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(12) Patent Application Publication

(10) Publication No. CN 105428720 A
(43) Publication Date 2016.03.23

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- (21) Application No. 201511016645.5
(22) Filing Date 2015.12.29
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(51) Int. Cl.
H01M 10/0568(2010.01)
H01M 10/052(2010.01)
H01M 10/0525(2010.01)

Claims 1 Page Specification 25 Pages

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- (54) Title
NON-AQUEOUS ELECTROLYTE, PREPARATION
METHOD THEREOF, AND LITHIUM SECONDARY BATTERY
(57) Abstract

The present invention provides a non-aqueous electrolyte, comprising a difluorophosphate and a non-aqueous solvent. The present invention uses difluorophosphate as an electrolyte salt in combination with a non-aqueous solvent to obtain a non-aqueous electrolyte, and the application of this non-aqueous electrolyte in a lithium secondary battery can improve the cycle retention rate of the lithium secondary battery. The results show that the initial specific capacity of the lithium secondary battery provided by the present invention can be as high as 256 mAh·g⁻¹, and the capacity retention rate of the lithium secondary battery after 500 charge-discharge cycles can be up to 89%.

1. A non-aqueous electrolyte, comprising a difluorophosphate and a non-aqueous solvent.
2. The non-aqueous electrolyte according to claim 1, wherein the concentration of the difluorophosphate is $0.1 \text{ mol} \cdot \text{L}^{-1}$ to $5.0 \text{ mol} \cdot \text{L}^{-1}$.
3. The non-aqueous electrolyte according to claim 1, wherein the non-aqueous solvent is selected from one or more of a chain ether compound, a carbonate compound, acetonitrile, N,N-dimethylacetamide, and dimethyl sulfoxide.
4. The non-aqueous electrolyte according to claim 3, wherein the chain ether compound is selected from dimethyl ether compounds;
the carbonate compound is selected from one or more of a chain carbonate and a cyclic carbonate, the chain carbonate is selected from one or more of dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, and a fatty acid ester derivative, and the cyclic carbonate is selected from one or more of ethylene carbonate, propylene carbonate, and γ -butyrolactone.
5. The non-aqueous electrolyte according to claim 1, further comprising a functional additive, wherein the functional additive is selected from one or more of a nitrile compound and a sulfate compound.
6. The non-aqueous electrolyte according to claim 5, wherein the nitrile compound is selected from one or more of succinonitrile and derivatives thereof, glutaronitrile and derivatives thereof, adiponitrile and derivatives thereof, pimelonitrile and derivatives thereof, suberonitrile and derivatives thereof, acetonitrile and derivatives thereof, acrylonitrile and derivatives thereof, and propionitrile and derivatives thereof;
the sulfate compound is selected from one or more of ethylene sulfite and derivatives thereof, propylene sulfate and derivatives thereof, ethylene sulfate and derivatives thereof, and propylene sulfite and derivatives thereof.
7. The non-aqueous electrolyte according to claim 1, further comprising a fluorine-containing alkali metal salt other than the difluorophosphate.
8. The non-aqueous electrolyte according to claim 7, wherein the fluorine-containing alkali metal salt other than the difluorophosphate is selected from one or more of lithium hexafluorophosphate, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethanesulfonate, lithium hexafluorosilicate, lithium bis(trifluoromethanesulfonyl)imide, lithium bis(fluorosulfonyl)imide, lithium bis(oxalato)borate, and lithium difluoro(oxalato)borate.
9. The non-aqueous electrolyte according to claim 7, wherein the concentration of the fluorine-containing alkali metal salt other than the difluorophosphate is $0 \text{ mol} \cdot \text{L}^{-1}$ to $1.0 \text{ mol} \cdot \text{L}^{-1}$.
10. A lithium secondary battery, comprising a positive electrode, a negative electrode, a separator, and an electrolyte, wherein the electrolyte is the non-aqueous electrolyte according to any one of claims 1 to 9.

NON-AQUEOUS ELECTROLYTE, PREPARATION METHOD THEREOF, AND LITHIUM SECONDARY BATTERY

TECHNICAL FIELD

[0001] The present invention belongs to the technical field of metal lithium secondary batteries, and particularly relates to a non-aqueous electrolyte, a preparation method thereof, and a lithium secondary battery.

BACKGROUND

[0002] With the lightening and miniaturization of electrical appliances in recent years, non-aqueous electrolyte secondary batteries having high energy density, such as lithium-ion secondary batteries, have been developed. In addition, with the expansion of the application field of such lithium-ion secondary batteries, researchers hope to further improve battery characteristics.

[0003] In order to improve battery characteristics such as load characteristics, cycle characteristics, storage characteristics, and low-temperature characteristics of such lithium-ion secondary batteries, various studies have been conducted on non-aqueous solvents and electrolytes. At present, most non-aqueous electrolytes in lithium secondary batteries use lithium hexafluorophosphate as the electrolyte salt and carbonate organic solvents as the non-aqueous solvent to prepare the non-aqueous electrolyte. However, lithium hexafluorophosphate is unstable and easily decomposes during the use of the battery, thereby affecting the cycle retention rate of the lithium secondary battery prepared using the above non-aqueous electrolyte.

SUMMARY

[0004] In view of this, the technical problem to be solved by the present invention is to provide a non-aqueous electrolyte, a preparation method thereof, and a lithium secondary battery. The non-aqueous electrolyte provided by the present invention has a good cycle retention rate.

[0005] The present invention provides a non-aqueous electrolyte, comprising a difluorophosphate and a non-aqueous solvent.

[0006] Preferably, the concentration of the difluorophosphate is $0.1 \text{ mol} \cdot \text{L}^{-1}$ to $5.0 \text{ mol} \cdot \text{L}^{-1}$.

[0007] Preferably, the non-aqueous solvent is selected from one or more of a chain ether compound, a carbonate compound, acetonitrile, N,N-dimethylacetamide, and dimethyl sulfoxide.

[0008] Preferably, the chain ether compound is selected from dimethyl ether compounds;

[0009] the carbonate compound is selected from one or more of a chain carbonate and a cyclic carbonate, the chain carbonate is selected from one or more of dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, methyl propyl carbonate, and a fatty acid ester derivative, and the cyclic carbonate is selected from one or more of ethylene carbonate, propylene carbonate, and γ -butyrolactone.

[0010] Preferably, it further comprises a functional additive, and the functional additive is selected from one or more of a nitrile compound and a sulfate compound.

[0011] Preferably, the nitrile compound is selected from one or more of succinonitrile and derivatives thereof, glutaronitrile and derivatives thereof, adiponitrile and derivatives thereof, pimelonitrile and derivatives thereof, suberonitrile and derivatives thereof, acetonitrile and derivatives thereof, acrylonitrile and derivatives thereof, and propionitrile and derivatives thereof;

[0012] the sulfate compound is selected from one or more of ethylene sulfite and derivatives thereof, propylene sulfate and derivatives thereof, ethylene sulfate and derivatives thereof, and propylene sulfite and derivatives thereof.

[0013] Preferably, it further comprises a fluorine-containing alkali metal salt other than the difluorophosphate.

[0014] Preferably, the fluorine-containing alkali metal salt other than the difluorophosphate is selected from one or more of lithium hexafluorophosphate, lithium tetrafluoroborate, lithium perchlorate, lithium hexafluoroarsenate, lithium trifluoromethanesulfonate, lithium hexafluorosilicate, lithium bis(trifluoromethanesulfonyl)imide, lithium bis(fluorosulfonyl)imide, lithium bis(oxalato)borate, and lithium difluoro(oxalato)borate.

[0015] Preferably, the concentration of the fluorine-containing alkali metal salt other than the difluorophosphate is $0 \text{ mol} \cdot \text{L}^{-1}$ to $1.0 \text{ mol} \cdot \text{L}^{-1}$.

[0016] The present invention also provides a lithium secondary battery, comprising a positive electrode, a negative electrode, a separator, and an electrolyte, wherein the electrolyte is the above-mentioned non-aqueous electrolyte.

