BATTERY
CHARACTERIZATION

THERMAL ANALYSIS & CALORIMETRY SOLUTIONS

• THERMAL SAFETY •
• THERMAL STABILITY •
• HEAT CAPACITY •
• CHARGE/DISCHARGE HEAT •
• SELF-DISCHARGE HEAT •

setaram
KEP TECHNOLOGIES

YOUR CHALLENGES

Batteries are essential power sources for every application from your new smartphone, to the development of electric vehicles, Internet of Things (IoT) and Industrial Internet of Things (IIoT).
As the development of these new technologies is linked with the autonomy of devices, one key element which makes a great difference is their battery. The demand for new, more powerful, higher energy density and faster charging batteries is growing quickly. In addition, so are the requirements for new materials and thermal safety testing.

Thermal analysis and calorimetry, including traditional TGA and DSC as well as isothermal calorimetry techniques, provide critical insights into batteries and battery components.

KEP Technologies understands your challenges and offers a choice of solutions that provide experimental control, instrument versatility and quality results.

COMMON BATTERIES - STUDIES & SOLUTIONS

This brochure presents some of our solutions in this field and we encourage you to contact us for more information.

During normal use, under abuse or uncontrolled conditions, battery materials may be exposed to high temperatures. It is a key thermal ageing and thermal safety issue for batteries. It requires testing by TGA or DSC to determine if there is a risk to trigger the decomposition of one or more battery materials at high temperature. Materials may include electrodes (anode or cathode), electrolyte, separators, etc.

Thermal Stability

In order to assess the maximum temperature attainable by a battery during its operation, it is necessary to perform a heat transfer calculation. For that purpose, the batteries thermophysical properties such as its Heat Capacity (C_p) must be accurately known. DSC and calorimetry can provide C_p measurements of constitutive materials or of a full battery.

Heat Capacity

Battery operations leading to risk of overheating include the critical charging and discharging phases (when the battery is used to supply power to the device). This challenge can be addressed by measuring the heat released during the charging and discharging operations of the rechargeable battery. Isothermal calorimetry is the ideal solution for this testing.

Charge / Discharge Heat

Self-discharge is a phenomenon in batteries in which internal chemical reactions reduce the stored charge of the battery even if the battery isn't used. Measurements of the heat flow of batteries during their self-discharge, helps by comparing their capacity to stay charged during long periods of time. It is a key technical specification of a battery and should be assessed to check performance.

Self-Discharge Heat

CUSTOMER TESTIMONIAL

"We chose the C80 due to its multi-modes and availability to use large number of specialized cells for a wide range of applications. There is the possibility of direct heat capacity measurements of solid materials in a wide temperature range. Also C80 has a possibility to use gas circulating cells (to work in controlled atmospheres). It will be used for measurements of specific heat capacity, phase transition temperatures and heat effects in lithium nickel dioxide material."

Mr. Oleg Bolotov - Scientific-research electrodynamics laboratory, LLC "Proton-21"

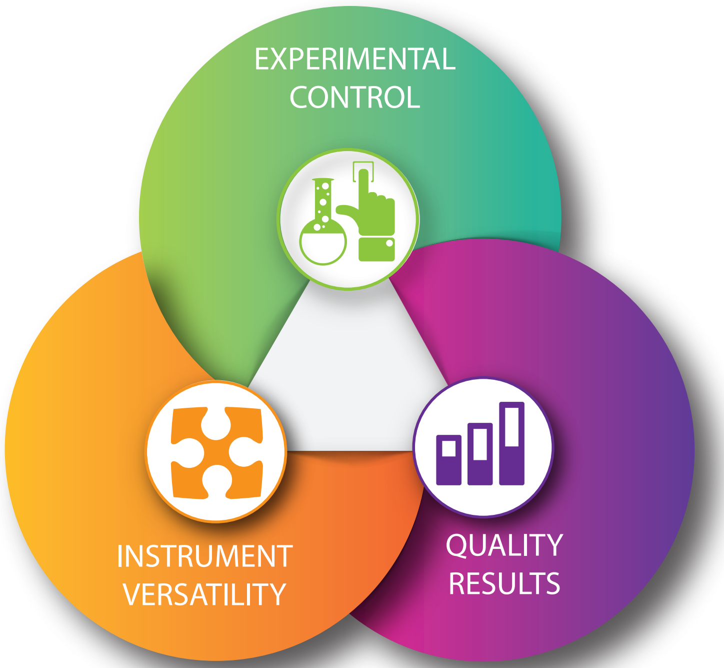
THE KEP TECHNOLOGIES ADVANTAGE

KEP Technologies is addressing it's offerings to the battery market by making available the widest and most versatile choice of solutions. Now you can consult with one company, KEP Technologies, to address your challenges across the broadest number of battery studies on the market.

