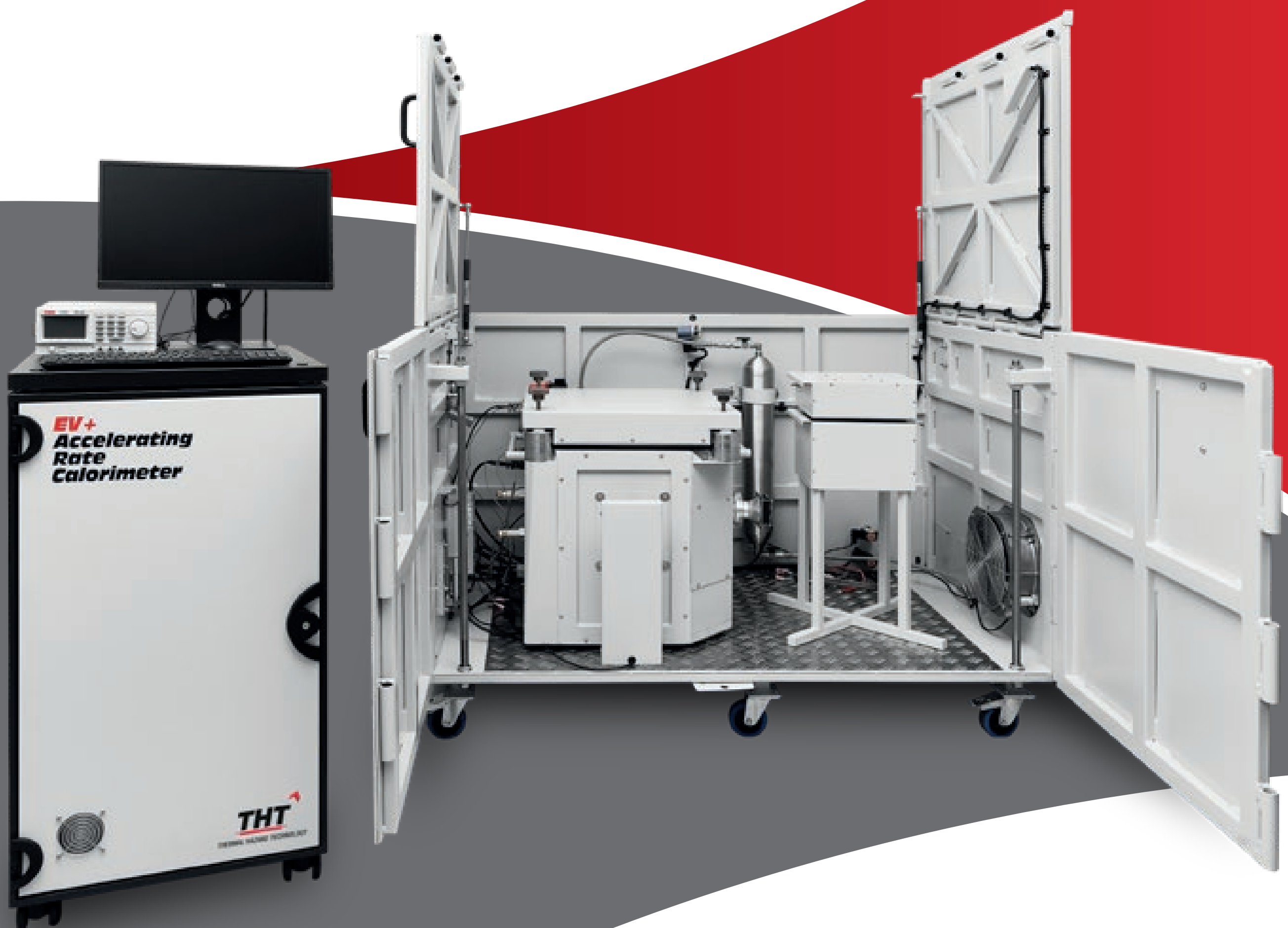
THT
THERMAL HAZARD TECHNOLOGY

ARC® Accelerating Rate Calorimeter

The World Benchmark Battery Testing Calorimeter Systems

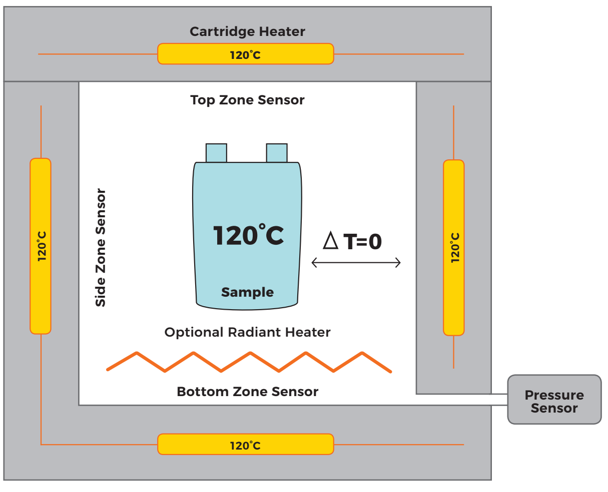


Lithium batteries are hazardous - it is important to determine both the effect of heat on lithium batteries and the heat that results from their use and abuse

Introduction

Adiabatic Calorimetry provides vital thermal data in battery development, safety, performance, efficiency and life.

