

CN102668221A Nonaqueous electrolyte solution and device comprising same

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NON-AQUEOUS ELECTROLYTE AND APPARATUS COMPRISING THE SAME

FIELD OF THE INVENTION

The present exemplary embodiment relates to a non-aqueous type electrolyte and an apparatus having the same.

BACKGROUND OF THE INVENTION

In devices such as lithium ion secondary batteries and capacitors, since lithium ion secondary batteries can realize high energy density, they are attracting attention as power sources for mobile phones and notebook computers, as well as as power sources for large-scale power storage and power sources for automobiles.

Although a lithium ion secondary battery can achieve a high energy density, the size thereof is increased, and the energy density is increased, and higher safety is expected. For example, in a large-scale power storage power supply and an automotive power supply, particularly high safety is expected, and as safety measures, structural design of a battery, a package, and the like, enhancement of a protective circuit, an electrode material, an additive having an overcharge protective function, enhancement of a shutdown function of a separator, and the like are performed.

Lithium ion secondary batteries use aprotic solvents such as cyclic carbonates and chain carbonates as the electrolyte solvent; these carbonates are characterized by having a low flash point and being combustible, although having a high dielectric constant and a high ion conductivity.

The way to further enhance the safety of the lithium ion secondary battery is to make the electrolyte flame-retardant. As a technique for making an electrolytic solution flame-retardant, a method of adding a phosphazene compound as a flame retardant has been disclosed.

For example, the nonaqueous electrolyte battery of Patent Document 1 uses a solution in which a lithium salt is dissolved in a phosphazene derivative as an electrolyte, or a solution in which a lithium salt is dissolved in a solvent to which an aprotic organic solvent of the phosphazene derivative is further added. It is thus disclosed that a risk of, for example, explosion or misfire is not generated even in an abnormal situation such as a short circuit, and excellent battery performance can be realized.

The nonaqueous electrolyte battery of Patent Document 2 uses a solution in which a lithium salt is dissolved in a chain phosphazene derivative as an electrolyte, or a solution in which a lithium salt is dissolved in a solvent of an aprotic organic solvent to which a phosphazene derivative is further added. It is thus disclosed that a risk of, for example, explosion or misfire is not generated even in a normal situation such as a short circuit, and excellent battery performance can be realized.

Patent Document 3 describes a non-aqueous electrolyte secondary battery having a positive electrode, a negative electrode, and a non-aqueous electrolyte containing a supporting salt, an organic solvent, and a phosphazene derivative, wherein the potential window of the phosphazene derivative is in the range of lower limit value+0.5 V or less and upper limit value+4.5 V or more, and the potential window of the organic solvent is in the range wider than the phosphazene derivative.

Patent Document 4 describes a non-aqueous electrolyte secondary battery having a positive electrode, a negative electrode, and a non-aqueous electrolyte containing a supporting salt and a phosphazene derivative, the lithium salt solution (0.5 mol/l) of which has an electrical conductivity of at least 2.0 mS/cm.

A technique is known which uses, as an additive, a substance which is reductively degraded at a potential higher than that of a carbonate used as a solvent for an electrolytic solution and forms an SEI (Solid Electrolyte Interface) which is a protective film having a high lithium ion permeability. It is known that since SEI has a large influence on charge/discharge efficiency, cycle characteristics, and safety, control of SEI at the negative electrode is important, and irreversible capacity of carbon materials and oxide materials can be reduced by SEI.

Patent Document 5 describes providing an excellent non-aqueous electrolyte containing a lithium salt and a non-aqueous solvent, which can secure safety and reliability in abnormal heating of a battery or the like by further introducing a cyclic carbonate having a carbon-carbon unsaturated bond and a phosphazene derivative based on the non-aqueous electrolyte in a molecule of 1% by mass or more and 25% by mass or less, and can also provide good battery performance such as cycle characteristics.

The nonaqueous electrolytic solution used in the battery disclosed in Patent Document 6 contains a non-aqueous solution containing a cyclic phosphazene compound and a difluorophosphate compound, and at least one cyclic sulfur-containing compound selected from the group consisting of 1,3-propane sultone, 1,3-butane sultone, 1,4-butane sultone, and 1,3,2-thiolane-2,2-dioxide, and a supporting salt. It is disclosed that excellent battery performance and high safety are imparted to a battery even under a high temperature environment.

REFERENCE LIST

Patent Document

Patent Document 1: JP 6-13108 A

Patent Document 2: JP11-144757A

Patent Document 3: JP2001-217005A

Patent Document 4: JP2001-217007A

Patent Document 5: JP2006-24380A

Patent Document 6: JP 2008-41413 A

SUMMARY OF THE INVENTION

Technical Problems

However, in Patent Documents 1 to 4 and 6, since the phosphazene compound is gradually reductively degraded on the negative electrode during long-term use, the capacity retention rate of the battery is sometimes greatly reduced.

In Patent Document 5, although the addition of vinyl carbonate that can form SEI inhibits the reductive degradation of the phosphazene compound, the addition of vinyl carbonate in an amount sufficient to inhibit the reductive degradation of the phosphazene compound for a long period of time causes an increase in resistance, and sometimes greatly reduces the charge/discharge characteristics of the battery.

Further, when the phosphazene compound and the difluorophosphate ester are degraded over a long period of time, the existence ratio of the flame retardant in the electrolytic solution decreases, and safety may decrease after long-term use. That is, in the case of adding a flame retardant that is reductively degraded, an amount of additive corresponding to the amount of the flame retardant added is required, and thus the resistance of the battery is greatly increased in some cases, while the capacity and ratio characteristics are sharply reduced.

That is, an object of the present exemplary embodiment is to provide a non-aqueous electrolyte solution having high flame retardancy and a good capacity retention ratio, and an apparatus including the non-aqueous electrolyte solution.

Solution to the Technical Problems

The nonaqueous electrolytic solution according to the present exemplary embodiment is an electrolytic solution used in an apparatus including a positive electrode, a negative electrode, and a nonaqueous electrolytic solution, and further includes a lithium salt and a compound having a phosphazene structure represented by the following formula (1), and further includes at least one disulfonate selected from a cyclic disulfonate represented by the following formula (2) and a chain disulfonate represented by the following formula (3) in an amount of 0.05 mass % or more and 12.0 mass % or less based on the total amount of the nonaqueous electrolytic solution.

wherein in Formula (1), X1 and X2 each independently represent a halogen element or a monovalent substituent; the monovalent substituent represents an alkyl group, an alkoxy group, an aryl group, an acyl group, an aryloxy group, an amino group, an alkylthio group, an arylthio group, a haloalkyl group, a haloalkoxy group, a haloaryl group, a haloacyl group, a haloaryloxy group, a haloamino group, a haloalkylthio group, or a haloarylthio group; n represents an integer of 3 or more and 5 or less; and Formula (1) may be cyclic.

[Equation 2]

wherein in Formula (2), Q represents an oxygen atom, a methylene group, or a single bond; A1 represents a substituted or unsubstituted alkylene group having 1 to 5 carbon atoms, a carbonyl group, a sulfinyl group, a substituted or unsubstituted perfluoroalkylene group having 1 to 5 carbon atoms, a substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms, a substituted or unsubstituted alkylene group having 1 to 6 carbon atoms, a substituted or unsubstituted perfluoroalkylene group having 1 to 6 carbon atoms, a substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms, which may be branched; and A2 represents a substituted or unsubstituted alkylene group which may be branched.

wherein in Formula (3), R1 and R4 each independently represent an atom or group selected from a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 5 carbon atoms, a substituted or unsubstituted fluoroalkyl group having 1 to 5 carbon atoms, a polyfluoroalkyl group having 1 to 5 carbon atoms, -SO₂ X11 (wherein X11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -SY11 (wherein Y11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -COZ (wherein Z is a hydrogen atom or a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), and a halogen atom; R2 and R3 each independently represent an atom or a group selected from the group consisting of substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms, substituted or unsubstituted alkoxy groups having 1 to 5 carbon atoms, substituted or unsubstituted phenoxy groups, substituted or unsubstituted fluoroalkyl groups having 1 to 5 carbon atoms, polyfluoroalkyl groups having 1 to 5 carbon atoms, substituted or unsubstituted fluoroalkoxy groups having 1 to 5 carbon atoms, polyfluoroalkoxy groups having 1 to 5 carbon atoms, hydroxyl groups, halogen atoms, -NX12 X13 (wherein X12 and X13 each independently represent a hydrogen atom or substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms), and -NY12 CONY13 Y14 (wherein Y12 to Y14 each independently represent a hydrogen atom or substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms).

In the nonaqueous electrolyte solution according to the present exemplary embodiment, a portion of the disulfonate ester contained in the nonaqueous electrolyte solution is substituted with a sultone compound represented by the following formula (4).

wherein in Formula (4), R8 to R13 each independently represent an atom or a group selected from a hydrogen atom, an alkyl group having 1 or more and 12 or less carbon atoms, a cycloalkyl group having 3 or more and 6 or less carbon atoms, and an aryl group having 6 or more and 12 or less carbon atoms; m represents an integer of 0 or more and 2 or less.

In the non-aqueous electrolyte solution according to the present exemplary embodiment, the non-aqueous electrolyte solution contains a compound having a phosphazene structure in an amount of 3.0% by mass or more and 20.0% by mass or less based on the total amount of the non-aqueous electrolyte solution.

In the non-aqueous electrolyte according to the present exemplary embodiment, the non-aqueous electrolyte is gelled with a polymer.

The apparatus according to the present exemplary embodiment is a lithium ion secondary battery or a capacitor, and includes the non-aqueous electrolyte.

According to the present exemplary embodiment, the introduction of the specific disulfonate having a large inhibitory effect on the reductive degradation of the compound having a phosphazene structure can suppress the reductive degradation of the compound having a phosphazene structure on the negative electrode active material. Therefore, an increase in resistance caused by reductive degradation of a compound having a phosphazene structure can be suppressed for a long period of time, and a good capacity retention ratio can be obtained. Further, according to the present exemplary embodiment, since reduction of the compound having a phosphazene structure can be suppressed for a long period of time, and an effective amount of the compound having a phosphazene structure remains in the electrolytic solution even after long-term use, high flame retardancy can be obtained for a long period of time. In addition, the amount of gas generated during the initial charge can be reduced.

The present exemplary embodiment can provide a non-aqueous electrolyte solution having high flame retardancy and a good capacity retention ratio, and an apparatus including the non-aqueous electrolyte solution.

DESCRIPTION OF THE DRAWINGS

FIG. 1 is a diagram illustrating a configuration of a positive electrode of a lithium ion secondary battery according to the present exemplary embodiment; FIG. (1a) shows a plan view of the positive electrode, and FIG. (1b) shows a side view of the positive electrode.

FIG. 2 is a diagram illustrating a configuration of a negative electrode of a lithium ion secondary battery according to the present exemplary embodiment; FIG. (2a) shows a plan view of the negative electrode, and FIG. (2b) shows a side view of the negative electrode.

FIG. 3 is a cross-sectional view illustrating a configuration of a battery element after a lithium ion secondary battery according to the present exemplary embodiment is wound.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, the present exemplary embodiment will be described in detail.

The nonaqueous electrolytic solution according to the present exemplary embodiment is an electrolytic solution used in an apparatus including a positive electrode, a negative electrode, and a nonaqueous electrolytic solution, and further includes a lithium salt and a compound having a phosphazene structure represented by the following formula (1), and further includes at least one disulfonate selected from a cyclic disulfonate represented by the following formula (2) and a chain disulfonate represented by the following formula (3) in an amount of 0.05 mass % or more and 12 mass % or less based on the total amount of the nonaqueous electrolytic solution.

wherein in Formula (1), X1 and X2 each independently represent a halogen element or a monovalent substituent; the monovalent substituent represents an alkyl group, an alkoxy group, an aryl group, an acyl group, an aryloxy group, an amino group, an alkylthio group, an arylthio group, a haloalkyl group, a haloalkoxy group, a haloaryl group, a haloacyl group, a haloaryloxy group, a haloamino group, a haloalkylthio group, or a haloarylthio group; n represents an integer of 3 or more and 5 or less; and Formula (1) may be cyclic.

[Equation 6]

wherein in Formula (2), Q represents an oxygen atom, a methylene group, or a single bond; A1 represents a branched substituted or unsubstituted alkylene group having 1 to 5 carbon atoms, a carbonyl group, a sulfinyl group, a branched substituted or unsubstituted perfluoroalkylene group having 1 to 5 carbon atoms, a branched substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms, an ether bond-containing and branched substituted or unsubstituted alkylene group having 1 to 6 carbon atoms, an ether bond-containing and branched substituted or unsubstituted perfluoroalkylene group having 1 to 6 carbon atoms, an ether bond-containing and branched substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms; and A2 represents a branched substituted or unsubstituted alkylene group.

wherein in Formula (3), R1 and R4 each independently represent an atom or group selected from a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 5 carbon atoms, a substituted or unsubstituted fluoroalkyl group having 1 to 5 carbon atoms, a polyfluoroalkyl group having 1 to 5 carbon atoms, -SO₂X11 (wherein X11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -SY11 (wherein Y11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -COZ (wherein Z is a hydrogen atom or a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), and a halogen atom; R2 and R3 each independently represent an atom or a group selected from the group consisting of substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms, substituted or unsubstituted alkoxy groups having 1 to 5 carbon atoms, substituted or unsubstituted

phenoxy groups, substituted or unsubstituted fluoroalkyl groups having 1 to 5 carbon atoms, polyfluoroalkyl groups having 1 to 5 carbon atoms, substituted or unsubstituted fluoroalkoxy groups having 1 to 5 carbon atoms, polyfluoroalkoxy groups having 1 to 5 carbon atoms, hydroxyl groups, halogen atoms, -NX₁₂X₁₃ (wherein X₁₂ and X₁₃ each independently represent a hydrogen atom or substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms), and -NY₁₂CONY₁₃Y₁₄ (wherein Y₁₂ to Y₁₄ each independently represent a hydrogen atom or substituted or unsubstituted alkyl groups having 1 to 5 carbon atoms).

