

BATTERY THERMAL PROTECTION SYSTEM AND APPLICATION THEREOF

5 TECHNICAL FIELD

The present invention relates to the technical field of safety protection of commercial lithium-ion batteries, and in particular, to a battery thermal protection system and application thereof.

10 BACKGROUND

An energy storage part and an energy conversion part of a lithium-ion battery pack exist in the same space, which is easy to cause an exothermic chain reaction in the case of over-charge, nail penetration, and collision, resulting in thermal runaway and fire and explosion of the whole battery pack. Research believes that thermal runaway is the most serious safety accident for traction batteries, directly threatening life safety of users. The problem of thermal runaway propagation in battery packs is solved mainly by means of thermal protection technology.

A battery set of an existing new-energy vehicle is usually fixedly placed in a metal housing, and then the batteries in the battery set are isolated and protected by a mica plate or an aerogel, but the effect is not very remarkable. Research believes that coating a thermal-protective coating on an aluminum housing of each single cell will be a way to delay the fire outbreak and explosion of a battery. For example, a Chinese invention patent application (publication number: CN 114 590 008 A) discloses a heat-insulating multilayer composite material for a cell module, and a preparation method and application thereof. A product having impact resistance and thermal insulation functions is obtained by pressing and molding a heat-insulating plate, a fiber substrate immersed in a resin matrix, and a heat-insulating film, but the problem of thermal runaway propagation cannot be effectively solved by relying on only the protective coating.

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SUMMARY

In order to solve the above problems, the present invention provides a novel battery thermal protection system, consisting of multifunctional coatings coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery and a fluid between cells in a module, which can greatly reduce damage of thermal runaway of a single cell to adjacent cells and the whole battery set, and block propagation of the thermal runaway.

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An aspect of the present invention provides a novel battery thermal protection system, consisting of multifunctional coatings coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery and a fluid between cells in a module, where the
5 multifunctional coatings are one or a combination of an organic coating, an inorganic coating, and an organic-inorganic hybrid coating, and the number of layers of the multifunctional coatings is 1-10.

As a preferred technical solution, the fluid is one of a circulating fluid, an intermittent fluid,
10 and a stationary fluid.

As a preferred technical solution, the fluid is selected from one or a combination of water, methanol, ethanol, ethylene glycol, glycerol, silicone oil, a fluorinated liquid, base oil, white oil, solvent oil, lubricating oil, insulating oil, heat conducting oil, and a thermal manage-
15 ment fluid, and is preferably a thermal management fluid.

As a preferred technical solution, the fluid has a kinematic viscosity (40°C, ASTM D7042) of 2-12 mm²/s, preferably 2-8 mm²/s.

20 As a preferred technical solution, the thermal management fluid has a pour point not greater than -50°C, preferably $\leq$ -66°C.

As a preferred technical solution, the organic-inorganic hybrid coating is prepared from at least an organosilicon resin, silicon dioxide, a silicate, and an organic solvent, and the
25 mass ratio of the organosilicon resin, the silicon dioxide, and the silicate is (3-4):(5-8):(0.5-1).

As a preferred technical solution, the materials for preparing the inorganic coating comprise at least a silicate, a metal oxide, and a dispersant, and the mass ratio of the silicate,
30 the metal oxide, and the dispersant is (5-6):(1-2):(2-4).

As a preferred technical solution, the organosilicon resin is CFS18350, from Weifang Fuller New Materials Co., Ltd.

35 As a preferred technical solution, the silicon dioxide has a particle size of 20-50 nm. Preferably, the silicon dioxide has a particle size of 30 ± 10 nm. The exemplary silicon dioxide

ZT-SP30P is purchased from Zhejiang Zhitainawei New Materials Co., Ltd. As a preferred technical solution, the organic solvent is at least one of propylene glycol methyl ether and ethylene glycol.

- 5 As a preferred technical solution, the dispersant includes a silane copolymer, which can be hydrolyzed to produce a silanol bond, with a preferred example being AKN-2300, and is purchased from Foshan Qianyou Chemical Co., Ltd. As a preferred technical solution, the silicate is at least one of sodium silicate and potassium silicate, and is preferably potassium silicate.

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As a preferred technical solution, the metal oxide is at least one of titanium oxide, zirconia, aluminum oxide, and magnesium oxide, and is preferably aluminum oxide. Preferably, the aluminum oxide has a particle size of 30-50 nm, and the exemplary aluminum oxide HN-L30 is purchased from Hangzhou Hengna New Materials Co., Ltd.

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As a preferred technical solution, the multifunctional coating includes an organic-inorganic hybrid coating and an inorganic coating.

