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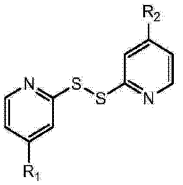
Claims 1 page, Specification 5 pages

(54) Title of Invention

A Non-Aqueous Electrolyte, Its Preparation Method, and a High-Voltage Lithium-Ion Battery

(57) Abstract

This invention discloses a non-aqueous electrolyte and its preparation method, along with a high-voltage lithium-ion battery. The electrolyte mainly includes organic solvents, conductive lithium salts, and additives. The organic solvents consist of at least one of the following: cyclic carbonate solvents, aromatic hydrocarbon solvents, and linear solvents. The conductive lithium salt concentration in the organic solvent ranges from 0.8 to 1.5 mol/L. The additive is used in an amount ranging from 0.01 to 10.0 wt.%, and it is at least one of the compounds represented by the general formula (1) below,



(I)

where R_1 and R_2 are selected from any one of hydrogen group, acetoxy, methoxy, ethoxy, benzene ring, cycloalkyl, C_1-C_4 alkenyl, carboxyl, ester, aliphatic carbonate, and fluorine and chlorine atoms. The addition of these compounds into the non-aqueous electrolyte improves the electrode/electrolyte interface film properties, thereby helping improve the cycle life of lithium-ion batteries operating at high voltages (greater than 4.2 V) and mitigate the problem of gas swelling during high-temperature storage.

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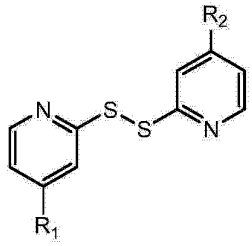
1. A non-aqueous electrolyte, comprising an organic solvent, a conductive lithium salt, and an additive, wherein the organic solvent is selected from at least one of cyclic carbonate solvents, aromatic hydrocarbon solvents, and linear solvents, and the additive is a substituted dipyridyl disulfide derivative, with the following structural formula:



where R_1 and R_2 are selected from any one of hydrogen group, acetoxy, methoxy, ethoxy, benzene ring, cycloalkyl, C_1-C_4 alkenyl, carboxyl, ester, aliphatic carbonate, and fluorine and chlorine atoms.

2. The non-aqueous electrolyte according to claim 1, wherein R_1 and R_2 respectively represent at least one of methoxy, ethoxy, phenyl, and fluorine atoms.

3. The non-aqueous electrolyte according to claim 1, wherein the substituted dipyridyl disulfide derivative is at least one of dipyridyl disulfide, bis(4-methoxy-pyridine) disulfide, bis(4-ethoxy-pyridine) disulfide, bis(4-phenyl-pyridine) disulfide, and bis(4-fluoro-pyridine) disulfide.

4. The non-aqueous electrolyte according to claim 1, wherein the concentration of the conductive lithium salt in the organic solvent is between 0.8–1.5 mol/L, and the additive is present in an amount of 0.01–10.0% by weight of the organic solvent.

5. The non-aqueous electrolyte according to claim 1, wherein the cyclic carbonate solvent is at least one of ethylene carbonate, propylene carbonate, fluorinated ethylene carbonate, γ-butyrolactone, and γ-valerolactone.

6. The non-aqueous electrolyte according to claim 1, wherein the aromatic hydrocarbon solvent is at least one of benzene, fluorobenzene, difluorobenzene, toluene, trifluorobenzene, and xylene; and the linear solvent is at least one of dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, ethyl acetate, methyl propyl carbonate, ethers, and fluorinated ethers.

7. The non-aqueous electrolyte according to claim 1, wherein the conductive lithium salt is at least one of $LiPF_6$, $LiBF_4$, $LiSO_3CF_3$, $LiClO_4$, $Li(CF_3SO_2)_2N$, and $LiC(CF_3SO_2)_3$.

8. The non-aqueous electrolyte according to claim 1, wherein it further includes commonly used additives selected from vinylene carbonate, ethylene vinyl carbonate, fluorinated ethylene carbonate, propane sultone, butane sultone, adiponitrile, succinonitrile, LiBOB, LiODFB, etc., and wherein these commonly used additives constitute 0.1–5.0% of the total mass of the electrolyte.

9. A method for preparing the electrolyte, comprising:

(1) mixing the organic solvents in proportion and using 5Å molecular sieves, calcium hydride, and lithium hydride to remove impurities and moisture;

(2) dissolving the conductive lithium salt in the organic solvents at room temperature, and stirring uniformly;

(3) adding the commonly used additives and stirring uniformly;

(4) adding the additives to prepare the non-aqueous electrolyte according to any of claims 1–8.

10. A high-voltage lithium-ion battery, comprising a positive electrode, a negative electrode, and a separator, wherein the positive electrode material is a lithium-containing transition metal oxide, the negative electrode material is at least one selected from carbon materials capable of lithium ion intercalation/extraction, lithium metal, silicon, tin, or their oxides; the separator is one of woven fabric, nonwoven fabric, and synthetic resin microporous membranes; and the lithium-ion battery further includes the non-aqueous electrolyte according to any of claims 1–9.

