

CN111342129A Electrolyte and electrochemical device

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Electrolyte and electrochemical device

Technical field

This application relates to the field of energy storage technology, and in particular to an electrolyte and an electrochemical device containing the electrolyte.

Background technique

Electrochemical devices represented by lithium ion batteries have the advantages of high energy density, high working voltage, low self-discharge rate, long cycle life, and no pollution. They have been widely used in computers, smart wearable devices, smart phones, and drones. , And electric vehicles and other fields. With the development of modern information technology and the expansion of the application range of lithium-ion batteries, the energy density of lithium-ion batteries in this field has higher requirements.

There are many factors that affect the energy density of lithium ion batteries. At present, increasing the charge cut-off voltage of lithium-ion batteries is one of the effective means to increase energy density, but the increase in voltage leads to poor stability of the positive electrode. How to solve the above problems to increase the energy density of lithium-ion batteries has become an urgent need in this field. The problem.

Summary of the invention

According to the inventor's research, although the nitrile additives can effectively improve the stability of the positive electrode and thus significantly improve the cycle performance of the electrochemical device, the nitrile additives may cause the elution of copper in the negative electrode current collector and thus affect the stability of the negative electrode. Especially when copper ions are eluted at the welding place of the tabs, it is easy to cause battery self-discharge and even safety problems.

The invention provides an electrochemical device, which can solve the self-discharge problem of the electrochemical device under high voltage while meeting the high-voltage cycle stability, and at the same time, is beneficial to improve safety characteristics.

In some embodiments, the present invention provides an electrochemical device, which includes a positive electrode, a negative electrode, a separator, and an electrolyte; wherein the electrolyte includes a nitrile compound, and the nitrile compound accounts for a mass fraction of the electrolyte. Is A%,

The negative electrode includes a current collector, and the current collector includes: a first zone and a second zone;

The first area is provided with a negative active material layer;

The second region does not include a negative active material layer;

The area of the second zone accounts for B% of the surface area of the current collector; and

$A \times B < 600$.

In some embodiments, the nitrile compound comprises at least one of a compound of formula I, a compound of formula II, a compound of formula III, a compound of formula IV, a compound of formula V, or a compound of formula VI:

Wherein, a, d, f, j, k, l, m, r, u, w and y are each independently an integer selected from 1 to 5, b, c, e, g, h, i, n, o, p, q, s, t, v, x are each independently an integer selected from 0 to 5; the mass fraction A% of the nitrile compound in the electrolyte is 0.1% to 10%.

In some embodiments, the nitrile compound includes at least one of the following compounds:

In some embodiments, the negative electrode has tabs, and the tabs are connected to the second region by welding, and $A \times B \leq 210$.

In some embodiments, the negative electrode has tabs, the number of tabs is not less than 1, the tabs are formed by cutting the current collector, and the tabs include an uncoated negative electrode active material layer Area, and $A \times B \leq 500$.

In some embodiments, at least one second zone is located at the edge of the current collector, wherein the distance between the tab closest to the edge of the current collector and the edge of the current collector is C, and $0 \leq C$ / The width of the tab ≤ 50 .

In some embodiments, at least one second area is located at the edge of the current collector, and the edge of the second area at the edge of the current collector is folded back or not; wherein when folded back, the width of the folded back area is D , And $0.1 \leq D/\text{tip width} \leq 20$.

In some embodiments, the current collector is copper foil, and the copper foil has one or more properties selected from the following:

- Copper purity $\geq 99.5\%$,
- The thickness is from 3 microns to 15 microns,
- The weight per unit area is 30g/m² to 150g/m²,
- Tensile strength $\geq 20\text{kg/mm}^2$, and
- Elongation $\geq 1.5\%$.

In some embodiments, the second zone is optionally covered with a substance capable of adhering to the second zone.

In some embodiments, the part of the tab is optionally covered by a substance capable of being glued thereon.

In some embodiments, the electrolyte further includes additives, the additives including 1,3-propane sultone, fluoroethylene carbonate, vinylene carbonate, 2,4-butane sultone, 1,4-butane sultone, methylene disulfonate, vinyl sulfate, succinic anhydride, ethoxypentafluorocyclotriphosphazene, 1,3-dioxane or propylene. At least one of group-1,3-sultones.

In some embodiments, wherein the electrolyte further includes an anion, the anion includes at least one of Cl⁻, Br⁻, SO₄²⁻, CO₃²⁻ or F⁻, and the content of the anion in the electrolyte Less than or equal to 1000ppm.

Another aspect of the present invention provides an electronic device including the electrochemical device as described above.

The additional aspects and advantages of the embodiments of the present application will be partially described, shown, or explained through the implementation of the embodiments of the present application in the subsequent description.

Description of the drawings

FIG. 1 is a top view of a negative electrode current collector in an embodiment of the application.

Fig. 2 is a side view of the current collector shown in Fig. 1 along the Z direction.

FIG. 3 is a top view of the negative electrode current collector in another embodiment of the application.

Fig. 4 is a side view of the current collector shown in Fig. 3 along the Z direction.

FIG. 5 is a side view of the negative electrode current collector in another embodiment of the application.

FIG. 6 is a side view of the negative electrode current collector in another embodiment of the application.

FIG. 7 is a side view of the negative electrode current collector in another embodiment of the application.

FIG. 8 is a top view of the negative electrode current collector in another embodiment of the application.

detailed description

The embodiments of this application will be described in detail below. The embodiments of this application should not be construed as limiting the scope of protection claimed by this application. Unless clearly indicated otherwise, the following terms used herein have the meanings indicated below.

As used herein, the terms "substantially", "substantially", "substantially", "substantially" and "about" are used to describe and illustrate small changes. When used in conjunction with an event or situation, the term can refer to an example in which the event or situation occurs precisely and an example in which the event or situation occurs very closely. For example, when used in conjunction with a value, the term may refer to a range of variation less than or equal to $\pm 10\%$ of the stated value, such as less than or equal to $\pm 5\%$, less than or equal to $\pm 4\%$, less than or equal to $\pm 3\%$, If less than or equal to $\pm 2\%$, less than or equal to $\pm 1\%$, less than or equal to $\pm 0.5\%$, less than or equal to $\pm 0.1\%$, or less than or equal to $\pm 0.05\%$, then the two values can be considered "substantially" the same.

In addition, sometimes amounts, ratios, and other numerical values are presented in range format herein. It should be understood that this type of range format is for convenience and brevity, and should be flexibly understood, not only including the values explicitly designated as range limits, but also encompassing all individual values or sub-ranges within the stated range, as if clearly Specify each value and subrange locally.

In the detailed description and claims, a list of items connected by the term "one of" may mean any one of the listed items. For example, if items A and B are listed, then the phrase "one of A and B" means only A or only B. In another example, if items A, B, and C are listed, then the phrase "one of A, B, and C" means only A; only B; or only C. Project A can contain a single element or multiple elements. Project B can contain a single element or multiple elements. Project C can contain a single element or multiple elements.

In the detailed description and claims, a list of items connected by the term "at least one of" can mean any combination of the listed items. For example, if items A and B are listed, then the phrase "at least one of A and B" or "at least one of A or B" means only A; only B; or A and B. In another example, if items A, B, and C are listed, then the phrase "at least one of A, B, and C" or "at least one of A, B, or C" means only A; or only B; C only; A and B (exclude C); A and C (exclude B); B and C (exclude A); or all of A, B, and C. Project A can contain a single element or multiple elements. Project B can contain a single element or multiple elements. Project C can contain a single element or multiple elements.

As used herein, the content of each component in the electrolyte is based on the total weight of the electrolyte.

1. Electrolyte

In some embodiments, the electrolyte of the present invention contains a nitrile compound, and the nitrile compound includes at least one of the compound of formula I, compound of formula II, compound of formula III, compound of formula IV, compound of formula V or compound of formula VI:

Wherein, a, d, f, j, k, l, m, r, u, w and y are each independently selected from 1, 2, 3, 4 or 5, b, c, e, g, h, i, n, o, p, q, s, t, v, x are each independently selected from 0, 1, 2, 3, 4, or 5; the mass fraction A% of the nitrile compound in the electrolyte is 0.1% to 10%, 0.3% to 8%, 1% to 6%, or 3% to 4%, in some embodiments, the A% is about 0.5%, about 1.5%, about 2.5%, about 3.5%, about 4.5%, about 5.5%, about 6.5%, about 7.5%, about 8.5%, or about 9.5%.

In some embodiments, the nitrile compound includes at least one of the following compounds:

In some embodiments, in order to further improve the performance of the lithium ion battery, the electrolyte further contains one or more of the following additives: 1,3-propane sultone (PS), fluoroethylene carbonate (FEC), vinylene carbonate (VC), 2,4-butane sultone, 1,4-butane sultone, methylene disulfonate (MMDs), vinyl sulfate (DTD)), succinic anhydride (SA), ethoxypentafluorocyclotriphosphazene, 1,3-dioxane (DOX) or propenyl-1,3-sultone.

In some embodiments, in order to inhibit the dissolution of copper in the electrolyte containing the nitrile compound, the electrolyte may also contain anions, such as at least one of the following inorganic anions, such as Cl⁻, Br⁻, SO₄²⁻, CO₃²⁻, or F⁻. In some embodiments, the content of the anion in the electrolyte is less than or equal to 1000 ppm.

In some embodiments, the electrolyte further includes a lithium salt and an organic solvent.

In some embodiments, the lithium salt is selected from one or more of inorganic lithium salt and organic lithium salt. In some embodiments, the lithium salt contains at least one of fluorine, boron, or phosphorus. In some

embodiments, the lithium salt is selected from one or more of the following lithium salts: lithium hexafluorophosphate (LiPF₆), lithium bistrifluoromethanesulfonimide (LiTFSI), bis(fluorosulfonyl) Lithium amide (abbreviated as LiFSI), bisoxalate boric acid (abbreviated as LiBOB), difluorooxalate boric acid (abbreviated as LiDFOB), lithium hexafluoroarsenate (abbreviated as LiAsF₆), lithium perchlorate (abbreviated as LiClO₄), trifluoro At least one of lithium methanesulfonate (LiCF₃SO₃).

In some embodiments, the concentration of the lithium salt is 0.5M to 1.5M. In some embodiments, the concentration of the lithium salt is 0.8M to 1.2M.

The organic solvent includes a cyclic ester and a chain ester, and the cyclic ester is selected from at least one of ethylene carbonate (EC), propylene carbonate (PC), γ -butyrolactone (BL) and butylene carbonate One; the chain ester is selected from dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), propyl ethyl carbonate, methyl formate (MF), ethyl formate (At least one of MA), ethyl acetate (EA), ethyl propionate (EP), propyl propionate (PP), methyl propionate, propyl acetate, methyl butyrate, and ethyl butyrate.

2. Electrochemical device

The electrochemical device of the present application includes any device that undergoes an electrochemical reaction, and specific examples thereof include all kinds of primary batteries, secondary batteries, fuel cells, solar cells, or capacitors. In particular, the electrochemical device is a lithium secondary battery, including a lithium metal secondary battery, a lithium ion secondary battery, a lithium polymer secondary battery, or a lithium ion polymer secondary battery. In some embodiments, the electrochemical device of the present application is an electrochemical device having a positive electrode having a positive electrode active material capable of occluding and releasing metal ions, and a negative electrode having a negative electrode active material capable of occluding and releasing metal ions. It includes any of the above-mentioned electrolytes of the present application.

Electrolyte

The electrolyte used in the electrochemical device of the present application is any of the above-mentioned electrolytes in the present application.

negative electrode

In the electrochemical device according to the present application, the negative electrode includes a current collector and a negative electrode active material layer provided on the current collector. The anode active material layer contains an anode active material. The specific types of negative electrode active materials are not subject to specific restrictions, and can be selected according to requirements.

The negative electrode can be prepared by a preparation method known in the art. For example, the negative electrode may be obtained by mixing an active material, a conductive material, and a binder in a solvent to prepare an active material composition, and coating the active material composition on a current collector.

The negative electrode active material includes a material that reversibly intercalates/deintercalates lithium ions. In some embodiments, the material that reversibly intercalates/deintercalates lithium ions includes a carbon material. In some embodiments, the carbon material may be any carbon-based negative active material commonly used in lithium ion rechargeable batteries. In some embodiments, the carbon material includes, but is not limited to: crystalline carbon, amorphous carbon, or a mixture thereof. The crystalline carbon may be amorphous, flake-shaped, flake-shaped, spherical or fibrous natural graphite or artificial graphite. Amorphous carbon can be soft carbon, hard carbon, mesophase pitch carbide, calcined coke and the like.

In some embodiments, the negative active material layer includes a negative active material. In some embodiments, the negative electrode active material includes, but is not limited to: lithium metal, structured lithium metal, natural graphite, artificial graphite, mesophase carbon microspheres (abbreviated as MCMB), hard carbon, soft carbon, silicon, silicon -Carbon composite, Li-Sn alloy, Li-Sn-O alloy, Sn, SnO, SnO₂, spinel structure lithiated TiO₂-Li₄Ti₅O₁₂, Li-Al alloy or any combination thereof.

In some embodiments, the negative active material layer may include a binder, and optionally a conductive material. The binder improves the bonding of the negative active material particles with each other and the bonding of the negative active material with the current collector. In some embodiments, the binder includes but

is not limited to: polyvinyl alcohol, carboxymethyl cellulose, hydroxypropyl cellulose, diacetyl cellulose, polyvinyl chloride, carboxylated polyvinyl chloride, polyvinyl fluoride, Polymers containing ethylene oxide, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, styrene butadiene rubber, acrylic (ester) styrene butadiene rubber, Epoxy resin, nylon, etc.

In some embodiments, the conductive material includes, but is not limited to: carbon-based materials, metal-based materials, conductive polymers, or mixtures thereof. In some embodiments, the carbon-based material is selected from natural graphite, artificial graphite, carbon black, acetylene black, Ketjen black, carbon fiber, or any combination thereof. In some embodiments, the metal-based material is selected from metal powder, metal fiber, copper, nickel, aluminum, silver. In some embodiments, the conductive polymer is a polyphenylene derivative.

In the electrochemical device according to the present application, the current collector of the negative electrode may be selected from copper foil, nickel foil, stainless steel foil, titanium foil, foamed nickel, foamed copper, conductive metal-coated polymer substrates, and combinations thereof. In some embodiments, the current collector includes copper foil.

In some embodiments, the copper foil is produced by electrolysis or rolling, the purity is greater than or equal to 99.5%, and the sum of the content of trace elements such as nickel, zinc, and chromium is less than or equal to 0.5% by weight;

In some embodiments, the copper foil has one or more properties selected from the following:

- Copper purity is greater than or equal to 99.5%;
- The thickness is 3 microns to 15 microns, for example, the thickness is about 4 microns, about 5 microns, about 6 microns, about 7 microns, about 8 microns, about 9 microns, about 10 microns, about 11 microns, about 12 microns, About 13 microns, or about 14 microns;
- The weight per unit area is 30g/m² to 150g/m², for example, the weight per unit area is about 50g/m², about 70g/m², about 90g/m², about 110g/m², or about 130g/m²;
- The tensile strength is greater than or equal to 20kg/mm², for example, the tensile strength is greater than or equal to 30kg/mm², greater than or equal to 40kg/mm², or greater than or equal to 50kg/mm²;
- The elongation is greater than or equal to 1.5%, for example, the elongation is greater than or equal to 2%, greater than or equal to 2.5%, greater than or equal to 3%, greater than or equal to 3.5%, or greater than or equal to 4%.

