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ScienceDirect

Procedia Engineering 211 (2018) 531–537

Procedia Engineering

www.elsevier.com/locate/procedia

2017 8th International Conference on Fire Science and Fire Protection Engineering (on the Development of Performance-based Fire Code)

Research and Development of Fire Extinguishing Technology for Power Lithium Batteries

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Abstract

By summarizing the previous experimental studies on fire extinguishing of lithium battery, it was found that the lithium battery fire extinguishing exhibits some essential characteristics,such as long duration, high temperature, large water consumption and great difficulty in extinction. The applicability of fire extinguishing agent for power lithium batteries was analysed in this work. Through the acupuncture experiment, the different efficiencies of fire extinguishing agents were compared. It is expected to provide some useful references for future safety design and prevention of such lithium batteries.

Peer-review under responsibility of the organizing committee of ICFSFPE 2017.

Key words: lithium batteries, fire, fire extinguishing agent

1. Introduction

In recent years, the demand for new energy sources is increasing with the increasingly serious environmental problem, and the new energy vehicles represented by electric vehicles gets more attention. By the end of 2015, the total annual production of new energy vehicles are nearly 380000, and the number of new energy vehicles shows explosive growth trend. It is expected that production and sales of electric cars in China will reach one million in 2017. China is now in a critical stage of the development of new energy automotive industry and thus the security of new energy vehicles becomes more sensitive. Safety accidents of new energy vehicles have their special internal reasons, because the battery serves as a high energy carrier. The thermal runaway occurs at low temperature, and it is not easy to eliminate such accidents. Many influential fire accidents have caused numerous economic loss, fatalities and severe social influence.Thermal self-ignition, fire and explosion phenomenon of electric vehicle battery make the safety of lithium-ion battery become the focus of attention. Questions about the safety and reliability of power battery of electric vehicles bring new problems and challenges for fire fighting and emergency rescue. Recently, the scholars in State Key Laboratory of Fire Science carried out fire extinguishing experiments on the technology of lithium battery fire prevention and control, but the research is still in the initial stage [1].

This study utlizes 18650# lithium-ion batteris to examine the efficiency of pure water, 5% F-500 solution and 5% self-made solution (anionic nonionic surfactants) on lithium battery fires. In addition, the water mist extinguishing system is applied to extinguish lithium battery fires, which provides an alternative method for such fires. This work reveals some fundamental insight into studying the technology of extinguishing large-scale lithium battery fires.

2. Characteristics of fire extinguishing for power lithium battery

Although the cause of electric vehicle fire is complex, one of the main reasons is the spontaneous ignition caused by power lithium battery. In the study of fire accidents of power lithium battery, NFPA [2] has carried out the lithium battery fire

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1877-7058
Peer-review under responsibility of the organizing committee of ICFSFPE 2017
10.1016/j.proeng.2017.12.045

experiment.

2.1. Fast burning and long duration

The power lithium battery causes a series of effects because of various incentives leading to thermal runaway. Once the heat accumulation of lithium battery is out of control, the battery would burn immediately.Figure 1 shows the lithium batteries fire extinguishing process carried out by NFPA. It only took a few seconds for the battery to transform to intense combustion, whereas the suppression process had lasted about 27 minutes [2].

2.2. High temperature

During the fire tests, NFPA used thermocouple to measure the temperature and found that the maximum temperature outside the battery is in the range of 283 to 1090 degrees, and the maximum temperature inside the battery is between 572 and 1121 degrees. The peak heat flux at a distance of 5 feet from the VFT device is 2.2kW/m^2 , and the value ranges from1.5 kW/m^2 to 2.1kW/m^2 when the distance is15, 20 and 25 feet individually. The maximum temperature and heat flux measured during the tests mostly occurred after the burner was terminated. It indicated that the battery fire was still very hot at that time. Therefore, the flame temperature is high enough to ignite other combustibles once the vehicle's power lithium battery burns.

2.3. Large water consumption

During the fire extinguishing tests, NFPA used water to put out the power lithium battery fire. In order to avoid the reignition, the fire extinguishing continued for a long time and the water consumption was larger than others. Although the increased amount of water extinguished the fire more thoroughly, it endangered the battery at thermal runaway temperature.

