

# Introduction

Li-ion batteries are currently being developed in many shapes and sizes. A variety of chemistries are being pioneered and new types are being developed. The safety issue that exists is well known and a major part of this development effort is to get a chemistry that gives good thermal stability under conditions of abuse and normal use.

Several test methods have been used but the Accelerating Rate Calorimeter has become recognised as a technique that can quantify their hazard potential.



Fig. 1

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To study larger batteries, perhaps as used for EV, HEV, storage or space use of a larger calorimeter is required. To accommodate such batteries we have also developed the EV-Accelerating Rate Calorimeter.

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# THT ARC

At Thermal Hazard Technology we have developed an Accelerating Rate Calorimeter and have modified this to be of specific use for battery testing. This instrument is now commercially available – and a testing service is available.

This technology is introduced here and examples show how it is used to gain safety information on Li-ion batteries.

The modified standard Accelerating Rate Calorimeter and a close up of the actual calorimeter are shown (Fig.1 & 2). The calorimeter can contain batteries of all shapes and sizes up to 26650 or mobile phone style prismatics and Lipolymer batteries.

Using special sample holders battery materials (e.g. anode or cathode material, electrolyte, SEI can be tested).



The pictures below show this calorimeter and illustrate how much larger it is when compared to the standard unit (Fig. 4). With these two calorimeters it is possible to perform safety tests on all types of Li-ion battery. Figures 5 and 6 show an 18650 battery as to be tested within the standard unit and a notebook battery pack to be tested in the EV system.



Fig. 3









Fig. 5

Fig. 6

Accelerating Rate Calorimeter testing of battery materials and components has been pioneered by Jeff Dahn and his group now based in Dalhousie University in Halifax, Nova Scotia. He has published data on many types of anode and cathode material and data on electrolyte material and SEI. We have concentrated on the testing of complete batteries.

Batteries can be tested either in open configuration, where their container becomes the 'sample holder' or it is possible to test the battery held within a purpose designed holder. In this way pressure information can be obtained.

However there is a risk of explosion that could cause damage to the instrument. To minimise this, a burst-disc assembly has been developed – to allow pressure relief.

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# Safety Testing of an 18650

The battery is contained within the Accelerating Rate Calorimeter and the test is performed by heating first to a chosen start temperature (below the onset of heat release or exothermic reaction). Subsequently the sample is heated in small heat steps.

After each heat step, there is a wait period to allow isothermal stability. After the heat step, there is a seek period where the system will determine if the battery is self-heating, i.e. if the temperature is rising.

When such exothermic reaction is observed, the instrument will switch to the adiabatic tracking mode. The self-heating reaction will be quantified with time.

Under the adiabatic (worst case) conditions, the heat output will usually accelerate – until either explosive decomposition or until the reaction has completed.

The battery can be tested under any conditions of charge. Typically with a charged 18650 reaction onset is observed near 90°C. The reaction accelerates until near 200°C explosive decomposition results. Discharged batteries will typically show onset at a temperature 20-40°C higher. A similar variation in onset temperature has been found with varying chemistries.

The time-temperature-pressure worst case data can then be presented in a variety of formats. The data can be presented on simple graphs, for example heat rise against temperature, graphs showing self-heating with temperature or it is possible to make kinetic and thermodynamic analysis of the data using the analysis software package, ARCCal+.



The same data can be presented as Time to Maximum Rate, where under worst case the time to explosion from any temperature can be determined. Such tests will quantify the safety and hazard potential of the battery itself.

We have produced two units that integrate within our Accelerating Rate Calorimeter to allow the battery under test to be subjected to normal use or abuse operations. In this way such in situ tests can be programmed within the instrument and the data produced obtained by the instrument PC for data analysis by a modified version of the software.

The Accelerating Rate Calorimeter becomes a dedicated Battery Safety Calorimeter.

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The Battery Safety Unit (BSU) allows various abuse testing to be carried out. The tests that may be programmed include shorting tests and overvoltage charging and discharging tests. The battery may be held within a pressure tight holder or may be simply suspended from the calorimeter lid.

Figure 8 shows how the leads are fed though from a battery holder – it also shows a prismatic battery sample holder.



Fig. 8

Shorting a battery will produce a rapid temperature rise, but this may or may not be sufficient to cause the explosive runaway to commence. Should this happen, the battery can be seen to have a significant risk factor.

The data from the mobile phone prismatic battery given below shows that for this example, shorting causes the temperature to rise 100°C in 2 minutes and the final temperature is high enough for the explosive reaction to occur. The battery underwent explosive decomposition 15 minutes after shorting occurred (Fig. 9).



Applying an overvoltage can be shown to cause either rapid self-heating to explosion or there may be 'shut-down' and the battery may be thermally stable to its usual decomposition temperature. Such differently observed behaviour is shown in Fig. 10 and 11 – indicating a remarkable difference in the safety behaviour of two rather similar batteries.



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Fig. 11

The Battery Cycler Unit (KSU) is the option that allows charging and discharging and multiple cycling under a variety of electrical conditions.

The unit integrates a commercial single channel cycler. Under isothermal or heat-wait-seek conditions the cycling can be carried out simultaneously with the thermal test. In this way it is possible to quantify the heat that may be generated or absorbed by discharging and charging cycles. But it is also possible to determine how the heat effects change with repeated cycling.

It is therefore possible to determine information on the efficiency and lifetime properties of the battery.

Figure 12 shows the heat release from continual discharge of a large EV-style battery will raise the temperature at a steady rate. In this test the discharging was stopped for fear of explosion.







Figure 13 shows the general pattern of heat production and absorption during repeated cycling. Here it is possible to observe the heat produced with each discharge cycle and the heat changes that occur with every charge cycle.

The charge cycle shows an initial heat absorption followed by heat output, the latter indicating inefficiency in energy conversion.

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### Summary

With the Battery Safety and Cycler Options the standard Accelerating Rate Calorimeter is a purpose developed Battery Safety Calorimeter.

This and the EV-ARC purpose designed for larger batteries may be used to study...

- battery components (anode, cathode, electrolyte, SEI)
- batteries (at various charge levels)
- batteries when shorted
- batteries when overcharged or over discharged
- batteries when charged, discharged, cycled ...batteries of any size, to obtain .safety, lifecycle or electrochemical efficiency data

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