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A Non-Aqueous Electrolyte, Its Preparation Method, and a High-Voltage Lithium-Ion Battery

Technical Field

[0001] This invention relates to the field of an electrolyte and its preparation method, as well as a high-voltage lithium-ion battery that contains this electrolyte. Specifically, it concerns a non-aqueous electrolyte and its preparation method, along with a high-voltage lithium-ion battery.

Background Art

[0002] Currently, non-aqueous secondary batteries, such as lithium-ion batteries, are widely used in portable electronic devices due to their advantages, including specific energy, compact size, light weight, no memory effect, and long cycle life. However, as portable electronic devices continue to evolve and the attention for electric vehicles increases, conventional lithium-ion batteries no longer meet these needs.

[0003] Currently, researchers focus on developing high-capacity and high-voltage (greater than 4.2V) positive electrode materials, such as improving the operating voltage of lithium cobalt oxides and lithium manganese oxides (greater than 4.2V), as well as developing high-voltage lithium nickel manganese composite oxides. However, these positive electrode materials tend to undergo structural changes at high operating voltages, causing transition metal dissolution and deposition on the negative electrode. Additionally, conventional organic electrolytes are more prone to decomposition at high voltages, and these factors lead to the deterioration of the high-voltage lithium-ion battery performance.

[0004] Moreover, the negative electrode materials for lithium-ion batteries are typically carbon-based or alloy materials capable of intercalating/extracting lithium ions, and non-aqueous electrolytes for commercial batteries are composed of lithium salts and organic carbonate solvents. However, during charging (especially under high-temperature and high-voltage conditions), the organic carbonate electrolytes undergo reduction and decomposition at the electrode surfaces as lithium ions intercalate into the negative electrode material. The solid decomposition products cover the electrode surface, increasing the internal resistance of the battery. The gaseous decomposition products, such as H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, C_3H_6, etc., lead to an increase in internal pressure of the battery, causing the battery to swell, impeding the movement of lithium ions, and resulting in performance degradation.

[0005] Research has shown that improving the electrode/electrolyte interface properties can effectively solve the related issues of non-aqueous electrolytes in lithium-ion batteries. The application of functional additives in the electrolytes of lithium-ion batteries plays a key role in enhancing the interface properties. This method has been widely researched due to its advantages such as being simple and achieving significant effects. For instance, the invention patent CN00129234.X improves the discharge capacity retention by adding diphenyl disulfide derivatives to the electrolyte. Chinese patent application No. 201310279092.7 discloses that thiophene-based thioether compounds can form a polymeric film on the positive electrode surface, inhibiting the oxidative decomposition of the electrolyte and improving high-voltage performance of batteries. These organic additives can improve the electrode/electrolyte interface properties, but the quantity of the additives must be strictly controlled. Additionally, the current development of high-voltage lithium-ion battery electrolyte additives remains limited, with relatively single-function effects. Therefore, it is essential to develop novel electrolyte additives to improve the electrode/electrolyte interface properties of lithium-ion batteries under high-temperature and high-voltage conditions.

Summary of the invention

[0006] In view of the issues in the background art, the objective of this invention is to provide a non-aqueous electrolyte and its preparation method, which can suppress battery swelling at high temperatures while maintaining a high discharge capacity retention for the battery.

[0007] The specific solution is as follows:

[0008] A non-aqueous electrolyte, comprising an organic solvent, a conductive lithium salt, and an additive, wherein the organic solvent is selected from at least one of cyclic carbonate solvents, aromatic hydrocarbon solvents, and linear solvents; and the additive is a substituted dipyridyl disulfide derivative, with the following structural formula:

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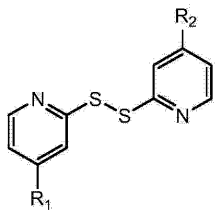
[0009]



[0010] where R_1 and R_2 are selected from any one of hydrogen group, acetoxy, methoxy, ethoxy, benzene ring, cycloalkyl, C_1-C_4 alkenyl, carboxyl, ester, aliphatic carbonate, and fluorine and chlorine atoms.

[0011] R_1 and R_2 respectively represent at least one of methoxy, ethoxy, phenyl, and fluorine atoms.

[0012] The substituted dipyridyl disulfide derivative is at least one of dipyridyl disulfide, bis(4-methoxy-pyridine) disulfide, bis(4-ethoxy-pyridine) disulfide, bis(4-phenyl-pyridine) disulfide, and bis(4-fluoro-pyridine) disulfide.

[0013] The concentration of the conductive lithium salt in the organic solvent is between 0.8 and 1.5 mol/L, and the additive is present in 0.01–10.0% by weight of the organic solvent.

[0014] The cyclic carbonate solvent is at least one of ethylene carbonate, propylene carbonate, fluorinated ethylene carbonate, γ-butyrolactone, and γ-valerolactone.