[0017] Compared with the prior art, the present invention provides a non-aqueous electrolyte comprising a difluorophosphate and a non-aqueous solvent. The present invention uses difluorophosphate as an electrolyte salt in combination with a non-aqueous solvent to obtain a non-aqueous electrolyte, and the application of this non-aqueous electrolyte in a lithium secondary battery can improve the cycle retention rate of the lithium secondary battery.

[0018] The results show that the initial specific capacity of the lithium secondary battery provided by the present invention can be as high as $256 \text{ mAh} \cdot \text{g}^{-1}$, and the capacity retention rate of the lithium secondary battery after 500 charge-discharge cycles can be up to 89%.

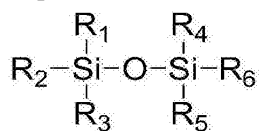
DETAILED DESCRIPTION

[0019] The present invention provides a non-aqueous electrolyte, comprising a difluorophosphate and a non-aqueous solvent.

[0020] The non-aqueous electrolyte provided by the present invention uses a difluorophosphate as an electrolyte salt. The present invention has no special limitation on the source of the difluorophosphate, which can be commercially available or prepared by oneself. In the present invention, the difluorophosphate is preferably prepared according to the following method:

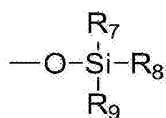
[0021] A) mixing and stirring an organic solvent, a fluoride salt, and a compound of Formula I to obtain a suspension;

[0022] B) introducing PF_5 gas into the suspension, heating to react, and then recrystallizing to obtain a difluorophosphate;



[0023] , Formula I;

[0024] In Formula I, R_1 to R_6 are each independently selected from H, a C1-C50 hydrocarbon group, a C1-C50 substituted hydrocarbon group, or a group having a structure of Formula II; or any two or more groups of R_1 to R_6 are bonded to each other to form a cyclic structure;



[0025] , Formula II;

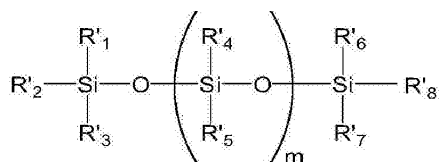
[0026] In Formula II, R_7 to R_9 are each independently selected from H, a C1-C50 hydrocarbon group, a C1-C50 substituted hydrocarbon group, or any one or more groups of R_7 to R_9 are further substituted by a group having the structure of Formula II.

[0027] The present invention first mixes and stirs an organic solvent, a fluoride salt, and a compound having the structure of Formula I to obtain a suspension;

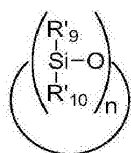
[0028] Specifically, the fluoride salt is dissolved in the organic solvent to obtain a mixed solution;

[0029] The mixed solution is mixed and stirred with the compound having the structure of Formula I to obtain a suspension.

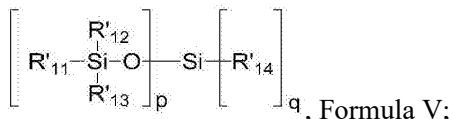
[0030] Preferably, the compound having the structure of Formula I is selected from compounds having a structure of Formula III, Formula IV, or Formula V;



[0031] , Formula III;



[0032] , Formula IV;



, Formula V;

[0033] wherein R'_1 to R'_{14} are each independently selected from H, a C1-C50 hydrocarbon group, and a C1-C50 substituted hydrocarbon group; $m \geq 0$; $n \geq 3$; $q \geq 1$, $p \geq 2$, and $p+q=4$.

[0034] More preferably, R'_1 to R'_{14} are each independently selected from H, a C1-C25 alkyl group, a C1-C25 substituted alkyl group, a C1-C25 alkenyl group, a C1-C25 substituted alkenyl group, a C1-C25 alkynyl group, a C1-C25 substituted alkynyl group, a phenyl group, and a substituted phenyl group; m is an integer of 0 to 5; n is an integer of 3 to 10; $q \geq 1$, $p \geq 2$, and $p+q=4$.

[0035] Most preferably, the compound having the structure of Formula I is selected from hexamethyldisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, hexamethylcyclotrisiloxane, octaphenylcyclotetrasiloxane, or trifluoropropylmethylcyclotrisiloxane.

[0036] In the present invention, the molar ratio of -Si-O-Si- in the compound having the structure of Formula I to the fluoride salt is > 2 , preferably 2 to 5.

[0037] The fluoride salt is preferably one or more of salts of metals in Group I, Group II, and Group V of the periodic table and quaternary onium salts, more preferably lithium fluoride, sodium fluoride, potassium fluoride, ammonium fluoride, or calcium fluoride.

[0038] The molar ratio of the fluoride salt to the non-aqueous solvent is $\geq 2 \text{ mol} \cdot \text{L}^{-1}$, preferably 2 to $4.5 \text{ mol} \cdot \text{L}^{-1}$, more preferably 3 to $4 \text{ mol} \cdot \text{L}^{-1}$, and most preferably $4 \text{ mol} \cdot \text{L}^{-1}$.

[0039] The organic solvent is selected from one or more of acetone, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and propylene glycol dimethyl ether.

[0040] After obtaining the suspension, PF_5 gas is introduced into the suspension, heated to react, and then recrystallized to obtain a difluorophosphate.

[0041] In the present invention, the temperature for introducing the PF_5 gas into the suspension is 0 to 25°C , preferably 10°C . After the introduction of the PF_5 gas is completed, a heating reaction is performed, wherein the temperature of the heating reaction is 40 to 80°C , preferably 60°C , and the time of the heating reaction is 6 to 15 hours, preferably 12 hours.

[0042] In the present invention, the difluorophosphate is preferably lithium difluorophosphate, sodium difluorophosphate, potassium difluorophosphate, ammonium difluorophosphate, or calcium difluorophosphate.

[0043] In the non-aqueous electrolyte, the concentration of the difluorophosphate is preferably $0.1 \text{ mol} \cdot \text{L}^{-1}$ to $5.0 \text{ mol} \cdot \text{L}^{-1}$, more preferably $0.8 \text{ mol} \cdot \text{L}^{-1}$ to $3.0 \text{ mol} \cdot \text{L}^{-1}$, and particularly preferably $1.0 \text{ mol} \cdot \text{L}^{-1}$ to $2.0 \text{ mol} \cdot \text{L}^{-1}$. In some embodiments of the present invention, the concentration of the difluorophosphate is $0.5 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $0.7 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $0.8 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $0.9 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $1.0 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $1.5 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $2.0 \text{ mol} \cdot \text{L}^{-1}$; in other embodiments of the present invention, the concentration of the difluorophosphate is $2.5 \text{ mol} \cdot \text{L}^{-1}$.

[0044] In the present invention, the non-aqueous solvent is selected from one or more of a chain ether compound, a carbonate compound, acetonitrile, N,N-dimethylacetamide, and dimethyl sulfoxide.

[0045] Preferably, the non-aqueous solvent is selected from chain ether compounds, preferably dimethyl ether compounds, and more preferably one or more of dimethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, triethylene glycol dimethyl ether, and propylene glycol dimethyl ether. The present invention uses a chain ether compound as the non-aqueous solvent to reduce the viscosity of the electrolyte.

[0046] Preferably, the non-aqueous solvent further comprises one or more of a chain carbonate, a cyclic carbonate, acetonitrile (AN), N,N-dimethylacetamide (DMF), dimethyl sulfoxide (DMSO), and derivatives of the above compounds. Wherein, the chain carbonate is preferably one or more of dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), diethyl carbonate (DEC), methyl propyl carbonate (MPC), and a fatty acid ester derivative, and the cyclic carbonate is preferably one or more of ethylene carbonate (EC), propylene carbonate (PC), and γ -butyrolactone (γ -BL). In the present invention, the chain carbonate can further reduce the viscosity of the electrolyte, increase the solubility of the electrolyte salt, and improve low-temperature characteristics such as the low-temperature load of the battery. The cyclic carbonate can improve the life of the lithium secondary battery.