The compound having a phosphazene structure exhibits flame retardancy, and therefore the compound represented by the above formula (1) is used. Examples of the compound represented by the above formula (1) include monoethoxypentafluorocyclotriphosphazene.

These compounds may be used alone or in combination of two or more. In the compound having the phosphazene structure represented by the above formula (1), X₁ and X₂ may each independently be a different group between units.

From the viewpoint of suppressing reductive degradation of the compound having a phosphazene structure, the compound represented by the above formula (2) is used as a cyclic disulfonate; and the compound represented by the above formula (3) is used as a chain disulfonate.

Representative examples of the compound represented by the above formula (2) are specifically shown in Table 1, and representative examples of the compound represented by the above formula (3) are specifically shown in Table 2, but the present exemplary embodiment is not limited thereto. These compounds may be used alone or in combination of two or more.

[Table 1]

[Table 2]

The proportion of at least one compound selected from the cyclic disulfonate compound represented by the above formula (2) and the chain disulfonate compound represented by the above formula (3) in the nonaqueous electrolyte solution is 0.05 mass % or more and 12 mass % or less based on the total amount of the nonaqueous electrolyte solution. When the proportion based on the total amount of the non-aqueous electrolyte solution is less than 0.05 mass %, the effect of the surface film in which the reductive degradation of the compound having a phosphazene structure is inhibited cannot be effectively obtained. On the other hand, if the proportion of the nonaqueous electrolyte solution is more than 12 mass %, the increase in viscosity of the nonaqueous electrolyte solution and the increase in resistance associated therewith cannot be suppressed, and battery characteristics cannot be further improved. The proportion is preferably 0.1% by mass or more and 10% by mass or less, and the effect of the surface film can be further improved by making the proportion in this range.

The nonaqueous electrolyte according to the present embodiment can reduce the amount of gas generated during initial charge, and is also preferable from the viewpoint of safety. This is conceivable because the simultaneous presence of the compound having a phosphazene structure and the disulfonate in the nonaqueous electrolytic

solution in the above-described ratio can form SEI into which the compound having a phosphazene structure is introduced by a reaction mechanism different from SEI formation using the nonaqueous electrolytic solution containing only the disulfonate.

In the nonaqueous electrolyte solution according to the present exemplary embodiment, a part of the disulfonate ester contained in the nonaqueous electrolyte solution is preferably substituted with a sultone compound represented by the following formula (4).

wherein in Formula (4), R8 to R13 each independently represent an atom or a group selected from a hydrogen atom, an alkyl group having 1 or more and 12 or less carbon atoms, a cycloalkyl group having 3 or more and 6 or less carbon atoms, and an aryl group having 6 or more and 12 or less carbon atoms; m represents an integer of 0 or more and 2 or less.

As the sultone compound represented by the above formula (4), for example, 1,3-propane sultone, 1,4-butane sultone, and derivatives thereof can be used, but are not limited thereto. These compounds may be used alone or in combination of two or more.

The nonaqueous electrolytic solution preferably contains a compound having a phosphazene structure in an amount of 3.0% by mass or more and 20.0% by mass or less based on the total amount of the nonaqueous electrolytic solution. The introduction of 3.0 mass % or more of the compound having a phosphazene structure based on the total amount of the non-aqueous electrolyte may provide a sufficient flame-retardant effect; the introduction of 20.0 mass % or less thereof may suppress the reduction in ion conductivity.

The non-aqueous electrolyte may be a gel electrolyte in which a polymer is gelled.

The non-aqueous electrolyte according to the present exemplary embodiment may contain an aprotic solvent. Examples of the aprotic solvent include cyclic carbonates such as propylene carbonate (PC), ethylene carbonate (EC), butylene carbonate (BC), and vinyl carbonate (VC), chain carbonates such as dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), and dipropyl carbonate (DPC), aliphatic carboxylic acid esters such as methyl formate, methyl acetate, and ethyl propionate, gamma lactones such as gamma butyrolactone, chain ethers such as 1,2-ethoxyethane (DEE) and ethoxymethoxyethane (EME), cyclic ethers such as tetrahydrofuran and 2-methyltetrahydrofuran; Dimethyl sulfoxide, 1,3-dioxolane, formamide, acetamide, dimethylformamide, dioxolane, acetonitrile, propionitrile, nitromethane, ethyl monoglyme, phosphoric triester, trimethoxymethane, dioxolane derivatives, sulfolane, methyl sulfolane, 1,3-dimethyl-2-imidazolidinone, 3-methyl-2-oxazolidinone, propylene carbonate derivatives, tetrahydrofuran derivatives, diethyl ether, anisole, N-methylpyrrolidone, and fluorocarboxylic acid esters. These aprotic organic solvents may be used alone or in the form of a mixture of two or more, but are not limited thereto.

Examples of the lithium salt contained as an electrolyte in the nonaqueous electrolyte according to the present exemplary embodiment include LiPF₆, LiBF₄, LiAsF₆, LiSbF₆, LiClO₄, LiAlO₄, LiN(C_qF_{2q+1}SO₂) (CrF_{2r+1}SO₂) (q and r are natural numbers), and LiCF₃SO₃. However, the lithium salt is not limited thereto.

As the negative electrode active material contained in the negative electrode of the apparatus having the nonaqueous electrolytic solution according to the present exemplary embodiment, one kind or two or more kinds selected from the group consisting of, for example, metallic lithium, a lithium alloy, and a material capable of absorbing and releasing lithium ions may be used. As the material capable of absorbing and releasing lithium ions, carbon materials, silicon, and oxides can be used.

As the carbon material, graphite, amorphous carbon, diamond-like carbon, carbon nanotubes, etc., which absorb lithium, and composite materials thereof can be used. In particular, graphite has high electron conductivity and is excellent in adhesion to a current collector containing a metal such as copper, and voltage flatness, and

contains only a small amount of impurities because it is formed at a high treatment temperature, which is preferably advantageous for improving negative electrode performance. Further, a composite material of high crystalline graphite and low crystalline amorphous carbon may be used.

As silicon and oxide, one of silicon, silicon oxide, tin oxide, indium oxide, zinc oxide, lithium oxide, phosphoric acid, and boric acid or a composite thereof can be used, and the composite preferably contains silicon oxide in particular. The structure is preferably in an amorphous state. This is because silicon oxide is stable, does not cause a reaction with other compounds, and does not introduce deterioration due to non-uniformity such as grain boundaries and defects due to amorphous structures. As the film forming method, a vapor deposition method, a CVD method, a sputtering method, or the like can be used.

The lithium alloy is composed of lithium and a metal capable of forming an alloy with lithium. For example, the lithium alloy is composed of a binary, ternary or higher multimetal alloy of a metal such as Al, Si, Pb, Sn, In, Bi, Ag, Ba, Ca, Hg, Pd, Pt, Te, Zn, and La and lithium. The metallic lithium and the lithium alloy are particularly preferably in an amorphous state. This is because the amorphous structure is difficult to cause deterioration caused by non-uniformity such as grain boundaries and defects.

The metal lithium and the lithium alloy can be suitably formed by a method such as a melt cooling method, a liquid quenching method, an atomization method, a vacuum evaporation method, a sputtering method, a plasma CVD method, a photo CVD method, a thermal CVD method, or a sol-gel method.

According to the present exemplary embodiment, examples of the positive electrode active material contained in the positive electrode of the apparatus having the nonaqueous electrolyte include lithium-containing composite oxides such as LiCoO_2 , LiNiO_2 , and LiMn_2O_4 . The transition metal portion of the lithium-containing composite oxide may be replaced with other elements.

A lithium-containing composite oxide having a stable state (plateau) of 4.5 V or more with respect to the counter electrode potential of metallic lithium may be used. Examples of the lithium-containing composite oxide include a spinel type lithium manganese composite oxide, an olivine type lithium-containing composite oxide, and an inverted spinel type lithium-containing composite oxide. Examples of the lithium-containing composite oxide include $\text{Li}_a(\text{M}_x\text{Mn}_{2-x})\text{O}_4$ (where $0 < x < 2$; and $0 < a < 1.2$). M is a compound selected from the group consisting of Ni, Co, Fe, Cr, and Cu.

In the present illustrative embodiment, examples of the gelling component used as a raw material of the polymer contained in the gel electrolyte include monomers, oligomers, and copolymer oligomers having two or more thermally polymerizable polymerization groups in one molecule thereof. Examples of the gelling component include an acrylic polymer-forming compound including bifunctional acrylates such as ethylene glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, propylene glycol diacrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butylene glycol diacrylate, and 1,6-hexanediol diacrylate, trifunctional acrylates such as trimethylolpropane triacrylate and pentaerythritol triacrylate, tetrafunctional acrylates such as ditrimethylolpropane tetraacrylate and pentaerythritol tetraacrylate, and methacrylate monomers. In addition to this, examples include monomers such as urethane acrylate and urethane methacrylate, copolymer oligomers thereof, and copolymer oligomers with acrylonitrile, but are not limited thereto.

As the polymer, a polymer which is soluble in a plasticizer and gelable, such as polyvinylidene fluoride, polyethylene oxide, and polyacrylonitrile, can also be used.

The gelling component is not limited to the above-mentioned monomers, oligomers and polymers, and any component that can gel can be used. The gelling component is not limited to one monomer, oligomer or polymer, and a mixture of two or more gelling components may be used as necessary. As the thermal polymerization initiator, benzoin, peroxide, or the like may be used as necessary, but the thermal polymerization initiator is not limited thereto.

In the battery configuration of the apparatus according to the present exemplary embodiment, as the electrode element, a laminate or a wound body may be used, and as the outer body, an aluminum laminate outer body or a metal outer body may be used. Further, the battery capacity is not limited. The apparatus according to the present exemplary embodiment is a lithium ion secondary battery, a capacitor, or the like, and the nonaqueous electrolytic solution according to the present exemplary embodiment may be used in the lithium ion secondary battery, the capacitor, or the like.

EXAMPLES

Hereinafter, the present embodiment will be described in detail by way of examples with reference to the accompanying drawings, but the present embodiment is not limited to the examples.

BRIEF DESCRIPTION OF DRAWINGS FIG. 1 is a diagram illustrating a configuration of a positive electrode of a lithium ion secondary battery. FIG. 1 shows a schematic view of the embodiment. FIG. 1(a) is a plan view of a positive electrode. FIG. (b) is a side view of the positive electrode.

FIG. 2 is a diagram illustrating a configuration of a negative electrode of a lithium ion secondary battery. FIG. 2 FIG. 2(a) is a plan view of the negative electrode. FIG. (b) is a side view of the negative electrode.

FIG. 3 is a cross-sectional view illustrating a configuration of a battery element after a lithium ion secondary battery is wound.

(Example 1)

First, the production of the positive electrode 1 will be described with reference to FIG. 1. 85 mass % of LiMn_2O_4 , 7 mass % of acetylene black as a conductive auxiliary agent, and 8 mass % of polyvinylidene fluoride as a binder were mixed; N-methylpyrrolidone was added to the mixture, and further mixed, thereby preparing a positive electrode slurry. The positive electrode slurry was applied onto both surfaces of an Al foil 2 having a thickness of 20 μm , a current collector was formed by a doctor blade method so that the thickness after rolling became 160 μm , dried at 120° C. for 5 minutes, and then subjected to a rolling step, thereby forming a positive electrode active material layer 14. Positive electrode active material uncoated portions 5 on which the positive electrode active material was not coated were provided on both end portions of the foil. The positive electrode material conductive tab 6 is welded to one positive electrode active material uncoated portion 5. The positive electrode active material single-sided coating portion 4 as one surface having the positive electrode active material coated on only one surface is provided close to the positive electrode active material uncoated portion 5 to which the positive electrode conductive tab 6 is welded, and the positive electrode active material double-sided coating portion 3 is provided further close thereto. A positive electrode 1 was thus prepared.

Next, the preparation of the negative electrode 7 will be described with reference to FIG. 2. 90% by mass of graphite, 1% by mass of acetylene black as a conductive auxiliary agent, and 9% by mass of polyvinylidene fluoride as a binder were mixed; N-methylpyrrolidone was added to the mixture, and further mixed, thereby preparing a negative electrode slurry. The negative electrode slurry was applied to both surfaces of a Cu foil 8 having a thickness of 10 μm , a current collector was formed by a doctor blade method so that the thickness after rolling became 120 μm , dried at 120° C. for 5 minutes, and then subjected to a rolling step, thereby forming a negative electrode active material application portion 9. A negative electrode active material uncoated portion 11 on which a negative electrode active material is not coated is provided on both end portions of the foil. The negative electrode material conductive tab 12 is welded on one of the ends. The negative electrode active material single-sided coating portion 10 as one surface having the negative electrode active material coated on only one surface is provided close to the negative electrode active material uncoated portion 11 to which the negative electrode conductive tab 12 is welded, and the negative electrode active material double-sided coating portion 9 is provided further close thereto. Thus, the negative electrode 7 was prepared.