[0015] The aromatic hydrocarbon solvent is at least one of benzene, fluorobenzene, difluorobenzene, toluene, trifluorobenzene, and xylene; and the linear solvent is at least one of dimethyl carbonate, ethyl methyl carbonate, diethyl carbonate, ethyl acetate, methyl propyl carbonate, ethers, and fluorinated ethers.

[0016] The conductive lithium salt is selected from at least one of $LiPF_6$, $LiBF_4$, $LiSO_3CF_3$, $LiClO_4$, $Li(CF_3SO_2)_2N$, and $LiC(CF_3SO_2)_3$.

[0017] The electrolyte further includes commonly used additives, which are at least one of vinylene carbonate, ethylene vinyl carbonate, fluorinated ethylene carbonate, propane sultone, butane sultone, adiponitrile, succinonitrile, LiBOB, LiODFB, etc. These commonly used additives constitute 0.1–5.0% by weight of the total mass of the non-aqueous electrolyte.

[0018] A method for preparing the electrolyte is as follows:

[0019] (1) Mix the organic solvents in the required proportions and use 5Å molecular sieves, calcium hydride, and lithium hydride to remove impurities and moisture;

[0020] (2) At room temperature, dissolve the conductive lithium salt in the organic solvents, and stir uniformly;

[0021] (3) Add the commonly used additives, and stir uniformly;

[0022] (4) Add the additives and prepare the non-aqueous electrolyte according to the invention.

[0023] Another objective of this invention is to provide a high-voltage lithium-ion battery, with the following specific solution:

[0024] A high-voltage lithium-ion battery, comprising a positive electrode, a negative electrode, and a separator, wherein the positive electrode material is a lithium-containing transition metal oxide, the negative electrode material is at least one of carbon materials capable of lithium ion intercalation/extraction, lithium metal, silicon or tin, and their oxides; the separator is one of woven fabric, nonwoven fabric, and synthetic resin microporous membrane; and the lithium-ion battery further includes the non-aqueous electrolyte according to the invention.

[0025] The advantages of this invention are as follows:

[0026] (1) The substituted dipyridyl disulfide derivative additives can improve the electrode/electrolyte interface properties, reduce the decomposition of the electrolyte, and prevent damage to the electrodes, thus improving the compatibility between the non-aqueous electrolyte and the active electrode materials;

[0027] (2) By adding the substituted dipyridyl disulfide derivatives and commonly used additives, an interface film forms on the electrode surface of the battery, which can reduce the dissolution of transition metals from the positive electrode, suppress the deposition and reduction of the transition metals on the negative electrode, and protect the electrode materials, which is beneficial for enhancing the high-temperature and high-voltage performance of lithium-ion secondary batteries and improving their cycle

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stability, while effectively suppressing gas swelling issues within the battery.

DETAILED DESCRIPTION

[0028] The following provides further explanation of the present invention through exemplary embodiments. However, the scope of the invention should not be limited to the embodiments; any modifications or changes that do not deviate from the essence of the invention can be understood by those skilled in the art and are within the scope of this invention's protection.

[0029] Embodiment 1

[0030] A non-aqueous electrolyte for high-voltage lithium-ion batteries, primarily comprising organic solvents, conductive lithium salts, and additives, where the organic solvent is composed of cyclic carbonate solvents (ethylene carbonate EC), aromatic hydrocarbon solvents (fluorobenzene FB), and linear carbonate solvents (ethyl methyl carbonate EMC) in a ratio of EC:EMC:FB = 3:6:1. The conductive lithium salt $LiPF_6$ has a concentration of 1.0 mol/L in the organic solvent, and the commonly used additives include 1.0wt.% vinylene carbonate and 1.0wt.% propane sultone. The additive is dipyridyl disulfide used at a concentration of 0.5wt.%.

[0031] The preparation method for the electrolyte is as follows:

[0032] (1) Mix the organic solvents in the required proportions and use 5Å molecular sieves, calcium hydride, and lithium hydride to remove impurities and moisture;

[0033] (2) At room temperature, dissolve the conductive lithium salt in the organic solvents, and stir uniformly;

[0034] (3) Add the commonly used additives vinylene carbonate and propane sultone, and stir uniformly;

[0035] (4) Add the dipyridyl disulfide additive to obtain the high-voltage lithium-ion battery non-aqueous electrolyte of this embodiment.

[0036] The high-voltage lithium-ion battery electrolyte of this invention was applied to a lithium cobalt oxide/graphite soft-pack battery. The cycling performance of the lithium cobalt oxide/graphite soft-pack battery was tested at room temperature with a voltage range of 3.0-4.4V and at a 1C charge/discharge rate.

[0037] After 200 charge-discharge cycles, the discharge capacity was 90.1% of the initial discharge capacity.

