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(54) **ELECTROLYTIC SOLUTION, ELECTROCHEMICAL DEVICE, SECONDARY BATTERY, AND LITHIUM-ION SECONDARY BATTERY**

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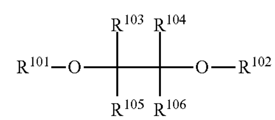
(57) **ABSTRACT**

The disclosure aims to provide an electrolytic solution with which an electrochemical device exhibiting excellent battery characteristics even with a negative electrode containing an alkali metal-containing material can be obtained. Provided is an electrolytic solution which is for use in a battery including a negative electrode containing an alkali metal-containing material, the electrolytic solution containing a solvent, the solvent including a compound (1) represented by the following formula (1):



wherein R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group, R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom.

ELECTROLYTIC SOLUTION, ELECTROCHEMICAL DEVICE, SECONDARY BATTERY, AND LITHIUM-ION SECONDARY BATTERY

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application is a Rule 53(b) Continuation of International Application No. PCT/JP2023/038046 filed Oct. 20, 2023, claiming priority based on Japanese Patent Application No. 2022-177357 filed Nov. 4, 2022, the respective disclosures of which are incorporated herein by reference in their entirety.

TECHNICAL FIELD

[0002] The disclosure relates to electrolytic solutions, electrochemical devices, secondary batteries, and lithium-ion secondary batteries.

BACKGROUND ART

[0003] Current electric appliances demonstrate a tendency to have a reduced weight and a smaller size, which leads to development of electrochemical devices such as lithium-ion secondary batteries having a high energy density. Further, electrochemical devices such as lithium-ion secondary batteries are desired to have improved characteristics as they are applied to more various fields. Improvement in battery characteristics will become more and more important particularly when lithium-ion secondary batteries are put in use for automobiles.

[0004] Patent Literature 1 discloses the use of an electrolytic solution containing a fluorinated diether represented by the formula I: $R^1—O—R^2—O—R^3$ (wherein R^1 and R^3 are each a fluorinated alkyl group and R^2 is an optionally fluorinated alkyl group) in a battery with a lithium metal negative electrode.

CITATION LIST

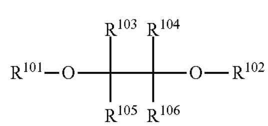
Patent Literature

[0005] Patent Literature 1: WO 2022/128233 A1

SUMMARY

[0006] The disclosure (1) relates to an electrolytic solution which is for use in a battery including a negative electrode containing an alkali metal-containing material, the electrolytic solution containing a solvent, the solvent including a compound (1) represented by the following formula (1):

[Chem. 1]



wherein R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group, R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom.

Advantageous Effects

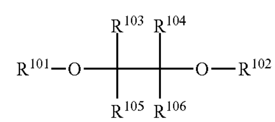
[0007] The disclosure can provide an electrolytic solution with which an electrochemical device exhibiting excellent battery characteristics even with a negative electrode containing an alkali metal-containing material can be obtained.

DESCRIPTION OF EMBODIMENTS

[0008] The disclosure will be specifically described hereinbelow.

[0009] The disclosure relates to an electrolytic solution which is for use in a battery including a negative electrode containing an alkali metal-containing material, the electrolytic solution containing a solvent, the solvent including a compound (1) represented by the following formula (1):

[Chem. 2]



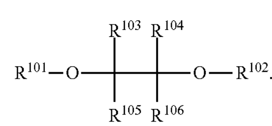
wherein R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group, R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom.

[0010] The electrolytic solution of the disclosure containing a solvent including the compound (1) can improve the battery characteristics (e.g., cycle characteristics, high-temperature storage characteristics) of electrochemical devices such as alkali metal ion secondary batteries including negative electrodes containing an alkali metal-containing material.

[0011] The electrolytic solution of the disclosure can also improve the performance of alkali metal dissolution/deposition.

[0012] The compound (1) is represented by the formula (1):

[Chem. 3]



[0013] In the formula (1), R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group. The non-fluorinated alkyl group preferably has a carbon number of 2 or less, more preferably 1.

