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Thermal runaway features of large format prismatic lithium ion battery using extended volume accelerating rate calorimetry

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HIGHLIGHTS

- Thermal runaway behavior of a 25 Ah prismatic Li-ion battery is evaluated using ARC.
- When thermal runaway happens, the temperature inside the battery is 870 °C or so.
- When thermal runaway happens, the temperature difference within the battery is 520 °C.
- The internal resistance is got by pulse current charging during thermal runaway test.
- The sharp drop of voltage is 15–40 s sooner than the sudden rise of temperature.

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ABSTRACT

In this paper, the thermal runaway features of a 25 Ah large format prismatic lithium ion battery with $Li(Ni_xCo_yMn_z)O_2$ (NCM) cathode are evaluated using the extended volume-accelerating rate calorimetry (EV-ARC). 4 thermocouples are set at different positions of the battery. The temperature inside the battery is 870 °C or so, much higher than that outside the battery. The temperature difference is calculated from the recorded data. The temperature difference within the battery stays lower than 1 °C for 97% of the test period, while it rises to its highest, approximately 520 °C, when thermal runaway happens. The voltage of the battery is also measured during the test. It takes 15–40 s from the sharp drop of voltage to the instantaneous rise of temperature. Such a time interval is beneficial for early warning of the thermal runaway. Using a pulse charge/discharge profile, the internal resistance is derived from the quotient of the pulse voltage and the current during the ARC test. The internal resistance of the battery increases slowly from 20 mΩ to 60 mΩ before thermal runaway, while it rises to 370 mΩ when thermal runaway happens indicating the loss of the integrity of the separator or the battery swell.

1. Introduction

Currently, lithium ion batteries are favored by researchers as a promising power source for electric vehicles (EVs). However, some hazards of the lithium ion battery have been reported [1]. The safety problems will undermine the confidence of the consumers and obstruct the commercialization of the EVs. Thus the safety issue of the lithium ion battery merits further study.

The thermal runaway behaviors of lithium ion battery have been reviewed several times [2–5]. Generally, when the temperature reaches approximately 90 °C, the self heating of the cell begins due to the start of the solid electrolyte interface (SEI) decomposition. Then follows the negative active material and electrolyte reaction, positive active material and electrolyte reaction, electrolyte decomposition, negative active material and binder reaction, etc. [1–6].

Accelerating rate calorimetry (ARC) is designed to study the exothermic chemical reactions by simulating an adiabatic condition [7]. Employing the ARC, some of the critical kinetic parameters, i.e. the onset temperature of the reaction and the enthalpy of the exothermic process, can be acquired. Not only has ARC been used to analyze the thermal behaviors of the components of the lithium ion battery [8–12], but also to evaluate the thermal hazard of the whole battery [13–15]. Shu and his group have completed a series of thermal abuse tests using a calorimetry named vent size package 2 (VSP2) [16–20], of which the functions are quite the same as those of the ARC.

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One single cell cannot meet the requirements of power and energy for the EVs, so it is a must to build battery packs with hundreds of single cells connected in parallel and series [21–24]. Large format lithium ion batteries are rapidly being developed to provide an alternative for the pack design [25,26]. Lithium ion cells with increased format have the advantage of reducing the number of basic units when integrated in a battery pack [27]. Reducing the number of cells increases reliability because the cells can be connected in series [28]. Thus some of the manufacturers of electric vehicles are favoring large format lithium ion battery.

However, the thermal behaviors of the scaled-up lithium ion batteries mutate under safety incidents, comparing with that of the small-sized cells [29]. A larger format battery is more vulnerable to thermal runaway because it contains more stored energy. The cooling performance is worse due to its lower surface:volume ratio. In addition, the scaled-up size leads to an increase of temperature difference within the battery [28]. Sensors, especially the thermocouples, have been employed to study the internal temperature and the temperature distribution of the lithium ion batteries [30–34]. The temperature difference within the battery is less than approximately 10 °C as reported in Refs. [31–34]. Kim [27,28] et al. have built models to simulate the temperature distribution of a large format cylindrical battery. The simulated temperature difference for normal operation condition is 10 °C or so [27]. However, for thermal runaway triggered by an internal short circuit, the temperature difference is approximately 600 °C [28].

