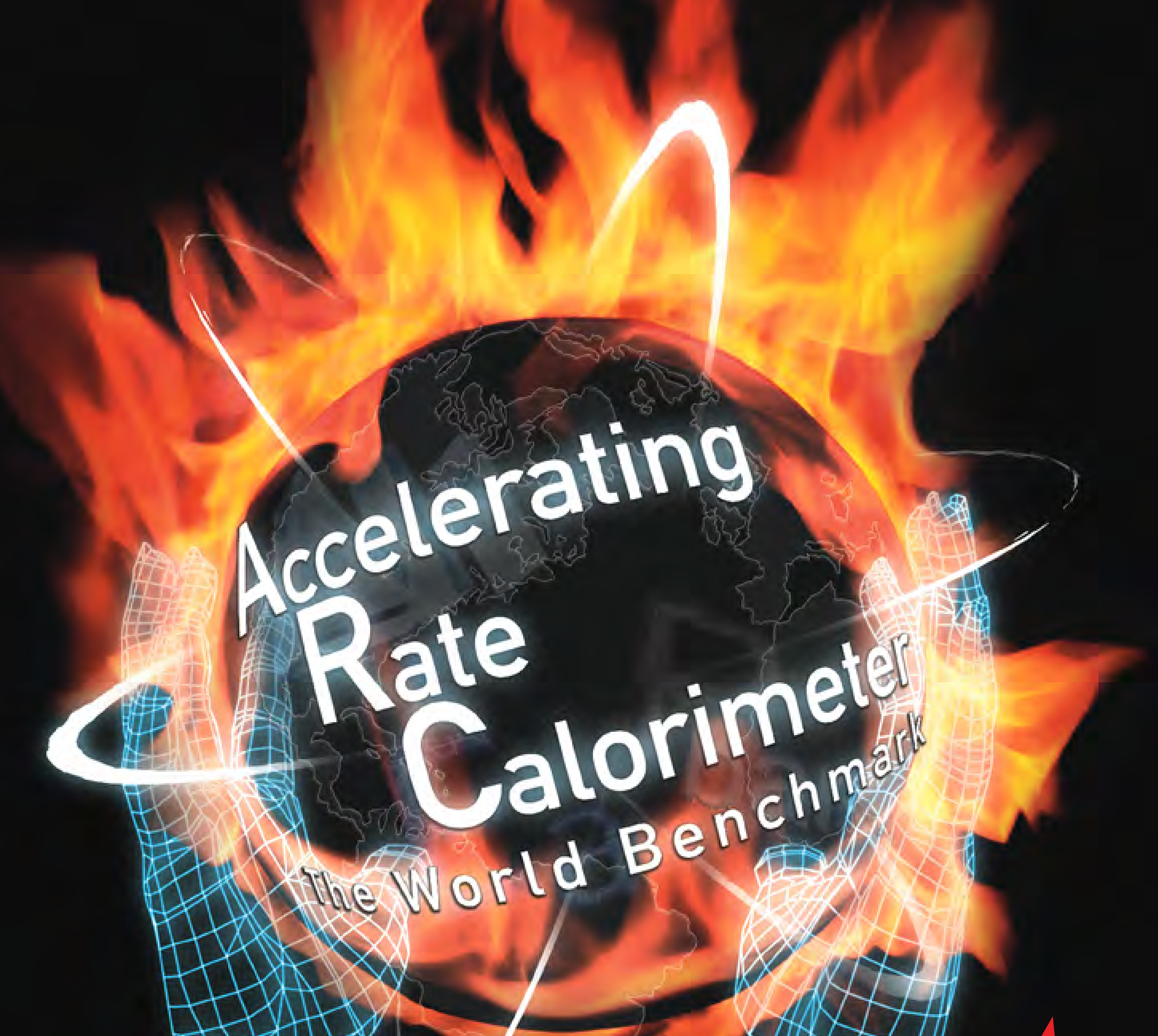
ARC®

The World Benchmark
Battery Testing Calorimeter Systems



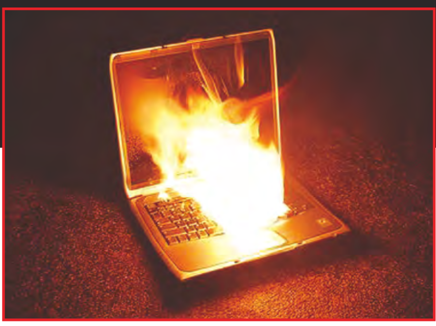
thermal hazard technology

Offices in ENGLAND, USA, CHINA, INDIA
Representation Worldwide

The ARC® Battery Test Systems
Battery Safety, Efficiency, Lifecycle, Performance,

Lithium Batteries & Heat...
Lithium batteries are recognised as hazardous - it is important to determine both the effect of heat on lithium batteries and the heat that results from their use and abuse.

ARC Calorimetry will give vital thermal data to areas of battery development, battery safety, battery performance efficiency and lifecycle.



Battery Safety and Battery Performance

The Accelerating Rate Calorimeter was devised by the Dow Chemical Company in the 1970's and was commercialised in 1980. This technology was developed to simulate exothermic runaway reactions from hazardous and reactive chemicals safely in the laboratory. For such a simulation an Adiabatic Calorimeter is appropriate and ARC technology embodies the best adiabatic control. In operation, the calorimeter temperature is controlled to always track or follow the sample temperature. Therefore as a sample self-heats and its temperature rises, so does the calorimeter temperature. Worst Case evaluation is made and a real life scenario simulated. Pressure can also be measured and the THT calorimeters can take very large batteries. In addition, the ARC will operate in isothermal mode with exceptional sensitivity and stability. The unique dynamic range allows for detection and measurement of very small heat release as well as the ability to quantify runaway explosive decompositions.

These operating conditions are also important for battery work. Uniquely the ARC has robustness and ruggedness to withstand damage should an explosive reaction occur and thus THT systems are designed to be safe in such circumstances.

Unrivalled Specification

Another key point necessary for many battery applications is the size of the calorimeter. Five options are available from THT (of those cylindrical in their internal shape) the smallest measures 10cm in diameter by 10cm in depth and is suitable for testing battery components in metal holders, coin cells, small prismatic, 18650 and other smaller 'domestic' batteries. The largest, 65cm by 50cm, will take large battery modules and packs used, for example, in applications from power tools to satellite and automotive applications.

In use to detect heat release, the system does not scan in temperature. Instead small heat steps are applied and after a wait period for isothermal equilibration, there is a seek period to detect heat release by temperature rise. When this occurs the system automatically switches to the Exotherm mode and tracks the heat release, by accurately following and recording the temperature rise.

These studies are routine for groups studying battery components in order to develop chemistries that optimise specific power requirements and increase their inherent safety. But ARC technology can allow much more to be achieved. Batteries, like reactive chemicals or explosives, will also release heat – they will react and decompose when heated, internal pressure may cause them to rupture and disintegrate. Accompanying this is typically smoke and fire as severe oxidation reactions occur between battery components and oxygen in the air.

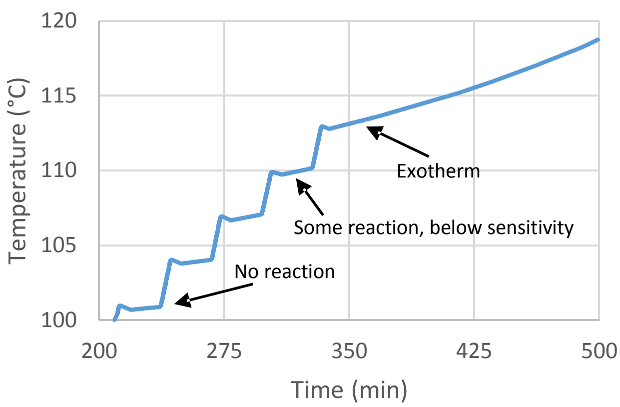
Due to the layout of the calorimeter it is simple to connect the battery to leads, allowing in-situ electrical measurement. With large batteries it is possible to apply multiple thermocouples to allow temperature distribution measurement over the battery surface. Connecting the battery to a cycler or battery test system allows vital temperature and pressure data to be obtained under conditions of charge, discharge (including of course the very fast discharge needed for automotive applications). Successive cycling and abuse testing such as short circuit, overvoltage and nail penetration and crush (internal short circuit) can be performed within the ARC calorimeter. The ARC is therefore an ideal tool to evaluate both performance and safety aspects of lithium batteries. 30 years after the technology was first available, the ARC remains the world benchmark calorimeter for scientists and engineers focusing in the area of chemical hazards. Today the latest generation ESARC with large volume calorimeters is the premier choice for those researching battery safety and the development of safer batteries and to evaluate the performance, efficiency and life-cycle of those batteries.

