# FUTURE ENERGY TECHNOLOGY – THERMAL HAZARDS OF LI-ION BATTERIES

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This article presents the adaptation of a well known Adiabatic Reaction Calorimeter (ARC*), to test the thermal safety of complete batteries and their components over a wide range of conditions. The resulting device, BTC, conforms to the basic design principles of the ARC* but focuses particularly on of flexibility of operation, allowing a wide range of tests to be performed easily and safely. Typical range of tests that are performed will be described and resulting thermal runaway data from commercial Li-ion batteries presented. A new development in this field, the measurement of heat generated while holding the battery temperature constant, using isothermal calorimeter, will also be discussed as this can be used to generate the basis for thermal management systems for high energy battery applications such as electric vehicles.

## 1. INTRODUCTION

Small scale fires involving new batteries in portable computers has already served to highlight the need for better and more extensive battery testing and this is even more important when the battery power levels increase by orders of magnitude and the total energy stored must run a commercial vehicle for hundreds of kilometres. Combined with the fact that a wide range of serious incidents are possible within battery driven cars and other large scale applications, the specification of a universal battery testing calorimeter becomes rather demanding.

Adiabatic calorimeters have become an accepted way to test the safety of batteries primarily because they represent an acceptable "worst case" approximation of the conditions under which batteries are likely to be used. The first commercial version the adiabatic calorimeter was the "ARC" developed by Dow Chemical in the late 1970s and although it has long ceased to exist, the name continues to be used. Essentially, these calorimeters allow the heat generated by the malfunction of a battery to be retained within the battery so that its temperature rises in proportion to the heat liberated and thus enables the consequences of malfunction to be realistically and unambiguously measured. In extreme cases, the temperature can continue to rise more and more quickly (often called a thermal runaway) leading to the generation of vast amounts of toxic chemical gases and the battery can physically disintegrate and possibly catch fire too. If the battery is placed inside a "test cell" that prevents gas release, very high pressures can be generated. The main reason for doing tests in closed containers (test cells) is to accommodate testing of liquids and other small samples (electrolytes, electrodes etc.). When complete batteries in tested in such containers the only advantage is that the amount of gas released can be more reliably measured based on pressure data – until the cell explodes if the pressure gets too high. In general, complete batteries don't need to be tested in closed cells and certainly not if the cells are large.

## 2. ADIABATIC TESTING – HOW AND WHY

An adiabatic calorimeter is essentially an electronic "oven" consisting of several "guard heaters" which control the oven temperature such that heat loss from the test battery is prevented, see Figure 1. The oven temperature relative to that of the battery has to be changed as the test is conducted at different temperatures and as the battery starts to self-heat.

The most common test determines the battery temperature at which problems of thermal runaway start and hence defines the maximum safe temperature. This involves use of a heat-wait-search (HWS) procedure that starts by heating the sample in small steps (see Figure 2) and at the end of each step, the system "waits" to see if the battery is generating heat that can be measured by a temperature rise (so called "search" step).

Doing the same test without an adiabatic calorimeter built for the job would have three main drawbacks:

- The correct maximum safe temperature would not be determined. More likely a temperature higher than the safe figure would be obtained (ie the battery would present a hazard at a lower temperature than predicted from a non-calorimetry test).
- The consequences of the thermal runaway would be understated in terms of severity and speed of incident. For example how hot the battery gets, the amount of fumes generated, the damage to the battery itself and of course how long it takes to produce these conditions would be less severe in a non-calorimetry test.
- A custom-built calorimeter provides a safe environment for operators to carry out the tests. The absence of such provisions can present a serious hazard to the operators.

Commercial calorimeters used for battery testing are either "standard" types that were originally developed for chemical testing or else "custom" units which have been modified for batteries. The former are useful for small scale work, typically for testing battery components and also complete batteries of size up to type 18650 (normally 65 mm high × 18 mm diameter) – see Figure 3 for example.

When large batteries and packs need to be tested, a completely different design is required and the Battery Testing Calorimeter (BTC) is specifically designed for this purpose – see Figure 4 where a normal lead-acid car battery is shown for scale. This has space for battery units measuring 35 cm in diameter and more than 50 cm high and as a result is constructed from thick steel plates to ensure safety under runaway conditions.