[0038] Embodiment 2

[0039] A preparation method for the non-aqueous electrolyte for lithium-ion batteries is the same as that of Embodiment 1, except that 1.0wt.% dipyridyl disulfide was used. The resulting non-aqueous electrolyte was applied to a full battery and tested for its performance using the same method as that of Embodiment 1.

[0040] After 200 charge-discharge cycles, the discharge capacity was 91.2% of the initial discharge capacity.

[0041] Embodiment 3

[0042] A preparation method for the non-aqueous electrolyte for high-voltage lithium-ion batteries is the same as that of Embodiment 1, except that 3.0 wt.% dipyridyl disulfide was used. The resulting non-aqueous electrolyte was applied to a full battery and tested for its performance using the same method as that of Embodiment 1.

[0043] After 200 charge-discharge cycles, the discharge capacity was 93.1% of the initial discharge capacity.

[0044] Embodiment 4

[0045] A preparation method for the non-aqueous electrolyte for high-voltage lithium-ion batteries is the same as that of Embodiment 1, except that 2.0 wt.% bis(4-methoxy-pyridine) disulfide was used. The resulting non-aqueous electrolyte was applied to a full battery and tested for its performance using the same method as that of Embodiment 1.

[0046] After 200 charge-discharge cycles, the discharge capacity was 92.6% of the initial discharge capacity.

[0047] Embodiment 5

[0048] A preparation method for the non-aqueous electrolyte for high-voltage lithium-ion batteries is the same as in Embodiment 1, except that 2.0 wt.% bis(4-ethoxy-pyridine) disulfide is used. The resulting non-aqueous electrolyte was applied to a full battery, and its performance was tested using the same method as

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that of Embodiment 1.

[0049] After 200 charge-discharge cycles, the discharge capacity was 91.4% of the initial discharge capacity.

[0050] Embodiment 6

[0051] A preparation method for the non-aqueous electrolyte for high-voltage lithium-ion batteries is the same as in Embodiment 1, except that 2.0 wt.% bis(4-phenyl-pyridine) disulfide is used. The resulting non-aqueous electrolyte was applied to a full battery, and its performance was tested using the same method as that of Embodiment 1.

[0052] After 200 charge-discharge cycles, the discharge capacity was 93.2% of the initial discharge capacity.

[0053] Embodiment 7

[0054] A preparation method for the non-aqueous electrolyte for high-voltage lithium-ion batteries is the same as in Embodiment 1, except that 1.0 wt.% bis(4-fluoro-pyridine) disulfide is used. The resulting non-aqueous electrolyte was applied to a full battery, and its performance was tested using the same method as that of Embodiment 1.

[0055] After 200 charge-discharge cycles, the discharge capacity was 90.5% of the initial discharge capacity.

[0056] Comparative Example 1

[0057] In this comparative example, the electrolyte for lithium-ion batteries mainly contains the following ingredients: organic solvents and aromatic hydrocarbon solvents (ethylene carbonate EC, ethyl methyl carbonate EMC, and fluorobenzene FB in a weight ratio of EC:EMC:FB = 3:6:1), with the conductive lithium salt $LiPF_6$ having a concentration of 1.0 mol/L in the organic solvent.

[0058] After 200 charge-discharge cycles, the discharge capacity was 73.7% of the initial discharge capacity.

[0059] Application Experiment of Embodiments and Comparative Example:

[0060] Charge-Discharge Testing Conditions: In order to measure the charge-discharge performance of batteries using the electrolyte prepared according to the present invention, the following procedure was conducted: lithium cobalt oxide positive electrode sheets and graphite negative electrode sheets were prepared according to conventional methods. The electrolyte prepared in Embodiment 1 was injected into these electrode sheets within a glove box, and 053048 soft-pack batteries were assembled. The prepared 053048 soft-pack batteries were tested using the Neware (BS-9300R model) battery testing system for charge-discharge performance. A battery prepared with the electrolyte from the comparative example was also tested for comparison. The batteries were cycled at a 1C charge/discharge rate within a voltage range of 3.0–4.4V. The results from the testing indicated that, after 200 cycles, the lithium-ion batteries prepared using the electrolyte of the present invention, with the addition of substituted dipyridyl disulfide derivatives, still maintained a high battery capacity, showing over 20% higher charge-discharge capacity compared to the batteries prepared with the conventional electrolyte in the comparative example.

[0061] High-temperature expansion performance test: The testing method adopted in the present invention is as follows:

[0062] High-temperature storage conditions: The battery is charged at 1C rate to the cutoff voltage, then charged at constant voltage until the cutoff current is below 0.1C, and end. The battery is stored in a 60°C high-temperature chamber for 7 days. The expansion rate is calculated using the following formula:

[0063]

$$\textbf{Expansion rate (\%)} = \frac{(T - T_0)}{T_0} \times 100 ,$$

[0064] where T is the battery thickness after high-temperature storage, and T_0 is the battery thickness before high-temperature storage.

