Accelerating Rate Calorimeter - ARC Technical Information Note 069 Stability of Li-Ion Batteries; Internal Pressure Measurement



Introduction

Calorimetric studies assessing the safety and thermal runaway potential of Lithium batteries have focussed on heat release. Much work has been presented from ARC testing. The ARC can measure pressure equally well assuming the test is carried out suitably. However in the case of a battery, there are two possibilities; external and internal pressure. The battery, being self contained, will show no external pressure until release of a venting disc or disintegration. The gas released will react with oxygen in the environment. Such tests may simply be carried out by enclosing the battery in a pressure-tight holder.

Earlier reported tests used a heavy close fitting container. Such a holder compromises thermal data and might explode upon rapid gas release. The usefulness of this data might be questioned since there would be no pressure rise from the start of the test until battery 'opening' occurs and then there would be a simple single rapid pressure rise. Perhaps of more interest is the development of internal pressure, how this increases with temperature and the temperature and pressure that can be withstood before opening.

For the first time we report calorimetric (thermal and pressure) data and though not shown here associated electrical data (voltage) can be recorded throughout the test. Tests have been carried out with 'specimen' 18650 batteries. For the test protocol, minor modifications are necessary to the ARC and to the battery itself. Here is reported the set up protocol, the experimentation and results.

Battery

In this leaflet the result from just one battery test is illustrated where the internal pressure is measured against the temperature. The test is with a 'standard type battery under standard conditions' and is designed to illustrate the method and utility of such testing. A commercial 18650 lithium-ion battery was used for these tests. Prior to the connection of the pressure tube, the battery was discharged to 3.1V at C/5 (440mA) until the current reached a minimum of100mA. After connection of the pressure tube the battery was charged to 4.1V at C/5 (440mA) and charging continued with a constant voltage of 4.1V until the current was below 100mA. The battery used was otherwise unused.

Procedure

To facilitate measurement of the internal battery pressure a small tube was attached to the base of the battery. To do this the battery together with the connecting tube and ancillary items was sited in a glove box filled with inert gas (Figure 1). The glove box contained a pillar drill. A hole was drilled carefully in the base of the battery case; the tube was inserted by 1mm and sealed in place with high temperature epoxy resin cement. This connecting tube had been pre-bent to a shape appropriate for the calorimeter, it had been filled with oil and the free end had attached a 1/16th inch Swagelok nut and ferrule set.

This was attached to a 'cap' to seal this free end. Sufficient epoxy resin was put around the base of the battery coving the tube position to make sure the two parts were sealed. No air could get into the battery. The assembly was left in the glove

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Fig 1

box for 24 hours for the epoxy resin to fully set. When removed from the glove box the cap was replaced by the pressure transducer and this assembly wassited within the calorimeter held by a light ceramic holder as shown (Figure 2).



Fig 2

The ARC had a 'side branch pressure connection' but it was not connected to the calorimeter itself 9Figure 3). The photographs illustrate the method, the battery and its position inside the calorimeter.





Attaching the pressure line to the battery inside a sealed environment (the internal material in the battery will react if exposed to oxygen).

Test Protocol

A standard ARC test was carried out. Heat-Wait-Seek steps were initiated at 60°C and the temperature and pressure were measured against time. Although not reported here, the battery voltage was also monitored against time. Voltage data shows the point of electrical failure in the battery. Data was recorded and analysed using standard ARCCal software.

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Results

The battery went into exotherm near 100° C. The graphs illustrate the results obtained (Figures 1, 2 & 3—front page). There is continual pressure rise from initial heating; the pressure rise mirrors the temperature rise. At 100° C as the exothermic reaction commences the internal pressure had risen to 4 bar. The pressure rises as the exotherm drives up the battery temperature. The battery remained intact until near 150° C when the internal pressure reached 12 bar. At this point there was a pressure decrease. However the pressure then rose again as the self-heating exotherm rate increased rapidly until, seven minutes later, when the temperature had risen to 160° C and the pressure reached 16 bar, there





Fig 4, 5 & 6

was dramatic pressure decrease due to full battery venting and disintegration. The test then automatically shut down.

The large graph above shows an exponential pressure rise interrupted only by a 2 bar drop in pressure at around 150°C (Figure 6).

Conclusions

The data illustrates the ability of the ARC to measure internal pressure alongside the thermal data for a lithium battery. The pressure shows increase prior to exothermic reaction and shows the speed of pressure increase as the exotherm accelerates. It illustrates the temperature and the pressure at which the battery will vent. The data in 'indicative of what may be achieved with other batteries, at other states of charge – and though not reported here it is possible to record simple the battery voltage during the test.

Reference

For further information on this type of test protocol, data and other related scientific reprints, please contact the author at martyn.ottaway@thermalhazardtechnology.com

Battery positioned inside calorimeter chamber on ceramic plinth. Cell has pressure line (silver) and current wires (red/black) connected.