2.4. Enhanced difficulty in extinguishing

The combustion reaction of power lithium battery generally occurs inside the battery. Water can not get access to the "fire", which is an important problem for fire fight. For the power battery pack, shell material of battery pack prevent fire extinguishing agent from acting on electrical core directly. So fire fighting is more difficult [3]. During tests, the total time spent on fighting fires exceeds the fire fighters' oxygen supply time and it poses a greater challenge to the personal security of fire fighters. Therefore, there is no effective method for the fire fighting of power lithium batteries, which belongs to the worldwide problem.

Figure 1 test: propane burner ignition (upper left); combustion(upper right); ignition off (left); the fire extinguishing started (right); fire again and inhibition again (lower left); the fire extinguishing completed (lower right)

2.5. Complexity of power lithium battery's fire extinguishing

A power battery is an energy storage unit whose fire is transformed from its electrical and chemical energy. When the electric and chemical energy is not consumed completely, the heat is in the sustained release stage. After the thermal runaway's expansion stage, the effectiveness of the fire suppression is very effective. This is the origin of the saying "why power fires can not be extinguished"., the development of the battery fire is very swift and violent especially for the ternary polymer lithium battery, and it releases oxygen itself. Consequently, it can hardly be extinguished after the fire spread.

Employing some specific methods can inhibit the occurrence and spread of fire. In addition to fire extinguishing at an open fire stage, the control of thermal runaway stage is also very important, such as the use of flame retardant materials, the addition of flame retardants in electrolyte. It is more important to develop the early warning technology. Study of the power battery fire on intelligent fire detection and flame retardant mechanism has been a breakthrough. However, there is rare effective breakthrough in the basic research about the technology of clean fire prevention and control, and its development has encountered considerable difficulties.

3. Research on fire extinguishing of lithium battery

At present the research on fire experiments of power lithium battery is highly concerned. The United States and the countries in Europe concerned about the fire safety of lithium batteries in the earlier times [4,5], such as the National Fire Protection Association (NFPA), the Federal Aviation Administration (FAA), and the Civil Aviation Authority (CAA). Recently, the scholars in the United States FM Global, the National Fire Protection Association (NFPA) and State Key Laboratory of Fire Science carried out fire extinguishing experiments on the technology of lithium battery fire's prevention and control, but the fire model was different [1].

3.1. Study on fire extinguishing of lithium batteries abroad

FAA has carried out the screening experiments of effective fire extinguishing agent fighting lithium battery fires, and evaluated their effectiveness through the fire simulation experiment and the experiment on cooling effect of fire extinguishing agents [6]. The experiment on cooling effect of fire extinguishing agent compared Halon1211 fire extinguishing agent with water based extinguishing agent such as water, AF-31, AF-21, A-B-D. It also compared gas fire extinguishing agent such as FM-200, FE-36, Halotron I with powder extinguishing agent and new fire extinguishing agent such as Purple-K and Novec1230. The results showed that the water based extinguishing agent has good cooling effect. With the increase of extinguishing agent's dosage, the cooling effect is more significant. And reducing the sprinkling capacity also has remarkable effects on the cooling effect. But non-water based extinguishing agent's cooling effect is not obvious. With the increase of extinguishing agent's dosage, the cooling capacity has little changes. Water based fire extinguishing agent's cooling ability was prioritized as AF-31, AF-21, A-B-D and Novec 1230.

Based on the experimental research on the fire extinguishing agent's cooling effect, FAA carried out the fire experiment of lithium battery. The experiment used a 18650# lithium-ion battery (battery capacity is 2600mAh, SOC is 50%). First, the heater of tube furnace was turned on, and then the heater of hexane was opened when the first battery's temperature was heated to 100℃. After the first battery was out of control, the fire extinguishing agents were sprayed. When the fire extinguishing agents is liquid at ambient temperature and pressure, such as water, AF-31, AF-21, A-B-D and Novec1230, they were sprinkled by a 500ml hand-held bottle. Other fire extinguishing agents, such as Halon1211, Halotron, I, FM-200, FE-36, CO2 and Purple-K, were sprayed by a hand-held bottle. After the fire was over, the heater was closed and data was recorded for about 20 minutes.The results showed that all thermal runaway of lithium battery occurred and spread in the absence of fire extinguishing agents, and only 500ml liquid fire extinguishing agents can effectively inhibit the spread of lithium-ion battery fire. Non-liquid fire extinguishing agents had no effect on lithium-ion battery.

