Test and research on suppressing fire of lithium-ion battery with water mist containing additive

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Abstract. In order to improve the fire extinguishing effect on lithium-ion battery fires, the paper experimented with compound solution of sodium dodecylbenzenesulfonate-dodecanol-sodium carbonate at a ratio of 3:2:2, polyfluoroalkyl betaine-alkyl glycoside-potassium carbonate at a ratio of 2:3:3 and monoalkyl ether phosphate potassium-fatty acid ester polyoxyethylene etherurea at a ratio of 3:2:3. The fire of the lithium-ion battery was extinguished with water mist containing additive compound solution by building lithium-ion battery fire extinguishing experimental platform. The experiment selected four different concentrations of 0.5%, 1%, 1.5%, and 2%. The results showed that the polyfluoroalkyl betaine-alkyl glycoside-potassium carbonate compound solution had better fire extinguishing effect in the early stage of thermal runaway, and the battery did not reignite. The sodium dodecylbenzenesulfonate-dodecanol-sodium carbonate compound solution took the least time to reduce the battery temperature to below 200°C. In the later period, the sodium dodecylbenzenesulfonate-dodecanol-sodium carbonate compound solution has the greatest advantage in cooling rate. In the gas absorption test, the sodium dodecylbenzenesulfonate-dodecanol-sodium carbonate compound solution has the best absorption effect on methane, and the polyfluoroalkyl betaine-alkyl glycoside-potassium carbonate compound solution releases CO. The concentration of the compound has a more obvious drop than the other two compound solutions.

1. Introduction
As an energy storage device, power batteries are vulnerable to external environmental stimuli and their own manufacturing defects to cause thermal runaway, causing fire and explosion[1]. At present, the research at home and abroad mainly focuses on the theory of thermal characteristics of power lithium-ion batteries, thermal stability of battery materials, and safety testing of single cell. Wang Qingsong et al [2-3] carried out lithium-ion battery fire hazard tests, gas tests and fire-fighting experiments. Experiments show that the water mist fire extinguishing system cannot effectively suppress or extinguish the fire of the 18650 lithium cobalt oxide lithium-ion battery. There are still many obstacles to the fire suppression of lithium-ion batteries, but there have been many related researches on the development of water mist and surfactants in fire suppression and explosion suppression[4-6]. In addition, the current research on potential safety hazards of lithium-ion batteries is still how to effectively control thermal runaway and avoid chain propagation. Its fire, especially the release of toxic and harmful gases, is an auxiliary research point for subsequent thermal runaway [7-9]. Zhu et al. [10] used water mist containing surfactants to conduct fire extinguishing experiment on lithium-ion batteries. The temperature and flame propagation speed of the surface of the lithium-ion batteries decreased, proving that the
water mist containing surfactants can effectively suppress thermal runaway of lithium batteries happened. At present, the research on the fire extinguishing of lithium-ion batteries is not deep enough, and the research on surfactants in extinguishing lithium-ion batteries and suppressing the explosion of toxic and harmful gases in fires is rarely involved.

2. Experimental

2.1. Experimental sample

Additive solution:
Anionic surfactant: Monoalkyl ether phosphate potassium (MAEPK), Sodium dodecylbenzene sulfonate (SDBS)
Nonionic surfactant: Fatty acid ester polyoxyethylene ether (FMEE)
Fluorocarbon surfactant: Polyfluoroalkyl betaine (PFAB)
Hydrocarbon surfactant: Alkyl glycoside (APG-0810)
Organic matter: Dodecanol (Shorthand D); Potassium carbonate (Shorthand E), Sodium carbonate (Shorthand F), Urea (Shorthand H)
Other samples: power lithium-ion phosphate battery cell (battery capacity is 12A•h)

2.2. Experimental platform

The fire extinguishing experimental platform consists of surfactant low-pressure water mist system, gas detection device, electric heater, thermocouple, wire mesh, lithium-ion battery cell, gas analysis device, and data recording device and computer.

During the experiment, the lithium-ion battery cell was placed on a wire mesh for heating, and an electric heater was placed under the wire mesh. When the lithium-ion battery started to catch fire, the fire test was performed. In the lithium-ion battery fire extinguishing test, after the thermal runaway of battery, the low-pressure water mist system is activated, and the fire extinguishing agent is sprayed on the lithium-ion battery 0.8m directly above the center of the battery. The working pressure is 1.2MPa and the flow rate is 20ml/s. The temperature changes of the lithium-ion battery and the environment are collected through three thermocouples T1, T2, T3. During the experiment, the T1 thermocouple was set in the middle of the lithium-ion battery, the T2 thermocouple was set at 20cm above the lithium-ion battery, and the T3 was set at the vent. The gas concentration change during the lithium-ion combustion process was recorded by gas analysis device.