ARC® Instrumentation

The ESARC

For safety studies and accurate detection, the Heat-Wait-Seek protocol of the ARC and automatic detection of exothermic reactions is illustrated below. For full details of the ESARC, its mode of operation data and analysis, please request the 28 page ARC brochure or visit www.thtuk.com, www.thtusa.com or www.thtchina.com.

Heat-Wait-Seek Protocol to Detect Self-Heating



ARC key aspects are:

- Excellent Adiabatic Control to 0.01°C
- Sensitivity to 0.002°C/min
- Measurement of Pressure and Temperature
- Choice of Calorimeter Size up to 65cm by 50cm
- Resultant Gas Collection facility

Ease of Use

- Simple Hardware Configuration
- Rapid experimental Set Up; 10 Minutes
- Intuitive Labview™ Software
- Up to $2m^3$ Working Volume

Versatile and Flexible Operation

- Any Chemical / Battery Type
- Many Different Battery Holders
- Quantifies Exotherms and Endotherms
- Isothermal and Isoperibolic Modes
- Evacuated, Inert or Air Atmosphere

Multiple Built-In Safety Features

- Rugged Robust Construction
- Explosion Resistant Containment Vessel
- 3mm Reinforced Steel
- Door Proximity Switch Cut-Out
- Software - Independent System Failsafe
- Automated Fume Extraction
- Fireproof and Explosion Containment

Calorimeter Choice

Batteries come in all shapes and sizes, so THT uniquely provides instrumentation to test both small and large batteries.

Standard ESARC
The standard ARC Calorimeter has an internal size of 10cm diameter by 10cm depth with optional 3cm height extension. This is ideal for testing battery components and smaller batteries, from Coin Cells to AA and 18650 to 26650, prismatic and smaller lithium polymer batteries. However this calorimeter is restricted to small batteries.

EV
To facilitate safety testing of large batteries, EV batteries and modules, THT developed the large volume calorimeter, the EVARC. The internal size of this EV calorimeter is 25cm diameter and 50cm depth. Using the same electronics and software of the ESARC, the EVARC can be operated with either the EV calorimeter or the standard calorimeter allowing full functionality of both instruments.

EV+
The EV+ calorimeter 40 x 44cm volume and is designed for safety and performance testing of EV cells and small modules.

It has been designed to fulfil requirements of SAND 2005-3123, SAE J2464. USABC / FreedomCAR and UN & UL tests.

The EV+ calorimeter is a low-pressure tight sealed unit. The lid to base seal is maintained by electromagnets. It is designed to vent with a modest over pressure and any gas generation can be led to collection facilities.

There is in built capability for gas collection, video monitoring, battery clamping, temperature distribution and cryogenic operation.

BPC
For battery performance studies and research of large format cells appropriate in the automotive and aerospace industries, THT has developed the battery performance calorimeter (BPC).

The BPC is also likely to be the calorimeter of choice in areas of Stationary Applications; for storage and 'peak shaving'. The BPC is 65cm diameter by 50cm depth and is housed in the EV+ containment vessel ensuring maximum safety in operation. The BPC uses the same electronics hardware and software as other THT ARC systems and can be acquired packaged together with the other calorimeters as a multi calorimetry system.

The BPC calorimeter housed in the EV+ containment blast box

A THT Battery Test system; the EV+ARC with electronics cabinet is shown

Battery Specific ARC Options

A range of options and kits are available to allow testing from battery components to abuse tests of EV battery modules. Many options are suitable for all calorimeters, some are specific to particular calorimeters.

Options can be acquired with the unit or added at any later date.

Battery Materials & Chemical Components Kit

Fundamental battery research begins at the component level. The ARC can be used to test battery component materials in the same way as it is used in traditional chemical applications. For battery components in ARC bombs or complete coin cells up to 18650 cylindrical cells, the standard calorimeter is used.

Battery component sample size ranges from 100mg to several grams. Bomb volume is 9ml for the standard ARC bomb or 1ml for the tube bomb. Larger holders are also available. The component kit contains appropriate sample holders and modified pressure lines to facilitate studies on battery components which should be prepared under inert conditions.

Battery Safety Holders & Canisters

THT has available a full range of battery holders which are suitable for all shapes and sizes of cell. There are standard holders for common battery sizes such as coin cells and 18650 as well as the more adaptable holders for various sizes of pouch cell. Both open and pressure-tight holders are available if pressure data is required. Holders are also available for larger cells used in automotive/aerospace applications.

In addition THT provides pressure certified canisters for various sizes of cell, to fit in standard, EV or EV+ calorimeters. Using these canisters, gas can be isolated and collected in a separate vessel then taken for analysis.

Integrated Battery Cycler - KSU Option

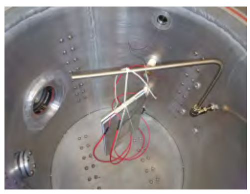
The THT KSU option is an integrated single or dual channel battery cycler. The voltage and current range may be supplied to match customer requirements, from milliamp level up to several hundred amps. The system is fully integrated with appropriate software to give a single turn-key instrument to allow rapid charge/discharge cycling ie tests under conditions of battery use. Voltage and current data is plotted concurrently with the standard temperature and pressure data. The ARC is designed to allow easy connection of large to small diameter wires to the battery sample. Stand-alone cyclers can also be easily used in conjunction with the ARC. The calorimeter electronics can be provided with an Electronic Trigger Unit which gives different output voltages depending on the ARC running mode (heat, wait, seek, cool etc.) and this voltage signal can be used to trigger a cycler or other equipment.

Short Circuit/Overcharge

Modules to carry out safe, in-situ short circuiting of cells may be purchased. The short-circuit option (SCO) allows remote shorting of cells in the ARC. The short is carried out through a low impedance contactor box. The short circuit current can be independently measured at high frequency via a current transducer to verify the severity of the shorting current.

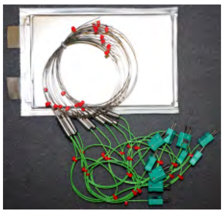
Overcharging can be carried out using the integrated KSU cycler, or on another stand alone power supply or cycler. Overcharge testing leads to an even more severe thermal runaway compared to standard thermal abuse tests.

Heat Capacity Option



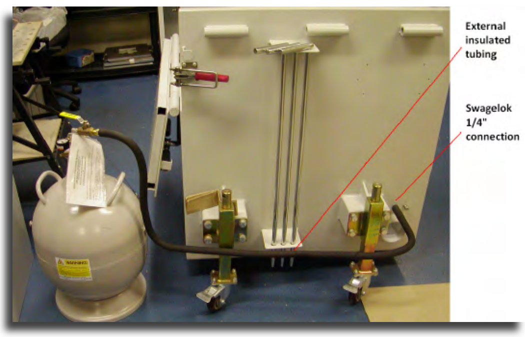
For design of thermal management systems in any battery application it is necessary to quantify the heat production rate. Measurement of heat production from ARC data requires knowledge of the sample's heat capacity. If the average heat capacity of the battery is known, the temperature and temperature rate data can be converted to heat/enthalpy (joules) and heat rate/power (watts). Option to measure battery heat capacity can be provided and are available in semi or fully automated form. To measure the heat capacity two or more cells are heated with a thin kapton-insulated heater and a precise power supply. In the fully automated form the power supply is integrated with the ARC system and the data is analysed with the ARCCal+ analysis software.

