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Heat release during thermally-induced failure of a lithium ion battery: Impact of cathode composition

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ABSTRACT

A novel experimental technique, Copper Slug Battery Calorimetry (CSBC), was employed for the measurement of the energetics and dynamics of the thermally-induced failure of 18650 form factor lithium ion batteries (LIBs) containing three different cathodes: lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC) and lithium iron phosphate (LFP). The heat capacity of these LIBs was evaluated to be $1.1 \pm 0.1\ \mathrm{J\,g^{-1}\,K^{-1}}$ for all three types. It was shown that the total heat generated inside the batteries increases with increasing amount of electrical energy stored. The maximum total internal heat generated by fully-charged LIBs was found to be 37.3 ± 3.3, 34.0 ± 1.8 and 13.7 ± 0.4 kJ/cell for LCO, NMC and LFP LIBs, respectively. Detailed modeling of heat transfer in the CSBC experiments was carried out to evaluate thermal conductivities of the LIBs and demonstrate that the assumptions associated with the CSBC experiment analysis are valid. Additionally, experiments were carried out in which the CSBC technique was combined with cone calorimetry to measure the heat produced in flaming non-premixed combustion of vented battery materials. The released combustion heat varied between 35 and 63 kJ/cell for LCO LIBs, 27 and 81 kJ/cell for NMC LIBs, and 36 and 50 kJ/cell for LFP LIBs.

1. Introduction

With the optimal combination of energy density, efficiency, cycle life and minimal memory effect [1], lithium ion batteries (LIBs) are the state-of-the-art energy storage devices and have been adopted in a wide variety of electrical and electronic systems. With their ever-growing market size and popularity, the safety of LIB-based devices remains an important consideration. When LIBs are subjected to environmental conditions outside their intended design envelope, they may fail irreversibly. More specifically, when exposed to excessive external heat, unintended exothermic reactions may be initiated. These reactions take place within and between the four primary components of an LIB: the anode (most commonly carbon), the cathode (typically, a lithium metal oxide), the electrolyte (lithium salt dissolved in a mixture of organic carbonates) and the separator (a thin layer of porous polymer). These reactions can produce a large amount of thermal energy at an increasing rate. At an early stage, these reactions are accompanied by venting of potentially combustible gases and aerosols; this stage is referred to as “safety venting” [1]. At a later stage, the battery can self-heat rapidly, while simultaneously ejecting a portion of the anode and cathode materials; this stage is usually referred to as “thermal runaway” [1,2].

Quantification of the energetics and dynamics of both stages of the failure process is necessary to understand the safety impact of various lithium ion cell and pack designs. Considerable research efforts have been dedicated to understanding energetics of the thermally-induced failure of LIBs. Differential scanning calorimetry (DSC) was used to study a number of electrode and electrolyte materials as well as their combinations. Yang et al. [3] employed DSC to investigate the most common anode material, graphite, at various states of charge (SOC). A sharp exothermic peak was detected at high temperature when samples contained more than 0.71 lithium ions per 6 carbon atoms. Maleki et al. [4] utilized DSC to examine the thermal stability of the graphite/$LiCoO_2$ battery chemistry. It was found that the total exothermic heats of decomposition for the anode (graphite) and cathode ($LiCoO_2$) were $697\ \mathrm{J\,g^{-1}}$ and $407\ \mathrm{J\,g^{-1}}$, respectively, and these heats decreased by about 60% with the removal of electrolyte (a mixture of organic carbonates and $LiPF_6$).

Von Sacken and co-authors [5] employed accelerating rate calorimetry (ARC) to show that a carbon intercalation anode material was superior to a lithium metal anode from the aspect of thermal stability. Richard and Dahn [6] used ARC to measure self-heating

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rate of a lithiated mesocarbon microbead (MCMB) material in different types of electrolyte. It was found that the amount of lithium in the MCMB, the nature of the electrolyte, the material surface area and the initial temperature in the experiment can all impact the thermal stability of this system. Ribière et al. [7] utilized a fire propagation apparatus to study flaming combustion of the materials ejected from a pouch form factor lithium ion cell. Recently, Walters and Lyon [8] used a bomb calorimeter (pressurized with nitrogen to exclude the heat produced in flaming combustion) to evaluate the total heat released during LIB failure. They found that for fully-charged T-Energy ICR18650 cells, which were also examined in the current study, the total heat was about 60 kJ/cell.