Each solution embodies our "Reimagine Material Characterization" value proposition by delivering the three core customer benefits of **Experimental Control, Instrument Versatility and Quality Results.**

We believe solutions that provide these benefits will deliver the highest value to our customers.

In addition to our core customer benefits, we are able to provide **customized solutions** by harnessing the engineering and project management of our highly skilled organization.



CUSTOMIZED SOLUTIONS

Modular design allows for upgraded and tailored functionality
Access to all previous non-proprietary custom requests
Open access to our engineering development team

INSTRUMENT

THEMYS ONE

- **HIGH SENSITIVITY BALANCE FOR THE DETECTION OF SMALL MASS VARIATIONS** specifically designed for TGA analysis.
- **CONVENIENCE OF ONE FURNACE** to reach temperatures as high as 1600°C.
- **PLUG AND PLAY INTERCHANGEABLE RODS** to perform TGA only, TG-DSC, TG-DTA, and 3D high sensitivity/Cp measurements.
- **EXTERNAL COUPLING CAPABILITY** including evolved gas analyzers

SPECIFICATIONS

Temperature range (°C)	room temperature to 1600
Isothermal and temperature scanning (°C/min)	0.01 to 100
Sample volume (ml)	up to 1 in TGA
Evolved gas analyzers (FTIR, MS, GCMS, MS-FTIR, or FTIR-GCMS) for performing qualitative and quantitative gas characterization	

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

THERMAL STABILITY OF GEL POLYMER ELECTROLYTE FOR LI-METAL BATTERIES

INTRODUCTION

While improved performance is a key factor in the development of new types of batteries, operational safety is also a major concern. Structural design of the electrolyte and components can be optimized to ensure the security in case of misuse. An example is provided here with the development and testing of self-shutdown gel polymer electrolyte (GPE) of lithium metal battery. The thermal stability of the components of the electrolyte membrane was tested by TGA technique.

EXPERIMENT

- Sample: electrolyte gel membrane SGPE-40 and PVDF-HFP@SiO_2
- Instrument/Technique: THEMYS ONE TGA
- Thermal profile: heating between 25 and 600°C at 5°C/min

RESULTS AND CONCLUSION

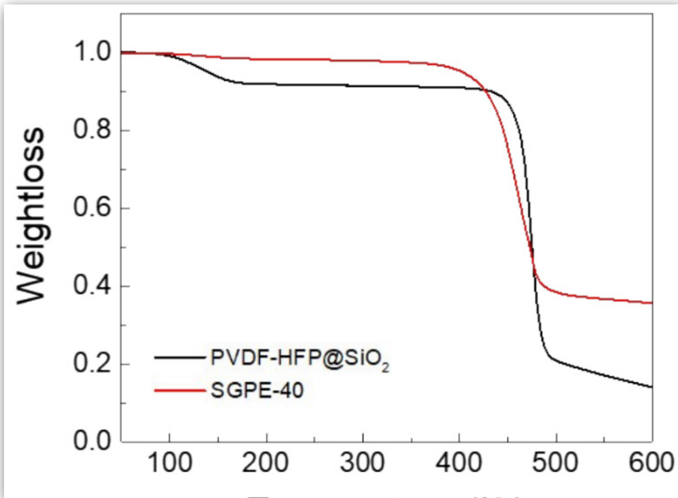


Figure 1 : Mass variation between 25 and 600°C of GPE

The components of the electrolyte have different thermal behavior. PVDF-HFP@SiO_2 looses about 10% of its mass between 100°C and 200°C but its main decomposition occurs above 425°C.
The main decomposition of SGPE-40 starts below 400°C, and is considered as less thermally stable.

However, both components of gel polymer electrolyte display a remarkable thermal stability up to a significantly higher temperature than other GPEs.