Through the research of this project, FAA found that the experimental results of fire extinguishing agents' cooling effect are similar to the experimental results of lithium battery fire extinguishing. It further testified that the cooling ability of fire extinguishing agents is the key factor to prevent the spread of lithium battery fire. Water based fire extinguishing agents had the best effect on the suppression of lithium battery fires, while gas extinguishing agents and dry powder extinguishing agents are ineffective in suppressing lithium battery fires.

3.2. The study on fire extinguishing of lithium battery in China

In order to reduce the risk of lithium battery fires, Wuhan Institute of China Classification Society [7] carried out the research on the effectiveness of extinguishing agent of fighting power lithium battery fire. They analyzed the effectiveness of carbon dioxide, dry powder and heptafluoropropane which inhibit lithium battery fire. They evaluated its effectiveness from three aspects such as the fire extinguishing time, the recrudescence rate and smoke effect synthetically.The experiment found that the carbon dioxide's extinguishing effect is poor and the resurgence of fire occurred. Dry powder extinguishing agent has little effect on the lithium battery, and explosion occurred even during the experiment. The best effect on extinguishing lithium battery fires is heptafluoropropane.

University of Science and Technology of China [8] carried out the research on the effectiveness of dry powder, carbon dioxide and heptafluoropropane of extinguishing lithium battery fires. It was found that heptafluoropropane has good effect, but also the resurgence of fire occurred.

Tianjin fire station of Ministry of public security [3] conducted the experiment of extinguishing lithium battery fires with the powder, carbon dioxide and AFFF fire extinguishing agent and water mist technology. The results showed that the carbon dioxide, dry powder, 3% AFFF can extinguish the open fire of 18650# lithium-ion batteries. Due to the thermal runaway of lithium-ion batteries, it continued to release heat, combustible gas and oxygen. It can not extinguish the fire completely. All of them appeared resurgence phenomenon. With the fire extinguishing agent's cooling ability increasing, the time of appearing resurgence prolonged. For completely extinguishing 18650# lithium-ion battery fires, it needs to improve the fire extinguishing agent's ability of cooling and absorbing heat. Water mist fire extinguishing technology can not inhibit the 18650# lithium-ion battery fires effectively. Some studies showed that [4,5] water mist containing surface active agent is an efficient and environmental fire extinguishing technology. The utility of lithium battery fire needs further study.

3.3. Application of F-500 micro capsule technology and water mist containing additives system in the lithium battery fire extinguishing

There are few studies on the micro capsule technology of explosive hydrocarbons in the literature, and the results of existing research are concentrated mainly in developed countries. The existing advanced technology is F-500 micro capsule's material technology, which is a new high efficiency fire extinguishing, explosion prevention and environmental technology developed by the American dangerous goods Control Arts Inc (HCT). In 2009, Bosch tested the extinguishing effect of water, foam, powder and F-500 on lithium battery fires. The tests found that F-500 is the first choice of lithium battery fire extinguishing agent.

In April 2013, German motor vehicle inspection association (DEKRA) selected three kinds of fire extinguishing agent, and studied the extinguishing effect on power lithium battery fire of electric vehicle [9]. According to the structure of electric vehicle's lithium battery, DEKRA used n-heptane to ignite lithium battery and set up fire model. They compared F-500 fire extinguishing agent's effect with water and powder fire extinguishing agent's effect on extinguishing lithium battery fire. Firefighters began to fight fire after n-heptane combustion's time at about 20min. Through simulation experiments, DEKRA found that water can successfully extinguish the lithium battery fire of electric vehicles. But there are many other problems, such as large water consumption and long extinguishing time. F-500 fire extinguishing agent can improve the efficiency of extinguishing lithium battery fires. The extinguishing time of extinguishing agent containing 1% F-500 is only fourteen seconds. The water consumption is greatly reduced. As a kind of micro cellular agent, F-500 can effectively inhibit class D (metal) fire in which no explosion exists. When the water is applied to class D (metal) fire, high temperature can make water into hydrogen and oxygen. The after-combustion and explosion will occur easily. Powder extinguishing agent can not cool the fire, and the fire will happen again. F-500 can reduce the surface tension of water. The formation of smaller droplets can make them penetrate into the internal of lithium battery. They quickly extinguished the fire and the fire will not happen again. F-500 forms a layer of protective film on the surface of the water forming a spherical micro capsule "chemical cocoon". The fuel elements of combustion were wrapped up in the micro capsule inhibiting combustion.The fast cooling ability of F-500 can quickly extinguish the fires and prevent the fire occurring again. These characteristics make F-500 not only apply to metal magnesium, metal titanium and other class D fire, but also apply to lithium battery fires.

