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### **ELECTROLYTE FOR SECONDARY BATTERY, SECONDARY BATTERY, BATTERY MODULE, BATTERY PACK, AND ELECTRIC APPARATUS**

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#### **Abstract**

This application provides an electrolyte for secondary battery, a secondary battery, a battery module, a battery pack, and an electric apparatus. The electrolyte for secondary battery includes a fluoroether solvent and an additive, where the additive includes one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive. In this application, with one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive added in an electrolyte containing the fluoroether solvent, interface stability of the secondary battery is significantly enhanced, and the cycling performance, storage stability, and overall safety of the secondary battery are improved.

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## **Background/Summary**

CROSS-REFERENCE TO RELATED APPLICATION [0001] This application is a continuation application of the PCT Application PCT/CN2022/140702 filed on Dec. 21, 2022, which is incorporated herein by reference in the entirety.

### **TECHNICAL FIELD**

[0002] This application relates to the field of secondary battery technologies, and in particular, to an electrolyte for secondary battery, a secondary battery, a battery module, and an electric apparatus.

### **BACKGROUND**

[0003] In recent years, secondary batteries have been widely used in energy storage power supply systems such as hydroelectric, thermal, wind, and solar power plants, and many other fields including electric tools, electric bicycles, electric motorcycles, electric vehicles, military equipment, and aerospace. With the widespread application of secondary batteries, higher requirements are being placed on their energy density, cycling performance, and other characteristics.

[0004] The electrolyte serves as a medium for ion transfer between the positive and negative electrodes. As an essential component of a secondary battery, it plays a crucial role in the rate performance, cycle life, and safety of the secondary battery. Liquid electrolytes, commonly referred to as electrolytes, typically possess excellent ion conductivity, endowing batteries with excellent kinetic performance. However, electrolytes have high reactivity, and are particularly prone to side reactions with the metal negative electrode, which hinders the effective improvement in the cycling performance and storage performance of batteries. Therefore, there is a need to further optimize the composition of the electrolyte to provide an electrolyte with stable electrochemical properties while capable of enhancing the overall electrochemical performance of the secondary battery.

### **SUMMARY**

[0005] This application is carried out in view of the preceding subject with a purpose to provide an electrolyte for secondary battery. With one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive added in a fluoroether solvent, which is obtained by direct fluorine substitution of ether molecules, an electrolyte having stable electrochemical properties is provided. Secondary batteries prepared using this electrolyte exhibit improved interface stability, high-temperature performance, cycling performance, and storage stability.

[0006] A first aspect of this application provides an electrolyte for secondary battery, including a fluoroether solvent and an additive, where the additive includes one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive. In any embodiment, the fluoroether solvent is obtained by directly substituting hydrogen bonded to carbon of the corresponding ether molecules with fluorine.

[0007] In any embodiment, a cation of the ionic liquid additive includes one or more of nitrogen-

containing onium ion and phosphorus-containing onium ion; and an anion of the ionic liquid additive includes one or more of halogen ion, phosphate ion, borate ion, sulfonimide compound anion, and sulfonylamide compound anion.

[0008] With one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive added in an electrolyte containing the fluoroether solvent, interface stability of the secondary battery can be significantly improved, and the cycling performance, storage stability, and overall safety of the secondary battery are enhanced.

[0009] In any embodiment, the cation of the ionic liquid additive includes one or more of 1-butyl-3-methylimidazolium, 1-benzyl-3-methylimidazolium, 3-methyl-1-ethoxycarbonylmethylimidazolium, 1-alkyl-3-methylimidazolium, 1-[(trimethylsilyl)methyl]benzotriazolium, N-alkyl-N-methylpiperidinium, 5-azoniumspiro[4.4]nonane, trihexyl(tetradecyl)phosphine ion, tetrabutylphosphine ion, and n-butyl-N-methylpyrrolidinium, and optionally 1-benzyl-3-methylimidazolium or 1-alkyl-3-methylimidazolium.

[0010] In any embodiment, the anion of the ionic liquid additive includes one or more of chloride ion, bromide ion, iodide ion, hexafluorophosphate, tetrafluoroborate, dicyandiamide anion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, and bis(trifluoromethylsulfonyl)imide anion, and optionally one or more of chloride ion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, and bis(trifluoromethylsulfonyl)imide anion.

[0011] In any embodiment, the ionic liquid additive includes one or more selected from 1-butyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-butyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-benzyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-benzyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-alkyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-chloride salt, and N-alkyl-N-methylpiperidine-tetrafluoroborate.

[0012] In any embodiment, the amide compound additive includes one or more of compounds represented by formula I, formula II, or formula III,

##STR00001## [0013] where R.sub.1 to R.sub.9 are each independently selected from hydrogen, silyl group, ketone carbonyl group, C.sub.1 to C.sub.3 alkyl group unsubstituted or substituted by at least one fluorine atom, and aryl group unsubstituted or substituted by at least one fluorine atom.

[0014] In any embodiment, the amide compound additive includes one or more of N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylacetoacetamide, 1,1,1-trifluoro-N,N-dimethylform sulfonamide, N,O-bis(trimethylsilyl)trifluoroacetamide, 2,3,6-trifluorobenzenesulfonamide, N,N-dimethyl-4-fluorobenzenesulfonamide, and N-methyl-N-trimethylsilane trifluoroacetamide.

[0015] In any embodiment, the cation shielding additive includes a salt whose cation is an alkali metal element or an alkaline earth metal element.

[0016] In any embodiment, the cation shielding additive includes one or more of lithium nitrate, lithium perchlorate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium bisoxaloborate, lithium difluoroxaloborate, lithium bis(fluorosulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide, potassium hexafluorophosphate, potassium bis-oxaloborate, potassium difluoro-oxaloborate, potassium bis(fluorosulfonyl)imide, potassium bis(trifluoromethylsulfonyl)imide, cesium nitrate, cesium hexafluorophosphate, cesium bis(fluorosulfonyl)imide, cesium chloride, cesium bromide, calcium nitrate, strontium nitrate, and barium nitrate.

[0017] In any embodiment, the alloy additive is a compound containing an element from family IVA or family VA.

[0018] In any embodiment, the alloy additive includes one or more of antimony trifluoride, antimony pentafluoride, tin difluoride, tin tetrafluoride, bismuth trichloride, and fumed silica.

[0019] In any embodiment, a mass percentage of the additive is 1-10% based on total mass of the electrolyte.

[0020] When the mass percentage of the additive is 1-10% based on the total mass of the electrolyte, a stable SEI film can be formed at the interface between the negative electrode and the electrolyte. In addition, an effective barrier can be constructed at the interface electric double layer to prevent the shuttle of certain ions and free radicals in the electrolyte and side reactions. This enhances the interface stability, cycling performance, and storage stability of the battery.

[0021] In any embodiment, the fluoroether solvent includes a compound represented by formula IV or a crown ether substituted by a fluorine atom,

##STR00002## [0022] where R.sub.7, R.sub.8, and R.sub.9 are each independently selected from hydrogen, and a straight-chain or branched-chain C.sub.1-C.sub.6 alkyl group unsubstituted or substituted by fluorine or a hydroxyl group, at least one of R.sub.7, R.sub.8, and R.sub.9 contains a fluorine atom, and R.sub.7 and R.sub.9 optionally are combined with oxygen to which R.sub.7 and R.sub.9 are connected and R.sub.8 connected to the oxygen, to generate a 5- or 6-membered saturated heterocyclic ring, where at least one hydrogen atom on the ring is substituted by fluorine or a fluoroalkyl group.

[0023] In any embodiment, the fluoroether solvent includes one or more of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane, 2-(2-ethoxyethoxy)-1,1,1-trifluoroethane, 1,2-bis(2,2-difluoroethoxy)ethane, 2-(2-(2,2-difluoroethoxy)ethoxy)-1,1,1-trifluoroethane, 1,2-bis(2,2,2-trifluoroethoxy)ethane, 1,1,1,3,3,3-hexafluoroisopropylmethyl ether, 2,2,2-trifluoroethyl-1,1,2,3,3,3-hexafluoropropyl ether, 2,2-bis(trifluoromethyl)-1,3-dioxolane, 2,2-dimethoxy-4-(Trifluoromethyl)-1,3-dioxopentane, 2-ethoxy-4-(trifluoromethyl)-1,3-dioxopentane, octafluorotetrahydrofuran, ethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol dimethyl ether substituted by at least one fluorine atom, triethylene glycol dimethyl ether substituted by at least one fluorine atom, tetraethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol diethyl ether substituted by at least one fluorine atom, diisopropyl ether substituted by at least one fluorine atom, dibutyl ether substituted by at least one fluorine atom, diethylene glycol dibutyl ether substituted by at least one fluorine atom, 1,4-diethoxybutane substituted by at least one fluorine atom, 15-crown ether-5 substituted by at least one fluorine atom, 12-crown ether-4 substituted by at least one fluorine atom, and 18-crown ether-6 substituted by at least one fluorine atom; and optionally at least one of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane, 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxopentane.

[0024] In any embodiment, a mass percentage of the fluoroether solvent is 20%-90% based on the total mass of the electrolyte.

[0025] In any embodiment, an electrolytic salt is a sodium salt, where the sodium salt includes one or more of sodium nitrate, sodium perchlorate, sodium hexafluorophosphate, sodium tetrafluoroborate, sodium tetrafluoroyttrate, sodium hexafluoroarsenate, sodium acetate, sodium trifluoroacetate, sodium bisoxaloborate, sodium difluoroxaloborate, tetrafluoroborate sodium phenylborate, sodium trifluoromethanesulfonate, sodium bis(fluorosulfonyl)imide, sodium bis(trifluoromethanesulfonyl)imide, and sodium (n-perfluorobutylsulfonyl)imide.

[0026] In any embodiment, a mass percentage of the electrolytic salt is 2%-70%, optionally 20%-70%, based on the total mass of the electrolyte.