In some embodiments, the copper foil is produced by electrolysis, has a purity greater than or equal to 99.5%, a thickness of about 6 microns, a tensile strength greater than or equal to 30 kg/mm², and an elongation greater than or equal to 3%.

In some embodiments, the copper foil has a certain degree of corrosion resistance, for example, using ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) at about 45° C. according to mass ratio It is 3:1:7 and the electrolyte with 1mol/L LiPF₆ content has no obvious color change after immersing for about 48 hours.

In some embodiments, the electrochemical device includes a positive electrode, a negative electrode, a separator, and an electrolyte; wherein the electrolyte includes a nitrile compound, and the nitrile compound accounts for A% by mass of the electrolyte; the negative electrode includes The current collector includes: a first region and a second region; wherein the first region is provided with a negative active material layer; and the second region does not include a negative active material layer. The area of the second zone accounts for B% of the surface area of the current collector, and A×B is less than 600, for example, A×B is less than 550, less than 500, less than 450, less than 400, less than 350, less than 300, less than 250, Less than 200, less than 150, less than 100, less than 50, less than 30, less than 15, or less than 5.

In some embodiments, the negative electrode has tabs, and the tabs are connected to the second region by welding, and A×B is less than 210. For example, A×B is less than 200, less than 150, less than 100, less than 50, less than 30, less than 15, or less than 10.

Figures 1 and 2 illustrate a schematic diagram of a current collector of a negative electrode in an embodiment of the present invention. The current collector includes: a first region 1 and a second region 2; wherein the first region is provided with a negative electrode active material layer (as shown in FIG. Shown in the middle gray area); the second area does not contain a negative active material layer. The negative electrode has a tab 3, which is connected to the second region by welding.

As shown in FIG. 2, in some embodiments, at least one second region is located at the edge of the current collector, wherein the distance between the tab closest to the edge of the current collector and the edge of the current collector is C , The width of the tab is W , and the range of " C/W " (that is, the ratio of C to W) is 0-50, for example, 5-40, 10-30, 15-40, or 20-30.

In some embodiments, the negative electrode has tabs, and the number of tabs is 1 to 150, for example, the number of tabs is 3, 5, 7, 9, 10, 15. One, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 110, 120, 130, or 140. The tabs are formed by cutting the current collector, and the tabs include areas where the negative electrode active material layer is not coated, and $A \times B$ is less than about 500; for example, $A \times B$ is less than 450, less than 400, and less than 350, Less than 300, less than 250, less than 200, less than 150, less than 100, less than 50, less than 30, less than 15 or less than 10.

3 and 4 illustrate schematic diagrams of a current collector of a negative electrode in another embodiment of the present invention. The current collector includes: a first region 1 and a second region 2; wherein the first region is provided with a negative electrode active material layer; The second region does not include a negative active material layer. The negative electrode has a plurality of tabs 3, the tabs are formed by cutting the current collector, and the tabs include regions where the negative electrode active material layer is not coated.

As shown in Figure 5, in some embodiments, at least one second area is located at the edge of the current collector, and the edge of the second area located at the edge of the current collector is folded back or not; wherein when folded back, The width of the turn-back area is D , the width of the tab is W , and the range of " D/W " (that is, the ratio of D to W) is 0.1 to 20, such as 2 to 18, 4 to 16, 6 to 14, 8 to 12, Or 9 to 10.

As shown in FIG. 6, in some embodiments, at least one second region is located at the edge of the current collector, and the negative electrode further includes one or more second regions that do not contain a negative electrode active material layer located in the middle of the current collector. .

In some embodiments, in order to reduce the surface area of the second zone as much as possible, the second zone is optionally covered with a substance capable of bonding to the second zone. For example, as shown in FIG. 7, a part of the second area is covered by, for example but not limited to, a polymer tape 4.

In some embodiments, the part of the tab is optionally covered with a substance capable of adhering to it. For example, as shown in FIG. 8, in order to reduce the dissolution of copper ions at the welding place between the tab and the second zone, the welding portion of the tab can be covered with, for example, but not limited to, a polymer tape.

In the negative electrode of the present invention, the first region (that is, the region provided with the negative electrode active material layer) may be located on the upper surface, the lower surface or both of the negative electrode current collector; the second region may be located on the negative electrode current collector At the edge and/or inside the second area, the second area also includes a tab welding part, a tab area formed by cutting, and an edge folding area.

positive electrode

The material of the positive electrode used in the electrochemical device of the present application can be prepared using materials, structures, and manufacturing methods known in the art. In some embodiments, the technology described in US9812739B can be used to prepare the positive electrode of the present application, which is incorporated into the present application by reference in its entirety.

In some embodiments, the positive electrode includes a current collector and a positive electrode active material layer on the current collector. The positive electrode active material includes at least one lithiated intercalation compound that reversibly intercalates and deintercalates lithium ions. In some embodiments, the positive active

material includes a composite oxide. In some embodiments, the composite oxide contains lithium and at least one element selected from cobalt, manganese, and nickel.

In some embodiments, the positive electrode active material is selected from one or more of lithium cobaltate, lithium manganate, lithium nickelate, or lithium nickel manganese cobalt ternary materials, and the negative electrode active material contains silicon or silicon oxide material. It can also be selected from graphite, hard carbon, mesophase carbon microspheres and any other negative electrode materials that can release lithium.

In some embodiments, the positive active material may have a coating on its surface, or may be mixed with another compound having a coating. The coating may include at least one selected from the oxide of the coating element, the hydroxide of the coating element, the oxyhydroxide of the coating element, the oxycarbonate of the coating element, and the hydroxycarbonate of the coating element. Kind of coating element compound. The compound used for the coating may be amorphous or crystalline.

In some embodiments, the coating element contained in the coating may include Mg, Al, Co, K, Na, Ca, Si, Ti, V, Sn, Ge, Ga, B, As, Zr or any of them. combination. The coating can be applied by any method as long as the method does not adversely affect the performance of the positive electrode active material. For example, the method may include any coating method known in the art, such as spraying, dipping, and the like.

The positive active material layer further includes a binder, and optionally a conductive material. The binder improves the bonding of the positive electrode active material particles to each other, and also improves the bonding of the positive electrode active material to the current collector.

In some embodiments, the binder includes, but is not limited to: polyvinyl alcohol, hydroxypropyl cellulose, diacetyl cellulose, polyvinyl chloride, carboxylated polyvinyl chloride, polyvinyl fluoride, ethylene-containing Oxygen polymers, polyvinylpyrrolidone, polyurethane, polytetrafluoroethylene, polyvinylidene fluoride, polyethylene, polypropylene, styrene butadiene rubber, acrylic (ester) styrene butadiene rubber, epoxy resin, Nylon etc.

In some embodiments, conductive materials include, but are not limited to: carbon-based materials, metal-based materials, conductive polymers, and mixtures thereof. In some embodiments, the carbon-based material is selected from natural graphite, artificial graphite, carbon black, acetylene black, Ketjen black, carbon fiber, or any combination thereof. In some embodiments, the metal-based material is selected from metal powder, metal fiber, copper, nickel, aluminum, silver. In some embodiments, the conductive polymer is a polyphenylene derivative.

In some embodiments, the current collector may be aluminum, but is not limited thereto.

The positive electrode can be prepared by a preparation method known in the art. For example, the positive electrode may be obtained by mixing an active material, a conductive material, and a binder in a solvent to prepare an active material composition, and coating the active material composition on a current collector. In some embodiments, the solvent may include N-methylpyrrolidone and the like, but is not limited thereto.

In some embodiments, the positive electrode is made by forming a positive electrode material using a positive electrode active material layer including lithium transition metal-based compound powder and a binder on a current collector.

In some embodiments, the positive active material layer can usually be made by the following operations: dry mixing the positive electrode material and the binder (conducting material and thickener used as needed) to form a sheet, The obtained sheet is press-bonded to the positive electrode current collector, or these materials are dissolved or dispersed in a liquid medium to form a slurry, and then coated on the positive electrode current collector and dried. In some embodiments, the material of the positive active material layer includes any material known in the art.

Isolation film

In some embodiments, the electrochemical device of the present application is provided with a separator between the positive electrode and the negative electrode to prevent short circuits. The material and shape of the isolation membrane used in the electrochemical device of the present application are not particularly limited, and it may be any technology disclosed in the prior art. In some embodiments, the isolation membrane includes

a polymer or an inorganic substance formed of a material that is stable to the electrolyte of the present application.

For example, the isolation film may include a substrate layer and a surface treatment layer. The substrate layer is a non-woven fabric, film or composite film with a porous structure, and the material of the substrate layer is selected from at least one of polyethylene, polypropylene, polyethylene terephthalate, and polyimide. Specifically, a polypropylene porous film, a polyethylene porous film, a polypropylene non-woven fabric, a polyethylene non-woven fabric, or a polypropylene-polyethylene-polypropylene porous composite film can be selected. The substrate layer can be one layer or multiple layers. When the substrate layer is multiple layers, the polymer composition of different substrate layers can be the same or different, and the weight average molecular weight is different; when the substrate layer is multiple layers, The closed cell temperature of the polymer of different substrate layers is different.

A surface treatment layer is provided on at least one surface of the substrate layer, and the surface treatment layer may be a polymer layer or an inorganic substance layer, or a layer formed by a mixed polymer and an inorganic substance.

The inorganic layer includes inorganic particles and a binder. The inorganic particles are selected from alumina, silica, magnesium oxide, titanium oxide, hafnium dioxide, tin oxide, ceria, nickel oxide, zinc oxide, calcium oxide, zirconium oxide, One or a combination of yttrium oxide, silicon carbide, boehmite, aluminum hydroxide, magnesium hydroxide, calcium hydroxide, and barium sulfate. The binder is selected from polyvinylidene fluoride, vinylidene fluoride-hexafluoropropylene copolymer, polyamide, polyacrylonitrile, polyacrylate, polyacrylic acid, polyacrylate, polyvinylpyrrolidone, polyvinyl ether, One or a combination of polymethyl methacrylate, polytetrafluoroethylene and polyhexafluoropropylene. The polymer layer contains a polymer, and the material of the polymer includes polyamide, polyacrylonitrile, acrylate polymer, polyacrylic acid, polyacrylate, polyvinylpyrrolidone, polyvinyl ether, polyvinylidene fluoride or poly(At least one of vinylidene fluoride-hexafluoropropylene).

Three, application

The electrochemical device of the embodiment of the present application has improved cycle performance and high temperature stability under over-discharge conditions, and is suitable for use in various electronic devices.

The use of the electrochemical device of the present application is not particularly limited, and it can be used for various known uses. For example, notebook computers, pen-input computers, mobile computers, e-book players, portable phones, portable fax machines, portable copiers, portable printers, headsets, video recorders, LCD TVs, portable cleaners, portable CD players, Mini discs, transceivers, electronic notebooks, calculators, memory cards, portable recorders, radios, backup power supplies, motors, cars, motorcycles, assisted bicycles, bicycles, lighting equipment, toys, game consoles, clocks, power tools, flashlights, Cameras, large household storage batteries or lithium-ion capacitors, etc.

Example

Hereinafter, examples and comparative examples are given to further specifically describe the present application, but as long as the gist is not deviated, the present application is not limited to these examples.

1. Preparation of lithium ion battery

(1)Preparation of negative electrode

(i) The negative electrode formed by welding the tab

Dissolve artificial graphite powder, sodium carboxymethyl cellulose (CMC), and styrene-butadiene rubber in water at a mass ratio of 96:2:2, mix thoroughly and stir to obtain negative electrode slurry, and evenly coat the negative electrode slurry to a thickness of 12 On the specific area of the copper foil of the micron negative current collector, the negative active material layer is obtained by baking at 120° C. for 1 hour, and then compacting, slitting, and welding tabs to obtain the negative electrode.

(ii) The negative electrode formed by cutting the tab

Dissolve artificial graphite powder, sodium carboxymethyl cellulose (CMC), and styrene-butadiene rubber in water at a mass ratio of 96:2:2, mix thoroughly and stir to obtain negative electrode slurry, and evenly coat the negative electrode slurry to a thickness of 12 On the specific area of the micron negative current collector copper foil, the negative active material layer is obtained by baking at 120° C. for 1 hour, and then compacting, cutting the tabs, and slitting to obtain the negative electrode.

(iii) Preparation method of the negative electrode with polymer tape in the second area of the negative electrode (Example 59)

Dissolve artificial graphite powder, sodium carboxymethyl cellulose (CMC), and styrene-butadiene rubber in water at a mass ratio of 96:2:2, mix thoroughly and stir to obtain negative electrode slurry, and evenly coat the negative electrode slurry to a thickness of 12 On the specific area of the copper foil of the negative electrode current collector of micrometers, the negative electrode active material layer is obtained by baking at 120°C for 1 hour, and then undergoes compaction, slitting, welding tabs, and in the second area (that is, the negative electrode slurry is not coated Area) pasted with a polymer tape made of acrylate to obtain a negative electrode.

(iv) Preparation method of the negative electrode (Example 60) with polymer tape at the welding of the tab

Dissolve artificial graphite powder, sodium carboxymethyl cellulose (CMC), and styrene-butadiene rubber in water at a mass ratio of 96:2:2, mix thoroughly and stir to obtain negative electrode slurry, and evenly coat the negative electrode slurry to a thickness of 12 On the specific area of the micron negative current collector copper foil, the negative active material layer is obtained by baking at 120°C for 1 hour, and then compacting, slitting, welding the tabs, and pasting the tab welding area with acrylic polymer Material tape to obtain a negative electrode.

(2)Preparation of positive electrode

(i) The positive electrode formed by welding the tab

The positive active material lithium cobalt oxide (molecular formula is LiCoO_2), the binder polyvinylidene fluoride (PVDF), and conductive graphite (Super-P) are dissolved in N-methylpyrrolidone (NMP) at a mass ratio of 96:2:2 Mix it evenly to make positive electrode slurry. The positive electrode slurry was uniformly coated on a positive electrode current collector aluminum foil with a thickness of about 12 microns, and baked at 120° C. for 1 hour to obtain a positive electrode active material layer, and then compacted, welded tabs, and slit to obtain a positive electrode.

(ii) The positive electrode formed by cutting the tab

The positive active material lithium cobalt oxide (the molecular formula is LiCoO_2), the binder polyvinylidene fluoride (PVDF), and conductive graphite (Super-P) are dissolved in N-methylpyrrolidone (NMP) at a mass ratio of 96:2:2 Mix it evenly to make positive electrode slurry. The positive electrode slurry was uniformly coated on a positive electrode current collector aluminum foil with a thickness of 12 microns, and baked at 120° C. for 1 hour to obtain a positive electrode active material layer. After that, the positive electrode was obtained by compacting, cutting tabs, and slitting.

(3)Preparation of electrolyte

In a dry argon atmosphere glove box, mix ethylene carbonate (EC), propylene carbonate (PC), and diethyl carbonate (DEC) in a mass ratio of 3:1:7, add LiPF_6 as a lithium salt, and add Specific types and amounts of additives (the types and amounts of added substances are shown in Table 1, and the content of each component in the electrolyte is based on the total weight of the electrolyte). The concentration of LiPF_6 in the electrolyte is about 1 mol/L.