Binxuan Xie, Shimou Chen, Yong Chen,Lili Liu, Self-shutdown function induced by sandwich-like gel polymer electrolytes for high safety lithium metal batteries, RSC Adv., 2021,11, 14036-14046

INSTRUMENT

CALVET

ISOTHERMAL OR TEMPERATURE SCANNING MODES
for increased flexibility

HEAT MEASUREMENT ACCURACY
with Calvet 3D sensor capturing 93-95% of all heat forms. The highest level on the market

CONVENIENT, INTERCHANGEABLE CELLS
to perform even the most demanding experiments using one instrument :
- Heat capacity and Self-discharge with standard cells
- Thermal stability with pressure measurement cells
- Charge / discharge with cells allowing the use of electrical wiring and connections to battery cycler

WIDE TEMPERATURE RANGE
with low temperature version CALVET CRYO and high temperature version CALVET HT

SPECIFICATIONS

	CALVET	CALVET CRYO	CALVET HT
Temperature range (°C)	Ambient to 300	-196 to 200	Ambient to 600
Temperature accuracy (°C)	+/-0.3 *	+/-0.5 **	+/-1*
Temperature precision (°C)	+/-0.15*	+/-0.25**	+/-0.5*
Programmable temperature scanning rate	0.001 to 2°C/min	0.01 to 1°C/min	0.01 to 2°C/min
Enthalpy accuracy	+/-0.4 *	+/-0.2 **	+/-1*
Calorimetric precision (%)	+/-0.4*	+/-0.5**	+/-1.5*
Cells (ml)	Up to 12.5 (standard cell)	Up to 12.5 (standard cell)	Up to 7
Battery sizes (mm)	Up to 15 diameter, 70 height. C80-22 (on request) up to 20	Up to 15 diameter, 70 height	
Pressure measured and controlled (bar [psi])	350 [5,075]; 600 [8,700]; 1000 [14,600]	100 [1,450]; 600 [8,700]; 1000 [14,600]	100 [1,450]; 300 [4,350]; 400 [5,800]

** Based on indium melting tests ** Based on naphthalene melting tests*

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

THERMAL STABILITY OF AN ELECTROLYTE UNDER TEMPERATURE SCANNING CONDITIONS

INTRODUCTION

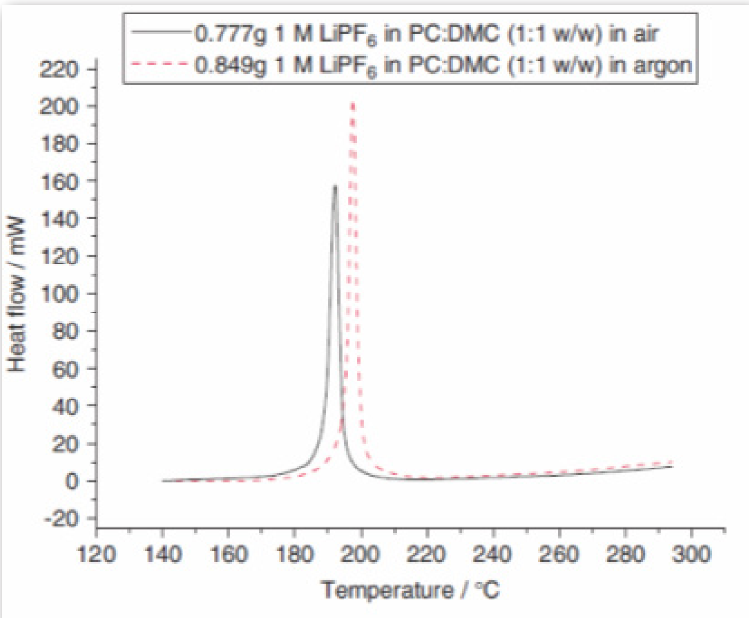
When the temperature of a Li-ion battery increases because of abusive conditions (e.g., short circuit, overcharge, heating) self-heating may be initiated. Various exothermic and endothermic reactions involving both the solution and the electrodes can occur inside the battery. The CALVET calorimeter is used with high pressure stainless steel vessels to study the thermal stability of several commonly used organic solvents and electrolytes and to investigate the kinetic process of the related reactions.

EXPERIMENT

• Instrument: CALVET.
• Vessel : High pressure stainless steel.
• Sample : Electrolyte LiPF6 in PC:DMC.
Ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) are the most widely used solvents and LiPF6 is the dominant solute used in practical lithium ion batteries.
• Method: Heating at 0.2°C/min to 300 °C in air or argon.