[0014] Examples of the non-fluorinated alkyl group include a methyl group (CH_3), an ethyl group (CH_3CH_2), a propyl group ($CH_3CH_2CH_2$), and an isopropyl group ($(CH_3)_2CH$). Preferred are a methyl group and an ethyl group, and more preferred is a methyl group.

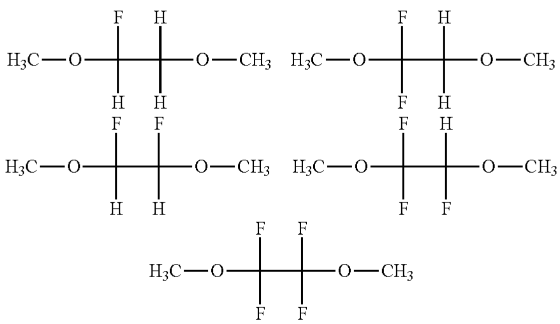
[0015] In the formula (1), R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom. As the number of halogen atoms increases, the acidity increases, resulting in further improvement of the battery characteristics. Thus, preferably, at least two of R^{103} to R^{106} are halogen atoms.

More preferably, at least three of R^{103} to R^{106} are halogen atoms. Most preferably, all of R^{103} to R^{106} are halogen atoms.

[0016] Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Preferred are a fluorine atom and a chlorine atom, and more preferred is a fluorine atom.

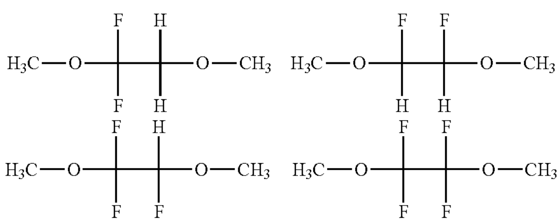
[0017] Examples of the compound (1) include compounds represented by the following formulas.

[Chem. 4]



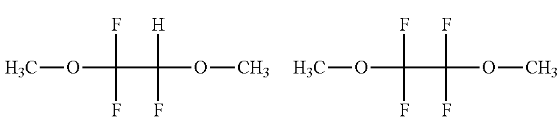
[0018] In particular, the compound (1) is preferably any of compounds represented by the following formulas.

[Chem. 5]



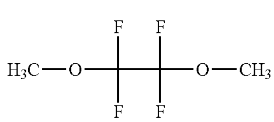
[0019] The compound (1) is more preferably any of compounds represented by the following formulas.

[Chem. 6]



[0020] The compound (1) is most preferably any of compounds represented by the following formulas.

[Chem. 7]



[0021] One of these compounds (1) may be used alone or two or more thereof may be used in any combination.

[0022] In the electrolytic solution of the disclosure, the compound (1) is preferably contained in an amount of 0.01 to 80% by volume relative to the solvent. The compound (1) in an amount within the above range can further improve the battery characteristics of electrochemical devices and the performance of alkali metal dissolution/deposition.

[0023] The amount of the compound (1) relative to the solvent is more preferably 0.1% by volume or more, still more preferably 1.0% by volume or more, further more preferably 5.0% by volume or more, further more preferably 10% by volume or more, further more preferably 20% by volume or more, further more preferably 30% by volume or more, particularly preferably 35% by volume or more, most preferably 40% by volume or more. The amount of the compound (1) is more preferably 70% by volume or less, still more preferably 60% by volume or less, particularly preferably 50% by volume or less, most preferably 45% by volume or less.

[0024] The solvent containing the compound (1) preferably further contains at least one selected from the group consisting of carbonates and carboxylates.

[0025] The carbonate may be either a cyclic carbonate or an acyclic carbonate.

[0026] The cyclic carbonate may be either a non-fluorinated cyclic carbonate or a fluorinated cyclic carbonate.

[0027] An example of the non-fluorinated cyclic carbonate is a non-fluorinated saturated cyclic carbonate. Preferred is a non-fluorinated saturated alkylene carbonate containing a C2-C6 alkylene group, and more preferred is a non-fluorinated saturated alkylene carbonate containing a C2-C4 alkylene group.