[0047] In the present invention, the chain ether compound and the chain carbonate are low-viscosity organic solvents, and the cyclic carbonate, acetonitrile (AN), N,N-dimethylacetamide (DMF), dimethyl sulfoxide (DMSO), and derivatives of the above compounds are high dielectric constant solvents. Wherein, the mixing ratio of the high dielectric constant solvent and the low-viscosity organic solvent in the present invention, expressed by volume ratio, is preferably 0:100 to 100:0, more preferably 10:90 to 80:20, and particularly preferably 15:85 to 50:50. By optimizing the ratio in this way, the increase in the viscosity of the non-aqueous electrolyte can be effectively suppressed, the degree of dissociation of the electrolyte salt can be further improved, and thereby the conductivity of the lithium-ion battery electrolyte during charge and discharge can be improved.

[0048] In the present invention, the non-aqueous solvent is preferably one or more of DME, DDME, TDME, PC, EC, AN, DMSO, and EMC.

[0049] In the present invention, the non-aqueous electrolyte further comprises a fluorine-containing alkali metal salt other than the difluorophosphate. The fluorine-containing alkali metal salt other than the difluorophosphate is preferably a fluorine-containing lithium salt, more preferably one or more of lithium hexafluorophosphate (LiPF_6), lithium tetrafluoroborate (LiBF_4), lithium perchlorate (LiClO_4), lithium hexafluoroarsenate (LiAsF_6), lithium trifluoromethanesulfonate (LiCF_3SO_3), lithium hexafluorosilicate (Li_2SiF_6), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), lithium bis(fluorosulfonyl)imide (LiFSI), lithium bis(oxalato)borate (LiBOB), and lithium difluoro(oxalato)borate (LiODFB), and most preferably LiPF_6 , LiTFSI , LiFSI , LiBOB , or LiODFB .

[0050] The concentration of the fluorine-containing alkali metal salt other than the difluorophosphate is preferably $0\text{ mol}\cdot\text{L}^{-1}$ to $1.0\text{ mol}\cdot\text{L}^{-1}$, more preferably $0.1\text{ mol}\cdot\text{L}^{-1}$ to $0.5\text{ mol}\cdot\text{L}^{-1}$.

[0051] Preferably, the non-aqueous electrolyte provided by the present invention further comprises a functional additive, and the functional additive is selected from one or more of a nitrile compound and a sulfate compound; the nitrile compound is preferably one or more of succinonitrile (BDN) and derivatives thereof, glutaronitrile (PDN) and derivatives thereof, adiponitrile (HDN) and derivatives thereof, pimelonitrile (PLN) and derivatives thereof, suberonitrile (SN) and derivatives thereof, acetonitrile (AN) and derivatives thereof, acrylonitrile (ACN) and derivatives thereof, and propionitrile (ECN) and derivatives thereof;

[0052] the sulfate compound is selected from one or more of ethylene sulfite (ES) and derivatives thereof, propylene sulfate (TS) and derivatives thereof, ethylene sulfate (DTD) and derivatives thereof, and propylene sulfite (PS) and derivatives thereof.

[0053] More preferably, the functional additive is selected from one or more of BDN, PDN, SN, AN, CAN, γ -BL, PS, and ES.

[0054] In the non-aqueous electrolyte, the addition amount of the functional additive is preferably 0 wt% to 10 wt%, preferably 1 wt% to 5 wt%.

[0055] The present invention also provides a preparation method of the above non-aqueous electrolyte, comprising the following steps:

- [0056] mixing a difluorophosphate and a non-aqueous solvent to obtain a non-aqueous electrolyte.
- [0057] In the present invention, the mixing is preferably performed under sealed conditions in an atmosphere of nitrogen or an inert gas. The inert gas is preferably argon or helium.
- [0058] In the present invention, the preparation method of the non-aqueous electrolyte comprises the following steps:
- [0059] mixing a difluorophosphate, a fluorine-containing alkali metal salt other than the difluorophosphate, and a non-aqueous solvent to obtain a non-aqueous electrolyte.
- [0060] In the present invention, the mixing is preferably performed under sealed conditions in an atmosphere of nitrogen or an inert gas. The inert gas is preferably argon or helium.
- [0061] In the present invention, the preparation method of the non-aqueous electrolyte can also be performed according to the following steps:
- [0062] mixing a difluorophosphate, a functional additive, a fluorine-containing alkali metal salt other than the difluorophosphate, and a non-aqueous solvent to obtain a non-aqueous electrolyte.
- [0063] In the present invention, the mixing is preferably performed under sealed conditions in an atmosphere of nitrogen or an inert gas. The inert gas is preferably argon or helium.
- [0064] In the present invention, the preparation method of the non-aqueous electrolyte can also be performed according to the following steps:
- [0065] mixing a difluorophosphate, a functional additive, and a non-aqueous solvent to obtain a non-aqueous electrolyte.
- [0066] In the present invention, the mixing is preferably performed under sealed conditions in an atmosphere of nitrogen or an inert gas. The inert gas is preferably argon or helium.
- [0067] The present invention also provides a lithium secondary battery, comprising a positive electrode, a negative electrode, a separator, and an electrolyte, wherein the electrolyte is the above-mentioned non-aqueous electrolyte.
- [0068] In the present invention, the types of the positive electrode, the negative electrode, and the separator are not particularly limited, and any types of positive electrode, negative electrode, and separator used in lithium secondary batteries known to those skilled in the art can be used.
- [0069] The positive electrode of the present invention is preferably prepared according to the following method:
- [0070] mixing a positive electrode active material, a conductive agent, a binder, and a solvent to prepare a positive electrode active material composition;
- [0071] directly coating the positive electrode material composition on an Al current collector and drying to prepare a positive electrode plate.
- [0072] In the present invention, the positive electrode active material can be any lithium-containing transition metal oxide, transition metal oxide, or transition metal sulfide commonly used in the art, preferably LiCoO_2 , $\text{LiMn}_x\text{O}_{2x}$ ($x=1, 2$), $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ ($0 \leq x < 1$), $\text{LiNi}_x\text{Co}_{1-x}\text{O}_2$ ($0 < x < 1$), LiFePO_4 , MoS_2 , SnS_2 , MoO_3 , or V_2O_5 , more preferably a lithium-containing transition metal oxide.
- [0073] The negative electrode of the present invention is preferably prepared according to the following method:
- [0074] mixing a negative electrode active material, a conductive agent, a binder, and a solvent to prepare a negative electrode active material composition;
- [0075] directly coating the negative electrode material composition on a Cu current collector and drying to prepare a negative electrode plate.
- [0076] The negative electrode active material can be metallic lithium, a lithium alloy, a lithium titanate material capable of doping and dedoping lithium ions, a carbon material capable of doping and dedoping lithium ions, tin oxide, niobium oxide, vanadium oxide, or titanium oxide capable of doping and dedoping lithium ions; or silicon capable of doping and dedoping lithium ions.
- [0077] Among the above negative electrode active materials, a carbon material capable of doping and dedoping lithium ions is preferred. The carbon material is preferably graphite or amorphous carbon, more preferably activated carbon, carbon fiber, carbon black, or natural graphite.
- [0078] In the present invention, the conductive agent for the positive electrode active material or the negative electrode active material is preferably carbon black; the binder for the positive electrode active material or the negative electrode active material can be selected from a vinylidene fluoride/hexafluoropropylene copolymer, polyvinylidene fluoride (PVDF), polyacrylonitrile, polymethyl methacrylate, polytetrafluoroethylene and mixtures thereof, or a

styrene-butadiene rubber-based polymer; the solvent for the positive electrode active material or the negative electrode active material can be selected from N-methylpyrrolidone (NMP), acetone, water, etc.

[0079] In the present invention, the amounts of the positive electrode active material, the negative electrode active material, the conductive agent, the binder, and the solvent can be those commonly used in the preparation of lithium-ion batteries.

[0080] In the present invention, the separator needs to have low resistance to the movement of ions of the electrolyte and good absorption capacity and wettability for the electrolyte. The separator is preferably a non-woven fabric or woven fabric of glass fiber, polyester, polyethylene, polytetrafluoroethylene, and combinations thereof. More preferably, it is a porous separator wound with polyethylene or polypropylene.