Until now, little research has been done on evaluating the thermal runaway features of large format lithium ion battery. Most of the existing experiments are conducted for 18,650 cells [14–20], or for batteries with a capacity of less than 1 Ah [13]. Models of the large format lithium ion battery are calling for experimental validation [27,28]. The size of the calorimetry restricted the former research on the large format lithium ion battery. Now Thermal Hazard Technology (THT) has developed a new type of ARC named extended volume-ARC (the EV-ARC). The EV-ARC provides a possible solution to test large samples, including the large format lithium ion battery [7].

In the Vehicle Battery Safety Roadmap Guidance [35], Dr. Doughty and Dr. Pesaran synthesized the performance of cells with variant cathode materials, i.e. $LiCoO_2$ (LCO), $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA), $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})_{0.9}O_2$ (NCM), $LiMn_2O_4$ (LMO) and $LiFePO_4$ (LFP). The cell with NCM cathode performs better in thermal runaway tests than those with the LCO and the NCA do, while it performs worse than those with the LMO and LFP do. However, the cell with NCM cathode has better high temperature durability and higher specific capacity than that with the LMO cathode does. Also the cell with NCM cathode costs less and has higher energy density than that with the LFP cathode does. Therefore cells with NCM cathode are of interest to be used in the recent applications of battery pack for electric vehicle.

In this paper, a 25 Ah prismatic battery with NCM cathode is tested by the EV-ARC. The thermal runaway features of the 25 Ah battery have been reported synthetically. The inside temperature has been recorded and the temperature difference within the battery during the thermal runaway process has been reported. The battery voltage is recorded, and the internal resistance is measured by exerting a pulse charging on the sample during the ARC test.

2. Experiment

2.1. The EV-ARC

The instrument used is the es-ARC with double systems, including a standard ARC and an EV-ARC, manufactured by THT, Fig. 1. The functions of the EV-ARC are quite the same as those pervasively used ARC. A common EV-ARC test also follows the heat-wait-seek method. The difference is that the calorimeter of the EV-ARC is much larger than that of the standard ARC. The calorimeter of the standard ARC has an internal size of 10 cm diameter by 10 cm depth, while the calorimeter of the EV-ARC has an internal size of 25 cm diameter and 50 cm depth.

Fig. 1. The illustration of the es-ARC with double systems made by the THT.

2.2. The 25 Ah NCM battery

The 25 Ah battery employed for the EV-ARC test is manufactured by AE Energy Co. Ltd. with NCM/Graphite as its electrodes. Fig. 2 shows the product dimensions of the 25 Ah NCM battery. Remember that the standard ARC calorimeter has an internal size of 10 cm diameter by 10 cm depth. The 25 Ah battery is too large to be held in the standard ARC.

Fig. 3 shows the C/5 (5 A) charging curve of the 25 Ah NCM battery.

2.3. The experiment settings

The 25 Ah battery is composed of two pouch cells connected in parallel wrapped by an aluminum shell, Fig. 4. The structure provides a convenience to insert a micro-thermocouple between the two pouch cells. Though the cover and the shell were separated, the

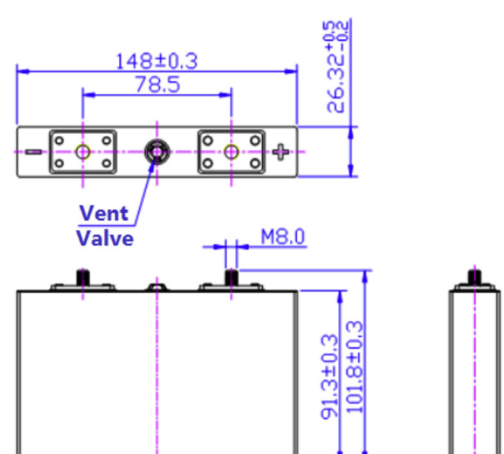

Fig. 2. The product dimensions of the 25 Ah NCM battery.