[0028] In order to give high permittivity and suitable viscosity, the non-fluorinated saturated cyclic carbonate preferably includes at least one selected from the group consisting of ethylene carbonate, propylene carbonate, cis-2,3-pentylene carbonate, cis-2,3-butylene carbonate, 2,3-pentylene carbonate, 2,3-butylene carbonate, 1,2-pentylene carbonate, 1,2-butylene carbonate, and butylene carbonate.

[0029] One non-fluorinated saturated cyclic carbonate may be used alone, or two or more thereof may be used in any combination at any ratio.

[0030] The non-fluorinated saturated cyclic carbonate, when contained, is preferably present in an amount of 5 to 90% by volume, more preferably 10 to 60% by volume, still more preferably 15 to 45% by volume, relative to the solvent.

[0031] The fluorinated cyclic carbonate is a cyclic carbonate containing a fluorine atom. A solvent containing a fluorinated cyclic carbonate can suitably be used at high voltage.

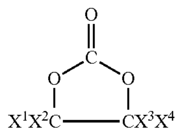
[0032] The term “high voltage” herein means a voltage of 4.2 V or higher. The upper limit of the “high voltage” is preferably 5.5 V, more preferably 5.4 V.

[0033] The fluorinated cyclic carbonate may be either a fluorinated saturated cyclic carbonate or a fluorinated unsaturated cyclic carbonate.

[0034] The fluorinated saturated cyclic carbonate is a saturated cyclic carbonate containing a fluorine atom. Specific examples thereof include a compound represented by the following formula (A):

[Chem. 8]

(A)



wherein X^1 to X^4 are the same as or different from each other, and are each —H, —CH_3, —C_2H_5, —F, a fluorinated alkyl group optionally containing an ether bond, or a fluorinated alkoxy group optionally containing an ether bond; at least one selected from X^1 to X^4 is —F, a fluorinated alkyl group optionally containing an ether bond, or a fluorinated alkoxy group optionally containing an ether bond. Examples of the fluorinated alkyl group include —CF_3, —CF_2H, and —CH_2F.

[0035] The presence of the fluorinated saturated cyclic carbonate in the electrolytic solution of the disclosure when applied to a high-voltage lithium-ion secondary battery, for example, can improve the oxidation resistance of the electrolytic solution, resulting in stable and excellent charge and discharge characteristics.

[0036] The term "ether bond" herein means a bond represented by —O—.

[0037] In order to give a good permittivity and oxidation resistance, one or two of X^1 to X^4 is/are each preferably —F, a fluorinated alkyl group optionally containing an ether bond, or a fluorinated alkoxy group optionally containing an ether bond.

[0038] In anticipation of a decrease in viscosity at low temperature, an increase in flash point, and improvement in solubility of an electrolyte salt, X^1 to X^4 are each preferably —H, —F, a fluorinated alkyl group (a), a fluorinated alkyl group (b) containing an ether bond, or a fluorinated alkoxy group (c).

[0039] The fluorinated alkyl group (a) is a group obtainable by replacing at least one hydrogen atom of an alkyl group by a fluorine atom. The fluorinated alkyl group (a) preferably has a carbon number of 1 to 20, more preferably 1 to 17, still more preferably 1 to 7, particularly preferably 1 to 5.

[0040] Too large a carbon number may cause poor low-temperature characteristics and low solubility of an electrolyte salt. Too small a carbon number may cause low solubility of an electrolyte salt, low discharge efficiency, and increased viscosity, for example.

[0041] Examples of the fluorinated alkyl group (a) having a carbon number of 1 include CFH_2—, CF_2H—, and CF_3—. In order to give good high-temperature storage characteristics, particularly preferred is CF_2H— or CF_3—. Most preferred is CF_3—.

[0042] In order to give good solubility of an electrolyte salt, preferred examples of the fluorinated alkyl group (a) having a carbon number of 2 or greater include fluorinated alkyl groups represented by the following formula (a-1):

$$R^{a1}—R^{a2}— \quad (a\text{-}1)$$

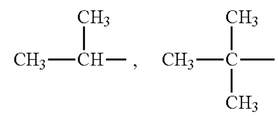
wherein R^{a1} is an alkyl group having a carbon number of 1 or greater and optionally containing a fluorine atom; R^{a2} is a C1-C3 alkylene group optionally containing a fluorine atom; and at least one of R^{a1} or R^{a2} contains a fluorine atom.