Multipoint Option for measurement of surface temperature variation (MPO)



Heat release from batteries is not spatially uniform. Heat may conduct through metal components or collector plates causing greater temperature rise at the terminals compared to the battery case. For applications such as Thermal Management it is vital to understand the variation in heat release over the battery surface. THT provides both semi and fully automatic options to permit surface temperature measurements. 8, 16 and 24 thermocouple kits are available and data may be logged concurrently with standard temperature and pressure data. The standard ARC system also contains two auxiliary thermocouples in addition to the primary tracking thermocouple.

Cryogenic Operation



Isothermal, battery cycling, multipoint and heat capacity testing is often needed over the full range of environmental temperatures to simulate real-world conditions faced by battery systems. To facilitate such testing THT provides a manual cooling option for the standard, EV and EV+ calorimeters. This permits rapid cooling and short-term cryogenic isothermal stability. In addition, the Cryogenic System Unit is a refrigeration system that is available with the standard ESARC to maintain a sub-ambient temperature in the blast box for long periods of time (minimum working temperature of -35°C). The BPC comes with a circulator and can maintain -30°C isothermal operation.

Nail Penetration & Crush Options

THT provides Nail Penetration & Crush options for smaller or larger batteries or varying shapes and constructions. The basic option is pneumatic without speed-control and has the capacity to crush the steel case of an 18650 cell. Interchangeable nail and crush heads can be selected and this option is connected to a pressurized gas cylinder (maximum pressure 150 bar). A range of configurations are available.

For speed-controlled testing, THT offers an electric motor-driven variable speed system. This motorised option allows controlled speed nail penetration. This is required in various industry testing standards and is valuable for larger batteries or modules when speed variation can give differences in results. Various gearings and two different motors are available to give a total of 8 possible configurations to suit customer requirements.

Video Monitoring

Video monitoring is standard in the EV+ calorimeter. The high resolution camera is air cooled for close proximity filming. Videos can be generated using ARC software where pictures are taken at specified intervals (good for long tests) or in real-time using separate video capture software. A dual window configuration allows a gas tight seal and easy cleaning between runs. There is also the possibility of using IR transparent windows and IR cameras for in-situ thermal imaging.

Gas Collection

Gas collection is achieved in the standard and EV calorimeters by use of sealed canisters or sample holders. These are placed internally within the calorimeter. The canisters have sealed ports to allow cables and thermocouples to pass through to the sample. Other ports allow for inertion of the canister atmosphere, pressure measurement and gas collection. The versatility of this approach means that a variety of external collection methods are possible.

The EV+ calorimeter is of a sealed construction with several integrated ports for gas collection. Automated gas sampling is possible using the SSS (single sample system) for a one-off sample or the SSU (system sampling unit) for up to four separate samples during a single test. Samples may be collected on a time, temperature or pressure basis, or at the end of the test.

Battery & Battery Component Testing

The application of the ARC to lithium batteries may be categorised into five groups:

1. Battery component testing for development of new battery chemistries: A fundamental research area where much work has been done within university & academic environments. Also applicable to companies developing novel cell chemistries, electrolytes or separator materials.

2. Single cells and battery modules for safety studies; testing and for safety in a range of abuse scenarios; typically carried out by battery manufacturers or OEMs. This is a key area of research in vehicle applications where thermal runaway poses a significant safety risk due to the quantity of cells in use.

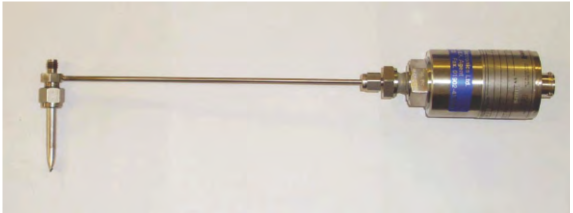
3. Battery heat output under normal conditions of use; cycling for heat release to determine battery efficiency or life time. Also includes measurement of cell heat capacity. Testing carried out in academic or industrial laboratories for applications ranging from consumer electronics to aerospace.

4. Fast charge/discharge battery performance studies. Important for EV, HEV and PHEV, battery packs & modules where rapid charging and discharging is essential to usability. The temperature distribution over the battery/module may vary making multipoint measurement useful. These tests can includes cycling at extreme temperatures.

5. Gas release studies using internal or external pressure measurement. Aiming to investigate quantity, speed and temperature of gas release. Secondary analysis (eg. GC-MS) is used to determine gas composition. Key for design of battery case (burst disk) or design of secondary enclosure for battery modules.

Battery Components

Evaluation of battery components to study new battery chemistries is key to enhanced battery performance and safety. Development is focused on increased energy density and increased thermal stability. Often improvement in one area may have a detrimental effect on another.

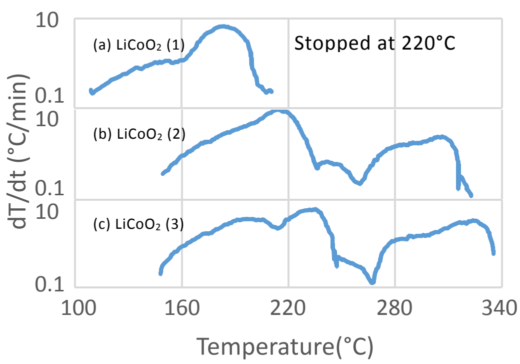


Normally it is the reaction of or an interaction between components that leads to heat release. Low temperature reactions may be SEI decomposition and anode material reaction. Higher temperature reactions may be oxidation of cathode material by electrolyte.

For component testing, sample preparation to make lithiated anode and de-lithiated cathode is often necessary. This is typically done by assembling prototype cells with specialist equipment. Pressure measurement is also important to analyse gas generation.

THT's battery components kit contains special sample holders and parts to facilitate simple sample loading in a glove box. Testing might include particle size variation, electrolyte variation and SoC (state of charge) variation etc.

With chemistry evaluation, mixes of 2 or 3 components typically are tested. ARC data can be complex, including multiple reactions, as illustrated from results published by Professor Dahn and reproduced with his permission.



Effect of Increasing Component Particle Size $LiCoO_2$ (a), (b), (c)

Safety Testing of Batteries

Batteries of varying shape and size may be tested in the ARC; they may be suspended from the lid section or they may be supported directly in the base of the calorimeter with an insulated stand. The simplest test is a "heat-wait-seek" thermal abuse test. This is the classic ARC test commonly found in scientific literature. It is possible to test batteries at any State of Charge, or age, and it is possible to connect cables to the battery terminals to measure voltage during the test. More advanced instrumentation can be used to measure cell impedance. Open or closed sample holders are available – but, as with all samples that undergo significant gas generation, rupture of a closed holder might occur.

A key difference between chemicals and batteries is that batteries function as their own 'holder'. This means initial pressure generation is contained inside the cell case. THT offer two possibilities to study pressure associated with batteries; internal pressure measurement (pressure generated inside the battery case) or external pressure measurement (pressure generated during cell venting).

Aside from onset of heat release (the beginning of the reaction), the ARC test will determine self heating at all temperatures – and thus gives much more information than hot box and other empirical tests. The final potential of the battery to contain pressure or to disintegrate in such an event is important; ejection of battery components will be associated with fire as the lithium reacts with air and the release of smoke and toxic or corrosive gas.