[0027] When the mass percentage of the electrolytic salt is 2%-70% based on the total mass of the electrolyte, a stable SEI film can be formed at the interface between the negative electrode and the electrolyte. In addition, an effective barrier can be constructed at the interface electric double layer to prevent the shuttle of ions and free radicals and side reactions, enhancing the interface stability of the battery.

[0028] A second aspect of this application provides a secondary battery, including the electrolyte according to the first aspect.

[0029] In any embodiment, the secondary battery includes one or more of lithium metal battery and

sodium metal battery.

[0030] In any embodiment, the secondary battery is a sodium metal battery with no negative electrode.

[0031] In any embodiment, the secondary battery includes a positive electrode plate, where the positive electrode plate includes a positive electrode active material, and the positive electrode active material includes one or more of Prussian blue compound, polyanionic compound, and layered oxide.

[0032] In any embodiment, a surface of particles of the positive electrode active material is provided with a coating layer, where the coating layer includes one or more of carbon material (amorphous graphite, graphen), polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), aluminum oxide, zinc oxide, titanium oxide, zirconium oxide, magnesium oxide, silicon oxide, lanthanum oxide, sodium fluoride, lithium fluoride, and aluminum fluoride.

[0033] The coating layer on the surface of positive electrode active material particles can prevent the occurrence of side reactions caused by direct contact between the surface of positive metal and the electrolyte. It also suppresses the dissolution of transition metals from the positive electrode and enhances the stability of the electrode/electrolyte interface.

[0034] In any embodiment, the coating layer has a thickness of 2 nm-1000 nm.

[0035] In any embodiment, the secondary battery includes a negative electrode plate, where the negative electrode plate includes a negative electrode current collector and a primer layer provided on at least one surface of the negative electrode current collector, and the primer layer includes one or more of carbon nanotube, graphite, graphene, silver composite carbon nanoparticle, and tin composite carbon nanoparticle.

[0036] In any embodiment, the negative electrode current collector includes at least one of metal foil, metal foam current collector, metal mesh current collector, carbon felt current collector, carbon cloth current collector, carbon paper current collector, and composite current collector.

[0037] In any embodiment, the primer layer has an areal density of 2 g/m.<sup>2</sup>-50 g/m.<sup>2</sup>.

[0038] In any embodiment, the primer layer has a thickness of 1 μm-100 μm.

[0039] A third aspect of this application provides a battery module, including the secondary battery according to the second aspect.

[0040] A fourth aspect of this application provides a battery pack, including the secondary battery according to the second aspect or the battery module according to the third aspect.

[0041] A fifth aspect of this application provides an electric apparatus, including at least one of the secondary battery according to the second aspect, the battery module according to the third aspect, or the battery pack according to the fourth aspect.

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## Description

### BRIEF DESCRIPTION OF DRAWINGS

[0042] FIG. 1 is a schematic diagram of a secondary battery according to an embodiment of this application;

[0043] FIG. 2 is an exploded view of the secondary battery according to the embodiment of this application in FIG. 1;

[0044] FIG. 3 is a schematic diagram of a battery module according to an embodiment of this application;

[0045] FIG. 4 is a schematic diagram of a battery pack according to an embodiment of this application;

[0046] FIG. 5 is an exploded view of the battery pack according to the embodiment of this application in FIG. 4; and

[0047] FIG. 6 is a schematic diagram of an electric apparatus using a secondary battery as a power

source according to an embodiment of this application.

## REFERENCE SIGNS

[0048] **1.** battery pack; **2.** upper box body; **3.** lower box body; **4.** battery module; **5.** secondary battery; **51.** housing; **52.** electrode assembly; and **53.** cover plate.

## DESCRIPTION OF EMBODIMENTS

[0049] The following discloses in detail embodiments of the binder, preparation method thereof, electrode, battery, and electric apparatus of this application, with appropriate reference to the accompanying drawings. However, there may be cases where unnecessary detailed descriptions are omitted. For example, detailed descriptions of well-known matters and repeated descriptions of actually identical structures have been omitted. This is to avoid unnecessarily prolonging the following description, for ease of understanding by persons skilled in the art. In addition, the accompanying drawings and the following descriptions are provided for persons skilled in the art to fully understand this application and are not intended to limit the subject matter recorded in the claims.

[0050] “Ranges” disclosed in this application are defined in the form of lower and upper limits. A given range is defined by one lower limit and one upper limit selected, where the selected lower and upper limits define boundaries of that particular range. Ranges defined in this method may or may not include end values, and any combinations may be used, meaning any lower limit may be combined with any upper limit to form a range. For example, if ranges of 60-120 and 80-110 are provided for a specific parameter, it is understood that ranges of 60-110 and 80-120 can also be used. In addition, if minimum values of a range are given as 1 and 2, and maximum values of the range are given as 3, 4, and 5, the following ranges can be used: 1-3, 1-4, 1-5, 2-3, 2-4, and 2-5. In this application, unless otherwise stated, a value range of “a-b” is a short representation of any combination of real numbers between a and b, where both a and b are real numbers. For example, a value range of “0-5” means that all real numbers in the range of “0-5” are listed herein, and “0-5” is just a short representation of a combination of these values. In addition, a parameter expressed as an integer greater than or equal to 2 is equivalent to disclosure that the parameter is, for example, an integer among 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, and so on.

[0051] Unless otherwise specified, all the embodiments and optional embodiments of this application can be combined with each other to form new technical solutions.

[0052] Unless otherwise specified, all the technical features and optional technical features of this application can be combined with each other to form new technical solutions.

[0053] Unless otherwise specified, all the steps in this application can be performed in the order described or in random order, preferably, in the order described. For example, a method including steps (a) and (b) indicates that the method may include steps (a) and (b) performed in order or may include steps (b) and (a) performed in order. For example, the foregoing method may further include step (c), which indicates that step (c) may be added to the method in any ordinal position, for example, the method may include steps (a), (b), and (c), steps (a), (c), and (b), steps (c), (a), and (b), or the like.

[0054] Unless otherwise specified, “include” and “contain” mentioned in this application are inclusive or may be exclusive. For example, the terms “include” and “contain” can mean that other unlisted components may also be included or contained, or only listed components are included or contained.

[0055] Unless otherwise specified, in this application, the term “or” is inclusive. For example, the phrase “A or B” means “A, B, or both A and B”. More specifically, any one of the following conditions satisfies the condition “A or B”: A is true (or present) and B is false (or not present); A is false (or not present) and B is true (or present); or both A and B are true (or present).

[0056] Ether solvents are commonly used in electrolytes for secondary batteries. However, ether solvents cannot be paired with all positive electrode active materials, especially layered oxides with high energy density and high working potential. The applicant has fortuitously discovered that

fluorinated ether solvents, namely fluoroether solvents, can effectively increase the absolute value of highest occupied molecular orbital (value of HOMO) of ether compounds, widens the electrochemical stability window of the electrolyte, and is able to pair with positive electrode materials with high operating potential, thereby improving the operating voltage of the battery. However, the direct application of fluoroether solvents in secondary batteries, especially in batteries with no negative electrode, still faces challenges such as poor cycling and storage performances.

#### [Electrolyte for Secondary Battery]

[0057] Based on this, this application provides an electrolyte for secondary battery, where the electrolyte for secondary battery includes a fluoroether solvent and an additive, where the additive includes one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive.

[0058] In this document, “fluoroether solvent” is a solvent generated by directly fluorinating ether solvent molecules. Unlike typical fluoroether inert diluents, the fluoroether solvent in this application is used as the main solvent in the electrolyte.

[0059] In this document, the term “additive” refers to a component in the electrolyte that is present in a smaller quantity and may be a gas, liquid, or solid. Conceptually, the distinction among an additive, a main solvent, and an electrolytic salt lies in their different proportions in the electrolyte. A solvent or salt with a smaller proportion can be collectively referred to as an additive.

[0060] In this document, the term “ionic liquid additive” refers to a salt added to the electrolyte in a smaller proportion, fully consisting of cations and anions, and exhibiting a liquid state at or near room temperature. Room temperature refers to  $25^{\circ}\text{C} \pm 5^{\circ}\text{C}$ .

[0061] In this document, the term “amide compound additive” refers to a compound added to the electrolyte in a smaller proportion, containing

##STR00003##

group.

[0062] In this document, the term “cation shielding additive” refers to a salt added to the electrolyte in a smaller proportion, capable of ionizing into cations. These cations play a role in excluding shuttle ions and free radicals that cause side reactions at the double-layer interface of the negative electrode.

[0063] In this document, the term “alloy additive” refers to a compound added to the electrolyte in a smaller proportion, containing an element capable of generating an alloy, within the SEI film, with the metal cations in the electrolytic salt.

[0064] In some embodiments, the additive includes an ionic liquid additive. In some embodiments, the additive includes an amide compound additive. In some embodiments, the additive includes a cation shielding additive. In some embodiments, the additive includes an alloy additive. In some embodiments, the additive is a mixture of an ionic liquid additive and an amide compound additive. In some embodiments, the additive is a mixture of an ionic liquid additive and a cation shielding additive. In some embodiments, the additive is a mixture of an ionic liquid additive and an alloy additive. In some embodiments, the additive is a mixture of an amide compound additive and an alloy additive. In this application, with one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive added in an electrolyte containing the fluoroether solvent, the occurrence of side reactions between the metal negative electrode and the electrolyte and the generation of unstable and fragile solid electrolyte interface (SEI) film can be suppressed, thereby significantly enhancing the interface stability of the secondary battery, and improving the cycling performance, storage stability, and overall safety of the secondary battery.

[0065] In some embodiments, a cation of the ionic liquid additive includes one or more of nitrogen-containing onium ion and phosphorus-containing onium ion. An anion of the ionic liquid additive includes one or more of halogen ion, phosphate ion, borate ion, sulfonimide compound anion, and sulfonylamide compound anion.