[0043] R^{a1} and R^{a2} each may further contain an atom other than carbon, hydrogen, and fluorine atoms.

[0044] R^{a1} is an alkyl group having a carbon number of 1 or greater and optionally containing a fluorine atom. R^{a1} is preferably a C1-C16 linear or branched alkyl group. The carbon number of R^{a1} is more preferably 1 to 6, still more preferably 1 to 3.

[0045] Specifically, for example, CH_3—, CF_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, $CH_3CH_2CH_2CH_2$—, and groups represented by the following formulas:

[Chem. 9]

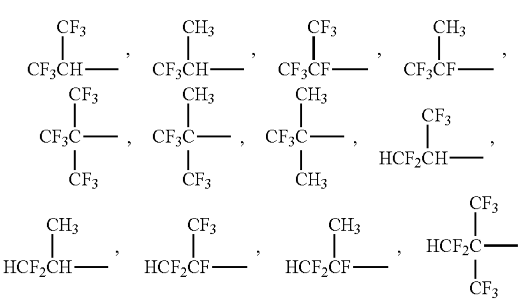


[0046] may be mentioned as linear or branched alkyl groups for R^{a1}.

[0047] Examples of R^{a1} which is a linear alkyl group containing a fluorine atom include CF_3—, CF_3CH_2—, CF_3CF_2—, $CF_3CH_2CH_2$—, $CF_3CF_2CH_2$—, $CF_3CF_2CF_2$—, $CF_3CH_2CF_2$—, $CF_3CH_2CH_2CH_2$—, $CF_3CF_2CH_2CH_2$—, $CF_3CH_2CF_2CH_2$—, $CF_3CF_2CF_2CH_2$—, $CF_3CF_2CF_2CF_2$—, $CF_3CF_2CH_2CF_2$—, $CF_3CH_2CH_2CH_2CH_2$—, $CF_3CF_2CH_2CH_2CH_2$—, $CF_3CH_2CF_2CH_2CH_2$—, $CF_3CF_2CF_2CH_2CH_2$—, $CF_3CF_2CF_2CF_2CH_2$—, $CF_3CF_2CH_2CF_2CH_2$—, $CF_3CF_2CH_2CH_2CH_2CH_2$—, $CF_3CF_2CF_2CF_2CH_2CH_2$—, $CF_3CF_2CH_2CF_2CH_2CH_2$—, HCF_2—, HCF_2CH_2—, HCF_2CF_2—, $HCF_2CH_2CH_2$—, $HCF_2CF_2CH_2$—, $HCF_2CH_2CF_2$—, $HCF_2CF_2CH_2CH_2$—, $HCF_2CH_2CF_2CH_2$—, $HCF_2CF_2CF_2CF_2$—, $HCF_2CF_2CH_2CH_2CH_2$—, $HCF_2CH_2CF_2CH_2CH_2$—, $HCF_2CF_2CF_2CF_2CH_2$—, $HCF_2CF_2CF_2CF_2CH_2CH_2$—, FCH_2—, FCH_2CH_2—, FCH_2CF_2—, $FCH_2CF_2CH_2$—, $FCH_2CF_2CF_2$—, $CH_3CF_2CH_2$—, $CH_3CF_2CF_2$—, $CH_3CF_2CH_2CF_2$—, $CH_3CF_2CF_2CF_2$—, $CH_3CH_2CF_2CF_2$—, $CH_3CF_2CH_2CF_2CH_2$—, $CH_3CF_2CF_2CF_2CH_2$—, $CH_3CF_2CF_2CH_2CH_2$—, $CH_3CH_2CF_2CF_2CH_2$—, $CH_3CF_2CH_2CF_2CH_2CH_2$—, $CH_3CF_2CH_2CF_2CH_2CH_2$—, $HCFClCF_2CH_2$—, $HCF_2CFClCH_2$—, $HCF_2CFClCF_2CFClCH_2$—, and $HCFClCF_2CFClCF_2CH_2$—.