[0065] Test results are shown in Table 1

[0066]

Embodiment	Expansion Rate after 7-Day High-Temperature Storage
Embodiment 1	2.10%

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Embodiment 2	1.90%
Embodiment 3	1.80%
Embodiment 4	2.00%
Embodiment 5	2.30%
Embodiment 6	2.10%
Embodiment 7	2.00%
Comparative Example 1	8.70%

[0067] From the above data, it can be concluded that the batteries prepared using the electrolyte of the present invention exhibit significantly lower expansion rates under high-temperature conditions, which greatly improves their safety performance.

[0068] The above provides specific descriptions of feasible embodiments of the present invention, but it should not be construed as limiting the scope of the invention's protection.

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DECLARATION OF TRANSLATOR

I, Johnson Wong, hereby declare as follows:

1. I personally prepared the attached translation from Chinese into English of the patent that is entitled "CN104051787A" in Chinese and "CN104051787A " in English (also attached).

2. The attached translation is, to the best of my knowledge, a true, full and accurate translation of the attached Chinese document.

3. I am competent to perform this translation, because I have 18 years of experience as a professional Chinese-to-English patent translator.

4. I declare under the penalty of perjury under the laws of the United States that the foregoing is true and correct; and further declare that I am aware that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 1001 of Title 18 of the United States Code.

Dated: 12-9-22

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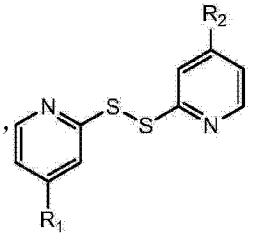
权利要求书1页 说明书5页

(54)发明名称

一种非水电解液及其制备方法以及一种高电压锂离子电池

(57)摘要

本发明公开了一种非水电解液及其制备方法以及一种高电压锂离子电池，电解液主要包括：有机溶剂、导电锂盐和添加剂，有机溶剂为环状碳酸酯溶剂、芳香烃溶剂和线性溶剂的一种以上组成，导电锂盐在有机溶剂中的浓度为0.8-1.5mol/L，所述添加剂为用量0.01-10.0wt.%的下述通式(I)表示的化合物中的至少一种，



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式中，R_1和R_2选自氢基、乙酰氧基、甲氧基、乙氧基、苯环、环烷基、C_1-C_4的烯基、羧基、酯基、脂肪族碳酸酯基以及氟原子、氯原子的任一种。非水电解液中添加了上述化合物后可以改善电极/电解液界面膜的性质，有利于提高锂离子电池高电压(大于4.2V)的循环寿命、以及抑制高温储存时的气胀问题。

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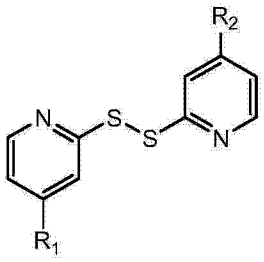
1. 一种非水电解液，包括有机溶剂、导电锂盐和添加剂，其中：所述有机溶剂选自环状碳酸酯溶剂、芳香烃溶剂和线性溶剂的一种以上，所述添加剂为：取代二硫化二吡啶衍生物，其结构式如下：



其中 R_1 和 R_2 选自氢基、乙酰氧基、甲氧基、乙氧基、苯环、环烷基、C_1-C_4 的烯基、羧基、酯基、脂肪族碳酸酯基以及氟原子、氯原子的任一种。

2. 根据权利要求 1 所述的非水电解液，其中：所述 R_1 和 R_2 分别代表甲氧基、乙氧基、苯基、氟原子一种以上。

3. 根据权利要求 1 所述的非水电解液，其中：该取代二硫化二吡啶衍生物为二硫化二吡啶，二硫化二（4- 甲氧基吡啶）、二硫化二（4- 乙氧基吡啶）、二硫化二（4- 苯基吡啶）、二硫化二（4- 氟吡啶）一种以上。

4. 根据权利要求 1 所述的非水电解液，其中：所述导电锂盐在有机溶剂中的浓度为 0.8-1.5mol/L，所述添加剂的用量为有机溶剂重量的 0.01-10.0%。

5. 根据权利要求 1 所述的电解液，其中：所述环状碳酸酯溶剂为碳酸乙烯酯、碳酸丙烯酯、氟代碳酸乙烯酯、γ- 丁内酯和 γ- 戊内酯一种以上。

6. 根据权利要求 1 所述的非水电解液，其中：所述芳香烃溶剂为苯、氟苯、二氟代苯、甲苯、三氟代苯、二甲苯的一种以上；所述线型溶剂为碳酸二甲酯、碳酸甲乙酯、碳酸二乙酯、乙酸乙酯、碳酸甲丙酯、醚类和氟代醚的一种以上。

7. 根据权利要求 1 所述的非水电解液，其中：所述导电锂盐为 $LiPF_6$、$LiBF_4$、$LiSO_3CF_3$、$LiClO_4$、$Li(CF_3SO_2)_2N$、$LiC(CF_3SO_2)_3$ 中的一种以上。

