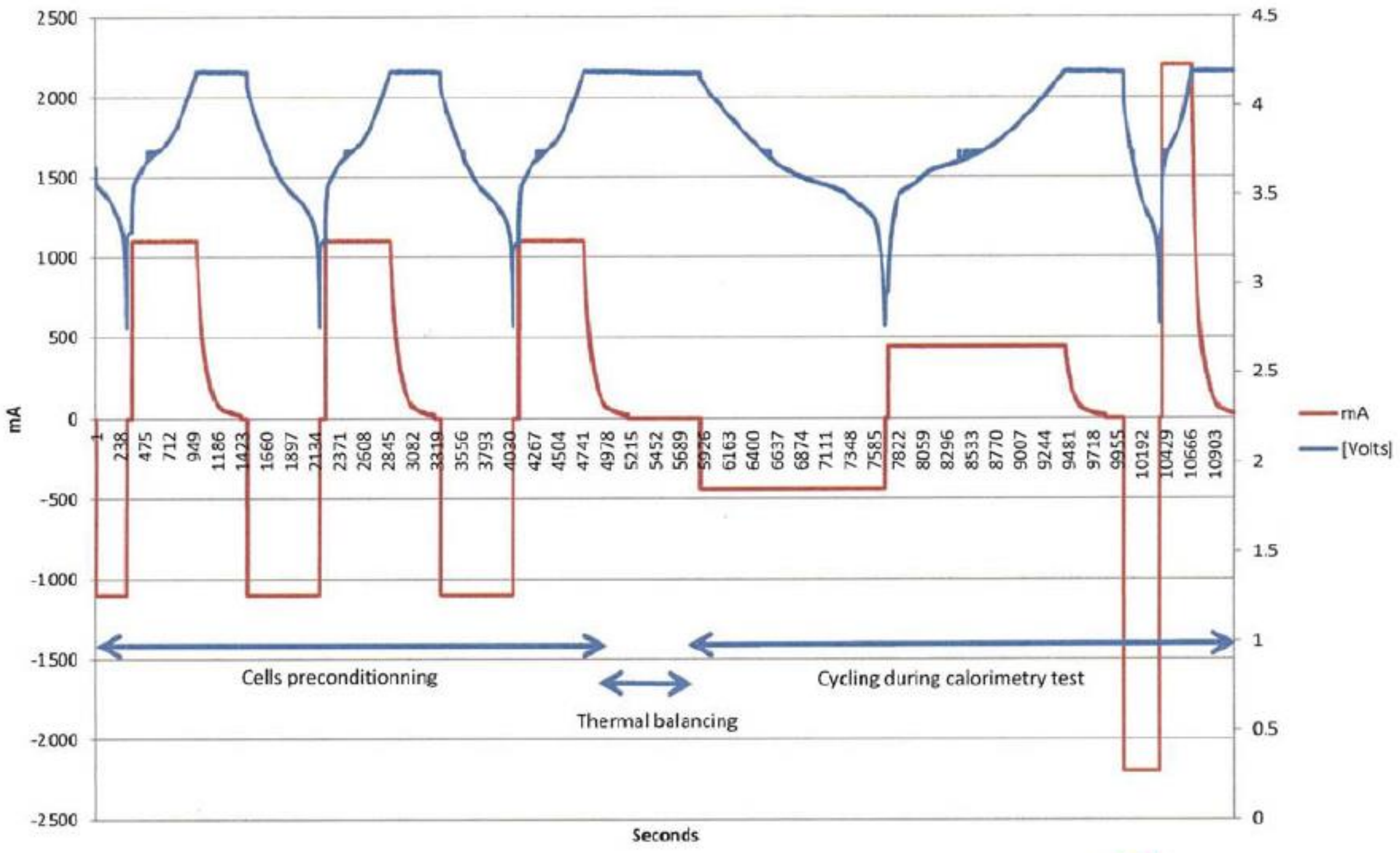
Battery under load



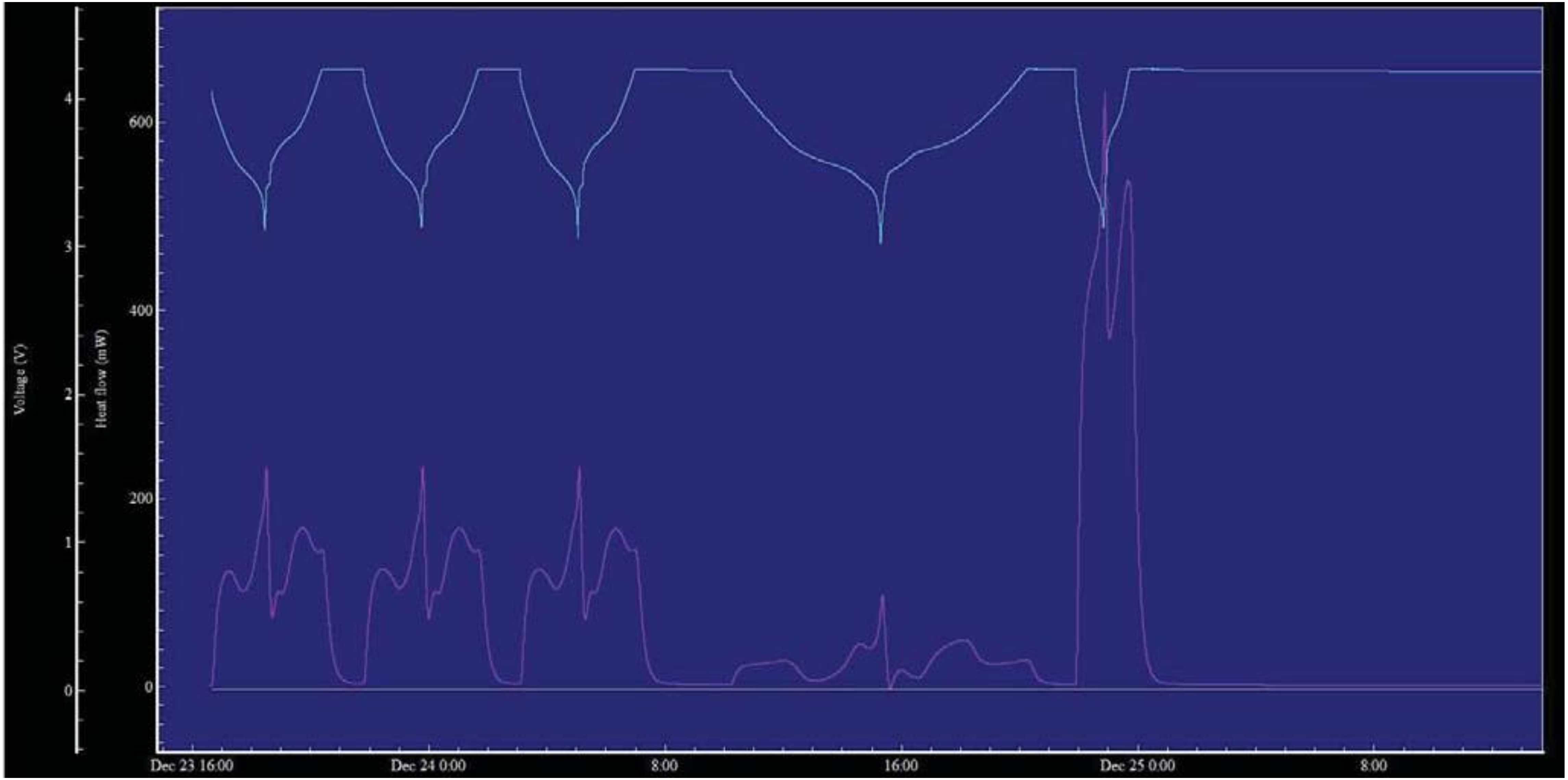




Experimental program