The lithium-ion battery was first commercialized in 1991 by Sony and Asahi Kasei. Offering what was considered acceptable stability combined with excellent energy density, the lithium-ion battery became a key component in the portable electronics revolution. As the energy density of these cells gradually increased to fulfil the power demands of new applications, dangerous thermal runaway events became more common. Researchers required a tool to understand these processes.



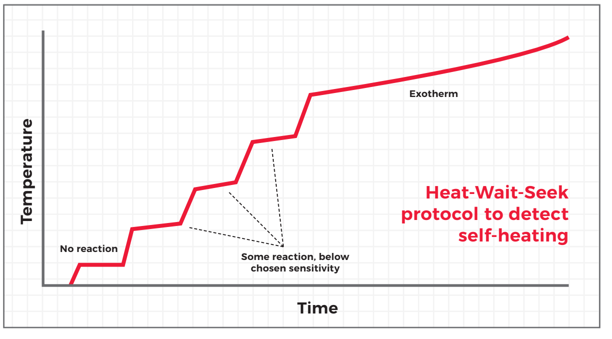
The Accelerating Rate Calorimeter (ARC) was devised by the Dow Chemical Company in the 1970s and was commercialised in 1980. This technology was developed to simulate exothermic runaway reactions from hazardous and reactive chemicals at safe laboratory scale. This is facilitated through adaptive adiabatic control: In operation, the calorimeter temperature aims to match the sample temperature while a reaction is occurring. Therefore as a sample self-heats and its temperature rises, so does the calorimeter temperature. There is minimal heat transfer between the sample and the surroundings. The "worst case" conditions are evaluated and a real life hazard scenario is simulated.

The wide 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 critical for battery work. The ARC is robust and rugged enough to withstand explosive battery decompositions, with the system designed to contain the significant energy released during thermal runaway.

For accurate detection of exothermic reactions the ARC employs a 'heat-wait-seek' (HWS) protocol which is slower, but far more accurate than a simple temperature scan. In HWS, small heat steps are applied and after a wait period for isothermal equilibrium, there is a seek period to detect heat release by temperature rise. When this occurs the system automatically switches to exotherm mode and tracks the heat release, accurately following and recording the temperature rise.

HWS tests are run on complete batteries at any state of charge or age.



A range of additional abuse tests can be performed under adiabatic conditions, including short circuit, overcharge, nail penetration and crush. The layout of the calorimeter enables easy connection to a battery cycler or test system, allowing vital temperature, voltage and current data to be obtained under conditions of charge and discharge (including the rapid discharge needed for automotive applications). Multiple thermocouples can be added to any test type. ARC experiments are also invaluable for groups studying battery components in order to develop chemistries that optimise specific power requirements and increase their inherent safety.

The ARC is therefore an ideal tool to evaluate both performance and safety aspects of lithium batteries

System Choice

Batteries come in many shapes and sizes. THT uniquely provides instrumentation to test components to large EV batteries in one system. This novel modular design allows extra features to be added as necessary without prohibitive upgrade costs. All feature advanced safety mechanisms, including automatic door locking, fume extraction, a software independent heating fail-safe and blast-proof reinforced steel enclosure.

ES ARC

9x10cm Chamber Size

- World's best-selling and benchmark adiabatic calorimeter
- Calorimeter choice: Standard only
- Sample range - components to small pouch/cylindrical
- Electronics housed in lower section with calorimeter sited in upper section blast box
- Working volume: 0.25m^3

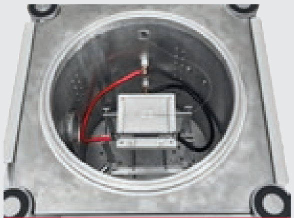
EV ARC

- Mid-sized system
- Calorimeter choice: Standard and EV
- Sample range: components (standard calorimeter) to EV batteries (EV calorimeter)
- Separate electronic cabinet with top opening blast box for calorimeter with fume extraction
- Working volume: 0.57m^3

25x50cm Chamber Size

EV+ ARC

- Largest system
- Calorimeter choice: Standard, EV and EV+
- Sample range: components (standard calorimeter) to small modules (EV+ calorimeter)
- EV+ calorimeter designed to fulfil requirements of Sandia 2005-3123, SAE J2464, USABC / FreedomCAR and UN & UL tests
- Working volume: 1.93m^3

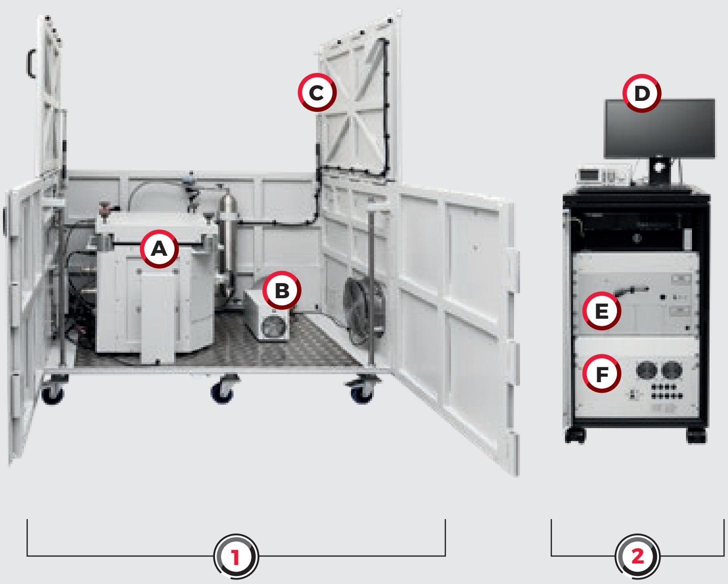


40x44cm Chamber Size

System breakdown

The ARC system can be divided into 2 parts:

The Blast Box – Where the experiment is carried out
The Electronics – For control and data acquisition



(1) Blast Box

A. The Calorimeter Assembly
Where the sample is tested

B. Optional Modules and Cabling
Additional equipment is fixed to the inside of the blast box

C. Blast Box
To protect the user including fume extraction

(2) Electronic Cabinet

D. The Workstation (PC)
The ARC software, allows the user to run tests and log data (Windows based)

E. The ESU/OSU
Control and data acquisition from the calorimeter and options

F. PSU/PSU+
Provides power to the ARC system

Calorimeter Choice

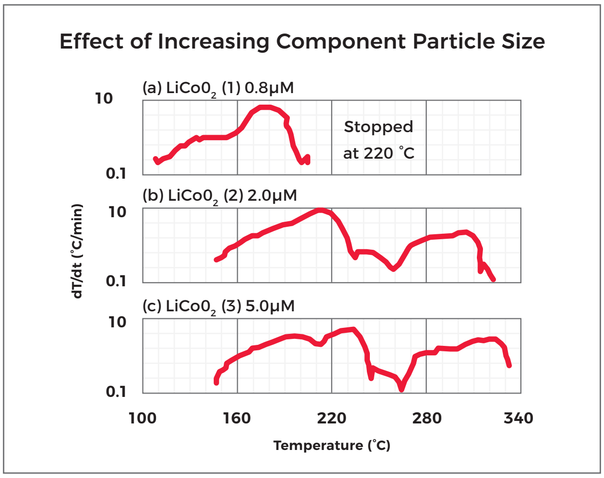
Calorimeter	Standard	EV	EV+
Applications			
Cell components	✓	✗	✗
Coin cells	✓	✗	✗
18650/small cylindrical	✓	✓	✓
Small pouch	✓	✓	✓
Mono cells	✓	✓	✓
Large pouch/prismatic/cylindrical	✗	✓	✓
Small modules	✗	✗	✓
Approximate capacity of DUT	50mAh to 5Ah	500mAh to 100Ah	1Ah to 130Ah
Features			
Video camera	✗	✗	✓
'Closed test' canister pressure measurement	✓	✓	✓
Integrated cables for current / voltage measurement	✗	✗	✓
Independent safety cutout	✓	✓	✓
Embedded heaters	✓	✓	✓
Options			
KSU Integrated single channel battery cycler – customer specified voltage and current range	✓	✓	✓
NPCO Pneumatic nail penetration and crush	✓	✓	✓
NPCO-CS Controlled speed nail penetration crush option	✗	✓	✓
CPU Automatic specific heat capacity measurement up to 200˚C	✓	✓	✓
MPO Multipoint thermocouple for spatial distribution measurement	✓	✓	✓
SCO Button operated electronic contactor for external shorting of batteries	✓	✓	✓
LNFO Liquid nitrogen flow for low temperature application, -40˚C start temperature	✓	✓	✓
SSU Gas collection, 4 samples – automatic collection at any time, temperature or pressure	✓	✓	✓
SSS Single sample gas collection during or after test into collection vessel, up to 4 litre sample	✓	✓	✓
PRU Pneumatic raising and lowering of calorimetrer lid	✓	✗	✗
RHA Motor driven lifting and rotation of calorimeter lid	✗	✓	✓
SGU Integrated unit for software-controlled spark generation	✗	✓	✓
IRU IR camera for in-situ thermal imaging	✗	✗	✓
ETU Provides output voltage signals based on test mode to trigger external tester	✓	✓	✓
UPS Maintains operation for up to 1hr in the event of power failure, includes smart shutdown routine	✓	✓	✗
VMO/CMO Separate options for logging cell voltage or short-circuit current without integrated cycler	✓	✓	✓

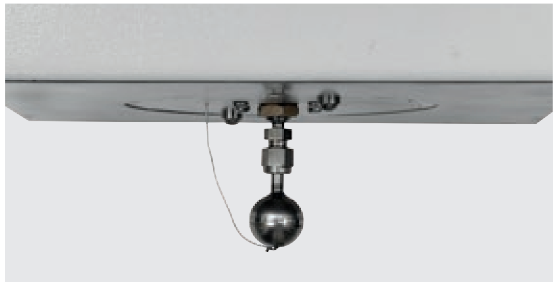
Calorimeter	Standard	EV	EV+
Chamber dimensions	9cm diameter x 10cm depth	25cm diameter x 50cm depth	40cm diameter x 44cm depth
Temperature range	Ambient* to 600˚C	Ambient* to 450˚C	Ambient* to 300˚C
Thermocouple specification	Resolution 0.001˚C Precision <0.2% Accuracy 0.7%	Resolution 0.001˚C Precision <0.2% Accuracy 0.7%	Resolution 0.001˚C Precision <0.2% Accuracy 0.7%
No. of heaters	8	8	8
Pressure range	0-200 bar	0-200 bar	0-14 bar
Sensitivity	0.005˚C/min	0.02˚C/min	0.02˚C/min
Safety	0.25m³ blast box	0.57m³ blast box	1.25m³ blast box
Control modes	Adiabatic Ramping Isothermal Isoperibolic Step Isothermal	Adiabatic Ramping Isothermal Isoperibolic Step Isothermal	Adiabatic Ramping Isothermal Isoperibolic Step Isothermal
Control / Analysis Software	NI Labview based	NI Labview based	NI Labview based
Electrical requirement	200-250V, 16A 3.5kW	200-250V, 16A 3.5kW	200-250V, 32A 7.0kW
Dimensions (L x W x H)	**Electronics Unit and Blast Box** 80cm x 70cm x 167cm **Blast Box (door open)** 80cm x 150cm x 167cm	**Electronics Unit** 55cm x 60cm x 107cm **Blast Box** 123cm x 98cm x 97cm **Blast Box (door open)** 123cm x 98cm x 192cm	**Electronics Unit** 55cm x 60cm x 107cm **Blast Box** 167cm x 105cm x 116cm **Blast Box (door open)** 187cm x 105cm x 194cm

