

MULTIFUNCTIONAL THERMAL PROTECTION COMPOSITE COATING AND PREPARATION METHOD 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 multifunctional thermal protection composite coating and a preparation method and application thereof.

10 BACKGROUND

In recent years, the popularity of new-energy vehicles has caused a sudden increase in the usage of lithium-ion batteries, and battery fire and explosion accidents have become increasingly frequent. A main reason for battery fire and explosion is that when a single cell in a lithium-ion battery pack is subjected to thermal runaway, heat is uncontrollably
15 rapidly transferred to the surrounding individual cells through an aluminum housing of the battery cell, resulting in thermal runaway and fire and explosion of the whole battery pack. Research suggests that coating a layer of thermal protection coating on an aluminum housing of each individual cell would be an effective strategy to delay battery fire and explosion.

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As is well known, there are three forms of heat transfer, namely thermal radiation, thermal convection, and thermal conduction. If it is desired to prevent heat distribution, these three heat transfer ways should be inhibited or delayed. A method to inhibit a single way of heat transfer is not ideal. Therefore, researchers suggested a design concept of a composite
25 coating of thermal protection and conducted extensive investigations. For example, a Chinese invention patent application (publication No.: CN 115 849 958 A) discloses a preparation method and application of a ceramic-based thermal protection coating. By constructing a thermal protection composite coating consisting of a pore sealing layer, a silicon-based anti-oxidation layer, and a heat-insulating and ablation-resistant layer, the
30 pore-sealing, anti-oxidation, and heat-insulating and ablation-resistant coatings having different functions are combined to fully realize their respective advantages to form a composite system with a three-layer structure and improve a temperature-resistant effect. A Chinese invention patent application (authorization announcement No.: CN 113 800 955 B) provides a multi-layer ceramic-based thermal protection composite coating and a
35 method of preparing the same and use thereof. A composite coating including a buffer layer, a strong self-healing anti-oxidation layer, an intermediate chemical barrier layer, a

ceramic thermal insulation layer, and a reinforced isolation layer sequentially from inside to outside is prepared by chemical vapor deposition, so as to prolong the service life of a material under the condition of high-temperature chemical oxidation and corrosion. A Chinese invention patent application (authorization announcement No.: CN 103 847 189 B) provides a thermal protection coating for a launch pad. The thermal protection coating includes an organic bottom layer and an organic-inorganic composite skin layer, and can withstand erosion of combustion gas flow, so that a metal back surface is at a temperature not greater than 200°C. Although a variety of thermal protection composite coatings have been developed, it is difficult to apply these composite coatings to thermal protection of aluminum housings of batteries because of factors such as high technical difficulty, complex preparation conditions, and thicker coatings. Therefore, it is still of great significance to continuously develop a simple and efficient method to prepare an ultra-thin multifunctional thermal protection composite coating for an aluminum housing of a battery.

15 SUMMARY

In order to solve the above problems, the present invention provides a design and preparation of a multifunctional thermal protection composite coating. The composite coating can controllably form a composite coating structure including a thermal conduction weakening layer, an air layer, and a thermal convection weakening layer during a fire process. While ensuring that the overall coating thickness is thin to meet the actual requirements of an aluminum housing of a battery, the design of three-layer composite structure can effectively weaken thermal conduction and thermal convection, and fully utilize functions of high temperature resistance, flame retardant, and thermal insulation.

25 An aspect of the present invention provides a multifunctional thermal protection composite coating, consisting of an organic-inorganic hybrid coating and an inorganic ceramic coating sequentially disposed on a surface of a base, wherein the materials for preparing the organic-inorganic hybrid coating comprise at least a polymer compound, an inorganic filler, and a solvent, and the materials for preparing the inorganic ceramic coating comprise at least an aqueous emulsion, a silicate, and an inorganic compound.

As a preferred technical solution, the composite coating of multifunctional thermal protection has a thickness of 1-1000 μm.

As a preferred technical solution, the polymer compound is selected from at least one of an organosilicon resin, an epoxy resin, and a polyurethane, and is preferably an organosilicon resin.

- 5 As a preferred technical solution, the organosilicon resin has a solid content of 50-60 wt%, preferably 50 ± 2 wt%. Preferably, the organosilicon resin is selected from at least one of CFS18050, CFS18250, CFS18350, CFS18450, CFS18550, CFS18650, CFS15030, CFS16030, CFS7060W, CFS7030W, and CFS6020W, and is preferably CFS18350, from Weifang Fuller New Materials Co., Ltd.