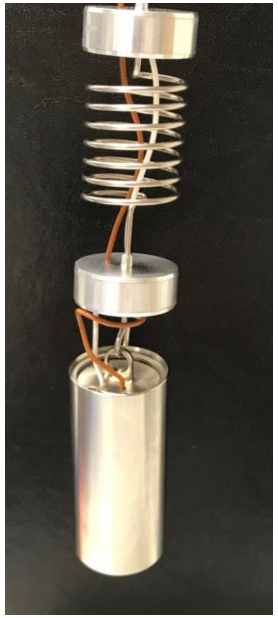


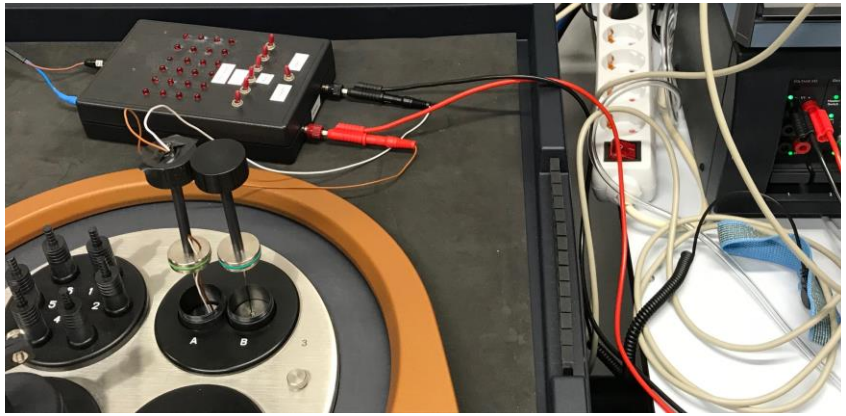
Results

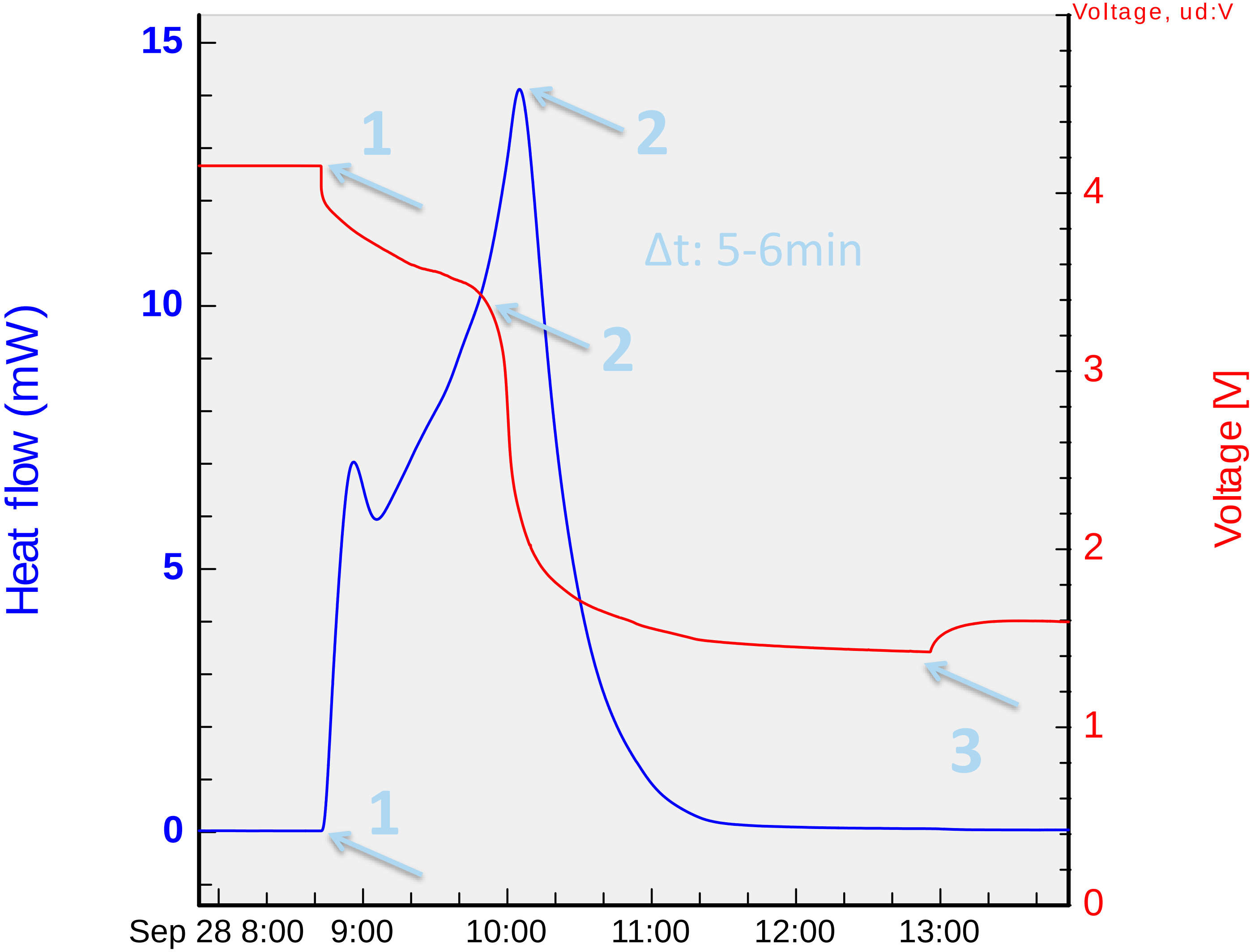


Voltage (V)
Heat flow (mW)
4
3
2
1
0
600
400
200
0
Dec 23 16:00
Dec 24 0:00
8:00
16:00
Dec 25 0:00
8:00

