APPLICATION**NOTE**

Measuring Thermal Runaway of 18650 Cells by Accelerating Rate Calorimetry

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Introduction

The cylindrical 18650 cell was introduced in the early '90s and quickly found applications in portable electronics. Today it has become the de facto industry standard for portable electronics. Compared with other battery technologies, lithium ion batteries have many advantages including high power density and high energy density. However, one of the major concerns of lithium ion batteries is that it may suffer thermal runaway if overheated or overcharged. Therefore, special attention must be paid to the safety measures associated with the use of such energy storage devices.

Accelerating Rate Calorimetry (ARC®) has been traditionally used for chemical process safety for the last 30 years. More recently, it has been used in assessing the risk of thermal runaway of lithium ion battery. By creating an adiabatic condition, the ARC® can simulate the "worst-case scenario" which can be found in some real-life situations (e.g., one 18650 cell running in the middle of a battery pack.).

Instrumentation

The calorimeter used in this note was the NETZSCH ARC® 254 (figure 1). The ARC® 254 is an accelerating rate calorimeter designed specifically to operatate in an adiabatic mode. The high tracking rate (up to 200 K/min) provides more reliable data and a wider range of applications. Many accessories are available for various battery testing requirements.

A standardized measuring technique called "heat-wait-search™" is used for thermal runaway test. Here, the sample is initially heated to a temperature just below the expected reaction temperature. If no self-heating occurs, the temperature is increased stepwise until the sample self-heating rate exceeds a certain threshold value (usually

1 NETZSCH ARC® 254

0.02 K/ min). The calorimeter switches to adiabatic mode and the furnace temperature will track the sample temperature to maintain an adiabatic condition.

For the analysis of lithium ion batteries, special sample vessel are available allowing the above-described "heat-wait-search" program to be carried out on an entire 18650 cell (figure 2).

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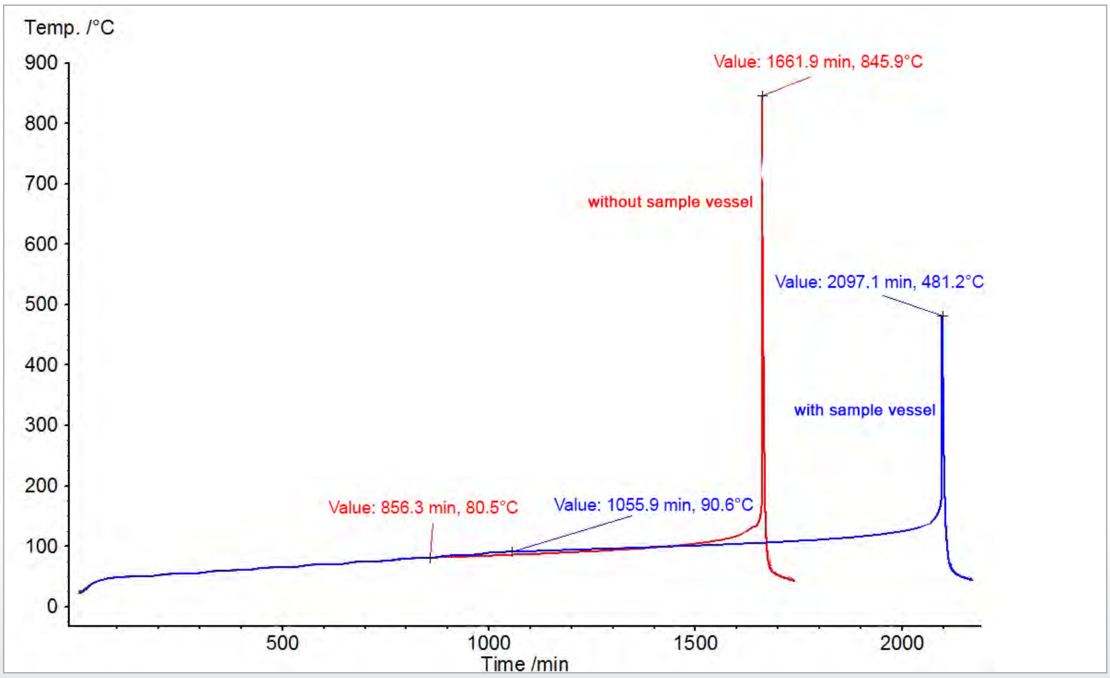
2 18650 cell vessel in ARC® 254 18650 cell mounted in ARC 254 18650 cell after thermal runaway

These closed vessels have the advantage of being able to capture the gas release and the pressure can be measured as a function of time and temperature. The disadvantage of using these vessels is that some of the heat from the reaction is absorbed by the vessel reducing the sensitivity of the measurement. In this note, both runs with and without sample vessels were conducted to show the effect of the sample vessel on test result.

Results

The results of an 18650 cell thermal runaway test are presented in the figure 3. Sample temperature is plotted as a function of time. The blue curve is from the 18650 test with sample vessel while the red curve is without vessel. In case of with vessel, the sample temperature was measured at the surface of the sample vessel. For the test without



3 Results of a “heat-wait-search” program with 18650 lithium ion cell

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without a sample vessel, the sample temperature was measured directly at the surface of the 18650 cell. In both cases the start temperature was 50°C and the temperature was increased stepwise by 5 K. After temperature stabilization the self-heating rate of the sample was measured for 20 minutes. If the self-heating exceeds a value of 0.02 K/min the instrument will switch to adiabatic mode and track the sample temperature as it begin to react exothermically. For the sample enclosed in a vessel, the self-heating rate exceeded the threshold value of 0.02 K/min and the start of the decomposition was detected at 90°C. This part of the exothermic reaction resulted from the decomposition of the solid electrolyte interface (SEI). The temperature of 90°C is a relevant value for assessing the thermal stability and safety of the cell. After 1000 minutes, the decomposition reaction accelerated rapidly and was associated with a rapid increase in temperature. This second part of the reaction resulted from a serial decompositions of the individual components within the cell. A maximum temperature of 481°C was reached. This value is also relevant for safety, since it can be correlated to the energy released during decomposition.

Compared with the data with vessel, the data without vessel shows a lower onset temperature of 80°C and a higher maximum temperature of 846°C. It is due to the thermal inertia of the tests. The sample vessel adsorbs some of the heat released from the cell during reaction.

The amount of heat adsorbed depends on the mass and heat capacity of the vessel. The ratio between the product of the sample mass and heat capacity to the product of the vessel mass and heat capacity is known as thermal inertia. When sample mass is large compared to the vessel mass, the thermal inertia approaches one. These tests are often called "low phi" tests. Here the test without vessel has a thermal inertia (Φ-factor) of one while the test with vessel has a $\Phi > 1$. It is important to understand the effect of thermal inertia when interpreting the data.

Conclusion

18650 lithium ion battery is commonly used in portable electronics. The information from the thermal runaway test on ARC® 254 allows for the determination of its potential thermal runaway risk which is associated with the cell chemistry. Measurement data can thus be used not only for cell construction and design, but also for conclusions to be drawn regarding proper handling, thermal safety and the degree of danger associated with improper storage or use. The effect of vessel (Φ-factor) is also demonstrated. Generally low phi test will give a lower onset temperature and higher maximum temperature.

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