8. 根据权利要求 1 所述的非水电解液，其中：还包括常用添加剂，所述常用添加剂为碳酸亚乙烯酯、碳酸乙烯亚乙酯、氟代碳酸乙烯酯、丙磺酸内酯、丁磺酸内酯、己二腈、丁二腈、LiBOB、LiODFB 等中的一种以上，所述常用添加剂占非水电解液总质量的 0.1-5.0%。

9. 一种电解液制备方法，电解液的配制方法是：

(1) 将有机溶剂按比例混合后用 5 Å 分子筛、氢化钙、氢化锂纯化除杂、除水；

(2) 在室温条件下，将导电锂盐溶解在上述有机溶剂中，并搅拌均匀；

(3) 加入常用添加剂，并搅拌均匀。

(4) 加入添加剂，制得权利要求 1-8 任一项所述的非水电解液。

10. 一种高电压锂离子电池，包括正极、负极和隔膜，其中：正极材料为含锂过渡金属氧化物，负极材料为可嵌入 / 脱出锂离子的碳材料、锂金属、硅或锡及其氧化物中的一种以上；隔膜为织布、无纺布、合成树脂微多孔膜的一种；锂离子电池还包括权利要求 1-9 任一项所述的非水电解液。

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一种非水电解液及其制备方法以及一种高电压锂离子电池

技术领域

[0001] 本发明涉及一种电解液及其制备方法以及包含该电解液高电压锂离子电池制备领域，尤其涉及一种非水电解液及其制备方法以及一种高电压锂离子电池。

背景技术

[0002] 目前，非水二次电池诸如锂离子电池因其比能量高、体积小、质量轻、无记忆效应、循环寿命长等优点广泛应用于便携式电子设备中。随着便携式电子设备的不断更新和人们对电动交通工具的关注，常规锂离子电池已经不能满足人们的需求。

[0003] 目前，研究者们主要通过开发高容量、高工作电压（大于 4.2V）的正极材料，如提高锂钴复合氧化物、锂锰复合氧化物的工作电压（大于 4.2V），开发高工作电压的锂镍锰复合氧化物等。然而，这些正极材料在高工作电压条件下容易发生结构改变，过渡金属发生溶解并在负极上沉积，另外常规有机电解液在高电压下更容易发生分解，这些因素导致了高电压锂离子电池性能的恶化。

[0004] 另外，锂离子电池的负极材料主要为可脱嵌锂的碳质或合金材料，而商品化电池的非水电解液是由锂盐和有机碳酸酯溶剂组成。然而，在充电时（尤其在高温、高电压条件下），锂离子在嵌入负极材料的过程中，有机碳酸酯电解液会在电极表面发生还原分解，分解的固体产物将覆盖在电极表面，增大电池内阻。而分解出的气体产物如 H_2、CO、CO_2、CH_4、C_2H_6、C_3H_8、C_3H_6 等将使电池内部压力增加，引起电池膨胀，妨碍锂离子的移动，使电池性能下降。

[0005] 研究发现，通过改善锂离子电池电极／电解液界面性质，可以有效解决锂离子电池非水电解液的相关问题。而锂离子电池电解液功能添加剂的应用对界面性质的改善起到了重要作用。由于该方法简单，效果显著等优点受到了广泛研究者的关注。如发明专利 CN00129234.X 通过向电解质中添加二硫化二苯衍生物来改进电池的放电容量保持率。中国专利申请号 201310279092.7 公布了噻吩基硫醚类化合物能够在正极表面形成聚合物膜，减小电解液的氧化分解，提高了电池的高电压性能。上述有机添加剂都能够对电极／电解液界面性质进行改善，然而对添加剂的使用量需要严格的掌控。另外，目前对高电压锂离子电池电解液添加剂的开发种类仍较少，效果单一。因而需要研发出新型电解液添加剂改善高温高电压锂离子电池的电极／电解液界面性质显得非常必要。

发明内容

[0006] 鉴于背景技术所存在的问题，本发明的目的在于提供一种非水电解液及其制备方法，该电解液可以在高温时抑制电池膨胀，同时使电池具有高放电容量保持率。

[0007] 具体方案如下：

[0008] 一种非水电解液，包括有机溶剂、导电锂盐和添加剂，其中：所述有机溶剂选自环状碳酸酯溶剂、芳香烃溶剂和线性溶剂的一种以上，所述添加剂为取代二硫化二吡啶衍生物，其结构式如下：

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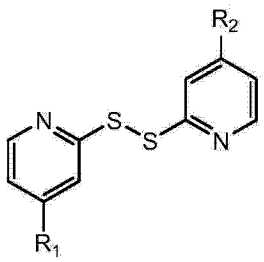
[0009]



[0010] 其中 R_1 和 R_2 选自氢基、乙酰氧基、甲氧基、乙氧基、苯环、环烷基、C_1-C_4 的烯基、羧基、酯基、脂肪族碳酸酯基以及氟原子、氯原子的任一种。