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As a preferred technical solution, the inorganic filler is selected from at least one of a zirconium compound, a silicon compound, a titanium compound, an aluminum compound, and a magnesium compound. Preferably, the inorganic filler is selected from at least one of zirconia, silicon dioxide, potassium silicate, sodium silicate, magnesium oxide, and
15 aluminum oxide. Preferably, the inorganic filler is a combination of silicon dioxide and potassium silicate or a combination of aluminum oxide, silicon dioxide, and potassium silicate.

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Preferably, the silicon dioxide has a particle size of 20-50 nm, and a loss on ignition (950°C , 2 h) $\leq 8\%$. Preferably, the silicon dioxide has a particle size of 30 ± 10 nm, and a loss on ignition (950°C , 2 h) $\leq 6\%$. The silicon dioxide VK-SP30T as an example is purchased from Crystal Clear Electronic Material Co., Ltd.

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As a preferred technical solution, the solvent is at least one of propylene glycol methyl ether and ethylene glycol.

As a preferred technical solution, the aqueous emulsion YF6189 as an example is purchased from Shanghai Chaozhan Industrial Development Co., Ltd.

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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 inorganic compound is at least one of silicon dioxide, titanium oxide, zirconia, aluminum oxide, aluminum hydroxide, and magnesium hydroxide, and is preferably aluminum oxide. Preferably, the aluminum oxide has a specific surface

area of 9-11 m²/g, and the aluminum oxide SAO-020 as example is purchased from Shandong Sinocera Functional Materials Co., Ltd.

- Another aspect of the present invention provides a method of preparing a multifunctional thermal protection composite coating, including at least the following steps:
- 5 S1: adding a polymer compound and an inorganic filler to a solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;
- S2: adding an inorganic compound and a silicate to an aqueous emulsion at a mass ratio, ultrasonic treating and stirring to obtain an inorganic ceramic coating;
- 10 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
- 15 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 ceramic coating.

As a preferred technical solution, the mass ratio of the polymer compound to the inorganic filler is 5:(5-15). Preferably, the organosilicon resin, silicon dioxide or a combination of silicon dioxide and aluminum oxide, and potassium silicate are at a mass ratio of 5:(5-10):1.

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As a preferred technical solution, a mass proportion of the organosilicon resin in the organic-inorganic hybrid coating is 50-60 wt%, preferably 50 ± 2 wt%.

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As a preferred technical solution, the mass ratio of the inorganic compound to the silicate is (10-15):1.

As a preferred technical solution, a mass proportion of the inorganic compound in the inorganic ceramic coating is 50-70 wt%, preferably 70 ± 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.

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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.

5 As a preferred technical solution, the pretreatment 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, sandblasting is performed on the aluminum plate by using 180-mesh corundum sand. The aluminum plate after sandblasting is ultrasonically cleaned by using ethanol until there are no particles adher-
10 ing to the surface of the aluminum plate, and then the aluminum plate is dried in the blast drying oven at 60°C 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
15 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.

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 .

20 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 $25 \pm 2^\circ\text{C}$ for 12 h.

As a preferred technical solution, in step S5, the single-layer coating film has a thickness
25 of 80-100 μm , and the inorganic ceramic coating has a thickness of 300-420 μm .

An objective of the present invention is to provide an ultra-thin thermal protection coating for an aluminum housing of a battery. During research, the inventors have found that by the pretreatment of the aluminum plate of the housing of the commercial lithium-ion bat-
30 tery, which is combined with a specific organic-inorganic hybrid coating, especially by optimization of the mass proportions of the polymer compound and the inorganic filler in the organic-inorganic hybrid coating, the provided organic-inorganic hybrid coating meets spraying process requirements, and at the same time, there is a strong bonding effect between the formed organic-inorganic hybrid coating and the pretreated aluminum plate, so
35 as to avoid the problem that the composite coating falls off after being subjected to fire. Further, the organosilicon resin CFS18350 having a solid content of $50 \pm 2 \text{ wt}\%$ is used,

and combined with silicon dioxide and potassium silicate, or aluminum oxide, silicon dioxide and potassium silicate, so that the provided organic-inorganic hybrid coating has strong adhesion and little volume change after being subjected to fire. However, during the thermal insulation performance test, it was found that the thermal insulation effect
5 needs to be further improved.