[0081] The present invention has no special limitation on the shape of the lithium secondary battery, which can be cylindrical, coin-shaped, or square. In the present invention, the shape of the battery has nothing to do with the basic structure, and design changes can be implemented according to the purpose.

[0082] The present invention uses difluorophosphate as an electrolyte salt in combination with a non-aqueous solvent to obtain a non-aqueous electrolyte, and the application of this non-aqueous electrolyte in a lithium secondary battery can improve the cycle retention rate of the lithium secondary battery.

[0083] The results show that the initial specific capacity of the lithium secondary battery provided by the present invention can be as high as $256 \text{ mAh}\cdot\text{g}^{-1}$, and the capacity retention rate of the lithium secondary battery after 500 charge-discharge cycles can be up to 89%.

[0084] In order to further understand the present invention, the non-aqueous electrolyte, the preparation method thereof, and the lithium secondary battery provided by the present invention will be described below with reference to examples, but the protection scope of the present invention is not limited by the following examples.

[0085] Examples 1 to 22

[0086] Examples 1 to 22 are specifically described, and the specific experimental operation steps are as follows: adding a fluoride salt, a compound having the structure of Formula I, and a non-aqueous solvent into a dry closed container protected by an inert gas, and mixing and stirring to form a suspension, then cooling to a low temperature (10°C), and introducing a certain amount of PF_5 gas at this temperature, then heating to 60°C to react for 12 hours. After the reaction is completed, cooling to room temperature, filtering to remove unreacted fluoride salt and other insoluble impurities, then removing the solvent by rotary evaporation, and then obtaining high-purity difluorophosphate through recrystallization, filtering to remove the recrystallization solvent (acetone: anhydrous ether = 1:4, v/v), drying the obtained crystals under reduced pressure at 80°C for 6 hours, weighing the obtained white powder, and calculating the yield. The results are shown in Table 1 for the reaction conditions and results of Examples 1 to 22.

[0087] As Examples 1 to 22, each example was reacted according to the combination of experimental conditions described in Table 1 below to prepare a difluorophosphate. In addition, evaluations regarding each example were performed, and the results are also shown in Table 1.

[0088] The solid obtained by drying under reduced pressure was analyzed by ion chromatography, and it was confirmed that the main product was difluorophosphate, and its purity was determined. The results are shown in Table 1.

[0089] The difluorophosphate was dissolved in deionized water at a concentration of 1 mmol/L, and then subjected to ion chromatography analysis according to the EPA 300.1 detection standard. In the ion chromatography, an ICS-3000 from DIONEX Corporation was used as the chromatographic column.

[0090] Gas chromatography was used to monitor the concentration of the compound having the structure of Formula I in the reaction system to determine the end point of the reaction. In the gas chromatography, a TC-1 (inner diameter $0.32 \text{ mm} \times 30 \text{ m} \times$ film thickness $0.25 \mu\text{m}$) from GL Science Corporation was used as the chromatographic column, and the measurement was performed by raising the temperature from 40°C at a heating rate of 5°C per minute.

[0091] The concentration of protonic acid (lithium hexafluorophosphate) in the reaction system was determined by an acid-base titration method. Assuming that all of the protonic acid is HF, the remaining concentration obtained by subtracting the concentration of the protonic acid from the concentration of the F anion was defined as the F anion concentration. The reaction liquid was analyzed by ion chromatography and an acid-base titration method to analyze the F anion concentration. The lower limit of the reliable quantitative value is $1.0 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$.

[0092] The difluorophosphate prepared in Example 8 was analyzed by ^{31}P -NMR and ^{19}F -NMR. The NMR was performed using deuterated DMSO as a solvent and TMS as a standard. The results are as follows:

[0093] ^{19}F -NMR (400 MHz; deuterated acetone solution):

[0094] -84.54 ppm (doublet, -83.33 ppm and -85.75 ppm respectively, coupling constant is 968 Hz);

[0095] ³¹P-NMR (202.61 MHz; deuterated acetone solution):

[0096] -18.00 ppm (triplet, -12.30 ppm, -18.00 ppm and -23.71 ppm respectively; coupling constant is 1155 Hz).

[0097] In addition, the following results were confirmed by the above NMR and the above gas chromatography: since there were no peaks determined to be derived from theoretically generated by-products and products other than these by-products, no impurities were detected.

[0098] Table 1 Reaction conditions and results of Examples 1 to 22

[0099]

	Fluoride salt		Solvent		Compound having the structure of Formula I		Phosphorus pentafluoride/mol	Reaction temperature/°C	Reaction time/h	Difluorophosphate		
	Type	Added amount g/mol	Type	Added amount ml	Type	Added amount g/mol				Product	Yield/%	Purity/%

[0100]

Example 1	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Lithium difluorophosphate	92.8	99.5
Example 2	Lithium fluoride	25.9/1	Diethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Lithium difluorophosphate	93.1	99.1
Example 3	Lithium fluoride	25.9/1	Triethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Lithium difluorophosphate	90.5	99.4
Example 4	Lithium fluoride	25.9/1	Acetone	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Lithium difluorophosphate	88.5	98.9
Example 5	Lithium fluoride	25.9/1	Propylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Lithium difluorophosphate	91.7	99.0
Example 6	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Octamethyltrisiloxane	260.2/1.1	1.1	60	12	Lithium difluorophosphate	93.5	99.5
Example 7	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Decamethyltetrasiloxane	227.8/0.73	1.1	60	12	Lithium difluorophosphate	90.8	99.4
Example 8	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Octamethylcyclotetrasiloxane	163.1/0.55	1.1	60	12	Lithium difluorophosphate	93.7	99.8
Example 9	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Hexamethylcyclotrisiloxane	244.7/1.1	1.1	60	12	Lithium difluorophosphate	91.9	99.6
Example 10	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Octaphenylcyclotetrasiloxane	436.2/0.55	1.1	60	12	Lithium difluorophosphate	89.1	99.1
Example 11	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Hexaphenylcyclotrisiloxane	654.3/1.1	1.1	60	12	Lithium difluorophosphate	89.5	99.0

[0101]

Example 12	Lithium fluoride	25.9/1	Ethylene glycol dimethyl ether	400	Trifluoropropylmethylcyclotrisiloxane	515.4/1.1	1.1	60	12	Lithium difluorophosphate	90.3	99.3
Example 13	Sodium fluoride	42.0/1	Ethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Sodium difluorophosphate	94.5	99.7
Example 14	Potassium fluoride	58.1/1	Ethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Potassium difluorophosphate	95.1	99.8
Example 15	Ammonium fluoride	37.1/1	Ethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Ammonium difluorophosphate	94.1	97.8
Example 16	Sodium fluoride	42.0/1	Ethylene glycol dimethyl ether	400	Octamethylcyclotetrasiloxane	163.1/0.55	1.1	60	12	Sodium difluorophosphate	95.3	99.8
Example 17	Potassium fluoride	58.1/1	Ethylene glycol dimethyl ether	400	Octamethylcyclotetrasiloxane	163.1/0.55	1.1	60	12	Potassium difluorophosphate	96.1	99.9
Example 18	Ammonium fluoride	37.1/1	Ethylene glycol dimethyl ether	400	Octamethylcyclotetrasiloxane	163.1/0.55	1.1	60	12	Ammonium difluorophosphate	93.9	97.9
Example 19	Potassium fluoride	58.1/1	Ethylene glycol dimethyl ether	400	Octaphenylcyclotetrasiloxane	436.2/0.55	1.1	60	12	Potassium difluorophosphate	91.5	98.8
Example 20	Potassium fluoride	58.1/1	Ethylene glycol dimethyl ether	400	Trifluoropropylmethylcyclotrisiloxane	515.4/1.1	1.1	60	12	Potassium difluorophosphate	92.1	99.6
Example 21	Calcium fluoride	78.1/1	Ethylene glycol dimethyl ether	400	Hexamethyldisiloxane	357.3/2.2	1.1	60	12	Calcium difluorophosphate	85.0	98.2
Example 22	Calcium fluoride	78.1/1	Ethylene glycol dimethyl ether	400	Octamethylcyclotetrasiloxane	163.1/0.55	1.1	60	12	Calcium difluorophosphate	86.0	97.7

[0102] From the results shown in Table 1 above, it can be seen that in Examples 1 to 22 using the preparation method of the difluorophosphate of the present invention, high-purity difluorophosphate can be obtained with a very high recovery rate by reacting under mild conditions for a relatively short time, using a fluoride salt, a compound having a specific structure, and phosphorus pentafluoride as raw materials.