(4)Preparation of isolation membrane

Use polypropylene isolation film about 12 microns thick

(5)Lithium-ion battery preparation

A polypropylene film of about 12 microns was used as the separator. Lay the positive electrode, the separator, and the negative electrode in order, so that the separator is in the middle of the positive and negative electrodes to separate them, and then wind and put them into an aluminum foil packaging bag. After baking at 80°C to remove water, inject the corresponding electrolyte. After vacuum packaging, standing, forming, shaping and other processes, the preparation of the lithium ion battery is completed.

2. Test on the copper foil used in the negative current collector

Copper foil thickness test: Use a micrometer to measure 5 points and take the average value.

Mass per unit area: Cut the copper foil into 100*100mm wide sheets and weigh, and calculate the mass per unit area. Mass per unit area = weight/area;

Tensile strength test: use a tensile testing machine to test, the length of the test sample is 200±0.5mm, the width is 15±0.25mm, the tensile speed is set to 50mm/min, the chuck distance of the testing machine is 125±0.1mm, test 5 For parallel samples, take the average value as the test result. During the test, the length of the sample is parallel to the axis of the fixture, and the sample is kept straight. The test temperature is 20±5°C

Elongation test: use a tensile testing machine to test, the length of the test sample is 200±0.5mm, the width is 15±0.25mm, the tensile speed is set to 50mm/min, the chuck distance of the testing machine is 125±0.1mm, and 5 samples are tested For parallel samples, take the average value as the test result. During the test, the length of the sample is parallel to the axis of the fixture, and the sample is kept straight. The test temperature is 20±5°C; elongation=stretched length/original length;

3. Lithium-ion battery performance test

(1)Cycle performance test

The lithium-ion battery was charged to 4.45V at a constant current of 1C at 45°C, left for 30 minutes, discharged to 3.0V at 1C, and charged and discharged 500 times.

Li-ion battery capacity retention rate (%)=discharge capacity of 500 cycles/first discharge capacity×100%.

(2)60°C high temperature storage test

Put the lithium-ion battery in a 25°C thermostat, charge it to 3.95V at a constant current of 0.5C, test the thickness of the battery, and then fully charge it to 4.45V, store the battery in a 60°C oven for 30 days, during which time, every 3 Test the thickness of the battery once a day. If the thickness growth rate of the battery relative to 3.95V is greater than 60%, stop the test.

Thickness growth rate = (thickness after storage-3.95V thickness) / 3.95V thickness x 100%

(3)Floating charge leakage current test

Put the lithium-ion battery at 45°C for 120 minutes, charge it to 4.45V at 1C, maintain the constant voltage charging state for 15 days, and record the current after 15 days.

(4)Battery squeeze test

Put the lithium-ion battery in a thermostat at 25°C, charge it to 4.45V at a constant current of 0.5C, then charge it to a current of 0.05C at a constant voltage, squeeze the battery with a pressure of 20KN, and observe whether the battery burns or explodes.

A. Prepare the electrolytes and lithium ion batteries of Examples 1 to 39 and Comparative Examples 1 to 6 according to the above method, wherein copper foil is used as the negative electrode current collector, and the copper foil is produced by electrolysis, with a purity of ≥99.5% and a thickness of 6 microns, tensile strength ≥30kg/mm², elongation ≥3%. The area of the second zone accounts for 18.2% of the surface area of the negative electrode. The connection method between the tab and the second zone is welding. The width w of the tab is 0.8cm. The distance C between the tab and the edge of the current collector is 2cm. It is located in the current collector. The width D of the edge-turn-back area of the second area of the edge is 1.8 cm. The positive

electrode tab is correspondingly prepared by welding. Test the cycle capacity retention rate, floating charge leakage current and 60°C high temperature storage test of the lithium ion battery with different cycles. The test results are shown in Table 2.

Table 1

Note: "/" means not added

Table 1 shows the examples and comparative examples when the ratio B% of the area of the fixed second region to the surface area of the negative electrode is 18.2%. Compared with Comparative Example 1 in which the nitrile compound is not contained in the electrolyte, the cycle performance of Examples 1 to 39 in which the specific nitrile compound in the range of 0.1% to 10% by weight is added to the electrolyte is significantly improved. From the comparison of Comparative Example 2 to Comparative Example 5 and Comparative Example 1, it can be seen that when the content of the nitrile compound is increased to 12% by weight so that the value of AxB reaches 218.2, the cycle performance is improved compared to Comparative Example 1, but improved The amplitude is reduced and the battery self-discharge is further improved. It can be seen from Comparative Example 6 that when the content of the nitrile compound increases to 15% so that AxB)210, the floating charge leakage current exceeds 50mA, which seriously affects the use of the battery. Therefore, when the electrolyte contains 0.1% to 10% by weight of the specific nitrile compound, when the connection method of the tab and the second zone is welding, A×B(210 can ensure the improvement of battery performance while introducing small Self-discharge. The addition of nitrile compounds can improve the cycle because the nitrile group can complex the metal ions on the cathode and stabilize the metal ion potential, thereby reducing the structural phase transition of the cathode material. At the same time, the nitrile compound can also be adsorbed on the cathode surface, reducing the cathode and the electrolyte. Contact, the combination of the two, can significantly improve the battery's cycle and floating performance; but at the same time, the nitrile compound has a certain solubility for the negative current collector copper foil, especially when the surface of the copper foil current collector without active material is exposed to the electrolyte In the middle, the solubility of the nitrile compound on the copper foil is greatly enhanced, and the eluted copper ions can be slowly reduced to elemental copper on the surface of the negative electrode during the charging and discharging process of the battery and deposited continuously, which eventually leads to a partial short circuit of the battery and deterioration of self-discharge. Although the nitrile compound will deteriorate the self-discharge of the battery, it has obvious advantages in the electrical performance of the battery. Therefore, we need to add a certain amount of nitrile compound to the electrolyte and control the area of the exposed empty copper foil within a certain range. Can take into account the battery's electrical performance and self-discharge;

B. Prepare the electrolytes and lithium ion batteries of Examples 40 to 52 and Comparative Example 8 according to the above method, wherein copper foil is used as the negative electrode current collector, and the copper foil is produced by electrolysis with a purity of $\geq 99.8\%$ and a thickness of 8 microns , Tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 3\%$; the connection between the tab and the second zone is welding, the tab width w is 0.8 cm, and the distance between the tab and the edge of the current collector is 2 cm; located at the edge of the current collector The width D of the folded-back area at the edge of the second zone is 2.5 cm. The positive electrode tab is correspondingly prepared by welding. Test the cycle capacity retention rate, floating charge leakage current and 60°C high temperature storage test of the lithium ion battery with different cycles. The test results are shown in Table 2.

Table 2

Table 2 shows the examples and comparative examples when the content of the nitrile compound in the electrolyte is fixed at 3% by weight. As shown in Examples 40 to 51, when the content of the nitrile compound in the electrolyte is fixed at 3% by weight, the battery cycle and storage performance is better. As the area of the second area of the negative electrode in the battery is adjusted, the value of $A \times B$ As shown in Comparative Example 8, when the value of $A \times B$ exceeds 210, the battery will have a serious self-discharge phenomenon, which will seriously affect the use of the battery. The negative electrode current collector in Example 52 does not have a second region (ie, B is 0.4), so that the value of $A \times B$ is 1.2. Compared with Comparative Example 8, the battery in Example 52 has better cycle performance and low leakage current.

C. Prepare the electrolytes and lithium ion batteries of Example 53 to Example 60 and Comparative Example 9 according to the above method, wherein copper foil is used as the negative electrode current collector, and the copper foil is produced by electrolysis with a purity of $\geq 99.8\%$ and a thickness of 6 microns, tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 2\%$. The connecting manner of the tabs and the second area is cutting, the number of tabs is 9, the width w of the tabs is 1.5cm, and the width D of the edge folding area of the second area at the edge of the current collector is 1.5cm. The positive electrode tab is prepared by cutting. Test the capacity retention rate, floating charge leakage current and 60°C high temperature storage test of different cycles of lithium-ion battery. The test results are shown in Table 3.

table 3

As shown in Table 3, Example 53 to Example 60 and Comparative Example 9 all adopted the method of cutting tabs to prepare batteries. From Example 53 to Example 59, it can be seen that adjusting the area ratio $B\%$ of the second zone has no significant effect on the battery capacity retention rate, but the battery self-discharge increases; when the amount of nitrile compound $A\%$ in Comparative Example 9 increases When it reaches 12% by weight and the area ratio of the second zone $B\%$ reaches 54%, and the value of $A \times B$ is 648, the self-discharge current reaches 40mA. The negative electrode current collector in Example 60 is all coated with active material, but there is no active material on the tabs (that is, $B\%=2.3\%$ is the proportion of the empty copper foil at the tabs), so the value of $A \times B$ is 6.9, which is comparable to Comparative Example 9. In comparison, the battery cycle and storage performance of Example 60 is better, and the leakage current is small. In summary, when the battery is prepared by cutting tabs, it is necessary to control the $A \times B$ within 600 to make the battery performance better.

D. Prepare the electrolytes and lithium-ion batteries of Examples 61 to 63 according to the above method, wherein copper foil is used as the negative electrode current collector, the copper foil is produced by electrolysis, the purity is $\geq 99.8\%$, the thickness is 6 microns, and the tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 2\%$. The connecting method of the tab and the second zone is welding, the tab width is 0.8cm, the distance C between the tab and the edge of the current collector is 2cm, and the width D of the edge folding area of the second zone at the edge of the current collector is 1.8cm. The positive electrode tab is correspondingly prepared by welding. Test the cycle capacity retention rate, floating charge leakage current and 60°C high temperature storage test of lithium-ion battery with different cycles. The test results are shown in Table 4.

Table 4

As shown in Table 4, in Example 61, a certain area of polymer adhesive was pasted on the copper foil area not coated with the active material layer to reduce the contact area between the copper foil and the electrolyte; it is comparable to Example 63 where the polymer tape is not pasted. Compared with Example 61, the leakage current is lower. In Example 62, the polymer tape covering a certain area at the tab welding position can also reduce the self-discharge of the battery compared with Example 63 where the polymer tape is not attached. Therefore, in the actual battery design, polymer tape can be covered at the welding area of the tabs on the negative electrode copper foil current collector and other empty copper foil areas that are not coated with negative active material or other can be bonded to the copper foil and tabs. To reduce the self-discharge of the battery.

E. Prepare the electrolytes and lithium ion batteries of Examples 64 to 70 according to the above method, wherein copper foil is used as the negative electrode current collector, the copper foil is produced by electrolysis, the purity is $\geq 99.8\%$, the thickness is 6 microns, and the tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 2\%$. The connecting method of the tab and the second zone is welding, the tab width is 0.8cm, the distance C between the tab and the edge of the current collector is 2cm, and the width D of the edge folding area of the second zone at the edge of the current collector is 1.8cm. The positive electrode tab is correspondingly prepared by welding. Test the cycle capacity retention rate, floating charge leakage current and 60 °C high temperature storage test of the lithium ion battery with different cycles. The test results are shown in Table 5.

table 5

Note: "/" means not added

Comparing Examples 64 to 69 with Example 70, it can be seen that adding other additives to the electrolyte containing a specific nitrile compound can significantly improve the battery cycle and the growth rate of floating thickness, and the addition of FEC can increase the negative electrode SEI. The LiF content of SEI effectively increases the stability of the anode SEI; the addition of additive VC can polymerize on the surface of the SEI to form a network protective layer, strengthen the flexibility of the SEI, and the addition of other additives, which can be used to a certain extent stabilize or strengthen the SEI protective layer, thus significantly improving the cycle performance of the cell; at the same time, because of the film-forming effect of the additive on the negative electrode, it can also reduce the deposition of copper ions on the negative electrode to a certain extent, reduce the self-discharge of the battery, and further improve the battery's overall electrical performance.

Therefore, it can be seen from the examples and comparative examples that nitrile compounds, as effective additives for improving cycle stability, have a greater impact on battery self-discharge. In order to improve battery long-term storage performance, it is necessary to control the content of nitrile compounds and the area of the empty copper foil area. Within a certain range, the battery capacity will not be significantly reduced after long-term storage. At the same time, adding a certain amount of other additives to the electrolyte can improve the battery's cycle and self-discharge, and ensure the battery's long-term cycle and storage performance.

F. Prepare the electrolytes and lithium-ion batteries of Examples 71 to 72 according to the above method, wherein copper foil is used as the negative electrode current collector, the copper foil is produced by electrolysis, the purity is $\geq 99.8\%$, the thickness is 6 microns, and the tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 2\%$; the connection between the tab and the second zone is welding, the tab width w is 0.8cm; the distance C between the tab and the edge of the current collector is 2cm; in embodiment 71, it is located at the edge of the current collector. The width D of the edge-turned-back area of the second zone is 1.8 cm, and the edge of the second zone at the edge of the current collector in Example 72 is not folded back. The positive electrode tab is

correspondingly prepared by welding. Test the cycle capacity retention rate, floating charge leakage current and squeeze test of different cycles of lithium-ion battery. See Table 6 for the test results.

Table 6

As shown in Table 6, the edge of the second region located at the edge of the current collector in Example 71 is folded back, and the edge of the second region located at the edge of the current collector in Example 72 does not turn back. The capacity retention rate and floating leakage current of the two are not Obvious difference, but the squeeze test shows that the use of folding back reduces the risk of burrs piercing the diaphragm at the tab welding point, so the battery has higher safety performance.

G. Prepare the electrolytes and lithium ion batteries of Examples 73 to 76 according to the above method, wherein copper foil is used as the negative electrode current collector, the copper foil is produced by electrolysis, the purity is $\geq 99.8\%$, the thickness is 6 microns, and the tensile strength $\geq 30\text{kg/mm}^2$, elongation $\geq 2\%$; the connection between the tab and the second zone is welding, the tab width W is 0.8cm; the distance C between the tab and the edge of the current collector is 2cm; The width D of the edge folding area is 1.8 cm. The positive electrode tab is correspondingly prepared by welding. Test the cycle capacity retention rate and floating charge leakage current of the lithium-ion battery with different cycles. The test results are shown in Table 7

Table 7

As shown in Table 7, when the electrolyte contains an appropriate amount of anions, such as Cl^- , it will improve the leakage current of the battery, but when the addition amount is too high, such as more than 1000ppm, the battery capacity retention rate will be more affected. Big. Therefore, while ensuring the electrical performance of the battery, an appropriate amount of anions can be added to the electrolyte to improve the floating charge leakage current;

The above are only a few embodiments of the present invention, and do not limit the present invention in any form. Although the present invention is disclosed as above in preferred embodiments, it is not intended to limit the present invention. Anyone familiar with the profession, Without departing from the scope of the technical solution of the present invention, making some changes or modifications using the technical content disclosed above is equivalent to an equivalent implementation case and falls within the scope of the technical solution.

References throughout the specification to "some embodiments", "partial embodiments", "one embodiment", "another example", "examples", "specific examples" or "partial examples" mean At least one embodiment or example in this application includes the specific feature, structure, material, or characteristic described in the embodiment or example. Therefore, descriptions appearing in various places throughout the specification, such as: "in some embodiments", "in embodiments", "in one embodiment", "in another example", "in an example", "In", "in a specific example" or "exemplified", which are not necessarily quoting the same embodiment or example in this application. In addition, the specific features, structures, materials or characteristics herein can be combined in one or more embodiments or examples in any suitable manner.

Although illustrative embodiments have been demonstrated and described, those skilled in the art should understand that the above-mentioned embodiments should not be construed as limiting the application, and the embodiments can be changed without departing from the spirit, principle, and scope of the application , Substitution and modification.

