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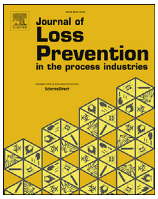

Combustion behavior of lithium iron phosphate battery induced by external heat radiation

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ABSTRACT

The combustion behavior of 50 Ah $LiFePO_4$/graphite battery used for electric vehicle is investigated in the ISO 9705 combustion room. The combustion is trigged by a 3 kW electric heater as an external thermal radiative source, and then the surface temperature, combustion behavior, heat release rate, flame temperature and mass loss rate are obtained. The thermal runaway occurs when the battery surface temperature reaches 126.7 ± 2.2 °C and releases the combustible gases. After its ignition, the combustion generally undergoes first jet fire stage, stable combustion stage, second even third jet fire stage, final stable combustion stage and extinguishes stage. The maximum heat release rate reaches 64.32 kW and the maximum heat release is 13.74 MJ. The heat release rate is closely synchronous with the mass loss rate, and the mass loss ratio reaches to 26.9%. These fundamental data can provide basic knowledge for the battery performance based fire safety design.

1. Introduction

Lithium ion batteries (LIBs) are most popular types of rechargeable battery with the best energy densities, no memory effect, and only a slow loss of charge. Therefore, they are widely used in portable electronics, electric vehicles (EV) and energy storage. However, the booming lithium ion batteries fire and explosion accidents have illustrated their high risk, whether they are in large batteries used in energy storage applications, or middle batteries used in electric vehicles, or even smaller batteries used in common electronic equipment (Wang et al., 2012).

Many accident shave shown that the fire or explosion accidents are directly caused by the overheating (Wang et al., 2012). Overheating may be caused by electrical shorting, rapid discharge, overcharging, manufacturers defect, poor design, or mechanical damage, among many other causes. Overheating leads to the decomposition of solid electrode interface (SEI) on graphite surface and the reduction of electrolyte. Once the quantity of heat produced by inner reactions accumulated more than dissipated, internal temperature and pressure could continual rising and result in the battery rupture and release flammable gases. The spilled gases will be ignited spontaneously and then cause to a fire finally.

Many efforts have being made to improve the LIBs safety. Materials inherent stability, including cathode, anode and electrolyte, are the key functional materials to improve the safety. The traditional $LiCoO_2$ based battery is more dangerous than other kind of materials based battery, such as $LiFePO_4$ and $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ batteries (Jhu et al., 2012), and $Li_4Ti_5O_{12}$ anode material shows better thermal stability than that of graphite (Wang et al., 2006; Yi et al., 2013). Lots of flame retardant additives were investigated to reduce the flammability of the electrolyte (Chen et al., 2009a, 2009b; Park et al., 2009; Wang et al., 2010; Xiang et al., 2007; Zhang, 2006), but the battery still has the potential of thermal runaway. To release the high pressure and heat, the safety vents, thermal fuse, positive temperature coefficient (PTC), shutdown separators and special battery management system (BMS) were developed to prevent the battery goes to fire (Wang et al., 2012). Some new kind of battery systems also under development to replace the current lithium ion battery, but it still a long way for application, such as lithium-air battery (Jung et al., 2012), lithium-sulfur battery (Kim et al., 2013). Therefore, at present and near future, the lithium ion battery dominates the market and will become the most widely used second power.

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Nomenclature

$\dot{Q}$	heat release rate(HRR), Js^{-1}
E	energy release per mass unit of oxygen, 13.1 MJ per kilogram of oxygen
$\dot{m}_e$	mass flow rate of exhausted gases
MLR	mass loss rate, $g\ s^{-1}$
S	stage
SOC	stage of charge
$\dot{X}_{O_2}^{A0}$	initial concentration of oxygen
$\dot{X}_{O_2}^{A}$	concentration of oxygen in combusted gases

Subscripts

e	expansion
fj	first jet fire
ml	mass loss
sc	stable combustion
sj	second jet fire
sm	smoking
ssc	second stable combustion
tj	third jet fire