In this work, a recently developed experimental technique, Copper Slug Battery Calorimetry (CSBC) [9], was utilized to investigate the thermally-induced failure of 18650 form factor commercial LIBs representing a range of cathode chemistries including lithium cobalt oxide (LCO), lithium nickel manganese cobalt oxide (NMC) and lithium iron phosphate (LFP). Some of the results presented here for NMC cells were reported in an earlier publication [9]. These results are repeated to provide a comprehensive comparison between the battery types.

The stand-alone version of the CSBC apparatus was used to measure the heat capacity of the LIB cells and to quantify the rate of heat generation inside the cells during the thermally-induced failure process. A computer model was constructed within the COMSOL Multiphysics environment [10] to simulate the heat transfer processes associated with the CSBC experiments. This model was used to elucidate thermal conductivities of the batteries and validate key assumptions employed in the calculation of the internal heat generation rate. In separate experiments, CSBC was combined with cone calorimetry [11] to determine the heat released in flaming combustion of the materials ejected from the battery. Together with the stand-alone CSBC experiments, these measurements provided a comprehensive evaluation of the energetics of the failure process and impact of SOC and cathode chemistry on this energetics.

2. Methods

2.1. Sample preparation

The three types of LIB cells analyzed in this study are shown in Fig. 1. Detailed specifications of these cells are given in Table 1. It should be noted that, while the main difference between the cells was the chemical structure of the cathode, other differences in structure and composition were likely to be present (due to the commercial nature of the tested specimens) and may have contributed to the observed differences in the failure dynamics.

Table 1
Specifications of tested LIB cells.

LIB type	LCO	NMC	LFP
LIB model	T-Energy ICR18650[12]	Panasonic CGR18650CG[13]	K2 18650E[14]
Cathode	lithium cobalt oxide	lithium nickel manganese cobalt oxide	lithium iron phosphate
Anode	carbon	carbon	carbon
Nominal capacity (mA h)	2600	2250	1500
Nominal voltage (V)	3.7	3.6	3.2
No. of safety vent ports	4	3	5
Mass without packaging (g)	44.00 ± 0.07	42.30 ± 0.04	38.60 ± 0.11

Prior to each experiment, the cell's plastic packaging was stripped off and it was charged to a specific SOC with an iCharger 208B using the constant current/constant voltage method. The selected SOCs were 0%, 25%, 50% and 100%. The open circuit voltages of the cells and the electrical energy stored in them, which was directly measured by the charger, are listed in Table 2. Due to the differences in the cathode chemistry and cell design choices, different cell types had significantly different electric capacities. Therefore, to provide adequate comparisons, the key quantities describing the failure process are presented in this manuscript as a function of the stored electrical energy (kJ), rather than SOC.

2.2. Copper slug battery calorimetry

A schematic of the CSBC apparatus is shown in Fig. 2. The primary component of the CSBC is a hollow cylinder (or slug) composed of nearly pure (99.5%) copper. This slug houses an LIB specimen. The top surface of the specimen is leveled with the upper edge of the slug so that the cell's safety vent ports are open to the atmosphere. The internal dimensions of the slug ensure a good thermal contact with 18650 form factor LIBs. An electric heater consisting of a resistive heating wire (OMEGA NI80-010-200) insulated with 3 M Ruban Isolant tape is tightly wrapped around the slug. This heater is used to initiate the failure process. It is powered by a DC power supply, BK Precision 1685B, employed in a controlled power mode.

The copper slug is housed inside a larger cylinder that consists of Gemcolite FG23-112HD ceramic fiber thermal insulation, which is used to minimize heat losses from the system to the environment. The temperature of the slug is monitored with an embedded type K thermocouple. This temperature is read at a frequency of

Fig. 1. Tested LIB cells with (left) and without (right) plastic packaging.