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(54)

Non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire and preparation method thereof.

(57)

The invention discloses a non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire and a preparation method thereof, wherein the non-conductive superfine water mist fire extinguishing agent comprises non-ionic fluorine surfactant, fatty alcohol polyoxyethylene ether, urea, dimethyl methylphosphonate and deionized water; by mass percent, non-ionic fluorine surfactant accounts for 0.25%, fatty alcohol polyoxyethylene ether accounts for 1.5%-2.5%, urea accounts for 0.32%-0.36%, dimethyl methylphosphonate accounts for 3.5%-4.5%, and the balance is deionized water. The invention adopts two types of additives to compound, the performance of the physical additive and the performance of the chemical additive are combined, and the special flame retardant dimethyl methylphosphonate for the lithium ion battery is introduced to achieve better fire extinguishing and flame retardant effects. Meanwhile, the non-ionic additive is selected as solvent, the deionized water is used as solvent, the performance of the non-overfire battery is protected while the fire is extinguished, and the loss of accidents is reduced to the maximum extent.

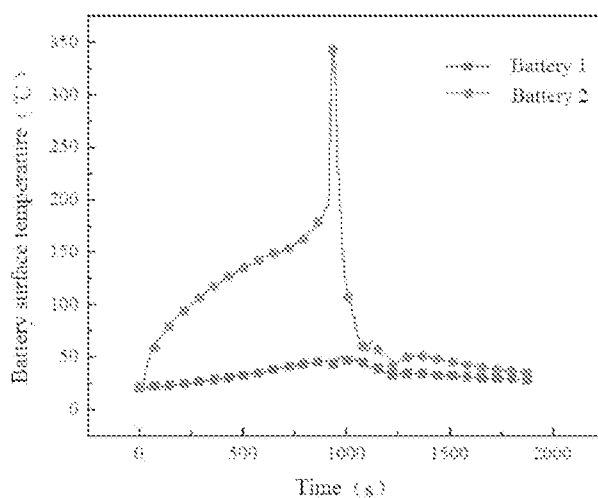


FIG 1

Non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire and preparation method thereof

Technical Field

The invention belongs to the technical field of lithium ion battery fire extinguishing agents, and particularly relates to a non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire and a preparation method thereof.

Background Art

The risk of lithium-ion battery fires has led to a lot of research on how to put them out. The Federal Aviation Administration has done a lot of experiments to select fire extinguishing agents which can inhibit the thermal runaway of lithium ion batteries. The final experimental results show that the commonly used Halon fire extinguishing agents can extinguish the fire of lithium ion batteries, but can not reduce the internal temperature of lithium ion batteries, and can eventually reignite. The results show that the internal temperature of lithium ion battery can be reduced by adding additives and using the physical or chemical action of additives, the fire of lithium ion battery can be inhibited and the reignition can be prevented. At present, the superfine water mist additives are mainly divided into two types, one is an inorganic salt and a chemical additive (such as NaCl, FeCl₂, KHCO₃, NH₄H₂PO₄, CO(NH₂)₂ and the like) which is decomposed to generate inert gas, and the inorganic salt additives ionize in water to generate a large number of metal ions, which may damage the performance of storage equipment instruments and lithium ion batteries; and the other is a surfactant which can only change the physical properties of superfine water mist, but cannot improve its fire extinguishing performance to a great extent. Both of them have some limitations.

Summary of the Invention

The invention aims to provide a non-conductive superfine water mist fire extinguishing agent for inhibiting fire of a lithium ion battery and a preparation method thereof, which solves the problems of superfine water mist fire extinguishing agent in the prior art, one is a large amount of metal ions are generated by ionization of a class of inorganic salt additives in water, and damage is caused to storage equipment instruments and performance of the lithium ion battery; and the other is a surfactant which

can only change the physical properties of superfine water mist, but cannot improve its fire extinguishing performance to a great extent.

In order to achieve the above objects, the specific technical scheme adopted by the invention is as follows:

A non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire, the fire extinguishing agent comprises non-ionic fluorine surfactant FC-4430, fatty alcohol polyoxyethylene ether AEO-9, urea, dimethyl methylphosphonate and deionized water;

by mass percent, non-ionic fluorine surfactant accounts for 0.25%, fatty alcohol polyoxyethylene ether accounts for 1.5%-2.5%, urea accounts for 0.32%-0.36%, dimethyl methylphosphonate accounts for 3.5%-4.5%, and the balance is deionized water.

In the superfine water mist fire extinguishing agent for lithium ion battery fire in the present application, the non-ionic fluorine surfactant effectively reduces the surface tension between water phases and enhances the atomization effect of the superfine water mist. Fatty alcohol polyoxyethylene ether belongs to one kind of surfactant, its HLB (hydrophilic-lipophilic balance value of a surfactant) value is 12.5, which can play a good dispersion effect, enhance the dispersion of fluorine surfactant in water, improve the uniform stability of solution. Urea decomposes at 160°C and reacts as follow: $\text{CO}(\text{NH}_2)_2 \rightarrow \text{NH}_3 + \text{HCNO}$ and $\text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{CO}_2$, the produced CO_2 and NH_3 incombustible gases can insulate the combustibles from the oxygen in the air and extinguish the suffocation. Dimethyl methylphosphonate by breaking down in flames to forms small molecules that interact with $\cdot\text{H}$ and $\cdot\text{OH}$ radicals, reduces flame strength and reduces the process of combustion chain reactions.

The invention adopts physical and chemical additives to compound, the performance of the two types of additives is combined, and the special flame retardant dimethyl methylphosphonate for the lithium ion battery is introduced to achieve better fire extinguishing and flame retardant effects. Meanwhile, the non-ionic additive is selected as a solute, the deionized water is used as a solvent, the performance of the non-overfire battery is protected while the fire is extinguished, and the loss of accidents is reduced to the maximum extent.

Further preferably, the fatty alcohol polyoxyethylene ether has a molecular formula of $\text{C}_{30}\text{H}_{62}\text{O}_{10}$ and a molecular weight of 582.

Further optimizing, the non-ionic fluorine surfactant accounts for 0.25%, fatty alcohol polyoxyethylene ether accounts for 2%, urea accounts for 0.36%, dimethyl methylphosphonate accounts for 3.5%, and the balance is deionized water.

Further optimizing, the conductivity of the non-conductive superfine water mist fire extinguishing agent is $27 \pm 2 \mu\text{S/cm}$.

The preparation method of the non-conductive superfine water mist fire extinguishing agent comprises the steps of weighing a non-ionic fluorine surfactant, fatty alcohol polyoxyethylene ether, urea and dimethyl methylphosphonate according to a mass ratio, sequentially adding into distilled water, fully stirring to prepare a fire extinguishing agent solution, and spraying the fire extinguishing agent solution through a high-pressure nozzle to form the superfine water mist fire extinguishing agent. The preparation method is simple, the preparation can be completed only by fully stirring the components, the concentration of the fire extinguishing agent is low, the cost is low, and the performance is stable.

Compared with the prior technology, the invention has the following beneficial effects:

1. The preparation method of the fire extinguishing agent is simple, the preparation can be completed only by fully stirring the components, the concentration of the fire extinguishing agent is low, the cost is low, and the performance is stable.
2. The fire extinguishing agent can enhance the advantages of the superfine water mist fire extinguishing technology, because the diameter of the superfine water mist droplets is small, the specific surface area of the droplets can be further increased through the non-ionic fluorine surfactant in the fire extinguishing agent, the physical heat absorption effect of the superfine water mist can be enhanced through the larger specific surface area, and the fatty alcohol polyoxyethylene ether can further reduce the surface tension of the water and enhance the heat absorption effect of the superfine water mist through improving the solubility and dispersibility of the non-ionic fluorine surfactant in the water.
3. The urea in the fire extinguishing agent belongs to heat-sensitive substances, is easy to decompose when heated, not only can the temperature be reduced, but also NH_3 and CO_2 generated by decomposition of the urea belong to incombustible gases, can play an asphyxiant role of diluting oxygen concentration, and enhances the fire extinguishing effect.
4. Dimethyl methylphosphonate is used as a special flame retardant for lithium ion batteries, so that

the dimethyl methylphosphonate can be sprayed on the surfaces of other lithium ion batteries in the form of superfine water mist while playing a fire extinguishing effect, and can be equivalent to a layer of flame retardant coating.

5. The components of the fire extinguishing agent are all non-ionic liquids, short circuit damage to the lithium ion battery cannot be caused in the fire extinguishing process, and the performance of the non-thermal runaway battery subjected to fire extinguishing by adopting the fire extinguishing agent is still good.

Brief Description of the Drawings

FIG. 1 is a graph showing the temperature change curve of using tap water superfine water mist to extinguish a fire of a lithium-ion battery pack in Example 2;

FIG. 2 is a graph showing the temperature change curve of using distilled water superfine water mist to extinguish a fire of a lithium-ion battery pack in Example 2;

FIG. 3 is a graph showing the temperature change curve of using superfine water mist of urea solutions with different concentrations in Example 3; wherein, 3(a) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the urea single-component solution with a concentration of 0.28%; 3(b) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the urea single-component solution with a concentration of 0.30%; 3(c) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the urea single-component solution with a concentration of 0.32%; 3(d) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the urea single-component solution with a concentration of 0.34%; 3(e) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the urea single-component solution with a concentration of 0.30%;

FIG. 4 is a graph showing the temperature change curve of using superfine water mist of fatty alcohol polyoxyethylene ether solutions with different concentrations in Example 3; wherein, 4(a) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the fatty alcohol polyoxyethylene ether single-component solution with a concentration of 0.5%; 4(b) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine

water mist of the fatty alcohol polyoxyethylene ether single-component solution with a concentration of 1%; 4(c) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the fatty alcohol polyoxyethylene ether single-component solution with a concentration of 1.5%; 4(d) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the fatty alcohol polyoxyethylene ether single-component solution with a concentration of 2%; 4(e) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the fatty alcohol polyoxyethylene ether single-component solution with a concentration of 2.5%;

