Applied Thermal Engineering 125 (2017) 1061–1074

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Research Paper

Study of the fire hazards of lithium-ion batteries at different pressures

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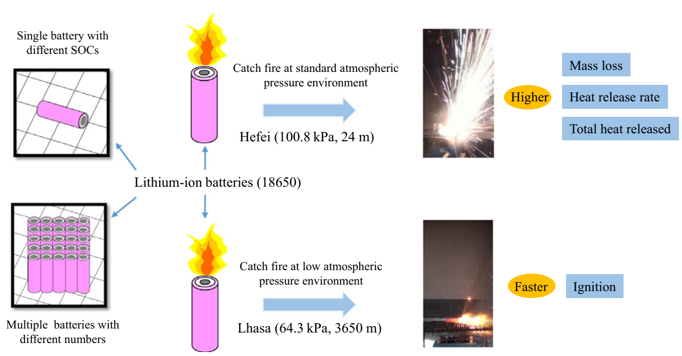
HIGHLIGHTS

- Pioneering study of lithium-ion battery fire at sub-standard atmospheric pressure.
- Comparisons with the fire hazards at the standard atmospheric conditions.
- Ignition, mass loss and HRR are related to the SOC and pressure.
- Empirical correlations are established to link the hazard parameters with pressure.
- The uncertainty in the heat release rate measurement is highlighted.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 October 2016
Revised 12 May 2017
Accepted 28 June 2017
Available online 14 July 2017

Keywords:
Lithium-ion battery
Atmospheric pressure
Mass loss
Heat release rate
Fire hazards

ABSTRACT

The fire behavior of lithium-ion battery is affected by the environment conditions. In this paper, an experimental study is performed to assess the fire hazards of lithium-ion batteries at different atmospheric pressures by means of the in-situ calorimeters built in a sea-level city Hefei (100.8 kPa, 24 m) and a high altitude city Lhasa (64.3 kPa, 3650 m), respectively. The fire hazards of lithium-ion batteries were characterized by measuring the ignition time, mass loss, heat release rate (HRR), and total heat release (THR). From the results, the ignition time of single battery decreases with the ascending of the state of charge (SOC), whiles the mass loss, and ejection energy increase with that at two pressures. The increment of altitude causes the battery to ignite faster, while the mass loss, heat release rate and total heat release both for single battery and bundle batteries decrease at low pressure. The total heat release in the bundle increases with the battery numbers in a power function. The coefficient of the proportionality is pressure dependent.

1. Introduction

With the development of lithium-ion batteries technology, it has been widely applied in various fields of applications, such as cameras, computers, mobile phones, electric vehicles etc. [1]. However, lithium-ion batteries contain highly energetic materials in contact with the flammable chemical electrolyte pertaining to organic solvents. Any abuse, including disposing in fire, overcharging, external short circuiting or crushing, can trigger spontaneous self-heating reactions, and lead to fire and explosion eventually [2]. Incidents of the related severe fires and explosions problems in airlines have been reported [3].

For this reason, various research works the thermal stability of the battery materials have been carried out to decrease the flammability and potential explosion of lithium-ion battery [4–9]. These studies mostly focused on the internal heating reactions inside the battery. The combustion behaviors of the batteries

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http://dx.doi.org/10.1016/j.applthermaleng.2017.06.131
1359-4311/

after heating are also important for understanding the hazard of the battery fire. Ribiere et al. [10] conducted a study of single 2.9 Ah $LiMn_2O_4$ battery combustion to investigate the process of battery fire, and it was found that even a single lithium-ion battery can release considerably intense heat and toxic gases. Ping et al. [11] performed the similar fire research to evaluate the safety of a large-size lithium-iron phosphate/graphite battery with the capacity of 50 A h based on the ISO 9705 Full-Scale Room Fire Test apparatus, and significant fire hazards were also observed. Fredrik Larsson et al. conducted the fire tests on commercial lithiumeiron phosphate cells and laptop battery packs, and the HRR was calculated using the method of oxygen consumption [12]. Fu et al. conducted an experimental study on burning behaviors of 18,650 lithium ion batteries using a cone calorimeter, and the effects of SOC on burning behaviors of lithium-ion batteries were also evaluated [13]. According to their studies, SOC is the main factor that account for the thermal runaway and the sustained fire. Normally, higher SOC battery gives higher HRR peaks and higher total HF emission for lower SOC values. Amandine Lecocq et al. [14] performed the combustion tests of 1.3 A h based LiFSI and $LiPF_6$ cells using Tewarson apparatus which also calculated HRR by analyzing the quantification of O_2, CO, and CO_2. Their obtained results reveal that critical thresholds are highly dependent on the nature of the salt, $LiPF_6$ or LiFSI, and on the SOC.

In practice, lithium-ion batteries are often used, stored and transported in bundles. Safety concerns over the shipment of lithium-ion batteries were highlighted after a United Parcel Service cargo plane carrying a significant number of lithium-metal and lithium-ion batteries crashed in Dubai in September 2010 [15]. In response to the questionable safety of lithium-ion batteries as cargo, the International Civil Aviation Organization (ICAO) made several updates for the Safe Transport of Dangerous Goods by Air regarding the transport of batteries [16]. US Federal Aviation Agency (FAA) also confirmed that the transport of multiple lithium batteries had a higher risk [17]. Therefore the fire behaviors of single and bundle batteries are identically important for developing fire protection.