[0103] Examples 23 to 204 and Comparative Examples 1 to 7

[0104] Preparation of Electrolyte

[0105] A valve, a thermometer, a pressure gauge, and a safety valve were installed on the lid of a SUS316L sealed container with a nominal volume of 1 L (actual volume 1.3 L) to serve as a reaction apparatus. After the reaction apparatus was sufficiently dried, it was placed in a glove box filled with an inert gas (nitrogen, argon, helium, etc.). The difluorophosphate, non-aqueous solvent, and functional additive were added to the reaction tank apparatus, and a stirring bar for a magnetic stirrer was placed therein. The lid was closed and sealed in this state, and the lithium salt was dissolved. Table 2 shows the formulated electrolyte formulations.

[0106] Table 2 Formulations of non-aqueous electrolytes containing difluorophosphate

[0107]

	Difluorophosphate		Other alkali metal salt		Non-aqueous solvent		Other additives	
	Type	Concentration/mol	Type	Concentration/mol	Type	Ratio v/v	Type	Content/%
Electrolyte 1	Li	1	-	-	DME	1	-	-
Electrolyte 2	Li	1	-	-	DDME	1	-	-
Electrolyte 3	Li	1	-	-	TDME	1	-	-
Electrolyte 4	Li	1	-	-	DME:DDME	1:1	-	-
Electrolyte 5	Li	1	-	-	DME:DDME:TDME	1:1:1	-	-
Electrolyte 6	Li	1.5	-	-	DME:DDME	1:1	-	-
Electrolyte 7	Li	2.0	-	-	DME:DDME	1:1	-	-
Electrolyte 8	Li	2.5	-	-	DME:DDME	1:1	-	-
Electrolyte 9	Li	1	-	-	DME:PC	9:1	-	-
Electrolyte 10	Li	0.9	LiPF ₆	0.1	DME:PC	9:1	-	-
Electrolyte 11	Li	0.8	LiPF ₆	0.2	DME:PC	9:1	-	-
Electrolyte 12	Li	0.7	LiPF ₆	0.3	DME:PC	9:1	-	-

[0108]

Electrolyte 14	Li	0.9	LiFSI	0.1	DME:PC	9:1	-	-
Electrolyte 15	Li	1	-	-	DME:EC	2:1	-	-
Electrolyte 16	Li	1	-	-	DME:EC	1:1	-	-
Electrolyte 17	Li	0.9	LiFSI	0.1	DME:EC	9:1	-	-
Electrolyte 18	Li	0.9	LiFSI	0.1	DME:EC	4:1	-	-
Electrolyte 19	Li	0.9	LiFSI	0.1	DME:EC	2:1	-	-
Electrolyte 20	Li	0.9	LiFSI	0.1	DME:EC	1:1	-	-
Electrolyte 21	Li	1	-	-	DME:AN	2:1	-	-
Electrolyte 22	Li	1.5	-	-	DME:AN	2:1	-	-
Electrolyte 23	Li	2.5	-	-	DME:AN	2:1	-	-
Electrolyte 24	Li	1	-	-	DME:DMSO	4:1	-	-
Electrolyte 25	Li	1.5	-	-	DME:DMSO	4:1	-	-
Electrolyte 26	Li	2.5	-	-	DME:DMSO	4:1	-	-

[0109] Table 2 (Continued) Formulations of non-aqueous electrolytes containing difluorophosphate

[0110]

	Difluorophosphate		Other alkali metal salt		Non-aqueous solvent		Other additives	
	Type	Concentration/mol	Type	Concentration/mol	Type	Ratio v/v	Type	Content/%
Electrolyte 27	Li	0.9	LiPF ₆	0.1	DME:AN	2:1	-	-
Electrolyte 28	Li	0.9	LiTFSI	0.1	DME:AN	2:1	-	-
Electrolyte 29	Li	0.9	LiFSI	0.1	DME:AN	2:1	-	-

[0111]

Electrolyte 30	Li	0.9	LiBOB	0.1	DME:AN	2:1	-	-
Electrolyte 31	Li	0.5	LiPF ₆	0.5	DME:DDME:TDME	1:1:1	-	-
Electrolyte 32	Li	0.9	LiPF ₆	0.1	DME:DDME	1:1	-	-
Electrolyte 33	Li	0.9	LiBOB	0.1	DME:DDME	1:1	-	-
Electrolyte 34	Li	0.9	LiODFB	0.1	DME:DDME	1:1	-	-
Electrolyte 35	Li	1	-	-	DME:DDME	1:1	BDN	5
Electrolyte 36	Li	1	-	-	DME:DDME	1:1	PDN	5
Electrolyte 37	Li	1	-	-	DME:DDME	1:1	SN	5
Electrolyte 38	Li	1	-	-	DME:DDME	1:1	AN	2
Electrolyte 39	Li	1	-	-	DME:DDME	1:1	ACN	1
Electrolyte 40	Li	1	-	-	DME:DDME	1:1	-BL	2
Electrolyte 41	Li	1	-	-	DME:DDME	1:1	PS	1
Electrolyte 42	Li	1	-	-	DME:DDME	1:1	ES	1
Electrolyte 43	Na	1	LiPF ₆	0.1	DME:DDME	1:1	-	-
Electrolyte 44	K	1	LiPF ₆	0.1	DME:DDME	1:1	-	-
Electrolyte 45	Ca	1	LiPF ₆	0.1	DME:DDME	1:1	-	-
Electrolyte A	-	-	LiPF ₆	1	EC:EMC:DMC	1:1:1	-	-
Electrolyte B	-	-	LiPF ₆	1.2	EC:DMC	3:7	-	-

[0112]

Electrolyte C	-	-	LiPF ₆	1	EC:DMC	3:7	-	-
Electrolyte D	-	-	LiPF ₆	1	EC:EMC	3:7	-	-
Electrolyte E	-	-	LiPF ₆	1.2	EC:EMC	3:7	-	-

[0113] Fabrication and Assembly of Secondary Batteries

[0114] Fabrication and Assembly of Secondary Battery 1

[0115] Fabrication of positive electrode 1: 90% of lithium cobaltate (LiCoO₂) as a positive electrode active material, 5% of acetylene black as a conductive material, and 5% of polyvinylidene fluoride (PVdF) as a binder were mixed in an N-methylpyrrolidone solvent to prepare a slurry. The obtained slurry was coated on both sides of an aluminum foil having a thickness of 15 μm, dried, and rolled with a press machine to a thickness of 80 μm, and then cut into a shape having an active material layer with a width of 100 mm and a length of 100 mm and an uncoated portion with a width of 30 mm to serve as a positive electrode.

[0116] Fabrication of negative electrode 1: 100 parts by weight of an aqueous dispersion of sodium carboxymethyl cellulose as a thickener (the concentration of sodium carboxymethyl cellulose was 1%) and 2 parts by weight of an aqueous dispersion of styrene-butadiene rubber as a binder (the concentration of styrene-butadiene rubber was 50%) were added to 98 parts by weight of an artificial graphite powder KS-44, and mixed with a disperser to prepare a slurry. The obtained slurry was coated on both sides of a copper foil having a thickness of 10 μm, dried, and rolled with a press machine to a thickness of 75 μm, and then cut into a shape having an active material layer with a width of 104 mm and a length of 104 mm and an uncoated portion with a width of 30 mm to serve as a negative electrode.