RESULTS AND CONCLUSION

A strong exothermic reaction starting above 160°C is seen. That reaction is shifted to higher temperatures under argon, meaning an improved thermal stability.



from Qingsong Wang and coll., Journal of Loss Prevention in the Process Industries - 19 (2006) 561–569

MEASUREMENT OF THE HEAT CAPACITY OF A FULL BATTERY

INTRODUCTION

Heat capacity measurements of a battery, together with additional measurements of heat source factors and heat transfer coefficients using other techniques, makes the calculation of the battery's temperature rise possible as well as to compare calculations with measured values.

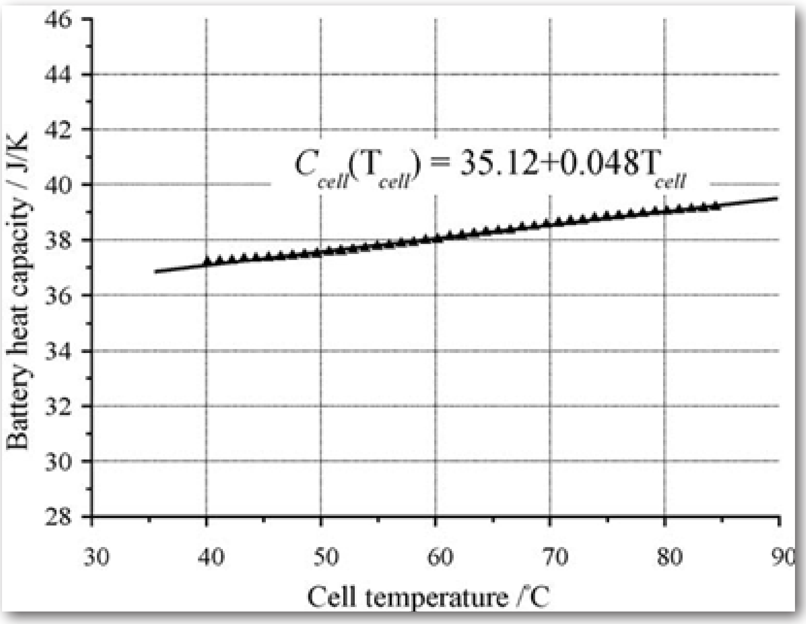
EXPERIMENT

- Instrument: CALVET.
- Vessel : Standard stainless steel vessel.
- Sample : A commercially available, cylindrical lithium-ion battery.
- Method: A temperature ramp from 20 to 90°C at 0.4°C/min.

RESULTS AND CONCLUSION

The heat capacity of the cell can be approximated by a linear function of temperature C_{cell} (J/◦C) = 35.12 + 0.048T (◦C).

Thanks to the CALVET measurements and the application of this method, the authors were able to plot the battery's heat capacity against temperature over the tested range and observe that the variation was almost linear.



Kazuo Onda et al, Journal of Power Sources 158 (2006) 535–542

MEASUREMENT OF THE HEAT PRODUCED BY A BATTERY WHEN IT IS CHARGING/ DISCHARGING

INTRODUCTION

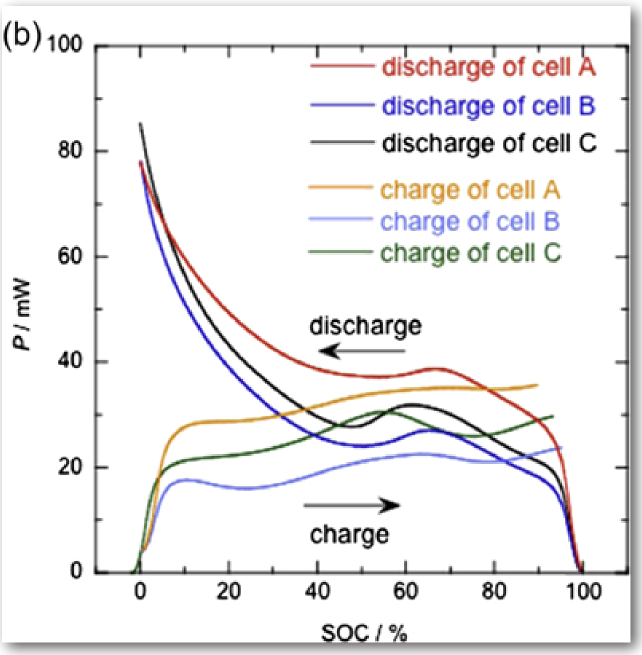
Isothermal calorimetry can measure the heat produced when a rechargeable battery is charged and discharged. The idea here is to assess the risks of damage to the battery if overheating occurs. The battery is connected using thin wires to an electrical cycling system before being placed in the sample holder.