The fabrication of the battery element will be described with reference to FIG. 3. The melted and cut portions of the two sheets of separators 13 including a polypropylene microporous film having a film thickness of 25 μm and a porosity of 55% and subjected to a hydrophilic treatment were fixed and wound to the winding core of the winding device, and the front ends of the positive electrode 1 and the negative electrode 7 were introduced. Under the condition that the opposite side of the connection portion of the positive electrode conductive tab 6 and the connection portion side of the negative electrode conductive tab 12 are made to be the front end sides of the positive electrode 1 and the negative electrode 7, respectively, the negative electrode 7 is disposed between two sheets of separators 13, the positive electrode 1 is disposed on the upper surface of the separators 13, and wound by rotating a winding core, thereby forming a battery element (hereinafter, referred to as J/R (gel roll)).

The J/R was stored in a printed laminated outer package, the positive electrode conductive tab 6 and the negative electrode conductive tab 12 were pulled out, one side of the laminated outer package was folded back, and heat fusion was performed in a state where the solution injection portion remained unfused.

An electrolytic solution was prepared by mixing 10% by mass of monoethoxypentafluorocyclotriphosphazene and 2% by mass of Compound No. 2 in Table 1 in an electrolytic solution containing 1.2 mol/l of LiPF₆ as a supporting salt and ethylene carbonate (EC)/diethyl carbonate (DEC) = 30/70 (volume ratio) as a solvent.

Then, the electrolytic solution was injected from the solution injection portion to vacuum-impregnate, and the solution injection portion was thermally fused to obtain a battery.

The obtained battery was subjected to CC-CV charging (constant current constant voltage charging, charging conditions: a CC current of 0.02 C, a CV time of 5 hours, and a temperature of 20° C.) to a battery voltage of 4.2 V, and then a discharge capacity obtained when discharged to a battery voltage of 3.0 V at 0.02 C was defined as an initial capacity; and a ratio of the obtained initial capacity to a design capacity was defined as an initial capacity (%), which was measured.

The ratio of the 2C capacity to the 0.2C capacity at 20°C of the obtained battery was defined as a ratio characteristic (%), and the ratio was measured.

The cycle test of the obtained battery includes CC-CV charging at an upper limit voltage of 4.2 V, a current of 1 C, and a CV time of 1.5 hours, and CC discharging at a lower limit voltage of 3.0 V, a current of 1 C, and all were performed at 45° C. The ratio of the discharge capacity at the 1000th cycle to the discharge capacity at the first cycle was defined as the capacity retention ratio, and the ratio was measured.

The combustion test was performed by placing the battery after the cycle test 10 cm above the front end of the flame of the gas burner. The combustion ability was evaluated as follows based on the state in which the electrolytic solution was vaporized and burned. A case where the electrolyte is not ignited is defined as A; a case where the flame is extinguished after 2-3 seconds of ignition even though it is ignited is defined as B; a case where the flame is extinguished within 10 seconds even though it is ignited is defined as C; and a case where combustion continues without being extinguished even after 10 seconds is defined as D.

(Example 2)

In Example 2, a battery was fabricated and evaluated in the same manner as in Example 1 except that 2 mass % of Compound No. 101 in Table 2 was mixed as an additive.

(Example 3)

In Example 3, a battery was prepared and evaluated as in Example 1 except that 4% by mass of Compound No. 101 in Table 2 was mixed as an additive.

(Example 4)

In Example 4, a battery was prepared and evaluated as in Example 1 except that 2 mass % of Compound No. 2 in Table 1 and 2 mass % of Compound No. 101 in Table 2 were mixed as additives.

(Example 5)

In Example 5, a battery was prepared and evaluated as in Example 1 except that 2 mass % of Compound No. 2 in Table 1 and 3 mass % of 1,3-propane sultone were mixed as additives.

(Example 6)

In Example 6, a battery was prepared and evaluated as in Example 1 except that 4% by mass of Compound No. 2 in Table 1 and 6% by mass of 1,3-propane sultone were mixed as additives.

(Example 7)

In Example 7, a battery was prepared and evaluated as in Example 6 except that 20% by mass of monoethoxypentafluorocyclotriphosphazene was added.

(Example 8)

In Example 8, a battery was prepared and evaluated as in Example 7 except that 25 mass % of monoethoxypentafluorocyclotriphosphazene was added.

(Example 9)

In Example 9, a battery was prepared and evaluated as in Example 1 except that 5 mass % of Compound No. 2 in Table 1 and 7 mass % of 1,3-propane sultone were mixed as additives.

(Comparative Example 1)

In Comparative Example 1, a battery was prepared and evaluated as in Example 6 except that monoethoxypentafluorocyclotriphosphazene was not added.

(Comparative Example 2)

In Comparative Example 2, a battery was prepared and evaluated as in Example 1 except that no additive was added.

(Comparative Example 3)

In Comparative Example 3, a battery was prepared and evaluated as in Example 1 except that 5 mass % of vinyl carbonate (VC) not corresponding to any one of the above formulas (2), (3), and (4) was added as an additive.

(Comparative Example 4)

In Comparative Example 4, a battery was prepared and evaluated as in Example 1 except that 3 mass % of propane sultone (PS) was mixed as an additive.

The results of the initial capacity, ratio characteristics, capacity retention ratio, and flame retardancy in Examples 1 to 9 and Comparative Examples 1 to 4 are shown in Table 3.

[Table 3]

No. 2 described in the list of additives in Table 3 represents Compound No. 2 in Table 1; No. 101 represents Compound No. 101 in Table 2; PS represents 1,3-propane sultone; and VC represents vinyl carbonate which does not correspond to any one of the above formulas (2), (3), and (4).

As shown in Examples 1 to 6 and 9 in Table 3, in the case where the amount of monoethoxypentafluorocyclotriphosphazene added was made a fixed amount and the amount of the additive was increased, the capacity retention ratio was very good. Further, in the battery combustion test after the cycle test, the electrolyte solution was not ignited or was ignited but was extinguished after 2 to 3 seconds of ignition. In contrast, in Comparative Example 1, the electrolyte solution was continuously burned in the battery

combustion test after the cycle test. In Comparative Example 2, the capacity retention rate was low, and further, in the battery combustion test after the cycle test, the electrolyte continued to burn. That is, it was found that the compound having a phosphazene structure was reductively degraded due to the absence of the additive, and became absent in its effective amount for combustion suppression. In addition, in Comparative Example 3 and Comparative Example 4, the flame retardancy was also slightly reduced as compared with the Examples, indicating that the additive was not sufficient for suppressing the reductive degradation of the compound having the phosphazene structure. As is clear from Examples 6, 7 and 9, although there is a possibility that the SEI is thickened and the resistance is increased by adding a large amount of the additive, the combustion suppressing effect is sufficiently maintained even after the cycle test. By Comparative Examples 8 and 7, since the amount of monoethoxypentafluorocyclotriphosphazene added exceeds 20 mass % decreases the ion conductivity of the electrolytic solution, the ratio characteristics slightly decrease, and since the excess phosphazene compound with respect to SEI gradually decreases and degrades in the long-term cycle test, the battery combustion suppressing effect after the long-term cycle test is slightly decreased.

Further, in Examples, the gas generation amount during the initial charge tended to decrease by comparison with each Comparative Example. This is conceivable because the simultaneous presence of the compound having a phosphazene structure and the disulfonate in the electrolytic solution can form SEI into which the compound having a phosphazene structure is introduced by a reaction mechanism different from SEI formation using a non-aqueous electrolytic solution containing only the disulfonate. However, assuming that since further reduction of the phosphazene compound present in the electrolytic solution can be suppressed on the SEI thus formed, there is a possibility that SEI using disulfonate ester introduced with the phosphazene compound has a larger reduction degradation suppressing effect on a certain electrolytic solution component containing the phosphazene compound. This effect is presumed to improve the life characteristics.

As is clear from the above, SEI using a specific disulfonate and a specific sultone compound can suppress reductive degradation of a compound having a phosphazene structure for a long period of time and provide a good capacity retention rate as a life characteristic, thereby providing high flame retardancy. Further, the balance between the amount of the compound having a phosphazene structure added and the amount of the additive is optimized, so that the ratio retention characteristic can be maintained and good life characteristics can be provided.

(Example 10)

Example 10 was carried out in the same manner as in Example 5 except that the electrolytic solution in Example 5 was used as the gel electrolyte. First, 10 mass % of monoethoxypentafluorocyclotriphosphazene, 2 mass % of Compound No. 2 in Table 1, and 3 mass % of PS were mixed in an electrolyte solution containing 1.2 mol/l of LiPF₆ and in which EC/DEC = 30/70 (volume ratio). Further, 3.8 mass % of triethylene glycol diacrylate and 1 mass % of trimethylolpropane triacrylate as a gelling agent were added and mixed well. Then, 0.5 mass % of tert-butyl peroxyvalate as a polymerization initiator was added. A pregel solution was thus prepared. Then, the pregel solution was injected from the solution injection portion for vacuum impregnation, and polymerized at 80° C. for 2 hours, thereby obtaining a lithium ion battery (lithium polymer battery).

(Comparative Example 5)

Comparative Example 5 was carried out in the same manner as in Example 10 except that the additive in Example 10 was not added.

The initial capacity, ratio characteristics, capacity retention ratio, and flame retardancy in Example 10 and Comparative Example 5 are shown in Table 4.

[Table 4]

No. 2 of the list of additives described in Table 4 represents Compound No. 2 in Table 1; and PS,1,3-propane sultone.

As is clear from Table 4, in the case of using a gel electrolyte instead of the liquid electrolyte, reduction degradation of a compound having a phosphazene structure can be suppressed for a long period of time by SEI using a disulfonate and a sultone compound, and a good capacity retention rate as a life property can be provided, so that high flame retardancy is provided.

(Example 11)

Example 11 was carried out in the same manner as in Example 6 except that graphite as the negative electrode material in Example 6 was changed to a silicon-based material. First, 90 mass % of silicon, 1 mass % of acetylene black as a conductive auxiliary agent, and 9 mass % of polyimide as a binder were mixed; N-methylpyrrolidone was added to the mixture, and further mixed, thereby producing a negative electrode slurry. This negative electrode slurry was coated on both surfaces of a Cu foil 8 having a thickness of 10 μm to form a current collector so that the thickness became 80 μm after rolling, dried at 120° C. for 5 minutes, then subjected to a rolling step, and further dried at 300° C. for 10 minutes, thereby forming a negative electrode active material coating portion 9.

(Comparative Example 6)

Comparative Example 6 was carried out in the same manner as in Example 11 except that the additive in Example 11 was not added. The cycle tests of Example 11 and Comparative Example 6 included CC-CV charging (upper limit voltage: 4.2 V, current: 1 C, and CV time: 1.5 hours) and CC discharging (lower limit voltage: 3.0 V, and current: 1 C), and both were performed at 45° C. The ratio of the discharge capacity at the 200th cycle to the capacity at the first cycle was defined as the capacity retention ratio.

The initial capacity, ratio characteristics, capacity retention ratio, and flame retardancy characteristics in Example 11 and Comparative Example 6 are shown in Table 5.

[Table 5]

No. 2 described in the additive column of Table 5 represents Compound No. 2 in Table 1; and PS represents 1,3-propane sultone.

As is clear from Table 5, in the case of using a silicon material instead of graphite, SEI using a disulfonate and a sulfoendoester compound can also suppress reductive degradation of a compound having a phosphazene structure for a long period of time, and can provide a good capacity retention rate as a life property, so that high flame retardancy is provided.

In summary, it can be confirmed that the present exemplary embodiment can provide a non-aqueous electrolyte having a good capacity retention rate and high flame retardancy and an apparatus including the non-aqueous electrolyte.

This application claims priority to Japanese Patent Application No. 2009-247185 filed on 10 and 28 of 2009, the disclosure of which is incorporated herein in its entirety.

In summary, the present invention has been described by referring to the embodiment (and the example), but the present invention is not limited to the embodiment (and the example). In the composition and details of the

present invention, various alterations and modifications that can be understood by those skilled in the art can be made within the scope of the present invention.