[0011] 所述 R_1 和 R_2 分别代表甲氧基、乙氧基、苯基、氟原子一种以上。

[0012] 该取代二硫化二吡啶衍生物为二硫化二吡啶，二硫化二（4- 甲氧基吡啶）、二硫化二（4- 乙氧基吡啶）、二硫化二（4- 苯基吡啶）、二硫化二（4- 氟吡啶）一种以上。

[0013] 所述导电锂盐在有机溶剂中的浓度为 0.8-1.5mol/L，所述添加剂的用量为有机溶剂重量的 0.01-10.0％。

[0014] 所述环状碳酸酯溶剂为碳酸乙烯酯、碳酸丙烯酯、氟代碳酸乙烯酯、γ－丁内酯和γ－戊内酯一种以上。

[0015] 所述芳香烃溶剂为苯、氟苯、二氟代苯、甲苯、三氟代苯、二甲苯的一种以上；所述线型溶剂为碳酸二甲酯、碳酸甲乙酯、碳酸二乙酯、乙酸乙酯、碳酸甲丙酯、醚类和氟代醚的一种以上。

[0016] 所述导电锂盐为 $LiPF_6$、$LiBF_4$、$LiSO_3CF_3$、$LiClO_4$、$Li(CF_3SO_2)_2N$、$LiC(CF_3SO_2)_3$ 中的一种以上。

[0017] 还包括常用添加剂，所述常用添加剂为碳酸亚乙烯酯、碳酸乙烯亚乙酯、氟代碳酸乙烯酯、丙磺酸内酯、丁磺酸内酯、己二腈、丁二腈、LiBOB、LiODFB 等中的一种以上，所述常用添加剂占非水电解液总质量的 0.1-5.0％。

[0018] 一种电解液制备方法，电解液的配制方法是：

[0019] (1) 将有机溶剂按比例混合后用 5 Å 分子筛、氢化钙、氢化锂纯化除杂、除水；

[0020] (2) 在室温条件下，将导电锂盐溶解在上述有机溶剂中，并搅拌均匀；

[0021] (3) 加入常用添加剂，并搅拌均匀。

[0022] (4) 加入添加剂，制得本发明的非水电解液。

[0023] 本发明的另一目的是提供一种高电压锂离子电池，具体方案如下：

[0024] 一种高电压锂离子电池，包括正极、负极和隔膜，其中：正极材料为含锂过渡金属氧化物，负极材料为可嵌入／脱出锂离子的碳材料、锂金属、硅或锡及其氧化物中的一种以上；隔膜为织布、无纺布、合成树脂微多孔膜的一种；锂离子电池还包括本发明的非水电解液。

[0025] 本发明的优点在于：

[0026] (1) 添加剂取代二硫化二吡啶衍生物能够改善电极／电解液界面性质，减少电解液的分解和对电极的破坏，改善非水电解液与活性电极材料的兼容性；

[0027] (2) 通过添加取代二硫化二吡啶衍生物和常用添加剂，在电池的电极表面形成界面膜能够减少过渡金属从正极上的溶出，抑制过渡金属在负极上的沉积和还原，保护电极

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材料，有利于提高锂二次电池的高温、高电压性能和循环稳定性，并有效抑制电池的气胀问题。

具体实施方式

[0028] 下面通过示例性的实施例对本发明进行进一步的阐述；但本发明的范围不应局限于实施例的范围，任何不偏离本发明主旨的变化或改变能够为本领域的技术人员所理解，都在本发明的保护范围以内。

[0029] 实施例 1

[0030] 一种高电压锂离子电池用非水电解液，主要包含有机溶剂、导电锂盐和添加剂，所述有机溶剂由环状碳酸酯溶剂（碳酸乙烯酯 EC），芳香烃溶剂（氟苯 FB）、线型碳酸酯溶剂（碳酸甲乙酯 EMC）组成，EC：EMC：FB ＝ 3:6:1。所述导电锂盐 $LiPF_6$ 在有机溶剂中的浓度为 1.0mol/L，所述常用添加剂为 1.0wt.％用量的碳酸亚乙烯酯和用量为 1.0wt.％的丙磺酸内酯，所述添加剂为二硫化二吡啶，用量 0.5wt.％。

[0031] 电解液的配制方法是：

[0032] (1) 将有机溶剂按比例混合后用 5 Å 分子筛、氢化钙、氢化锂纯化除杂、除水；

[0033] (2) 在室温条件下，将导电锂盐溶解在上述有机溶剂中，并搅拌均匀；

[0034] (3) 加入常用添加剂碳酸亚乙烯酯和丙磺酸内酯，并搅拌均匀。

[0035] (4) 加入添加剂二硫化二吡啶，即得本实施例所述高电压锂离子电池非水电解液。

[0036] 将本发明的高电压锂离子电池电解液用于钴酸锂 / 石墨软包装电池，测试钴酸锂 / 石墨软包装电池在常温环境下 3.0-4.4V，1C 倍率充放电的循环性能。