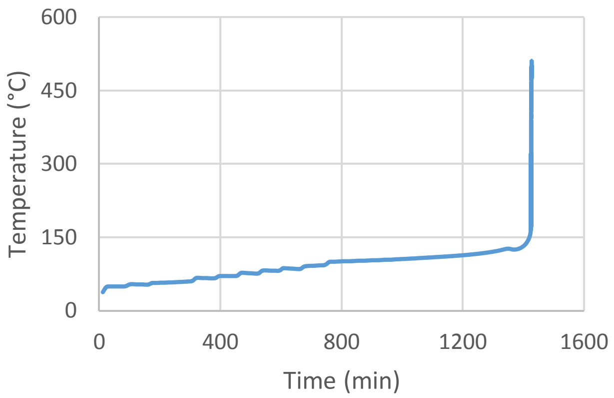
THT has developed sealed canisters that will accommodate various sizes of battery and be gas tight to facilitate pressure measurement. These canisters allow for thermal and electrical measurement. The standard ARC system allows for temperature measurement of the battery, the canister air temperature (key for calculating gas volume) and the canister surface temperature. The canister may be evacuated or filled with inert gas. In addition to measurement of pressure it is possible during or after the test to sample gas for analysis. If connected to external analytical instrumentation there is the potential to analyse gas generation in real time, but gas flow must be carefully controlled.

The order of exothermic reactions shown from a fully charged 18650 metal oxide battery are typically SEI, anode, separator melting (endotherm) and cathode reacting with electrolyte – as shown. Above 200°C the battery may disintegrate or the reaction may go to completion without disintegration of the battery.

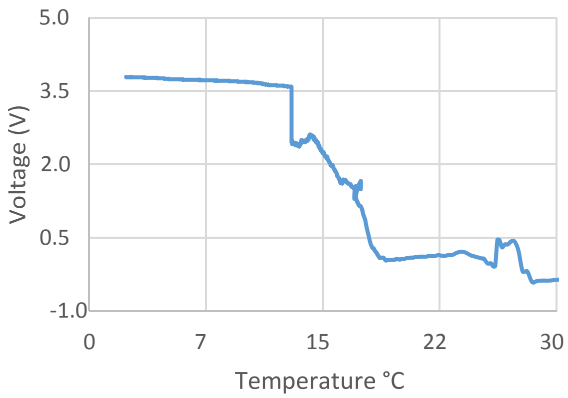
Batteries at different States of Charge or of different ages will give different heat release profiles. Voltage measurement often shows that batteries will retain their voltage until well into exothermic decomposition. Data may be complex as illustrated below.

Internal pressure measurement is simply achieved by attaching a sealed fine pressure line to the battery in a glove box. Data shown below indicates pressure increase to 4bar prior to the exothermic decomposition commencing. As decomposition proceeds the internal pressure increases and it is not until above 12 bar that the battery disintegrates and there is gas release.

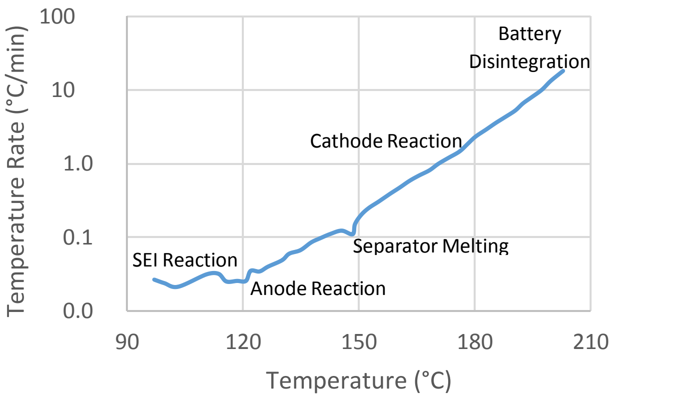
Battery Thermal Stability Test



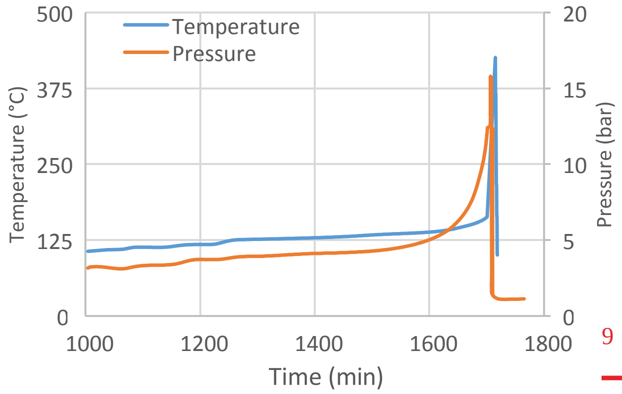
Voltage Against Temperature Graph



The Exotherm Portion has Overlapping Reactions



Internal Pressure During Test



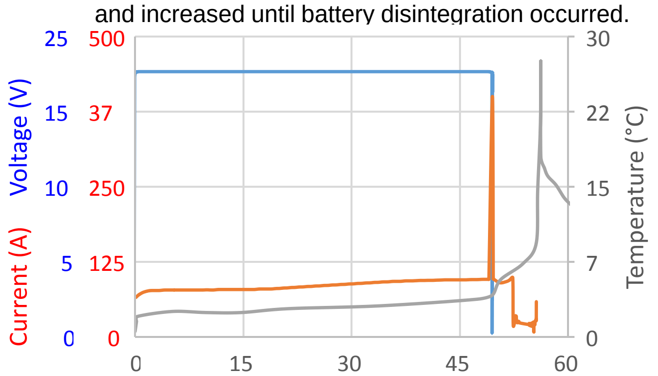
Use & Abuse Testing of Lithium Batteries

Testing of Batteries under Abuse conditions

Lithium batteries can fail dramatically when physically or electrically abused. Many abuse tests have been proposed and several are detailed as standard tests by organisations working within the battery industry. Prescribed tests typically give an empirical pass or fail result. The ARC has the potential here to accomplish a range of tests in which abuse conditions are simulated, generating quantitative thermodynamic and kinetic information. These tests may be carried out with smaller batteries in the standard ESARC system or with large batteries in the EVARC or EV+ARCsystems.

Options are available from THT to allow either manual or automated (software controlled) abuse tests on batteries to be carried out within the ARC calorimeter. Several examples are given below.

Lithium batteries, if overcharged, are known to self heat and can lead to disintegration. Overcharging increases the energy loading of the cell beyond its working limit. The energy is released during decomposition. In this example, the battery was subjected to charging at 450mA to a 20V upper limit. After 200 minutes the battery voltage increased above 4V with associated temperature rise. After 500 minutes there was rapid temperature rise (and the current supply was switched off). The exothermic reactions continued and increased until battery disintegration occurred.

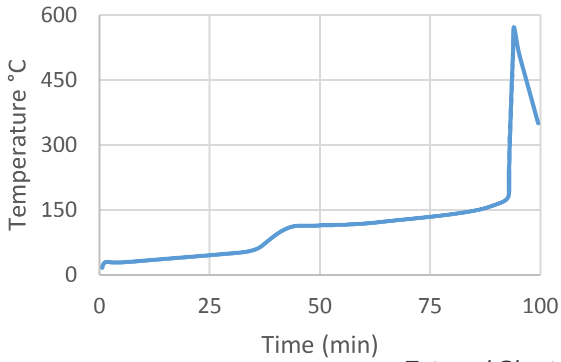


Overvoltage Test

External shorting of a battery within the ARC is simply achieved by connecting the positive and the negative battery terminals through low impedance wire. For higher capacity batteries, thicker cables are required to handle the large current flow that occurs during shorting. The test is rapid (1-2 hours) and carried out with the instrument at a constant temperature.

Shorting gives a temperature increase that is tracked by the calorimeter and the amount of heat released can be quantified. Shorting may or may not lead to a complete thermal runaway depending on the battery.