By further combination with the inorganic ceramic coating, the inventors sequentially spray the organic-inorganic hybrid coating and the inorganic ceramic coating onto the surface of the aluminum plate of the housing of the commercial lithium-ion battery to form the multi-
10 functional thermal protection composite coating including the organic-inorganic hybrid coating and the inorganic ceramic coating. In particular, the thicknesses of the organic-inorganic hybrid coating and the inorganic ceramic coating are controlled, thus achieving an excellent thermal insulation effect with the ultra-thin composite coating, meeting fire-proof and thermal insulation requirements of the commercial lithium-ion battery, and hav-
15 ing low cost. In addition, the implementation method is simple, and can be suitable for large-scale industrial production and application. Further, by controlling the mass proportions of aluminum oxide and the silicate in the inorganic ceramic coating, a large number of bubbles are generated in the provided composite coating while being subjected to fire. While abundant air chambers are formed in the coating, a part of a top layer is separated
20 from a bottom layer to form a large number of air layers, and finally a composite coating structure including a thermal conduction weakening layer, an air layer, and a thermal convection weakening layer is formed. It is ensured that the overall coating thickness is thin to meet the actual requirements, and functions of high temperature resistance, flame retardant, and thermal insulation are brought into full play.

25 According to the present invention, by optimization of the design of the composite coating, an impact of external heat on cells inside the aluminum housing is comprehensively reduced from two aspects, i.e., weakening thermal conduction and weakening thermal convection, thus greatly improving safety of the commercial lithium-ion battery.

30 A third aspect of the present invention provides the application of a multifunctional thermal protection composite coating on a surface of an aluminum housing of a commercial lithium-ion battery.

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Beneficial effects

1. The present invention provides a design and preparation of a multifunctional thermal protection composite coating. The composite coating can controllably form a composite coating structure including a thermal conduction weakening layer, an air layer, and a thermal convection weakening layer during a fire process. While ensuring that the overall coating thickness is thin to meet the actual requirements of an aluminum housing of a battery, the design of three-layer composite structure design can effectively weaken thermal conduction and thermal convection, and fully realize functions of high temperature resistance, flame retardant, and thermal insulation.
2. According to the present invention, by the pretreatment of the aluminum plate of the housing of the commercial lithium-ion battery, combined with a specific organic-inorganic hybrid coating, especially by optimization of the mass proportions of the polymer compound and the inorganic filler in the organic-inorganic hybrid coating, the provided organic-inorganic hybrid coating meets spraying process requirements, and at the same time, there is a strong bonding effect between the formed organic-inorganic hybrid coating and the pretreated aluminum plate, so as to avoid the problem that the composite coating falls off after being subjected to fire.
3. According to the present invention, by further combination with the inorganic ceramic coating, the inventors sequentially spray the organic-inorganic hybrid coating and the inorganic ceramic coating onto the surface of the aluminum plate of the housing of the commercial lithium-ion battery to form the multifunctional thermal protection composite coating including the organic-inorganic hybrid coating and the inorganic ceramic coating. In particular, the thicknesses of the organic-inorganic hybrid coating and the inorganic ceramic coating are controlled, thus achieving an excellent thermal insulation effect with the ultra-thin composite coating, meeting fire-proof and thermal insulation requirements of the commercial lithium-ion battery and having low cost. In addition, the implementation method is simple and can be suitable for large-scale industrial production and application.
4. According to the present invention, by controlling the mass proportions of aluminum oxide and the silicate in the inorganic ceramic coating, a large number of bubbles are generated in the provided composite coating while being subjected to fire. While abundant air chambers are formed in the coating, a part of a top layer is separated from a bottom layer to form a large number of air layers, and finally a composite coating structure including a thermal conduction weakening layer, an air layer, and a thermal convection weakening layer is formed. It is ensured that the overall coating thickness is thin to meet the actual requirements, and functions of high temperature resistance, flame retardant, and thermal insulation are fully realized.

5. According to the present invention, by optimization of the design of the composite coating, an impact of external heat on cells inside the aluminum housing is comprehensively reduced from two aspects, i.e., weakening thermal conduction and weakening thermal convection, thus greatly improving safety of the commercial lithium-ion battery.

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BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is optical photos of the multifunctional thermal protection composite coating provided in Example 1 before (a) and after (b) being subjected to fire.

10 **FIG. 2** is scanning electron microscope (SEM) front views (a and b) and side views (c and d) of the composite coating of multifunctional thermal protection provided in Example 1 after being subjected to fire.