CN111342129A Electrolyte and electrochemical device

Data originating from sources other than the EPO may not be accurate, complete, or up to date.

The wording below is an initial machine translation of the original publication. To generate a version using the latest translation technology, go to the original language text and use Patent Translate.

1. An electrochemical device, which comprises a positive electrode, a negative electrode, a separator and an electrolyte; wherein,

The electrolyte contains a nitrile compound, and the mass fraction of the nitrile compound in the electrolyte is A%,

The negative electrode includes a current collector, and the current collector includes: a first zone and a second zone;

The first area is provided with a negative active material layer;

The second region does not include a negative active material layer;

The area of the second zone accounts for B% of the surface area of the current collector; and

$A \times B \geq 600$.

2. The electrochemical device according to claim 1, wherein the nitrile compound comprises at least one of a compound of formula I, a compound of formula II, a compound of formula III, a compound of formula IV, a compound of formula V or a compound of formula VI:

Wherein, a, d, f, j, k, l, m, r, u, w and y are each independently an integer selected from 1 to 5, b, c, e, g, h, i, n, o, p, q, s, t, v, x are each independently an integer selected from 0 to 5; the mass fraction A% of the nitrile compound in the electrolyte is 0.1% to 10%.

3. The electrochemical device according to claim 1, wherein the nitrile compound comprises:

At least one of

.

4.4. The electrochemical device according to claim 1, wherein the negative electrode has a tab, the tab being connected to the second region by welding, and $A \times B \geq 210$.

5.The electrochemical device according to claim 1, wherein the negative electrode has tabs, the number of tabs is not less than 1, the tabs are formed by cutting the current collector, and the tabs contain Coating the area of the negative electrode active material layer, and $A \times B \leq 500$.

6.The electrochemical device according to claim 4 or 5, wherein at least one second region is located at the edge of the current collector, wherein the distance between the tab closest to the edge of the current collector and the edge of the current collector is C, and $0 \leq C/\text{tab width} \leq 50$.

7.The electrochemical device according to claim 1, wherein at least one second region is located at the edge of the current collector, and the edge of the second region located at the edge of the current collector is folded back or not; wherein when folded back, The width of the turn-back area is D, and $0.1 \leq D/\text{tab width} \leq 20$.

8.The electrochemical device according to claim 1, wherein the current collector is copper foil, and the copper foil has one or more properties selected from the following:

Copper purity $\geq 99.5\%$,

The thickness is from 3 microns to 15 microns,

The weight per unit area is 30g/m² to 150g/m²,

Tensile strength $\geq 20\text{kg/mm}^2$, and

Elongation $\geq 1.5\%$.

9.The electrochemical device according to claim 1, wherein the second region is optionally covered with a substance capable of adhering to the second region.

10.The electrochemical device according to claim 4 or 5, wherein the part of the tab is optionally covered with a substance capable of bonding thereon.

11.The electrochemical device according to claim 1, wherein the electrolytic solution further contains an additive, the additive comprising 1,3-propane sultone, fluoroethylene carbonate, vinylene carbonate, 2,4- Butane sultone, 1,4-butane sultone, methylene methane disulfonate, vinyl sulfate, succinic anhydride, ethoxy pentafluorocyclic triphosphazene, 1,3-diox At least one of heterocyclohexane or propenyl-1,3-sultone.

12.The electrochemical device according to claim 1, wherein the electrolyte further contains an anion, the anion including at least one of Cl⁻, Br⁻, SO₄²⁻, CO₃²⁻ or F⁻, the anion being in the The content in the electrolyte is less than or equal to 1000 ppm.

13.An electronic device comprising the electrochemical device according to any one of claims 1-12.



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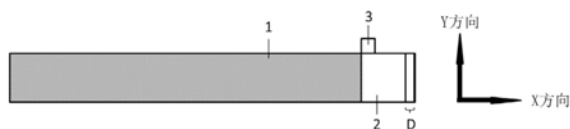
权利要求书2页 说明书17页 附图2页

(54)发明名称

一种电解液及电化学装置

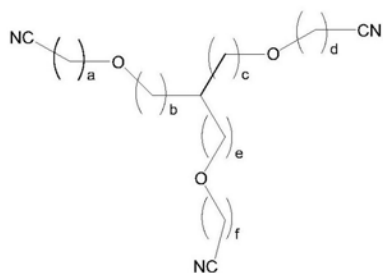
(57)摘要

本申请涉及一种电解液及电化学装置。特别地,本申请提供一种含有腈化合物的电解液及包含该电解液的锂离子电池,当将腈化合物占所述电解液的质量比率与负极集流体上不包含负极活性物质的区域面积占所述集流体的表面积比率的乘积限定在一定范围时,可在改善电化学装置循环稳定性的同时降低电化学装置的自放电,并改善电化学装置长期存储性能。

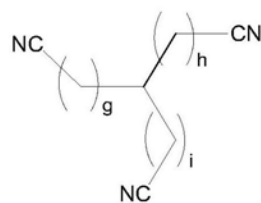


1. 一种电化学装置,其包含正极、负极、隔离膜及电解液;其中,
 所述电解液包含腈化合物,所述腈化合物占所述电解液的质量分数为A%,
 所述负极包括集流体,所述集流体包含:第一区和第二区;
 所述第一区设置有负极活性物质层;
 所述第二区不包含负极活性物质层;
 所述第二区的面积占所述集流体的表面积的B%;且
 $A \times B < 600$ 。

2. 根据权利要求1所述的电化学装置,其中所述腈化合物包含式I化合物、式II化合物、式III化合物、式IV化合物、式V化合物或式VI化合物中的至少一种:



式 I ,



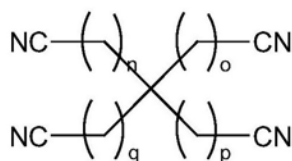
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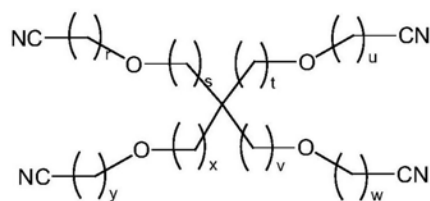
式 III ,



式 IV ,



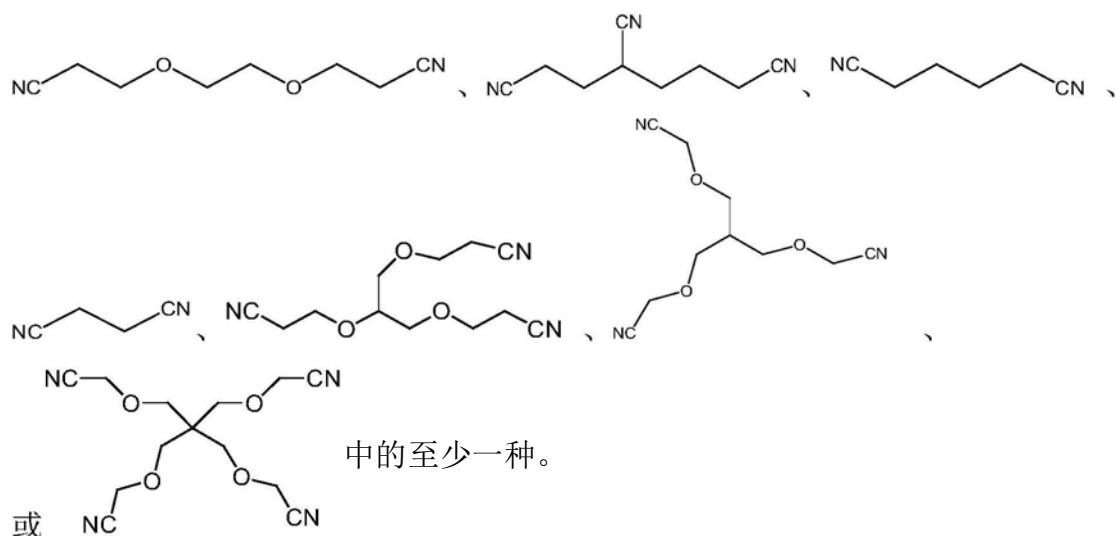
式 V 及



式 VI ,

其中,a、d、f、j、k、l、m、r、u、w和y各自独立的选自1至5的整数,b、c、e、g、h、i、n、o、p、q、s、t、v、x各自独立的选自0至5的整数;所述腈化合物占所述电解液的质量分数A%为0.1%至10%。

3. 根据权利要求1所述的电化学装置,其中所述腈化合物包含:



4. 根据权利要求1所述的电化学装置,其中所述负极具有极耳,所述极耳是通过焊接连

接至所述第二区形成的,且 $A \times B < 210$ 。

5. 根据权利要求1所述的电化学装置,其中所述负极具有极耳,所述极耳个数不小于1,所述极耳是通过裁切所述集流体形成的,所述极耳包含未涂覆负极活性物质层区域,且 $A \times B < 500$ 。

6. 根据权利要求4或5所述的电化学装置,其中至少有一个第二区位于所述集流体的边缘,其中距离所述集流体边缘最近的极耳与所述集流体的边缘之间的距离为C,且 $0 \leq C/\text{极耳宽度} \leq 50$ 。

7. 根据权利要求1所述的电化学装置,其中至少有一个第二区位于所述集流体的边缘,位于所述集流体边缘的所述第二区的边缘回折或不回折;其中当回折时,回折区域的宽度为D,且 $0.1 \leq D/\text{极耳宽度} \leq 20$ 。

8. 根据权利要求1所述的电化学装置,其中所述集流体为铜箔,所述铜箔具有选自如下的一种或多种性质:

铜纯度 $\geq 99.5\%$,

厚度为3微米至15微米,

单位面积的重量为 $30\text{g}/\text{m}^2$ 至 $150\text{g}/\text{m}^2$,

拉伸强度 $\geq 20\text{kg}/\text{mm}^2$,及

延伸率 $\geq 1.5\%$ 。

9. 根据权利要求1所述的电化学装置,其中所述第二区任选地被能够粘附在所述第二区上的物质覆盖。

10. 根据权利要求4或5所述的电化学装置,其中所述极耳的部位任选地被能够粘接在其上的物质覆盖。

11. 根据权利要求1所述的电化学装置:其中所述电解液进一步中包含添加剂,所述添加剂包含1,3-丙烷磺酸内酯、氟代碳酸乙烯酯、碳酸亚乙烯酯、2,4-丁烷磺酸内酯、1,4-丁烷磺酸内酯、甲烷二磺酸亚甲酯、硫酸乙烯酯、丁二酸酐、乙氧基五氟环三磷腈、1,3-二氧杂环己烷或丙烯基-1,3-磺酸内酯中的至少一种。

12. 根据权利要求1所述的电化学装置:其中所述电解液进一步包含阴离子,所述阴离子包括 Cl^- 、 Br^- 、 SO_4^{2-} 、 CO_3^{2-} 或 F^- 中的至少一种,所述阴离子在所述电解液中的含量小于或等于1000ppm。

13. 一种电子装置,其包括根据权利要求1-12中任一权利要求所述的电化学装置。

一种电解液及电化学装置

技术领域

[0001] 本申请涉及储能技术领域,尤其涉及一种电解液和包含该电解液的电化学装置。

背景技术

[0002] 以锂离子电池为代表的电化学装置具有能量密度高,工作电压高,自放电率低,循环寿命长,无污染等优点,已被广泛应用于计算机、智能穿戴设备、智能手机、无人机,以及电动汽车等领域。随着现代信息技术的发展和锂离子电池应用范围的拓展,本领域锂离子电池的能量密度有了更高的要求。

[0003] 影响锂离子电池的能量密度的因素有很多。目前,提高锂离子电池充电截止电压是提升能量密度的有效手段之一,但电压的提高导致正极稳定性变差,如何解决上述问题以提高锂离子电池的能量密度已成为本领域目前亟需解决的问题。

发明内容

[0004] 经发明人研究发现,虽然腈类添加剂能够有效改善正极稳定性从而对电化学装置的循环性能等有明显的改善,但是腈类添加剂可能导致负极集流体中的铜溶出从而影响负极的稳定性,特别是在极耳焊接处有铜离子溶出时易引起电池自放电甚至安全问题。

[0005] 本发明提供了一种电化学装置,其能在满足高电压的循环稳定性下,解决高电压下电化学装置的自放电问题,同时,有利于提升安全特性。

[0006] 在一些实施例中,本发明提供了一种电化学装置,其包含正极、负极、隔离膜及电解液;其中,所述电解液包含腈化合物,所述腈化合物占所述电解液的质量分数为A%,

[0007] 所述负极包括集流体,所述集流体包含:第一区和第二区;

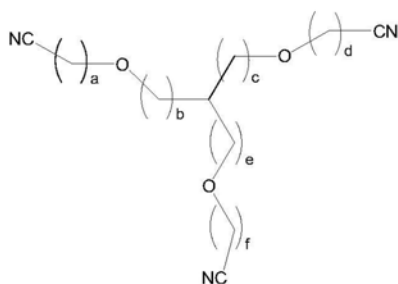
[0008] 所述第一区设置有负极活性物质层;

[0009] 所述第二区不包含负极活性物质层;

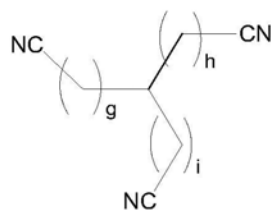
[0010] 所述第二区的面积占所述集流体的表面积的B%;且

[0011] $A \times B < 600$ 。

[0012] 在一些实施例中,所述腈化合物包含式I化合物、式II化合物、式III化合物、式IV化合物、式V化合物或式VI化合物中的至少一种:



式 I,



式 II,

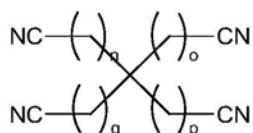
[0013]



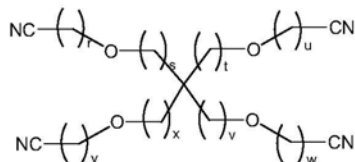
式 III,



式 IV,



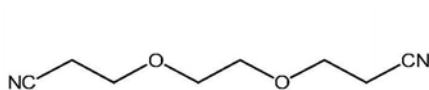
式 V、及



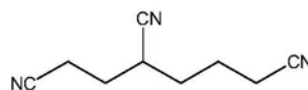
式 VI,

[0014] 其中, $a, d, f, j, k, l, m, r, u, w$ 和 y 各自独立的选自 1 至 5 的整数, $b, c, e, g, h, i, n, o, p, q, s, t, v, x$ 各自独立的选自 0 至 5 的整数; 所述腈化合物占所述电解液的质量分数 $A\%$ 为 0.1% 至 10%。

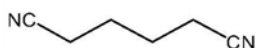
[0015] 在一些实施例中, 所述腈化合物包含下述中的至少一种化合物:



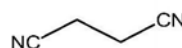
化合物 1、



化合物 2、

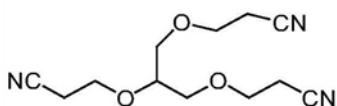


化合物 3、

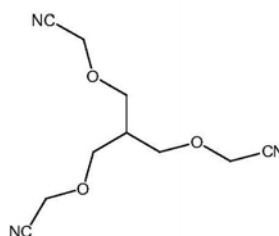


化合物 4、

[0016]