Button cell battery- Li R2032 - Discharge

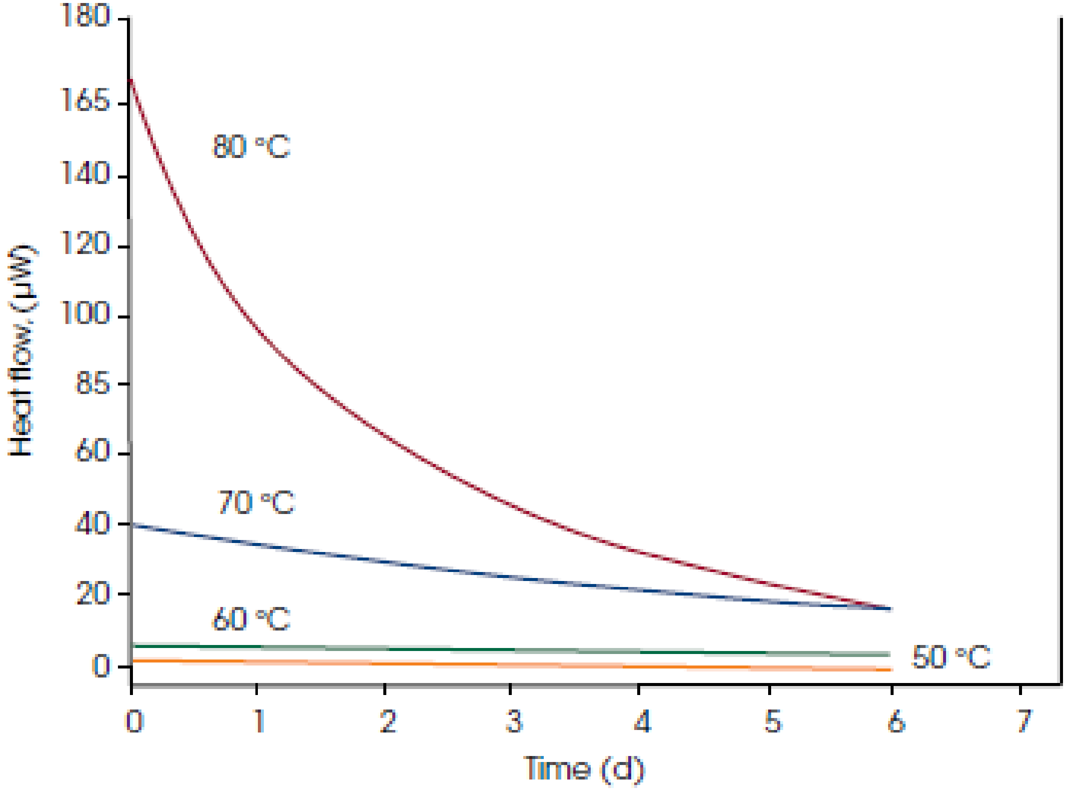


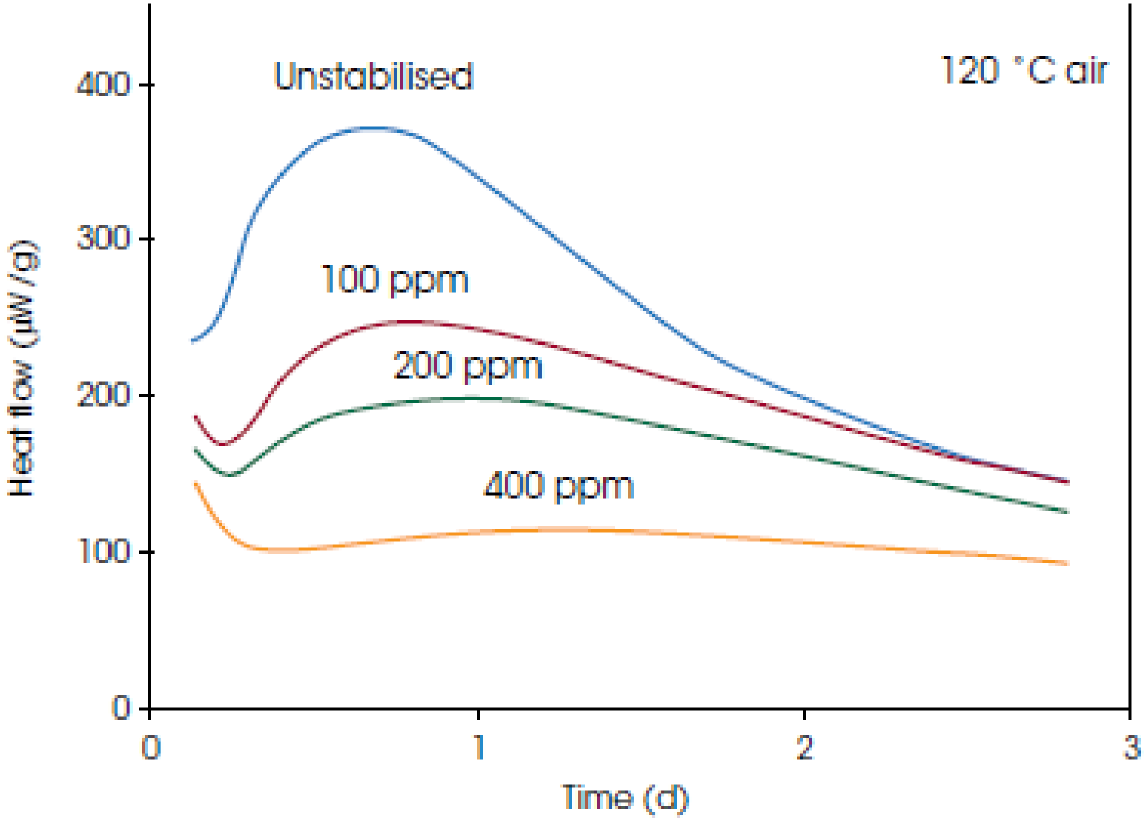




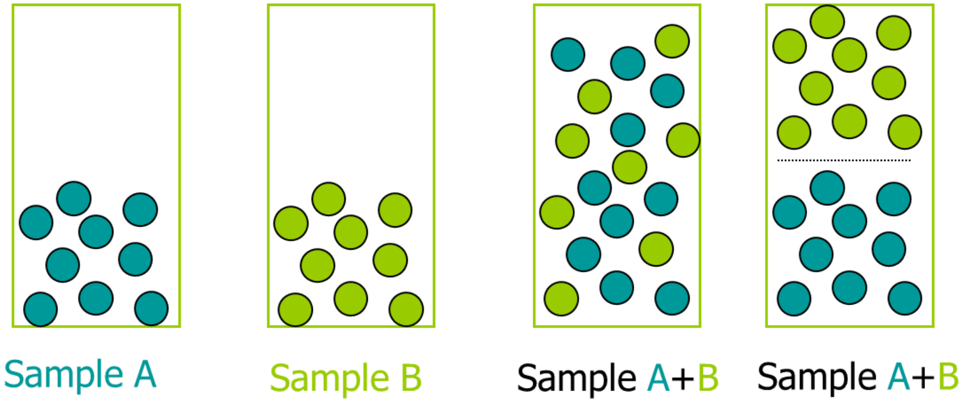
Stability and Compatibility

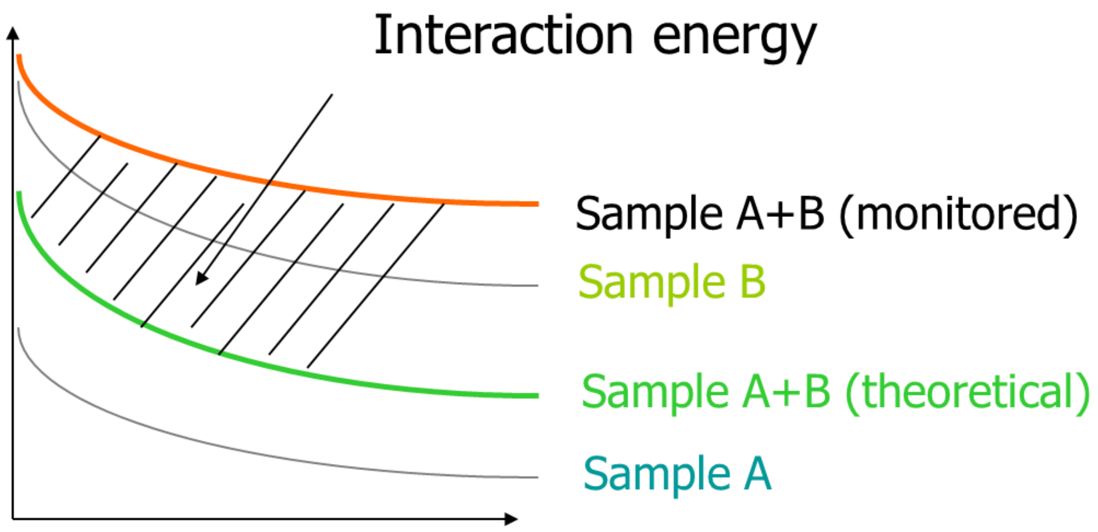
Battery individual component stability measurements