[0066] In some embodiments, the cation of the ionic liquid additive includes one or more of 1-butyl-3-methylimidazolium, 1-benzyl-3-methylimidazolium, 3-methyl-1-ethoxycarbonylmethylimidazolium, 1-alkyl-3-methylimidazolium, 1-[(trimethylsilyl)methyl]benzotriazolium, N-alkyl-N-methylpiperidinium, 5-azoniumspiro[4.4]nonane, trihexyl(tetradecyl)phosphine ion, tetrabutylphosphine ion, and n-butyl-N-methylpyrrolidinium, and optionally 1-benzyl-3-methylimidazolium or 1-alkyl-3-methylimidazolium.

[0067] In some embodiments, the anion of the ionic liquid additive includes one or more of chloride ion, bromide ion, iodide ion, hexafluorophosphate, tetrafluoroborate, dicyandiamide anion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, and bis(trifluoromethylsulfonyl)imide anion, and optionally one or more of chloride ion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, and bis(trifluoromethylsulfonyl)imide anion.

[0068] In some embodiments, the ionic liquid additive includes one or more selected from 1-butyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-butyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-benzyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-benzyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-alkyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-chloride salt, and N-alkyl-N-methylpiperidine-tetrafluoroborate.

[0069] With an ionic liquid additive, especially an ionic liquid containing bis(fluorosulfonyl)imine and bis(trifluoromethylsulfonyl)imine, added to the fluoroether solvent, the SEI film generated at the negative electrode can be strengthened, reducing direct reactions between the negative electrode and fluoroether solvent molecules or free radicals. In addition, the ionic liquid additive can play a role of excluding solvent molecules at the electric double layer between the negative electrode and the electrolyte, further reducing direct reactions between the negative electrode and fluoroether solvent molecules or radicals, synergistically enhancing the stability at the interface between the negative electrode and electrolyte, and further improving the cycling and storage performance of the battery at room temperature and high temperatures. In some embodiments, the amide compound additive includes one or more compounds represented by formula I, formula II, or formula III,

##STR00004## [0070] where R.sub.1 to R.sub.9 are each independently selected from hydrogen, silyl group, ketone carbonyl group, C.sub.1-C.sub.3 alkyl group unsubstituted or substituted by at least one fluorine atom, and aryl group unsubstituted or substituted by at least one fluorine atom.

[0071] In this document, the term “silyl group” refers to —Si(R.sub.10)(R.sub.11)(R.sub.12) group, where R.sub.10, R.sub.11, and R.sub.12 are each independently selected from hydrogen and substituted or unsubstituted C.sub.1-3 alkyl group. In an example, the silyl group includes, but is not limited to, —SiH.sub.3 and —Si(CH.sub.3).sub.3.

[0072] In this document, the term “ketone carbonyl group” is an —R—CO—R'— group, where both R and R' are hydrocarby groups.

[0073] In this document, the term “aryl group” refers to an aromatic ring system in which at least one ring is aromatic, including but not limited to phenyl, biphenyl, indanyl, 1-naphthyl, 2-naphthyl, and tetrahydronaphthyl.

[0074] In this document, the term “C.sub.1-3 alkyl group” is a straight-chain or branched hydrocarbon chain group including carbon and hydrogen atoms, without unsaturation, having from one to three carbon atoms, and attached to the rest of the molecule via a single bond.

[0075] In this document, the term “substituted” refers to at least one hydrogen atom of the compound or chemical moiety being replaced by another chemical moiety or a substituent, where the substituent is independently selected from hydroxy group, mercapto group, amino group, cyano group, nitro group, aldehyde group, halogen atom, alkenyl group, alkynyl group, aryl group, heteroaryl group, C.sub.1-6 alkyl group, and C.sub.1-6 alkoxy group.



[0076] In some embodiments, the amide compound additive includes one or more of N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylacetoacetamide, 1,1,1-trifluoro-N,N-dimethylform sulfonamide, N,O-bis(trimethylsilyl)trifluoroacetamide, 2,3,6-trifluorobenzenesulfonamide, N,N-dimethyl-4-fluorobenzenesulfonamide, and N-methyl-N-trimethylsilane trifluoroacetamide.

[0077] When the amide compound additive is added to the fluoroether solvent, the SEI film generated at the negative electrode will contain an inorganic nitride. The presence of the inorganic nitride improves film stability, thereby significantly enhancing the electrochemical stability of the battery. In addition, some amide compound additives have Lewis basicity and can coordinate with Lewis acidic species in the fluoroether solvent, preventing further reactions between Lewis acidic components in the electrolyte and the negative electrode. This further enhances the stability of the negative electrode interface of the battery. Through the foregoing effects, amide compound additives can significantly improve the cycling and storage performances of secondary batteries, especially metal batteries (including batteries with no negative electrode).

[0078] In some embodiments, the cation shielding additive includes a salt whose cation is an alkali metal element or an alkaline earth metal element.

[0079] In this document, alkali metal elements refer to the metal elements of family IA in the periodic table of elements, excluding hydrogen (H). In some embodiments, the cation shielding additive includes lithium, potassium, or cesium.

[0080] In this document, alkaline earth metal elements refer to the metal elements of family IIA in the periodic table of elements. In some embodiments, the cation shielding additive includes calcium, strontium, or barium.

[0081] In some embodiments, the cation shielding additive includes one or more of lithium nitrate, lithium perchlorate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium bisoxaloborate, lithium difluoroxaloborate, lithium bis(fluorosulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide, potassium hexafluorophosphate, potassium bis-oxaloborate, potassium difluoro-oxaloborate, potassium bis(fluorosulfonyl)imide, potassium bis(trifluoromethylsulfonyl)imide, cesium nitrate, cesium hexafluorophosphate, cesium bis(fluorosulfonyl)imide, cesium chloride, cesium bromide, calcium nitrate, strontium nitrate, and barium nitrate.

[0082] With the cation shielding additive added in the fluoroether solvent, a cation different from metal ions in the electrolyte salt can be introduced. The cation in the cation shielding additive can exclude, through the double electric layer at the negative electrode interface, shuttle ions and free radicals that cause side reactions, and can guide the uniform deposition and stripping of metal ions of the electrolytic salt at the negative electrode. Moreover, some anions contained in the cation shielding additive can also increase the inorganic components in the SEI film and stabilize the SEI, thereby further enhancing the negative electrode interface stability of the battery and improving the cycling and storage performances of a secondary battery, especially a metal battery (including a battery with no negative electrode). In some embodiments, the alloy additive is a compound containing an element from family IVA or family VA.

[0083] In some embodiments, the alloy additive includes one or more of antimony trifluoride, antimony pentafluoride, tin difluoride, tin tetrafluoride, bismuth trichloride, and fumed silica.

[0084] In this paper, the term “fumed silica (Fumed silica)”, also known as fumed white carbon black, is an amorphous nano-silica particle.

[0085] When a foregoing alloy additive is added to the fluoroether electrolyte, a double layer SEI film is formed at the negative electrode. One layer of the SEI film is rich in alloy components formed by IVA or VA group elements in conjunction with sodium, while the other layer of the SEI film is rich in inorganic substances such as sodium fluoride. This enhances the stability of the SEI film and suppresses dendrite formation at the negative electrode, thereby improving the cycling performance and storage stability of the secondary battery. Additionally, it reduces gas generated

and contributes to overall battery safety.

[0086] In some embodiments, a mass percentage of the additive is 1-10% based on total mass of the electrolyte.

[0087] In some embodiments, the mass percentage of the additive is optionally 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, and 10% based on the total mass of the electrolyte.

[0088] When the mass percentage of the additive is 1-10% based on the total mass of the electrolyte, a stable SEI film can be generated at the interface between the negative electrode and the electrolyte, and the ion transport in the battery will not be affected due to excessively thick SEI film, thus improving the comprehensive performance of the battery.

[0089] In some embodiments, the ether solvent is a fluoroether solvent, and the fluoroether solvent includes a compound represented by formula IV or a crown ether substituted by a fluorine atom or a fluoroalkyl group,

##STR00005## [0090] where R.sub.7, R.sub.8, and R.sub.9 are each independently selected from hydrogen, and a straight-chain or branched-chain C.sub.1-C.sub.6 alkyl group unsubstituted or substituted by fluorine or a hydroxyl group, at least one of R.sub.7, R.sub.8, and R.sub.9 contains a fluorine atom, and R.sub.7 and R.sub.9 optionally are combined with oxygen to which R.sub.7 and R.sub.9 are connected and R.sub.8 connected to the oxygen, to generate a 5- or 6-membered saturated heterocyclic ring, where at least one hydrogen atom on the ring is substituted by fluorine or a fluoroalkyl group.

[0091] In this document, the term “C.sub.1-6 alkyl group” can be understood with reference to the definition of the term “C.sub.1-3 alkyl”.

[0092] In this document, “fluoroalkyl group” refers to an alkyl group containing at least one fluorine atom.

[0093] In some embodiments, the fluoroether solvent includes one or more of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane

##STR00006##

2-(2-ethoxyethoxy)-1,1,1-trifluoroethane

##STR00007##

1,2-bis(2,2-difluoroethoxy)ethane

##STR00008##

2-(2-(2,2-difluoroethoxy)ethoxy)-1,1,1-trifluoroethane

##STR00009##

1,2-bis(2,2,2-trifluoroethoxy)ethane

##STR00010##

1,1,1,3,3,3-hexafluoroisopropylmethyl ether, 2,2,2-trifluoroethyl-1,1,2,3,3,3-hexafluoropropyl ether, 2,2-bis(trifluoromethyl)-1,3-dioxolane, 2,2-dimethoxy-4-(Trifluoromethyl)-1,3-dioxopentane, 2-ethoxy-4-(trifluoromethyl)-1,3-dioxopentane, octafluorotetrahydrofuran, ethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol dimethyl ether substituted by at least one fluorine atom, triethylene glycol dimethyl ether substituted by at least one fluorine atom, tetraethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol diethyl ether substituted by at least one fluorine atom, diisopropyl ether substituted by at least one fluorine atom, dibutyl ether substituted by at least one fluorine atom, diethylene glycol dibutyl ether substituted by at least one fluorine atom, 1,4-diethoxybutane substituted by at least one fluorine atom, 15-crown ether-5 substituted by at least one fluorine atom, 12-crown ether-4 substituted by at least one fluorine atom, and 18-crown ether-6 substituted by at least one fluorine atom; and optionally at least one of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane, and 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxopentane.