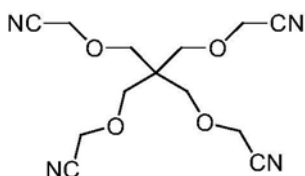


化合物 5、



化合物 6、

或



化合物 7。

[0017]

[0018] 在一些实施例中, 所述负极具有极耳, 所述极耳是通过焊接连接至所述第二区形成的, 且 $A \times B < 210$ 。

[0019] 在一些实施例中, 所述负极具有极耳, 所述极耳个数不小于 1, 所述极耳是通过裁切所述集流体形成的, 所述极耳包含未涂覆负极活性物质层区域, 且 $A \times B < 500$ 。

[0020] 在一些实施例中, 至少有一个第二区位于所述集流体的边缘, 其中距离所述集流

体边缘最近的极耳与所述集流体的边缘之间的距离为C,且 $0 \leq C/\text{极耳宽度} \leq 50$ 。

[0021] 在一些实施例中,至少有一个第二区位于所述集流体的边缘,位于所述集流体边缘的所述第二区的边缘回折或不回折;其中当回折时,回折区域的宽度为D,且 $0.1 \leq D/\text{极耳宽度} \leq 20$ 。

[0022] 在一些实施例中,所述集流体为铜箔,所述铜箔具有选自如下的一种或多种性质:

[0023] -铜纯度 $\geq 99.5\%$,

[0024] -厚度为3微米至15微米,

[0025] -单位面积的重量为 $30\text{g}/\text{m}^2$ 至 $150\text{g}/\text{m}^2$,

[0026] -拉伸强度 $\geq 20\text{kg}/\text{mm}^2$,及

[0027] -延伸率 $\geq 1.5\%$ 。

[0028] 在一些实施例中,所述第二区任选地被能够粘附在所述第二区上的物质覆盖。

[0029] 在一些实施例中,所述极耳的部位任选地被能够粘接在其上的物质覆盖。

[0030] 在一些实施例中,所述电解液进一步中包含添加剂,所述添加剂包含1,3-丙烷磺酸内酯、氟代碳酸乙烯酯、碳酸亚乙烯酯、2,4-丁烷磺酸内酯、1,4-丁烷磺酸内酯、甲烷二磺酸亚甲酯、硫酸乙烯酯、丁二酸酐、乙氧基五氟环三磷腈、1,3-二氧杂环己烷或丙烯基-1,3-磺酸内酯中的至少一种。

[0031] 在一些实施例中,其中所述电解液进一步包含阴离子,所述阴离子包括 Cl^- 、 Br^- 、 SO_4^{2-} 、 CO_3^{2-} 或 F^- 中的至少一种,所述阴离子在所述电解液中的含量小于或等于1000ppm。

[0032] 本发明的另一个方面提供了一种电子装置,所述电子装置包括如上所述的电化学装置。

[0033] 本申请实施例的额外层面及优点将部分地在后续说明中描述、显示、或是经由本申请实施例的实施而阐释。

附图说明

[0034] 图1为本申请一个实施例中负极集流体的俯视图。

[0035] 图2为图1所示集流体沿Z方向的侧视图。

[0036] 图3为本申请又一实施例中负极集流体的俯视图。

[0037] 图4为图3所示集流体沿Z方向的侧视图。

[0038] 图5为本申请又一实施例中负极集流体的侧视图。

[0039] 图6为本申请再一实施例中负极集流体的侧视图。

[0040] 图7为本申请又一实施例中负极集流体的侧视图。

[0041] 图8为本申请又一实施例中负极集流体的俯视图。

具体实施方式

[0042] 本申请的实施例将会被详细的描述在下文中。本申请的实施例不应该被解释为对本申请要求保护范围的限制。除非另外明确指明,本文使用的下述术语具有下文指出的含义。

[0043] 如本文中所使用,术语“大致”、“大体”、“大体上”、“实质”及“约”用以描述及说明小的变化。当与事件或情形结合使用时,所述术语可指代其中事件或情形精确发生的例子

以及其中事件或情形极近似地发生的例子。举例来说,当结合数值使用时,术语可指代小于或等于所述数值的 $\pm 10\%$ 的变化范围,例如小于或等于 $\pm 5\%$ 、小于或等于 $\pm 4\%$ 、小于或等于 $\pm 3\%$ 、小于或等于 $\pm 2\%$ 、小于或等于 $\pm 1\%$ 、小于或等于 $\pm 0.5\%$ 、小于或等于 $\pm 0.1\%$ 、或小于或等于 $\pm 0.05\%$,那么可认为所述两个数值“大体上”相同。

[0044] 另外,有时在本文中以范围格式呈现量、比率和其它数值。应理解,此类范围格式是用于便利及简洁起见,且应灵活地理解,不仅包含明确地指定为范围限制的数值,而且包含涵盖于所述范围内的所有个别数值或子范围,如同明确地指定每一数值及子范围一般。

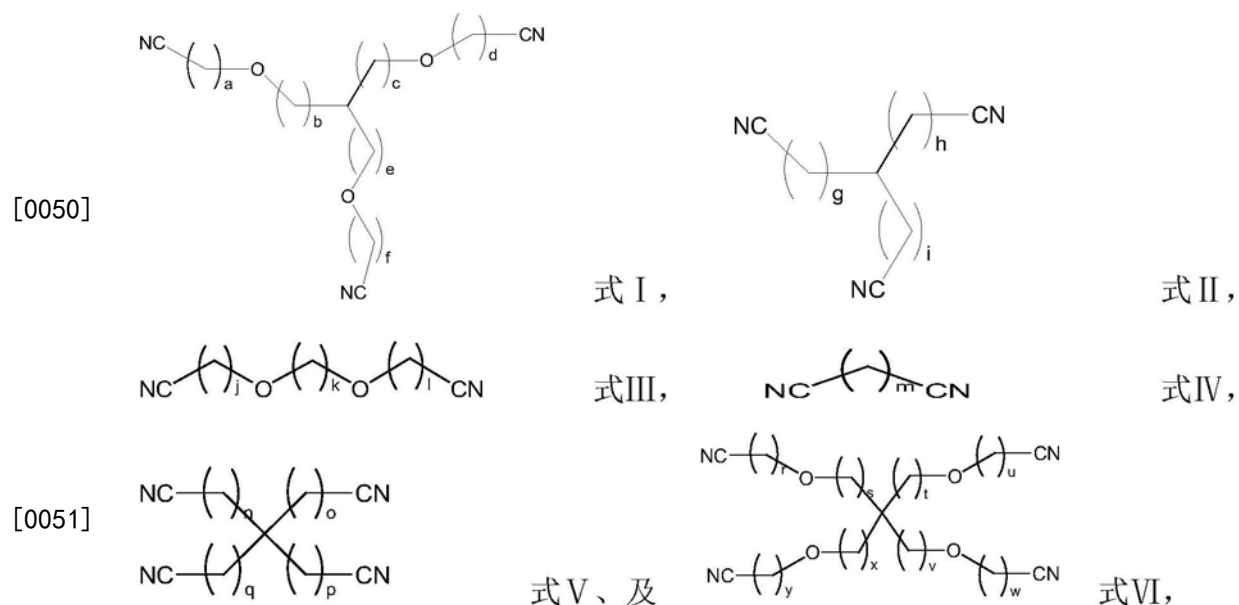
[0045] 在具体实施方式及权利要求书中,由术语“中的一者”连接的项目的列表可意味着所列项目中的任一者。例如,如果列出项目A及B,那么短语“A及B中的一者”意味着仅A或仅B。在另一实例中,如果列出项目A、B及C,那么短语“A、B及C中的一者”意味着仅A;仅B;或仅C。项目A可包含单个元件或多个元件。项目B可包含单个元件或多个元件。项目C可包含单个元件或多个元件。

[0046] 在具体实施方式及权利要求书中,由术语“中的至少一者”连接的项目的列表可意味着所列项目的任何组合。例如,如果列出项目A及B,那么短语“A及B中的至少一者”或“A或B中的至少一者”意味着仅A;仅B;或A及B。在另一实例中,如果列出项目A、B及C,那么短语“A、B及C中的至少一者”或“A、B或C中的至少一者”意味着仅A;或仅B;仅C;A及B(排除C);A及C(排除B);B及C(排除A);或A、B及C的全部。项目A可包含单个元件或多个元件。项目B可包含单个元件或多个元件。项目C可包含单个元件或多个元件。

[0047] 如本文中所使用,电解液中各组分的含量均为基于电解液的总重量得到的。

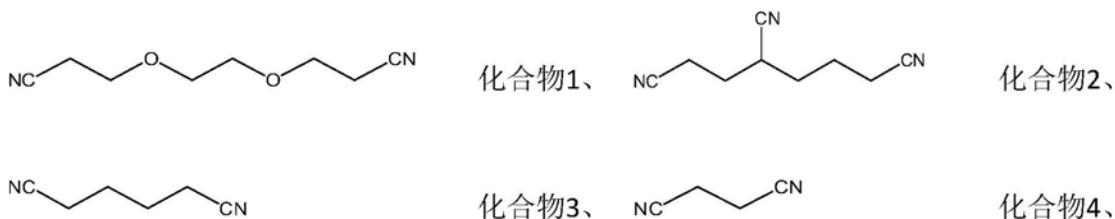
[0048] 一、电解液

[0049] 在一些实施例中,本发明的电解液中包含腈化合物,所述腈化合物包含式I化合物、式II化合物、式III化合物、式IV化合物、式V化合物或式VI化合物中的至少一种:

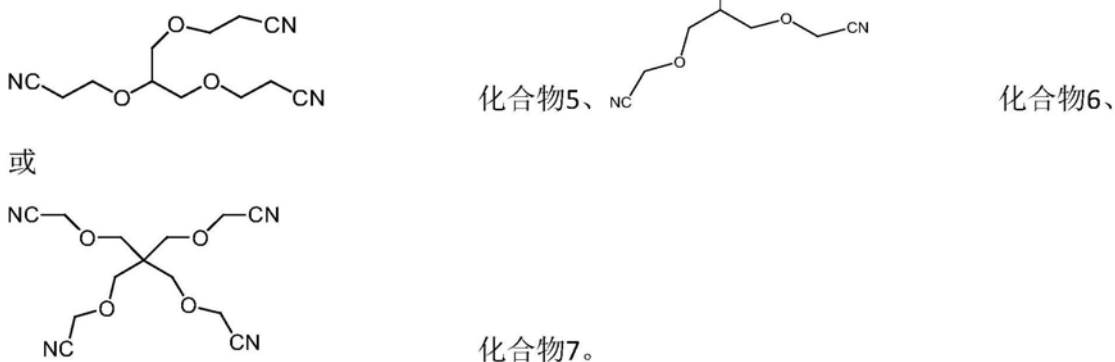


[0052] 其中,a、d、f、j、k、l、m、r、u、w和y各自独立的选自1、2、3、4或5,b、c、e、g、h、i、n、o、p、q、s、t、v、x各自独立的选自0、1、2、3、4或5;所述腈化合物占所述电解液的质量分数A%为0.1%至10%、0.3%至8%、1%至6%、或3%至4%,在一些实施例中,所述A%为约0.5%、约1.5%、约2.5%、约3.5%、约4.5%、约5.5%、约6.5%、约7.5%、约8.5%或约9.5%。

[0053] 在一些实施例中,所述腈化合物包含下述中的至少一种化合物:



[0054]



[0055] 在一些实施例中,为进一步改善锂离子电池的性能,所述电解液中还包含以下添加剂中的一种或多种:1,3-丙烷磺酸内酯(PS)、氟代碳酸乙烯酯(FEC)、碳酸亚乙烯酯(VC)、2,4-丁烷磺酸内酯、1,4-丁烷磺酸内酯、甲烷二磺酸亚甲酯(MMDS)、硫酸乙烯酯(DTD)、丁二酸酐(SA)、乙氧基五氟环三磷腈、1,3-二氧杂环己烷(DOX)或丙烯基-1,3-磺酸内酯。

[0056] 在一些实施例中,为抑制含有腈化合物的电解液引起铜的溶出,所述电解液中还含有阴离子,例如如下无机阴离子中的至少一种,如 Cl^- 、 Br^- 、 SO_4^{2-} 、 CO_3^{2-} 、或 F^- 。在一些实施例中,所述阴离子在所述电解液中的含量小于或等于1000ppm。

[0057] 在一些实施例中,所述电解液进一步包括锂盐和有机溶剂。

[0058] 在一些实施例中,所述锂盐选自无机锂盐和有机锂盐中的一种或多种。在一些实施例中,所述锂盐含有氟元素、硼元素或磷元素中的至少一种。在一些实施例中,所述锂盐选自如下锂盐中的一种或多种:六氟磷酸锂(LiPF_6)、双三氟甲烷磺酰亚胺锂(简称为LiTFSI)、双(氟磺酰)亚胺锂(简称为LiFSI)、双草酸硼酸(简称为LiBOB)、二氟草酸硼酸(简称为LiDFOB)、六氟砷酸锂(简称为 LiAsF_6)、高氯酸锂(简称为 LiClO_4)、三氟甲磺酸锂(简称为 LiCF_3SO_3)中的至少一种。

[0059] 在一些实施例中,所述锂盐的浓度为0.5M至1.5M。在一些实施例中,所述锂盐的浓度为0.8M至1.2M。

[0060] 所述有机溶剂包含环状酯和链状酯,所述环状酯选自碳酸乙烯酯(EC)、碳酸丙烯酯(PC)、 γ -丁内酯(BL)和碳酸丁烯酯中的至少一种;所述链状酯选自碳酸二甲酯(DMC)、碳酸二乙酯(DEC)、碳酸甲乙酯(EMC)、碳酸丙乙酯、甲酸甲酯(MF)、甲酸乙酯(MA)、乙酸乙酯(EA)、丙酸乙酯(EP)、丙酸丙酯(PP)、丙酸甲酯、乙酸丙酯、丁酸甲酯、丁酸乙酯中的至少一种。

[0061] 二、电化学装置

[0062] 本申请的电化学装置包括发生电化学反应的任何装置,它的具体实例包括所有种类的一次电池、二次电池、燃料电池、太阳能电池或电容器。特别地,该电化学装置是锂二次电池,包括锂金属二次电池、锂离子二次电池、锂聚合物二次电池或锂离子聚合物二次电池。在一些实施例中,本申请的电化学装置是具备具有能够吸留、放出金属离子的正极活性物质的正极以及具有能够吸留、放出金属离子的负极活性材料的负极的电化学装置,其特征在于,包含本申请的上述任何电解液。

[0063] 电解液

[0064] 本申请的电化学装置中使用的电解液为本申请的上述任何电解液。

[0065] 负极

[0066] 在根据本申请所述的电化学装置中,负极包括集流体和设置在集流体上的负极活性材料层。负极活性材料层包含负极活性材料。负极活性材料的具体种类均不受到具体的限制,可根据需求进行选择。

[0067] 负极可以通过本领域公知的制备方法制备。例如,负极可以通过如下方法获得:在溶剂中将活性材料、导电材料和粘合剂混合,以制备活性材料组合物,并将该活性材料组合物涂覆在集流体上。

[0068] 负极活性材料包括可逆地嵌入/脱嵌锂离子的材料。在一些实施例中,可逆地嵌入/脱嵌锂离子的材料包括碳材料。在一些实施例中,碳材料可以是在锂离子可充电电池中通常使用的任何基于碳的负极活性材料。在一些实施例中,碳材料包括、但不限于:结晶碳、非晶碳或它们的混合物。结晶碳可以是无定形的、片形的、小片形的、球形的或纤维状的天然石墨或人造石墨。非晶碳可以是软碳、硬碳、中间相沥青碳化合物、煅烧焦等。

