Journal of Power Sources 398 (2018) 55–66

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Characterization of behaviour and hazards of fire and deflagration for high-energy Li-ion cells by over-heating

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HIGHLIGHTS

- Critical incident heat flux that activates deflagration or/and fire is found.
- Duration, evolution and key parameters of fire and deflagration are characterized.
- Underlying reactions for fire and deflagration occurrence are determined.
- Hazards like temperatures of cell and flame and mass of ejected gas are quantified.
- Revised oxygen consumption method is developed and the heat release is specified.

ARTICLE INFO

Keywords:
$LiNiCoAlO_2$ cell
Fire behaviour
Deflagration
Thermal hazard
Over-heating

ABSTRACT

Fire and deflagration are extreme manifestation of thermal runaway (TR) of Li-ion cells, and they are characterized for fully charged $LiNiCoAlO_2$ (LNCA) 18650 cells in this investigation. The cells are over-heated using a cone calorimeter under different incident heat fluxes. When the cells are exposed to the incident heat flux larger than 35 kW m^{-2}, both fire and deflagration present. The pressure valve opens when the temperature of the cell is higher than 132 °C. The fire occurs with the valve opening when the concentration of the venting vapour in the air is higher than the lower flammability limit. The deflagration happens after the cell temperature arrives about 200 °C, and is mainly arising from the cathode decomposition, the combustion of solvents and the anode relevant thermal reactions. The extreme temperatures of the cell and the flame during deflagration are over than 820 and 1035 °C, respectively. The production of CO_x, mass loss, heat release rate (HRR) are quantitative identified, and are found increase as the increasing incident heat flux. Based on revised oxygen consumption method, the HRR and liberated heat during the fire and deflagration for the cells are up to 11.8 ± 0.05 kW and 163.1 ± 1.5 kJ, respectively.

1. Introduction

State-of-the-art commercial Li-ion batteries (LIBs), which possess high energy density, good cycling stability and long lifetime, currently dominant the power sources for portable electronics and are increasingly used in electric vehicles (EV) and grids storage. On the other hand, as revealed by many investigators [1–3], thermal runaway (TR) and its propagation in LIB modules and packs may result in fire and/or explosions under abnormal operations, such as overheating, overcharging, short circuit, puncture, compression or crashing. To enhance the safety of LIBs, numerous efforts have been devoted to developing new cell materials, chemistry, novel cell design and improved battery thermal management systems (BTMS) [4–7]. Although various progress has been achieved, incidents and recalls related to LIBs have still occurred in the consumer market for mobile phones, laptops and EVs as well as airplanes [8,9]. To meet the ever increasing requirements for high energy and power density LIBs, some relatively new chemistry systems with high energy density have entered the commercial market. However, the potential risk and associated hazards are not well understood or quantified.

$LiNiCoAlO_2$ (LNCA) is a type of relatively new cathode material which has already been commercially used in LIBs in recent years.

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https://doi.org/10.1016/j.jpowsour.2018.07.044
Received 31 May 2018; Received in revised form 28 June 2018; Accepted 10 July 2018
0378-7753/

Comparing with traditional $LiCoO_2$, $LiMn_2O_4$, $LiFePO_4$ and other cathode materials, LNCA has higher specific capacity, which makes LNCA based cells attractive to the EV application. However, the thermal stability issue of LNCA cells at high temperature is still a problem which hinders its wide application [10]. In order to gain insight of TR and its propagation of LNCA cells, some investigators have conducted failure tests to analyse the behaviour of LNCA cells during TR. Golubkov et al. [11] studied the parameters of TR for two types of 18650 cells (LNCA cells and $LiFePO_4$ cells) using thermal ramp tests to measure the onset and maximum temperature, the composition and quantity of the vent gas. They also examined the dependence of the TR behaviour on the state of charge (SOC). Duh et al. [12] performed TR tests of LNCA cells with 100% SOC. They measured the TR parameters and calculated the enthalpy change liberated by TR of the cells based on adiabatic temperature rise. The averaged enthalpy change during TR was found to be (30.9 ± 4.6) kJ for 18650 LNCA cells. Lammer et al. [13] proposed holistic analysis of thermally induced TR of 18650 LNCA cells. The heat emissions and maximum total gas emission of TR were found to be 31 kJ and 5459 cm^3, respectively. The above studies provided details about TR behaviour and key indicating parameters, and potential mechanisms associated with the thermal stability deterioration of LNCA cells. However, to the best of our knowledge, the fire and deflagration behaviour of LNCA cells have not been quantitatively investigated. When fire or deflagration occurs in LNCA cells, more heat could be released than that when there is only venting without ignition. The energy liberated during TR are typically determined by two methods: (1) multiplying the temperature rise with the heat capacity and the mass for the cell body, or/and gaseous species or/and the sealed canister. The energy during TR is determined by the contribution from heat change of cell body, or/and gaseous species or/and the sealed canister [12,14–16]; and (2) the estimated heat of combustion of the flammable LIB composites such as electrolyte, separator, binder and packaging [17,18]. Neither method takes into account the subsequent effect of potential deflagration, which can result in rapid temperature rise and huge energy release with a short time.