DESCRIPTION OF REFERENCE NUMBERS

- 1 Positive electrode
- 2 Al foil
- 3 Positive electrode active material double-sided coating portion
- 4 Positive electrode active material single-sided coating portion
- 5 Positive electrode active material uncoated portion
- 6 positive electrode conductive tab
- 7 negative electrode
- 8 Cu foil
- 9 Negative electrode active material double-sided coating portion
- 10 negative electrode active material single-sided coating portion
- 11 negative electrode active material uncoated portion
- 12 negative electrode conductive tab
- 13 spacer
- 14 Positive electrode active material layer
- 15 negative electrode active material layer

CN102668221A Nonaqueous electrolyte solution and device comprising same

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

1. A non-aqueous electrolyte for use in an apparatus comprising a positive electrode, a negative electrode, and a non-aqueous electrolyte, wherein

the nonaqueous electrolyte solution contains a lithium salt and a compound having a phosphazene structure represented by the following formula (1), and

The non-aqueous electrolyte further contains at least one disulfonate selected from the group consisting of a cyclic disulfonate represented by the following formula (2) and a chain disulfonate represented by the following formula (3) in an amount of 0.05 mass % or more and 12.0 mass % or less based on the total amount of the non-aqueous electrolyte solution:

wherein in Formula (1), X1 and X2 each independently represent a halogen element or a monovalent substituent; the monovalent substituent represents an alkyl group, an alkoxy group, an aryl group, an acyl group, an aryloxy group, an amino group, an alkylthio group, an arylthio group, a haloalkyl group, a haloalkoxy group, a haloaryl group, a haloacyl group, a haloaryloxy group, a haloamino group, a haloalkylthio group, or a haloarylthio group; n represents an integer of 3 or more and 5 or less; and Formula (1) may be cyclic;

wherein in Formula (2), Q represents an oxygen atom, a methylene group, or a single bond; A1 represents a substituted or unsubstituted alkylene group having 1 to 5 carbon atoms, a carbonyl group, a sulfinyl group, a substituted or unsubstituted perfluoroalkylene group having 1 to 5 carbon atoms, a substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms, a substituted or unsubstituted alkylene group having 1 to 6 carbon atoms, a substituted or unsubstituted perfluoroalkylene group having 1 to 6 carbon atoms, a substituted or unsubstituted perfluoroalkylene group having 1 to 6 carbon atoms, or a substituted or unsubstituted fluoroalkylene group having 2 to 6 carbon atoms, which may be branched; and A2 represents a substituted or unsubstituted alkylene group which may be branched;

wherein in Formula (3), R1 and R4 each independently represent an atom or group selected from a hydrogen atom, a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms, a substituted or unsubstituted alkoxy group having 1 to 5 carbon atoms, a substituted or unsubstituted fluoroalkyl group having 1 to 5 carbon atoms, a polyfluoroalkyl group having 1 to 5 carbon atoms, -SO₂ X11 (wherein X11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -SY11 (wherein Y11 is a substituted or unsubstituted alkyl group having 1 to 5 carbon atoms), -COZ (wherein Z is a hydrogen atom or a substituted or unsubstituted

alkyl group having 1 to 5 carbon atoms), and a halogen atom; and R₂ and R₃ each independently represent an atom or a group selected from the group consisting of substituted or unsubstituted alkyl having 1 to 5 carbon atoms, substituted or unsubstituted alkoxy having 1 to 5 carbon atoms, substituted or unsubstituted phenoxy, substituted or unsubstituted fluoroalkyl having 1 to 5 carbon atoms, polyfluoroalkyl having 1 to 5 carbon atoms, substituted or unsubstituted fluoroalkoxy having 1 to 5 carbon atoms, polyfluoroalkoxy having 1 to 5 carbon atoms, hydroxy, halogen atom, -NX₁₂X₁₃ (wherein X₁₂ and X₁₃ each independently represent a hydrogen atom or substituted or unsubstituted alkyl having 1 to 5 carbon atoms), and -NY₁₂CONY₁₃Y₁₄ (wherein Y₁₂ to Y₁₄ each independently represent a hydrogen atom or substituted or unsubstituted alkyl having 1 to 5 carbon atoms).

2.A nonaqueous electrolytic solution according to claim 1, wherein a portion of the disulfonate ester contained in the nonaqueous electrolytic solution is substituted with a sultone compound represented by the following formula (4):

[Equation 4]

wherein in Formula (4), R₈ to R₁₃ each independently represent an atom or a group selected from a hydrogen atom, an alkyl group having 1 or more and 12 or less carbon atoms, a cycloalkyl group having 3 or more and 6 or less carbon atoms, and an aryl group having 6 or more and 12 or less carbon atoms; and m represents an integer of 0 or more and 2 or less.

3.A nonaqueous electrolytic solution according to claim 1 or 2, wherein the compound having a phosphazene structure is contained in an amount of 3.0% by mass or more and 20.0% by mass or less based on the total amount of the nonaqueous electrolytic solution.

4.A nonaqueous electrolytic solution according to any one of claims 1 to 3, wherein the nonaqueous electrolytic solution is gelled with a polymer.

5.A device which is a lithium ion secondary battery or a capacitor, the device comprising the non-aqueous electrolyte according to any one of claims 1 to 4.



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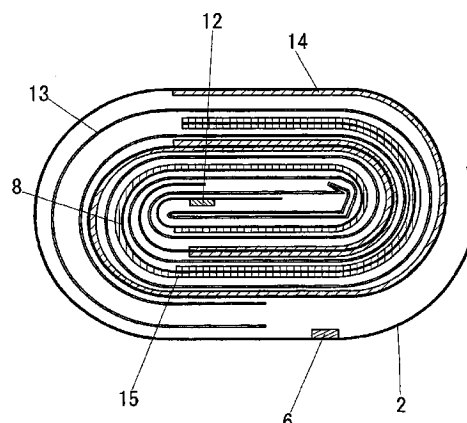
权利要求书 3 页 说明书 17 页 附图 3 页

(54) 发明名称

非水型电解液以及包含其的设备

(57) 摘要

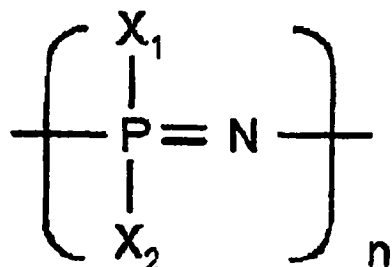
提供具有高阻燃性和良好容量保持率的非水型电解液、以及包含该非水型电解液的设备。非水型电解液被用于包含正极、负极和非水型电解液的设备中,并且含有锂盐和具有磷腈结构的化合物,并且基于该非水型电解液的总量进一步包含 0.05 质量%以上且 12.0 质量%以下的选自环状二磺酸酯和链状二磺酸酯中的至少一种二磺酸酯。



1. 一种用于包含正极、负极以及非水型电解液的设备中的非水型电解液,其中该非水型电解液包含锂盐和具有下述式(1)所示的磷腈结构的化合物,且

基于该非水型电解液的总量进一步包含 0.05 质量%以上且 12.0 质量%以下的选自下述式(2)所示的环状二磺酸酯和下述式(3)所示的链状二磺酸酯中的至少一种二磺酸酯:

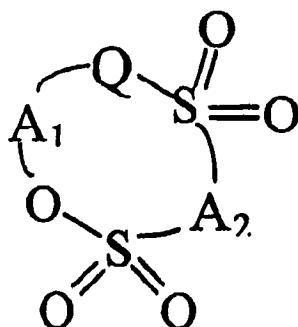
[式1]



(1)

其中在式(1)中, X_1 和 X_2 各自独立地表示卤素元素或一价取代基;该一价取代基表示烷基、烷氧基、芳基、酰基、芳氧基、氨基、烷硫基、芳硫基、卤代烷基、卤代烷氧基、卤代芳基、卤代酰基、卤代芳氧基、卤代氨基、卤代烷硫基或卤代芳硫基;n表示3以上且5以下的整数;且式(1)可为环状;

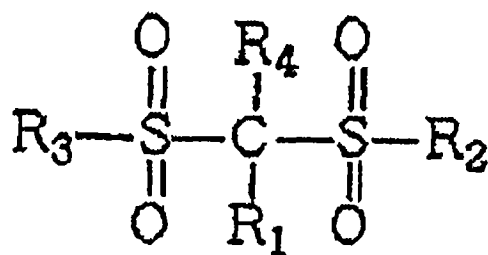
[式2]



(2)

其中在式(2)中, Q表示氧原子、亚甲基或单键; A_1 表示可以分支的取代或未取代的具有1至5个碳原子的亚烷基、羰基、亚磺酰基、可以分支的取代或未取代的具有1至5个碳原子的全氟亚烷基、可以分支的取代或未取代的具有2至6个碳原子的氟亚烷基、含有醚键且可以分支的取代或未取代的具有1至6个碳原子的亚烷基、含有醚键且可以分支的取代或未取代的具有1至6个碳原子的全氟亚烷基、或含有醚键且可以分支的取代或未取代的具有2至6个碳原子的氟亚烷基;且 A_2 表示可以分支的取代或未取代的亚烷基;

[式3]

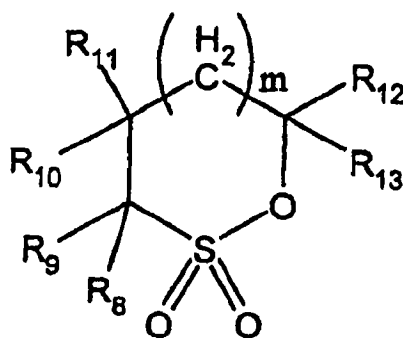


(3)

其中在式 (3) 中, R_1 和 R_4 各自独立地表示选自氢原子、取代或未取代的具有 1 至 5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、 $-\text{SO}_2\text{X}_{11}$ (其中 X_{11} 为取代或未取代的具有 1 至 5 个碳原子的烷基)、 $-\text{SY}_{11}$ (其中 Y_{11} 为取代或未取代的具有 1 至 5 个碳原子的烷基)、 $-\text{COZ}$ (其中 Z 为氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和卤素原子中的原子或基团; 且 R_2 和 R_3 各自独立地表示选自取代或未取代的具有 1 至 5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的苯氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、取代或未取代的具有 1 至 5 个碳原子的氟烷氧基、具有 1 至 5 个碳原子的多氟烷氧基、羟基、卤素原子、 $-\text{NX}_{12}\text{X}_{13}$ (其中 X_{12} 和 X_{13} 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和 $-\text{NY}_{12}\text{CONY}_{13}\text{Y}_{14}$ (其中 Y_{12} 至 Y_{14} 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 中的原子或基团。

2. 根据权利要求 1 所述的非水型电解液, 其中所述非水型电解液中所含的二磺酸酯的部分被下述式 (4) 所示的磺内酯化合物取代:

[式 4]



(4)

其中在式 (4) 中, R_8 至 R_{13} 各自独立地表示选自氢原子、具有 1 个以上且 12 个以下碳原子的烷基、具有 3 个以上且 6 个以下碳原子的环烷基、和具有 6 个以上且 12 个以下碳原子的芳基中的原子或基团; 且 m 表示 0 以上且 2 以下的整数。

3. 根据权利要求 1 或 2 所述的非水型电解液, 其中, 基于该非水型电解液的总量包含 3.0 质量%以上且 20.0 质量%以下的所述具有磷腈结构的化合物。

4. 根据权利要求 1 至 3 中任一项所述的非水型电解液, 其中该非水型电解液利用聚合物进行了凝胶化。

5. 一种设备,其为锂离子二次电池或电容器,该设备包含根据权利要求1至4中任一项所述的非水型电解液。

非水型电解液以及包含其的设备

技术领域

[0001] 本示意性实施方式涉及非水型电解液和具有其的设备。

背景技术

[0002] 在例如锂离子二次电池和电容器的设备中,由于锂离子二次电池可实现高能量密度,因此它们作为手机和笔记本电脑的电源,也作为大型电力储藏用电源和汽车用电源引人关注。

[0003] 虽然锂离子二次电池可实现高能量密度,但大型化使得能量密度变得巨大,更高的安全性受到期待。例如,在大型电力储藏用电源和汽车用电源中,期待特别高的安全性,而作为安全措施,施行了:电池、封装等的结构设计、保护电路、电极材料、具有过充电保护功能的添加剂、隔离物的关闭功能的增强等。

[0004] 锂离子二次电池使用例如环状碳酸酯和链状碳酸酯的非质子溶剂作为电解质溶剂;这些碳酸酯的特征在于:虽然具有高的介电常数和高的离子传导性,但具有低的闪点且是可燃的。

[0005] 进一步增强锂离子二次电池安全性的方式是使电解液变得阻燃。作为用于使电解液变得阻燃的技术,已经公开了添加磷腈化合物作为阻燃剂的方法。

[0006] 例如,专利文献 1 的非水电解质电池使用一种溶液,其中锂盐溶解在磷腈衍生物中作为电解质,或者使用一种溶液,其中锂盐溶解在进一步添加了磷腈衍生物的非质子有机溶剂的溶剂中。由此公开了即使在例如短路非正常情形下也不会产生例如爆炸或失火的危险,并且可实现优异的电池性能。

[0007] 专利文献 2 的非水电解质电池使用一种溶液,其中锂盐溶解在链状磷腈衍生物中作为电解质,或者使用一种溶液,其中锂盐溶解在一种其中进一步添加了磷腈衍生物的非质子有机溶剂的溶剂中。由此公开了即使在例如短路非正常情形下也不会产生例如爆炸或失火的危险,并且可实现优异的电池性能。

[0008] 专利文献 3 描述了一种非水型电解液二次电池,其具有正极、负极以及含有支持盐、有机溶剂和磷腈衍生物的非水型电解液,其中磷腈衍生物的电势窗在下限值 +0.5V 以下和上限值 +4.5V 以上的范围内,有机溶剂的电势窗在比磷腈衍生物更宽的范围内。

[0009] 专利文献 4 描述了一种非水型电解液二次电池,其具有正极、负极以及含有支持盐和磷腈衍生物的非水型电解液,其锂盐溶液 (0.5mol/l) 具有至少 2.0mS/cm 的电导率。