[0048] Examples of R^{a1} which is a branched alkyl group containing a fluorine atom include those represented by the following formulas.

[Chem. 10]



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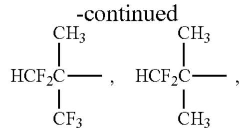
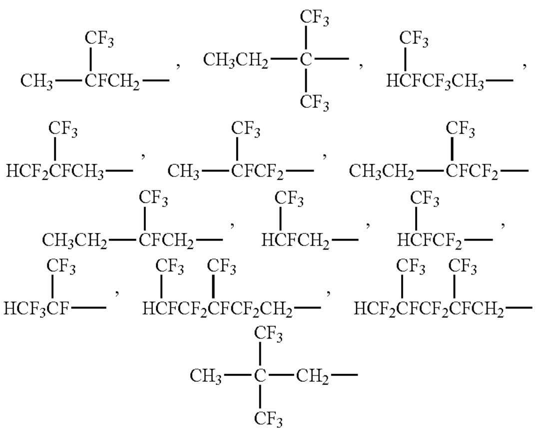


[Chem. 11]



[0049] The presence of a branch such as CH_3— or CF_3— may easily cause high viscosity. Thus, the number of such branches is more preferably small (one) or zero.

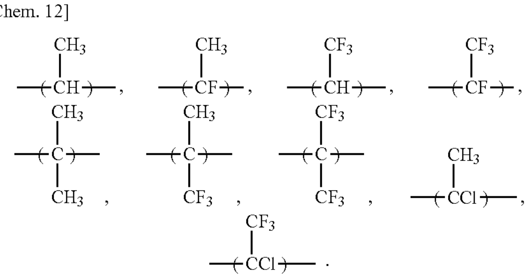
[0050] R^{a2} is a C1-C3 alkylene group optionally containing a fluorine atom. R^{a2} may be either linear or branched. Examples of a minimum structural unit constituting such a linear or branched alkylene group are shown below. R^{a2} is constituted by one or combination of these units.

(i) Linear Minimum Structural Units

[0051] —CH_2—, —CHF—, —CF_2—, —CHCl—, —CFCl—, —CCl_2—

(ii) Branched Minimum Structural Units

[Chem. 12]



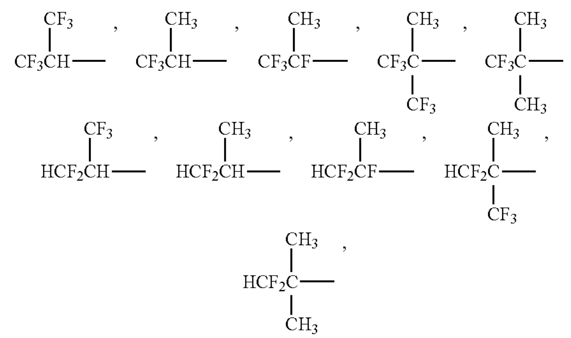
[0052] Preferred among these exemplified units are Cl-free structural units because such units may not be dehydrochlorinated by a base, and thus may be more stable.

[0053] R^{a2} which is a linear group consists only of any of the above linear minimum structural units, and is preferably —CH_2—, —CH_2CH_2—, or CF_2—. In order to further improve the solubility of an electrolyte salt, —CH_2— or —CH_2CH_2— is more preferred.

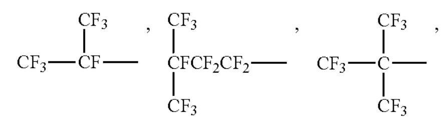
[0054] R^{a2} which is a branched group includes at least one of the above branched minimum structural units. A preferred example thereof is a group represented by —(CX^aX^b)— (wherein X^a is H, F, CH_3, or CF_3; X^b is CH_3 or CF_3; when X^b is CF_3, X^a is H or CH_3). Such a group can much further improve the solubility of an electrolyte salt.