EXPERIMENT

• Instrument: CALVET.
• Vessel : Customized vessel
• Sample: Cylindrical Li-ion batteries, State of Charge ranging between 50 and 90%.
Stored between 436 and 652 days. Storage temperature ranging between 20 and 50°C.
• Method: Isothermal testing at 25°C. The battery is fitted in the calorimeter, connected to an external battery charging/discharging system through lead wires (<1% heat loss) up to high current (450 mA).

RESULTS AND CONCLUSION

At a high rate of charging and discharging (on the chart: 450 mA), the cell stored at 50°C (cell A) shows larger heat generation probably because of leakage of the electrolyte solution. To limit the temperature increase and thus preserve safety, improving the sealing would be an effective measure.



Saito et al, Journal of Power Sources 244 (2013) 294-299

SELF DISCHARGE OF LITHIUM BATTERIES

INTRODUCTION

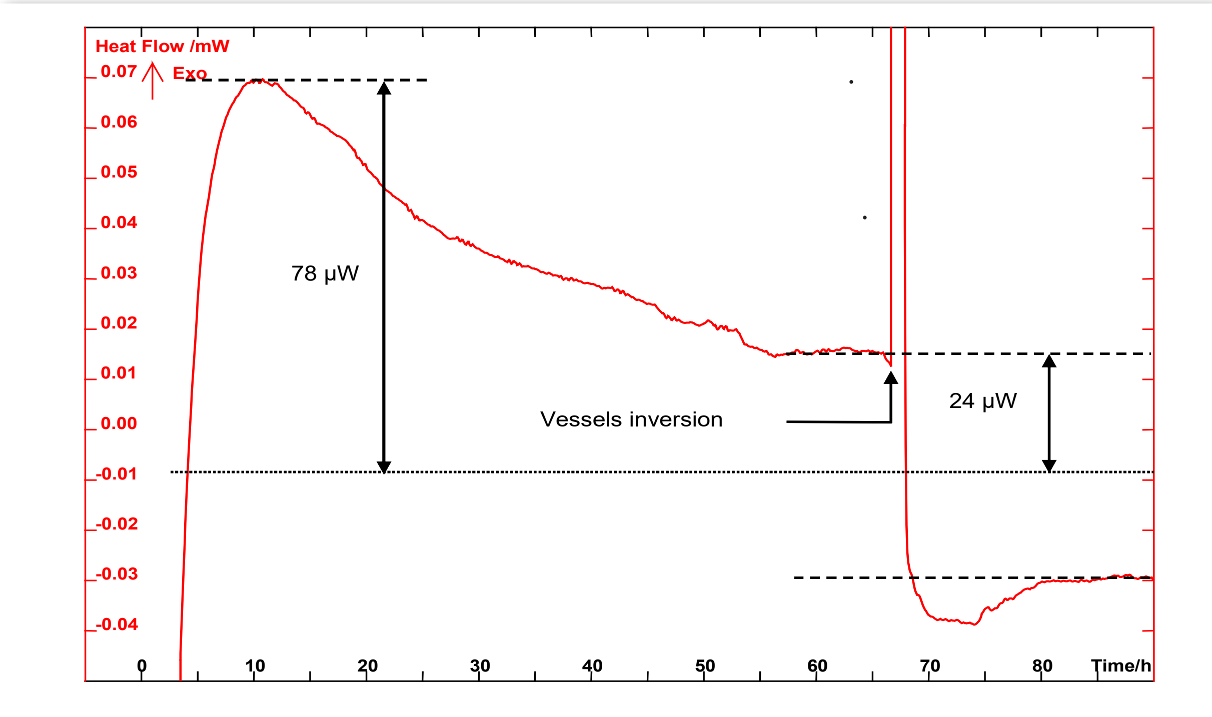
Self-discharge is a phenomenon in batteries in which internal chemical reactions reduce the stored charge of a battery even if the battery isn't used. Measurement of the heat flow of a battery during its self-discharge thus helps compare its capacity to stay charged during long periods of time versus other batteries. The method of measurement of self-discharge heat using an isothermal calorimeter consists of placing a sample holder containing a battery in the reference side of the calorimeter where the self-discharge heat is produced. The two sample holders are swapped and the difference of calorimetric signal level before and after swapping is used to determine the self-discharge heat.