[0117] Assembly of secondary battery 1: The positive electrode and the negative electrode were overlapped and wound together with a polyethylene separator so that the positive electrode and the negative electrode were not in direct contact with each other, to prepare an electrode body. The terminals of the positive electrode and the negative electrode were housed in a battery can such that they were exposed to the outside. Then, 5 mL of the electrolyte described later was injected therein, followed by riveting and molding to prepare a 18650-type cylindrical battery, which was designated as secondary battery 1.

[0118] Fabrication and Assembly of Secondary Battery 2

[0119] A battery was fabricated in the same manner as secondary battery 1, except that lithium nickel manganese cobaltate (LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂) was used instead of lithium cobaltate as the positive electrode active material, and the charging voltage was set to 4.30 V, which was designated as secondary battery 2.

[0120] Fabrication and Assembly of Secondary Battery 3

[0121] A battery was fabricated in the same manner as secondary battery 1, except that lithium iron phosphate (LiFePO₄) was used instead of lithium cobaltate as the positive electrode active material, and the charging voltage was set to 4.20 V, which was designated as secondary battery 3.

[0122] Fabrication and Assembly of Secondary Battery 4

[0123] 73.2 parts by weight of silicon and 8.1 parts by weight of copper as non-carbon materials, and 12.2 parts by weight of artificial graphite powder (trade name "KS-6" manufactured by Timcal Corporation) were used as a negative electrode active material. 54.2 parts by weight of an N-methylpyrrolidone solution containing 12 parts by weight of poly(vinylidene fluoride) (hereinafter abbreviated as "PVDF") and 50 parts by weight of N-methylpyrrolidone were added thereto, and mixed with a disperser to prepare a slurry. The obtained slurry was uniformly coated on a copper foil having a thickness of 18 μm as a negative electrode current collector, naturally dried, and finally dried under reduced pressure at 85°C for 24 hours. Then, it was pressed so that the electrode density was about 1.5 g·cm⁻³, and punched into a disk shape with a diameter of 12.5 mm to prepare a negative electrode (silicon alloy negative electrode). Except for this, a battery was fabricated in the same manner as secondary battery 1, which was designated as secondary battery 4.

[0124] Fabrication and Assembly of Secondary Battery 5

[0125] 90 parts by weight of a negative electrode active material (Li_{4/3}Ti_{5/3}O₄), 5% of acetylene black as a conductive material, and 5% of polyvinylidene fluoride (PVDF) as a binder were mixed in an N-methylpyrrolidone solvent to prepare a slurry. The obtained slurry was coated on one side of a rolled copper foil having a thickness of 10 μm, dried,

and rolled with a press machine to a thickness of 90 μm , and then cut into a shape having an active material layer with a width of 104 mm and a length of 104 mm and an uncoated portion with a width of 30 mm to serve as a negative electrode. Except for this, a battery was fabricated in the same manner as secondary battery 1, which was designated as secondary battery 5.

[0126] Fabrication and Assembly of Secondary Battery 6

[0127] Except that lithium nickel manganese cobaltate ($\text{Li}_{1.2}\text{Ni}_{1/6}\text{Mn}_{1/6}\text{Co}_{4/6}\text{O}_2$) was used instead of lithium cobaltate as the positive electrode active material, and the charging voltage was set to 4.8 V. Except for this, a battery was fabricated in the same manner as secondary battery 1, which was designated as secondary battery 6.

[0128] Fabrication and Assembly of Secondary Battery 7

[0129] Except that lithium nickel manganese cobaltate ($\text{Li}_{1.2}\text{Ni}_{1/6}\text{Mn}_{1/6}\text{Co}_{4/6}\text{O}_2$) was used instead of lithium cobaltate as the positive electrode active material, and the charging voltage was set to 3.45 V. Except for this, a battery was fabricated in the same manner as secondary battery 5, which was designated as secondary battery 7.

[0130] Examples 23 to 204 and Comparative Examples 1 to 7

[0131] As Examples 23 to 204 and Comparative Examples 1 to 7, experiments were performed according to the combinations of experimental conditions (types of electrolyte and secondary battery) shown in Table 2 and Table 3 for each example/comparative example, and the evaluation items described below were evaluated. The results are also shown in Table 3.

[0132] Evaluation of Secondary Batteries

[0133] The evaluation of the secondary batteries was performed under the following conditions for each battery.

[0134] Evaluation of Secondary Battery 1

[0135] Cycle Retention Rate

[0136] Initial charge and discharge: The battery was charged to 4.3 V by a constant current constant voltage charging method at 0.2 C at 25°C, and then discharged to 3.0 V at a constant current of 0.2 C. This was subjected to 5 cycles to stabilize the battery. The discharge capacity at the 5th cycle at this time was taken as the initial capacity. Moreover, the current value of the 1-hour discharge rated capacity was taken as 1 C.

[0137] Cycle test: The battery subjected to the initial charge and discharge was subjected to 500 cycles of charge and discharge at 60°C as follows: charging to 4.3 V at a constant current constant voltage of 1 C, and then discharging to 3.0 V at a constant current of 1 C. The ratio of the discharge capacity at the 500th cycle to the discharge capacity at the 1st cycle at this time was taken as the cycle retention rate.

[0138] Evaluation of Secondary Battery 2

[0139] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner.

[0140] Evaluation of Secondary Battery 3

[0141] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner, except that the charging voltage in each test was changed from 4.3 V to 4.2 V, and the discharge voltage was changed from 3.0 V to 2.5 V.

[0142] Evaluation of Secondary Battery 4

[0143] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner, except that the discharge voltage in each test was changed from 3.0 V to 2.5 V.

[0144] Evaluation of Secondary Battery 5

[0145] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner, except that the charging voltage in each test was changed from 4.3 V to 2.7 V, and the discharge voltage was changed from 3.0 V to 1.9 V.

[0146] Evaluation of Secondary Battery 6

[0147] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner, except that the charging voltage in each test was changed from 4.3 V to 4.8 V, and the discharge voltage was changed from 3.0 V to 1 V.

[0148] Evaluation of Secondary Battery 7

[0149] The same items as in the evaluation of secondary battery 1 were evaluated in the same manner, except that the charging voltage in each test was changed from 4.3 V to 3.45 V, and the discharge voltage was changed from 3.0 V to 0.5 V.

[0150] Table 3 Performance measurement of secondary batteries

[0151]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 23	Electrolyte 1	Secondary battery 1	155	67
Example 24	Electrolyte 2	Secondary battery 1	155	68
Example 25	Electrolyte 3	Secondary battery 1	155	67
Example 26	Electrolyte 4	Secondary battery 1	155	66
Example 27	Electrolyte 5	Secondary battery 1	155	65
Example 28	Electrolyte 6	Secondary battery 1	154	68
Example 29	Electrolyte 7	Secondary battery 1	154	67
Example 30	Electrolyte 8	Secondary battery 1	155	67
Comparative Example 1	Electrolyte A	Secondary battery 1	155	65
Example 31	Electrolyte 9	Secondary battery 1	155	67
Example 32	Electrolyte 10	Secondary battery 1	157	69
Example 33	Electrolyte 11	Secondary battery 1	157	70
Example 34	Electrolyte 12	Secondary battery 1	158	71

[0152]

Example 35	Electrolyte 13	Secondary battery 1	158	72
Example 36	Electrolyte 14	Secondary battery 1	158	78
Example 37	Electrolyte 15	Secondary battery 1	155	69
Example 38	Electrolyte 16	Secondary battery 1	157	71
Example 39	Electrolyte 17	Secondary battery 1	158	79
Example 40	Electrolyte 18	Secondary battery 1	159	81
Example 41	Electrolyte 19	Secondary battery 1	156	80
Example 42	Electrolyte 20	Secondary battery 1	157	80
Example 43	Electrolyte 21	Secondary battery 1	156	78

[0153] Table 3 [Continued]