[0069] 在一些实施例中,负极活性材料层包括负极活性材料。在一些实施例中,负极活性材料包括、但不限于:锂金属、结构化的锂金属、天然石墨、人造石墨、中间相微碳球(简称为MCMB)、硬碳、软碳、硅、硅-碳复合物、Li-Sn合金、Li-Sn-O合金、Sn、SnO、SnO₂、尖晶石结构的锂化TiO₂-Li₄Ti₅O₁₂、Li-Al合金或其任意组合。

[0070] 在一些实施例中,负极活性材料层可以包括粘合剂,并且可选地包括导电材料。粘合剂提高负极活性材料颗粒彼此间的结合和负极活性材料与集流体的结合。在一些实施例中,粘合剂包括但不限于:聚乙烯醇、羧甲基纤维素、羟丙基纤维素、二乙酰基纤维素、聚氯乙烯、羧化的聚氯乙烯、聚氟乙烯、含亚乙基氧的聚合物、聚乙烯吡咯烷酮、聚氨酯、聚四氟乙烯、聚偏1,1-二氟乙烯、聚乙烯、聚丙烯、丁苯橡胶、丙烯酸(酯)化的丁苯橡胶、环氧树脂、尼龙等。

[0071] 在一些实施例中,导电材料包括、但不限于:基于碳的材料、基于金属的材料、导电聚合物或它们的混合物。在一些实施例中,基于碳的材料选自天然石墨、人造石墨、碳黑、乙炔黑、科琴黑、碳纤维或其任意组合。在一些实施例中,基于金属的材料选自金属粉、金属纤维、铜、镍、铝、银。在一些实施例中,导电聚合物为聚亚苯基衍生物。

[0072] 在根据本申请所述的电化学装置中,负极的集流体可以选自铜箔、镍箔、不锈钢箔、钛箔、泡沫镍、泡沫铜、覆有导电金属的聚合物基底和它们的组合。在一些实施例中,所述集流体包括铜箔。

[0073] 在一些实施例中,所述铜箔由电解或压延生成,纯度大于或等于99.5%,镍、锌、铬

等微量元素含量之和小于或等于0.5重量%；

[0074] 在一些实施例中,所述铜箔具有选自如下的一种或多种性质:

[0075] ●铜纯度大于或等于99.5%；

[0076] ●厚度为3微米至15微米,例如所述厚度为约4微米、约5微米、约6微米、约7微米、约8微米、约9微米、约10微米、约11微米、约12微米、约13微米、或约14微米；

[0077] ●单位面积的重量为30g/m²至150g/m²,例如所述单位面积的重量为约50g/m²、约70g/m²、约90g/m²、约110g/m²、或约130g/m²；

[0078] ●拉伸强度大于或等于20kg/mm²,例如所述拉伸强度大于或等于30kg/mm²、大于或等于40kg/mm²、或大于或等于50kg/mm²；

[0079] ●延伸率大于或等于1.5%,例如所述延伸率大于或等于2%、大于或等于2.5%、大于或等于3%、大于或等于3.5%、或大于或等于4%。

[0080] 在一些实施例中,所述铜箔由电解生成,纯度大于或等于99.5%,厚度为约6微米,拉伸强度大于或等于30kg/mm²,延伸率大于或等于3%。

[0081] 在一些实施例中,所述铜箔具有一定程度的抗腐蚀性,例如,在约45℃下用碳酸乙烯酯(EC)、碳酸丙烯酯(PC)、碳酸二乙酯(DEC)按照质量比为3:1:7, LiPF₆含量为1mol/L的电解液浸泡约48小时后无明显颜色变化。

[0082] 在一些实施例的电化学装置中包含正极、负极、隔离膜及电解液;其中,所述电解液包含腈化合物,所述腈化合物占所述电解液的质量分数为A%;所述负极包括集流体,所述集流体包含:第一区和第二区;其中所述第一区设置有负极活性物质层;所述第二区不包含负极活性物质层。所述第二区的面积占所述集流体的表面积的B%,且A×B小于600,例如A×B小于550、小于500、小于450、小于400、小于350、小于300、小于250、小于200、小于150、小于100、小于50、小于30、小于15、或小于5。

[0083] 在一些实施例中,所述负极具有极耳,所述极耳是通过焊接连接至所述第二区形成的,且A×B小于210。例如A×B小于200、小于150、小于100、小于50、小于30、小于15、或小于10。

[0084] 图1和图2演示了本发明实施例中负极的集流体的示意图,所述集流体包含:第一区1和第二区2;其中所述第一区设置有负极活性物质层(如图中灰色区域所示);所述第二区不包含负极活性物质层。所述负极具有极耳3,所述极耳是通过焊接连接至所述第二区形成的。

[0085] 如图2所示,在一些实施例中,至少有一个第二区位于所述集流体的边缘,其中距离所述集流体边缘最近的极耳与所述集流体的边缘之间的距离为C,极耳宽度为W,且“C/W”(即C与W的比值)的范围为0至50,例如5至40、10至30、15至40、或20至30。

[0086] 在一些实施例中,所述负极具有极耳,所述极耳个数为1至150个,例如,所述极耳个数为3个、5个、7个、9个、10个、15个、20个、25个、30个、35个、40个、45个、50个、60个、70个、80个、90个、100个、110个、120个、130个、或140个;所述极耳是通过裁切所述集流体形成的,所述极耳包含未涂覆负极活性物质层区域,且A×B小于约500;例如A×B小于450、小于400、小于350、小于300、小于250、小于200、小于150、小于100、小于50、小于30、小于15或小于10。

[0087] 图3和图4演示了本发明又一实施例中负极的集流体的示意图,所述集流体包含:第一区1和第二区2;其中所述第一区设置有负极活性物质层;所述第二区不包含负极活性

物质层。所述负极具有多个极耳3,所述极耳是通过裁切所述集流体形成的,所述极耳包含未涂覆负极活性物质层区域。

[0088] 如图5所示,在一些实施例中,至少有一个第二区位于所述集流体的边缘,位于所述集流体边缘的所述第二区的边缘回折或不回折;其中当回折时,回折区域的宽度为D,极耳宽度为W,且“D/W”(即D与W的比值)的范围为0.1至20,例如2至18、4至16、6至14、8至12、或9至10。

[0089] 如图6所示,在一些实施例中,至少有一个第二区位于所述集流体的边缘,所述负极还包括位于集流体中间的一个或多个不包含负极活性物质层的第二区。

[0090] 在一些实施例中,为尽可能降低第二区的表面积,所述第二区任选地被能够粘接在所述第二区上的物质覆盖。例如,如图7所示,所述第二区的一部分被,例如但不限于,聚合物胶带4覆盖。

[0091] 在一些实施例中,所述极耳的部位任选地被能够粘附在其上的物质覆盖。例如,如图8所示,为减少极耳与第二区焊接处的铜离子溶出,所述极耳焊接部分可以用,例如但不限于,聚合物胶带覆盖。

[0092] 在本发明的负极中,所述第一区(即设置有负极活性物质层的区域)可以位于负极集流体的上表面、下表面或者两者之上;所述第二区可以位于负极集流体的边缘和/或内部,所述第二区还包括极耳焊接处、裁切形成的极耳区域、边缘回折区域。

[0093] 正极

[0094] 本申请的电化学装置中使用的正极的材料可以使用本领域公知的材料、构造和制造方法制备。在一些实施例中,可以采用US9812739B中记载的技术制备本申请的正极,其以全文引用的方式并入本申请中。

[0095] 在一些实施例中,正极包括集流体和位于该集流体上的正极活性材料层。正极活性材料包括可逆地嵌入和脱嵌锂离子的至少一种锂化插层化合物。在一些实施例中,正极活性材料包括复合氧化物。在一些实施例中,该复合氧化物含有锂以及从钴、锰和镍中选择的至少一种元素。

[0096] 在一些实施例中,正极活性材料选自钴酸锂、锰酸锂、镍酸锂或锂镍锰钴三元材料中的一种或多种,所述负极活性材料含有硅或硅氧材料,还可任选自石墨、硬碳、中间相碳微球等可实现脱嵌锂的任意负极材料。

[0097] 在一些实施例中,正极活性材料可以在其表面上具有涂层,或者可以与具有涂层的另一化合物混合。该涂层可以包括从涂覆元素的氧化物、涂覆元素的氢氧化物、涂覆元素的羟基氧化物、涂覆元素的碳酸氧盐和涂覆元素的羟基碳酸盐中选择的至少一种涂覆元素化合物。用于涂层的化合物可以是非晶的或结晶的。

[0098] 在一些实施例中,在涂层中含有的涂覆元素可以包括Mg、Al、Co、K、Na、Ca、Si、Ti、V、Sn、Ge、Ga、B、As、Zr或它们的任意组合。可以通过任何方法来施加涂层,只要该方法不对正极活性材料的性能产生不利影响即可。例如,该方法可以包括对本领域公知的任何涂覆方法,例如喷涂、浸渍等。

[0099] 正极活性材料层还包括粘合剂,并且可选地包括导电材料。粘合剂提高正极活性材料颗粒彼此间的结合,并且还提高正极活性材料与集流体的结合。

[0100] 在一些实施例中,粘合剂包括,但不限于:聚乙烯醇、羟丙基纤维素、二乙酰基纤维

素、聚氯乙烯、羧化的聚氯乙烯、聚氟乙烯、含亚乙基氧的聚合物、聚乙烯吡咯烷酮、聚氨酯、聚四氟乙烯、聚偏1,1-二氟乙烯、聚乙烯、聚丙烯、丁苯橡胶、丙烯酸(酯)化的丁苯橡胶、环氧树脂、尼龙等。

[0101] 在一些实施例中,导电材料包括,但不限于:基于碳的材料、基于金属的材料、导电聚合物和它们的混合物。在一些实施例中,基于碳的材料选自天然石墨、人造石墨、碳黑、乙炔黑、科琴黑、碳纤维或其任意组合。在一些实施例中,基于金属的材料选自金属粉、金属纤维、铜、镍、铝、银。在一些实施例中,导电聚合物为聚亚苯基衍生物。

[0102] 在一些实施例中,集流体可以是铝,但不限于此。

[0103] 正极可以通过本领域公知的制备方法制备。例如,正极可以通过如下方法获得:在溶剂中将活性材料、导电材料和粘合剂混合,以制备活性材料组合物,并将该活性材料组合物涂覆在集流体上。在一些实施例中,溶剂可以包括N-甲基吡咯烷酮等,但不限于此。

[0104] 在一些实施例中,正极通过在集流体上使用包括锂过渡金属系化合物粉体和粘结剂的正极活性物质层形成正极材料而制成。

[0105] 在一些实施例中,正极活性物质层通常可以通过如下操作来制作:将正极材料和粘结剂(根据需要而使用的导电材料和增稠剂等)进行干式混合而制成片状,将得到的片压接于正极集流体,或者使这些材料溶解或分散于液体介质中而制成浆料状,涂布在正极集流体上并进行干燥。在一些实施例中,正极活性物质层的材料包括任何本领域公知的材料。

[0106] 隔离膜

[0107] 在一些实施例中,本申请的电化学装置在正极与负极之间设有隔离膜以防止短路。本申请的电化学装置中使用的隔离膜的材料和形状没有特别限制,其可为任何现有技术中公开的技术。在一些实施例中,隔离膜包括由对本申请的电解液稳定的材料形成的聚合物或无机物等。

[0108] 例如隔离膜可包括基材层和表面处理层。基材层为具有多孔结构的无纺布、膜或复合膜,基材层的材料选自聚乙烯、聚丙烯、聚对苯二甲酸乙二醇酯和聚酰亚胺中的至少一种。具体的,可选用聚丙烯多孔膜、聚乙烯多孔膜、聚丙烯无纺布、聚乙烯无纺布或聚丙烯-聚乙烯-聚丙烯多孔复合膜。基材层可以为一层或多层,当基材层为多层时,不同的基材层的聚合物的组成可以相同,也可以不同,重均分子量不同;当基材层为多层时,不同的基材层的聚合物的闭孔温度不同。

[0109] 基材层的至少一个表面上设置有表面处理层,表面处理层可以是聚合物层或无机物层,也可以是混合聚合物与无机物所形成的层。

[0110] 无机物层包括无机颗粒和粘结剂,无机颗粒选自氧化铝、氧化硅、氧化镁、氧化钛、二氧化铪、氧化锡、二氧化铈、氧化镍、氧化锌、氧化钙、氧化锆、氧化钪、碳化硅、勃姆石、氢氧化铝、氢氧化镁、氢氧化钙和硫酸钡中的一种或几种的组合。粘结剂选自聚偏氟乙烯、偏氟乙烯-六氟丙烯的共聚物、聚酰胺、聚丙烯腈、聚丙烯酸酯、聚丙烯酸、聚丙烯酸盐、聚乙烯吡咯烷酮、聚乙烯醚、聚甲基丙烯酸甲酯、聚四氟乙烯和聚六氟丙烯中的一种或几种的组合。聚合物层中包含聚合物,聚合物的材料包括聚酰胺、聚丙烯腈、丙烯酸酯聚合物、聚丙烯酸、聚丙烯酸盐、聚乙烯吡咯烷酮、聚乙烯醚、聚偏氟乙烯或聚(偏氟乙烯-六氟丙烯)中的至少一种。

[0111] 三、应用

[0112] 本申请实施例的电化学装置具有提高的循环性能及在过放电条件下的高温稳定特性,适合使用在各种电子设备中。

[0113] 本申请的电化学装置的用途没有特别限定,可以用于公知的各种用途。例如笔记本电脑、笔输入型计算机、移动电脑、电子书播放器、便携式电话、便携式传真机、便携式复印机、便携式打印机、头戴式立体声耳机、录像机、液晶电视、手提式清洁器、便携CD机、迷你光盘、收发机、电子记事本、计算器、存储卡、便携式录音机、收音机、备用电源、电机、汽车、摩托车、助力自行车、自行车、照明器具、玩具、游戏机、钟表、电动工具、闪光灯、照相机、家庭用大型蓄电池或锂离子电容器等。

[0114] 实施例

[0115] 以下,举出实施例和比较例对本申请进一步具体地进行说明,但只要不脱离其主旨,则本申请并不限于这些实施例。

[0116] 一. 锂离子电池的制备

[0117] (1) 负极的制备

[0118] (i) 极耳经焊接形成的负极

[0119] 将人造石墨粉末、羧甲基纤维素钠(CMC)、丁苯橡胶按质量比96:2:2溶于水中,充分混合搅拌得到负极浆料,将负极浆料均匀地涂布在厚度为12微米的负极集流体铜箔的特定区域上,在120℃烘烤1小时得到负极活性材料层,之后经过压实、分切、焊接极耳、得到负极。

[0120] (ii) 极耳经裁切形成的负极

[0121] 将人造石墨粉末、羧甲基纤维素钠(CMC)、丁苯橡胶按质量比96:2:2溶于水中,充分混合搅拌得到负极浆料,将负极浆料均匀地涂布在厚度为12微米的负极集流体铜箔的特定区域上,在120℃烘烤1小时得到负极活性材料层,之后经过压实、裁切极耳、分切、得到负极。