FIG. 5 is a graph showing the temperature change curve of using superfine water mist of non-ionic fluorine surfactant solutions with different concentrations in Example 3; wherein, 5(a) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the non-ionic fluorine surfactant single-component solution with a concentration of 0.05%; 5(b) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the non-ionic fluorine surfactant single-component solution with a concentration of 0.1%; 5(c) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the non-ionic fluorine surfactant single-component solution with a concentration of 0.15%; 5(d) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the non-ionic fluorine surfactant single-component solution with a concentration of 0.2%; 5(e) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the non-ionic fluorine surfactant single-component solution with a concentration of 0.25%;

FIG. 6 is a graph showing the temperature change curve of using superfine water mist of dimethyl methylphosphonate solutions with different concentrations in Example 3; wherein, 6(a) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the dimethyl methylphosphonate single-component solution with a concentration of 2%; 6(b) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the dimethyl methylphosphonate single-component solution with a concentration of 4%; 6(c) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the dimethyl methylphosphonate single-component solution with a concentration of 6%; 6(d) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist

of the dimethyl methylphosphonate single-component solution with a concentration of 8%; 6(e) is the temperature change curve of the lithium ion battery pack fire extinguished by the superfine water mist of the dimethyl methylphosphonate single-component solution with a concentration of 10%;

FIG. 7 is a graph showing the temperature change curve of using superfine water mist of extinguishing agent solutions of different composite schemes in Example 4; wherein, 7(a) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 1 in Table 7; 7(b) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 2 in Table 7; 7(c) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 3 in Table 7; 7(d) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 4 in Table 7; 7(e) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 5 in Table 7; 7(f) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 6 in Table 7; 7(g) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 7 in Table 7; 7(h) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 8 in Table 7; 7(i) is a temperature change curve of lithium ion battery pack fire extinguished by the superfine water mist of the compound fire extinguishing agent with sequence number 9 in Table 7;

FIG. 8 is a graph showing the temperature change curve of using superfine water mist of compound fire extinguishing agent in Example 5;

FIG. 9 is a graph showing the temperature change curve of using superfine water mist of compound fire extinguishing agent in Example 6;

FIG. 10 is a graph showing voltage-current curves of three mediums of tap water, distilled water and fire extinguishing agent in Example 7.

Detailed Description of the Invention

The technical solutions in the embodiments of the present invention will be clearly and completely described below in conjunction with the accompanying drawings in the embodiments of the present invention. Obviously, the embodiments described are only a few, but not all, embodiments of the present invention. Based on the embodiments of the present invention, all other embodiments obtained by a person of ordinary skill in the art without involving any inventive effort are within the scope of the present invention.

In the present application, a corresponding water mist solution is configured according to the specific requirements in each of the following examples.

In the implementation process, the temperature of a laboratory is controlled to be about 25°C, two lithium ion batteries are arranged on a battery fixing support in parallel as a group, the side surfaces of the two lithium ion batteries are in contact, and the two lithium ion batteries are recorded as a battery 1 and a battery 2 according to a thermal runaway sequence, the models of the battery 1 and the battery 2 are the same, and both are 18650 type lithium ion batteries, 2600 mAh and 100% SOC; each group of experiments corresponds to one group of lithium ion battery packs. Cr₂₀Ni₈₀ nichrome resistance wires are wound on the surfaces of each group of batteries 1, no resistance wires need to be wound on the batteries 2, and the heating resistance wires are supplied by a direct-current voltage-stabilizing power supply with the power of about 20 W to cause the thermal runaway of batteries 1; the high-pressure atomizing spray head is fixedly arranged at a height of about 15 cm from the upper part of the lithium ion battery pack, the spraying pressure of the spray head is set to be 6 MPa, the aperture of the spray head is 3 mm, and the spraying angle is 120°.

In the application, the non-ionic fluorine surfactant, fatty alcohol polyoxyethylene ether, urea and dimethyl methylphosphonate are all existing products. The non-ionic fluorine surfactant is produced by 3M Company, US, the fatty alcohol polyoxyethylene ether is produced by Zhongxin Chemical Co., Ltd., the molecular formula of the fatty alcohol polyoxyethylene ether is C₃₀H₆₂O₁₀, and the molecular weight is 582. Urea is produced by Sinopharm Chemical Reagent Co., Ltd., and dimethyl methylphosphonate is produced by Beijing Letai Chemical Co., Ltd. The deionized water is produced by Gaoke Group Environmental Protection Biotechnology Co., Ltd.

Example 1:

Under the condition of not spraying superfine water mist, the thermal runaway experiment of the lithium ion battery is carried out.

The thermal resistance wire is heated to cause the thermal runaway of the battery 1, the stable combustion flame is developed after the initial injection fire is formed, and cause the thermal runaway of the battery 2, the thermal runaway and the transmission phenomenon occur. The experimentally recorded data are shown in Table 1:

Table 1 Thermal runaway and propagation process parameters of lithium ion batteries sprayed without superfine water mist

Sequence Number	Safety valve opening temperature (°C)	Thermal runaway initial temperature (°C)	Highest temperature (°C)	Flame duration (s)
Battery 1	162.1	216.1	740	59
Battery 2	156.3	224.7	841.3	42

Referring to Table 1, the duration of the battery 1 can reach 59 s, and the thermal runaway of the battery 2 can be caused without any control thermal runaway measures, so that the battery 2 is dangerous.

Example 2:

The thermal runaway experiment of lithium ion battery was carried out by using tap water and distilled water superfine water mist respectively.

The experiment was carried out in two groups, denoted as the first group and the second group, each group comprising battery 1 and battery 2.

The thermal resistance wires of the two groups of experiments are heated to cause thermal runaway of the batteries 1 in the two groups of experiments, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the lithium ion batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying.

The first group adopts a high-pressure nozzle to spray tap water to form superfine water mist, and the second group adopts a high-pressure nozzle to spray distilled water to form superfine water mist.

The data of the two groups of experiments are shown in Table 2. The first group, after spraying the tap

water superfine mist, the battery 1 was extinguished 5 s after spraying, 287 s was required for the initial temperature drop to below the safe temperature of 50°C, and cooling rate from the maximum temperature to 50°C were 1.137°C/s and 1.158°C/s.

In the second group, after spraying distilled water superfine water mist, the battery 1 was extinguished 6 s after spraying, and 174 s was needed for the initial temperature drop to below the safe temperature 50°C, and cooling rate from the maximum temperature to 50°C was 1.158°C/s.

Table 2 Relevant parameters of tap water and distilled water superfine water mist fire extinguishing process with different concentrations of urea solution

Sequence Number	Safety valve opening temperature (°C)	Thermal runaway initial temperature (°C)	Highest temperature (°C)	Extinguishing Time (s)	Time for cooling to 50°C (s)	Maximum cooling rate (°C/s)	Conductivity (μs/cm)
Tap water	148.4	192.4	344.4	5	287	1.137	297
Distilled water	142.8	196.6	316.8	6	174	1.538	2

Referring to FIGS. 1 and 2, the batteries 2 of the first group and the second group do not cause thermal runaway by adopting a tap water and distilled water superfine water mist fire extinguishing and cooling mode. Wherein, compared with the first group and the second group, when the distilled water superfine water mist is adopted for fire extinguishing, the fire extinguishing rate is relatively fast, and a large temperature rise phenomenon occurs after the superfine water mist is sprayed for fire extinguishing and cooling, as shown in FIG. 1. Because tap water is not filtered or distilled, and contains a certain amount of impurities such as suspended substances, colloidal substances, soluble substances and small molecular organic matters, the surface tension of the tap water is larger than that of distilled water, and the specific surface area of droplets is smaller, so that the fire extinguishing and cooling effect is poorer than that of distilled water; meanwhile, due to the fact that the spraying time of the tap water superfine water mist is long (287 s), the temperature of the battery is cooled slowly, and the temperature rising phenomenon cannot occur, as shown in FIG. 2. Therefore, the cooling rate of the tap water superfine water mist is slow, the temperature rise after fire extinguishing is small, but after the temperature reaches 50°C, the cooling time of the distilled water superfine water mist is short, so

that the fire extinguishing temperature rise of the distilled water superfine water mist is large and the duration time is long, if the lithium ion batteries reach a certain amount, fire re-combustion of the lithium ion batteries can be caused, or a heat transmission phenomenon is caused, and a great potential safety hazard is left.

However, in the first group, when the tap water superfine water mist is used for extinguishing and cooling, lots of metal ions are generated by ionization, and the conductivity is 297 $\mu\text{s}/\text{cm}$, so that the performance of a storage device instrument and a lithium ion battery can be damaged.

Example 3:

The thermal runaway experiments of lithium ion batteries were carried out with different concentrations of single-component superfine water mist.

The single component means that only one component is added, and the balance is distilled water.

In this example, the experiment was performed in four groups, designated as a third group, a fourth group, a fifth group and a sixth group. In the third group, urea and distilled water are mixed to form a single-component fire extinguishing agent, five parts concentration-value single-component superfine water mist fire extinguishing agent are prepared according to different mass of added urea, each part corresponds to a group of lithium ion battery thermal runaway experimental batteries, and each group of lithium ion batteries comprises a battery 1 and a battery 2. The thermal resistance wires of all the battery packs are heated to cause thermal runaway of the batteries 1 in the five groups of lithium ion battery packs, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. Experimental data as shown in Table 3 and FIGS. 3(a)-3(e), the battery 2 corresponding to the third group of five parts concentration-value single-component superfine water mist fire extinguishing agent did not cause thermal runaway.

Table 3 Relevant parameters of superfine water mist fire extinguishing process with different concentrations of urea solution

Concentration	Safety valve opening temperature	Thermal runaway initial temperature	Highest temperature (°C)	Extinguishing Time (s)	Time for cooling to	Maximum cooling rate (°C)	Conductivity ($\mu\text{s}/\text{cm}$)
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	re (°C)	re (°C)			50°C (s)	/s)	
0.28%	136.9	182.9	291.2	2	108	1.990	5
0.30%	134.3	191.4	303.5	3	107	1.433	6
0.32%	143.5	191.6	318.2	3	116	1.496	12
0.34%	140.9	199.1	306.5	2	134	2.475	20
0.36%	146.6	196.8	353.5	4	180	1.967	20

In the fourth group, fatty alcohol polyoxyethylene ether and distilled water are mixed to form a single-component fire extinguishing agent, five parts concentration-value single-component superfine water mist fire extinguishing agent are prepared according to different mass of added fatty alcohol polyoxyethylene ether, each part corresponds to a group of lithium ion battery thermal runaway experimental batteries, and each group of lithium ion batteries comprises a battery 1 and a battery 2. The thermal resistance wires of all the battery packs are heated to cause thermal runaway of the batteries 1 in the five groups of lithium ion battery packs, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. Experimental data as shown in Table 4 and FIGS. 4(a)-4(e), the battery 2 corresponding to the fourth group of five parts concentration-value single-component superfine water mist fire extinguishing agent did not cause thermal runaway.