[0094] The direct fluorination modification of ether molecules can increase the absolute value of the highest occupied molecular orbital (HOMO) of the ether, thereby widening the electrochemical stability window of the corresponding electrolyte after the electrolytic salt is dissolved. This

enhances the electrochemical stability of the electrolyte, allowing the electrolyte to be paired with positive electrode active materials with higher potential, and improving the use voltage of the secondary battery.

[0095] In some embodiments, a mass percentage of the fluoroether solvent is 20%-90% based on the total mass of the electrolyte.

[0096] In some embodiments, the mass percentage of the fluoroether solvent is 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, and 90% based on the total mass of the electrolyte.

[0097] Unlike using the fluoroether solvent as an inert diluent, incorporating the fluoroether solvent in the electrolyte with a higher mass percentage as the primary solvent can effectively enhance the electrochemical stability of the electrolyte. This allows the electrolyte to be paired with cathode active materials with higher potentials, thereby boosting the use voltage of the secondary battery.

[0098] In some embodiments, an electrolytic salt is a sodium salt, where the sodium salt includes one or more of sodium nitrate, sodium perchlorate, sodium hexafluorophosphate, sodium tetrafluoroborate, sodium tetrafluoroyttrate, sodium hexafluoroarsenate, sodium acetate, sodium trifluoroacetate, sodium bisoxaloborate, sodium difluoroxaloborate, tetrafluoroborate sodium phenylborate, sodium trifluoromethanesulfonate, sodium bis(fluorosulfonyl)imide, sodium bis(trifluoromethanesulfonyl)imide, and sodium (n-perfluorobutylsulfonyl)imide.

[0099] In some embodiments, a mass percentage of the electrolytic salt is 2%-70%, optionally 20%-70%, based on the total mass of the electrolyte.

[0100] In some embodiments, the mass percentage of the electrolytic salt is 2%, 5%, 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, and 70%, based on the total mass of the electrolyte.

[0101] When the mass percentage of the electrolytic salt is 2% to 70% based on the total mass of the electrolyte, the electrolytes provided in this application can effectively improve the chemical stability and cycling and storage performances of the battery. When the mass percentage of the electrolytic salt is 20%-70% based on the total mass of the electrolyte, high concentration of electrolytic salt can further reduce the free solvent molecules in the solvent, mitigate the side reactions between the solvent and the negative electrode, and improve the cycling performance, storage performance, and high temperature performance of the battery.

[Secondary Battery]

[0102] In some embodiments, the secondary battery includes the foregoing electrolyte.

[0103] In some embodiments, the secondary battery is a lithium metal battery or a sodium metal battery.

[0104] A lithium metal battery is a battery whose negative electrode is made of lithium metal, and lithium ions are used to migrate back and forth between the positive and negative electrodes.

[0105] A sodium metal battery refers to a battery where the negative electrode is made of sodium metal, and sodium ions are used to migrate back and forth between the positive and negative electrodes.

[0106] In some embodiments, the secondary battery is a sodium metal battery with no negative electrode. The sodium metal battery with no negative electrode does not use a negative electrode active material. Instead, it solely uses a negative electrode current collector as the negative electrode. During the initial charging process, sodium deposition occurs on the negative electrode, and during discharge, sodium returns to the positive electrode, realizing a charge and discharge cycle. Due to the absence of a negative electrode material and the use of a negative electrode current collector, a battery with no negative electrode can effectively overcome the drawbacks of a sodium metal battery and achieve a higher energy density compared to a battery with a metal sodium negative electrode.

[0107] Although a fluoroether solvent can effectively enhance the electrochemical stability of a battery, it causes more obvious side reactions in a battery with no negative electrode. In this

application, with one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive added in the fluoroether solvent, a stable SEI film is generated at the electrode/electrolyte interface. In addition, an effective barrier is constructed at the interface electric double layer to prevent the shuttle of certain ions and free radicals and side reactions, greatly improving the cycling performance and storage stability of the sodium battery with no negative electrode.

[0108] In some embodiments, the secondary battery includes a positive electrode plate, where the positive electrode plate includes a positive electrode active material, and the positive electrode active material includes one or more of Prussian blue compound, polyanionic compound, and layered oxide.

[0109] The transition metal in a layered transition metal oxide may be at least one of Mn, Fe, Ni, Co, Cr, Cu, Ti, Zn, V, Zr, and Ce. Alternatively, the layered transition metal oxide is, for example,  $\text{Na}_x\text{MO}_{1-x}$ , where M is one or more of Ti, V, Mn, Co, Ni, Fe, Cr, and Cu, and  $0 < x \leq 1$ .

[0110] The polyanionic compound may be a compound with a metal ion, a transition metal ion, and a tetrahedral  $(\text{YO})_n^{n-}$  anionic unit. The metal ion may be one of sodium ion, lithium ion, potassium ion, and zinc ion; the transition metal may be at least one of Mn, Fe, Ni, Co, Cr, Cu, Ti, Zn, V, Zr, and Ce; Y may be at least one of P, S, and Si; and n represents the valence state of  $(\text{YO})_n^{n-}$ .

[0111] The Prussian blue compound may be a compound with a sodium ion, a transition metal ion, and a cyanide ion ( $\text{CN}^-$ ). The transition metal may be at least one of Mn, Fe, Ni, Co, Cr, Cu, Ti, Zn, V, Zr, and Ce. The Prussian blue compound may be, for example,  $\text{Na}_a\text{Me}_b\text{Me}'_c(\text{CN})_6$ , where Me and Me' are each independently at least one of Ni, Cu, Fe, Mn, Co, and Zn, and  $0 < a \leq 2$ ,  $0 < b < 1$ ,  $0 < c < 1$ .

[0112] In some embodiments, the positive electrode active material includes one or more of  $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ,

$\text{Na}(\text{Cu}_{1/9}\text{Ni}_{2/9}\text{Fe}_{1/3}\text{Mn}_{1/3})\text{O}_2$ ,

$\text{Na}_{2/3}\text{Ni}_{1/6}\text{Mn}_{2/3}\text{Cu}_{1/9}\text{Mg}_{1/18}\text{O}_2$ ,

$\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ,  $\text{NaFePO}_4$ ,

$\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ,  $\text{Na}_{1/9}\text{CoFe}(\text{CN})_6$ ,  $\text{Na}_2\text{NiFe}(\text{CN})_6$ , and  $\text{NaMnFe}(\text{CN})_6$ .

[0113] The sodium metal battery with no negative electrode can exhibit good cycling performance in ether electrolyte, especially demonstrates excellent cycling performance when paired with a polyanionic positive electrode material, including sodium vanadium phosphate ( $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ ) and sodium iron pyrophosphate ( $\text{Na}_4\text{Fe}_3(\text{PO}_4)_2\text{P}_2\text{O}_7$ ). A layered oxide has higher energy density and when combined with the electrolyte provided in this application, its defects of low coulombic efficiency and poor cycling performance when used in an ether electrolyte can be effectively solved.

[0114] In some embodiments, a surface of particles of the positive electrode active material is provided with a coating layer, where the coating layer includes one or more of carbon material (amorphous carbon, graphite, graphen, and the like), polyaniline, polypyrrole, Poly(3,4-ethylenedioxythiophene), aluminum oxide, zinc oxide, titanium oxide, zirconium oxide, magnesium oxide, silicon oxide, lanthanum oxide, sodium fluoride, lithium fluoride, and aluminum fluoride.

[0115] The coating of the coating layer can effectively enhance the stability of the positive electrode active material, reduce the metal dissolution and particle fragmentation of the positive electrode active material during cycling, and improve the cycling performance and storage stability of the battery.

[0116] In some embodiments, the coating layer has a thickness of 2 nm-1000 nm.

[0117] An appropriately thick coating layer can effectively improve the performance and prevent

the increase in resistance of the positive electrode film caused by an excessively thick coating layer, which would lead to a decrease in battery performance.

[0118] In some embodiments, the secondary battery includes a negative electrode plate, where the negative electrode plate includes a negative electrode current collector and a primer layer provided on at least one surface of the negative electrode current collector, and the primer layer includes one or more of carbon nanotube, graphite, graphene, silver composite carbon nanoparticle, and tin composite carbon nanoparticle.

[0119] In some embodiments, the primer layer has an areal density of 2 g/m.<sup>2</sup>–50 g/m.<sup>2</sup>.

[0120] In some embodiments, the primer layer has a thickness of 1 μm–100 μm.

[0121] The primer layer within the foregoing ranges can effectively guide the negative electrode deposition, reduce the formation of sodium dendrites at the negative electrode, and improve the uniformity of sodium metal deposition. Moreover, a primer layer with an appropriate areal density and thickness can truly make the absence of a negative electrode possible, enhancing the energy density and safety performance of the battery.

[0122] In some embodiments, the current collector of the sodium metal battery with no negative electrode includes at least one of metal foil, metal foam current collector, metal mesh current collector, carbon felt current collector, carbon cloth current collector, carbon paper current collector, and composite current collector.

[0123] In some embodiments, the metal foil may be copper foil, aluminum foil, stainless steel foil, and titanium foil, and the metal foam current collector may be copper foam, aluminum foam, nickel foam, and the like. The metal mesh current collector may be copper mesh, aluminum mesh, and stainless steel mesh. The composite current collector includes a current collector with a primer layer or a current collector with a polymer base film. The composite current collector may be a sandwich structure, with the polymer base film in the middle and metal foils on two sides. The composite current collector can also have a metal foil on one side of the polymer base film. The polymer base film may be one of polyamide, polyterephthalate, polyimide, polyethylene, polypropylene, polystyrene, polyvinyl chloride, acrylonitrile-butadiene-styrene copolymer, polybutylene terephthalate ester, poly(p-phenylene terephthalamide), polypropylene, polyoxymethylene, epoxy resin, phenolic resin, polytetrafluoroethylene, polyvinylidene fluoride, silicone rubber, and polycarbonate. In some embodiments, the secondary battery may include an outer package. The outer package may be used for packaging the electrode assembly and the electrolyte.