* -40˚C with LNFO option

Component Testing

- Standard calorimeter.
- Testing of anode and cathode materials, component mixtures, lithiated carbon, delithiated oxide and electrolyte.
- Allows evaluation of the change in self-heating of the material, including novel formulations, particle size and particle shape.





Standard ARC bomb

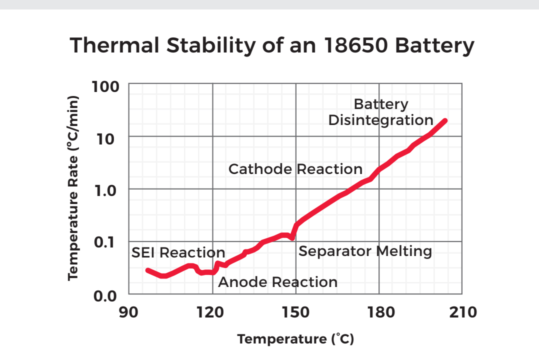
Tube bomb

Cell Testing

The simplest battery ARC test is a “heat-wait-seek” thermal abuse experiment run in either an“open” or “closed” configuration.

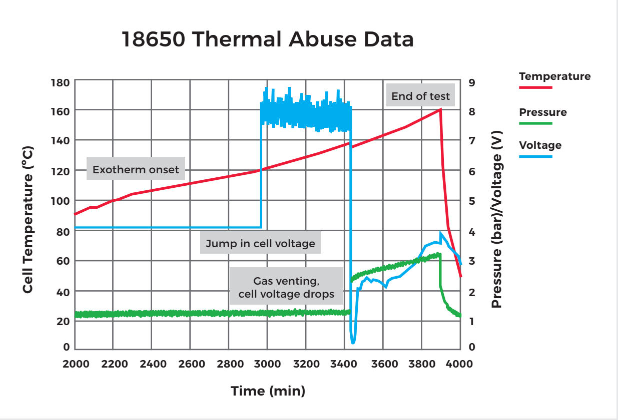
Open Test

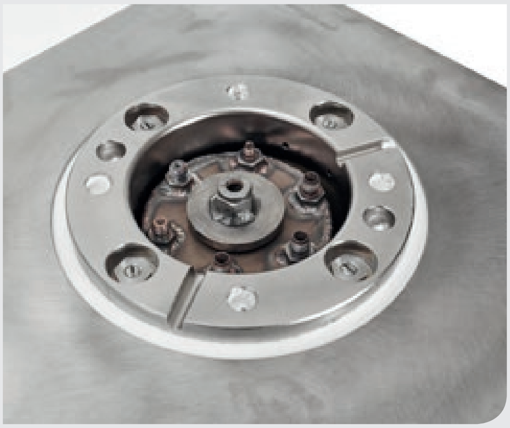
- Cell placed directly in the calorimeter chamber with a thermally isolated holder to support the cell.
- Open test provides best thermal data, as no thermal barrier created by the presence of a canister.
- Gas vented from the cell leaves the calorimeter and is extracted from the ARC.
- Allows optical or IR monitoring of cell when utilising EV+ calorimeter.



Closed Test

- Cell placed inside a sealed canister which is then placed in the calorimeter chamber.
- Gases resulting from the test are captured inside the canister.
- Heat from these gases transfers into the canister and the temperature rise in the canister gives an indication of the thermal energy contained in the venting gases.
- Pressure and cell voltage are measured providing information about the condition of the cell throughout the test.