Table 4 Relevant parameters of superfine water mist fire extinguishing process with different concentrations of fatty alcohol polyoxyethylene ether solution

Concentrati on	Safety valve opening temperatu re (°C)	Thermal runaway initial temperatu re (°C)	Highest temperatu re (°C)	Extinguishi ng Time (s)	Time for cooling to 50°C (s)	Maximu m cooling rate (°C /s)	Conductivi ty (μs/cm)
0.5%	139.4	198.3	282.9	3	165	1.866	4
1%	131.2	200.9	306.9	3	203	1.768	6
1.5%	151.7	203.8	325.6	4	165	1.890	16
2%	130.6	187.5	312.7	3	122	2.34	28
2.5%	135.7	198.5	246.2	3	202	1.070	35

In the fifth group, non-ionic fluorine surfactant and distilled water are mixed to form a single-component fire extinguishing agent, five parts concentration-value single-component superfine water mist fire extinguishing agent are prepared according to different mass of added non-ionic

fluorine surfactant, each part corresponds to a group of lithium ion battery thermal runaway experimental batteries, and each group of lithium ion batteries comprises a battery 1 and a battery 2. The thermal resistance wires of all the battery packs are heated to cause thermal runaway of the batteries 1 in the five groups of lithium ion battery packs, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. Experimental data as shown in Table 5 and FIGS. 5(a)-5(e), the battery 2 corresponding to the fifth group of five parts concentration-value single-component superfine water mist fire extinguishing agent did not cause thermal runaway.

Table 5 Relevant parameters of superfine water mist fire extinguishing process with different concentrations of non-ionic fluorine surfactant solution

Concentration	Safety valve opening temperature (°C)	Thermal runaway initial temperature (°C)	Highest temperature (°C)	Extinguishing Time (s)	Time for cooling to 50°C (s)	Maximum cooling rate (°C/s)	Conductivity (μs/cm)
0.05%	133.4	200.8	301.2	3	158	1.677	3
0.1%	142.8	200.3	365.8	4	165	1.212	6
0.15%	139.2	205.2	350.7	4	229	1.524	5
0.2%	138.4	201.9	481.4	4	217	2.548	7
0.25%	134.1	190.4	314.8	3	223	2.171	23

In the sixth group, dimethyl methylphosphonate and distilled water are mixed to form a single-component fire extinguishing agent, five parts concentration-value single-component superfine water mist fire extinguishing agent are prepared according to different mass of added dimethyl methylphosphonate, each part corresponds to a group of lithium ion battery thermal runaway experimental batteries, and each group of lithium ion batteries comprises a battery 1 and a battery 2. The thermal resistance wires of all the battery packs are heated to cause thermal runaway of the batteries 1 in the five groups of lithium ion battery packs, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. Experimental data as shown in Table 6 and FIGS. 6(a)-6(e), the battery 2 corresponding to the sixth group of five parts concentration-value

single-component superfine water mist fire extinguishing agent did not cause thermal runaway.

Table 6 Relevant parameters of superfine water mist fire extinguishing process with different concentrations of dimethyl methylphosphonate solution

Concentration	Safety valve opening temperature (°C)	Thermal runaway initial temperature (°C)	Highest temperature (°C)	Extinguishing Time (s)	Time for cooling to 50°C (s)	Maximum cooling rate (°C/s)	Conductivity (μs/cm)
2%	135.8	192.5	313.7	3	147	0.955	18
4%	140.7	200.7	323.6	3	210	1.77	44
6%	150.4	210.6	289.5	2	205	1.235	60
8%	130.6	196.4	303.4	3	348	0.376	66
10%	156.1	240.3	431.1	4	1406	0.283	73

Referring to FIGS. 3-6 and Tables 3-6, embodiments relate to the following parameters: safety valve opening temperature, thermal runaway initial temperature, maximum temperature, fire extinguishing time, time cooling to 50°C, interval cooling rate from maximum temperature to 50°C (hereinafter referred to as maximum cooling rate), conductivity and the like. However, since the safety valve opening temperature and the thermal runaway initial temperature are recorded before the superfine water mist fire extinguishing agent is sprayed, they cannot be used as a parameter for judging the fire extinguishing and cooling effects of the fire extinguishing agent; through experiments, the fire extinguishing time of each mass concentration component in the embodiment is similar and is about 3 s, the difference of the fire extinguishing time is small, the fire extinguishing cooling effect of the fire extinguishing agent cannot be judged, the difference of the maximum cooling rate is large, and therefore the maximum cooling rate is selected as the main parameter for judging the fire extinguishing cooling effect of the fire extinguishing agent.

By comparing the maximum cooling rate, the optimal concentrations of the four single components are respectively determined as follows: 0.34% urea ($\text{CO}(\text{NH}_2)_2$), 2% fatty alcohol polyoxyethylene ether (AEO-9), 0.2% non-ionic fluorine surfactant (FC-4430), 4% dimethyl methylphosphonate (DMMP).

Example 4:

In the embodiment, four substances including urea, non-ionic fluorine surfactant, fatty alcohol polyoxyethylene ether and dimethyl methylphosphonate are taken as four factors (a fire extinguishing

agent prepared from the four substances is called a compound fire extinguishing agent, and a solvent is distilled water), and the optimal concentration of the single-component superfine water mist corresponding to the four substances in the Example 3 and the concentration of the adjacent interval are taken as three factors. Four-level three-factor orthogonal superfine water mist fire extinguishing and cooling experiment was carried out by the compound preparation solution shown in Table 7.

In the embodiment, the four-level three-factor orthogonal experiment is carried out in nine groups, as shown by the sequence number in Table 7, each group of composite fire extinguishing agents with different concentrations is subjected to a thermal runaway experiment corresponding to one group of lithium ion batteries, and each group of lithium ion batteries comprises a battery 1 and a battery 2.

Table 7 Composite fire extinguishing agent superfine water mist fire extinguishing agent group distribution ratio scheme

Sequence Number	Urea $\text{CO}(\text{NH}_2)_2$ (%)	non-ionic Fluorine Surfactant FC-430 (%)	Fatty polyoxyethylene AEO-9 (%)	alcohol ether	Dimethyl methylphosphonate (DMMP) (%)
1	0.32	0.15	1.5		3.5
2	0.32	0.2	2		4
3	0.32	0.25	2.5		4.5
4	0.34	0.15	2		4.5
5	0.34	0.2	2.5		3.5
6	0.34	0.25	1.5		4
7	0.36	0.15	2.5		4
8	0.36	0.2	1.5		4.5
9	0.36	0.25	2		3.5

The thermal resistance wires of all nine groups of battery packs are heated to cause thermal runaway of the corresponding batteries 1, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. Experimental results data as shown in Table 8 and FIGS. 7(a)-7 (i), no thermal runaway was caused in batteries 2 corresponding to all nine groups of experimental batteries. The sequence numbers of Table 8 correspond one-to-one to the sequence numbers of Table 7.

Table 8 Relevant parameters of superfine water mist fire extinguishing process with different concentrations of composite additive solution

Sequenc	Safety	Thermal	Highest	Extinguishi	Time	Maximu	Conductivi
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e Number	valve opening temperatu re (°C)	runaway initial temperatu re (°C)	temperatu re (°C)	ng Time (s)	for cooling to 50°C (s)	m cooling rate (°C /s)	ty (μs/cm)
1	145.5	190.2	357.6	3	338	1.023	25
2	130.9	174.4	317.9	2	136	1.042	30
3	130.9	201.8	377.4	3	166	2.170	28
4	142.6	214.7	308.9	2	165	1.242	27
5	141.9	200.4	273.6	2	165	1.521	27
6	144.2	192	388.7	3	142	2.267	33
7	143	195.5	272.3	2	210	1.417	25
8	147.1	198.5	303.1	2	247	1.224	30
9	144.1	212.8	274.9	2	110	2.607	27
Tap water	148.4	192.4	344.4	5	287	1.137	297

As shown in Table 8, the fire extinguishing time of the superfine water mist of the composite fire extinguishing agent in each proportion is similar and is about 2 s, and the cooling and extinguishing rate of the superfine water mist of the solution corresponding to the concentration of the ninth formula is the fastest, so that the optimal concentration of the compound fire extinguishing agent solution is determined as follows: 0.36% urea, 2.5% fatty alcohol polyoxyethylene ether, 0.25% non-ionic fluorine surfactant 3.5% dimethyl methylphosphonate. Referring to Table 8, the component composite superfine water mist fire extinguishing agent has a cooling rate of 2.607 °C/s, which is 2.3 times that of the conventional tap water superfine water mist (see sequence number 10 in Table 8), and has a good fire extinguishing effect, and at the same time, the fire extinguishing agent has a conductivity of 27 μS/cm, which is 10 times lower than that of tap water.

By comparing the fire-extinguishing and cooling effects of the compound solution in Table 8, it was found that the compound fire-extinguishing agent solution corresponding to three concentrations of sequence numbers 3, 6 and 9 in Table 7 had a relatively fast cooling and fire-extinguishing rate. In the three compound modes, the content of non-ionic fluorine surfactant was 0.25%, and the content was relatively high, so it was verified by this example, non-ionic fluorine surfactants play a dominant role in compound fire extinguishing agents.

In the experiment for determining the optimal concentration of the single-component fire extinguishing agent in the Example 3, the optimal concentration of the fatty alcohol polyoxyethylene

ether is 2%; in this example, the concentration of the fatty alcohol polyoxyethylene ether in the compound fire extinguishing agent solution corresponding to sequence number 9 in Table 8 was 2%, so it was confirmed by this example that the fatty alcohol polyoxyethylene ether was mainly used for improving the solubility and dispersibility of the non-ionic fluorine surfactant.