[0010] 已知一种技术,其使用一种物质作为添加剂,该物质在比用作电解液溶剂的碳酸酯的电势更高的电势下还原降解、并形成作为具有高锂离子渗透率的保护膜 SEI (Solid Electrolyte Interface, 固体电解质界面)。已知由于 SEI 对充电/放电效率、循环特性和安全性具有很大影响,因此在负极处的 SEI 的控制很重要,碳材料和氧化物材料的不可逆容量可通过 SEI 而降低。

[0011] 专利文献 5 描述了提供一种含有锂盐和非水溶剂的优异的非水型电解液,其通过在分子中进一步引入具有碳-碳不饱和键的环状碳酸酯和基于非水型电解液的 1 质量%以

上且 25 质量%以下的磷腈衍生物,可在电池的非正常加热等中确保安全性和可靠性,且还可提供良好的电池性能,例如循环特性。

[0012] 用于专利文献 6 中公开的电池的非水型电解液含有非水溶液,该非水溶液含有环状磷腈化合物和二氟磷酸酯化合物,以及选自 1,3- 丙烷磺内酯、1,3- 丁烷磺内酯、1,4- 丁烷磺内酯和 1,3,2- 二氧化硫杂环戊烷 -2,2- 二氧化物构成的组中的至少一种环状含硫化合物、以及支持盐。其公开了即使在高温环境下,也会对电池赋予优异的电池性能和高安全性。

[0013] 引用列表

[0014] 专利文献

[0015] 专利文献 1 :JP6-13108A

[0016] 专利文献 2 :JP11-144757A

[0017] 专利文献 3 :JP2001-217005A

[0018] 专利文献 4 :JP2001-217007A

[0019] 专利文献 5 :JP2006-24380A

[0020] 专利文献 6 :JP2008-41413A

发明内容

[0021] 技术问题

[0022] 然而,在专利文献 1 至 4 和 6 中,由于磷腈化合物在长期使用过程中会在负极上逐渐还原降解,因此有时电池的容量保持率大大降低。

[0023] 在专利文献 5 中,虽然可形成 SEI 的碳酸乙烯基酯的添加会抑制磷腈化合物的还原降解,但以足够长期抑制磷腈化合物的还原降解的量添加碳酸乙烯基酯则会引起电阻增加,有时会大大降低电池的充电 / 放电特性。

[0024] 而且,在磷腈化合物和二氟磷酸酯经长时期而降解时,电解液中的阻燃剂的存在比率降低,在长期使用之后,有时会降低安全性。也就是说,在添加会被还原降解的阻燃剂的情形中,需要相应于添加的阻燃剂的量的一定量的添加剂,且由此在某些情形中电池的电阻大大增加,而容量和比率特性急剧降低。

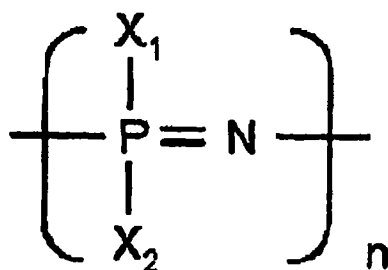
[0025] 也就是说,本示意性实施方式的目的是提供具有高阻燃性和良好容量保持率的非水型电解液以及包含该非水型电解液的设备。

[0026] 技术问题的解决方案

[0027] 根据本示意性实施方式的非水型电解液是一种用于包含正极、负极和非水型电解液的设备中的电解液,且含有锂盐和具有下述式 (1) 所示的磷腈结构的化合物,且进一步含有基于该非水型电解液的总量的 0.05 质量%以上且 12.0 质量%以下的选自下述式 (2) 所示的环状二磺酸酯和下述式 (3) 所示的链状二磺酸酯中的至少一种二磺酸酯。

[0028]

[式 1]

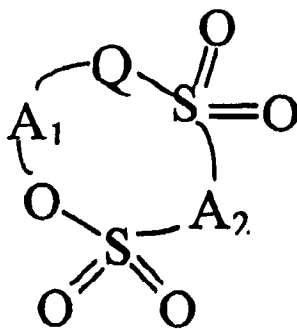


(1)

[0029] 其中在式 (1) 中, X_1 和 X_2 各自独立地表示卤素元素或一价取代基; 该一价取代基表示烷基、烷氧基、芳基、酰基、芳氧基、氨基、烷硫基、芳硫基、卤代烷基、卤代烷氧基、卤代芳基、卤代酰基、卤代芳氧基、卤代氨基、卤代烷硫基或卤代芳硫基; n 表示 3 以上且 5 以下的整数; 且式 (1) 可为环状。

[0030] [式 2]

[0031]

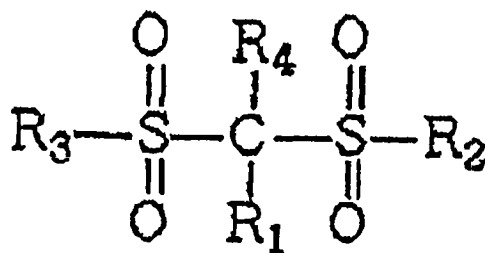


(2)

[0032] 其中在式 (2) 中, Q 表示氧原子、亚甲基或单键; A_1 表示可以分支的取代或未取代的具有 1 至 5 个碳原子的亚烷基、羰基、亚磺酰基、可以分支的取代或未取代的具有 1 至 5 个碳原子的全氟亚烷基、可以分支的取代或未取代的具有 2 至 6 个碳原子的氟亚烷基、含有醚键且可以分支的取代或未取代的具有 1 至 6 个碳原子的亚烷基、含有醚键且可以分支的取代或未取代的具有 1 至 6 个碳原子的全氟亚烷基、或含有醚键且可以分支的取代或未取代的具有 2 至 6 个碳原子的氟亚烷基; A_2 表示可以分支的取代或未取代的亚烷基。

[0033]

[式 3]



(3)

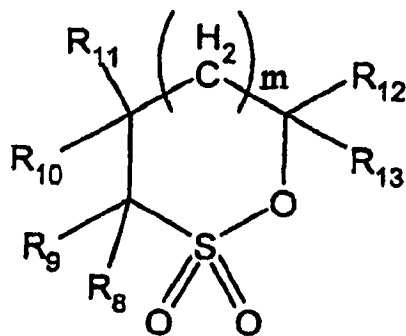
[0034] 其中在式 (3) 中, R_1 和 R_4 各自独立地表示选自氢原子、取代或未取代的具有 1 至

5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、 $-\text{SO}_2\text{X}_{11}$ (其中 X_{11} 为取代或未取代的具有 1 至 5 个碳原子的烷基)、 $-\text{SY}_{11}$ (其中 Y_{11} 为取代或未取代的具有 1 至 5 个碳原子的烷基)、 $-\text{COZ}$ (其中 Z 为氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和卤素原子中的原子或基团; R_2 和 R_3 各自独立地表示选自取代或未取代的具有 1 至 5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的苯氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、取代或未取代的具有 1 至 5 个碳原子的氟烷氧基、具有 1 至 5 个碳原子的多氟烷氧基、羟基、卤素原子、 $-\text{NX}_{12}\text{X}_{13}$ (其中 X_{12} 和 X_{13} 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和 $-\text{NY}_{12}\text{CONY}_{13}\text{Y}_{14}$ (其中 Y_{12} 至 Y_{14} 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 中的原子或基团。

[0035] 在根据本示意性实施方式的非水型电解液中, 该非水型电解液中所含的二磺酸酯的部分被下述式 (4) 所示的磺内酯化合物取代。

[0036]

[式 4]



(4)

[0037] 其中在式 (4) 中, R_8 至 R_{13} 各自独立地表示选自氢原子、具有 1 个以上且 12 个以下碳原子的烷基、具有 3 个以上且 6 个以下碳原子的环烷基、和具有 6 个以上且 12 个以下碳原子的芳基中的原子或基团; m 表示 0 以上且 2 以下的整数。

[0038] 在根据本示意性实施方式的非水型电解液中, 基于该非水型电解液的总量, 该非水型电解液含有 3.0 质量%以上且 20.0 质量%以下的具有磷腈结构的化合物。

[0039] 在根据本示意性实施方式的非水型电解液中, 该非水型电解液利用聚合物进行了凝胶化。

[0040] 根据本示意性实施方式的设备为锂离子二次电池或电容器, 且包含该非水型电解液。

[0041] 根据本示意性实施方式, 对具有磷腈结构的化合物的还原降解具有大的抑制作用的特定二磺酸酯的引入可抑制具有磷腈结构的化合物在负极活性物质上的还原降解。因此, 可长期抑制由具有磷腈结构的化合物的还原降解导致的电阻的增加, 并可得到良好的容量保持率。进一步地, 根据本示意性实施方式, 由于可长期抑制具有磷腈结构的化合物的还原、并且即使在长期使用之后电解液中仍然存在有效量的具有磷腈结构的化合物, 因此可长期获得高阻燃性。另外, 还可减少初次充电时的气体发生量。

[0042] 本示意性实施方式可提供具有高阻燃性和良好容量保持率的非水电解液以及包

含该非水电解液的设备。

附图说明

[0043] 图 1 为阐释根据本示意性实施方式的锂离子二次电池的正极的构成的图；图 (1a) 表示正极的平面图，图 (1b) 表示正极的侧面图。

[0044] 图 2 为阐释根据本示意性实施方式的锂离子二次电池的负极的构成的图；图 (2a) 表示负极的平面图，图 (2b) 表示负极的侧面图。

[0045] 图 3 为阐释根据本示意性实施方式的锂离子二次电池被卷绕之后的电池元件的构成的截面图。

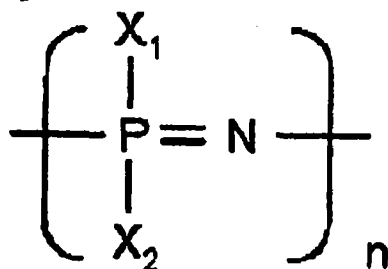
具体实施方式

[0046] 下文中将详细描述本示意性实施方式。

[0047] 根据本示意性实施方式的非水型电解液是用于包含正极、负极和非水型电解液的设备中的电解液，并且含有锂盐和具有下述式 (1) 所示的磷腈结构的化合物，且基于该非水型电解液的总量进一步含有 0.05 质量%以上且 12 质量%以下的选自下述式 (2) 所示的环状二磺酸酯和下述式 (3) 所示的链状二磺酸酯中的至少一种二磺酸酯。

[0048]

[式 5]

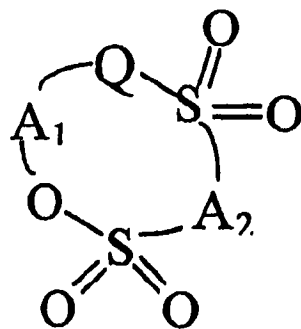


(1)

[0049] 其中在式 (1) 中， X_1 和 X_2 各自独立地表示卤素元素或一价取代基；该一价取代基表示烷基、烷氧基、芳基、酰基、芳氧基、氨基、烷硫基、芳硫基、卤代烷基、卤代烷氧基、卤代芳基、卤代酰基、卤代芳氧基、卤代氨基、卤代烷硫基或卤代芳硫基； n 表示 3 以上且 5 以下的整数；且式 (1) 可为环状。

[0050] [式 6]

[0051]

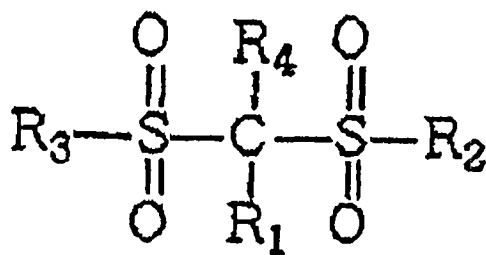


(2)

[0052] 其中在式 (2) 中, Q 表示氧原子、亚甲基或单键; A₁ 表示可以分支的取代或未取代的具有 1 至 5 个碳原子的亚烷基、羰基、亚磺酰基、可以分支的取代或未取代的具有 1 至 5 个碳原子的全氟亚烷基、可以分支的取代或未取代的具有 2 至 6 个碳原子的氟亚烷基、含有醚键且可以分支的取代或未取代的具有 1 至 6 个碳原子的亚烷基、含有醚键且可以分支的取代或未取代的具有 1 至 6 个碳原子的全氟亚烷基、含有醚键且可以分支的取代或未取代的具有 2 至 6 个碳原子的氟亚烷基; A₂ 表示可以分支的取代或未取代的亚烷基。

[0053]

[式 7]



(3)

[0054] 其中在式 (3) 中, R₁ 和 R₄ 各自独立地表示选自氢原子、取代或未取代的具有 1 至 5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、-SO₂X₁₁ (其中 X₁₁ 为取代或未取代的具有 1 至 5 个碳原子的烷基)、-SY₁₁ (其中 Y₁₁ 为取代或未取代的具有 1 至 5 个碳原子的烷基)、-COZ (其中 Z 为氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和卤素原子中的原子或基团; R₂ 和 R₃ 各自独立地表示选自取代或未取代的具有 1 至 5 个碳原子的烷基、取代或未取代的具有 1 至 5 个碳原子的烷氧基、取代或未取代的苯氧基、取代或未取代的具有 1 至 5 个碳原子的氟烷基、具有 1 至 5 个碳原子的多氟烷基、取代或未取代的具有 1 至 5 个碳原子的氟烷氧基、具有 1 至 5 个碳原子的多氟烷氧基、羟基、卤素原子、-NX₁₂X₁₃ (其中 X₁₂ 和 X₁₃ 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 和 -NY₁₂CONY₁₃Y₁₄ (其中 Y₁₂ 至 Y₁₄ 各自独立地表示氢原子或取代或未取代的具有 1 至 5 个碳原子的烷基) 中的原子或基团。