- As a preferred technical solution, a preparation method of the multifunctional coating includes at least the following steps:

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S1: adding an organosilicon resin, silicon dioxide, and a silicate to an organic solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;

S2: adding a silicate and a metal oxide to a dispersant at a mass ratio, ultrasonic treating and stirring to obtain an inorganic coating;

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S3: pretreating an aluminum plate of a housing of a commercial lithium-ion battery to obtain the pretreated aluminum plate;

S4: spraying the organic-inorganic hybrid coating onto a surface of the pretreated aluminum plate, drying to obtain a single-layer coating film, and repeating the step to obtain an organic-inorganic hybrid coating; and

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S5: spraying the inorganic ceramic coating onto a surface of the organic-inorganic hybrid coating, drying to obtain a single-layer coating film, and repeating the step to obtain an inorganic coating.

- A total mass proportion of the organosilicon resin, the silicon dioxide, and the silicate in the organic-inorganic hybrid coating is 50-60 wt%, preferably 50 ± 2 wt%.

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As a preferred technical solution, the ultrasonic treating specifically includes: ultrasonic treating by an ultrasonic cleaning machine with power of 180 W for 20-60 min, preferably 30 min.

- 5 As a preferred technical solution, the stirring specifically includes: stirring by a magnetic stirrer at a stirring speed of 600-1000 r/min for 0.5-1.5 h.

As a preferred technical solution, the pretreating specifically includes: taking the aluminum plate of the housing of the commercial lithium-ion battery, ultrasonically cleaning the aluminum plate by using acetone and ethanol for 30 min respectively, and then completely
10 drying the aluminum plate in a blast drying oven at 60°C. Then, the sandblasting is performed by using 180-mesh corundum sand. The aluminum plate after sandblasting is ultrasonically cleaned by using ethanol until there are no particles adhering to a surface of the aluminum plate, and then the aluminum plate is dried in the blast drying oven at 60°C
15 to obtain the pretreated aluminum plate.

As a preferred technical solution, the drying in step S4 specifically includes: drying at 20-30°C for 10-12 h and then drying at 60-80°C for 0.5-2 h. Preferably, the drying in step S4 specifically includes: drying at $25 \pm 2^\circ\text{C}$ for 12 h and then drying at $70 \pm 2^\circ\text{C}$ for 1 h.
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As a preferred technical solution, in step S4, the single-layer coating film has a thickness of 80-100 μm , and the organic-inorganic hybrid coating has a thickness of 80-200 μm .

As a preferred technical solution, the drying in step S5 specifically includes: drying at 20-30°C for 10-12 h. Preferably, the drying in step S5 specifically includes: drying at $25 \pm 2^\circ\text{C}$
25 for 12 h.

As a preferred technical solution, in step S5, the single-layer coating film has a thickness of 80-100 μm , and the inorganic ceramic coating has a thickness of 300-420 μm .
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In the early stage, the inventors designed and coated a multifunctional coating on the surface of an aluminum housing of each cell of a battery to effectively weaken thermal conduction and thermal convection, but it was found during heating test that the problem of thermal runaway propagation still occurred. During research, the inventors have found
35 that by assembling cells coated with multifunctional coatings into a module and immersing the module in a fluid, the fluid enters gaps between the cells and surrounds a whole cell

- set, and when a single cell is subjected to thermal runaway, a high temperature is generated. The heat is first blocked and weakened by the multifunctional thermal protection composite coating, and the spread heat passes through the fluid again, so that on one hand, the heat is absorbed by the fluid (specific heat capacity), and on the other hand, the heat is conducted out by the fluid (thermal conduction), thus greatly reducing damage of thermal runaway of a single battery cell to adjacent cells and the whole battery set, and blocking the propagation of the thermal runaway. Especially, by combining the multifunctional coating including the organic-inorganic hybrid coating and the inorganic coating with the thermal management fluid having a kinematic viscosity of 2-8 mm²/s and a pour point of $\leq -66^{\circ}\text{C}$, so that the thermal runaway time can be prolonged by about two hours, an influence of cells subjected to thermal runaway on adjacent cells can be greatly reduced, and the propagation of the thermal runaway is blocked, while the silicone oil and the fluorinated liquid may cause problems such as sealing and environmental harm.
- A second aspect of the present invention provides the application of a novel battery thermal protection system in a cell module of a lithium-ion battery.