In the compound fire extinguishing agent solution corresponding to the sequence number 9 in the Table 8, the urea solution is 0.36%, and the relative concentration is high. As urea mainly undergoes decomposition reaction in the fire extinguishing process to produce non-combustible gas and reduce the oxygen content in the space, the fire extinguishing effect is positively correlated with the concentration of the urea solution, and finally tends to be stable. However, in the experiment of superfine water mist of single urea solution, the urea solution with mass concentration of 0.34% had the best fire extinguishing and cooling effect, because the superfine water mist of single component urea had relatively large surface tension, the water mist could not make the urea solution play its best role. In the compound fire extinguishing agent solution, when the surface tension of the solution is reduced by the non-ionic fluorine surfactant and the fatty alcohol polyoxyethylene ether, the urea solution can fully play its role, so when the mass concentration is 0.36%, the synergistic fire extinguishing and cooling effect of the non-ionic fluorine surfactant and the fatty alcohol polyoxyethylene ether is the best.

As the fire extinguishing mechanism of dimethyl methylphosphonate is mainly the elementary reaction between phosphorus-containing small molecules and H, O, OH radicals in the flame combustion reaction process, the superfine water mist fire extinguishing agent can extinguish the flame within 2-3 s in the fire extinguishing process, so dimethyl methylphosphonate has low contribution to the fire extinguishing process, and dimethyl methylphosphonate is a special flame retardant for lithium ion batteries which can be used as a flame-retardant coating to be sprayed on the surface of a non-thermal runaway battery to play a flame-retardant role.

Based on the analysis, in the practical application process, the mass concentration can be adjusted in a certain range according to the cost of each component of the fire extinguishing agent on the basis of ensuring the fire extinguishing and cooling, and the fire extinguishing agent has a large cooling rate in three groups of experiments of sequence numbers 3, 6 and 9 in Table 8, namely a good fire extinguishing effect, and the corresponding concentration range of each component of the compound

fire extinguishing agent is as follows: the mass concentration of non-ionic fluorine surfactant was 0.25%, the mass concentration of urea was 0.32%-0.36%, the mass concentration of fatty alcohol polyoxyethylene ether was 1.5%-2.5%, the mass concentration of dimethyl methylphosphonate was 3.5%-4.5%, and the balance was distilled water. The mass concentration is equivalent to the mass percent.

Example 5:

Based on the mass concentration range in Example 4, a compound fire extinguishing agent solution having a mass concentration of 0.25% non-ionic fluorine surfactant, 0.32% urea, 1.5% fatty alcohol polyoxyethylene ether, 3.5% dimethyl methylphosphonate, and 0.25% non-ionic fluorine surfactant was prepared and subjected to a superfine water mist fire extinguishing experiment.

The thermal resistance wires of experimental battery packs are heated to cause thermal runaway of the batteries 1, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. The experiment data are shown in Table 9.

Table 9 Relevant parameters of minimum boundary mass concentration superfine water mist fire extinguishing process with different concentrations of urea solution

Sequence Number	Safety valve opening temperature (°C)	Thermal runaway initial temperature (°C)	Highest temperature (°C)	Extinguishing Time (s)	Time for cooling to 50°C (s)	Maximum cooling rate (°C/s)	Conductivity (μs/cm)
1	152.1	193.9	378.6	3	153	2.283	25

Referring to Table 9 and FIG. 8, the concentration of the superfine water mist extinguishes the lithium ion battery fire, the maximum cooling rate is 2.283 °C/s, and no thermal runaway occurred in the battery 2, which has good fire extinguishing and cooling efficiency.

Example 6:

Based on the mass concentration range in Example 4, a compound fire extinguishing agent solution having a mass concentration of 0.36% urea, 2.5% fatty alcohol polyoxyethylene ether, 4.5% dimethyl methylphosphonate, and 0.25% non-ionic fluorine surfactant was prepared and subjected to a superfine

water mist fire extinguishing experiment.

The thermal resistance wires of experimental battery packs are heated to cause thermal runaway of the batteries 1, and when the thermal runaway of the batteries 1 generates spraying flame, the high-pressure pump machine is started to spray superfine water mist, so that the spraying fire of the batteries 1 is inhibited, and the lithium ion batteries are cooled to below 50°C by continuous spraying. The experiment data are shown in Table 10.

Table 10 Relevant parameters of maximum boundary mass concentration superfine water mist fire extinguishing process with different concentrations of urea solution

Sequenc e Number	Safety valve opening temperatur e (°C)	Thermal runaway initial temperatur e (°C)	Highest temperatur e (°C)	Extinguishin g Time (s)	Time for coolin g to 50°C (s)	Maximu m cooling rate (°C /s)	Conductivit y (μs/cm)
1	141.7	206.3	358.7	2	152	2.402	29

Referring to Table 10 and FIG. 9, the concentration of the superfine water mist extinguishes the lithium ion battery fire, the maximum cooling rate is 2.402 °C /s, and no thermal runaway occurred in the battery 2, which has good fire extinguishing and cooling efficiency.

Example 7:

Two wiring terminals were fixed in a beaker by 1500 W high power direct current regulated power supply, and the voltage was gradually increased to 450 V. The conductivity of tap water, distilled water and the non-conductive compound fire extinguishing agent solution of Example 4 were compared. Referring to FIG. 10, among others, the conductivity is the lowest in distilled water, the current is 30 mA at a voltage of 450 V, the current is 70 mA in a non-conductive fire extinguishing agent, and the current of a direct current regulated power supply can reach 410 mA in tap water. Therefore, the conductivity of the non-conductive superfine water mist fire extinguishing agent is similar to that of distilled water, and does not cause performance damage to a non-thermal runaway battery after being sprayed, so it has good non-conductivity.

In combination with the above Examples 1-7, the fire extinguishing agent disclosed by the invention has the advantages of good fire extinguishing effect, high efficiency, no short circuit damage to the lithium ion battery in the fire extinguishing process, and the preparation method of the fire

extinguishing agent is simple.

It should be understood that the specific embodiments described herein are merely illustrative of the invention and are not intended to limit the invention. Any modification, equivalent replacement, improvement, etc. made within the spirit and principle of the present invention should be included in the protection scope of the present invention.

CLAIMS

1. A non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire, characterized in that the components of the non-conductive superfine water mist fire extinguishing agent comprises a non-ionic fluorine surfactant, a fatty alcohol polyoxyethylene ether, a urea, a dimethyl methylphosphonate and a deionized water;

by mass percent, the non-ionic fluorine surfactant accounts for 0.25%, the fatty alcohol polyoxyethylene ether accounts for 2%, the urea accounts for 0.36%, the dimethyl methylphosphonate accounts for 3.5%, and the balance is deionized water;

a preparation method of the non-conductive superfine water mist fire extinguishing agent comprises the steps of weighing the non-ionic fluorine surfactant, the fatty alcohol polyoxyethylene ether, the urea and the dimethyl methylphosphonate according to a mass ratio, sequentially adding into distilled water, fully stirring to prepare a fire extinguishing agent solution, and spraying the fire extinguishing agent solution through a high-pressure atomizing nozzle to form the superfine water mist fire extinguishing agent;

the fatty alcohol polyoxyethylene ether is AEO-9, the molecular formula is $C_{30}H_{62}O_{10}$, and the molecular weight is 582.

2. The non-conductive superfine water mist fire extinguishing agent for inhibiting lithium ion battery fire of claim 1, characterized in that the conductivity of the non-conductive superfine water mist fire extinguishing agent is $27 \pm 2 \mu S/cm$.

REVENDICATIONS

1. Agent extincteur à brouillard d'eau ultra-fin non conducteur pour inhiber le feu de batteries au lithium-ion, caractérisé en ce que: les composants de l'agent extincteur à brouillard d'eau ultra-fin non conducteur comprennent l'agent tensioactif fluoré non ionique, l'éther polyoxyéthylène d'alcool gras, l'urée, le méthylphosphonate de diméthyle et l'eau désionisée;

Calculé en pourcentage massique, l'agent tensioactif fluoré non ionique représente 0,25%, l'éther polyoxyéthylène d'alcool gras représente 2%, l'urée représente 0,36%, le méthylphosphonate de diméthyle représente 3,5% et le reste est de l'eau désionisée;

Le procédé de préparation de l'agent extincteur à brouillard d'eau ultra-fin non conducteur est le suivant: peser l'agent tensioactif fluoré non ionique, l'éther polyoxyéthylène d'alcool gras, l'urée et le méthylphosphonate de diméthyle en proportion massique, puis ajouter-les en séquence à l'eau distillée, remuer bien pour faire la solution d'agent extincteur, puis vaporiser-la à travers la buse d'atomisation à haute pression pour former l'agent extincteur à brouillard d'eau ultra-fin;

Ledit éther polyoxyéthylène d'alcool gras est AEO-9, la formule moléculaire est $C_{30}H_{62}O_{10}$ et le poids moléculaire est 582.

2. Agent extincteur à brouillard d'eau ultra-fin non conducteur pour inhiber le feu de batteries au lithium-ion selon la revendication 1, dans lequel la conductivité dudit agent extincteur à brouillard d'eau ultra-fin non conducteur est de $27 \pm 2 \mu S / cm$.