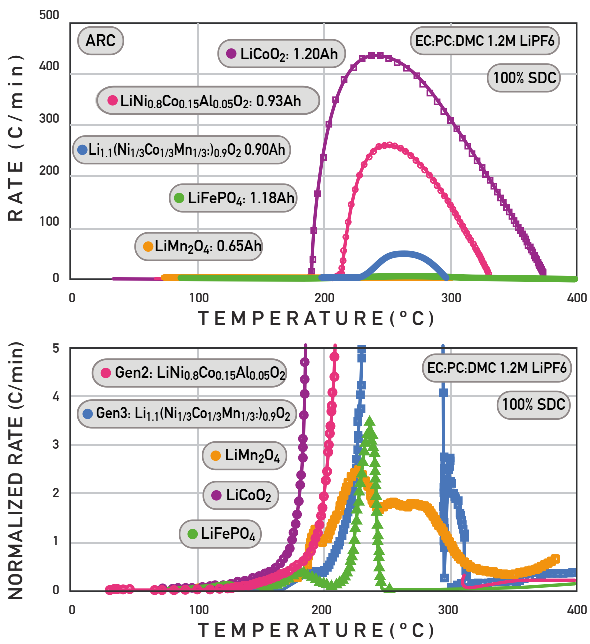
The result shown is from a fully charged battery. Shorting leads to a temperature rise of 100°C. After charge is depleted the battery continues to self-heat until disintegration occurs. This will not happen for all battery chemistries and does not happen for this battery type if it is fully discharged. In the discharged state, a temperature rise of 30°C occurs. This temperature rise is not sufficient to lead to runaway and Heat-Wait-Seek steps occur.



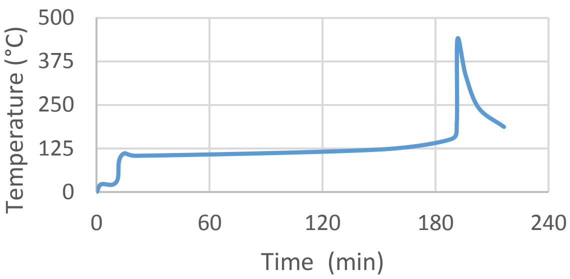
External Short Circuit

Some newer batteries have internal fuses which are triggered by excessive current flow to prevent thermal runaway via short circuiting. As battery development has progressed; variation in chemistry has led to batteries that are thermally stable at higher temperatures and undergo much smaller exothermic reactions i.e. giving less heat release. These batteries are safer, but it is naive to say they are completely safe. Data shown for Generation 1 to 5 of cathode material has been published by Dr E. Peter Roth at Sandia National Laboratories and is shown with his permission.

Comparison of Cathode Materials and Reduction in Heat Output

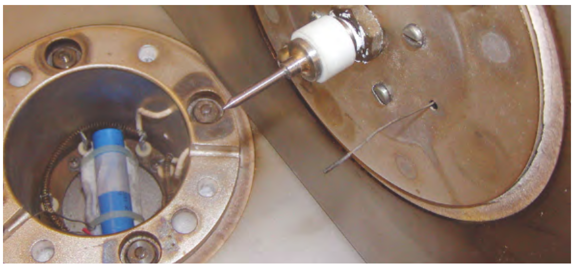


Nail penetration testing aims to simulate the effect of an internal short circuit. The test is specified in various industry standards as a way to internally short a battery in a relatively straightforward and repeatable manner. Real internal shorting may have a number of possible causes such as cell deformation, lithium dendrite formation or any type of puncturing. The nail penetration test can be carried out in the ARC in a manual or automatic mode. The battery is held on a support frame and the nail is driven through the battery. The thermal response is measured. Of key importance is whether the battery temperature will be raised enough to initiate a disintegration reaction. In the example shown, nail penetration results in a temperature rise of near 100°C and a further temperature rise, after the battery had shorted, led slowly to battery decomposition.



Nail Penetration

Such tests are illustrated here with ‘model’ 18650 batteries. These are often the choice in development studies. However using the EVARC and EV+ARC, these same tests can be carried out with larger battery packs and modules. As described earlier, various types of nail penetration system are available from THT.



Testing of Batteries under Use Conditions

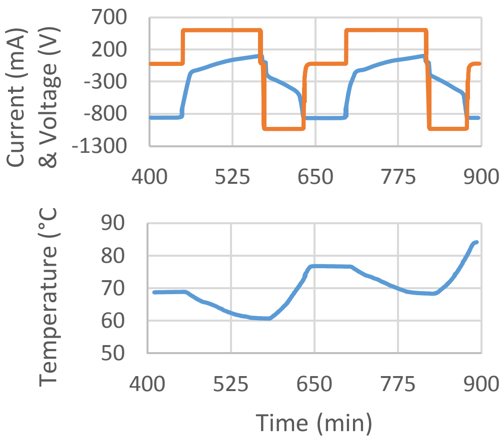
Quantifying the heat generated by lithium batteries during conditions of use allows for an understanding of their efficiency and gives information that is important in determining operating conditions and any thermal or safety issues that may result during normal operation. Variation in heat release from batteries as they age will give indication of battery life time. Heat release relates to cell internal resistance although heat generation may not be significant in applications where discharge is slow and gradual eg discharging the battery in a smart phone.

In applications such as electric vehicles or power tools where rapid and large discharge is needed, this can result in a much greater heat release and temperature rise.

The KSU Option for the ARC is a single or dual channel cycler integrated with ARC electronics. Several versions are available with differing voltage and current ranges. In the same way, a stand-alone cycler may be used in conjunction with the ARC and such cyclers are generally readily available in battery research labs. In the latter case there will be two sets of data that need to be synchronised post-test.

Often in cycling tests, the battery within the ARC is surrounded by a jacket of insulation. This reduces heat loss and better data can be obtained from tests carried out either isothermally or adiabatically. Repeated cycling is often implemented. Tests may be carried out with a few cycles in the ARC (when the battery is fresh), the battery removed and repeated cycling performed outside the ARC. Then the test is repeated (with the aged battery) inside the ARC. The change in thermal effect and speed of charge discharge will give a measure of capacity change with time, a change of internal resistance. The efficiency and lifetime characteristics of the battery are determined. The data illustrated below shows a simple two cycle charge and discharge with heat effects, both endothermic and exothermic processes. The associated thermal behaviour may be more complex as illustrated in many publications using the THT calorimeters for this work. Contact THT for a reference list.

Battery Cycling



Again such application can be realised not just with smaller (e.g. 18650) batteries but with large batteries, packs and modules. Cycle life is one key advantage of lithium batteries over different chemistries; cycle life is important in satellite and space application where there may be a day – night charge – discharge rotation. It is similarly important in stationary applications designed for peak shaving and storage.

Calorimeter Choice EV+

EV+ Calorimeter
The EV+ Calorimeter has been designed for EV cells and small modules and to meet the needs of testing necessary with EV batteries.

Many prescribed 'standard' tests call for calorimetry and also call for abuse testing (eg SAND, SAE). Tests call for video monitoring, gas detection/analysis, nail penetration and crush under controlled conditions. The EV+ calorimeter from THT has been designed to accommodate many of these - and more whilst gaining quality information on heat release.

Key features of the EV+ are its size and its ability to:-

- Have good calorimetric performance
- Incorporate the range of appropriate options

The EV+ is a cylindrical calorimeter 40cm in diameter and 44cm depth. Unlike other THT adiabatic calorimeters the lid seals to the base unit. This seal is restricted to below 1 bar and is maintained by electromagnets. This allows for inertion of the environment and the ability to collect products of battery disintegration. A gas collection line is standard.

Standard on the EV+ calorimeter are:-

- Integrated cables for current & voltage measurement
- Video camera (with light)
- Ability for battery pressure and temperature measurement
- Ability for purging, evaluation, inerting
- Gas collection port

The calorimeter is ready for addition of further options:-

Sub Ambient Operation, Cryogenic Option
Calorimeter Ready.
Pressure tight ports provided in calorimeter which can be blanked off or used if cryogenic (LNFO) option is available operates to -50°C.

Heat Capacity Measurement Cp Option
Calorimeter Ready
Pressure tight ports provided in calorimeter which can be blanked off or used if Heat Capacity Option (CPO) is available.

Surface Area Heat Distribution, Multipoint Option
Calorimeter Ready
Pressure tight ports provided in calorimeter which can be blanked off or used with 8, 16 or 24 thermocouple Multipoint Option (MPO).