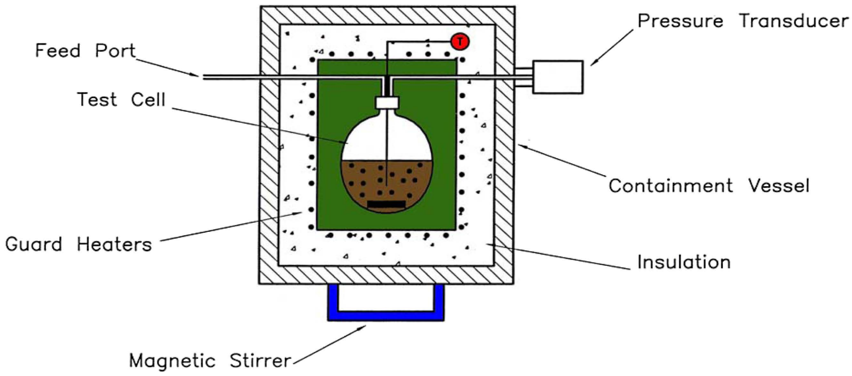


**Figure 1.** Principle components of an adiabatic calorimeter

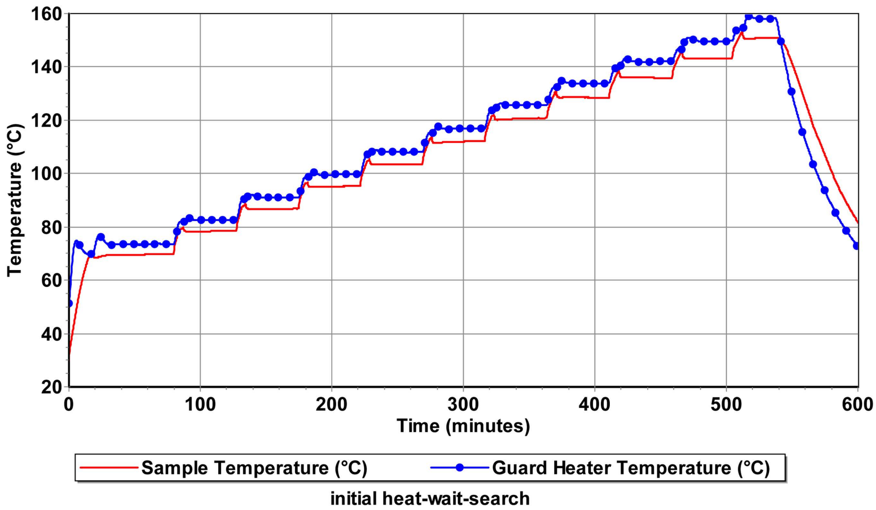


**Figure 2.** Heat-wait-search testing routine for thermal stability

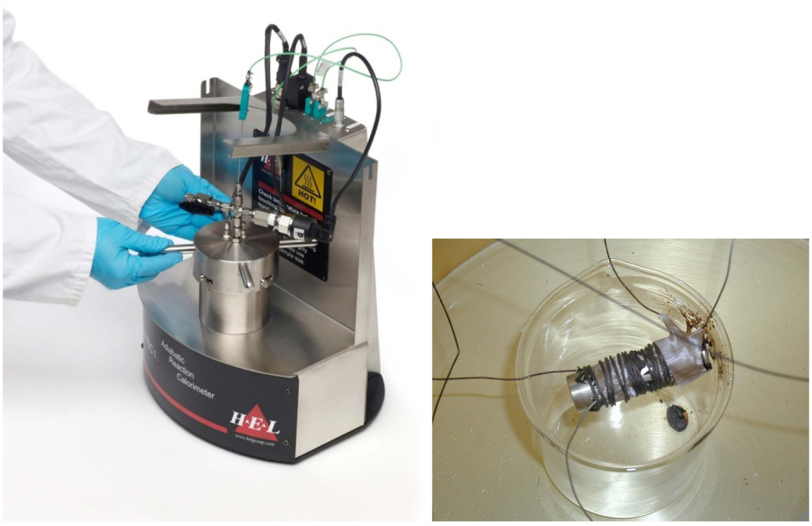

**Figure 3.** Phi-tec I - standard "ARC-type" adiabatic calorimeter for small scale thermal stability testing. An 18650 battery shown after test is such a unit


**Figure 4.** Custom designed Battery Testing Calorimeter (BTC) for larger scale testing

## 3. SAFE WORKING TEMPERATURE AND THERMAL RUNAWAY OF BATTERIES

The heat-wait-search procedure described earlier can be used with cells and large battery packs alike to determine the maximum safe temperature.