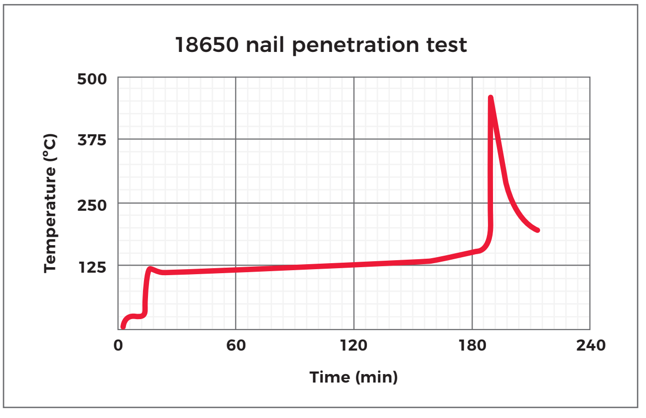
Canister Selection

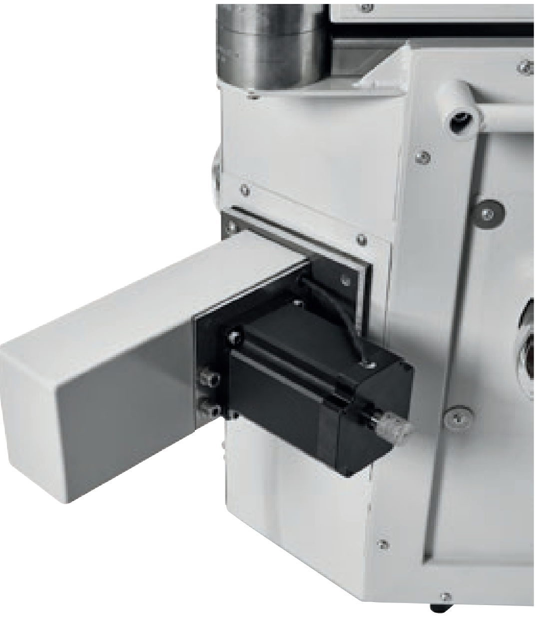
- As a general rule, a cell may generate 3 bar per amp-hour at peak pressure, but this can vary significantly, depending on cell SoC and chemistry. The peak pressure in the vessel should be below the safe operating pressure.
- Gas collection cylinders can increase the volume for gas dissipation and thus lower the peak pressure.

The nail penetration test is an industry standard method to simulate an internal short in a cell

Nail Penetration & Crush

- Option allowing testing on small to large cells.
- Available in pneumatic or motorised form.
- Speeds from 0.5mm/sec to 10cm/sec.
- Forces up to 34000N.

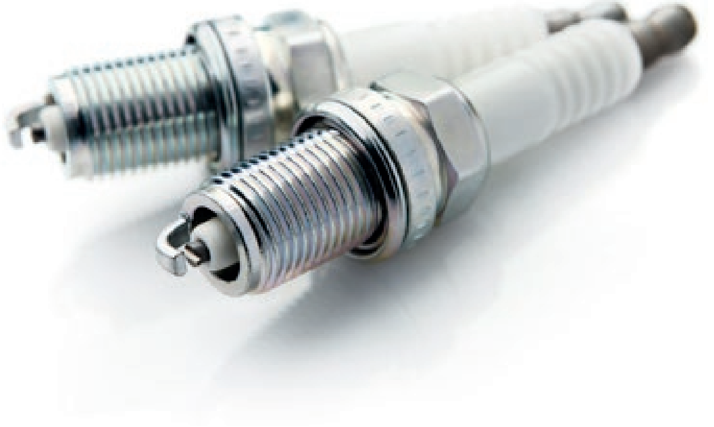




Spark Generation

- The severity of a thermal runaway and cell decomposition can depend on the presence of a spark. Without a spark, flammable gases may fail to ignite. In a real world failure scenario it is likely that an ignition source would be present.
- The SGU uses a spark-plug to create a continuous spark source at a single point. In order to correctly position the spark plug next to the cell vent region, there is a frame supplied with the SGU which can support cylindrical or prismatic format cells.
- Controlled via the ARC software of the test. The firing conditions for the SGU are as follows:
- **Activate at the start of test**
- **Activate at a set temperature**
- **Activate when the ARC enters exotherm mode (e.g. a reaction is detected in the cell)**

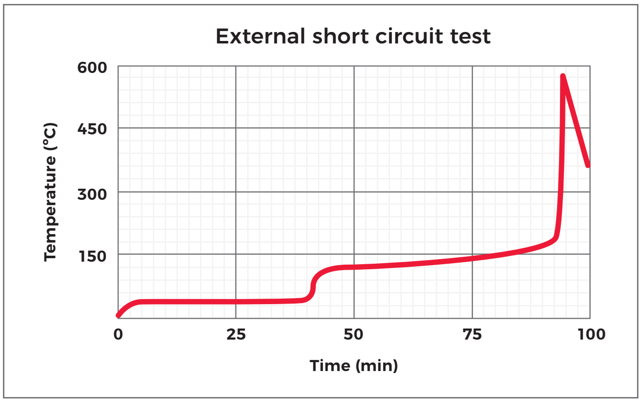
The SGU is available for EV and EV+ calorimeters and if used with the EV+ allows the ignition event to be filmed.



Abuse Testing

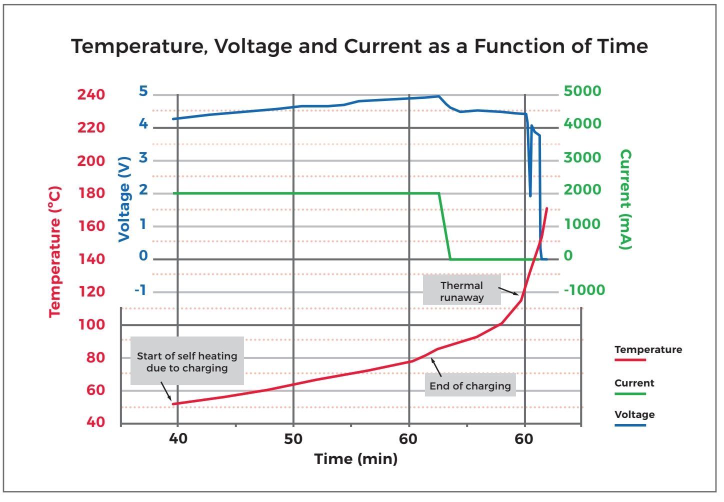
Short Circuit

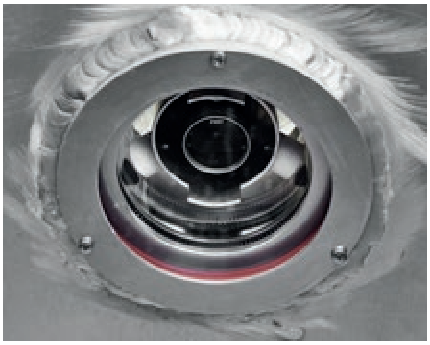
- Short-circuit option (SCO) allows remote shorting of cells in the ARC.
- Short is carried out through a low impedance contactor box.
- Short circuit current can be independently measured at high frequency via a current transducer to verify the severity of the shorting current.
- Designed to carry a load of up to 2750A for 10 seconds.
- SCO activation button on electronics unit.