Figure 2 comparison of pre

4. Experiment of lithium battery fire extinguishing

4.1. Experimental samples

The experimental sample is a commercial iron phosphate lithium-ion battery. The total capacity of the battery is 80A·h. It is connected in series by four 20A·h cells, and the weight of each battery is 2375±3g.

4.2. Experimental method

In order to simulate the daily common state of charge, the pre-cycle of battery was carried out between 3~4.5V before the tests. Circulation ratio was 0.2 C.When it was in a desired state of charge (50%SOC), the battery was prodded. Acupuncture experiment was carried out in a special acupuncture extrusion stage. Acupuncture equipped with thermocouples installed in the puncture fixture. The diameter of steel needle was 5mm and it penetrated into the single battery of 50% SOC at a rate of 30mm/s. The thermocouples were attached to the surface of the battery and measured the variation and distribution of temperature. Tests were conducted in two groups. One group was used to observe the phenomenon of lithium battery fire, and the other group was used to perform extinguishing fire tests when thermal runaway of lithium battery occurred. The extinguishing effect of pure water was compared with that of 5% F-500 solution and 5% self-made solution (anionic nonionic surfactants) to evaluate the fire extinguishing technology of water mist containing additives. Anionic nonionic surfactant combines many advantages of anionic and nonionic surfactants. It shows excellent characteristics such as good water solubility, high temperature resistance, easy degradation and high efficient foaming ability.

4.3. Experimental phenomena and results

SOC of the battery has a great influence on the results of the acupuncture experiment. The SOC is controlled at 50% to repeat tests. After the battery was prodded, a little amount of liquid was sprayed immediately to produce a lot of white smoke. The surface temperature of the battery increased rapidly. It reached a high temperature of 813.7℃ at 29s as shown in Fig. 3. After the occurrence of thermal runaway, the fire behavior of lithium batteries was roughly divided into the following five stages: (1) The expansion of the battery took place after the acupuncture. Gas and internal material were sprayed from the small hole. The battery was seriously deformed and a large amount of smoke could be observed. (2) At 14s, the battery emitted a hissing explosion and spurt a large amount of white aerosol which is probably made up of electrolyte droplet. The white aerosol was ignited instantaneously and emitted a strong jet flame. (3) The battery entered a steady combustion state and lasted about 15s. (4) At 29s, the battery flame was enhanced. (5) After a period of time, the flame went out gradually and ended at 1637s.

According to Fig. 4, it is found that 5% F-500 solution and 5% self-made solution have significant extinguishing effect on lithium battery fire in the tests. Compared to that of pure water, the extinguishing time of them are shortened by more than half. The two solutions can reduce the temperature of the lithium battery rapidly and extinguish the flame quickly. There is little difference between the extinguishing times of the two solutions. The self-made solution is slightly better than the F-500 solution. Pure water is very unstable in the early stage of flame suppression. The stability of flame suppression effect of both solutions is much better than that of pure water. Compared to spraying pure water, spraying 5% self-made solution and F-500 solution weakens the combustion intensity of lithium battery flame obviously. After spraying for 4s, it could inhibit the combustion of lithium battery very well.The experiment results infer that fuel molecules are absorbed and wrapped by solution after spraying self-made solution or F-500 solution. And thus the combustion reaction can be terminated. Compared to the flame effect, the inert effect of F-500 solution is closed to that of self-made solution. Meanwhile, the smoke control of F-500 is slightly better than that of self-made solution after ignition and the intensity of flame after ignition is better controlled, which is obviously superior to pure water.

According to the experiment of fire extinguishing effectiveness, utilization of pure water as the extinguishing agent to extinguish the lithium battery fires has defects, such as long extinguishing time and harmful products with "black smoke". While the scenario of a certain percentage of additives is added in water, extinguishing time is greatly shortened. The fire enhancement is effectively suppressed. And a large amount of "black smoke" translates into "white smoke" at the same time. Self-made solution and F-500 solution show excellent fire extinguishing effect in the experiments. In the process of extinguishing lithium battery fires, self-made solution and F-500 solution could absorb and wrap hydrocarbon molecules quickly. Hydrocarbon molecules produced by combustion is wrapped and insulated from oxygen.The combustion could be prevented and inert. Flame intensity and combustion time are both reduced. The harmful products of combustion are reduced and the visibility in the fire is increased. Consequently, the rapid and safe extinguishing effect is reached finally.