[0154]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 44	Electrolyte 22	Secondary battery 1	156	77
Example 45	Electrolyte 23	Secondary battery 1	157	76
Example 46	Electrolyte 24	Secondary battery 1	156	76
Example 47	Electrolyte 25	Secondary battery 1	156	76
Example 48	Electrolyte 26	Secondary battery 1	156	75
Example 49	Electrolyte 27	Secondary battery 1	156	74
Example 50	Electrolyte 28	Secondary battery 1	156	80
Example 51	Electrolyte 29	Secondary battery 1	157	81
Example 52	Electrolyte 30	Secondary battery 1	157	82
Example 53	Electrolyte 31	Secondary battery 1	156	85
Example 54	Electrolyte 32	Secondary battery 1	156	86
Example 55	Electrolyte 33	Secondary battery 1	156	87
Example 56	Electrolyte 34	Secondary battery 1	156	87

[0155]

Example 57	Electrolyte 35	Secondary battery 1	156	89
Example 58	Electrolyte 36	Secondary battery 1	156	88
Example 59	Electrolyte 37	Secondary battery 1	156	85
Example 60	Electrolyte 38	Secondary battery 1	156	81
Example 61	Electrolyte 39	Secondary battery 1	156	82
Example 62	Electrolyte 40	Secondary battery 1	156	87
Example 63	Electrolyte 41	Secondary battery 1	156	85
Example 64	Electrolyte 42	Secondary battery 1	156	85

[0156] Table 3 [Continued]

[0157]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 65	Electrolyte 43	Secondary battery 1	156	67
Example 66	Electrolyte 44	Secondary battery 1	156	65
Example 67	Electrolyte 45	Secondary battery 1	156	63
Example 68	Electrolyte 9	Secondary battery 2	160	71
Example 69	Electrolyte 10	Secondary battery 2	160	72
Example 70	Electrolyte 11	Secondary battery 2	160	70
Example 71	Electrolyte 12	Secondary battery 2	160	77
Example 72	Electrolyte 13	Secondary battery 2	160	72
Example 73	Electrolyte 14	Secondary battery 2	161	73
Example 74	Electrolyte 15	Secondary battery 2	161	68
Example 75	Electrolyte 16	Secondary battery 2	161	69
Example 76	Electrolyte 17	Secondary battery 2	161	68
Example 77	Electrolyte 18	Secondary battery 2	161	67

[0158]

Example 78	Electrolyte 19	Secondary battery 2	162	66
Example 79	Electrolyte 20	Secondary battery 2	161	67
Example 80	Electrolyte 21	Secondary battery 2	161	59
Example 81	Electrolyte 22	Secondary battery 2	162	61
Example 82	Electrolyte 23	Secondary battery 2	160	62
Example 83	Electrolyte 24	Secondary battery 2	161	61
Example 84	Electrolyte 25	Secondary battery 2	161	60

[0159] Table 3 [Continued]

[0160]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 85	Electrolyte 26	Secondary battery 2	161	59
Example 86	Electrolyte 27	Secondary battery 2	161	60
Example 87	Electrolyte 28	Secondary battery 2	161	58
Example 88	Electrolyte 29	Secondary battery 2	161	58
Example 89	Electrolyte 30	Secondary battery 2	161	60
Example 90	Electrolyte 31	Secondary battery 2	161	72
Example 91	Electrolyte 32	Secondary battery 2	161	78
Example 92	Electrolyte 33	Secondary battery 2	161	80
Example 93	Electrolyte 34	Secondary battery 2	161	81
Example 94	Electrolyte 35	Secondary battery 2	161	83
Example 95	Electrolyte 36	Secondary battery 2	161	81
Example 96	Electrolyte 37	Secondary battery 2	161	84
Example 97	Electrolyte 38	Secondary battery 2	161	80
Example 98	Electrolyte 39	Secondary battery 2	160	81

[0161]

Example 99	Electrolyte 40	Secondary battery 2	160	85
Example 100	Electrolyte 41	Secondary battery 2	159	86
Example 101	Electrolyte 42	Secondary battery 2	160	84
Example 102	Electrolyte 43	Secondary battery 2	160	75
Example 103	Electrolyte 43	Secondary battery 2	161	74
Example 104	Electrolyte 44	Secondary battery 2	160	77
Comparative Example 2	Electrolyte B	Secondary battery 2	162	75

[0162] Table 3 [Continued]

[0163]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 105	Electrolyte 2	Secondary battery 3	166	59
Example 106	Electrolyte 4	Secondary battery 3	166	60
Example 107	Electrolyte 5	Secondary battery 3	166	58
Example 108	Electrolyte 10	Secondary battery 3	166	58
Example 109	Electrolyte 17	Secondary battery 3	165	61
Example 110	Electrolyte 18	Secondary battery 3	165	60
Example 111	Electrolyte 19	Secondary battery 3	167	63
Example 112	Electrolyte 20	Secondary battery 3	167	61
Example 113	Electrolyte 21	Secondary battery 3	167	62
Example 114	Electrolyte 24	Secondary battery 3	167	63
Example 115	Electrolyte 27	Secondary battery 3	167	61
Example 116	Electrolyte 31	Secondary battery 3	167	64
Example 117	Electrolyte 34	Secondary battery 3	167	60
Example 118	Electrolyte 35	Secondary battery 3	167	61

[0164]

Example 119	Electrolyte 38	Secondary battery 3	167	60
Example 120	Electrolyte 39	Secondary battery 3	166	59
Example 121	Electrolyte 41	Secondary battery 3	167	66
Example 122	Electrolyte 42	Secondary battery 3	167	65
Example 123	Electrolyte 43	Secondary battery 3	167	58
Example 124	Electrolyte 44	Secondary battery 3	167	57
Comparative Example 3	Electrolyte C	Secondary battery 3	167	59

[0165] Table 3 [Continued]

[0166]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 125	Electrolyte 2	Secondary battery 4	155	59
Example 126	Electrolyte 4	Secondary battery 4	155	60
Example 127	Electrolyte 5	Secondary battery 4	156	58
Example 128	Electrolyte 10	Secondary battery 4	156	58
Example 129	Electrolyte 17	Secondary battery 4	155	61
Example 130	Electrolyte 18	Secondary battery 4	155	62
Example 131	Electrolyte 19	Secondary battery 4	155	68
Example 132	Electrolyte 20	Secondary battery 4	155	60
Example 133	Electrolyte 21	Secondary battery 4	155	61
Example 134	Electrolyte 24	Secondary battery 4	155	63
Example 135	Electrolyte 27	Secondary battery 4	155	61
Example 136	Electrolyte 31	Secondary battery 4	155	64
Example 137	Electrolyte 34	Secondary battery 4	155	60
Example 138	Electrolyte 35	Secondary battery 4	155	61

[0167]

Example 139	Electrolyte 38	Secondary battery 4	155	65
Example 140	Electrolyte 39	Secondary battery 4	155	66
Example 141	Electrolyte 41	Secondary battery 4	155	64
Example 142	Electrolyte 42	Secondary battery 4	155	65
Example 143	Electrolyte 43	Secondary battery 4	155	64
Example 144	Electrolyte 44	Secondary battery 4	155	63
Comparative Example 4	Electrolyte D	Secondary battery 4	155	65

[0168] Table 3 [Continued]

[0169]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 145	Electrolyte 2	Secondary battery 5	161	83
Example 146	Electrolyte 4	Secondary battery 5	161	80
Example 147	Electrolyte 5	Secondary battery 5	161	88
Example 148	Electrolyte 10	Secondary battery 5	161	88
Example 149	Electrolyte 17	Secondary battery 5	161	80
Example 150	Electrolyte 18	Secondary battery 5	162	82
Example 151	Electrolyte 19	Secondary battery 5	161	88
Example 152	Electrolyte 20	Secondary battery 5	161	80
Example 153	Electrolyte 21	Secondary battery 5	161	81
Example 154	Electrolyte 24	Secondary battery 5	161	83
Example 155	Electrolyte 27	Secondary battery 5	161	87
Example 156	Electrolyte 31	Secondary battery 5	161	84
Example 157	Electrolyte 34	Secondary battery 5	161	85
Example 158	Electrolyte 35	Secondary battery 5	161	87