EXPERIMENT

• Instrument: CALVET.
• Vessel : Standard vessel stainless steel.
• Sample : Batteries of type CR1220 are studied.
The temperature of the calorimeter was maintained at 70°C.
• Method : 9 batteries were superimposed inside the vessel. Between adjacent batteries a layer of paper is inserted to electrically insulate the batteries from each other.

RESULTS AND CONCLUSION

• After the introduction, the calorimetric output passes by a maximum of 78 µW. (or 78/9 = 8.7 µW per battery).
• After 65 hours the two vessels : measure and reference are inverted. The mid-point between the trace obtained before inversion and the trace after 80 hours gives the position of "calorimetric zero".
• It means that after 55 hours the 9 batteries dissipate 24 µW which corresponds to 24/9 = 2.7 µW for each battery.



INSTRUMENT

CALVET LV

HIGHEST HEAT MEASUREMENT ACCURACY
with Calvet 3D sensors capturing 93-95% of all heat forms, the highest level on the market

MODIFIABLE TEMPERATURE CONDITIONS
for increased flexibility and replications of real life conditions

CONVENIENT, INTERCHANGEABLE CELLS
to perform varied experiments in one instrument:

- Self-discharge with standard cells
- Charge/discharge with cells allowing the use of electrical wiring and connections to battery cycler
- Single or twin measurements

LARGE CELL VOLUME
to test battery sizes up to 33mm diameter and 100mm height, including the standard 18650, 21700 or D-type batteries

SPECIFICATIONS

	CALVET LV 17mm	CALVET LV 35mm
Temperature range (°C)	ambient to 200	
Temperature accuracy (°C)	+/-0.4 *	
Isothermal and temperature scanning rate (°C/hour)	< 2 between two isotherms	
Enthalpy accuracy	+/-0.2 *	
Cells (ml)	Up to 12.5	Up to 100
Battery sizes (mm)	Up to 15 diameter, 70 height	Up to 33 diameter, 100 height

** Based on indium melting tests*

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SELF DISCHARGE OF BATTERIES

INTRODUCTION

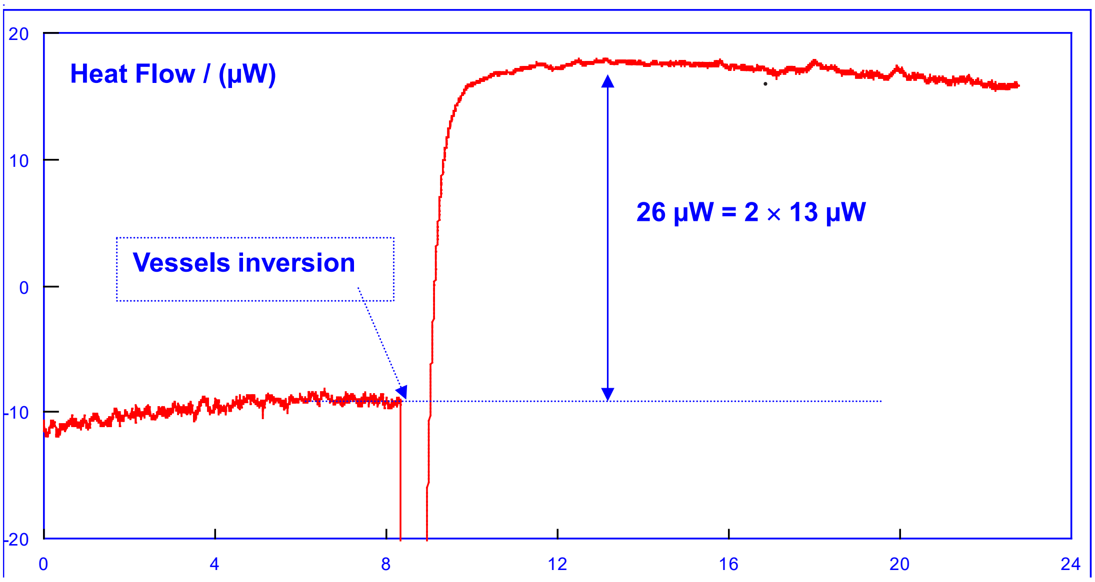
Self-discharge is a phenomenon in batteries in which internal chemical reactions reduce the stored charge of a battery even if the battery isn't used. Measurement of the heat flow of a battery during its self-discharge thus helps compare its capacity to stay charged during long periods of time versus other batteries. The method of measurement of self-discharge heat using an isothermal calorimeter consists of placing a sample holder containing a battery in the reference side of the calorimeter where the self-discharge heat is produced. The two sample holders are swapped and the difference of calorimetric signal level before and after swapping is used to determine the self-discharge heat.