3. Results and discussion

3.1. Experimental research on fire extinguishing of different kinds of compound additive solution

The tension value of the compound solution reaches the minimum compound ratio through the tension test. When the evaporation of water mist and take away heat makes the efficiency of fire extinguishing further improved. Therefore, we choose the SDBS-D-F compound solution with the concentration of 1% and the compounding ratio of 3:2:2, PFAB-APG0810-E compounding solution of 2:3:3 and MAEPK-FMEE-H of 3:2:3 compound solution. Because of the change of emulsifying property, the interfacial tension and interfacial energy may affect the fire-extinguishing performance, and the infiltration ability of surfactant will be changed. Figure 1, Figure 2 and Figure 3 show the relationship between the time of extinguishing the water mist containing compound additives and the temperature.

According to the time and temperature variation diagram of the fire extinguishing, the difference of lithium-ion battery temperature with time after different compound solutions are released can be calculated. Because the lithium-ion battery will cause thermal runaway at about 200°C and cause fire, this article uses the compound solution fine water mist to reduce the temperature of the lithium-ion battery to reach below 200°C as a control index.
When the temperature of the power lithium-ion battery reaches the maximum, the fire extinguishing agent will be released after the temperature is maintained for a period of time. It can be concluded that after the release of PFAB-APG0810-E compound solution, the time for lithium-ion battery to drop from the highest temperature of 693°C to 593°C is 25s, but it takes 191s to drop to below 200°C. After the release of MAEPK-FMEE-H compound solution, the lithium-ion battery fell from the highest temperature of 613°C to 513°C in 121s, and the temperature fell below 200°C in 200s. After the release of SDBS-D-F compound solution, the lithium-ion battery fell from the highest temperature of 625°C to 525°C in 78s, and the temperature fell below 200°C in 169s. After releasing the extinguishing agent of the compound solution, the PFAB-APG0810-E compound solution made the battery temperature decreased obviously in the initial stage, which indicated that the PFAB-APG0810-E compound solution released in the early stage of thermal runaway had better fire extinguishing effect. However, the SDBS-D-F compound takes the least time to reduce the battery temperature to below 200°C, which indicates that the later cooling rate SDBS-D-F compound solution has greater advantages. When the cooling rate of fire extinguishing agent is greater than the heat release rate of lithium-ion battery, the temperature begins to drop rapidly.

3.2 Experimental research on fire extinguishing with different concentration of compound additive solution

Four kinds of compound additive solutions with different concentrations of 0.5%, 1%, 1.5% and 2% were selected in the experiment. Through the research on the fire extinguishing characteristics of lithium-ion battery with different concentrations of compound solution, the optimal compound proportion and surfactant concentration were found out for the fire extinguishing application of lithium-ion battery. According to the classification of different types of surfactants, the research plots the fire temperature of the lithium-ion battery at different concentrations with time. The temperature is the highest temperature of the lithium-ion battery after spraying the water mist containing additives. It can be seen from Figure 4, Figure 5 and Figure 6 that the SDBS-D-F compound solution has the good fire extinguishing effect when the solution concentration is 1%. At this time, the maximum temperature is 420°C, and the fire extinguishing time is 30s. The PFAB-APG0810-E compound solution has the best
The effect of extinguishing the lithium-ion battery fire at concentration of 1.5%. At this time, the maximum temperature is 280 ℃, and the fire extinguishing time after spraying took 25s. For the MAEPK-FMEE-H compound solution has the best fire-extinguishing effect on the lithium-ion battery when the concentration is 2%. At this time, the maximum temperature is 350 ℃. Fluorosurfactants have the ability to reduce the surface tension of aqueous solutions, but it cannot reduce the interfacial tension of water and oil. In order to improve the wetting performance of their aqueous solutions, hydrocarbon chain surfactant that can reduce the interfacial tension of water and oil must be added. From the experimental results, it is concluded that the compound solution of 1.5% concentration of fluorosurfactant and hydrocarbon surfactant has better fire extinguishing effect than the anion-organic and anion-nonionic compound solution.

![Figure 4. SDBS-D-F compound solution](image1)
![Figure 5. PFAB-APG0810-E compound solution](image2)

3.3. Experimental research on gas absorption of different kinds of compound additive solution

Lithium-ion batteries have a high fire risk, and they are easy to reignite after the fire is extinguished. The generation of flammable gases is one of the important reasons for reignition and explosion of the lithium-ion batteries. It can effectively inhibit the explosion and combustion of lithium-ion batteries through the release of surfactant to inhibit and absorb combustible gas. 1% concentration of SDBS-D-F compound solution, 1.5% concentration of MAEPK-FMEE-H, and 2% concentration of PFAB-APG0810-E compound solution were selected for fire gas analysis of the water mist extinguishing lithium-ion battery.