The test data for a pouch type Li-ion battery with a 5Ah rating is shown in Figure 5.

In this experiment the "search" procedure starts at around 35 C and since no heat generation is detected (temperature remains constant) the battery is heated again. This stepwise heating followed by a wait period before search, is repeated until self-heating within the battery can be detected (at around 120 C); this is essentially the maximum safe temperature.

When this point is detected, the instrument simply controls the oven (or guard heaters) so that adiabatic conditions are maintained, which means that the battery keeps heating itself until chemicals are consumed or more likely, it blows up or catches fire, often generating lots of toxic products at the same time.

In most cases (as here), the pouch will rupture at some elevated temperature and this often gives the impression that the runaway has stopped – see the sudden fall in temperature after exceeding 300 C, in Figure 5. This fall is often due to the thermocouples measuring the temperature being moved so that they are no longer in close contact with the battery and not because the runway has stopped. The state of the battery before and after the runaway is shown in Figure 6.

## 4. CHARGING AND DISCHARGING LIMITS LEADING TO BATTERY EXPLOSION

While the thermal stability of normal (undamaged) batteries is of huge interest it is also important to determine how the results change under abnormal conditions or when a battery is charged and discharged at too fast a rate. There are huge pressures to speed up charging/discharging; in the context of EVs, charging is the equivalent of filling a tank with fuel and the discharge rate determines the car speed. If the

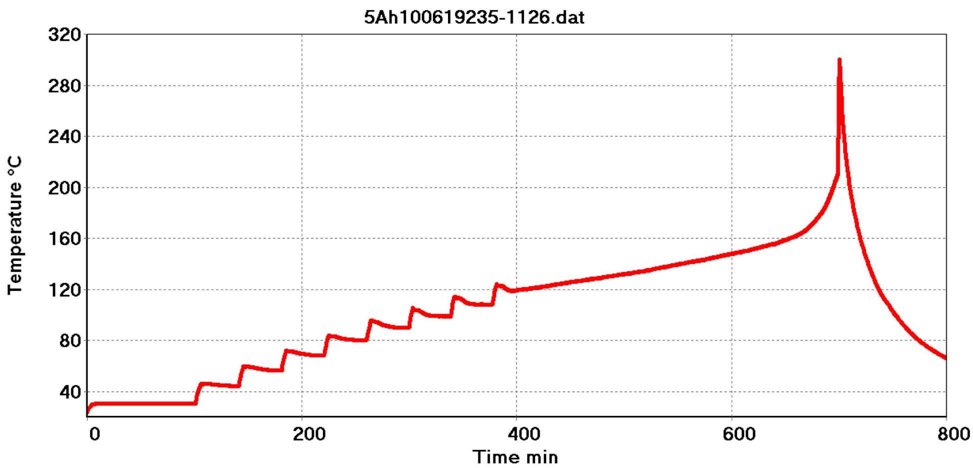


**Figure 5.** Heat-Wait-Search Test to determine thermal stability of pouch type Li-ion battery

**Figure 6.** Pouch battery before and after heat-wait-search Test

battery is connected to a cycler (see Figure 7), while placed in the BTC, changes in the battery temperature during charging/discharging cycles can be measured. The cycler can be programmed to repeat this operation for many days and thereby also provide information about the longer term stability of the battery.

The advantage of placing the battery sample in the BTC during such a test is that the temperature changes will indicate accurately the energy changes taking place in what is close to being a worst case situation where no cooling of the battery is taking place. Results for a 3-cell Li-ion polymer battery are shown in Figure 8.

During charging (at 2A), the battery cools (endothermic reaction) and when discharging (at 3A) heat is produced leading to a rise in temperature. However, overall, there is a rise in temperature after each cycle as the discharge produces much more heat than the cooling effect of charging. Eventually the temperature stabilises at between 55 and 65C.

