Thermal Runaway in Li-ion—getting the missing data

Most modern high energy batteries, not only Li-ion, contain highly reactive and potentially explosive chemicals as exemplified by the recent Boeing incident. Testing techniques exist that can predict these problems yet are rarely used and not widely understood. The most important of the tests aim to define the safe working limits: safe temperature, maximum discharge current and maximum safe voltage. Yet some of these parameters are often missing on battery data sheets and even when they are quoted, there is little supporting evidence. Jasbir Singh of HEL Ltd describes how that information can be obtained.

These important working parameters are often mixed up with the whole range of so-called “abuse” tests that are specified for Li-ion batteries. In reality these particular “abuse” tests are special, both because they are much more fundamental to the use of batteries and because the data can only be obtained on special equipment, called an adiabatic calorimeter.

This article will present the main “abuse” tests designed to understand fire and explosion risk resulting in thermal runaway of commercial Li-ion and other modern batteries.

Discussion will also focus on an important issue that is not addressed by “abuse” tests, namely the prevention of these problems through a better understanding and design of batteries and heat management systems. A new experimental method will be presented, isothermal calorimetry, which can address this.

Small scale fires involving new batteries, exemplified by, for example, the recent grounding of the entire fleet of Boeing 787-Dreamliners, has already illustrated the fact that Li-ion batteries are potentially dangerous. The United States' FAA has listed 132 previous aircraft incidents between 1991 and 2012 that involved “smoke, fire, extreme heat or explosion” in which battery powered devices were implicated and 62 of these incidents involved Li-ion batteries. The result of the Boeing incident, (see figure 1), was rather confined and though expensive for the companies involved, it did not lead to any injuries. This will not always be the case and when larger numbers of more powerful cells are used, for example in EVs, the situation can be far more serious. Commercial pressures such as the need to drive EVs more quickly, over greater distances and charge the batteries in minutes rather than hours, will increase the importance of battery testing.

The safety testing of batteries is 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 (such as falling from a height, exposure to fire or crushing) and hence are described as “abuse” tests. However, some of the most important tests need to be done in a special device called an adiabatic calorimeter while others
require no defined apparatus and test methods can be set up to suit the battery size and potential hazard.

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:

a. **Mechanical Abuse**
   Tests in this category include shock, drop, penetration, roll-over, immersion and crush. Penetration is one of the important tests due to the severity of hazard that can result as the battery is internally shorted (by penetration with metallic nail) and all the energy stored in the battery can be released within seconds, potentially leading to a rapid temperature rise followed by a fire or explosion.

b. **Thermal Abuse**
   These tests include high temperature (essentially fire) exposure, thermal stability, temperature cycling (without thermal management), and passive propagation resistance. Thermal stability is by far the most important and complex of these and without an adiabatic calorimeter the data is meaningless, as will be explained later. The objective of the test is to specify the maximum temperature at which a battery can safely be used but if this is not measured in the adiabatic calorimeter the figure reported will higher than is actually true.

c. **Electrical Abuse**
   Tests in this category include short circuit, overcharge voltage, over-discharge current and separator shut-down. The objective of short circuit and separator shut down is simply to demonstrate the consequence off these faults in the battery. The tests need to be performed in a protective environment as consequences similar to shortening by nail penetration are possible. The overcharge (i.e the safe maximum voltage) and over-discharge (i.e the maximum safe discharging current), are important in defining the normal use of a battery and hence the figures are worthy of special care. To get reliable values, the test must be performed adiabatically. This will define the working boundaries of the battery and consequences of exceeding these boundaries. This is similar to the thermal stability test, which defines the safe temperature boundary, using also an adiabatic calorimeter.

As a consequence, adiabatic calorimeters are slowly becoming an accepted way to test the safe working boundaries, of batteries primarily because they represent an acceptable "worst case" approximation of the conditions under which batteries are likely to be used. It is a special piece of equipment for performing an important few "abuse" tests.

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 (Ref 3). Essentially, these calorimeters allow the heat generated by the mal-function 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. This is therefore a realistic simulation of an accident, using real battery samples, but performed in a laboratory and possibly photographed.

**Abuse Testing and Adiabatic Calorimeters – how and why**

An adiabatic calorimeter is essentially an electronic "oven" consisting of several "guard heaters" which control the oven temperature distribution such that heat loss from the test battery is prevented, see Figure 2. 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 (or thermally
runaway).

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 3) 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). The data in figure 3
shows that the sample being
tested, did not thermally runaway
at any temperature.

Doing the same “abuse” test
without an adiabatic calorimeter
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 be perceived to be
less hazardous).

- 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.