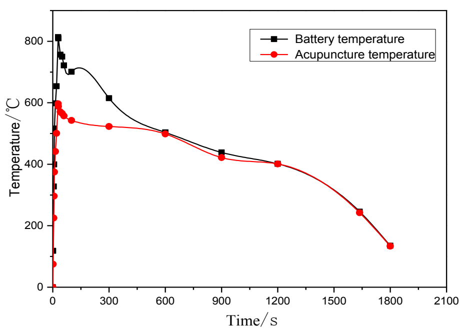

Figure 3 Surface temperature profiles of acupuncture experimental cel

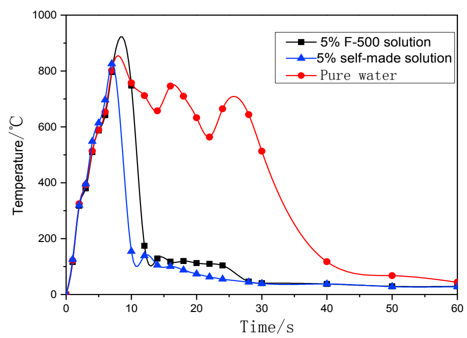

Figure 4 Comparison of the effect of fire extinguishing agents

5. Problems and Prospects

(1) Currently, the fire extinguishing media of lithium batteries mainly includes water, foam, dry powder, alkyl halide and carbon dioxide etc. Water mist fire extinguishing system has the characteristics such as low water consumption, cheap fire extinguishing medium, little damage to the object protected and green environmental protection. It has been concentrated in the field of fire protection in recent years. However, there are many problems in water mist fire extinguishing system. The uniformity of the water mist cannot be warranted.The liquid droplets reach the combustion surface with a certain amount of impulse. It is very difficult for water mist system to extinguish block fire. It is easy to extinguish class B (liquid) fire and it is difficult to extinguish class A (solid) fire. There is no guarantee of any water damage to objects.Water mist extinguishing system is not movable. The fire extinguishing properties are affected by droplet size, velocity distribution, impulse and geometric characteristics of nozzle. In recent years, the study on water mist extinguishing technology has been conducted extensively. But the water mist fire extinguishing system containing additives is still at the laboratory research stage. The results show that the extinguishing efficiency of water mist fire extinguishing system containing additives is obviously improved compared to the ordinary one.The study on fire extinguishing materials and fire prevention technologies for lithium batteries has become an important part in the field of fire science.

(2) The experimental studies have shown that lithium-ion batteries have high fire risk. The oxidation of lithium metal is over in a flash when the battery is heated up. The energy is the electrical energy and chemical energy contained in other substances. There are dozens of toxic and harmful substances such as five phosphorus pentafluoride, phosphine, hydrogen fluoride and hydrogen. These are the root of batteries combustion and reignition. According to the toxic and harmful gas coming from power lithium battery fire, hydrogen fluoride is regard as a model. Using the organic aggregates of surface active agent to absorb hydrogen fluoride gas is investigated. The feasibility of reducing hydrogen fluoride gas concentration is investigated. The absorption of surfactant mixtures of hydrogen fluoride is studied. Through a comprehensive analysis of the absorption performance and stability, the absorbent system with good absorption effect on hydrogen fluoride gas is screened. It reveals some fundamental insight into using the organic aggregates of surface active agent to absorb five phosphorus pentafluoride, phosphine, hydrogen and other gases.

(3) China has not yet formulated and promulgated the specifications and guidelines for emergency rescue of electric vehicles. The Chinese existing national standards for fire emergency rescue have not covered the specific contents of electric vehicles fire emergency rescue. It is very difficult for fire fighters to deal with the fire of electric vehicles. Therefore, according to the fire extinguishing experiment of power lithium battery, fundamental research on fire fighting should be combined with the emergency rescue. Furthermore, technical manual or standard specification needs to be established. To meet the needs of the fire work, normalization of the operation of fire fighters and emergency rescue should also be standardized.

Acknowledgments

This work is supported by the natural science research project of Jiangsu higher education institutions. (NO.17KJA620004)

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