Lithium iron phosphate ($LiFePO_4$) is kind of Lithium ion rechargeable battery which uses $LiFePO_4$ as a cathode material. $LiFePO_4$ is an intrinsically safer cathode material than $LiCoO_2$ and $Li[Ni_{0.1}Co_{0.8}Mn_{0.1}]O_2$ (Jiang and Dahn, 2004) and then is widely used in electric vehicles. This is because that Fe—P—O bond is stronger than the Co—O bond, so that when abused, (short-circuited, overheated, etc.) the oxygen atoms are much harder to remove. However, many fire accidents were reported for this kind of EV batteries (Wang et al., 2012), which indicates that when the $LiFePO_4$ battery volume is big enough and under extreme conditions, it also undergoes fire risk. The lithium ion battery fire behavior has not been taken the deserved attention, and the amount of data relative to the fire behavior of large batteries is limited. The first research on the fire-induced hazards of lithium ion battery was investigated by fire calorimetry (Ribiere et al., 2012). Combustion tests were performed on commercial pouch cells by means of the Fire Propagation Apparatus, in which the standard decomposition or combustion gases were analyzed to quantify thermal and toxic threat parameters governing the fire risk namely the rate of heat release and the effective heat of combustion as well as the toxic product releases. However, the battery capacity is 2.9 Ah, which is much smaller than the general electrical vehicle battery. The Fire Protection Research Foundation of the NFPA published the report on the suppressant research and other information relative to fire and safety issues in small-capacity lithium ion batteries (Mikolajczak et al., 2011). The document serves as a fine place to start when developing a sound understanding of the fire and explosion risk issues associated with lithium batteries. FM global published the report on flammability characterization of lithium ion battery in bulk storage (Ditch and de Vries, 2013), and large scale 18,650 packs combustion characterization and sprinkler effect were detected. However, much work is required to understand the special combustion behavior of large scale lithium ion battery.

At present work, ISO 9705 room fire test apparatus was employed to study the combustion behavior of $LiFePO_4$ battery. Tests were performed on 50 Ah commercial EV LIBs with 50% and 100% states of charge are reported, and the heat release rate (HRR), thermal runaway temperature, flame zone temperature, mass loss rate are analyzed and discussed to propose the possible mechanisms to understand the lithium ion battery combustion behavior.

2. Experiments

2.1. Experimental set up

Based on ISO9705 full-scale room fire test for surface products, an experimental system was set to detect the combustion behavior of LIB under external radiation as shown in Fig. 1. The system comprises four main subsystems, which are the HRR measurement, temperature measurement, mass loss measurement and video record subsystems.

HRR measurement is mainly used to identify the combustion gas products of CO and CO_2. The combustion flow rate of the product—air mixture is measured by a pilot tube. Sample gas is firstly inhaled from the ring sampler and then is filtrated and dewatered. Finally, the sample gas is tested by the oxygen analyzer to get the online quantification of O_2, CO and CO_2. Based on the oxygen consumption principle, the HRR of combustion can be calculated by the consumed oxygen, and regardless of where and how this heat disperses. The HRR can be calculated as.

$$\dot{Q} = 1.10E\dot{m}_e\left(\frac{X_{O_2}^{A0}-X_{O_2}^{A}}{1.105-1.5X_{O_2}^{A}}\right) \tag{1}$$

where $\dot{X}_{O_2}^{A0}$ is the initial concentration of oxygen, $\dot{X}_{O_2}^{A}$ is the concentration of oxygen in combusted gases, $\dot{m}_e$ is the mass flow rate of exhausted gases. E is the energy release per mass unit of oxygen, it was taken as 13.1 MJ per kilogram of oxygen.

The battery was fixed on a steel support, as shown in Fig. 2. Under 80 mm away from it, one 3 kW electric heater without any other fuel burner was used to avoid the interference on the combustion results. In order to decrease the propagating distance of the combustion smoke, the battery was right below the exhaust hood, not in the room or the corner.

One pre-experiment was performed to ensure where the gases will spill, the expected fire scale and the possibility of explosion. The results inform that the gases will spill from the safety valve where is close to the anode tab. Although the battery not exploded, to ensure the experiment is under control, one steel cage, with steel wire is 1.5 mm in diameter and the mesh is 50 mm × 50 mm, was made to cover the battery during the experiment. And then, one thermocouple (TC 5) were placed at the battery upper middle surface to detect the battery temperature, and three thermocouples, TC 1, 2 and 3 were placed at 30 mm, 130 mm and 230 mm away from the anode tab to detect the jet flame temperature. The forth thermocouples, TC 4, was placed 120 mm above TC 2 to detect the plume temperature. The 25 type K (chromel—alumel) thermocouples were employed to measure the temperature of the battery combustion flame.

An electronic balance was used to currently measure the mass loss of the battery. Two camera videos were protected by fire proofing boards were mounted at the outside of the exhaust hood to monitor the combustion behavior and the flame shape.

2.2. Materials

Two commercial lithium iron phosphate/graphite batteries with the capacity of 50 Ah were used to study the combustion behaviors. The battery size is 353 mm in length, 100 mm in width and 28 mm in heights. The state of charge (SOC) presents how many energy was stored in battery and the two batteries were designed as 50% and 100% SOC, which were numbered as no. 1 and no. 2,

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