Beneficial effects

1. The present invention provides a novel battery thermal protection system, consisting of multifunctional coatings coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery and a fluid between cells in a module, which can greatly reduce damage of thermal runaway of a single cell to adjacent cells and the whole battery set, and block propagation of the thermal runaway.
2. According to the present invention, by assembling cells coated with multifunctional coatings into a module and immersing the module in a fluid, the fluid enters gaps between the cells and surrounds a whole cell set, and when a single cell is subjected to thermal runaway, a high temperature is generated. The heat is first blocked and weakened by the multifunctional thermal protection composite coating, and the spread heat passes through the fluid again, so that on one hand, the heat is absorbed by the fluid (specific heat capacity), and on the other hand, the heat is conducted out by the fluid (thermal conduction), thus greatly reducing damage of thermal runaway of a single battery cell to adjacent cells and the whole battery set, and blocking the propagation of the thermal runaway.
3. According to the present invention, by combining the multifunctional coating including the organic-inorganic hybrid coating and the inorganic coating with the thermal management fluid having a kinematic viscosity of 2-8 mm²/s and a pour point of $\leq -66^{\circ}\text{C}$, so that the thermal runaway time can be prolonged by about two hours, an influence of cells sub-

jected to thermal runaway on adjacent cells can be greatly reduced, and the propagation of the thermal runaway is blocked.

BRIEF DESCRIPTION OF DRAWINGS

5 **FIG. 1** is a diagram showing a result of a thermal diffusion test of a cell module assembled in Example 1.

FIG. 2 is a diagram showing a result of a thermal diffusion test of a cell module assembled in a control example.

10 DETAILED DESCRIPTION OF EMBODIMENTS

Example 1

In an aspect, Example 1 of the present invention provides a novel battery thermal protection system, consisting of multifunctional coatings coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery and a fluid between cells in a
15 module.

The cell of the commercial lithium-ion battery being model 15119-24Ah is purchased from Suzhou Phylion Battery Co., Ltd.

20 The fluid is a stationary fluid.

The fluid is a thermal management fluid, which has a kinematic viscosity (40°C, ASTM D7042) of 7.137 mm²/s and a pour point of -66°C, the exemplary fluid being BluEV TF 8005, and is purchased from Fuchs Lubricants (China) Ltd.

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The materials for preparing the organic-inorganic hybrid coating comprise an organosilicon resin, silicon dioxide, a silicate, and an organic solvent, and the mass ratio of the organosilicon resin, the silicon dioxide, and the silicate is 35:58:7.

30 The materials for preparing the inorganic coating comprise a silicate, a metal oxide, and a dispersant, and the mass ratio of the silicate, the metal oxide, and the dispersant is 5.74:1.26:3.

The organosilicon resin is CFS18350, from Weifang Fuller New Materials Co., Ltd.

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The silicon dioxide has a particle size of 30 ± 10 nm. The exemplary silicon dioxide is ZT-SP30P purchased from Zhejiang Zhitainawei New Materials Co., Ltd.

The organic solvent is propylene glycol methyl ether.

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The exemplary dispersant is AKN-2300 purchased from Foshan Qianyou Chemical Co., Ltd. The silicate is potassium silicate.

The metal oxide is aluminum oxide, and the aluminum oxide has a particle size of 30-50 nm. The exemplary aluminum oxide is HN-L30 purchased from Hangzhou Hengna New Materials Co., Ltd.

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The multifunctional coating includes an organic-inorganic hybrid coating and an inorganic coating.

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A preparation method of the multifunctional coating includes the following steps:

S1: adding an organosilicon resin, silicon dioxide, and a silicate to an organic solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;

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S2: adding a silicate and a metal oxide to a dispersant at a mass ratio, ultrasonic treating and stirring to obtain an inorganic coating;

S3: pretreating an aluminum plate of a housing of a commercial lithium-ion battery to obtain the pretreated aluminum plate;

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S4: spraying the organic-inorganic hybrid coating onto a surface of the pretreated aluminum plate, drying to obtain a single-layer coating film, and repeating the step to obtain an organic-inorganic hybrid coating; and

S5: spraying the inorganic ceramic coating onto a surface of the organic-inorganic hybrid coating, drying to obtain a single-layer coating film, and repeating the step to obtain an inorganic coating.

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A total mass proportion of the organosilicon resin, the silicon dioxide, and the silicate in the organic-inorganic hybrid coating is 50 ± 2 wt%.

The ultrasonic treating specifically includes: ultrasonic treating by an ultrasonic cleaning machine with power of 180 W for 30 min.

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The stirring specifically includes: stirring by a magnetic stirrer at a stirring speed of 1000 r/min for 1 h.

5 The pretreating specifically includes: taking the aluminum plate of the housing of the commercial lithium-ion battery, ultrasonically cleaning the aluminum plate by using acetone and ethanol for 30 min respectively, and then completely drying the aluminum plate in a blast drying oven at 60°C. Then, the sandblasting is performed by using 180-mesh corundum sand. The aluminum plate after sandblasting is ultrasonically cleaned by using ethanol until there are no particles adhering to a surface of the aluminum plate, and then
10 the aluminum plate is dried in the blast drying oven at 60°C to obtain the pretreated aluminum plate.

The drying in step S4 specifically includes: drying at $25 \pm 2^\circ\text{C}$ for 12 h and then drying at $70 \pm 2^\circ\text{C}$ for 1 h.