Controlled Speed Nail Penetration & Crush Option
Calorimeter Ready
The latest THT Nail Penetration option allows functionality to SAND 2005-3123 & SAE J2464 specification. (EC-CS-NPCO). The NP option is pressure tight to the calorimeter (it allows in situ gas collection and video monitoring during operation). Nail penetration and crush of samples can be performed at various user defined speeds. Different force levels can be achieved with customised gearing configurations.

In built safety features are standard to the EV+ calorimeter and it is housed within the THT 'EBE' (EV Blast Enclosure). Multiple shut down features add to the fail safe mode of operation.

The modular nature of the THT ARC system enables upgrade possibilities at moderate cost.

Gas Collection Option
Calorimeter Ready
One bar overpressure as standard. Higher pressures are available with additional hardware. The SSS/SSU options allow automatic gas collection at predetermined test temperatures to auxiliary cylinders, which can then be removed for external analysis.

Calorimeter Choice BPC & IBC

The Battery Performance Calorimeter (BPC)
Thermal Management, Efficiency & Lifecycle Studies.

The Battery Performance Calorimeter (BPC) is a large volume calorimeter developed for research studies of larger (EV) cells and modules. The BPC utilise ARC electronics and software and is modular with the standard EV and EV+ calorimeters.

The BPC is designed to quantify heat changes during charge and discharge – at conditions that simulate use of the battery.

The BPC is not appropriate for stability, safety and abuse studies where battery disintegration is possible. The BPC has an upper temperature limit of 200°C but operates down to -30°C. Cryogenic operation is possible by linking to a refrigerated circulating bath.

A key and unique feature of the BPC is the 'Thermal Diode' heating system that allows current flow through the calorimeter. This eliminates need for conductive leads or cables to carry current. At high power operation such loads do cause major heat loss and data error in calorimeters with no 'thermal guard'.

The calorimeter has a depth of 50cm but its cross section is elliptical (50-65cm) maximising useful volume for large batteries.

In conjunction with the THT surface area (multipoint) heat measurement option, the BPC is ideally suited for gaining information appropriate for Thermal Management.

The BPC with THT ARC software and electronics can be used within the adiabatic, isothermal or isoperibolic modes. The choice of mode relates to the studies undertaken.

Key options used with the BPC are the surface area (multipoint) option and the heat capacity option. The BPC complements the other calorimeters available from THT.

The Isothermal Battery Calorimeters (IBC)

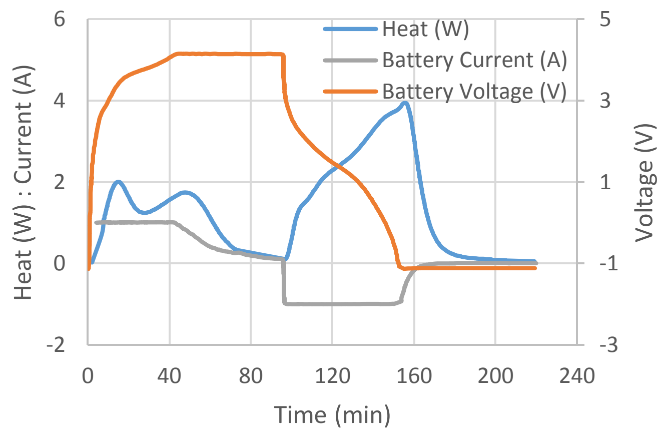
THT have a range of isothermal battery calorimeters which complement the ARC-based calorimeters.

The need for true isothermal calorimeters is when charge / discharge or self discharge isothermal testing is appropriate.

The isothermal battery calorimeters are fully described in their specific brochure.

Isothermal calorimeters have higher sensitivity than adiabatic calorimeters but have a more limited range of applications. Their temperature range is limited and they are not appropriate for safety abuse testing when battery disintegration or high temperatures may result.

The THT range of isothermal calorimeters includes size specific calorimeters, all of which can be connected to external cyclers. The high sensitivity of these units allows the measurement of small coin cells.



EV+ Options: Sub-Ambient Testing & Thermal Distribution

EV+ Calorimeter

Larger batteries and modules have application requirements that extend from the application of smaller batteries.

With large batteries there is still a need for stability and safety testing. Large cells are often used in applications where rapid charge/discharge is required. Ideal charge times for electric vehicles for example would be in the order of minutes rather than hours. This in turn introduces more significant thermal issues which must be addressed. The following options were devised with large format batteries in mind.

Cryogenic Applications

There is the need to evaluate battery performance and thermal aspects of its operation at all environmental temperatures. These may be to a temperature of -30°C or below. Temperatures where electrodes could freeze!

The THT LNFO option allows such testing at modest cost. Testing can be performed at sub-zero temperatures by cooling with a flow of ultra cold nitrogen / liquid nitrogen. The LNFO option is easily attached to the EV or EV+ calorimeter.

Surface Temperature Determination
MultiPoint Option

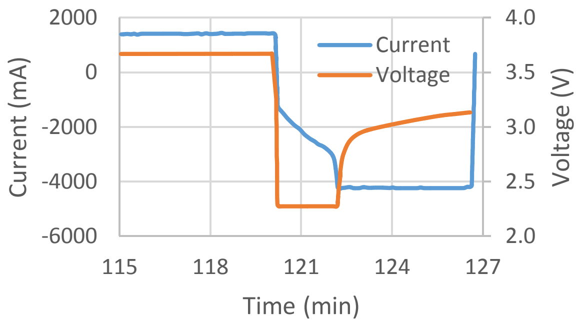
For larger batteries and modules it is key to determine where heat release under use or abuse is focused – how the temperature rise varies through the unit.

The MultiPoint option provides a multiple thermocouple facility to achieve measurement of thermal distribution over the surface of the battery, pack or module. The MultiPoint is available with 8,16 or 24 thermocouples to be positioned where appropriate. The temperature at all points is recorded and control can be at any of these positions.

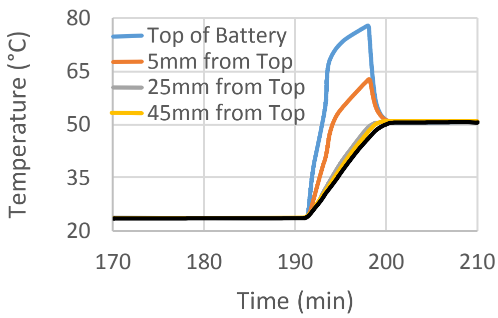
MultiPoint calorimeter tests obtain data more accurately than open bench tests. In the calorimeter the environment is controlled and unknown and un-quantified heat loss is minimised. Conditions are worst case and the final equilibrated battery temperature is recorded. Heat effects using such calorimeters are carefully quantified.

Multipoint data is illustrated for a small battery (18650)

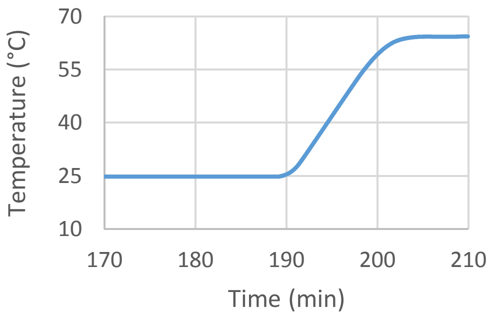
Cycler Data



Spatial Temperature of Battery



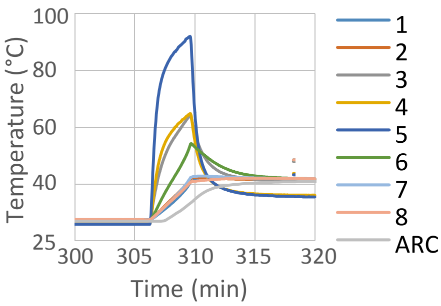
Control Temperature as a Function of Time



Note the timescale of the test, the speed of heat release and temperature increase – and that this is primarily at the anode. The speed of battery thermal equilibration is illustrated. The discharge profile shows the spatial temperatures across the battery and the calorimeter temperature.