[0124] In some embodiments, the outer package of the secondary battery may be a hard shell, for example, a hard plastic shell, an aluminum shell, or a steel shell. The outer package of the secondary battery may alternatively be a soft pack, for example, a soft pouch. Material of the soft pack may be plastic, which, for example, may be polypropylene, polybutylene terephthalate, and polybutylene succinate.

[0125] This application does not impose any special limitations on a shape of the secondary battery, and the secondary battery may be cylindrical, rectangular, or of any other shapes. For example, FIG. 1 shows a secondary battery 5 of a rectangular structure as an example.

[0126] In some embodiments, referring to FIG. 2, the outer package may include a housing 51 and a cover plate 53. The housing 51 may include a base plate and side plates connected to the base plate, and the base plate and the side plates enclose an accommodating cavity. The housing 51 has an opening communicating with the accommodating cavity, and the cover plate 53 can cover the opening to seal the accommodating cavity. The positive electrode plate, the negative electrode plate, and the separator may be made into an electrode assembly 52 through winding or lamination. The electrode assembly 52 is enclosed in the accommodating cavity. The electrolyte infiltrates into the electrode assembly 52. The secondary battery 5 may include one or more electrode assemblies 52, and persons skilled in the art may make choices according to actual requirements.

[0127] In some embodiments, the secondary battery may be assembled into a battery module, and

the battery module may include one or more secondary batteries. The quantity may be chosen by persons skilled in the art according to use and capacity of the battery module.

[0128] FIG. 3 shows a battery module 4 as an example. Referring to FIG. 3, in the battery module 4, a plurality of secondary batteries 5 may be sequentially arranged in a length direction of the battery module 4. Certainly, the batteries may alternatively be arranged in any other manners. Further, the plurality of secondary batteries 5 may be fastened through fasteners.

[0129] Optionally, the battery module 4 may further include a housing with accommodating space, and the plurality of secondary batteries 5 are accommodated in the accommodating space.

[0130] In some embodiments, the battery module may be further assembled into a battery pack, and the battery pack may include one or more battery modules. The quantity may be chosen by persons skilled in the art according to use and capacity of the battery pack.

[0131] FIG. 4 and FIG. 5 show a battery pack 1 as an example. Referring to FIG. 4 and FIG. 5, the battery pack 1 may include a battery box and a plurality of battery modules 4 arranged in the battery box. The battery box includes an upper box body 2 and a lower box body 3. The upper box body 2 can cover the lower box body 3 to form an enclosed space for accommodating the battery module 4. The plurality of battery modules 4 may be arranged in the battery box in any manner.

[0132] In addition, this application further provides an electric apparatus. The electric apparatus includes at least one of the secondary battery, the battery module, or the battery pack provided in this application. The secondary battery, the battery module, or the battery pack may be used as a power source for the electric apparatus or an energy storage unit of the electric apparatus. The electric apparatus may include a mobile device (for example, a mobile phone or a notebook computer), an electric vehicle (for example, a battery electric vehicle, a hybrid electric vehicle, a plug-in hybrid electric vehicle, an electric bicycle, an electric scooter, an electric golf vehicle, or an electric truck), an electric train, a ship, a satellite system, an energy storage system, or the like, but is not limited thereto.

[0133] The secondary battery, the battery module, or the battery pack may be selected for the electric apparatus based on requirements for using the electric apparatus.

[0134] FIG. 6 shows an electric apparatus as an example. This electric apparatus is a battery electric vehicle, a hybrid electric vehicle, a plug-in hybrid electric vehicle, or the like. To satisfy a requirement of the electric apparatus for high power and high energy density of the secondary battery, a battery pack or a battery module may be used.

[0135] In another example, the apparatus may be a mobile phone, a tablet computer, a notebook computer, or the like. The apparatus usually requires to be light and thin, and a secondary battery may be used as a power source.

## EXAMPLES

[0136] The following describes examples of this application. The examples described below are illustrative and only used for explaining this application, and cannot be construed as limitations on this application. Examples whose technical solutions or conditions are not specified are made in accordance with technical solutions or conditions described in literature in the field or made in accordance with product instructions. The reagents or instruments used are conventional products that are commercially available if no manufacturer is indicated.

### Example 1

#### I. Preparation Method

##### 1. Preparation of Positive Electrode Plate

[0137] A positive electrode active material sodium ferric pyrophosphate coated with carbon ( $\text{Na}_{0.4}\text{Fe}_{0.3}(\text{PO})_{0.4}\text{P}_{0.2}\text{O}_{0.7}\text{C}$ ), a binder polyvinylidene fluoride (PVDF), and a conductive agent conductive carbon black (super-P) were dispersed at a mass ratio of 96%:2%:2% in a N-methylpyrrolidone (NMP) solvent and well stirred to prepare the positive electrode slurry. The prepared slurry was applied onto a surface of an aluminum foil with a coating machine according to the mass requirement per unit area of the positive electrode active material

and then dried, followed by cold pressing of the coated electrode plate at a designed density of 2.5 g/cm<sup>3</sup> with a cold pressing machine, to obtain a final positive electrode plate.

## 2. Preparation of Negative Electrode Plate

[0138] Carbon nanotubes and sodium carboxymethyl cellulose were added at a mass ratio of 1:2 into water. The resulting mixture was stirred into a uniform slurry and the slurry was applied onto the negative electrode current collector, followed by drying and cutting to obtain a negative electrode plate with no negative structure, where the areal density of the primer layer was 10 g/m<sup>2</sup>, and thickness of the primer layer was 5 μm.

## 3. Separator

[0139] A polyethylene film (PE separator) was used as a separator.

## 4. Preparation of Electrolyte

[0140] In an argon atmosphere glove box (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm), a 20 wt. % of bis(fluorosulfonyl)imide sodium salt was dissolved in a 70 wt. % 2,2,3,3-Tetrafluoro-1,4-dimethoxybutane organic solvent. Then, a 10 wt. % 1,1,1-trifluoro-N,N-dimethylmethanesulfonamide additive was dissolved in the organic solvent. The mixture was well stirred to obtain the electrolyte of Example 1.

## 5. Preparation of Battery

[0141] The positive electrode plate, the separator, and the negative electrode plate were stacked in sequence so that the separator was sandwiched between the positive electrode plate and the negative electrode plate for separation, and the electrolyte was added, to assemble a button cell.

[0142] See Table 1 for example parameters.

[0143] In Examples 2-39, the compositions of the electrolytes for secondary battery were adjusted, and the example parameters are shown in Table 1. The mass ratios of the additives in Examples 15-19 were 1:1.

[0144] In Examples 40-43, the positive electrode active materials were

Na[Cu<sub>0.1</sub>Ni<sub>0.2</sub>Fe<sub>0.1</sub>Mn<sub>0.3</sub>]O<sub>2</sub>, and the example parameters of other components are shown in Table 1.

[0145] In Examples 44-47, the positive electrode active materials were ZrO<sub>2</sub> coated Na<sub>0.2</sub>Ni<sub>0.1</sub>Mn<sub>0.2</sub>Cu<sub>0.1</sub>Mg<sub>0.1</sub>O<sub>2</sub>, and the example parameters of other components are shown in Table 1.

[0146] In Comparative Examples 1-23, the compositions of the electrolytes or the positive electrode active materials of the secondary battery were adjusted, and the example parameters are shown in Table 1. The preparation method was basically the same as that of Example 1.

## II. Battery Performance Test

### (1) Electrochemical Stability Window Test

[0147] The window test of the electrolyte was carried out by using an electrochemical workstation with a test temperature of 25° C., a voltage range of 1.0 V-5.0 V, and a scanning rate of 0.1 mV/s. The use window of the electrolyte was determined based on the starting position of the peak potential in the CV curve. Cyclic voltammetry (CV) tests in this experiment were performed on a 1470 multi-channel electrochemical workstation of the Solartron Company in the United Kingdom.

### (2) Room-Temperature/High-Temperature Cycling Performance

[0148] At 25/60° C. and normal pressure (0.1 MPa), the battery was charged at a constant current of 0.1 C to a voltage of 4 V (for layered oxide positive electrode) or 3.7 V (sodium ferric pyrophosphate positive electrode). Then, the battery was charged at a constant voltage of 4/3.7 V to a current of 0.01 C, and then discharged at a constant current of 0.1 C to a voltage of 3.0 V. This was the first charge-discharge cycle. Then the battery was charged at a constant current of 1 C to a voltage of 4/3.7 V, then charged at a constant voltage of 4/3.7 V to a current of 0.1 C, and then discharged at a constant current of 1 C to a voltage of 3.0 V. The first cycle discharge capacity was defined as 100% and the number of cycles when the discharge capacity was 80% was recorded.

### (3) Room-Temperature/High-Temperature Storage Performance

[0149] At 25/60° C. and normal pressure (0.1 MPa), the battery was charged at a constant current of 0.1 C to 4 V (for layered oxide positive electrode) or 3.7 V (for sodium ferric pyrophosphate positive electrode), then charged at a constant voltage of 4/3.7 V to a current of 0.01 C, and then discharged at a constant current of 0.1 C to 3 V to obtain the pre-storage discharge capacity (Cd1). The sodium battery was charged at a constant current of 0.1 C to 4/3.7 V at 25° C., and then charged at a constant voltage of 4/3.7 V until the current dropped to 0.01 C, so as to charge the battery to 100% SOC through this step. The battery was stored in a constant temperature environment of 25/60° C. and the number of storage days when the storage capacity retention rate of the battery was 80% was recorded.

[0150] The test method for the post-storage discharge capacity (Cdn) was as follows: at 25/60° C., the battery was charged at a constant current of 0.1 C to 4/3.7 V, then charged at a constant voltage of 4/3.7 V until the current dropped to 0.01 C, and then discharged at a constant current of 0.1 C to 3 V to obtain the discharge capacity of the sodium battery after storage for n days, which was recorded as Cdn.

[0151] Storage capacity retention rate=post-storage discharge capacity (Cdn)/pre-storage discharge capacity(Cd1)\*100%.