FIG. 3 is a comparison diagram of test results of thermal insulation performance of a blank control (a), Example 1(b), Comparative Example 1(c), and Comparative Example 2(d).

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DETAILED DESCRIPTION OF EMBODIMENTS

Example 1

In an aspect, Example 1 of the present invention provides a multifunctional thermal protection composite coating, consisting of an organic-inorganic hybrid coating and an inorganic ceramic coating sequentially on a surface of a base, wherein the materials for preparing the organic-inorganic hybrid coating comprise a polymer compound, an inorganic filler, and a solvent, and the materials for preparing the inorganic ceramic coating comprise an aqueous emulsion, a silicate, and an inorganic compound.

25 The polymer compound is an organosilicon resin. The exemplary organosilicon resin has a solid content of 50 ± 2 wt% and is CFS18350 purchased from Weifang Fuller New Materials Co., Ltd.

The inorganic filler is a combination of silicon dioxide and potassium silicate.

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The silicon dioxide has a particle size of 30 ± 10 nm, and a loss on ignition (950°C , 2 h) $\leq$ 6%. The exemplary silicon dioxide is VK-SP30T purchased from Crystal Clear Electronic Material Co., Ltd.

35 The solvent is propylene glycol methyl ether.

The exemplary aqueous emulsion is YF6189 purchased from Shanghai Chaozhan Industrial Development Co., Ltd.

The silicate is potassium silicate.

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The inorganic compound is aluminum oxide. The aluminum oxide has a specific surface area of 9-11 m²/g, and the exemplary aluminum oxide is SAO-020 purchased from Shandong Sinocera Functional Materials Co., Ltd.

- 10 In another aspect, Example 1 of the present invention provides a method of preparing a multifunctional thermal protection composite coating, including the following steps:
- S1: adding a polymer compound and an inorganic filler to a solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;
- S2: adding an inorganic compound and a silicate to an aqueous emulsion at a mass ratio,
- 15 ultrasonic treating and stirring to obtain an inorganic ceramic coating;
- 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
- 20 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 ceramic coating.

- 25 The mass ratio of organosilicon resin, silicon dioxide, and potassium silicate is 5:10:1.

A mass proportion of the organosilicon resin in the organic-inorganic hybrid coating is 50 wt%.

- 30 The mass ratio of the inorganic compound to the silicate is 10:1.

A mass proportion of the inorganic compound in the inorganic ceramic coating is 70 wt%.

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

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

5 The pretreatment 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 on the aluminum plate by using 180-mesh corundum sand. The aluminum plate after sandblasting is ultrasonically
10 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 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 .

Example 2

25 Example 2 of the present invention provides a multifunctional thermal protection composite coating 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, silicon dioxide, and potassium silicate is 5:5:1.

30 Example 3

Example 3 of the present invention provides a multifunctional thermal protection composite coating 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 100 μm .
35 In step S5, the single-layer coating film has a thickness of 100 μm , and the organic-inorganic hybrid coating has a thickness of 400 μm .

Example 4

Example 4 of the present invention provides a multifunctional thermal protection composite coating and a preparation method thereof, and its specific implementations are the same as those of Example 1, except that the silicon dioxide is replaced by a combination of aluminum oxide and silicon dioxide, and the mass ratio of the aluminum oxide to the silicon dioxide is 1:1.

Example 5

Example 5 of the present invention provides a multifunctional thermal protection composite coating and a preparation method thereof, and its specific implementations are the same as those of Example 1, except that the mass ratio of the inorganic compound to the silicate is 15:1.

Comparative Example 1

Comparative Example 1 of the present invention provides an inorganic ceramic coating and a preparation method thereof. The materials for preparing the inorganic ceramic coating comprise an aqueous emulsion, a silicate, and an inorganic compound. The exemplary aqueous emulsion is YF6189 purchased from Shanghai Chaozhan Industrial Development Co., Ltd.

The silicate is potassium silicate.

The inorganic compound is aluminum oxide. The aluminum oxide has a specific surface area of 9-11 m²/g, and the exemplary aluminum oxide is SAO-020 purchased from Shandong Sinocera Functional Materials Co., Ltd.

The method of preparing the inorganic ceramic coating includes the following steps:

S1: adding an inorganic compound and a silicate to an aqueous emulsion at a mass ratio, ultrasonic treating and stirring to obtain an inorganic ceramic coating;
S2: pretreating an aluminum plate of a housing of a commercial lithium-ion battery to obtain the pretreated aluminum plate; and
S3: spraying the inorganic ceramic coating onto a surface of the pretreated aluminum plate, drying to obtain a single-layer coating film, and repeating the step to obtain an inorganic ceramic coating.