With a single large pouch cell the data might be more complex

Data here illustrates a 100 amp discharge experiment



EV+ Options: Heat Capacity, Thermal Management & Abuse Testing

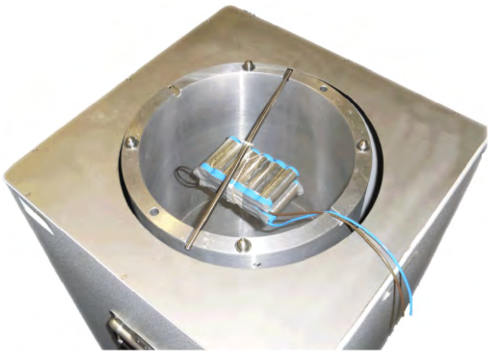
Heat Capacity

A value for the overall heat capacity of the battery is needed to allow conversion of standard calorimeter data to units of joules (heat) and watts (power or speed of heat release).

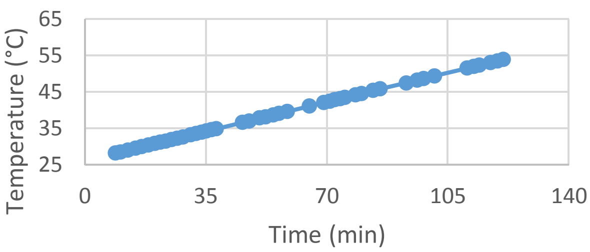
There are many methods by which heat capacity can be determined though typically these involve an additional heater. The heater is in contact with 1 or more batteries, power is supplied and the temperature rise of the battery relates to the heat capacity.

The THT Heat Capacity Option is supplied with heaters appropriate for batteries of the size to be measured. The unit utilises aluminium reference samples. The method is automatic and leads directly to determination of the 'overall' heat capacity.

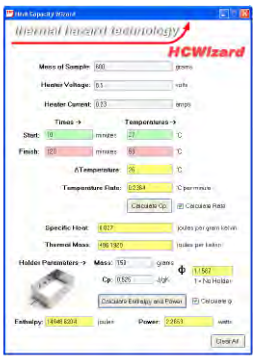
The THT ARC data analysis software has ability to take in sample heat capacity and generate automatically Enthalpy and Power graphs.



Battery pack wrapped in aluminium tape suspended within the calorimeter



The raw data is shown above. Taking the value for the temperature rate (at or averaged over a temperate range), the mass of the battery pack and the voltage and current supplied to the heater, we can then calculate the Cp value and heat capacity at any temperature using the heat capacity wizard software.



From this test the wizard calculated an average (mean) Cp value over the entire temperature range of the experiment of 0.83 J/gK.

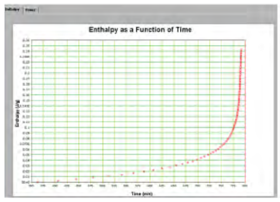
Thermal management of EV Batteries

Utilising the THT EV options, key information is available for thermal management of EV batteries. The battery may be subjected to EV use conditions by charge/discharge with an EV test system (eg Bitrode FTV, dSpace coupled to high power charge and load units or stand alone high power charge and load units). The test system might apply repeated charge-discharge cycles or a prescribed drive scenario.

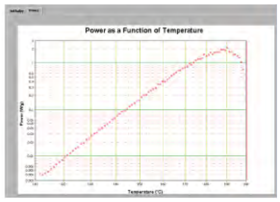
The ARC/EV+ calorimeter, equipped with Multipoint and Heat Capacity options, will give the fundamental data used to help design thermal management systems. Initially the specific heat capacity must be available. This value is simply put in to a MultiPoint Test allowing for generation of Enthalpy and Power graphs.

Software Set Up for MultiPoint

Screen Display During Test



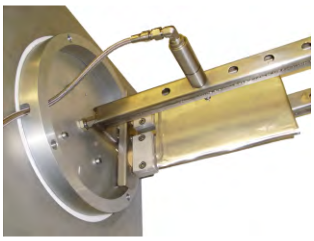
Enthalpy at One Point

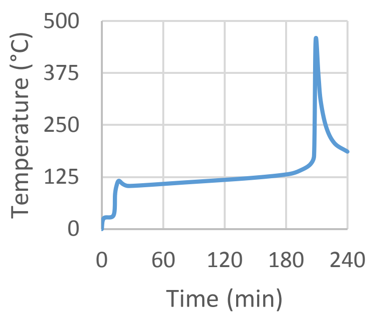


Power at One Point

Nail penetration and crush – controlled speed

Tests call for nail penetration at defined speeds and crush tests to be terminated at voltage drop. The THT NPCO option addresses these testing requirements and can be added to the EV or EV+ calorimeter.





Data from a nail penetration test, shown above. Initially the system was held isothermally before nail penetration commenced. Following the penetration the cell led into complete thermal disintegration (in fully adiabatic conditions).

Papers

We are pleased to see more and more papers in the Scientific Literature detailing important studies and data from testing Li Ion Batteries. A selection of recent papers citing the use of the THT ARC are listed below.

2015

Thermal runaway propagation model for designing a safer battery pack with 25 Ah $LiNi_xCo_yMn_zO_2$ large format lithium ion battery.
Xuning Feng, Xiangming He, *et al*
Applied Energy 154 (2015): 74-91

Characterization of penetration induced thermal runaway propagation process within a large format lithium ion battery module
Xuning Feng, Jing Sun, *et al*
Journal of Power Sources 275 (2015) 261-273

Interaction of cyclic ageing at high-rate and low temperatures and safety in lithium-ion batteries
Meike Fleischhammer, Thomas Waldmann, *et al*
Journal of Power Sources 274 (2015) :432-439

2014

Electro-thermal analysis and integration issues of lithium ion battery for electric vehicles
L.H. Saw, Y. Ye, A.A.O. Tay
Applied Energy 131 (2014): 97–107

Thermal and overcharge abuse analysis of a redox shuttle for overcharge protection of LiFePO4
Joshua Lamb, Christopher J, *et al*
Journal of Power Sources 247 (2014): 1011-1017

Thermal runaway features of large format prismatic lithium ion battery using extended volume accelerating rate Calorimetry
Xuning Feng, Mou Fang, *et al*
Journal of Power Sources 255 (2014): 294-301

Simultaneous estimation of thermal parameters for large-format laminated lithium-ion batteries
Jianbo Zhang, Bin Wu, *et al*
Journal of Power Sources 259 (2014): 106-116

Characterization of large format lithium ion battery exposed to extremely high temperature
Xuning Feng, Jing Sun *et al*
Journal of Power Sources 272 (2014): 457-467

2013

Lithium-ion capacitors: Electrochemical performance and thermal behavior
Patricia H. Smitha, Thanh N. Trana, *et al*
Journal of Power Sources 243 (2013): 982–992

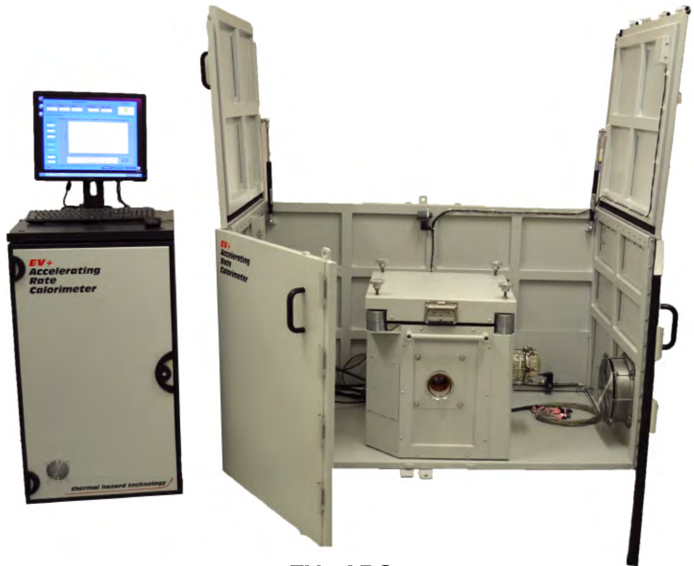
Thermal characterization of a high-power lithium-ion battery: Potentiometric and calorimetric measurement of entropy changes
Akram Eddahech, Olivier Briat, *et al*
Energy 61 (2013): 432–439

Users

THT has a range of adiabatic and isothermal safety and reaction calorimeters. Our instruments are currently utilised in leading pharmaceutical and chemical companies, the majority of the world's lithium battery manufacturers as well as government laboratories and universities worldwide.