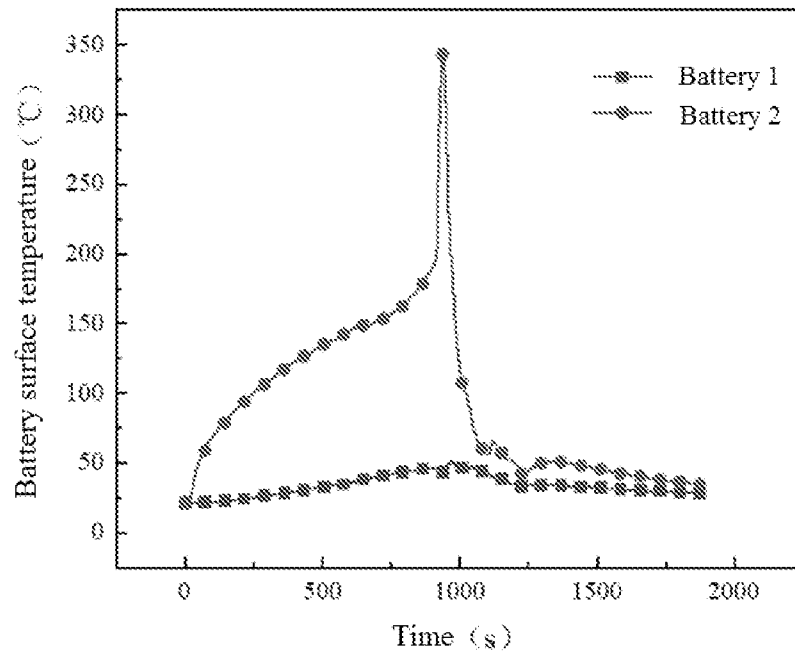


FIG 1

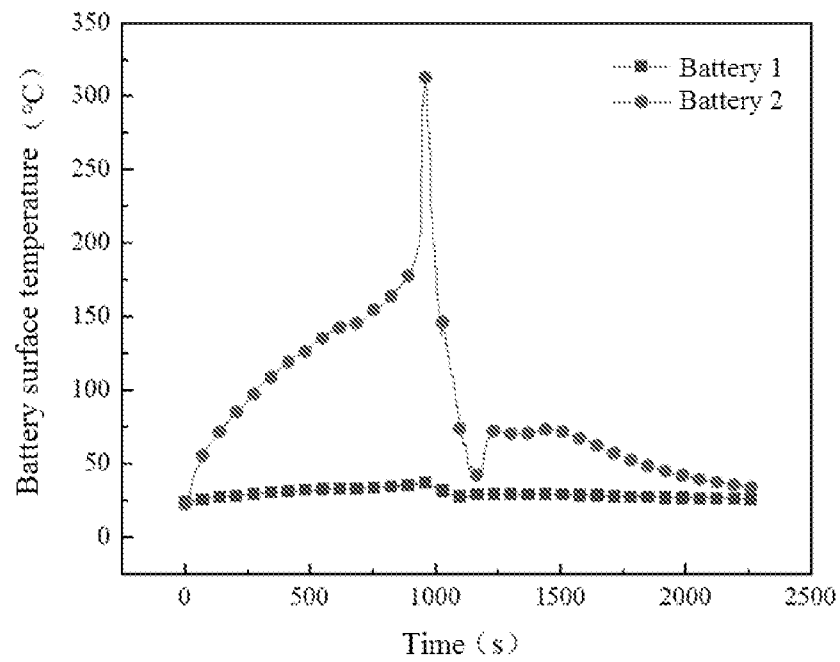
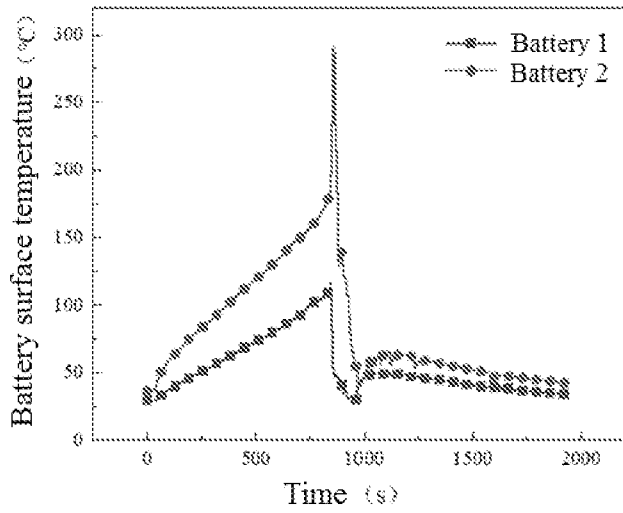
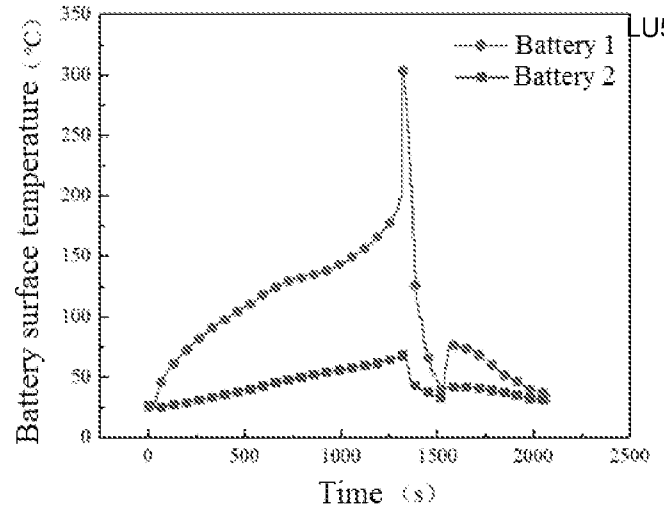


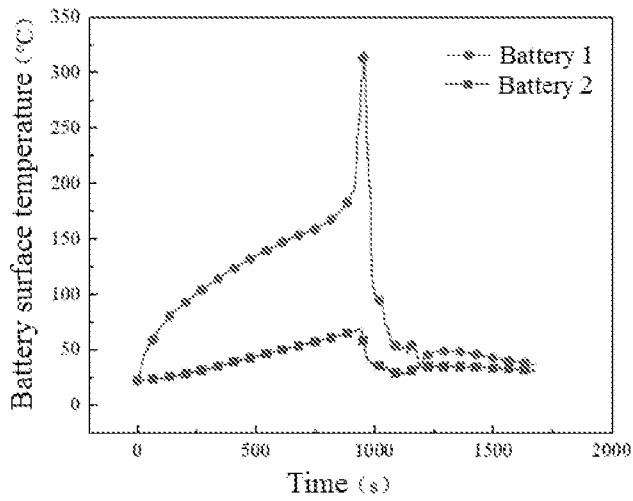
FIG 2



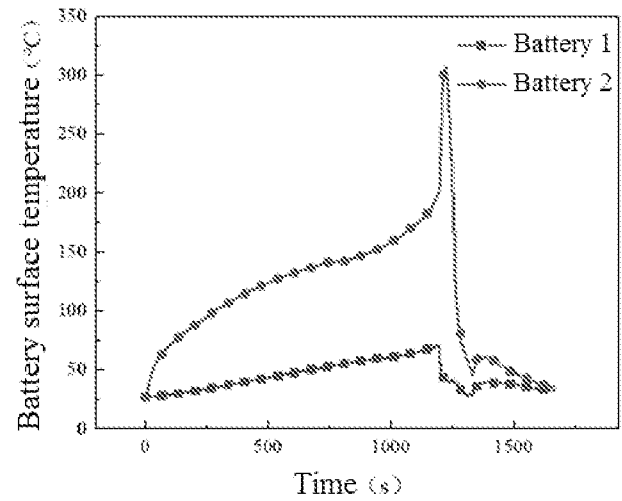
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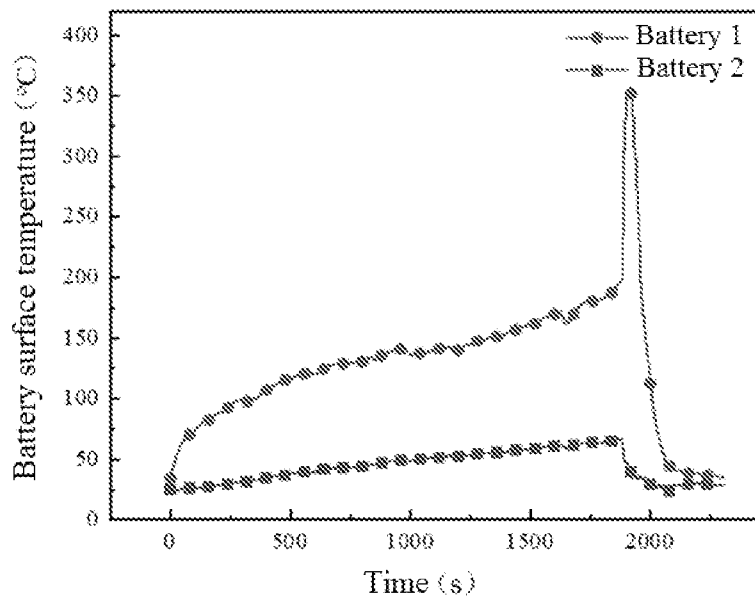
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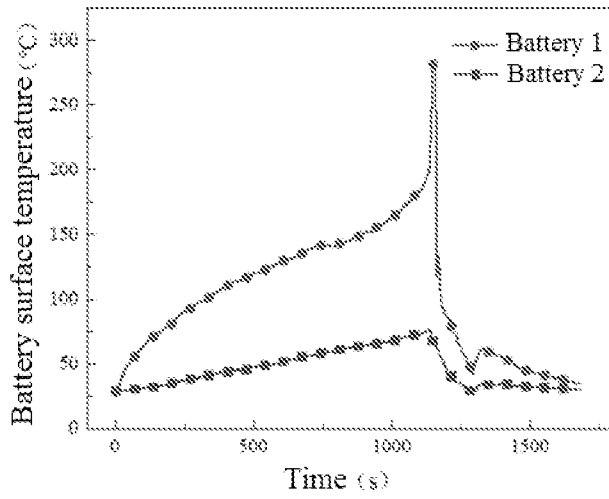


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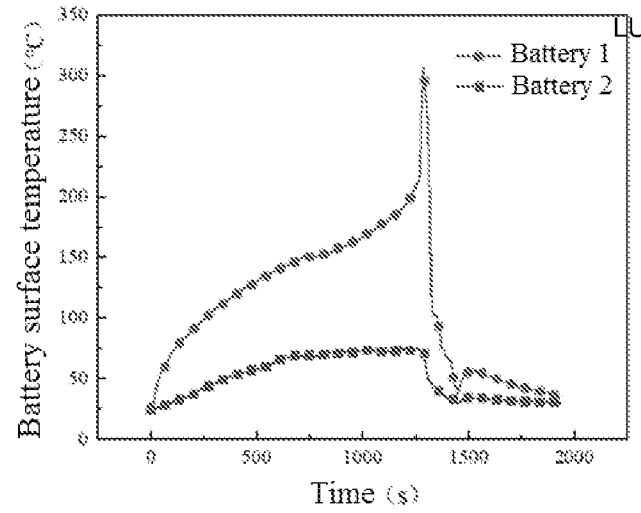