In this example, the charging/discharging rates are quite safe and although the battery temperature rises, it does not lead to a problem and safe long term cycling is demonstrated.

The same battery was then subjected faster rates of charging and discharging, again while inside the BTC. As before, the temperature rises during discharging (now 15A) and falls during charging (now 5A), but overall there is now a continued rise in temperature and after only a few cycles the battery goes into thermal runaway – the battery being around 110 C when it does so. The results are shown in Figure 9. The BTC can also be fitted with a video camera and some selected images from this are shown in Figure 10.

At this elevated temperature the battery quickly develops an internal short and therefore can no longer be charged. As a result the cycler switches back and forth frantically (hence the pink lines). Clearly, at this discharge rate, the battery would most definitely need to be cooled to prevent runaway, though the cooling duty is not known from this test.


**Figure 7.** BTC calorimeter connected to Cycler

## 5. THERMAL MANAGEMENT DUTY

The changes in battery temperature reported above – which eventually lead to thermal runaway – confirm the fact that heat is produced during cycling but the amount of heat is not directly quantified. Quantification is possible by multiplying the temperature rise by the specific heat of the battery pack. This will not produce precise information as battery specific heat is difficult to measure in a calorimeter due to the uneven nature of the device. It is however now possible to measure this heat directly rather than from adiabatic data. Ideally, this should be done while holding the battery temperature constant – as a battery management system would attempt to do.

This requires the use of isothermal (as opposed to adiabatic) calorimetry and such calorimeters are normally stand-alone devices built for this sole purpose. The BTC (originally designed to be adiabatic) can however be configured to operate in this mode with the addition of extra software and hardware features.

Typical data from this mode operation is shown in Figure 11. Now, the system holds the temperature of the battery pack constant by heating/cooling the as charging/discharging takes place. The data corresponds to heat generation rate in a Li-ion polymer (3-cell) battery at two different discharge rates – 10A and 20A. Hence if these batteries were part of a power system, the cooling rate needed could be calculated directly from this information.

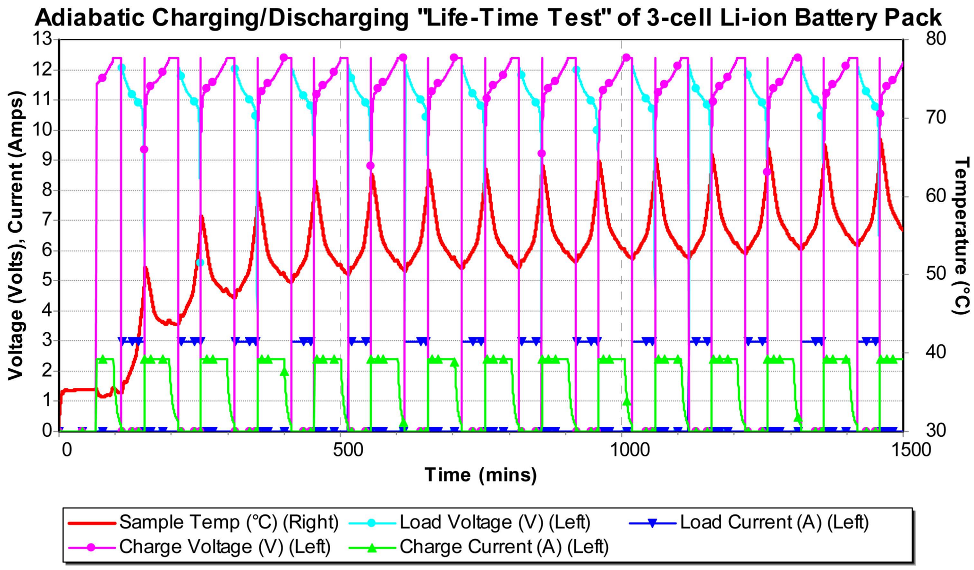


**Figure 8.** Cyclic charging/discharging a battery pack inside BTC

Notice that under adiabatic conditions, this same battery type resulted in a thermal runaway at 15A discharge rate; here, with active cooling to control the temperature, 20A has been achieved without the problem.