Selected Users of THT ARC	
ATL	Mitsubishi
BAK	NASA
BMW	Nissan
Boeing	Nokia
CEA	NREL
Eagle Pitcher	Panasonic
FAA	Samsung
GM	Sandia National Labs
Hitachi	Sanyo
Hyundai - Kia	Shin Kobe
ITRI	Sony
KIT	Tianjin Institute of Power Sources
Kokam	Toyota
LG	Underwriters Laboratories
Lishen	ZSW

EV ARC



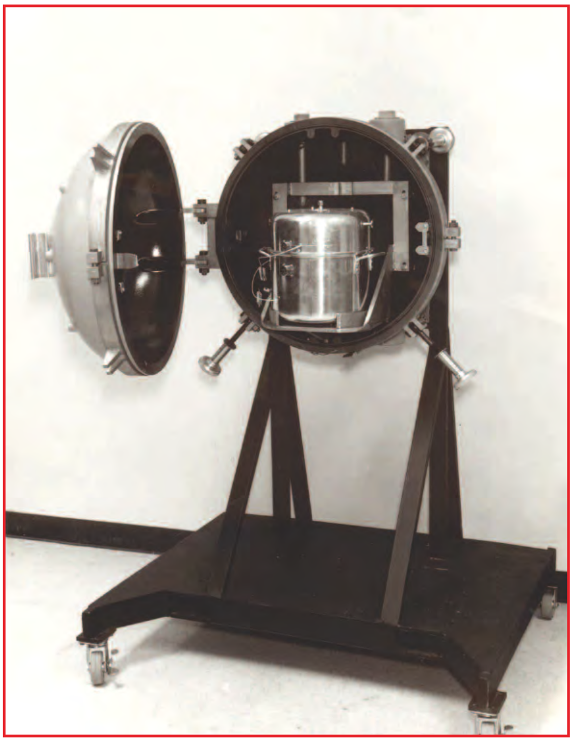
EV+ ARC

BPC

History

History

The ARC has been the unique adiabatic calorimeter of choice from the late 1970s to today.



The original ARC

Accelerating Rate Calorimeter has a long history of being the favoured technology to study lithium batteries. Clearly this is down to the ARC's...

- Ability to accommodate large samples
- Rugged and Robust construction
- Possibility to connect cables in-situ to allow charge and discharge
- Quality adiabatic control

Lithium and sulphur dioxide batteries were being investigated over 30 years ago – the first publication known to THT being *Eber W. B & Ernst D. W, Power Sources Symposium June 1982; Safety Studies of the Li/SO_2 system using Accelerating Rate Calorimetry.* The Li/SO_2 battery being a primary cell considered for defence applications.

However the major impetus for Lithium battery use was triggered by the advent of the Li-ion secondary 18650 cells pioneered from the mid 1990's by Sony. Sony was the first company to buy a THT ARC system for battery studies.

Initial studies were using 18650 cells and centred on stability and safety – and improvements to stability with changes in chemistry. This work either at cell level or at component level was the primary work carried out in the later 1990's and early 2000's.

The focus on safety at this time was crucial due to applications in cell phones and laptop computers – and well documented incidents that led to hugely expensive 'recalls'. The manufacturers were predominately Japanese companies.

From the year 2000, application areas expanded rapidly; large format (prismatic and pouch cells) appeared. The potential to use the ARC to study cells and small modules in situ under a variety of use and abuse conditions was realised. Within the period of 2000 - 2010 THT worked with organisations around the world to implement the options described in this brochure.

From 2005 and until today large format cells have become more established for high power applications. This led to challenges that THT has met with the large format calorimeters EV+ and BPC.

Key users of THT ARC systems now are Tier 1 automotive OEM's, their suppliers and specifiers.

It seems likely that most application areas have been addressed though in the future new challenges will no doubt arise which THT will aim to fulfil.

4 Key Tangible Benefits from THT

- Latest Hardware and latest Labview Software
- Highest Sensitivity, Widest Performance Features
- Large Volume EVARC and BPC Calorimeters
- Integrated Cycler & Battery Abuse Options

4 Key Intangible Benefits

- Largest Global Customer Base
- Most Experienced Technical Personnel
- Lifetime FREE Phone & -E-Mail Support
- Worldwide Offices & Support

Specification

ARC Common Components

- Safety; up to 2 cubic meter containment vessels (allows options); reinforced 3mm steel; proximity switch, door interlock.
- Electronics 3kVA or 7kVA power supply system
- Workstation with Microsoft Windows and NI Labview™; flat screen monitor, keyboard and mouse
- Real Time software in NI Labview; on-the-fly conditions change and full control; remote operation
- Remote User; ability to transfer operation of system to any allowed PC over network or internet
- Virtual Technician; ability to set up multiple tests in one method
- Modes; Adiabatic; quasi Isothermal; true Isothermal; Isoperibolic, Ramping
- Operation in air, vacuum, inert gas, reactive gas, flowing gas
- Adiabatic control to 0.01°C
- Pressure resolution 0.005bar; precision 0.02%; accuracy 0.05%
- Sample holders; ARC Bombs, low phi holders, tube bombs, special open or closed holders for any battery type
- Data Analysis software in Labview with ability that includes
  - Graphical and tabulation of raw data including Phi Corrected tmr plots
  - Data Conversion to Enthalpy, Power, Gas Generation
  - Kinetic Modelling for thermodynamic and kinetic data analysis
  - Phi Correction through kinetic modelling
  - Report generation in Microsoft Word, Excel, html
  - Analysis of 9 data sets; 3 analyses on each data set, 5 merge datasets
- Temperature resolution 0.001°C; precision 0.01%; thermocouples external and internal
- Vacuum to 200 bar pressure range (10-2000 bar with alternative transducers)
- Lifetime email and phone support, 1 Year warranty
- Testing to CE, UL, VCCI, CSA standards

Standard Calorimeter

- Fully compliant to ASTM E1981 E27
- Calorimeter design to Dow Patents of 1980 and 1984
- 10cm diameter 10cm depth calorimeter
- Temperature range 0-600°C (-40°C with cryogenic system)
- Sensitivity: 0.002°C/min to 200°C, 0.005°C/min to 400°C; 0.010°C/min to 500°C
- Tracking Rate to 20°C/min
- Gas Collection via canister
- Pneumatic Nail Penetration Option

EV Calorimeter

- 25cm diameter 50cm depth
- Temperature range 0-400°C (-60°C with cryogenic system)
- Sensitivity 0.02°C/min
- Gas collection via canister
- Collar for abuse testing
- Thermally guarded cable insert
- Pneumatic or Control Speed Nail Penetration Crush option

EV+ Calorimeter

- 40cm diameter 44cm depth
- Temperature range 0-300°C (-60°C with cryogenic system)
- Sealed lid designed for integral gas collection
- Automatic electronic safe lid lift
- Sealed lid pressure limits 0 to 1 bar over pressure
- Integrated video monitor
- Integrated Inert gas purging facility
- Integrated Battery Cable Connectors
- Pneumatic or Control Speed Nail Penetration Crush option

BPC

- 50 x 65cm elliptical x 50cm depth
- Temperature range -35 to 200°C (with refrigerated circulating bath)
- Sensitivity 0.01°C/min
- Integrated Battery Cables

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