[0170]

Example 159	Electrolyte 38	Secondary battery 5	160	82
Example 160	Electrolyte 39	Secondary battery 5	159	81
Example 161	Electrolyte 41	Secondary battery 5	160	84
Example 162	Electrolyte 42	Secondary battery 5	161	85
Example 163	Electrolyte 43	Secondary battery 5	161	84
Example 164	Electrolyte 44	Secondary battery 5	160	82
Comparative Example 5	Electrolyte D	Secondary battery 5	162	73

[0171] Table 3 [Continued]

[0172]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 165	Electrolyte 2	Secondary battery 6	255	65
Example 166	Electrolyte 4	Secondary battery 6	255	66
Example 167	Electrolyte 5	Secondary battery 6	255	68
Example 168	Electrolyte 10	Secondary battery 6	255	77
Example 169	Electrolyte 17	Secondary battery 6	255	72
Example 170	Electrolyte 18	Secondary battery 5	255	71
Example 171	Electrolyte 19	Secondary battery 6	256	75
Example 172	Electrolyte 20	Secondary battery 6	256	70
Example 173	Electrolyte 21	Secondary battery 6	256	74
Example 174	Electrolyte 24	Secondary battery 6	256	73
Example 175	Electrolyte 27	Secondary battery 6	255	69
Example 176	Electrolyte 31	Secondary battery 6	255	74
Example 177	Electrolyte 34	Secondary battery 6	255	75
Example 178	Electrolyte 35	Secondary battery 6	255	77

[0173]

Example 179	Electrolyte 38	Secondary battery 6	255	72
Example 180	Electrolyte 39	Secondary battery 6	256	71
Example 181	Electrolyte 41	Secondary battery 6	255	74
Example 182	Electrolyte 42	Secondary battery 6	255	75
Example 183	Electrolyte 43	Secondary battery 6	255	73
Example 184	Electrolyte 44	Secondary battery 6	255	73
Comparative Example 6	Electrolyte E	Secondary battery 6	255	67

[0174] Table 3 [Continued]

[0175]

	Electrolyte	Battery	Initial specific capacity/mAh·g ⁻¹	Cycle retention rate /%
Example 185	Electrolyte 2	Secondary battery 7	251	82
Example 186	Electrolyte 4	Secondary battery 7	251	87
Example 187	Electrolyte 5	Secondary battery 7	251	85
Example 188	Electrolyte 10	Secondary battery 7	251	85
Example 189	Electrolyte 17	Secondary battery 7	249	81
Example 190	Electrolyte 18	Secondary battery 7	251	81
Example 191	Electrolyte 19	Secondary battery 7	251	85
Example 192	Electrolyte 20	Secondary battery 7	250	83
Example 193	Electrolyte 21	Secondary battery 7	251	82
Example 194	Electrolyte 24	Secondary battery 7	251	83
Example 195	Electrolyte 27	Secondary battery 7	250	81
Example 196	Electrolyte 31	Secondary battery 7	251	87
Example 197	Electrolyte 34	Secondary battery 7	251	88
Example 198	Electrolyte 35	Secondary battery 7	249	87

[0176]

Example 199	Electrolyte 38	Secondary battery 7	249	83
Example 200	Electrolyte 39	Secondary battery 7	249	82
Example 201	Electrolyte 41	Secondary battery 7	251	87
Example 202	Electrolyte 42	Secondary battery 7	251	83
Example 203	Electrolyte 43	Secondary battery 7	249	85
Example 204	Electrolyte 44	Secondary battery 7	248	83
Comparative Example 7	Electrolyte E	Secondary battery 7	249	68

[0177] From the results in Table 3, the following conclusions can be drawn:

[0178] First, comparing Examples 23 to 30 with Comparative Example 1, Examples 23 to 30 using the non-aqueous electrolyte of the present invention show a slight improvement in cycle retention rate compared with Comparative Example 1.

[0179] Comparing Examples 31 to 64 with Comparative Example 1, Examples 31 to 64 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 1.

[0180] In addition, comparing Examples 65 to 67 with Comparative Example 1, Examples 65 to 67 using the non-aqueous electrolyte of the present invention show a slight improvement in cycle retention rate compared with Comparative Example 1.

[0181] Furthermore, comparing Examples 68 to 79 with Comparative Example 2, in the case where a cyclic carbonate is added to the non-aqueous electrolyte, Examples 68 to 79 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 2.

[0182] Comparing Examples 80 to 89 with Comparative Example 2, in the case where acetonitrile or DMSO is added to the non-aqueous electrolyte, Examples 80 to 89 using the non-aqueous electrolyte of the present invention show a slight decrease in cycle retention rate compared with Comparative Example 2.

[0183] Comparing Examples 90 to 104 with Comparative Example 2, in the case where other alkali metal lithium salts or functional additives are added to the non-aqueous electrolyte, Examples 90 to 104 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 2.

[0184] Comparing Examples 105 to 124 with Comparative Example 3, in the case where other solvents, lithium salts, or other functional additives are added to the non-aqueous electrolyte, Examples 105 to 124 using the non-aqueous electrolyte of the present invention show a slight improvement in cycle retention rate compared with Comparative Example 3.

[0185] Comparing Examples 125 to 144 with Comparative Example 4, in the case where other solvents, lithium salts, or other functional additives are added to the non-aqueous electrolyte, Examples 125 to 144 using the non-aqueous electrolyte of the present invention show a comparable cycle retention rate compared with Comparative Example 4.

[0186] Comparing Examples 145 to 164 with Comparative Example 5, in the case where other solvents, lithium salts, or other functional additives are added to the non-aqueous electrolyte, Examples 145 to 164 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 5.

[0187] Comparing Examples 165 to 184 with Comparative Example 6, in the case where other solvents, lithium salts, or other functional additives are added to the non-aqueous electrolyte, Examples 165 to 184 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 6.

[0188] Comparing Examples 185 to 204 with Comparative Example 7, in the case where other solvents, lithium salts, or other functional additives are added to the non-aqueous electrolyte, Examples 185 to 204 using the non-aqueous electrolyte of the present invention show a significant improvement in cycle retention rate compared with Comparative Example 7.

[0189] From the above results, it can be seen that the non-aqueous electrolyte secondary battery using the non-aqueous electrolyte of the present invention is excellent in large-current discharge characteristics and cycle retention rate, and is also excellent in high-temperature storage characteristics and cycle characteristics.

[0190] The present invention can be preferably used in any field where difluorophosphates are used, such as catalysts for reaction lubricating oils, bactericides for toothbrushes, stabilizers for vinyl chloride polymers, and preservatives for wood. In addition, the present invention can also be preferably used in fields such as non-aqueous electrolyte secondary batteries.

[0191] The above descriptions are merely preferred embodiments of the present invention. It should be pointed out that for those of ordinary skill in the art, without departing from the principles of the present invention, several improvements and modifications can also be made, and these improvements and modifications should also be considered as falling within the protection scope of the present invention., and these improvements and modifications should also be considered as falling within the protection scope of the present invention.



DECLARATION OF TRANSLATOR

I, Zhang Zhihui, hereby declare as follows:

1. I personally performed the attached translation from Chinese into English of [Foreign Patent / Application Publication No. CN 105428720 A], published/issued 2016.03.23, and entitled "[一种非水电解液及其制备方法以及一种锂二次电池]" ("NON-AQUEOUS ELECTROLYTE, PREPARATION METHOD THEREOF, AND LITHIUM SECONDARY BATTERY").
2. The attached translation is, to the best of my knowledge, a true, full and accurate English translation of the above-identified Chinese-language document.
3. I am competent to perform this translation because I hold a Master of Translation and Interpreting (MTI) in English from Qufu Normal University, as well as a Level 2 Certificate in Written Translation from the China Accreditation Test for Translators and Interpreters (CATTI).
4. I declare under penalty of perjury under the laws of the United States that the foregoing is true and correct, and I further declare that I am aware that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of any patent or proceeding resulting therefrom.

Dated: June 11, 2026

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