[0122] (iii) 负极第二区有聚合物胶带的负极(实施例59)的制备方法

[0123] 将人造石墨粉末、羧甲基纤维素钠(CMC)、丁苯橡胶按质量比96:2:2溶于水中,充分混合搅拌得到负极浆料,将负极浆料均匀地涂布在厚度为12微米的负极集流体铜箔的特定区域上,在120℃烘烤1小时得到负极活性材料层,之后经过压实、分切、焊接极耳、并在第二区(即未涂覆负极浆料的区域)贴上材质为丙烯酸酯的聚合物胶带,得到负极。

[0124] (iv) 极耳焊接处有聚合物胶带的负极(实施例60)的制备方法

[0125] 将人造石墨粉末、羧甲基纤维素钠(CMC)、丁苯橡胶按质量比96:2:2溶于水中,充分混合搅拌得到负极浆料,将负极浆料均匀地涂布在厚度为12微米的负极集流体铜箔的特定区域上,在120℃烘烤1h得到负极活性材料层,之后经过压实、分切、焊接极耳、并在极耳焊接区域贴上材质为丙烯酸酯的聚合物胶带,得到负极。

[0126] (2) 正极的制备

[0127] (i) 极耳经焊接形成的正极

[0128] 将正极活性材料钴酸锂(分子式为 LiCoO_2)、粘结剂聚偏二氟乙烯(PVDF)、导电石墨(Super-P)按质量比96:2:2溶于N-甲基吡咯烷酮(NMP)中混合均匀制成正极浆料。将正极浆料均匀地涂布在厚度为约12微米的正极集流体铝箔上,120℃烘烤1小时得到正极活性材料层,之后经过压实、焊接极耳、分切、得到正极。

[0129] (ii) 极耳经裁切形成的正极

[0130] 将正极活性材料钴酸锂(分子式为 LiCoO_2)、粘结剂聚偏二氟乙烯(PVDF)、导电石墨(Super-P)按质量比96:2:2溶于N-甲基吡咯烷酮(NMP)中混合均匀制成正极浆料。将正极浆料均匀地涂布在厚度为12微米的正极集流体铝箔上,120℃烘烤1小时得到正极活性材料层,之后经过压实、裁切极耳、分切得到正极。

[0131] (3) 电解液的制备

[0132] 在干燥的氩气气氛手套箱中,将碳酸乙烯酯(EC)、碳酸丙烯酯(PC)、碳酸二乙酯(DEC)按照质量比为3:1:7混合,加入 LiPF_6 作为锂盐,加入特定种类和量的添加剂(添加的物质种类和量如表1所示,电解液中各组分的含量均为基于电解液的总重量得到的)。电解液中 LiPF_6 的浓度为约1mol/L。

[0133] (4) 隔离膜的制备

[0134] 选用约12微米厚的聚丙烯隔离膜

[0135] (5) 锂离子电池的制备

[0136] 以约12微米的聚丙烯薄膜作为隔离膜。将正极、隔离膜、负极按顺序叠好,使隔离膜处于正负极中间起到隔离的作用,然后卷绕、装入铝箔包装袋,在80℃烘烤除水后,注入相应电解液,经过真空封装、静置、化成、整形等工序,即完成锂离子电池的制备。

[0137] 二. 对负极集流体采用的铜箔的测试

[0138] 铜箔厚度测试:使用千分尺测量5个点后取平均值。

[0139] 单位面积质量:将铜箔切成100*100mm宽片料称重,计算单位面积质量。单位面积质量=重量/面积;

[0140] 拉伸强度测试:使用拉伸试验机测试,测试样本长度为 $200 \pm 0.5\text{mm}$,宽度为 $15 \pm 0.25\text{mm}$,设置50mm/min的拉伸速度,试验机夹头距离为 $125 \pm 0.1\text{mm}$,测试5个平行样,取平均值为测试结果,测试时试样长度方向与夹具轴线平行,并保持样品直线状,实验温度为 $20 \pm 5^\circ\text{C}$

[0141] 延伸率测试:使用拉伸试验机测试,测试样本长度为 $200 \pm 0.5\text{mm}$,宽度为 $15 \pm 0.25\text{mm}$,设置50mm/min的拉伸速度,试验机夹头距离为 $125 \pm 0.1\text{mm}$,测试5个平行样,取平均值为测试结果,测试时试样长度方向与夹具轴线平行,并保持样品直线状,实验温度为 $20 \pm 5^\circ\text{C}$;延伸率=拉伸长度/原始长度;

[0142] 三. 锂离子电池性能测试

[0143] (1) 循环性能测试

[0144] 将锂离子电池在45℃条件下,以恒定电流1C充电至4.45V,搁置30分钟,1C放电至3.0V,循环充放电500次。

[0145] 锂离子电池容量保持率(%) = 循环500次放电容量/首次放电容量 $\times 100\%$ 。

[0146] (2) 60℃高温存储测试

[0147] 将锂离子电池放至25℃恒温箱中,以恒定电流0.5C充电至3.95V,测试电池的厚度,后满充至4.45V,将电池放在60℃烘箱中存储30天,期间,每3天测试一次电池厚度,如果电池相对3.95V时的厚度增长率大于60%,则停止测试。

[0148] 厚度增长率 = (存储后的厚度-3.95V时的厚度)/3.95V时的厚度 $\times 100\%$

[0149] (3) 浮充漏电流测试

[0150] 将锂离子电池在45℃条件下搁置120min,1C充电至4.45V,保持恒压充电状态15天,记录15天后电流大小。

[0151] (4) 电池挤压测试

[0152] 将锂离子电池放至25℃恒温箱中,以恒定电流0.5C充电至4.45V,然后恒压充电至电流为0.05C,用20KN的压力挤压电池,观察电池是否燃烧、爆炸。

[0153] A.按照上述方法制备实施例1至39和对比例1至6的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.5\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延伸率 $\geq 3\%$ 。第二区的面积占负极表面积的比例B%为18.2%,极耳与第二区的连接方式为焊接,极耳宽度w为0.8cm,极耳距离集流体边缘距离C为2cm,位于集流体边缘的第二区的边缘回折区域的宽度D为1.8cm。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及60℃高温存储测试,测试结果请见表2。

[0154] 表1

[0155]

	膈化合物	膈化合物占 电解液的质量 分数 A (%)	第二区面积占集 流体表面积比例 B (%)	AxB	容量保 持率(%)	浮充漏 电流 (mA)	60℃高温存储 测试(%)
实施例 1	化合物 1	0.3	18.2	5.46	70	4	48
实施例 2	化合物 1	1	18.2	18.2	78	5	35
实施例 3	化合物 1	3	18.2	54.6	75	7	15
实施例 4	化合物 1	5	18.2	91	74	9	14
实施例 5	化合物 1	10	18.2	182	67	20	14
实施例 6	化合物 2	1	18.2	18.2	87	6	33
实施例 7	化合物 2	3	18.2	54.6	86	8	15
实施例 8	化合物 2	10	18.2	182	72	18	14
实施例 9	化合物 3	0.3	18.2	5.46	72	4	47
实施例 10	化合物 3	1	18.2	18.2	84	7	36
实施例 11	化合物 3	3	18.2	54.6	79	9	18
实施例 12	化合物 3	10	18.2	182	72	23	18
实施例 13	化合物 5	0.3	18.2	5.46	70	3	50
实施例 14	化合物 5	1	18.2	18.2	82	5	32
实施例 15	化合物 5	3	18.2	54.6	81	6	13
实施例 16	化合物 5	5	18.2	91	75	9	10
实施例 17	化合物 5	10	18.2	182	70	19	10
实施例 18	化合物 6	1	18.2	18.2	81	3	23
实施例 19	化合物 6	3	18.2	54.6	81	4	14
实施例 20	化合物 6	10	18.2	182	70	23	14
实施例 21	化合物 7	0.3	18.2	5.46	70	3	51
实施例 22	化合物 7	1	18.2	18.2	85	5	35
实施例 23	化合物 7	3	18.2	54.6	83	6	13
实施例 24	化合物 7	10	18.2	182	70	19	13
实施例 25	化合物 1+化合物 2	1.5+1.5	18.2	54.6	81	5	37
实施例 26	化合物 1+化合物 3	1.5+1.5	18.2	54.6	83	4	35

[0156]

实施例 27	化合物 1+化合物 4	1.5+1.5	18.2	54.6	81	5	34
实施例 28	化合物 1+化合物 5	1.5+1.5	18.2	54.6	83	3	35
实施例 29	化合物 1+化合物 6	1.5+1.5	18.2	54.6	87	3	33
实施例 30	化合物 1+化合物 7	1.5+1.5	18.2	54.6	85	3	37
实施例 31	化合物 2+化合物 5	1.5+1.5	18.2	54.6	83	5	34
实施例 32	化合物 2+化合物 6	1.5+1.5	18.2	54.6	83	8	35
实施例 33	化合物 2+化合物 7	1.5+1.5	18.2	54.6	81	4	30
实施例 34	化合物 3+化合物 6	1.5+1.5	18.2	54.6	80	5	37
实施例 35	化合物 3+化合物 7	1.5+1.5	18.2	54.6	85	4	35
实施例 36	化合物 1+化合物 2 +化合物 3	1+1+1	18.2	54.6	81	3	35
实施例 37	化合物 2+化合物 4 +化合物 5	1+1+1	18.2	54.6	84	2.9	35
实施例 38	化合物 3+化合物 4 +化合物 6	1+1+1	18.2	54.6	84	4	36
实施例 39	化合物 5+化合物 6 +化合物 7	1+1+1	18.2	54.6	87	4	36
对比例 1	/	0	18.2	0	61	2.5	严重胀气停止 测试
对比例 2	化合物 2	12	18.2	218.2	56	45	20
对比例 3	化合物 3	12	18.2	218.2	54	38	23
对比例 4	化合物 5	12	18.2	218.2	56	43	21
对比例 5	化合物 6	12	18.2	218.2	59	36	18
对比例 6	化合物 7	15	18.2	345	51	51	19

[0157] 注：“/”代表未加入

[0158] 表1显示当固定第二区的面积占负极表面积的比例B%为18.2%时的实施例和对比例。相比于电解液中不含腈化合物的对比例1,电解液中加入范围在0.1重量%至10重量%的特定腈化合物的实施例1至实施例39的循环性能得到明显改善。从对比例2至对比例5与对比例1的比较可以看出,当增加腈化合物的含量至12重量%从而使AxB的值达到218.2时,循环性能相对于对比例1虽有改善,但改善幅度降低,同时电池自放电进一步提高。从对比例6可以看出,当腈化合物的含量增加到15%从而使AxB>210时,浮充漏电流超过50mA,严重影响电池使用。因此,对于电解液中含有0.1重量%至10重量%的特定腈化合物的情况,当极耳与第二区的连接方式为焊接时,A×B<210可保证电池性能提高的同时引入较小的自放电。加入腈化合物能改善循环是因为腈基可以络合阴极上的金属离子,稳定金属离子电位,从而降低阴极材料的结构相变,同时,腈化合物还可吸附在阴极表面,减少阴极与电解液的接触,二者结合,可显著改善电池的循环和浮充性能;但同时腈化合物对负极集流体铜箔具有一定的溶解性,尤其是当表面无活性物质负载的铜箔集流体暴露在电解液中时,腈化合物对铜箔的溶解性大大增强,溶出的铜离子在电池的充放电过程中可在负极表面慢慢被还原成单质铜并不断沉积,最终导致电池局部短路并恶化自放电。虽然腈化合物会恶化电池自放电,但其对电池电性能具有明显优势,因此,我们需要在电解液中添加一定含量的腈化合物并将其与暴露的空铜箔面积控制在一定范围内,方可兼顾电池的电性能和自放电;

[0159] B.按照上述方法制备实施例40至52以及对比例8的电解液以及锂离子电池,其中,

用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为8微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延伸率 $\geq 3\%$;极耳与第二区的连接方式为焊接,极耳宽度w为0.8厘米,极耳距离集流体边缘距离C为2cm;位于集流体边缘的第二区的边缘回折区域的宽度D为2.5cm。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及60℃高温存储测试,测试结果请见表2。

[0160] 表2

	腈化合物	腈化合物占 电解液的质量 分数 A (%)	第二区面积 占集流体表 面积比例 B (%)	AxB	容量保 持率 (%)	浮充漏电流 (mA)	60℃高温存储 测试(%)
实施例 40	化合物 2	3	9.1	27.3	83	8	32
实施例 41	化合物 3	3	17.6	52.8	88	8	32
实施例 42	化合物 4	3	21.9	65.7	88	15	30
实施例 43	化合物 5	3	23	69	86	16	35
实施例 44	化合物 6	3	27	81	85	17	34
实施例 45	化合物 7	3	31	93	81	11	34
实施例 46	化合物 2+化合物 3	1.5+1.5	17.6	52.8	81	6	37
实施例 47	化合物 3+化合物 4	1.5+1.5	17.6	52.8	81	3	34
实施例 48	化合物 3+化合物 5	1.5+1.5	21.9	65.7	81	6	36
实施例 49	化合物 3+化合物 5 +化合物 7	1+1+1	23	69	81	21	36
实施例 50	化合物 2+化合物 4 +化合物 5	1+1+1	23	69	81	23	35
实施例 51	化合物 2+化合物 4 +化合物 6	1+1+1	23	69	81	23	35
实施例 52	化合物 2	3	0.4	1.2	82	0.6	35
对比例 8	化合物 2	3	85	255	70	47	37

[0162] 表2显示当电解液中腈化合物的含量固定为3重量%时的实施例和对比例。如实施例40至实施例51所示,将电解液中腈化合物的含量固定为3重量%时,电池循环和存储性能较优,随着调整电池中负极的第二区的面积使AxB的值增大,电池浮充漏电流有所增加,如对比例8所示,当AxB的值超过210时,电池出现严重自放电现象,严重影响电池使用。实施例52中的负极集流体无第二区(即B为0.4)从而AxB的值为1.2,与对比例8相比,实施例52电池循环性能较优,漏电流很小。

[0163] C.按照上述方法制备实施例53至实施例60和对比例9的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延伸率 $\geq 2\%$ 。极耳与第二区的连接方式为裁切,极耳个数为9个,极耳宽度w为1.5cm,位于集流体边缘的第二区的边缘回折区域的宽度D为1.5cm。正积极耳对应的采用裁切方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及60℃高温存储测试,测试结果请见表3。

[0164] 表3

[0165]

	腈化合物	腈化合物占 电解液的质量 分数 A (%)	第二区面积 占集流体表面 面积比例 B (%)	AxB	容量保持 率 (%)	浮充漏电 流(mA)	60℃高温存储测 试(%)
实施例 53	化合物 1	3	18.1	54.3	83	2	34
实施例 54	化合物 2	3	22.5	67.5	85	3	28
实施例 55	化合物 4	3	36.7	110.1	86	6	29
实施例 56	化合物 5	3	54	162	83	21	32
实施例 57	化合物 1+化合物 2	1.5+1.5	18.1	54.3	84	4	33
实施例 58	化合物 2+化合物 4	1.5+1.5	18.1	54.3	81	3	33
实施例 59	化合物 2+化合物 4+ 化合物 5	1.5+1.5+1.5	18.1	54.3	83	4	26
实施例 60	化合物 2	3	2.3	6.9	83	0.2	31
对比例 9	化合物 5	12	54	648	80	40	15