[0055] 作为具有磷腈结构的化合物, 由于显示阻燃性, 因此使用上述式 (1) 所示的化合物。上述式 (1) 所示的化合物的实例包括单乙氧基五氟环三磷腈。

[0056] 这些化合物可单独使用或两种以上同时使用。在具有上述式 (1) 所示磷腈结构的化合物中, 在单元之间, X₁ 和 X₂ 可各自独立地为不同的基团。

[0057] 从抑制具有磷腈结构的化合物的还原降解的观点来看, 将上述式 (2) 所示的化合物用作环状二磺酸酯; 将上述式 (3) 所示的化合物用作链状二磺酸酯。

[0058] 上述式 (2) 所示的化合物的代表实例具体示于表 1 中, 上述式 (3) 所示的化合物的代表实例具体示于表 2 中, 但本示意性实施方式并不受其限定。这些化合物可单独使用或两种以上同时使用。

[0059] [表 1]

[0060]

化合物No.	化学结构	化合物No.	化学结构	化合物No.	化学结构	化合物No.	化学结构
1		8		15		22	
2		9		16			
3		10		17			
4		11		18			
5		12		19			
6		13		20			
7		14		21			

[0061] [表 2]

[0062]

化合物No.	化学结构	化合物No.	化学结构	化合物No.	化学结构
101		109		117	
102		110		118	
103		111		119	
104		112		120	
105		113			
106		114			
107		115			
108		116			

[0063] 基于该非水型电解液的总量,在非水型电解液中,选自上述式(2)所示的环状二磺酸酯化合物和上述式(3)所示的链状二磺酸酯中的至少一种化合物的比例为0.05质量%以上且12质量%以下。基于非水型电解液的总量的该比例低于0.05质量%时,不能有效地获得其中具有磷腈结构的化合物的还原降解被抑制的表面膜的效果。相反,如果基于非水型电解液的总量的该比例超过12质量%,则非水型电解液的粘性的上升和与之相伴的电阻的升高得不到抑制,从而不能进一步提高电池特性。该比例优选为0.1质量%以

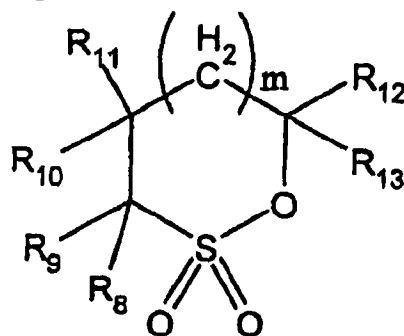
上且 10 质量%以下,并且使该比例在这一范围中可进一步提高表面膜的效果。

[0064] 根据本实施方式的非水型电解液可减少初次充电时的气体发生量,从安全性的观点来看其也是优选的。这是可想到的,因为非水电解液中具有磷腈结构的化合物和二磺酸酯以上述比例同时存在可通过与利用仅含有二磺酸酯的非水电解液的 SEI 形成不同的反应机制来形成引入具有磷腈结构的化合物的 SEI。

[0065] 在根据本示意性实施方式的非水型电解液中,该非水型电解液中所含的二磺酸酯的一部分优选被下述式 (4) 所示的磺内酯化合物取代。

[0066]

[式 8]



(4)

[0067] 其中在式 (4) 中, R_8 至 R_{13} 各自独立地表示选自氢原子、具有 1 个以上且 12 个以下碳原子的烷基、具有 3 个以上且 6 个以下碳原子的环烷基、和具有 6 个以上且 12 个以下碳原子的芳基中的原子或基团; m 表示 0 以上且 2 以下的整数。

[0068] 可使用例如 1,3-丙烷磺内酯、1,4-丁烷磺内酯及其衍生物作为上述式 (4) 所示的磺内酯化合物,但不限于此。这些化合物可单独使用或两种以上同时使用。

[0069] 基于非水型电解液的总量,非水型电解液优选含有 3.0 质量%以上且 20.0 质量%以下的具有磷腈结构的化合物。基于非水型电解液的总量引入 3.0 质量%以上的具有磷腈结构的化合物可提供足够的阻燃效果;其 20.0 质量%以下的引入可抑制离子传导性的降低。

[0070] 非水型电解液可利用聚合物凝胶化的凝胶电解质。

[0071] 根据本示意性实施方式的非水型电解液可含有非质子溶剂。非质子溶剂的实例包含例如碳酸亚丙酯 (PC)、碳酸亚乙酯 (EC)、碳酸亚丁酯 (BC) 和碳酸乙烯基酯 (VC) 的环状碳酸酯,例如碳酸二甲酯 (DMC)、碳酸二乙酯 (DEC)、碳酸甲乙酯 (EMC) 和碳酸二丙酯 (DPC) 的链状碳酸酯,例如甲酸甲酯、醋酸甲酯和丙酸乙酯的脂肪族羧酸酯,例如 γ -丁内酯的 γ -内酯,例如 1,2-乙氧基乙烷 (DEE) 和乙氧基甲氧基乙烷 (EME) 的链状醚,例如四氢呋喃和 2-甲基四氢呋喃的环状醚;二甲基亚砜、1,3-二氧杂环戊烷、甲酰胺、乙酰胺、二甲基甲酰胺、二氧杂环戊烷、乙腈、丙腈、硝基甲烷、乙基单甘醇二甲醚、磷酸三酯、三甲氧基甲烷、二氧杂环戊烷衍生物、环丁砜、甲基环丁砜、1,3-二甲基-2-咪唑烷酮、3-甲基-2-噁唑烷酮、碳酸亚丙酯衍生物、四氢呋喃衍生物、乙醚、苯甲醚、N-甲基吡咯烷酮以及氟代羧酸酯。这些非质子有机溶剂可单独使用或以两种以上的混合物的形式使用,但不限于此。

[0072] 根据本示意性实施方式的非水型电解液中所含有作为电解质的锂盐的实例包括: LiPF_6 、 LiBF_4 、 LiAsF_6 、 LiSbF_6 、 LiClO_4 、 LiAlO_4 、 $\text{LiN}(\text{C}_q\text{F}_{2q+1}\text{SO}_2)(\text{C}_r\text{F}_{2r+1}\text{SO}_2)$ (q 和 r 为自然数)

以及 LiCF_3SO_3 。但该锂盐不限于此。

[0073] 作为具有根据本示意性实施方式的非水型电解液的设备的负极中所含的负极活性物质,可以使用选自例如金属锂、锂合金和可吸收并释放锂离子的材料构成的组中的一种或两种以上的物质。作为可吸收并释放锂离子的材料,可使用碳材料或硅以及氧化物。

[0074] 作为碳材料,可使用吸收锂的石墨、无定形碳、金刚石样碳、碳纳米管等及它们的复合材料。特别地,石墨具有高的电子传导性,并且在与包含例如铜的金属的集电体的粘附性、以及电压平坦性方面优异,并且由于是在高处理温度下形成,因而仅含有少量的杂质,这对于提高负极性能优选地有利。进而,还可使用高结晶石墨和低结晶无定形碳的复合材料等。

[0075] 作为硅和氧化物,可使用硅、氧化硅、氧化锡、氧化镉、氧化锌、氧化锂、磷酸和硼酸中的一种或它们的复合物,且该复合物优选特别含有氧化硅。结构优选为无定形状态。这是由于氧化硅是稳定的,不会导致与其它化合物的反应,且由于无定形结构不会引入由例如晶粒边界和缺陷的非均匀性引起的劣化。作为成膜方法,可使用气相沉积法、CVD 法、溅射法等。

[0076] 锂合金由锂和可与锂形成合金的金属构成。例如,锂合金由例如 Al、Si、Pb、Sn、In、Bi、Ag、Ba、Ca、Hg、Pd、Pt、Te、Zn 以及 La 的金属与锂的二元、三元以上的多金属合金构成。金属锂和锂合金特别优选为无定形状态。这是因为无定形结构难以引起由例如晶粒边界和缺陷的非均匀性引起的劣化。

[0077] 金属锂和锂合金可通过融体冷却方式、液体急冷方式、雾化方式、真空蒸镀方式、溅射方式、等离子体 CVD 方式、光 CVD 方式、热 CVD 方式和溶胶-凝胶方式等方式而适宜形成。

[0078] 根据本示意性实施方式,具有非水型电解液的设备的正极中所含的正极活性物质的实例包括含锂复合氧化物,例如 LiCoO_2 、 LiNiO_2 和 LiMn_2O_4 。该含锂复合氧化物的过渡金属部分可被其它元素替代。

[0079] 可使用相对于金属锂的对电极电势具有 4.5V 以上的稳定状态 (plateau) 的含锂复合氧化物。该含锂复合氧化物的实例包括尖晶石型锂锰复合氧化物、橄榄石型含锂复合氧化物以及倒尖晶石型含锂复合氧化物。该含锂复合氧化物的实例包括 $\text{Li}_a(\text{M}_x\text{Mn}_{2-x})\text{O}_4$ (其中, $0 < x < 2$; 且 $0 < a < 1.2$ 。M 为选自 Ni、Co、Fe、Cr 和 Cu 构成的组中的至少一者) 所示的化合物。

[0080] 在本示意性实施方式中,用作凝胶电解质中所含的聚合物的原材料的凝胶化成分的实例包括在其一分子中具有两个以上可热聚合的聚合基团的单体、低聚物和共聚低聚物。该凝胶化成分的实例包括:形成丙烯酸聚合物的化合物,其包括双官能性丙烯酸酯例如乙二醇二丙烯酸酯、二甘醇二丙烯酸酯、三甘醇二丙烯酸酯、四甘醇二丙烯酸酯、丙二醇二丙烯酸酯、一缩二丙二醇二丙烯酸酯、二缩三丙二醇二丙烯酸酯、1,3-丁二醇二丙烯酸酯、1,4-丁二醇二丙烯酸酯和 1,6-己二醇二丙烯酸酯,三官能性丙烯酸酯例如三羟甲基丙烷三丙烯酸酯和季戊四醇三丙烯酸酯,四官能性丙烯酸酯例如双三羟甲基丙烷四丙烯酸酯和季戊四醇四丙烯酸酯,以及甲基丙烯酸酯单体。除此之外,该实例包括例如氨基甲酸酯丙烯酸酯和氨基甲酸酯甲基丙烯酸酯的单体,它们的共聚低聚物以及与丙烯腈的共聚低聚物,但不限于此。

[0081] 作为该聚合物,还可使用溶解于增塑剂中且可凝胶化的聚合物,例如聚偏氟乙烯、聚环氧乙烷和聚丙烯腈。

[0082] 凝胶化成分不限于上述单体、低聚物和聚合物,只要是可凝胶化的成分均可使用。该凝胶化成分不限于一种单体、低聚物或聚合物,可以根据需要使用二至数种凝胶化成分的混合物。作为热聚合引发剂,可以根据需要使用苯偶姻、过氧化物等,但热聚合引发剂不限于此。

[0083] 在根据本示意性实施方式的设备的电池构成中,作为电极元件,可使用层叠体或卷绕体;作为外包装体,可使用铝层叠外包装体或金属外包装体。进而,电池容量没有限制。本示意性实施方式的设备为锂离子二次电池、电容器等,并且根据本示意性实施方式的非水型电解液可用于该锂离子二次电池、电容器等中。

[0084] 实施例

[0085] 下文中,将参照附图通过实施例详细描述本实施方式,但本实施方式不限于该实施例。

[0086] 图1为阐释锂离子二次电池的正极的构成的图。图1(a)表示正极的平面图,图1(b)表示正极的侧面图。

[0087] 图2为阐释锂离子二次电池的负极的构成的图。图2(a)表示负极的平面图,图2(b)表示负极的侧面图。

[0088] 图3为阐释了锂离子二次电池被卷绕之后的电池元件的构成的截面图。

[0089] (实施例1)

[0090] 首先,通过图1说明正极1的制作。将85质量%的 LiMn_2O_4 、7质量%的作为导电辅助剂的乙炔黑和8质量%的作为粘接剂的聚偏氟乙烯混合;将N-甲基吡咯烷酮添加至该混合物,并进一步混合,由此制作正极浆料。将该正极浆料涂布在具有 $20\mu\text{m}$ 厚度的Al箔2的两面上,通过刮刀法形成集电体,以使辊压后的厚度变成 $160\mu\text{m}$,在 120°C 干燥5分钟,随后经辊压步骤,由此形成正极活性物质层14。其上没有涂布正极活性物质的正极活性物质未涂布部5被设置在该箔的两端部上。正极材料导电翼片6被焊接在一个正极活性物质未涂布部5上。作为具有仅在一个表面上涂布的正极活性物质的一个表面的正极活性物质单面涂布部4被设置为接近于焊接了正极导电翼片6的正极活性物质未涂布部5,正极活性物质两面涂布部3被设置为进一步与其接近。由此制作正极1。