[0152] The test results of the foregoing examples and comparative examples are shown in Table 1 and Table 2.

TABLE-US-00001

| TABLE 1  | Positive electrode Mass No.  | active material  | Sodium salt percentage   |
|--|--|--|--|
| Fluoroether Example 1  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 2  |
| Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 3  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   |
| 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 4  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane |
| Example 5  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 6  |
| Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 7  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   |
| 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 8  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane |
| Example 9  | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 10   |
| Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 11   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   |
| 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 12   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane |
| Example 13   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 14   |
| Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 15   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   |
| 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 16   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane |
| Example 17   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 18   |
| Carbon coated Bis(fluorosulfonyl)imide 20%                                   | 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 19   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   |
| 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane | Example 20   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | F3DEE sodium ferric sodium pyrophosphate                                     |
| Example 21   | Carbon coated Bis(fluorosulfonyl)imide 20%                                   | PFTTHF sodium ferric sodium pyrophosphate                                    | Example 22   |



Carbon coated Bis(fluorosulfonyl)imide 20% HME sodium ferric sodium pyrophosphate Example 23 Carbon coated Bis(fluorosulfonyl)imide 20% F5DEE sodium ferric sodium pyrophosphate Example 24 Carbon coated Bis(fluorosulfonyl)imide 20% F3DEE sodium ferric sodium pyrophosphate Example 25 Carbon coated Bis(fluorosulfonyl)imide 20% PFTHF sodium ferric sodium pyrophosphate Example 26 Carbon coated Bis(fluorosulfonyl)imide 20% HME sodium ferric sodium pyrophosphate Example 27 Carbon coated Bis(fluorosulfonyl)imide 20% F5DEE sodium ferric sodium pyrophosphate Example 28 Carbon coated Bis(trifluoro 20% 1,2- sodium ferric methanesulfonyl)imide bis(2,2- pyrophosphate sodium difluoroethoxy)ethane Example 29 Carbon coated Sodium 20% 1,2- sodium ferric hexafluorophosphate bis(2,2- pyrophosphate difluoroethoxy)ethane Example 30 Carbon coated Sodium 20% 1,2- sodium ferric bisoxaloborate bis(2,2- pyrophosphate difluoroethoxy)ethane Example 31 Carbon coated Bis(fluorosulfonyl)imide 24% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 32 Carbon coated Bis(fluorosulfonyl)imide 22% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 33 Carbon coated Bis(fluorosulfonyl)imide 17% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 34 Carbon coated Bis(fluorosulfonyl)imide 15% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 35 Carbon coated Bis(fluorosulfonyl)imide 2% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 36 Carbon coated Bis(fluorosulfonyl)imide 10% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 37 Carbon coated Bis(fluorosulfonyl)imide 30% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 38 Carbon coated Bis(fluorosulfonyl)imide 50% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 39 Carbon coated Bis(fluorosulfonyl)imide 70% 2,2,3,3- sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Example 40

Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 41

Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 42

Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 43

Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 44 ZrO.sub.2 coated

Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 45 ZrO.sub.2 coated

Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4 dimethoxybutane Example 46 ZrO.sub.2 coated

Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Example 47 ZrO.sub.2 coated

Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 Bis(fluorosulfonyl)imide 20% 2,2,3,3- sodium tetrafluoro-1,4- dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 25% 2,2,3,3- Example 1 sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 20% 2,2,3,3- Example 2 sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 25% F3DEE Example 3 sodium ferric sodium pyrophosphate Comparative Carbon coated Bis(fluorosulfonyl)imide 25% PFTHF Example 4 sodium ferric sodium pyrophosphate Comparative Carbon coated Bis(fluorosulfonyl)imide 25% HME Example 5 sodium ferric sodium pyrophosphate Comparative Carbon coated Bis(fluorosulfonyl)imide 25% F5DEE Example 6 sodium ferric sodium pyrophosphate Comparative Carbon coated Bis(trifluoro 25% 2,2,3,3- Example 7 sodium ferric methanesulfonyl)imide tetrafluoro-1,1- pyrophosphate sodium dimethoxybutane Comparative

Carbon coated Sodium 25% 2,2,3,3- Example 8 sodium ferric hexafluorophosphate tetrafluoro-1,2-  
pyrophosphate dimethoxybutane Comparative Carbon coated Sodium 25% 2,2,3,3- Example 9  
sodium ferric bisoxaloborate tetrafluoro-1,3- pyrophosphate dimethoxybutane Comparative Carbon  
coated Bis(fluorosulfonyl)imide 2% 2,2,3,3- Example 10 sodium ferric sodium tetrafluoro-1,4-  
pyrophosphate dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 10%  
2,2,3,3- Example 11 sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane  
Comparative Carbon coated Bis(fluorosulfonyl)imide 30% 2,2,3,3- Example 12 sodium ferric  
sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane Comparative Carbon coated  
Bis(fluorosulfonyl)imide 50% 2,2,3,3- Example 13 sodium ferric sodium tetrafluoro-1,4-  
pyrophosphate dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 70%  
2,2,3,3- Example 14 sodium ferric sodium tetrafluoro-1,4- pyrophosphate dimethoxybutane  
Comparative Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20%  
2,2,3,3- Example 15 sodium tetrafluoro-1,4- dimethoxybutane Comparative ZrO.sub.2 coated  
Bis(fluorosulfonyl)imide 20% 2,2,3,3- Example 16  
Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 sodium tetrafluoro-1,4-  
dimethoxybutane Comparative Carbon coated Bis(fluorosulfonyl)imide 20% Ethylene Example 17  
sodium ferric sodium glycol pyrophosphate dimethyl ether Comparative Carbon coated  
Bis(fluorosulfonyl)imide 20% Ethylene Example 18 sodium ferric sodium glycol pyrophosphate  
dimethyl ether Comparative Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2  
Bis(fluorosulfonyl)imide 20% Ethylene Example 19 sodium glycol dimethyl ether Comparative  
ZrO.sub.2 coated Bis(fluorosulfonyl)imide 20% Ethylene Example 20  
Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 sodium glycol dimethyl ether  
Comparative Carbon coated Bis(fluorosulfonyl)imide 20% Ethylene Example 21 sodium ferric  
sodium glycol pyrophosphate diethyl ether Comparative  
Na[Cu.sub.1/9Ni.sub.2/9Fe.sub.1/3Mn.sub.1/3]O.sub.2 Bis(fluorosulfonyl)imide 20% Ethylene  
Example 22 sodium glycol diethyl ether Comparative ZrO.sub.2 coated Bis(fluorosulfonyl)imide  
20% Ethylene Example 23 Na.sub.2/3Ni.sub.1/6Mn.sub.2/3Cu.sub.1/9Mg.sub.1/18O.sub.2 sodium  
glycol diethyl ether Mass Mass No. percentage Additive percentage Example 1 75% 1-butyl-3- 5%  
methylimidazole bis(fluorosulfonyl)imide salt Example 2 75% 1-butyl-3- 5% methylimidazole  
bis(trifluoromethylsulfonyl)- amide salt Example 3 75% 1-alkyl-3- 5% methylimidazole  
bis(fluorosulfonyl)amide salt Example 4 75% 1-alkyl-3- 5% methylimidazole chloride Example 5  
75% N-alkyl-N- 5% methylpiperidine tetrafluoroborate Example 6 75% 1,1,1- 5% trifluorofluoro-  
N,N- dimethylmethanesulfonamide Example 7 75% N,N- 5% dimethylformamide Example 8 75%  
2,3,6- 5% trifluorobenzene sulfonamide Example 9 75% Lithium nitrate 5% Example 10 75%  
Potassium 5% bisoxaloborate Example 11 75% Lithium 5% bis(trifluoromethanesulfonyl)- imide  
Example 12 75% Antimony 5% trifluoride Example 13 75% Fumed silica 5% Example 14 75% Tin  
difluoride 5% Example 15 75% 1-butyl-3- 5% methylimidazole bis(fluorosulfonyl)imide salt +  
1,1,1- trifluorofluoro- N,N- dimethylmethanesulfonamide Example 16 75% 1-butyl-3- 5%  
methylimidazole chloride + lithium hexafluorophosphate Example 17 75% 1-butyl-3- 5%  
methylimidazole chloride + antimony pentafluoride Example 18 75% 1,1,1- 5% trifluorofluoro-  
N,N- dimethylmethanesulfonamide + lithium hexafluorophosphate Example 19 75% 1,1,1- 5%  
trifluorofluoro- N,N- dimethylmethanesulfonamide + antimony pentafluoride Example 20 75% 1-  
butyl-3- 5% methylimidazole/ bis(fluorosulfonyl)imide Example 21 75% 1-butyl-3- 5%  
methylimidazole/ bis(fluorosulfonyl)imide Example 22 75% 1-butyl-3- 5% methylimidazole/  
bis(fluorosulfonyl)imide Example 23 75% 1-butyl-3- 5% methylimidazole/  
bis(fluorosulfonyl)imide Example 24 75% 1,1,1- 5% trifluorofluoro- N,N-  
dimethylmethanesulfonamide Example 25 75% 1,1,1- 5% trifluorofluoro- N,N-  
dimethylmethanesulfonamide Example 26 75% 1,1,1- 5% trifluorofluoro- N,N-  
dimethylmethanesulfonamide Example 27 75% 1,1,1- 5% trifluorofluoro- N,N-  
dimethylmethanesulfonamide Example 28 75% 1,1,1- 5% trifluorofluoro- N,N-

dimethylmethanesulfonamide Example 29 75% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 30 75% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 31 75% 1,1,1- 1% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 32 75% 1,1,1- 3% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 33 75% 1,1,1- 8% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 34 75% 1,1,1- 10% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 35 93% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 36 85% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 37 65% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 38 45% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 39 25% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 40 75% 1-butyl-3- 5% methylimidazole/  
 bis(fluorosulfonyl)imide Example 41 75% 1,1,1- 5% trifluorofluoro- N,N-  
 dimethylmethanesulfonamide Example 42 75% Lithium nitrate 5% Example 43 75% Antimony 5%  
 trifluoride Example 44 75% 1-butyl-3- 5% methylimidazole bis(fluorosulfonyl)imide Example 45  
 75% 1,1,1- 5% trifluorofluoro- N,N- dimethylmethanesulfonamide Example 46 75% Lithium 5%  
 hexafluorophosphate Example 47 75% Tin tetrafluoride 5% Comparative 75% // Example 1  
 Comparative 80% // Example 2 Comparative 75% // Example 3 Comparative 75% // Example 4  
 Comparative 75% // Example 5 Comparative 75% // Example 6 Comparative 75% // Example 7  
 Comparative 75% // Example 8 Comparative 75% // Example 9 Comparative 98% // Example 10  
 Comparative 90% // Example 11 Comparative 70% // Example 12 Comparative 50% // Example  
 13 Comparative 30% // Example 14 Comparative 80% // Example 15 Comparative 80% //  
 Example 16 Comparative 75% 1-butyl-3- 5% Example 17 methylimidazole/  
 bis(fluorosulfonyl)imide Comparative 80% // Example 18 Comparative 80% // Example 19  
 Comparative 80% // Example 20 Comparative 75% // Example 21 Comparative 75% // Example  
 22 Comparative 75% // Example 23