All the studies mentioned above were conducted in normal atmosphere. However there are situations where the lithium-ion battery fires occur in an environment with low pressure that is quite different from the standard atmospheric condition, such as at high elevation, in airplanes or spacecraft. The fire behavior of lithium-ion batteries may be affected by these environmental conditions. Chen et al. [18] found that the thermal runaway chemical reactions inside the battery shell caused pressure build-up and eventually led to rupture of the shell, with violently releasing of solid and gaseous combustibles. The rupture of the battery shell is related to the pressure differential between inside and outside. The reduction in outside or ambient pressure may lead to earlier rupture and hence higher fire hazard.

The altitude or the ambient pressure can significantly affect fire characteristics of combustibles[19]. Studies of common fuels, such as n-heptane [20-24], wood [25], cardboards [26,27], and other solid combustible [28], under high altitude or low pressure conditions have been investigated and indicates that ambient pressure has obvious effects on the fuels combustion behaviors. However, there are few studies concerned with the fire characteristics of lithium-ion batteries at low pressure. In order to fill in the gap and ascertain the effect of pressure on ignition and burning behavior of lithium-ion batteries, more studies are needed.

In this paper, the fire behaviors of single and bundle 18,650 $LiCoO_2$ batteries were experimentally examined at two ambient pressures, i.e. at a high-altitude city Lhasa (64.3 kPa, 3650 m) and a close to sea-level city Hefei (100.8 kPa, 24 m). The fire hazards of single battery (with different SOCs) and bundle batteries (with 100% SOC) at two pressures were quantitatively investigated. The fire hazards were evaluated in terms of time to ignition, mass loss, peak burning intensity, HRR and amount of heat release per unit battery. Based on the experimental results, the fire behaviors of lithium-ion batteries under different situations were revealed.

2. Electrochemical reactions inside lithium-ion batteries

The electrochemical reactions of commercially available $LiCoO_2$ lithium-ion battery during charging and discharging are represented by [29]:

$$\text{Cathode}: \text{LiCoO2} \underset{\overleftarrow{discharge}}{\overset{\overrightarrow{charge}}{\rule{2em}{0.4pt}}} xLi + +\text{Li}_{1-x}\text{CoO}_2 + \text{e} \tag{1}$$

$$\text{Anode}: \text{xLi}^+ + e + 6\text{C} \underset{\overleftarrow{discharge}}{\overset{\overrightarrow{charge}}{\rule{2em}{0.4pt}}} \text{LixC}_6 \tag{2}$$

The overall reaction equation can be expressed as:

$$\text{LiCoO}_2 + 6\text{C} \underset{\overleftarrow{discharge}}{\overset{\overrightarrow{charge}}{\rule{2em}{0.4pt}}} \text{Li}_{1-x}\text{CoO}_2 + \text{LixC}_6 \tag{3}$$

The usage of batteries involves complex chemical reactions and some of them are exothermic. The heat generated by these exothermic reactions usually disperses to the surrounding environment. However, if the heat is not effectively dispersed or when external heat is applied to the batteries, the resultant temperature increase will accelerate some exothermic reactions which will lead to thermal runaway reactions.

When the temperature gradually increases to approximately 120 °C, the lithium batteries experience a solid-electrolyte interphase decomposition. The separator (see Fig. 1) breaks down at temperatures about 130 °C and then induces an internal short circuit [30] and generates heat. A thermal runaway reaction occurs after the self-generated heating reaching a critical temperature. The charged $LiCoO_2$ have the disproportionation reaction as

$$\text{Li}_{1-x}\text{CoO}_2 \to (1-\text{x})\text{LiCoO}_2 + \frac{x}{3}\text{Co}_3\text{O}_4 + \frac{x}{3}\text{O}_2 \tag{4}$$

where x is determined by the stage of charge as shown in Reaction (3). The anode material graphite [C in Eq. (3)] is not considered to be reactive with oxygen because its high stability.

However, at high temperatures, the compound Co_3O_4 decomposes further and releases more oxygen, which can oxidize the electrolyte and generate more heat [30]. These reactions are summarized below.

$$\text{Co}_3\text{O}_4 \to 3\text{CoO} + \frac{1}{2}\text{O}_2 \tag{5}$$

$$\text{CoO} \to \text{Co} + \frac{1}{2}\text{O}_2 \tag{6}$$

$$2\text{LiCoO}_2 + \text{CO}_2 \to \text{Li}_2\text{CO}_3 + 2\text{Co} + \frac{3}{2}\text{O}_2 \tag{7}$$

$$\text{O}_2 + \text{electrolyte} \to \text{CO}_2 + \text{H}_2\text{O} + \text{heat} \tag{8}$$

Eqs. (4)–(7) describe the oxygen producing reactions that mainly take place inside the battery. The exothermic reaction of oxygen and electrolyte is considered to be a major contribution to the heat generation of the battery system.

Since these oxidizing reactions may not be completed, the product gas will contain CO, CO_2.

$$\text{O}_2 + \text{electrolyte} \to \text{CO} + \text{H}_2\text{O} + \text{heat} \tag{9}$$

$$2\text{CO} + \text{O}_2 \to 2\text{CO}_2 + \text{heat} \tag{10}$$