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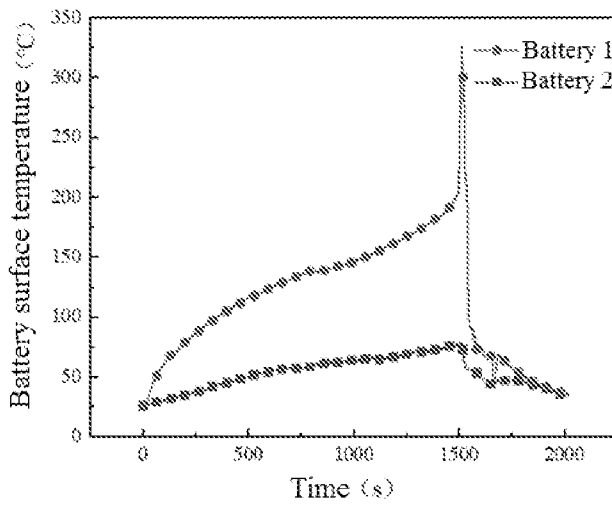
FIG 3



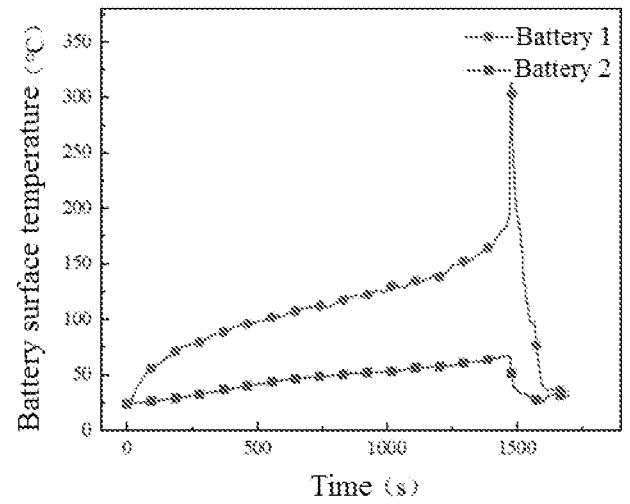
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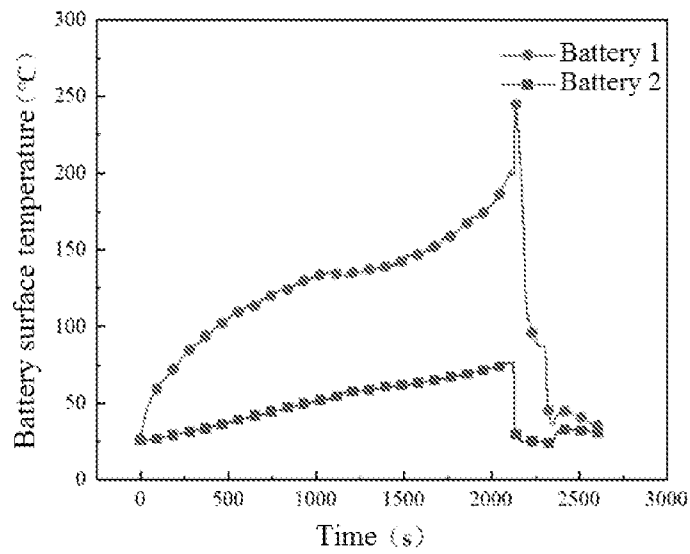
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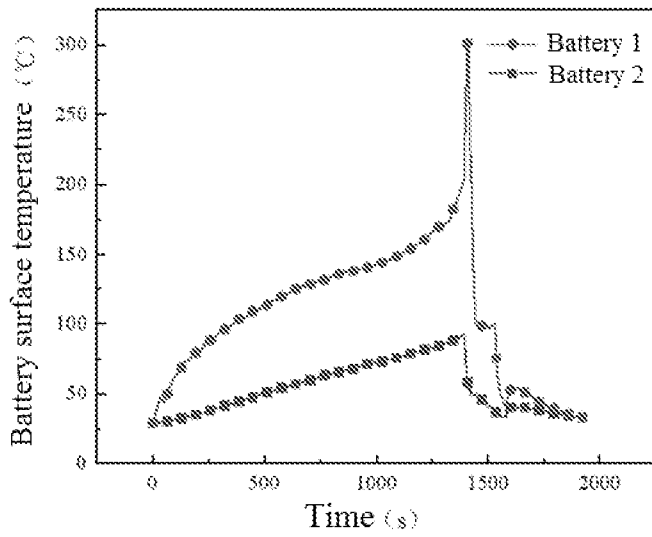


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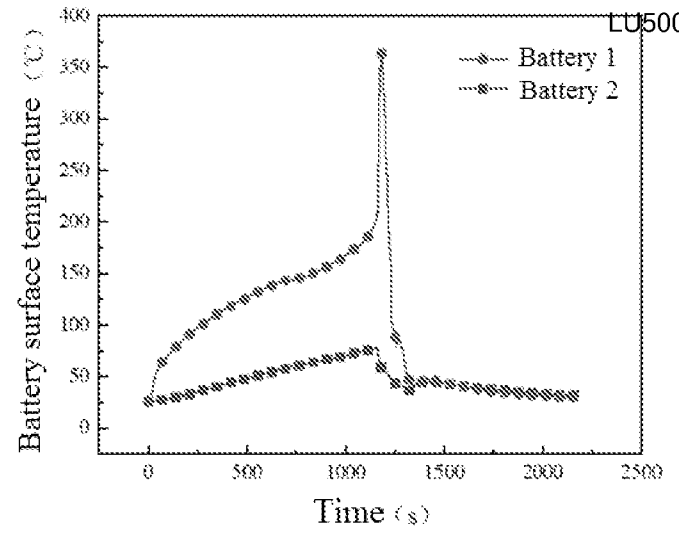


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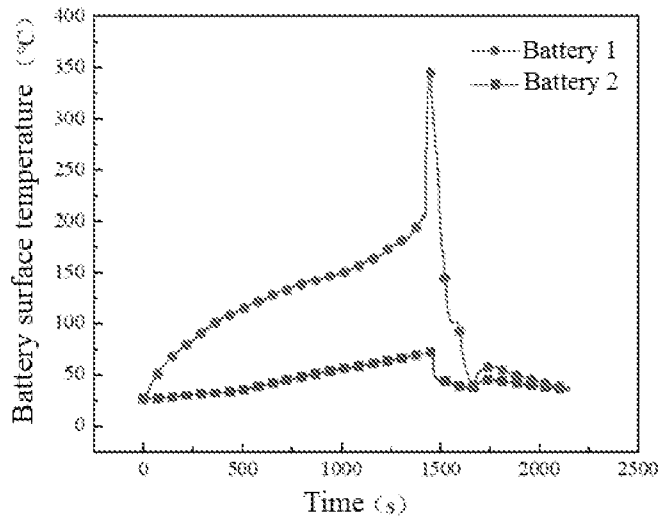
FIG 4



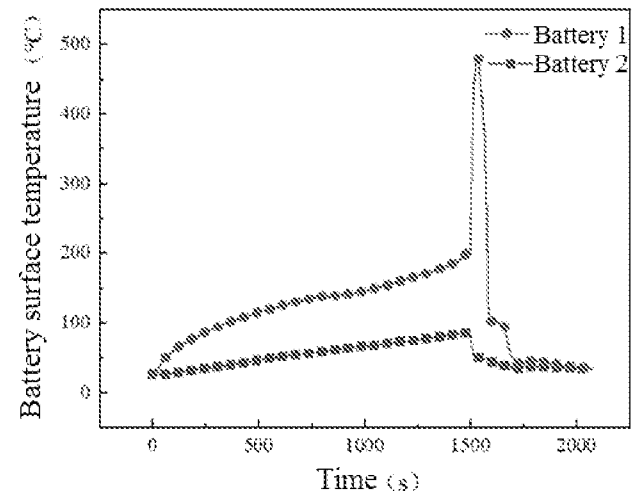
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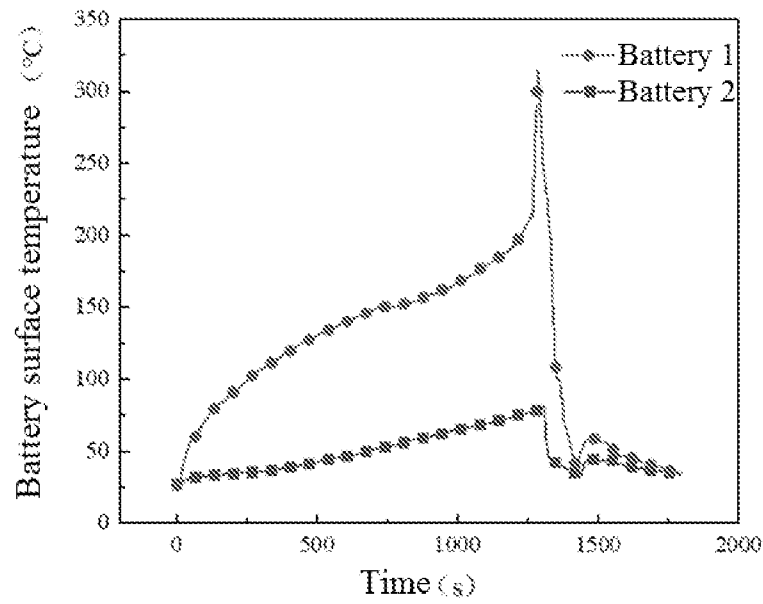
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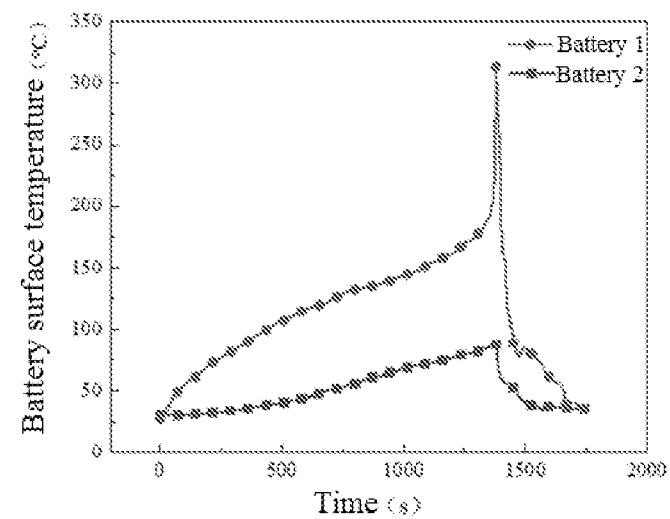