TABLE-US-00002 TABLE 2 Cycles for 80% Cycles for 80% Electrochemical capacity retention  
 capacity retention Storage days at Storage days at stability rate/cycle (25° C., rate/cycle (60° C.,  
 room temperature high temperature window width 1 C charge- 1 C charge- for 80% capacity for  
 80% capacity No. (V, 25° C.) discharge rate) discharge rate) retention rate retention rate Example 1  
 4.2 750 300 87 55 Example 2 4.3 1000 600 109 68 Example 3 4.3 950 250 96 40 Example 4 4.1  
 600 100 67 28 Example 5 4.3 700 100 82 36 Example 6 4.2 2000 900 323 201 Example 7 4.1 1200  
 350 164 87 Example 8 4.2 1000 300 168 80 Example 9 4.0 700 150 123 43 Example 10 4.1 750  
 200 118 58 Example 11 4.1 700 200 101 52 Example 12 4.0 800 300 123 63 Example 13 4.2 900  
 250 137 54 Example 14 4.0 800 300 130 48 Example 15 4.2 2500 1100 353 254 Example 16 4.1  
 500 150 62 46 Example 17 4.1 600 150 71 42 Example 18 4.3 1700 850 284 157 Example 19 4.2  
 1800 800 291 165 Example 20 4.4 1400 500 163 67 Example 21 4.5 1000 200 138 57 Example 22  
 4.4 800 300 156 79 Example 23 4.2 1200 250 135 42 Example 24 4.3 1500 650 174 86 Example 25  
 4.4 1000 650 136 78 Example 26 4.3 950 400 166 89 Example 27 4.1 1250 300 146 45 Example 28  
 4.2 1000 250 98 57 Example 29 4.2 1200 200 91 43 Example 30 4.2 850 150 76 37 Example 31 4.1  
 1000 200 129 54 Example 32 4.1 1800 800 267 145 Example 33 4.1 2050 1000 318 241 Example  
 34 4.0 1900 950 309 257 Example 35 3.9 1500 800 228 176 Example 36 4.0 1800 800 269 164  
 Example 37 4.1 2000 850 308 223 Example 38 4.2 2150 950 338 218 Example 39 4.4 2300 1000  
 330 231 Example 40 4.2 450 200 65 42 Example 41 4.2 800 500 148 97 Example 42 4.0 300 100  
 52 30 Example 43 4.0 200 50 41 21 Example 44 4.2 650 250 84 58 Example 45 4.2 900 650 167  
 122 Example 46 4.0 450 250 64 38 Example 47 4.0 250 100 47 19 Comparative 4.1 600 100 23 13  
 Example 1 Comparative 4.1 600 100 37 10 Example 2 Comparative 4.2 500 100 19 8 Example 3  
 Comparative 4.3 400 50 13 7 Example 4 Comparative 4.3 500 100 22 11 Example 5 Comparative  
 4.1 300 50 14 9 Example 6 Comparative 4.2 700 200 12 8 Example 7 Comparative 4.2 600 150 17  
 10 Example 8 Comparative 4.2 500 100 9 3 Example 9 Comparative 3.8 500 50 13 8 Example 10

Comparative 3.9 550 100 17 10 Example 11 Comparative 4.0 800 250 46 20 Example 12  
 Comparative 4.2 1300 300 55 21 Example 13 Comparative 4.4 1800 500 103 34 Example 14  
 Comparative 3.9 100 50 4 2 Example 15 Comparative 3.9 100 50 7 5 Example 16 Comparative 4.0  
 1000 200 251 69 Example 17 Comparative 3.8 700 150 65 8 Example 18 Comparative 3.8 50 0 3 1  
 Example 19 Comparative 3.8 50 0 2 1 Example 20 Comparative 3.9 600 100 45 11 Example 21  
 Comparative 3.9 150 50 12 4 Example 22 Comparative 3.9 200 50 15 5 Example 23

[0153] Table 1 and Table 2 show that the electrolyte of the sodium battery with no negative electrode in Examples 1 to 47 includes a fluoroether solvent and an additive, where the fluoroether solvent is used as the main solvent of the electrolyte, and the additive is selected from one or more of ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive. In Examples 1-5, the ionic liquid additive is used as the additive; in Examples 6-8, the amide compound additive is used as the additive; in Examples 9-11, the cation shielding additive is used as the electrolyte additive; in Examples 12-14, the alloy additive is used as the additive; and in Examples 15-19, one or a combination of more is selected from ionic liquid additive, amide compound additive, cation shielding additive, and alloy additive is used as the additive. Compared with Comparative Example 18 in which ether solvent is used as the main solvent, in Examples 1-47, the batteries exhibit wider electrochemical stability window, and the electrolytes have better electrochemical stability.

[0154] In addition, it can be seen from the comparison between Examples 1-19 and Comparative Examples 1 and 2, comparison between Examples 20-27 and Comparative Examples 3-6, comparison between Examples 28-30 and Comparative Examples 7-9, comparison between Examples 35-39 and Comparative Examples 10-14, comparison between Examples 40-43 and Comparative Example 15, comparison between Examples 44-47 and Comparative Example 15, that the addition of an additive in the electrolyte can significantly improve the storage performance of a battery with no negative electrode at both room temperature and high temperatures.

[0155] Examples 1-14 shows that an amide compound additive provides more significant improvement in the cycling and storage performance of a battery with no negative electrode. Examples 1-5 show that 1-butyl-3-methylimidazole bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole bis(fluorosulfonyl)amide salt, 1-butyl-3-methylimidazole bis(fluorosulfonyl)imide salt, and N-alkyl-N-methylpiperidine tetrafluoroborate can provide more effective improvement than 1-alkyl-3-methylimidazole chloride in the cycling and storage performance of a battery with no negative electrode. 1-butyl-3-methylimidazole bis(trifluoromethylsulfonyl)amide salt provides most significant improvement in the cycling and storage performance of a battery with no negative electrode at room temperature and high temperatures. Examples 9-11 show that among the cation shielding additives, potassium bisoxaloborate provides better improvement in the cycling and storage performance of a battery with no negative electrode. Examples 12 to 14 show that among the alloy additives, fumed silica can provide more effective improvement in the cycling and storage performance of a battery.

[0156] Examples 15 to 19 show that the addition of two different types of additives can also provide effective improvement in the cycling and storage performance of a battery. In Example 17, the addition of both the ionic liquid additive 1-butyl-3-methylimidazole bis(fluorosulfonyl)imide salt and the amide compound additive 1,1,1-trifluorofluoro-N,N-dimethylmethanesulfonamide exhibits a synergistic effect. Compared with the battery with no negative electrode and no additive in Comparative Example 1, at room temperature, the number of cycles of the battery with no negative electrode when reaching 80% capacity retention rate is increased by 3 times, and the number of storage days is increased by 5 times, and at high temperatures, the number of cycles is increased by 10 times, and the number of storage days is increased by 18 times.

[0157] Examples 20-27 show that the additives provided in this application are suitable for fluoroether solvents, and can effectively improve the cycling and storage performance of the batteries with electrolyte systems using different fluoroether solvents as the main solvent,

improving the electrochemical stability and cycling life of the batteries.

[0158] Examples 28-30 show that the electrolyte provided in this application is suitable for a variety of different sodium salts, and the batteries can show excellent cycling and storage performance.

[0159] Examples 6 and 31-34 show that when the mass percentage of the additive is 1-10% based on the total mass of the electrolyte, the batteries can exhibit a wider electrochemical window and excellent cycling and storage performance at room temperature and high temperatures.

[0160] Examples 6 and 35-39 show that when the mass percentage of the fluoroether solvent is 20%-90% based on the total mass of the electrolyte, the batteries can exhibit a wider electrochemical window and excellent cycling and storage performance at room temperature and high temperatures. Examples 6 and 31-39 show that when the mass percentage of the electrolytic salt is 2-70% based on the total mass of the electrolyte, the batteries can exhibit a wider electrochemical window and excellent cycling and storage performance at room temperature and high temperatures. In addition, it can be seen from the comparison between Examples 6, 31-36, and 37-39 that when the mass percentage of the electrolytic salt is 20%-70%, the battery demonstrates superior electrochemical window stability and cycling and storage performance.

[0161] It can be seen from the comparison between Examples 40-47 and Comparative Examples 18-23 that the electrolyte provided in this application is suitable for a variety of cathode materials. Whether for a polyanionic compound or layered oxide, the electrolyte can effectively improve the electrochemical stability window width and cycling performance and storage stability of the battery.

[0162] It should be noted that this application is not limited to the foregoing embodiments. The foregoing embodiments are merely examples, and embodiments having substantially the same constructions and the same effects as the technical idea within the scope of the technical solutions of this application are all included in the technical scope of this application. In addition, without departing from the essence of this application, various modifications made to the embodiments that can be conceived by persons skilled in the art, and other manners constructed by combining some of the constituent elements in the embodiments are also included in the scope of this application.