[0055] For example, CF_3CF_2—, HCF_2CF_2—, H_2CFCF_2—, CH_3CF_2—, CF_3CHF—, CH_3CF_2—, $CF_3CF_2CF_2$—, $HCF_2CF_2CF_2$—, $H_2CFCF_2CF_2$—, $CH_3CF_2CF_2$—, and those represented by the following formulas:

[Chem. 13]



[Chem. 14]



may be mentioned as preferred examples of the fluorinated alkyl group (a).

[0056] The fluorinated alkyl group (b) containing an ether bond is a group obtainable by replacing at least one hydrogen atom of an alkyl group containing an ether bond by a fluorine atom. The fluorinated alkyl group (b) containing an ether bond preferably has a carbon number of 2 to 17. Too large a carbon number may cause high viscosity of the fluorinated saturated cyclic carbonate. This may also cause the presence of many fluorine-containing groups, resulting in poor solubility of an electrolyte salt due to reduction in permittivity, and poor miscibility with other solvents. Accordingly, the carbon number of the fluorinated alkyl group (b) containing an ether bond is preferably 2 to 10, more preferably 2 to 7.

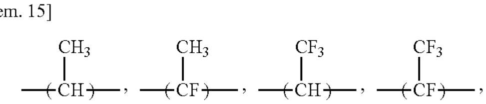
[0057] The alkylene group which constitutes the ether moiety of the fluorinated alkyl group (b) containing an ether bond is a linear or branched alkylene group. Examples of a minimum structural unit constituting such a linear or branched alkylene group are shown below.

(i) Linear Minimum Structural Units

[0058] —CH_2—, —CHF—, —CF_2—, —CHCl—, —CFCl—, —CCl_2—

(ii) Branched Minimum Structural Units

[Chem. 15]



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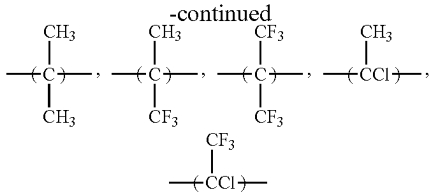


[0059] The alkylene group may be constituted by one of these minimum structural units, or may be constituted by multiple linear units (i), by multiple branched units (ii), or by a combination of a linear unit (i) and a branched unit (ii). Preferred examples will be mentioned in detail later.

[0060] Preferred among these exemplified units are Cl-free structural units because such units may not be dehydrochlorinated by a base, and thus may be more stable.

[0061] A still more preferred example of the fluorinated alkyl group (b) containing an ether bond is a group represented by the following formula (b-1):

$$R^3—(OR^4)_{n1}— \quad \text{(b-1)}$$

wherein R^3 is preferably a C1-C6 alkyl group optionally containing a fluorine atom; R^4 is preferably a C1-C4 alkylene group optionally containing a fluorine atom; n1 is an integer of 1 to 3; and at least one of R^3 or R^4 contains a fluorine atom.

[0062] Examples of R^3 and R^4 include the following groups, and any appropriate combination of these groups can provide the fluorinated alkyl group (b) containing an ether bond represented by the formula (b-1). Still, the groups are not limited thereto.

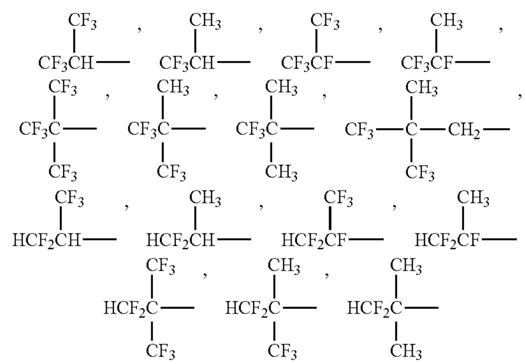
[0063] (1) R^3 is preferably an alkyl group represented by the formula: $X^c{}_3C—(R^5)_{n2}—$, wherein three X^cs are the same as or different from each other, and are each H or F; R^5 is a C1-C5 alkylene group optionally containing a fluorine atom; and n2 is 0 or 1.

[0064] When n2 is 0, R^3 may be $CH_3—$, $CF_3—$, $HCF_2—$, or $H_2CF—$, for example.