Overcharge

- Overcharge carried out using integrated KSU option, or stand-alone power supply or cycler.
- ARC tracks rapid heating of cell during overcharge procedure to maintain adiabaticity.

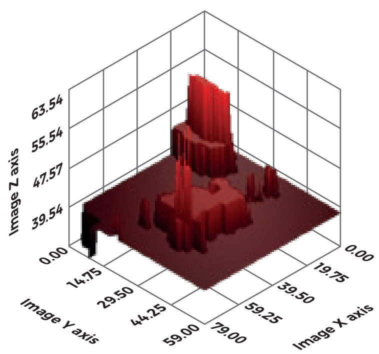




Video Monitoring

- Air cooled high resolution camera 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.
- Optional IR camera with IR transparent window for in-situ thermal imaging.
- IR is used to determine the spatial temperature distribution on the surface of the battery. In cycling tests this could help determine the areas of significant heat generation (e.g. the tabs).
- During safety testing the IR camera identifies the hottest points on the cell during a thermal runaway and the temperature of venting gas. It removes the need to attach many different thermocouples to the cell surface.

X and Y axis correspond to each pixel of the image, Z axis is the temperature identified within the IR image



Gas Collection

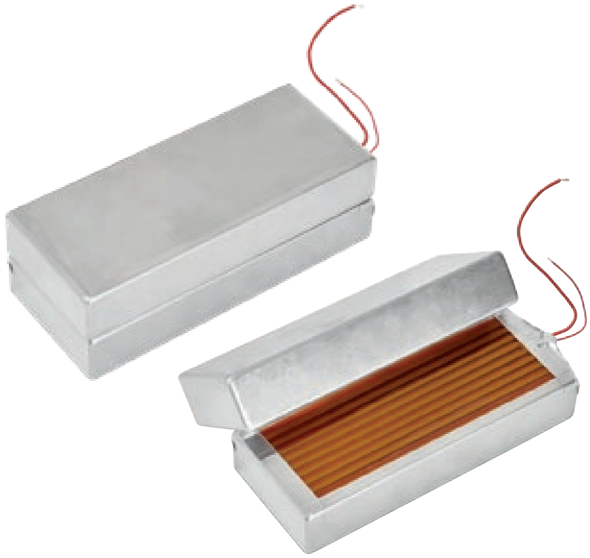
- Purpose designed options allow collection of vented gas after test or at a temperature or time prior to the end of test.
- Manual option for gas collection through a non-return valve.
- Automated option for collection of up to 4 gas samples at selected temperature or pressure values.

Performance Tests

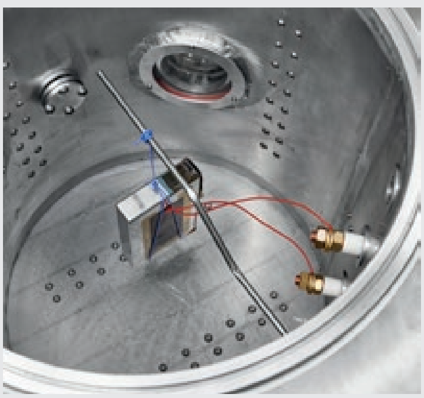
Heat Capacity

For design of thermal management systems in any battery application it is necessary to quantify the heat production rate during use. 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).
The heat capacity option enables this.

- Range of heater mats for different cell sizes.
- Thin Kapton-insulated heater.
- In the fully automated form the power supply is integrated with the ARC system and heat capacity is calculated with the ARCCal+ analysis software.
- Applicable to all battery formats.

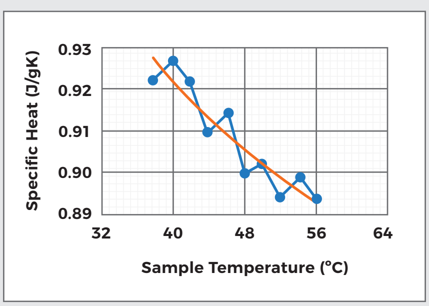


Specific heat capacity determination



To test specific heat capacity, the battery sample with heater is suspended in the calorimeter either from the lid or side connection points. The heater is wired to the variable DC power supply which is automatically controlled using the ARC software. Once the test is complete, the data can be loaded in the ARCCal+ software package. This software generates a graph and best-fit equation relating heat capacity to sample temperature. In this way the change in heat capacity with cell temperature can be determined.