## 6. BTC FOR BATTERY "ABUSE TESTS"

The safety testing of Li-ion batteries is also defined in various procedures and some of this data is for example necessary before the batteries can be shipped. These tests mostly involve subjecting batteries to extreme conditions and hence are described as "abuse" tests. Some of them need to be done in and adiabatic calorimeter while others can benefit from the availability of such a device as a means for containing heat and smoke that is often generated as well providing more reliable "worst case" data. Many of the test procedures also specify photographic or video records.

One of the most widely quoted procedures for abuse testing is produced by SAE International (ref 1) and another is by Sandia National Laboratories (ref 2). Most of the tests in these guides are quite similar.

Typically the abuse tests are divided into three categories with several different tests in each:

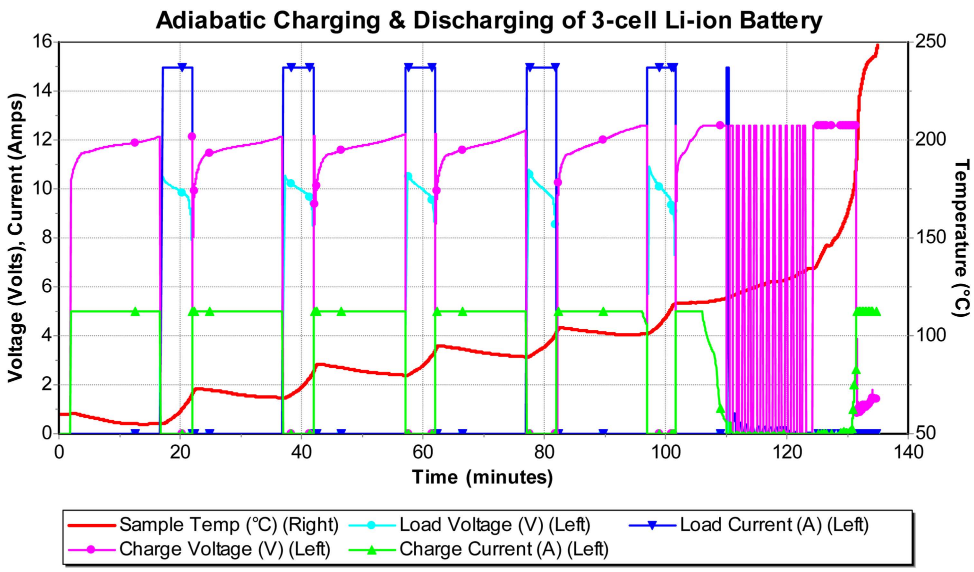


**Figure 9.** Thermal runaway resulting from fast charging/discharging rate

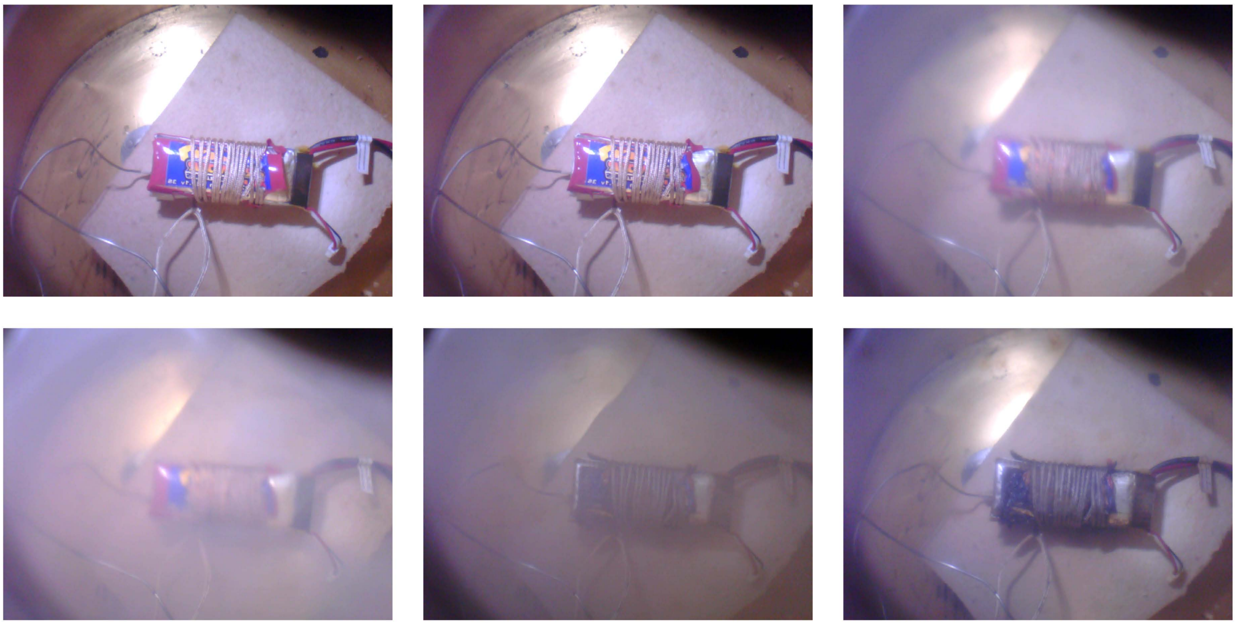

**Figure 10.** Battery undergoing thermal decomposition: Images from Video camera integrated into BTC

(a) Mechanical Abuse Tests
Tests in this category include shock, drop, penetration, Roll-over, immersion and crush. Penetration is one of the important tests and can benefit from being done in the BTC as the test chamber will provide protection in the event of fumes and fire and the any temperature increase can be measured as well as videoed.

(b) Thermal Abuse Tests
Tests include high temperature (essentially fire) exposure, thermal stability, temperature cycling without thermal management, and passive propagation resistance.
Thermal stability is similar to a heat-wait search test and the cycling and passive propagation tests both should ideally be performed in a BTC to get worse case scenario data.