[0091] 接着,通过图2说明负极7的制作。将90质量%的石墨、1质量%的作为导电辅助剂的乙炔黑和9质量%的作为粘接剂的聚偏氟乙烯混合;将N-甲基吡咯烷酮添加至混合物,并进一步混合,由此制作负极浆料。将该负极浆料涂布在具有 $10\mu\text{m}$ 厚度的Cu箔8的两面上,通过刮刀法形成集电体,以使辊压后的厚度变成 $120\mu\text{m}$,在 120°C 干燥5分钟,随后经辊压步骤,由此形成负极活性物质涂布部9。其上没有涂布负极活性物质的负极活性物质未涂布部11被设置在该箔的两端部上。负极材料导电翼片12被焊接在一个该端部上。作为具有仅在一个表面上涂布的负极活性物质的一个表面的负极活性物质单面涂布部10被设置为接近于焊接了负极导电翼片12的负极活性物质未涂布部11,并且负极活性物质两面涂布部9被设置为进一步与其接近。由此制作负极7。

[0092] 通过图3说明电池元件的制作。将两片隔离物13的熔融且切断部分固定并卷绕至卷绕装置的卷绕芯,并引入正极1和负极7的前端,所述隔离物13包括具有 $25\mu\text{m}$ 膜厚

和 55% 孔隙率并经受了亲水处理的聚丙烯微孔膜。在使正极导电翼片 6 的连接部的相反侧和负极导电翼片 12 的连接部侧分别作为正极 1 和负极 7 的前端侧的条件下,将负极 7 布置在两片隔离物 13 之间,将正极 1 布置在隔离物 13 的上表面上,并通过旋转卷绕芯进行卷绕,由此形成电池元件(下文中,称为 J/R(凝胶卷))。

[0093] 将 J/R 收纳在印花的层叠外包装体中;将正极导电翼片 6 和负极导电翼片 12 拉出;将层叠外包装体的一侧向后折叠,并在溶液注射用部分保持未熔合的状态下进行热熔合。

[0094] 通过将 10 质量%的单乙氧基五氟环三磷腈和 2 质量%的表 1 中的化合物 No. 2 混合在含有作为支持盐的 1.2mol/l 的 LiPF_6 和作为溶剂的碳酸亚乙酯(EC)/碳酸二乙酯(DEC) = 30/70(体积比)的电解液中来制作电解液。

[0095] 然后,将该电解液从溶液注射用部分注入以进行真空浸渗,将溶液注射用部分热熔合,由此得到电池。

[0096] 将所得的电池进行 CC-CV 充电(恒流恒压充电,充电条件:0.02C 的 CC 电流,5 小时的 CV 时间以及 20℃ 的温度)至 4.2V 的电池电压,且之后以 0.02C 放电至 3.0V 的电池电压时所获得的放电容量定义为初始容量;将所得的初始容量相对于设计容量的比例定义为初始容量(%),对其进行了测定。

[0097] 将所得的电池在 20℃ 的 2C 容量相对于 0.2C 容量的比例定义为比率特性(%),对其进行了测定。

[0098] 所得电池的循环试验包括 4.2V 的上限电压、1C 的电流、以及 1.5 小时的 CV 时间的 CC-CV 充电、以及 3.0V 的下限电压、1C 的电流的 CC 放电,且均在 45℃ 下进行。第 1000 次循环时的放电容量相对于第一次循环时的放电容量的比例被定义为容量保持率,对其进行了测定。

[0099] 通过将循环试验后的电池放置在气体燃烧器的火焰的前端上方 10cm 来进行燃烧试验。根据电解液挥发并燃烧的状态对燃烧能力作出如下评价。电解液不被引燃的情形被定义为 A;即使被引燃但在引燃 2-3 秒之后火焰熄灭的情形被定义为 B;即使被引燃但火焰在 10 秒之内熄灭的情形被定义为 C;即使 10 秒之后燃烧仍然持续而不熄灭的情形被定义为 D。

[0100] (实施例 2)

[0101] 在实施例 2 中,除了混合 2 质量%的表 2 中的化合物 No. 101 作为添加剂之外,以实施例 1 中相同的方式制作并评价电池。

[0102] (实施例 3)

[0103] 在实施例 3 中,除了混合 4 质量%的表 2 中的化合物 No. 101 作为添加剂之外,如实施例 1 制作并评价电池。

[0104] (实施例 4)

[0105] 在实施例 4 中,除了混合 2 质量%的表 1 中的化合物 No. 2 和 2 质量%的表 2 中的化合物 No. 101 作为添加剂之外,如实施例 1 制作并评价电池。

[0106] (实施例 5)

[0107] 在实施例 5 中,除了混合 2 质量%的表 1 中的化合物 No. 2 和 3 质量%的 1,3-丙烷磺内酯作为添加剂之外,如实施例 1 制作并评价电池。

[0108] (实施例 6)

[0109] 在实施例 6 中,除了混合 4 质量%的表 1 中的化合物 No. 2 和 6 质量%的 1,3- 丙烷磺内酯作为添加剂之外,如实施例 1 制作并评价电池。

[0110] (实施例 7)

[0111] 在实施例 7 中,除了添加 20 质量%的单乙氧基五氟环三磷腈之外,如实施例 6 制作并评价电池。

[0112] (实施例 8)

[0113] 在实施例 8 中,除了添加 25 质量%的单乙氧基五氟环三磷腈之外,如实施例 7 制作并评价电池。

[0114] (实施例 9)

[0115] 在实施例 9 中,除了混合 5 质量%的表 1 中的化合物 No. 2 和 7 质量%的 1,3- 丙烷磺内酯作为添加剂之外,如实施例 1 制作并评价电池。

[0116] (比较例 1)

[0117] 在比较例 1 中,除了不添加单乙氧基五氟环三磷腈之外,如实施例 6 制作并评价电池。

[0118] (比较例 2)

[0119] 在比较例 2 中,除了不添加添加剂之外,如实施例 1 制作并评价电池。

[0120] (比较例 3)

[0121] 在比较例 3 中,除了添加不对应于上述式 (2)、(3) 和 (4) 中任一者的 5 质量%的碳酸乙烯基酯 (VC) 作为添加剂之外,如实施例 1 制作并评价电池。

[0122] (比较例 4)

[0123] 在比较例 4 中,除了混合 3 质量%的丙烷磺内酯 (PS) 作为添加剂之外,如实施例 1 制作并评价电池。

[0124] 实施例 1 至 9、和比较例 1 至 4 中的初始容量、比率特性、容量保持率以及阻燃性的结果示于表 3 中。

[0125] [表 3]

[0126]

	负极活性物质/电解质	添加的磷腈化合物的量(质量%)	添加剂	添加的添加剂的量(质量%)	初始容量(%)	在 2C/0.2C 容量下的比率特性(%)	第 1000 次循环时的容量保持率(%)	燃烧能力
实施例 1	石墨/液体	10	No.2	2	90	78	70	B
实施例 2	石墨/液体	10	No.101	2	90	78	70	B
实施例 3	石墨/液体	10	No.101	4	88	76	73	A
实施例 4	石墨/液体	10	No.2/ No.101	4	86	75	72	A
实施例 5	石墨/液体	10	No.2/PS	5	89	77	74	A
实施例 6	石墨/液体	10	No.2/PS	10	82	65	75	A
实施例 7	石墨/液体	20	No.2/PS	10	79	60	68	A
实施例 8	石墨/液体	25	No.2/PS	10	75	55	58	B
实施例 9	石墨/液体	10	No.2/PS	12	74	54	75	A
比较例 1	石墨/液体	0	No.2/PS	5	89	82	75	D
比较例 2	石墨/液体	10	-	-	71	88	38	D
比较例 3	石墨/液体	10	VC	5	85	58	61	C
比较例 4	石墨/液体	10	PS	3	92	59	68	C

[0127]

[0128] 表 3 中添加剂一列中描述的 No. 2 表示表 1 中的化合物 No. 2 ;No. 101 表示表 2 中的化合物 No. 101 ;PS 表示 1,3- 丙烷磺内酯 ;以及 VC 表示不对应于上述式 (2)、(3) 和 (4) 中任一者的碳酸乙烯基酯。

[0129] 如表 3 中实施例 1 至 6 和 9 中所示,在使添加的单乙氧基五氟环三磷腈的量为固定量、并增加添加剂的量的情形下,容量保持率非常好。进而在循环试验后的电池燃烧试验中,电解液不被引燃、或者虽然被引燃但在引燃 2 至 3 秒之后熄灭。相反,在比较例 1 中,在循环试验之后的电池燃烧试验中,电解液持续燃烧。在比较例 2 中,容量保持率低,且进而在循环试验后的电池燃烧试验中,电解液持续燃烧。也就是说,发现由于不存在添加剂,因而具有磷腈结构的化合物被还原降解,变得不存在用于燃烧抑制的其有效的量。另外,在比较例 3 和比较例 4 中,与实施例相比阻燃性也稍微降低,表明添加剂不足以用于抑制具有磷腈结构的化合物的还原降解。由实施例 6、7 和 9 可知,虽然存在添加大量的添加剂使 SEI 变厚并使电阻增加的可能性,但尤其是燃烧抑制效果在循环试验之后也得以充分地维持。通过对比实施例 8 和 7,由于添加的单乙氧基五氟环三磷腈的量超过 20 质量%会降低电解液

的离子传导性,因此比率特性稍微降低,且由于相对于 SEI 的过量的磷腈化合物在长期循环试验中会渐渐还原降解,因此使得长期循环试验后的电池燃烧抑制效果稍微降低。

[0130] 进而,通过与各比较例进行比较,在实施例 10 中,初次充电时气体发生量倾向于降低。这是可想到的,因为电解液中具有磷腈结构的化合物和二磺酸酯的同时存在可通过与利用仅含有二磺酸酯的非水电解液的 SEI 形成不同的反应机制来形成引入具有磷腈结构的化合物的 SEI。然而,假设因为存在于电解液中的磷腈化合物的进一步还原可在这样形成的 SEI 上被抑制,则存在利用引入磷腈化合物的二磺酸酯的 SEI 对于含有磷腈化合物的某电解液成分具有更大的还原降解抑制效果的可能性。推测该效果使寿命特性良好。

[0131] 由上述可知,使用特定的二磺酸酯和特定的磺内酯化合物的 SEI 可长期抑制具有磷腈结构的化合物的还原降解,并提供作为寿命特性的良好的容量保持率,从而可提供高阻燃性。进而,使添加的具有磷腈结构的化合物的量和添加剂的量之间的平衡为最佳,使得可维持比率保持特性并提供良好的寿命特性。

[0132] (实施例 10)

[0133] 除了使用实施例 5 中的电解液作为凝胶电解质之外,以如实施例 5 中相同的方式进行实施例 10。首先,将 10 质量%的单乙氧基五氟环三磷腈、2 质量%的表 1 中的化合物 No. 2 和 3 质量%的 PS 混合于含有 1.2mol/l 的 LiPF_6 且其中 EC/DEC = 30/70 (体积比) 的电解液中。进一步添加 3.8 质量%的三甘醇二丙烯酸酯和作为凝胶化剂的 1 质量%的三羟甲基丙烷三丙烯酸酯并良好混合。然后,添加作为聚合引发剂的 0.5 质量%的过氧化特戊酸叔丁酯。由此制作预凝胶溶液。然后,将该预凝胶溶液从溶液注射用部分注入用于真空浸渗,并在 80°C 聚合 2 小时,由此得到锂离子电池 (锂聚合物电池)。

[0134] (比较例 5)

[0135] 除了不添加实施例 10 中的添加剂之外,以与实施例 10 相同的方式进行比较例 5。

[0136] 实施例 10 和比较例 5 中的初始容量、比率特性、容量保持率以及阻燃性示于表 4 中。

[0137] [表 4]

[0138]

	负极活性物质/电解质	添加的磷腈化合物的量(质量%)	添加剂	添加的添加剂的量(质量%)	初始容量(%)	在 2C/0.2C 容量下的比率特性(%)	第 1000 次循环时的容量保持率(%)	燃烧能力
实施例 10	石墨/聚合物	10	No.2/PS	5	89	75	76	A
比较例 5	石墨/聚合物	10	-	-	72	75	40	C

[0139] 描述在表 4 中的添加剂一列的 No. 2 表示表 1 中的化合物 No. 2;以及 PS, 1, 3- 丙

烷磺内酯。

[0140] 由表 4 可清楚,在使用凝胶电解质代替液体电解液的情形中,利用二磺酸酯和磺内酯化合物的 SEI 可长期抑制具有磷腈结构的化合物的还原降解,并可提供作为寿命特性的良好的容量保持率,使得提供高阻燃性。

[0141] (实施例 11)

[0142] 除了将实施例 6 中作为负极材料的石墨改为硅系材料之外,以与实施例 6 中相同的方式进行实施例 11。首先,将 90 质量%的硅、1 质量%的作为导电辅助剂的乙炔黑和 9 质量%的作为粘接剂的聚酰亚胺混合;将 N-甲基吡咯烷酮添加至混合物,并进一步混合,由此制造负极浆料。将该负极浆料涂布在具有 10 μm 厚度的 Cu 箔 8 的两面上以形成集电体,以使在辊压后厚度变成 80 μm ,在 120°C 干燥 5 分钟,然后经辊压步骤,并且另外在 300°C 下干燥 10 分钟,由此形成负极活性物质涂布部 9。

[0143] (比较例 6)

[0144] 除了不添加实施例 11 中的添加剂之外,以与实施例 11 中相同的方式进行比较例 6。实施例 11 和比较例 6 的循环试验包括 CC-CV 充电(上限电压:4.2V,电流:1C,以及 CV 时间:1.5 小时)以及 CC 放电(下限电压:3.0V,以及电流:1C),且二者均在 45°C 下进行。将第 200 次循环时的放电容量相对于第一次循环时的容量的比例定义为容量保持率。