[0166] 如表3所示,实施例53至实施例60及对比例9均采用裁切极耳的方式制备电池。从实施例53至实施例59可以看出,调整第二区面积比例B%对电池的容量保持率的影响不显著,但电池自放电加剧;当对比例9中的腈化合物的量A%增至12重量%且第二区面积占比B%达到54%从而AxB的值为648时,自放电电流达到40mA。实施例60中的负极集流体全部涂覆活性材料,但极耳上无活性材料(即B%=2.3%为极耳处空铜箔占比)从而AxB的值为6.9,与对比例9相比,实施例60电池循环和存储性能较优,漏电流很小。综上,当采用裁切极耳方式制备电池时,需控制AxB在600以内,才能使电池性能较优。

[0167] D. 按照上述方法制备实施例61至63的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延伸率 $\geq 2\%$ 。极耳与第二区的连接方式为焊接,极耳宽度为0.8cm,极耳距离集流体边缘距离C为2cm,位于集流体边缘的第二区的边缘回折区域的宽度D为1.8cm。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及60℃高温存储测试,测试结果请见表4。

[0168] 表4

[0169]

	腈化合物	腈化合物占电 解液的质量分 数 A (%)	AxB	容量保持率 (%)	浮充漏电 流(mA)	60℃高温存储测 试(%)
实施例 61	化合物 1	3	42	85	4	35
实施例 62	化合物 1	3	75	84	8	34
实施例 63	化合物 1	3	76.8	85	12	34

[0170] 如表4所示,实施例61中在未涂覆活性物质层的铜箔区域粘贴一定面积的聚合物胶从而降低铜箔与电解液的接触面积;与未粘贴聚合物胶带的实施例63相比,实施例61具有更低的漏电流;实施例62中在极耳焊接处覆盖一定面积的聚合物胶带,与未粘贴聚合物胶带的实施例63相比,也可降低电池的自放电。因此,在实际的电池设计中,可在负极铜箔集流体上极耳焊接处及其它未涂覆负极活性物质的空铜箔区覆盖聚合物胶带或者其他可粘接在铜箔和极耳上的物质,来降低电池的自放电。

[0171] E. 按照上述方法制备实施例64至70的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延

伸率 $\geq 2\%$ 。极耳与第二区的连接方式为焊接,极耳宽度为0.8cm,极耳距离集流体边缘距离C为2cm,位于集流体边缘的第二区的边缘回折区域的宽度D为1.8cm。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及60℃高温存储测试,测试结果请见表5。

[0172] 表5

	腈化合物	腈化合物占电解液的质量分数 A (%)	其他添加剂及其占电解液的质量分数 (%)	AxB	容量保持率 (%)	浮充漏电流(mA)	60℃高温存储测试(%)
实施例 64	化合物 1	3	PS 1	52.5	87%	5	25
实施例 65	化合物 2	3	FEC+PS 1+1	52.5	84%	3	23
[0173] 实施例 66	化合物 4	3	PS+VC 1+0.5	52.5	86%	2.4	17
实施例 67	化合物 5	3	DTD+SA 1+0.5	52.5	86%	8	16
实施例 68	化合物 2	3	MMDS+VC 0.5+0.5	52.5	85%	7	17
实施例 69	化合物 4	3	PS+VC+DTD 1+0.5+1	52.5	88%	10	15
实施例 70	化合物 1	3	/	52.5	75%	11	36

[0174] 注:“/”代表未加入

[0175] 实施例64至实施例69与实施例70相比可以看出,在含有特定腈化合物的电解液中进一步添加其它添加剂,可明显改善电池循环和浮充厚度增长率,添加剂FEC的加入可增加负极SEI的LiF含量,有效的增加了阳极SEI的稳定性;添加剂VC的加入,可在SEI表层聚合形成网状保护层,加强了SEI的柔韧性,以及其它添加剂的添加,都可在一定程度上稳定或强化SEI保护层,因此对电芯循环性能改善明显;同时,因为添加剂在负极的成膜作用,还可在一定程度上降低铜离子在负极的沉积,降低电池的自放电,进一步提升电池的整体电性能。

[0176] 因此,从实施例和对比例可知,腈化合物作为有效的改善循环稳定性添加剂,对电池的自放电影响较大,为了提高电池长期存储性能,需要将腈化合物的含量与空铜箔区域面积控制在一定范围以内,才能保证电池在长期存储后容量无明显的降低,同时,在电解液中添加一定含量的其它添加剂,可改善电池的循环和自放电,保证电池的长循环和存储性能。

[0177] F.按照上述方法制备实施例71至72的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg}/\text{mm}^2$,延伸率 $\geq 2\%$;极耳与第二区的连接方式为焊接,极耳宽度w为0.8cm;极耳距离集流体边缘距离C为2cm;实施例71中位于集流体边缘的第二区的边缘回折区域的宽度D为1.8cm,实施例72中位于集流体边缘的第二区的边缘不回折。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流及挤压测试,测试结果请见表6。

[0178] 表6

[0179]

	腈化合物	腈化合物占电解液的质量分数 A(%)	AxB	容量保持率(%)	浮充漏电流(mA)	挤压测试
实施例 71	化合物 2	3	52.5	84%	5	不燃烧
实施例 72	化合物 2	3	52.5	83%	6	燃烧

[0180] 如表6所述,实施例71中位于集流体边缘的第二区的边缘回折,实施例72中位于集流体边缘的第二区的边缘不回折,二者容量保持率及浮充漏电流无明显差异,但挤压测试显示,采用回折的方式降低了极耳焊接处毛刺刺穿隔膜的风险,因此电池具有更高的安全性。

[0181] G.按照上述方法制备实施例73至76的电解液以及锂离子电池,其中,用铜箔作为负极集流体,所述铜箔由电解生成,纯度 $\geq 99.8\%$,厚度为6微米,拉伸强度 $\geq 30\text{kg/mm}^2$,延伸率 $\geq 2\%$;极耳与第二区的连接方式为焊接,极耳宽度W为0.8cm;极耳距离集流体边缘距离C为2cm;集流体边缘的第二区的边缘回折区域的宽度D为1.8cm。正极极耳对应地采用焊接方式制备。测试锂离子电池不同循环次数循环容量保持率、浮充漏电流,测试结果请见表7

[0182] 表7

[0183]

	腈化合物	腈化合物占电解液的质量分数 A(%)	AxB	Cl-含量(ppm)	容量保持率(%)	浮充漏电流(mA)
实施例 73	化合物 5	3	36.9%	100	81%	7
实施例 74	化合物 5	3	36.9%	500	82%	6
实施例 75	化合物 5	3	36.9%	1000	80%	5
实施例 76	化合物 5	3	36.9%	1100	75%	4

[0184] 如表7所述,当在电解液中含有适量的阴离子,如 Cl^- 时,对电池的漏电流有改善作用,但当添加量偏高,如超过1000ppm时,对电池的容量保持率影响较大。因此在保证电池电性能的同时,可在电解液中添加适量的阴离子,改善浮充漏电流;

[0185] 以上所述,仅是本发明的几个实施例,并非对本发明做任何形式的限制,虽然本发明以较佳实施例揭示如上,然而并非用以限制本发明,任何熟悉本专业的技术人员,在不脱离本发明技术方案的范围,利用上述揭示的技术内容做出些许的变动或修饰均等同于等效实施案例,均属于技术方案范围内。

[0186] 整个说明书中对“一些实施例”、“部分实施例”、“一个实施例”、“另一举例”、“举例”、“具体举例”或“部分举例”的引用,其所代表的意思是在本申请中的至少一个实施例或举例包含了该实施例或举例中所描述的特定特征、结构、材料或特性。因此,在整个说明书中的各处所出现的描述,例如:“在一些实施例中”、“在实施例中”、“在一个实施例中”、“在另一个举例中”,“在一个举例中”、“在特定举例中”或“举例”,其不必然是引用本申请中的相同的实施例或示例。此外,本文中的特定特征、结构、材料或特性可以以任何合适的方式在一个或多个实施例或举例中结合。

[0187] 尽管已经演示和描述了说明性实施例,本领域技术人员应该理解上述实施例不能被解释为对本申请的限制,并且可以在不脱离本申请的精神、原理及范围的情况下对实施例进行改变,替代和修改。

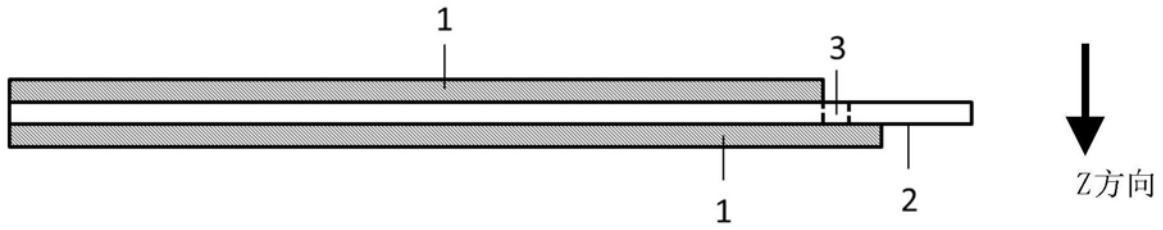


图1



图2

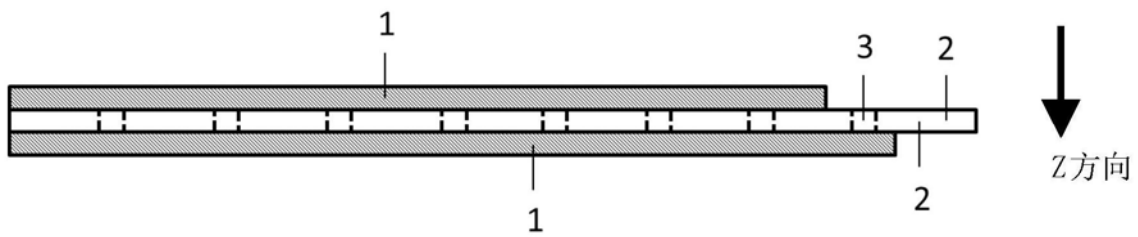


图3

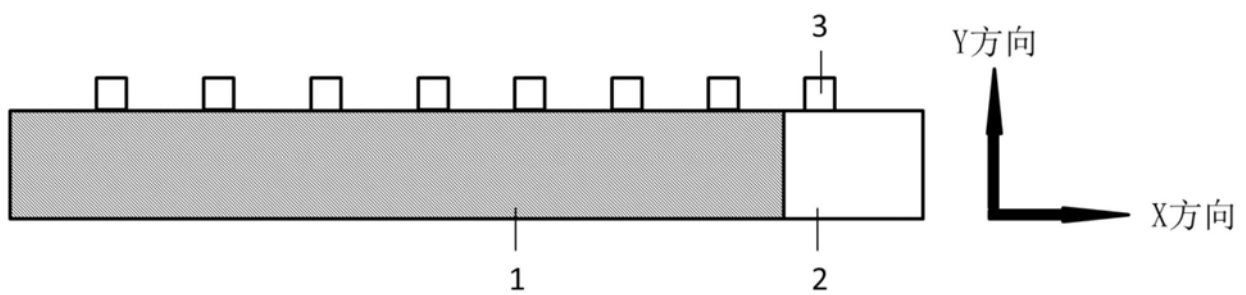


图4

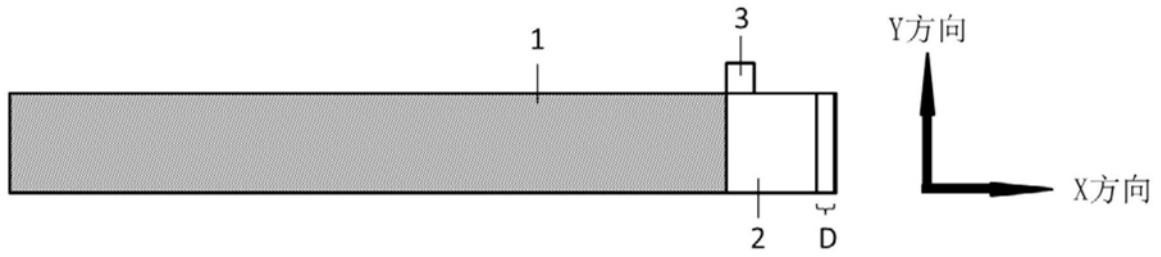


图5

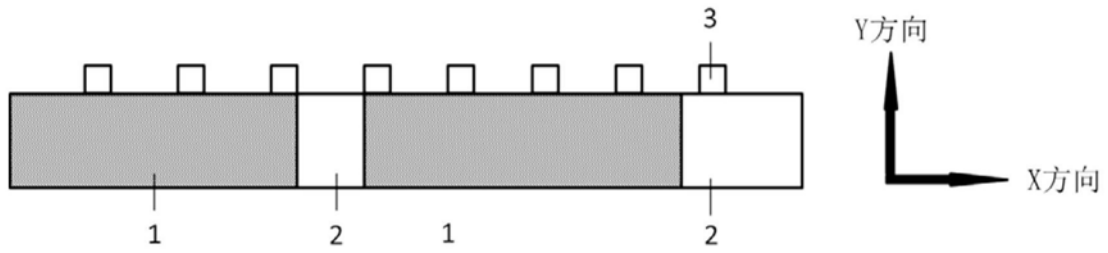


图6

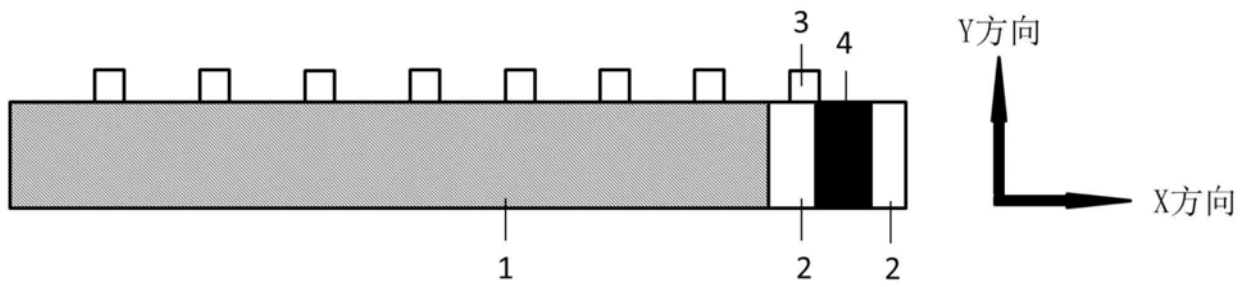


图7

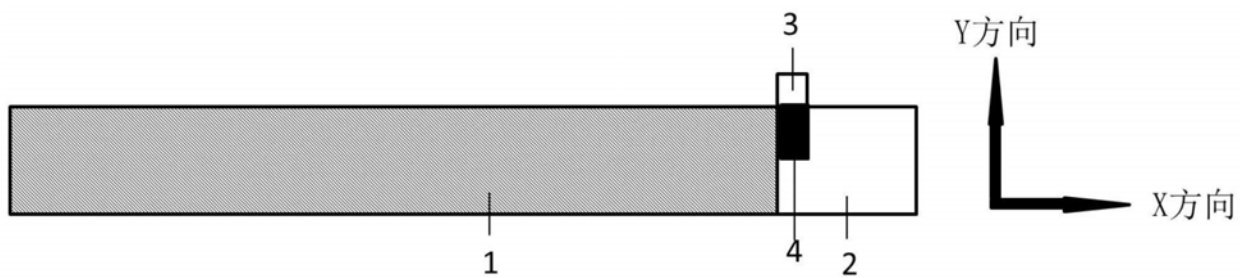


图8