[0065] When n2 is 1, specific examples of R^3 which is a linear group include $CF_3CH_2—$, $CF_3CF_2—$, $CF_3CH_2CH_2—$, $CF_3CF_2CH_2—$, $CF_3CF_2CF_2—$, $CF_3CH_2CF_2—$, $CF_3CH_2CH_2CH_2—$, $CF_3CF_2CH_2CH_2—$, $CF_3CH_2CF_2CH_2—$, $CF_3CF_2CF_2CH_2—$, $CF_3CF_2CF_2CF_2—$, $CF_3CF_2CH_2CF_2—$, $CF_3CH_2CH_2CH_2CH_2—$, $CF_3CF_2CH_2CH_2CH_2—$, $CF_3CH_2CF_2CH_2CH_2—$, $CF_3CF_2CF_2CH_2CH_2—$, $CF_3CF_2CF_2CF_2CH_2—$, $CF_3CF_2CH_2CF_2CH_2—$, $CF_3CF_2CH_2CH_2CH_2CH_2—$, $CF_3CF_2CF_2CF_2CH_2CH_2—$, $CF_3CF_2CH_2CF_2CH_2CH_2—$, $HCF_2CH_2—$, $HCF_2CF_2—$, $HCF_2CH_2CH_2—$, $HCF_2CF_2CH_2—$, $HCF_2CH_2CF_2—$, $HCF_2CF_2CH_2CH_2—$, $HCF_2CH_2CF_2CH_2—$, $HCF_2CF_2CF_2CF_2—$, $HCF_2CF_2CH_2CH_2CH_2—$, $HCF_2CH_2CF_2CH_2CH_2—$, $HCF_2CF_2CF_2CF_2CH_2—$, $HCF_2CF_2CF_2CF_2CH_2CH_2—$, $FCH_2CH_2—$, $FCH_2CF_2—$, $FCH_2CF_2CH_2—$, $CH_3CF_2—$, $CH_3CH_2—$, $CH_3CF_2CH_2—$, $CH_3CF_2CF_2—$, $CH_3CH_2CH_2—$, $CH_3CF_2CH_2CF_2—$, $CH_3CF_2CF_2CF_2—$, $CH_3CH_2CF_2CF_2—$, $CH_3CH_2CH_2CH_2—$, $CH_3CF_2CH_2CF_2CH_2—$, $CH_3CF_2CF_2CF_2CH_2—$, $CH_3CF_2CF_2CH_2CH_2—$, $CH_3CH_2CF_2CF_2CH_2—$, $CH_3CF_2CH_2CF_2CH_2CH_2—$, $CH_3CH_2CF_2CF_2CH_2CH_2—$, and $CH_3CF_2CH_2CF_2CH_2CH_2—$.

[0066] When n2 is 1, those represented by the following formulas:

[Chem. 16]



may be mentioned as examples of R^3 which is a branched group.

[0067] The presence of a branch such as $CH_3—$ or $CF_3—$ may easily cause high viscosity. Thus, R^3 is more preferably a linear group.

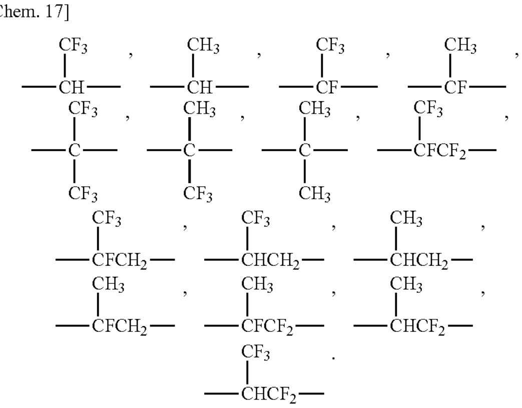
[0068] (2) In $—(OR^4)_{n1}—$ of the formula (b-1), n1 is an integer of 1 to 3, preferably 1 or 2. When n1 is 2 or 3, R^4s may be the same as or different from each other.

[0069] Preferred specific examples of R^4 include the following linear or branched groups.