The mass ratio of the inorganic compound to the silicate is 10:1.

A mass proportion of the inorganic compound in the inorganic ceramic coating is 70 wt%.

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

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

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The pretreatment 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 on the aluminum plate 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 to obtain the pretreated aluminum plate.

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

The single-layer coating film has a thickness of 100 μm , and the inorganic ceramic coating has a thickness of 500 μm .

- 25 Comparative Example 2

Comparative Example 2 of the present invention provides an organic-inorganic hybrid coating and a preparation method thereof. The materials for preparing organic-inorganic hybrid coating comprise a polymer compound, an inorganic filler, and a solvent, and the polymer compound is an organosilicon resin. The exemplary organosilicon resin has a solid content of $50 \pm 2 \text{ wt}\%$ and is CFS18350 purchased from Weifang Fuller New Materials Co., Ltd.

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The inorganic compound is a combination of silicon dioxide and potassium silicate.

The silicon dioxide has a particle size of 30 ± 10 nm, and a loss on ignition (950°C , 2 h) $\leq$ 6%. The exemplary silicon dioxide is VK-SP30T purchased from Crystal Clear Electronic Material Co., Ltd.

5 The solvent is propylene glycol methyl ether.

The method of preparing the organic-inorganic hybrid coating includes the following steps:

S1: adding a polymer compound and an inorganic filler to a solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;

10 S2: pretreating an aluminum plate of a housing of a commercial lithium-ion battery to obtain the pretreated aluminum plate; and

S3: 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.

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The mass ratio of organosilicon resin, silicon dioxide, and potassium silicate is 5:10:1.

A mass proportion of the organosilicon resin in the organic-inorganic hybrid coating is 50 wt%.

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

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

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The pretreatment 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 on the aluminum plate 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 to obtain the pretreated aluminum plate.

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The drying 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.

In step S4, the single-layer coating film has a thickness of 100 μm , and the organic-inorganic hybrid coating has a thickness of 500 μm .

Blank control

The blank control of the present invention is the pretreated aluminum plate in Example 1.

10 **Performance test method**

1. Optical photo characterization: The appearance and heat resistance of the composite coating were characterized by optical photos of the composite coating provided in Examples 1-5 before and after being subjected to fire. Results are shown in Table 1, and the optical photos of the composite coating provided in Example 1 before and after being subjected to fire are shown in FIG. 1.
2. SEM characterization: The structure of the composite coating was characterized by the SEM front views and side views of the composite coating provided in Examples 1-5 after being subjected to fire. Results are shown in Table 1, and the SEM front views and side views of the composite coating provided in Example 1 after being subjected to fire are shown in FIG. 2.
3. Thermal insulation performance: The thermal insulation effects of Examples 1-5, Comparative Examples 1 and 2 and blank control were tested by using a thermal insulation experimental device (self-made), in which a surface subjected to fire was the surface provided with a coating, with a flame temperature of 800°C . Results are shown in Table 1 and FIG. 3.

Table 1

Example	Optical photo characterization results	SEM characterization results	Thermal insulation performance test results
Example 1	The surface of the composite coating was smooth and flat, and adhered closely to the aluminum plate. After being subjected to fire, the composite coating did not fall off, and a	The SEM front views show that the coating was composed of a large number of irregular particles, and a large number of micron-sized pores were distributed on the whole plane of the coating. The SEM side views show	The composite coating showed a better thermal insulation effect, with a temperature maintained at 156°C after being subjected to fire for 5 min.