Fire or deflagration resulting from LIB TR and TR propagation poses serious potential hazards. Key characteristics which should be investigated include the duration of fire and/or deflagration, the evolution of the TR and its propagation, the critical parameters at the onset of fire and deflagration, the time to ignition and the critical incident heat flux that activate fire and deflagration. The resulting hazards including extreme temperatures of both the cell and the flame, heat released by the fire and/or deflagration and the ejected gases need to be quantified as such information is not only important to aid the design of robust and reliable battery module and BTMS but also crucial for effective fire protection and emergency response and evacuation.

In the present study, laboratory tests have been conducted by subjecting LNCA cells to radiant panels. The results have been analysed to derive the critical condition for TR and the evolution from venting to fire and deflagration. Measurements have been conducted for the cell surface temperature, flame temperature, heat release rate, time to ignition, duration of ignition, mass loss and production of CO_x. The energy source and energy loss of the cells during the tests are analysed. Recommendations have been formulated for thermal management and fire protection.

2. Experimental setup

2.1. The test rig

The schematic of the test rig is shown in Fig. 1. A radiant heater of cone calorimeter was placed above the cell to imitate different heating conditions. Two K-type (chromel–alumel) thermocouples (0.5 mm diameter) with a response time of 1 s and accuracy of ± 1.5 °C were either sticking around the testing cell or hanging on the upside of the cell to obtain the surface temperature of the cell and the flame temperature while fire jetting. Since the cathode material of the experiment is unstable under high temperature, to prevent the test system from being damaged during the experiment, the protection screen of the cone calorimeter was put down to prevent the exploding electrolyte injection and jet fire from widely spreading and fire jetting. The combustion products such as toxic gases were collected by the cone calorimeter and were transported away through a ventilation system. To prevent the system from being damaged by the injected electrolyte and jet fire, the cell was placed up on a flame–protection shield with holder. A weighing sensor was placed underneath the flame-protection shield to simultaneously measure the mass loss of the testing cell. A digital camera which was protected by the protection screen of the cone calorimeter was used to record the burning behaviour and jetting process of the tested cell. The exhaust hood was set to collect the combustion products mixed with ambient air and an oxygen analyzer was used to measure the oxygen depletion during the test. The heat release rate can be measured based on the combustion products and oxygen depletion. Each test was ended after the flame was extinguished without any suspicious phenomenon. All tests were repeated three times to reduce the test errors.

2.2. Cell fabrication and cycling

The cells (Panasonic) are 18650 cylinders with dimension of 18 mm in diameter and 65.2 mm in height. Their typical capacity is 3.2 A h and the total mass is about 48.5 ± 0.05 g. Cells were pre-cycled using a cycler (Neware) at 0.1C current rate within 2.5–4.2 V for three cycles and then followed by a constant voltage charging at 4.2 V, to achieve 100% SOC. In order to ensure the accuracy of the SOC, the charge and discharge cycling was completed within 10 h before the fire test.

The plastic packaging of all the testing cells were stripped before experiment to eliminate the influence of thermal decomposition of the packaging.

2.3. Thermal analysis and structure characterization of cell materials

After the cell was dissembled, the electrolyte was collected, the separator and the electrode were picked out and washed with DMC. The washed separator and electrode were then dried in the vacuum oven overnight under 40 °C. Thermal stabilities of the cell materials were studied by differential scanning calorimetry (DSC, Mettler Toledo). Separator, electrode and electrolyte with specific mass were added and sealed in the DSC crucible. The whole process was performed in the argon filled glove box. The sampling robot pierced the lid of hermetically sealed crucible immediately before the test. The DSC test was run in a nitrogen filled environment to prevent the samples from contacting with air. A heating rate of 10 °C/min from 50 °C to 500 °C was used for the test. The heat flow was calculated based on the weight of the entire sample. X-ray powder diffraction (XRD) was carried out using a Bruker Analytical X-ray System with Cu Kα radiation source filtered by a thin nickel plate.

3. Methodology

To interpret the complex progression of a cell from being over-heated to TR, and eventually to occurrence of fire or deflagration, mathematical model is built in this study. The model considers the intricate energy transport within and outside of the cell, including thermal radiation from the heater and possible fire or deflagration outside of the cell, the thermal reactions taking place in the cell, the effect of the venting vapour and ejecta, the thermal energy transformed from the electrical energy stored in the cell, and the heat dissipation arising from heat transfer to the atmosphere caused by convection and radiation.

During the over-heating tests, the cells were exposed to the radiating heat panel. Once the fire or deflagration occurs, the cells were