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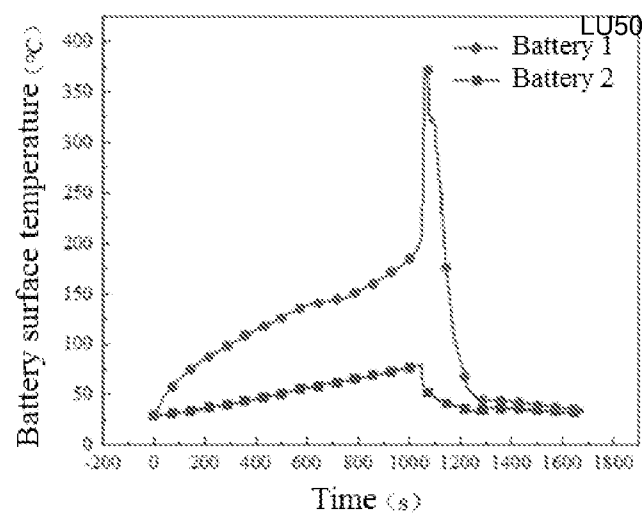


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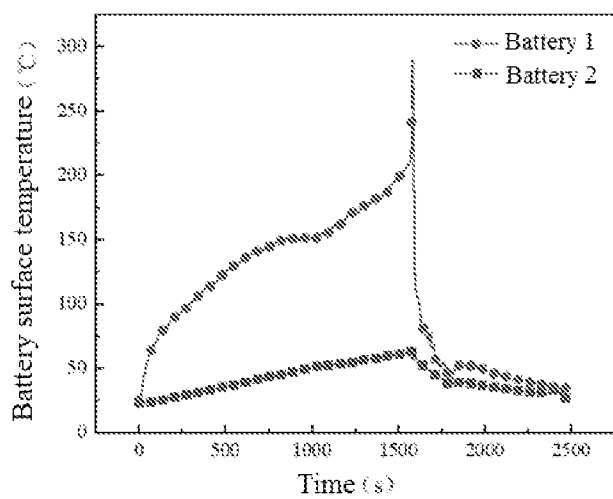
FIG 5



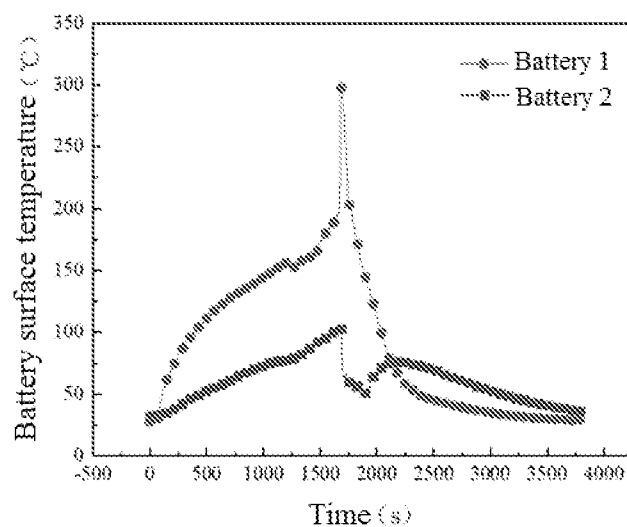
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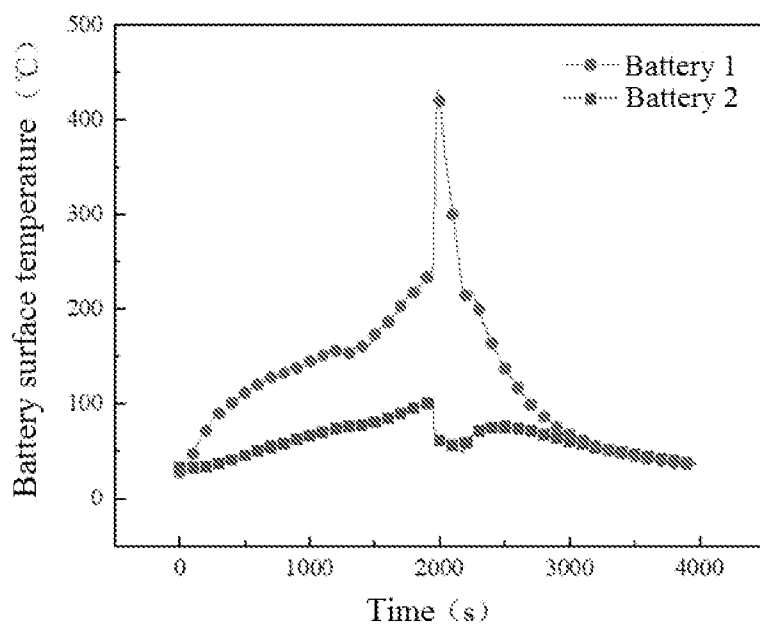
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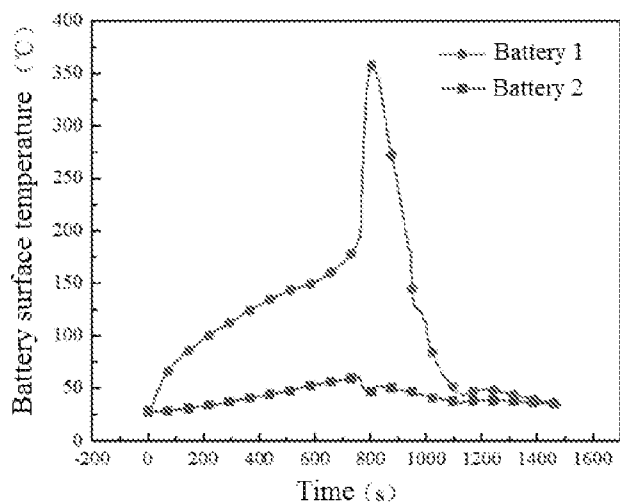


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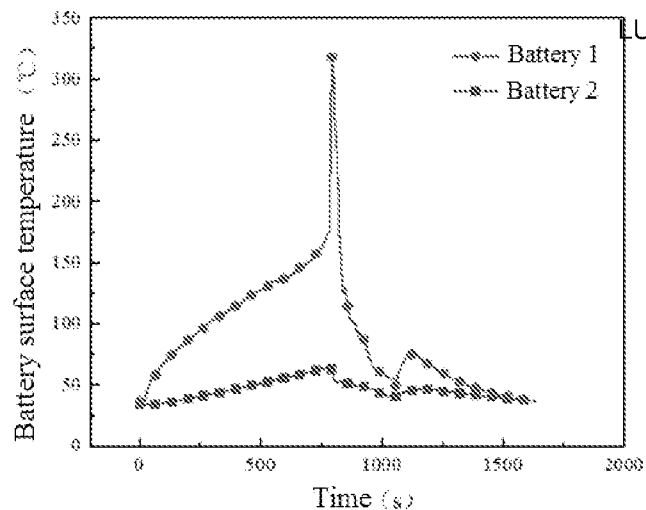


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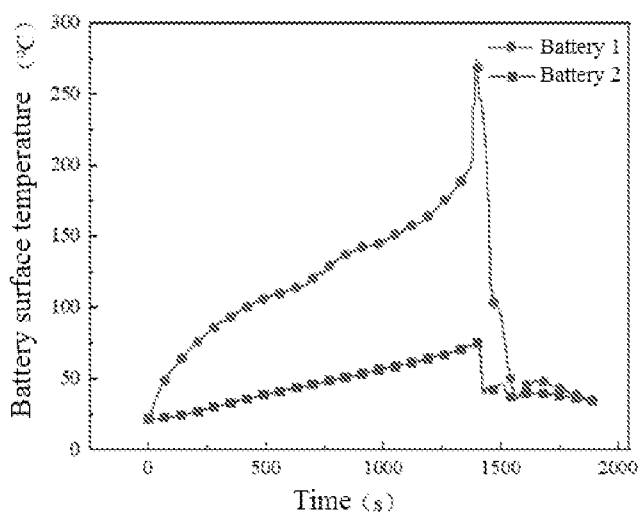
FIG 6