EXPERIMENT

• Instrument: CALVET LV.
• Vessel: Standard vessel in stainless steel.
• Sample : 6 watch batteries of Li-I type.
Available space for the sample inside the vessel :
- diameter : 32.7 mm
- height : 111.2 mm
- volume : 93.3 ml
Atmosphere : air.
• Method : Isotherm at 27.4°C for 24 hours.

RESULTS AND CONCLUSION

During the first 8 hours, the CALVET LV monitors the heat flow dissipated by the batteries. After this time, the two vessels (measure and reference) are inverted.
After another 4 hours the heat flow is stable again.
• The deviation of heat flow before, and after the inversion (26 µW) is twice as high as the heat flow dissipated by the 6 batteries : 13µW (= 26 µW / 2).
• Each battery dissipates an average heat flow of 2.2 µW (=13 µW / 6).



HEAT GENERATED DURING CHARGING/DISCHARGING OF SODIUM ION CELL

INTRODUCTION

With lithium reserves facing increasing constraints, there is a pressing demand for the exploration of more sustainable alternatives, notably in the domain of large-scale electrical energy storage. Sodium-ion batteries are emerging as a promising option compared to the established lithium-ion batteries.

The charging and discharging processes in batteries generate heat. Measuring this heat generation in conditions corresponding to normal use of the battery or even in abnormal/abusive conditions is important to predict temperature elevation and potential safety issues. This measurement can be done isothermally in a calorimeter equipped with wires to connect the battery.

EXPERIMENT

- Sample: Sodium ion coin cell connected to a battery cycler
- Instrument: CALVET LV
- Condition: Isothermal at 25°C, charging between 2V and 4V at 0.2C

RESULTS AND CONCLUSION

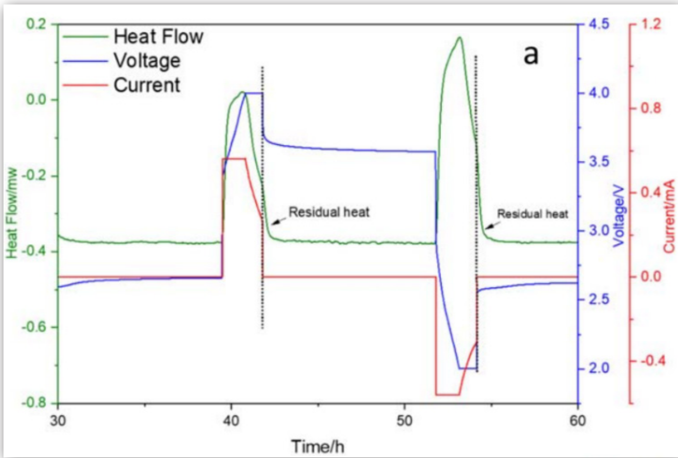


Figure 1 : Heat measurement during charging and discharging at 0.2C of $Na_{0.53}MnO_2$/HC half-cell

During charging and discharging processes, exothermic peaks are measured, which means heat is released by the cells.
After the charging/discharging is completed, some residual heat is still evolved, due to thermal mass and lag.

More heat is generated during the discharging process than the charging. This is explained by larger irreversible heat generation caused by internal resistance.
Integration of peaks provides the total heat generated by charging/discharging process, which can be used to predict temperature elevation.

Ijaz Ul Mohsin, Carlos Ziebert, Magnus Rohde and Hans Jürgen Seifert, Comprehensive Electrochemical, Calorimetric Heat Generation and Safety Analysis of Na0.53MnO2 Cathode Material in Coin Cells, J. Electrochem. Soc. 168 050544, 2021

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