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In step S4, the single-layer coating film has a thickness of 100 μm , and the organic-inorganic hybrid coating has a thickness of 200 μm .

The drying in step S5 specifically includes: drying at $25 \pm 2^\circ\text{C}$ for 12 h.

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In step S5, the single-layer coating film has a thickness of 100 μm , and the inorganic ceramic coating has a thickness of 300 μm .

A preparation method of the novel battery thermal protection system includes: assembling
25 cells of a commercial lithium-ion battery with a surface of an aluminum housing coated with multifunctional coatings into a cell module and immersing the cell module in a fluid, and allowing the fluid to enter gaps between the cells and surround the whole cell module.

Example 2

30 Example 2 of the present invention provides a novel battery thermal protection system and a preparation method thereof, and its specific implementations are the same as those of Example 1, except that the thermal management fluid has a kinematic viscosity (40°C, ASTM D7042) of 2.09 mm^2/s and a pour point of -81°C , the exemplary fluid being BluEV TF 8004, and is purchased from Fuchs Lubricants (China) Ltd.

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Example 3

Example 3 of the present invention provides a novel battery thermal protection system and a preparation method thereof, and its specific implementations are the same as those of Example 1, except that the mass ratio of organosilicon resin, the silicon dioxide, and the silicate is 40:52:8.

Example 4

Example 4 of the present invention provides a novel battery thermal protection system and a preparation method thereof, and its specific implementations are the same as those of Example 1, except that in step S4, the single-layer coating film has a thickness of 100 μm, and the organic-inorganic hybrid coating has a thickness of 300 μm. In step S5, the single-layer coating film has a thickness of 100 μm, and the organic-inorganic hybrid coating has a thickness of 200 μm.

Control example

The control example of the present invention is a battery thermal protection system without a fluid, wherein the battery thermal protection system specifically consists of a multifunctional coating coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery. The cell of the commercial lithium-ion battery being model 15119-24Ah is purchased from Suzhou Phylion Battery Co., Ltd. A composition and a preparation method of the multifunctional coating are the same as those in Example 1, and the cells of the commercial lithium-ion battery with the surface of the aluminum housing coated with the multifunctional coating are assembled into a cell module.

Performance test method

The cell modules assembled in the examples and the control example underwent thermal diffusion tests by heating by means of a heating package whose heating power was 300 W. The heating was performed and was stopped when the cells were subjected to thermal runaway. Thermal runaway times of the cell modules and whether propagation of thermal runaway occurred were recorded. Thermal runaway times and whether prorogation of thermal runaway occurred were recorded. Results are shown in Figs. 1, 2 and Table 1.

Table 1

Example	Thermal runaway time	Does prorogation of thermal runaway occur?
Example 1	120 min	No
Example 2	118 min	No
Example 3	110 min	No
Example 4	113 min	No
Control example	17 min	Yes

CLAIMS

1. Battery thermal protection system, characterized in that it consists of multifunctional coatings coated on a surface of an aluminum housing of each cell of a commercial lithium-ion battery and a fluid between cells in a module, wherein the multifunctional coatings are one or a combination of an organic coating, an inorganic coating, and an organic-inorganic hybrid coating, and the number of layers of the multifunctional coatings is 1-10.
2. Battery thermal protection system according to claim 1, characterized in that the fluid is one of a circulating fluid, an intermittent fluid, and a stationary fluid.
3. Battery thermal protection system according to claim 1 or 2, characterized in that the fluid is selected from one or a combination of water, methanol, ethanol, ethylene glycol, glycerol, silicone oil, a fluorinated liquid, base oil, white oil, solvent oil, lubricating oil, insulating oil, heat conducting oil, and a thermal management fluid.
4. Battery thermal protection system according to any one of claims 1 to 3, characterized in that the fluid has a kinematic viscosity of 2-12 mm²/s.
5. Battery thermal protection system according to claim 3 or 4, characterized in that the thermal management fluid has a pour point not greater than -50°C.
6. Battery thermal protection system according to any one of claims 1 to 5, characterized in that the materials for preparing the organic-inorganic hybrid coating comprise at least an organosilicon resin, silicon dioxide, a silicate, and an organic solvent.

7. Battery thermal protection system according to any one of claims 1 to 6, characterized in that the materials for preparing the inorganic coating comprise at least a silicate, a metal oxide, and a dispersant.
8. Battery thermal protection system according to claim 6, characterized in that the organosilicon resin, the silicon dioxide, and the silicate are at a mass ratio of (3-4):(5-8):(0.5-1).
9. Battery thermal protection system according to claim 7, characterized in that the mass ratio of the silicate, the metal oxide, and the dispersant is (5-6):(1-2):(2-4).
10. Use of the battery thermal protection system according to any one of claims 1 to 9 in a cell module of a lithium-ion battery.