[0037] 经过 200 次充放电循环后，放电容量为初始放电容量的 90.1％

[0038] 实施例 2

[0039] 一种锂离子电池非水电解液的制备方法与实施例 1 相同，所不同的是，使用 1.0wt.％用量的二硫化二吡啶，将如此制备的非水电解液按照与实施例 1 相同的方法应用于全电池中测试其性能。

[0040] 经过 200 次充放电循环后，放电容量为初始放电容量的 91.2％

[0041] 实施例 3

[0042] 一种高电压锂离子电池用非水电解液的制备方法与实施例 1 相同，所不同的是，使用 3.0wt.％用量的二硫化二吡啶，将如此制备的非水电解液按照与实施例 1 相同的方法应用于全电池中测试其性能。

[0043] 经过 200 次充放电循环后，放电容量为初始放电容量的 93.1％

[0044] 实施例 4

[0045] 一种高电压锂离子电池用非水电解液的制备方法与实施例 1 相同，所不同的是，使用 2.0wt.％用量的二硫化二（4- 甲氧基吡啶），将如此制备的非水电解液按照与实施例 1 相同的方法应用于全电池中测试其性能。

[0046] 经过 200 次充放电循环后，放电容量为初始放电容量的 92.6％

[0047] 实施例 5

[0048] 一种高电压锂离子电池用非水电解液的制备方法与实施例 1 相同，所不同的是，使用 2.0wt.％用量的二硫化二（4- 乙氧基吡啶），将如此制备的非水电解液按照与实施例

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1 相同的方法应用于全电池中测试其性能。

[0049] 经过 200 次充放电循环后，放电容量为初始放电容量的 91.4%

[0050] 实施例 6

[0051] 一种高电压锂离子电池用非水电解液的制备方法与实施例 1 相同，所不同的是，使用 2.0wt.%用量的二硫化二（4- 苯基吡啶），将如此制备的非水电解液按照与实施例 1 相同的方法应用于全电池中测试其性能。

[0052] 经过 200 次充放电循环后，放电容量为初始放电容量的 93.2%

[0053] 实施例 7

[0054] 一种高电压锂离子电池用非水电解液的制备方法与实施例 1 相同，所不同的是，使用 1.0wt.%用量的二硫化二（4- 氟吡啶），将如此制备的非水电解液按照与实施例 1 相同的方法应用于全电池中测试其性能。

[0055] 经过 200 次充放电循环后，放电容量为初始放电容量的 90.5%

[0056] 对比例 1、

[0057] 本对比例的锂离子电池电解液，主要包含如下原料：有机溶剂和芳香烃溶剂（碳酸乙烯酯 EC、碳酸甲乙酯 EMC 及氟苯 FB，EC、EMC 及 FB 的重量比为 EC：EMC：FB ＝ 3:6:1），导电锂盐 $LiPF_6$ 在有机溶剂中的浓度为 1.0mol/L。

[0058] 经过 200 次充放电循环后，放电容量为初始放电容量的 73.7%

[0059] 实施例和对比例的应用实验：

[0060] 充放电测试条件：为了测量使用本发明制得的电解液的电池充放电性能，进行以下操作：按照常规方法制备钴酸锂正极片、石墨负极片，使用实施例 1 制备得到电解液在手套箱中注液使用上述极片制备 053048 型软包装电池，用新威（BS-9300R 型）电池测试系统对制备的 053048 型电池进行充放电测试，同时与对比例电解液制备的电池进行比较。电池在电压 3.0-4.4V 的范围以 1C 充放电倍率循环。通过测试结果得出，本发明的电解液中加入取代二硫化二吡啶衍生物后，用本发明的电解液制备的锂离子电池 200 次循环后仍然有很高的电池容量，和对比例中的普通电解液制备的电池相比，充放电容量高出 20%以上。

[0061] 高温膨胀性能测试方面，本发明采用的测试方法为：

[0062] 高温存储实验条件：电池以 1C 倍率恒电流充电至截止电压，恒电压充电至截止电流小于 0.1C 结束。置于 60℃高温箱中存储 7 天。膨胀率计算方式为下式：

[0063]

$$膨胀率(\%) = \frac{(T - T_0)}{T_0} \times 100$$

[0064] 其中，T 为高温存储后的电池厚度，T_0 为高温存储前的电池厚度。

[0065] 测试结果如表 1

[0066]

实施例	高温放置 7 天膨胀率
实施例 1	2.10%

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实施例 2	1.90%
实施例 3	1.80%
实施例 4	2.00%
实施例 5	2.30%
实施例 6	2.10%
实施例 7	2.00%
对比例 1	8.70%

[0067] 通过以上数据可以得出，采用本发明的电解液制备的电池，高温放置膨胀率明显低，安全性能大大提高。

[0068] 以上是针对本发明的可行实施例的具体说明，但并不能限制本发明的保护范围。

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