![Figure 6. MAEPK-FMEE-H compound solution](image3)
![Figure 7. CH₄ and CO content change chart](image4)

The whole process of the battery from heating to burning to extinguishing is represented by (A)-(E) in Figure 7, (A) represents heating the battery; (B) represents the first half of the battery thermal runaway; (C) represents the second half battery thermal runaway; (D) represents the stable period after the temperature reaches the highest point; (E) represents the period after the release of the fire extinguishing agent. Figure 7 shows the maximum gas concentration at each stage, as can be seen from the figure, the volume concentration of some gases changed before and after surfactant release. After the release of the SDBS-D-F compound solution, the CO did not change much, but the concentration of CH₄ decreased. In the same period, the concentration of CH₄ dropped from the highest 1.236g/m³ to 0.743g/m³ after the release of SDBS-D-F compound solution. After the release of the
PFAB-APG0810-E compound solution, the concentration of CH₄ dropped from the highest 1.453 g/m³ to 0.9 g/m³. After the MAEPK-FMEE-H compound solution was released, the concentration of CH₄ decreased from 1.389 g/m³ to 1.13 g/m³. It can be seen that the SDBS-D-F compound solution and PFAB-APG0810-E compound solution have certain absorption effect on methane, but the SDBS-D-F compound solution has better absorption effect than the PFAB-APG0810-E compound solution. For CO gas, the trend of CO gas concentration after SDBS-D-F compound solution release is similar to that after MAEPK-FMEE-H release. And the CO concentration after the release of the PFAB-APG0810-E compound solution drops from 1.432 g/m³ to 0.993 g/m³, significantly lower than SDBS-D-F compound solution and MAEPK-FMEE-H. The compound solution mainly composed of PFAB-APG0810-E is mainly composed of K⁺ element with strong activity, and its solution contains more potassium ions. The speed of interaction between K⁺ and OH⁻ is 2-3 times that of Na⁺ and OH⁻. When urea is decomposed under heat at high temperature, it will release carbon monoxide, carbon dioxide and other gases, which may increase the concentration of carbon monoxide and other gases in the gas.

4. Conclusion
The PFAB-APG0810-E compound solution makes the lithium-ion battery temperature drop significantly, indicating that the PFAB-APG081-E compound solution releases in the early stage of thermal runaway to have a better fire extinguishing effect. The SDBS-D-F compound solution takes the least time to reduce the battery temperature to below 200°C, and SDBS-D-F compound solution has a greater advantage in the later cooling rate. The combination of fluorocarbon surfactant, hydrocarbon surfactant and potassium carbonate additive has better fire extinguishing effect than the anion-organic-sodium carbonate, anion-non-ion-urea compound solution, which can effectively suppress the fire and reduce lithium-ion battery temperature. SDBS-D-F compound solution and PFAB-APG0810-E compound solution have certain absorption effect on methane, but SDBS-D-F compound solution has better absorption effect than PFAB-APG0810-E compound solution.

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References
[1] Si Ge, Wang Qingsong. (2012) Fire risk and related research progress of lithium-ion batteries. J. Fire Science and Technology, 31 (9): 994 – 996.
[2] Qingsong Wang, Guangzheng Shao, Qiangling Duan and Jinhua Sun. (2016) The efficiency of heptafluoropropane fire extinguishing agent on suppressing the lithium titanate battery fire. J. Fire Technology, 52(2): 387-396.
[3] Ping P, Wang Q S, Huang P F, et al. (2015) Study of the fire behavior of high-energy lithium-ion batteries with full-scale burning test. J. Journal of Power Sources, 285: 80-89.
[4] Li Yi, Yu Dongxing. (2015) Experimental study on fire extinguishing of typical bond ion batteries. J. Journal of Safety and Environment, 15 (6): 120-125.
[5] T.Ohsaki, T.Kishi,T. Kubokiet al. (2005) Overcharge reaction of lithium-ion batteries. J. Journal of Power Sources, 146: 97-100.
[6] Gu Na. (2010) The absorption and application of surfactant organic aggregates to methane. D. China University of Mining and Technology.
[7] Lisbona, D, Snee, T. (2011) A review of hazards associated with primary lithium and lithium-ion batteries. Process Saf. Environ. Prot, 89: 434–442.
[8] Wang Q, Ping P, Zhao X, Chu G, Sun J, Chen C. (2012) Thermal runaway caused fire and explosion of lithium ion battery. J. Power Sources , 208: 210–224.
[9] Zhang Zengzhi, Zhang Chaojie, Xing Ruifeng. (2015) Experimental study on the absorption of methane by anionic surfactant-vegetable oil compound system. J. Functional Materials, 46(21): 21018-21022.

[10] Zhu M X, Zhu S B, Gong J H, et al. (2018) Experimental study on fire and explosion characteristics of power lithium batteries with surfactant water mist. J. Procedia Engineering, 211: 1083-1090.