[0145] 实施例 11 和比较例 6 中的初始容量、比率特性、容量保持率以及阻燃特性示于表 5 中。

[0146] [表 5]

[0147]

	负极活性物质/电解质	添加的磷腈化合物的量(质量%)	添加剂	添加的添加剂的量(质量%)	初始容量(%)	在 2C/0.2C 容量下的比率特性(%)	第 1000 次循环时的容量保持率(%)	燃烧能力
实施例 11	硅/液体	10	No.2/PS	10	76	70	71	B
比较例 6	硅/液体	10	-	-	66	70	33	D

[0148] 描述在表 5 的添加剂列中的 No. 2 表示表 1 中的化合物 No. 2;以及 PS 表示 1,3-丙烷磺内酯。

[0149] 由表 5 可清楚,在使用硅材料代替石墨的情形中,利用二磺酸酯和磺内酯化合物的 SEI 也可长期抑制具有磷腈结构的化合物的还原降解,并可提供作为寿命特性的良好的容量保持率,使得提供高阻燃性。

[0150] 综上,可确定本示意性实施方式可提供具有良好容量保持率和高阻燃性的非水型电解液和包含该非水型电解液的设备。

[0151] 本申请主张 2009 年 10 月 28 日提交的日本专利申请 No. 2009-247185 的优先权,其公开的内容全部并入本文。

[0152] 综上,通过参照实施方式(和实施例)描述了本发明,但本发明不限于该实施方式

(和该实施例)。在本发明的组成和细节中,可在本发明的范围内作出对于本领域技术人员可理解的各种变形和修改。

[0153] 符号说明

[0154] 1 正极

[0155] 2 Al 箔

[0156] 3 正极活性物质两面涂布部

[0157] 4 正极活性物质单面涂布部

[0158] 5 正极活性物质未涂布部

[0159] 6 正极导电翼片

[0160] 7 负极

[0161] 8 Cu 箔

[0162] 9 负极活性物质两面涂布部

[0163] 10 负极活性物质单面涂布部

[0164] 11 负极活性物质未涂布部

[0165] 12 负极导电翼片

[0166] 13 隔离物

[0167] 14 正极活性物质层

[0168] 15 负极活性物质层

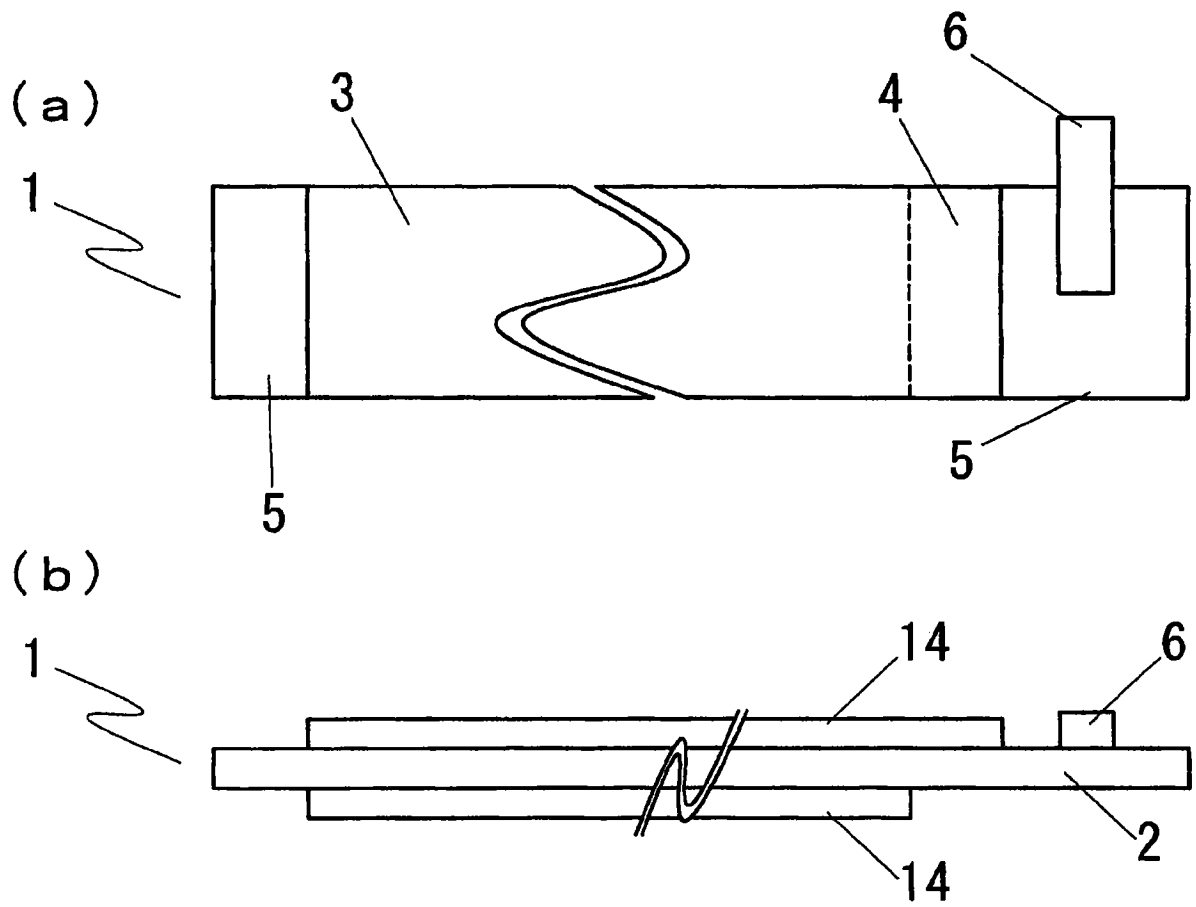


图 1

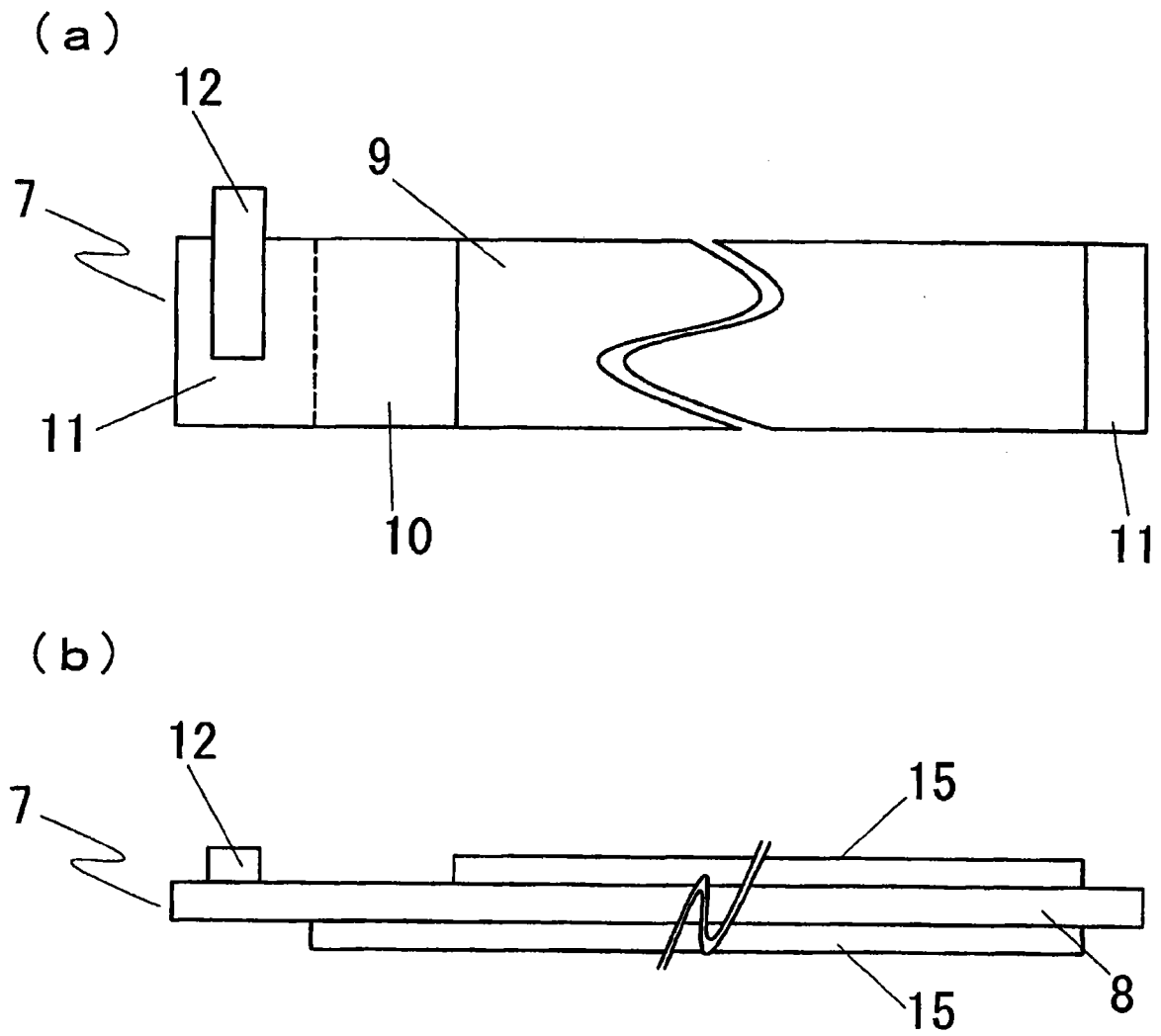


图 2

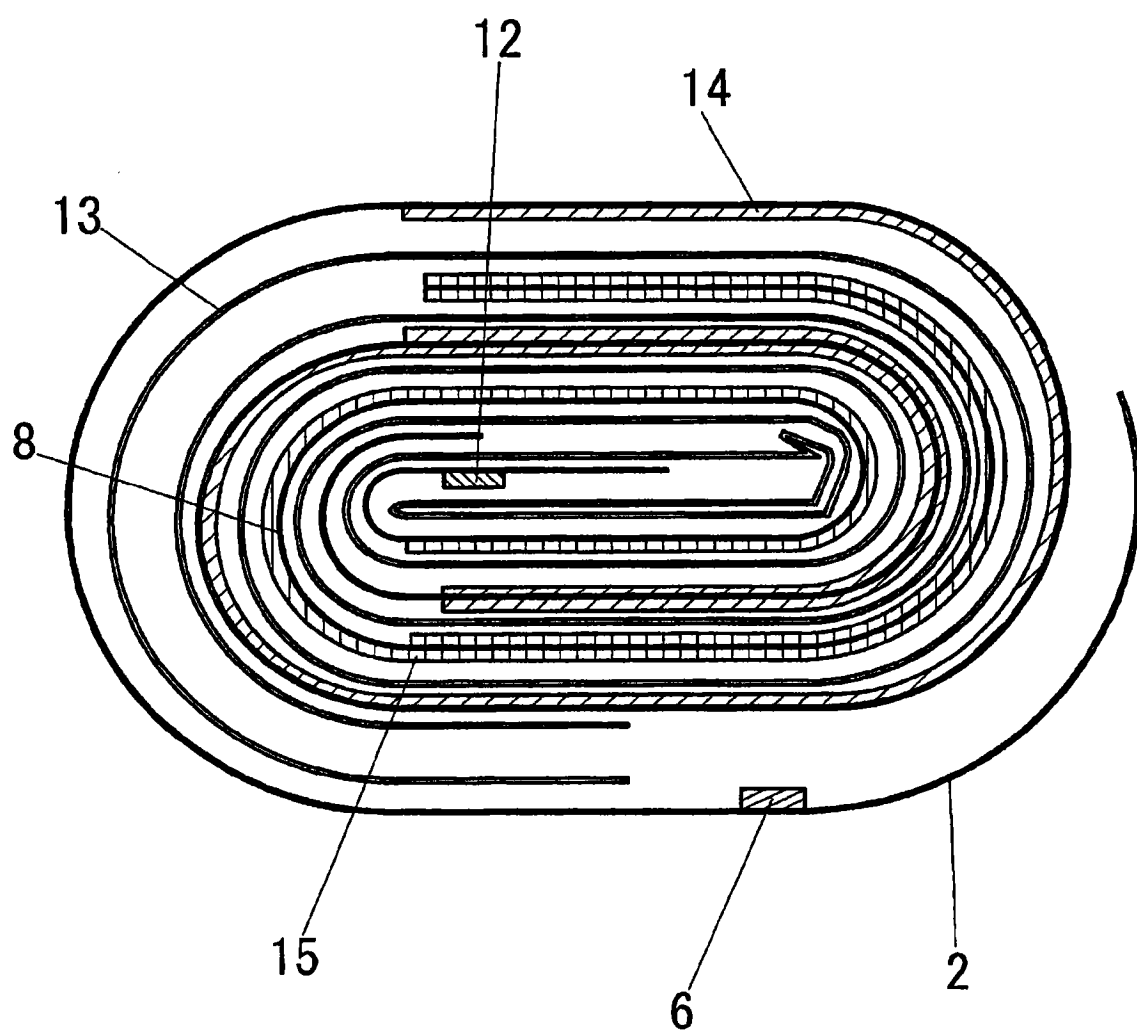


图 3