Heat capacity of a small module

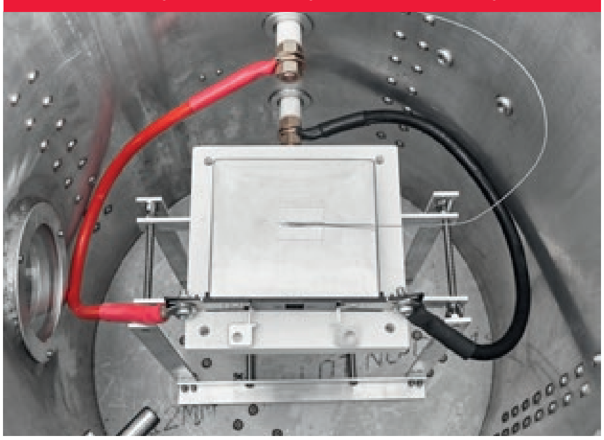


Charge & Discharge

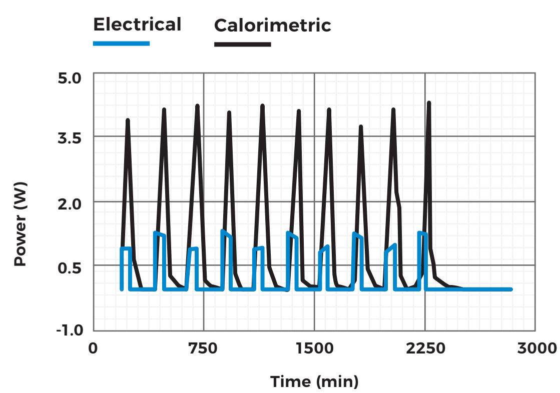
Cycling of cells in the ARC may be carried out adiabatically (chamber temperature tracks sample temperature) or isoperibolically (chamber maintains a constant temperature) depending on the test requirement. Adiabatic cycling inside the ARC allows measurement of the heat released from the cell during cycling once the heat capacity is measured. The ARC is designed to allow easy cable access between cell and cycler for all calorimeters and cell types.

- KSU option - Integrated single or dual channel battery cycler.
- Voltage Range: 0 V > 50V.
- Current Range: 1mA > 600A.
- Integrated software - one data file for synchronised temperature, pressure, current and voltage measurement.
- 3rd party cyclers can be activated using signals from the Electronic Trigger Unit 5V output.

Battery in use (Lifecycle and efficency)



Charge/Discharge Cycles



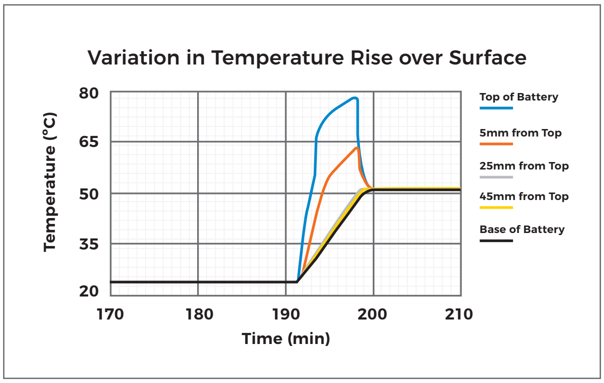
Measurement of surface temperature variation

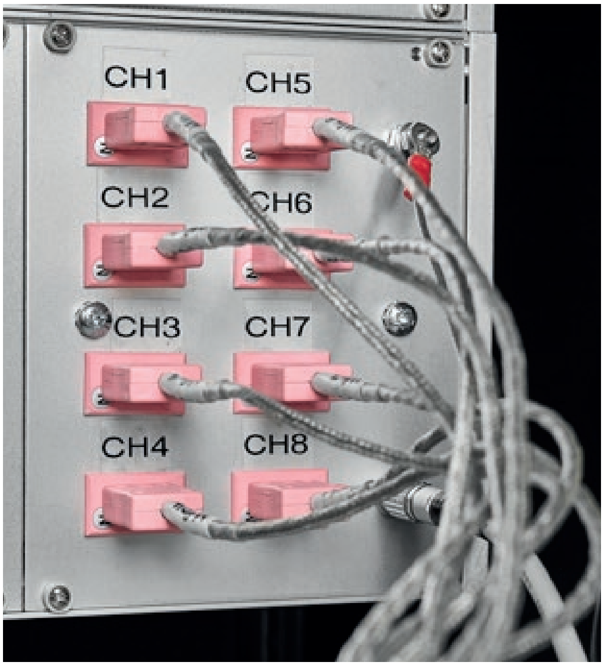
Heat release from batteries is not spatially uniform. Heat may conduct through metal components or collector plates causing greater temperature rise at the terminals compared to the battery case.

The MultiPoint Option (MPO) provides a multiple thermocouple facility to achieve measurement of thermal distribution over the surface of the battery, pack or module.

- 8, 16 or 24 thermocouple configurations.
- Temperature from all thermocouples is recorded in single ARC data file.
- MultiPoint calorimeter tests obtain data more accurately than open bench tests. In the calorimeter the environment is controlled and unknown and unquantified heat loss is minimised. Conditions are worst case and the final equilibrated battery temperature is recorded. Heat effects using such calorimeters are carefully quantified.
- Multi-track functionality enables adiabatic tracking of hottest measured point throughout the test.