When large batteries and
packs need to be tested, a custom
calorimeter 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 only. This
instrument has
space for battery
units measuring,
if necessary, up
to 50cm and 50cm
high (though normal
versions are smaller)
and as a result is
constructed from thick
steel plates to ensure
safety under fire and
explosion conditions.

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 runaway has stopped. The state of the battery before and after the runaway is shown in figure 6.

**Overcharging and Over-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 commercial 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 battery is connected to a cycler while placed in the BTC (see figure 7), 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, 2.2Ah 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 65°C.

In this example, the charging/discharging currents 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 to higher charging and discharging currents, 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 temperature being around 110°C when it does so.

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). 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.

Clearly, at this discharge current, the battery would most definitely need to be cooled to prevent runaway, though the cooling duty is not known from this test.

The overcharging (voltage) test is similar to the over-discharge (current) discussed above except that now the current is at a normal (and safe) value but the battery is charged to higher voltages until it starts to thermally degrade.

Photograph of a 8Ah Li-ion pouch battery based on NMC-graphite chemistry after overcharging to 5V (instead of long term safe figure of 4.5V) is shown in figure 11.
Preventing Thermal runaway through Thermal Management

Discussion of battery safety should not only look at abuse testing but also include prevention of the problem and hence the design of necessary protection systems and possibly also better batteries. 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 and without this, design of cooling (thermal management) systems is guess work.

A calorimetry method that is new to the battery industry has been shown to provide both the information needed for thermal control and potentially provide an insight into battery performance and hence, enable better design. This new technique is 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 12, involving a charging step followed by discharge. As is done, the battery is heated and cooled by the calorimeter, as necessary, to hold the battery temperature constant. The amount of heating and cooling needed is measured and displayed, as the test proceeds. Notice that for this battery type, the charging is endothermic (ie a cooling event) and the battery needs to be heated, while the discharge is exothermic (ie heating event) and the battery has to be cooled.

The effect of changes in the discharge current (while holding the temperature constant) for this same battery (Li-polymer, rated to 2.2Ah) is shown in figure 13. From this information, it is possible to specify the demand on a thermal management system as discharge current is varied and hence design the cooling system to handle the worst rate. Notice that under adiabatic conditions, this same battery type resulted in a thermal...

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**Figure 12**: Illustration of typical data from isothermal BTC for charging and discharging of a Li-ion polymer battery at 50°C.

**Figure 13**: Heat generation at different discharge currents (fixed temperature).

**Figure 14**: Change in heat generation with temperature (fixed discharge current).

**Figure 15**: Capacity change with temperature, at fixed charging/discharging currents.
runaway at a discharge rate of 15A; here, with active cooling to control the temperature, 20A has been achieved without problem.

The amount of heat produced, for a fixed discharge current, varies with the temperature of the battery and this relationship can also be quantified in the isothermal BTC. The resulting profile for the 8.8Ah NMC-graphite battery, over a temperature range of 0 to 60°C is shown in figure 14. Clearly, as the temperature is lowered, the amount of heat generated increases - by a factor of 3 in fact, showing the demand on the thermal management unit can vary enormously.

The ability to measure heat generation rate from a battery as a function of both discharge current and battery temperature is a huge step forward for battery developers and safety system designers alike.

Charging/discharging of batteries over a range of temperatures in the isothermal BTC can also reveal other useful information about battery performance, not related to safety. For example, changes in battery capacity with temperature can be also be deduced from the same experiment. As an example, the charge and discharge capacity profiles for the same NMC-graphite type battery are shown in figure 15. The area under the current plots represents the battery capacity at each temperature; this area is clearly decreasing as temperature is lowered. The pertinent battery capacity data is summarised in figure 16 which shows a 70% drop in capacity; experiments reveal that for a Li-ion polymer battery, the capacity drop is only 20% over the same temperature range.

Finally, a detailed look at the heat generation profiles reveals that battery discharging involves a number consecutive steps, both exothermic and endothermic, some fast and some very slow, see this is the precisely what adiabatic calorimeters do. Too often, battery data sheets provide no reference to these key measurements or else information is obtained using equipment that is unsuitable.

In addition to providing the safe envelope of use, these tests provide an understanding of the severity of incidents (without risk of injury to operators) if the safe envelope is transgressed. Also, photographic recording of the event can be provided for training use and information exchange more widely.

While adiabatic testing is already somewhat established, its use is still very limited and as a result the hazard potential of batteries is rarely understood.

A different but complementary testing method, isothermal calorimetry, is even less well appreciated but could be fundamental to providing data needed in the design of thermal management systems in high energy applications such as EVs. Isothermal calorimetry can potentially provide a bridge between battery developers and application engineers.

References

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