	large number of evenly distributed bubbles appeared on the surface of the coating.	that there were a large number of air holes distributed in a top coating, which can effectively inhibit thermal convection and prevent rapid transfer of heat.	
Example 2	The surface of the composite coating was smooth and flat, and adhered closely to the aluminum plate. After being subjected to fire, the composite coating did not fall off, and a large number of evenly distributed bubbles appeared on the surface of the coating.	The SEM front views show that the coating was comprised of a large number of irregular particles, and a large number of micron-sized pores of different sizes were distributed on the whole plane of the coating. The SEM side views show that there were a large number of air holes distributed in a top coating.	The composite coating showed a better thermal insulation effect, with a temperature maintained at 160°C after being subjected to fire for 5 min.
Example 3	The surface of the composite coating was smooth and flat, and adhered closely to the aluminum plate. After being subjected to fire, the composite coating did not fall off, and a large number of evenly distributed bubbles appeared on the surface of the coating.	The SEM front views show that the coating was comprised of a large number of irregular particles, and a large number of micron-sized pores of different sizes were distributed on the whole plane of the coating. The SEM side views show that there were a large number of air holes distributed in a top coating.	The composite coating showed a better thermal insulation effect, with a temperature maintained at 160°C after being subjected to fire for 5 min.
Example 4	The surface of the composite coating was smooth and flat, and adhered closely to the aluminum plate. After being subjected to fire, the composite coating	The SEM front views show that the coating was comprised of a large number of irregular particles, and a large number of micron-sized pores of different sizes were distributed on the whole	The composite coating showed a better thermal insulation effect, with a temperature maintained at 160°C after being subjected to fire for 5 min.

	did not fall off, and a large number of evenly distributed bubbles appeared on the surface of the coating.	plane of the coating. The SEM side views show that there were a large number of air holes distributed in a top coating.	
Example 5	The surface of the composite coating was smooth and flat, and adhered closely to the aluminum plate. After being subjected to fire, the composite coating did not fall off, and a large number of evenly distributed bubbles appeared on the surface of the coating.	The SEM front views show that the coating was comprised of a large number of irregular particles, and a large number of micron-sized pores of different sizes were distributed on the whole plane of the coating. The SEM side views show that there were a large number of air holes distributed in a top coating.	The composite coating showed a better thermal insulation effect, with a temperature maintained at 165°C after being subjected to fire for 5 min.
Blank control	-	-	The pretreated aluminum plate had a poor thermal insulation effect, with a temperature maintained at 413°C after being subjected to fire for 5 min.
Comparative Example 1	-	-	The inorganic ceramic coating had a poor thermal insulation effect, with a temperature maintained at 205°C after being subjected to fire for 5 min.
Comparative Example 2	-	-	The organic-inorganic hybrid coating had a poor thermal insulation effect, with a temperature maintained at 295°C after being sub-

			jected to fire for 5 min.
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CLAIMS

1. Multifunctional thermal protection composite coating, characterized in that it consists of an organic-inorganic hybrid coating and an inorganic ceramic coating sequentially disposed on a surface of a base, wherein the materials for preparing the organic-inorganic hybrid coating comprise at least a polymer compound, an inorganic filler, and a solvent, and the materials for preparing the inorganic ceramic coating comprise at least an aqueous emulsion, a silicate, and an inorganic compound.
2. Multifunctional thermal protection composite coating according to claim 1, characterized in that the polymer compound is selected from at least one of an organosilicon resin, an epoxy resin, and a polyurethane.
3. Multifunctional thermal protection composite coating according to claim 1 or 2, characterized in that the inorganic filler is selected from at least one of a zirconium compound, a silicon compound, a titanium compound, an aluminum compound, and a magnesium compound.
4. Multifunctional thermal protection composite coating according to claim 3, characterized in that the inorganic filler is at least one of silicon dioxide, titanium oxide, zirconia, aluminum oxide, aluminum hydroxide, and magnesium hydroxide.
5. Method of preparing the multifunctional thermal protection composite coating according to any one of claims 1 to 4, characterized in that it includes at least the following steps:
S1: adding a polymer compound and an inorganic filler to a solvent at a mass ratio, ultrasonic treating and stirring to obtain an organic-inorganic hybrid coating;
S2: adding an inorganic compound and a silicate to an aqueous emulsion at a mass ratio, ultrasonic treating and stirring to obtain an inorganic ceramic coating;

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

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 ceramic coating.

6. Method of preparing the multifunctional thermal protection composite coating according to claim 5, characterized in that the mass ratio of the polymer compound to the inorganic filler is 5:(5-15).
7. Method of preparing the multifunctional thermal protection composite coating according to claim 6, characterized in that the mass ratio of the inorganic compound to the silicate is (10-15):1.
8. Method of preparing the multifunctional thermal protection composite coating according to claim 7, characterized in that 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 .
9. Method of preparing the multifunctional thermal protection composite coating according to claim 8, characterized in that in step S5, the single-layer coating film has a thickness of 80-100 μm , and the organic-inorganic hybrid coating has a thickness of 300-420 μm .
10. Use of the multifunctional thermal protection composite coating according to any one of claims 1 to 4 on a surface of an aluminum housing of a commercial lithium-ion battery.