Heat Release Distribution





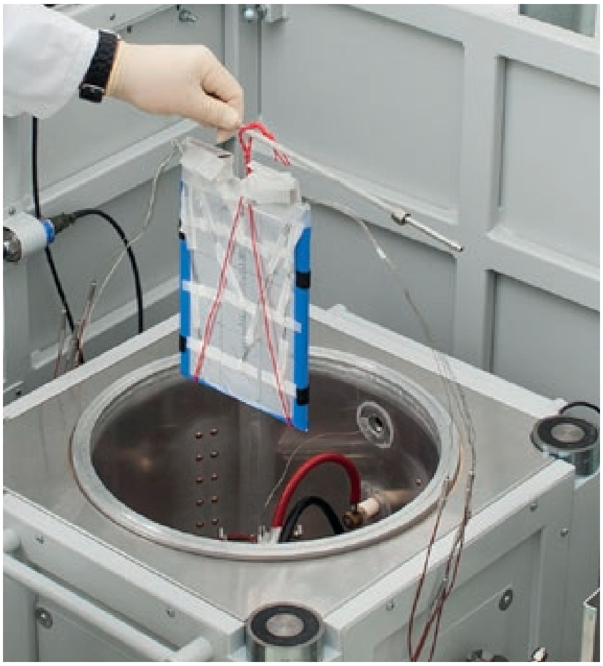
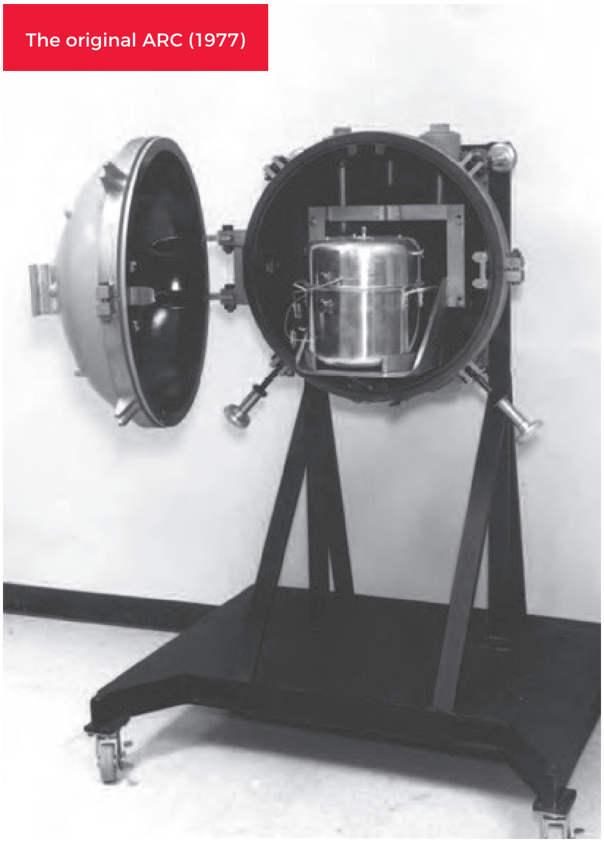


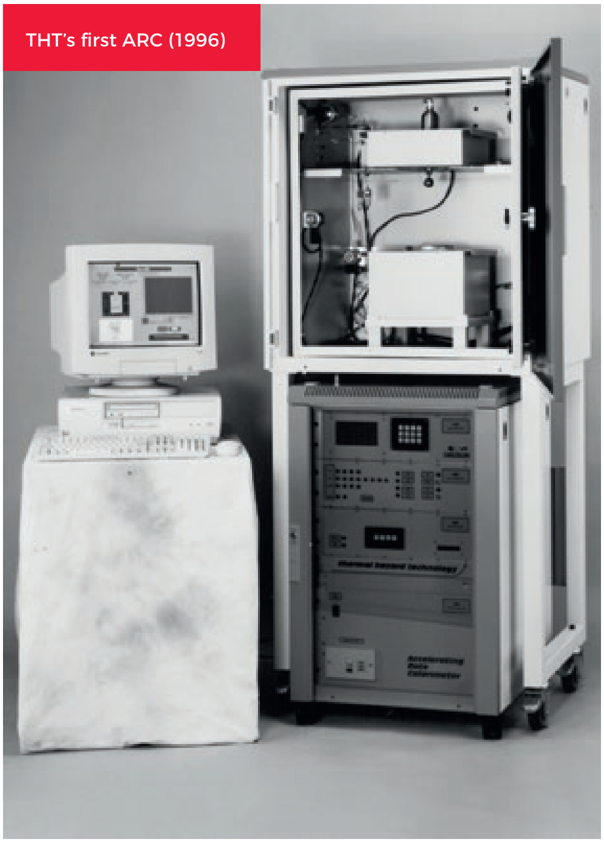
Image courtesy of Dr Carlos Ziebert, Head of Battery Safety Centre, Karlsruhe Institute of Technology.

EV+ inbuilt current and thermocouple ports allow for convenient test set-up

History

Accelerating rate calorimetry has a long history of being the favoured technology to study lithium batteries.





Lithium and sulphur dioxide batteries were being investigated by ARC over 35 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/SO2 system using Accelerating Rate Calorimetry.

ARC calorimetry is our passion and our core business. We have been working with the ARC since the 1980s and developed our first ARC in 1996. As the industry has evolved, so have our products. 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.

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 leading to the development of specific options (e.g. NPCO: nail penetration and crush option).

"ARC calorimetry is our passion and core business."

From the mid 2000s onwards, large format cells became more established for higher power applications. This led to test requirements that THT has met with the large format EV+ calorimeter. THT continues to develop new calorimetric systems to address the challenges faced by the battery industry.

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

Selected Users of THT ARC

Our range of adiabatic calorimeters are utilised in the majority of the world's lithium battery manufacturers as well as government laboratories and universities worldwide.

Service & Support

THT offer expert training with lifetime email and telephone support. Operating to ISO9001 THT enjoys an exceptional reputation amongst leading scientific and industrial organisations worldwide.

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