## Claims

1. An electrolyte for secondary battery, comprising: a fluoroether solvent; and an additive, wherein the additive comprises at least one of an ionic liquid additive, an amide compound additive, a cation shielding additive, or an alloy additive.

2. The electrolyte according to claim 1, wherein a cation of the ionic liquid additive comprises one or more of nitrogen-containing onium ion or phosphorus-containing onium ion; and an anion of the ionic liquid additive comprises one or more of halogen ion, phosphate ion, borate ion, sulfonimide compound anion, or sulfonylamide compound anion.

3. The electrolyte according to claim 1, wherein a cation of the ionic liquid additive comprises one or more of 1-butyl-3-methylimidazolium, 1-benzyl-3-methylimidazolium, 3-methyl-1-ethoxycarbonylmethylimidazolium, 1-alkyl-3-methylimidazolium, 1-[(trimethylsilyl)methyl]benzotriazolium, N-alkyl-N-methylpiperidinium, 5-azoniumspiro[4.4]nonane, trihexyl(tetradecyl)phosphine ion, tetrabutylphosphine ion, n-butyl-N-methylpyrrolidinium, 1-benzyl-3-methylimidazolium, or 1-alkyl-3-methylimidazolium.

4. The electrolyte according to claim 2, wherein the anion of the ionic liquid additive comprises one or more of chloride ion, bromide ion, iodide ion, hexafluorophosphate, tetrafluoroborate, dicyandiamide anion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, or bis(trifluoromethylsulfonyl)imide anion, and optionally one or more of chloride ion, bis(fluorosulfonyl)amide anion, bis(trifluoromethylsulfonyl)amide anion, bis(fluorosulfonyl)imide anion, or bis(trifluoromethylsulfonyl)imide anion.

5. The electrolyte according to claim 1, wherein the ionic liquid additive comprises one or more selected from 1-butyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-butyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-benzyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-benzyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-bis(fluorosulfonyl)imide salt, 1-alkyl-3-methylimidazole-bis(trifluoromethylsulfonyl)amide salt, 1-alkyl-3-methylimidazole-chloride salt, or N-alkyl-N-methylpiperidine-tetrafluoroborate.

6. The electrolyte according to claim 1, wherein the amide compound additive comprises one or more of compounds represented by formula I, formula II, or formula III, ##STR00011## wherein R.sub.1 to R.sub.9 are each independently selected from hydrogen, silyl group, ketone carbonyl group, C.sub.1-C.sub.3 alkyl group unsubstituted or substituted by at least one fluorine atom, and aryl group unsubstituted or substituted by at least one fluorine atom, and wherein the amide compound additive comprises one or more of N,N-dimethylformamide, N,N-dimethylacetamide, N,N-dimethylacetoacetamide, 1,1,1-trifluoro-N,N-dimethylform sulfonamide, N,O-bis(trimethylsilyl)trifluoroacetamide, 2,3,6-trifluorobenzenesulfonamide, N,N-dimethyl-4-fluorobenzenesulfonamide, or N-methyl-N-trimethylsilane trifluoroacetamide.

7. The electrolyte according to claim 1, wherein the cation shielding additive comprises a salt whose cation is an alkali metal element or an alkaline earth metal element.

8. The electrolyte according to claim 1, wherein the cation shielding additive comprises one or more of lithium nitrate, lithium perchlorate, lithium hexafluorophosphate, lithium tetrafluoroborate, lithium bisoxaloborate, lithium difluoroxaloborate, lithium bis(fluorosulfonyl)imide, lithium bis(trifluoromethanesulfonyl)imide, potassium hexafluorophosphate, potassium bis-oxaloborate, potassium difluoro-oxaloborate, potassium bis(fluorosulfonyl)imide, potassium bis(trifluoromethylsulfonyl)imide, cesium nitrate, cesium hexafluorophosphate, cesium bis(fluorosulfonyl)imide, cesium chloride, cesium bromide, calcium nitrate, strontium nitrate, or barium nitrate, and wherein the alloy additive is a compound containing an element from family IVA or family VA.

9. The electrolyte according to claim 1, wherein the alloy additive comprises one or more of antimony trifluoride, antimony pentafluoride, tin difluoride, tin tetrafluoride, bismuth trichloride, or fumed silica.

10. The electrolyte according to claim 1, wherein: a mass percentage of the additive is 1-10% based on total mass of the electrolyte; and the fluoroether solvent is an ether solvent, and the fluoroether solvent comprises a compound represented by formula IV or a crown ether substituted by a fluorine atom, ##STR00012## wherein R.sub.7, R.sub.8, and R.sub.9 are each independently selected from hydrogen, and a straight-chain or branched-chain C.sub.1-C.sub.6 alkyl group unsubstituted or substituted by fluorine or a hydroxyl group, at least one of R.sub.7, R.sub.8, and R.sub.9 contains a fluorine atom, and R.sub.7 and R.sub.9 optionally are combined with oxygen to which R.sub.7 and R.sub.9 are connected and R.sub.8 connected to the oxygen, to generate a 5- or 6-membered saturated heterocyclic ring, wherein at least one hydrogen atom on the ring is substituted by fluorine or a fluoroalkyl group, and wherein the fluoroether solvent comprises one or more of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane, 2-(2-ethoxyethoxy)-1,1,1-trifluoroethane, 1,2-bis(2,2-difluoroethoxy)ethane, 2-(2-(2,2-difluoroethoxy)ethoxy)-1,1,1-trifluoroethane, 1,2-bis(2,2,2-trifluoroethoxy)ethane, 1,1,1,3,3,3-hexafluoroisopropylmethyl ether, 2,2,2-trifluoroethyl-1,1,2,3,3,3-hexafluoropropyl ether, 2,2-bis(trifluoromethyl)-1,3-dioxolane, 2,2-dimethoxy-4-(Trifluoromethyl)-1,3-dioxopentane, 2-ethoxy-4-(trifluoromethyl)-1,3-dioxopentane, octafluorotetrahydrofuran, ethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol dimethyl ether substituted by at least one fluorine atom, triethylene glycol dimethyl ether substituted by at least one fluorine atom, tetraethylene glycol dimethyl ether substituted by at least one fluorine atom, diethylene glycol diethyl ether substituted by at least one fluorine atom, diisopropyl ether substituted by at least one fluorine atom, dibutyl ether substituted by at least one fluorine atom, diethylene glycol dibutyl ether substituted by at least one fluorine

atom, 1,4-diethoxybutane substituted by at least one fluorine atom, 15-crown ether-5 substituted by at least one fluorine atom, 12-crown ether-4 substituted by at least one fluorine atom, or 18-crown ether-6 substituted by at least one fluorine atom; and optionally at least one of 2,2,3,3-tetrafluoro-1,4-dimethoxybutane, 2,2-dimethoxy-4-(trifluoromethyl)-1,3-dioxopentane.

**11.** The electrolyte according to claim 1, wherein: a mass percentage of the fluoroether solvent is 20%-90% based on a total mass of the electrolyte; and the electrolyte further comprising an electrolytic salt that is a sodium salt, wherein the sodium salt comprises one or more of sodium nitrate, sodium perchlorate, sodium hexafluorophosphate, sodium tetrafluoroborate, sodium tetrafluoroyttrate, sodium hexafluoroarsenate, sodium acetate, sodium trifluoroacetate, sodium bisoxaloborate, sodium difluoroxaloborate, tetrafluoroborate sodium phenylborate, sodium trifluoromethanesulfonate, sodium bis(fluorosulfonyl)imide, sodium bis(trifluoromethanesulfonyl)imide, or sodium (n-perfluorobutylsulfonyl)imide, wherein a mass percentage of the electrolytic salt is 2%-70%, or 20%-70%, based on the total mass of the electrolyte.

**12.** A secondary battery, comprising: an electrolyte comprising: a fluoroether solvent; and an additive, wherein the additive comprises at least one of an ionic liquid additive, an amide compound additive, a cation shielding additive, or an alloy additive.

**13.** The secondary battery according to claim 12, wherein the secondary battery comprises at least one of lithium metal battery or sodium metal battery, and wherein the secondary battery is a sodium metal battery with no negative electrode.

**14.** The secondary battery according to claim 12, wherein the secondary battery comprises a positive electrode plate, wherein the positive electrode plate comprises a positive electrode active material, and the positive electrode active material comprises one or more of Prussian blue compound, polyanionic compound, or layered oxide, and wherein a surface of particles of the positive electrode active material comprises a coating layer, wherein the coating layer comprises one or more of carbon material, polyaniline, polypyrrole, poly(3,4-ethylenedioxythiophene), aluminum oxide, zinc oxide, titanium oxide, zirconium oxide, magnesium oxide, silicon oxide, lanthanum oxide, sodium fluoride, lithium fluoride, or aluminum fluoride.

**15.** The secondary battery according to claim 14, wherein the coating layer has a thickness between 2 nm and 1000 nm.

**16.** The secondary battery according to claim 12, wherein the secondary battery comprises a negative electrode plate, wherein the negative electrode plate comprises a negative electrode current collector and a primer layer is disposed on at least one surface of the negative electrode current collector, and the primer layer comprises one or more of carbon nanotube, graphite, graphene, silver composite carbon nanoparticle, or tin composite carbon nanoparticle.

**17.** The secondary battery according to claim 16, wherein the negative electrode current collector comprises at least one of metal foil, metal foam current collector, metal mesh current collector, carbon felt current collector, carbon cloth current collector, carbon paper current collector, or composite current collector.

**18.** The secondary battery according to claim 16, wherein the primer layer has an areal density between 2 g/m<sup>2</sup> and 50 g/m<sup>2</sup>.

**19.** The secondary battery according to claim 16, wherein the primer layer has a thickness between 1 μm and 100 μm.

**20.** An electric apparatus, comprising: at least one secondary battery, the at least one secondary battery including an electrolyte comprising: a fluoroether solvent; and an additive, wherein the additive comprises at least one of an ionic liquid additive, an amide compound additive, a cation shielding additive, or an alloy additive.

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