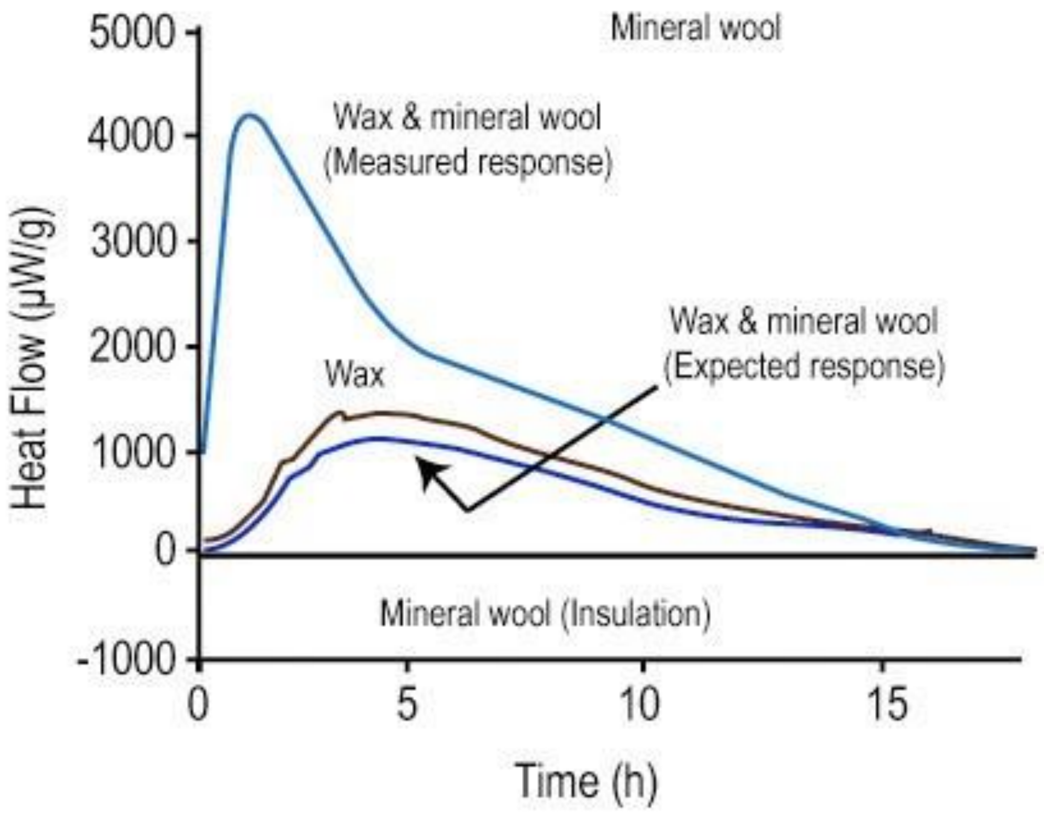
Battery component compatibility testing





Theoretical curve ≠ Monitored curve → Not compatible !

Compatibility Between Wax and Mineral Wool



Data provided by Svensson, *Bodycote Materials AB*, Sweden (2003)

Summary of using TAM for battery testing

- Only method that directly measures the occurrence of non-current producing reactions under load
- Very sensitive method to assess self-discharge, sometimes the only method
- Non-destructive
- Simple
- Continuous

In addition to whole device testing individual component stability and compatibility can be evaluated

Thanks!