(c) Electrical Abuse Tests
Tests in this category include short circuit, over-charge, over-discharge and separator shut-down.

These tests will often lead to generation of fumes and possibly a fire, so would benefit from the operator protection and data collection provided by a BTC. In addition, as stated earlier, worse-case consequences would be realised if the incidents were initiated under adiabatic conditions. As an

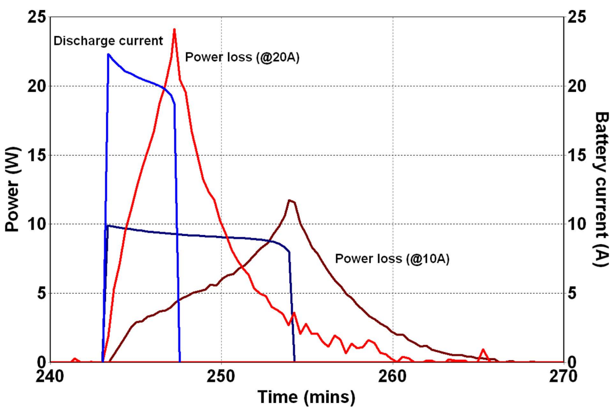


**Figure 11.** Heat generation in Li-ion polymer battery at two different discharge rates using isothermal version of BTC


**Figure 12.** Li-ion Battery after overcharging test in BTC

example, the state of a Li-ion battery subjected to overcharging inside the BTC is shown in Figure 12.

## 7. CONCLUSIONS

The understanding of hazards from of Li-ion and other emerging high energy battery technologies requires calorimetry tools that are fairly common place in the chemical industry. The reliability of the data has withstood the scrutiny of over 30 years of use and therefore provides an ideal platform for this application.

While adiabatic testing is somewhat more established, its use is still very limited and as a result the hazard potential of batteries is rarely understood. The value of isothermal data is even less well appreciated but could be fundamental to providing data need in the design of thermal management systems in high energy applications such as EVs.

## REFERENCES

1. Battery Standards Safety Committee, Electric and Hybrid Electric Vehicle Rechargeable Energy Storage Systems (RESS) Safety and Abuse Testing, Surface Vehicle Recommended Practice, SAE International, J2464, Nov 2009.
2. Doughty, D. H. and Craft, C. C, Electric Energy Storage System and Abuse Test Manual for Electric and Hybrid Electric Vehicle applications, Sandia National Laboratories, Report SAND2005-3123, 2006.