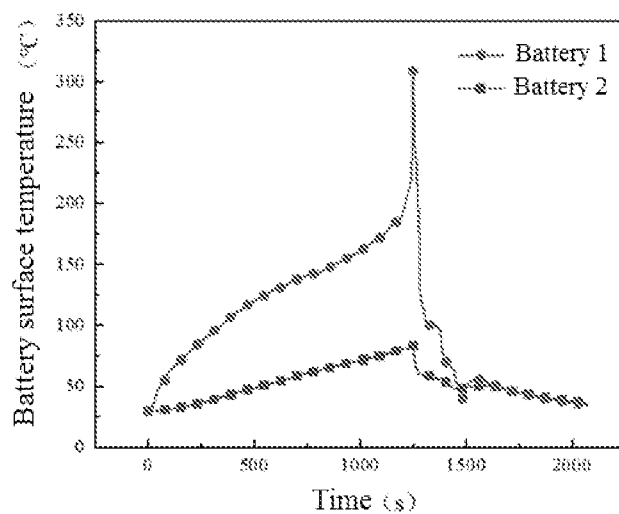
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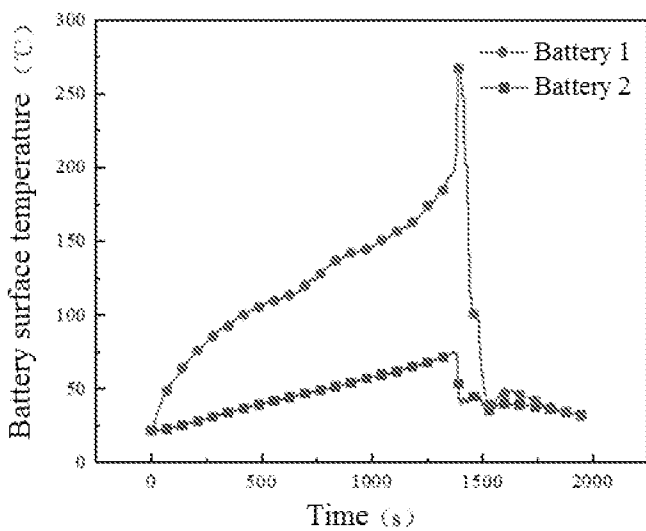
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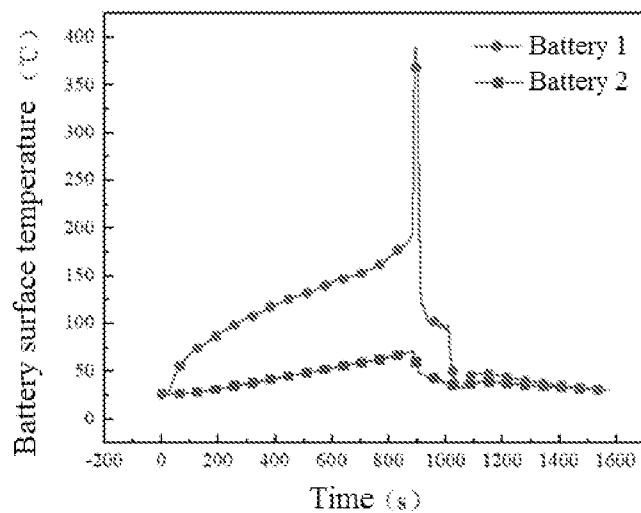
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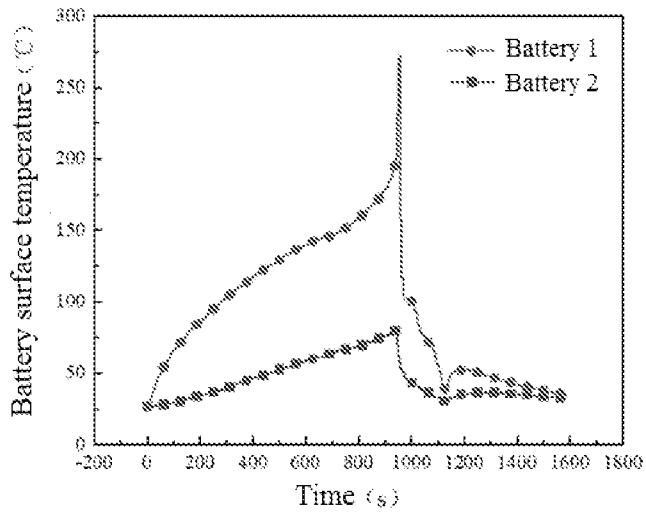
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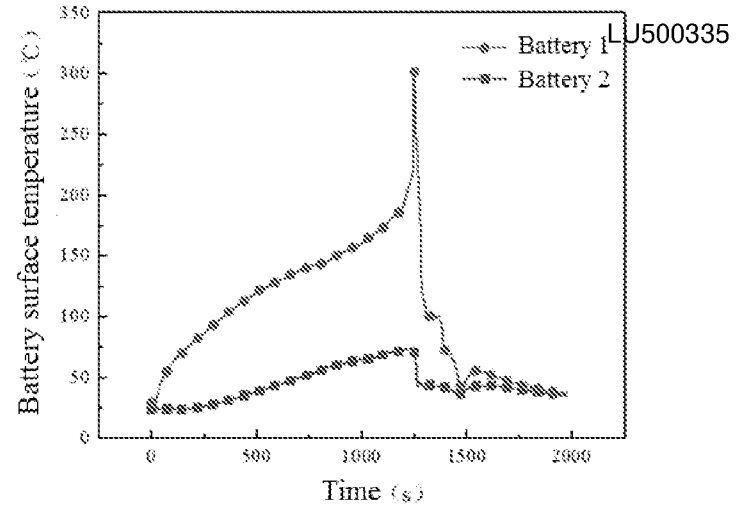
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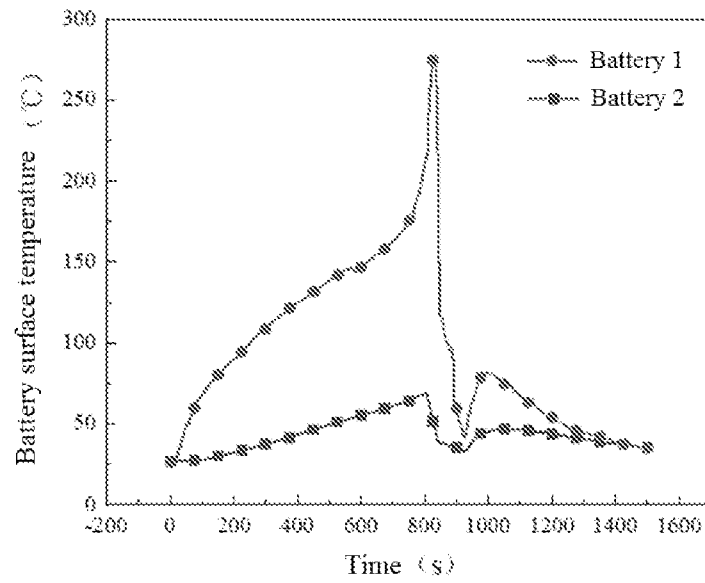
(f)



(g)



(h)



(i)

FIG 7

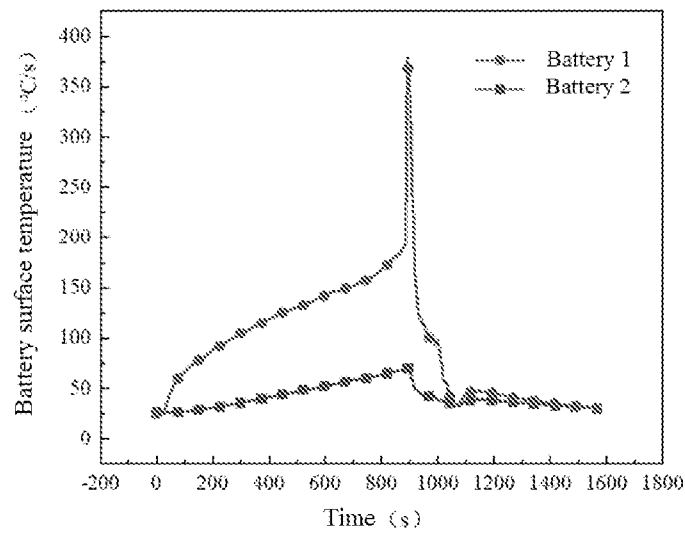


FIG 8

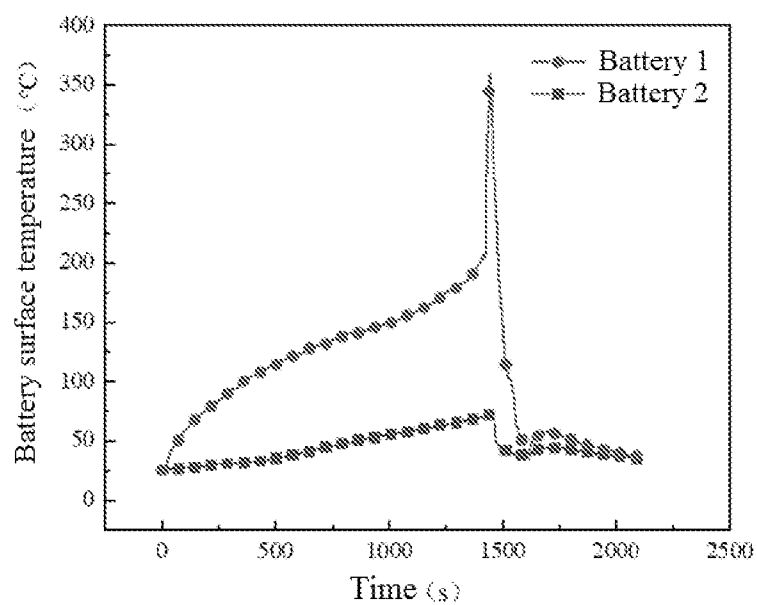


FIG 9

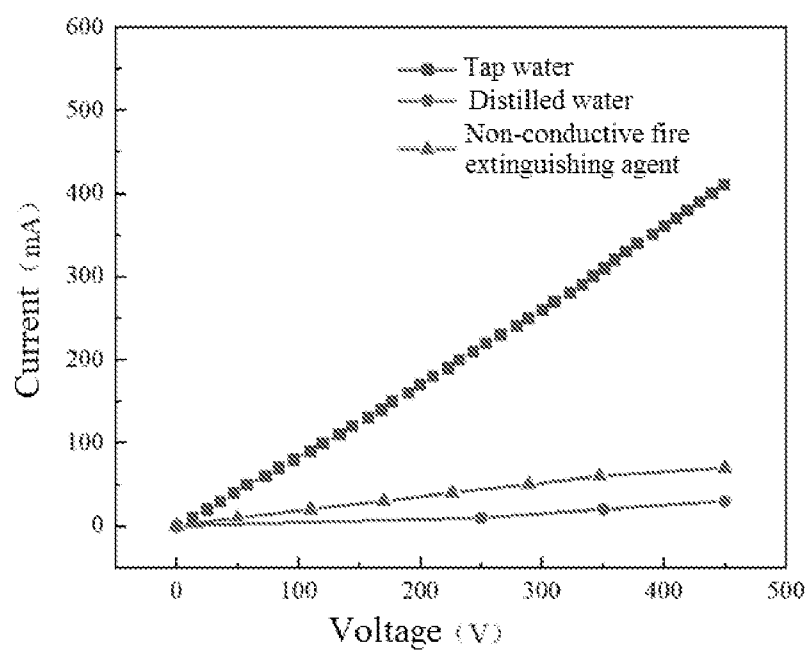


FIG10