[0070] Examples of the linear groups include $—CH_2—$, $—CHF—$, $—CF_2—$, $—CH_2CH_2—$, $—CF_2CH_2—$, $—CF_2CF_2—$, $—CH_2CF_2—$, $—CH_2CH_2CH_2—$, $—CH_2CH_2CF_2—$, $—CH_2CF_2CH_2—$, $—CH_2CF_2CF_2—$, $—CF_2CH_2CH_2—$, $—CF_2CF_2CH_2—$, $—CF_2CH_2CF_2—$, and $—CF_2CF_2CF_2—$.

[0071] Those represented by the following formulas:

[Chem. 17]



may be mentioned as examples of the branched groups.

[0072] The fluorinated alkoxy group (c) is a group obtainable by replacing at least one hydrogen atom of an alkoxy group by a fluorine atom. The fluorinated alkoxy group (c) preferably has a carbon number of 1 to 17, more preferably 1 to 6.

[0073] The fluorinated alkoxy group (c) is particularly preferably a fluorinated alkoxy group represented by

$X^d{}_3C—(R^6)_{n3}—O—$, wherein three X^ds are the same as or different from each other, and are each H or F; R^6 is preferably a C1-C5 alkylene group optionally containing a fluorine atom; n3 is 0 or 1; and any of the three X^ds contain a fluorine atom.

[0074] Specific examples of the fluorinated alkoxy group (c) include fluorinated alkoxy groups in which an oxygen atom binds to an end of an alkyl group mentioned as an example for R^{a1} in the formula (a-1).

[0075] The fluorinated alkyl group (a), the fluorinated alkyl group (b) containing an ether bond, and the fluorinated alkoxy group (c) in the fluorinated saturated cyclic carbonate each preferably have a fluorine content of 10% by mass or more. Too less a fluorine content may cause a failure in sufficiently achieving an effect of reducing the viscosity at low temperature and an effect of increasing the flash point. Thus, the fluorine content is more preferably 12% by mass or more, still more preferably 15% by mass or more. The upper limit thereof is usually 76% by mass.

[0076] The fluorine content of each of the fluorinated alkyl group (a), the fluorinated alkyl group (b) containing an ether bond, and the fluorinated alkoxy group (c) is a value calculated based on the corresponding structural formula by the following formula:

$$\{(\text{Number of fluorine atoms} \times 19)/(\text{Formula weight of group})\} \times 100\ (\%).$$

[0077] In order to give good permittivity and oxidation resistance, the fluorine content in the whole fluorinated saturated cyclic carbonate is preferably 10% by mass or more, more preferably 15% by mass or more. The upper limit thereof is usually 76% by mass.

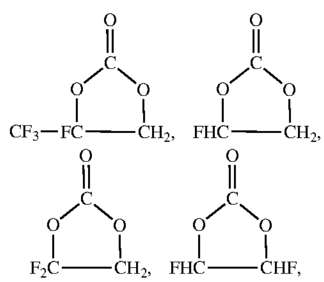
[0078] The fluorine content in the fluorinated saturated cyclic carbonate is a value calculated based on the structural formula of the fluorinated saturated cyclic carbonate by the following formula:

$$\{(\text{Number of fluorine atoms} \times 19)/(\text{Molecular weight of fluorinated saturated cyclic carbonate})\} \times 100\ (\%).$$

[0079] Specific examples of the fluorinated saturated cyclic carbonate include the following.

[0080] Specific examples of the fluorinated saturated cyclic carbonate in which at least one selected from X^1 to X^4 is —F include those represented by the following formulas.

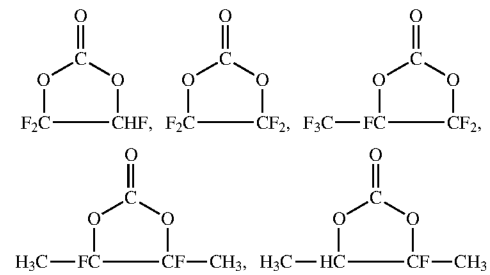
[Chem. 18]



[0081] These compounds have a high withstand voltage and give good solubility of an electrolyte salt.

[0082] Alternatively, those represented by the following formulas:

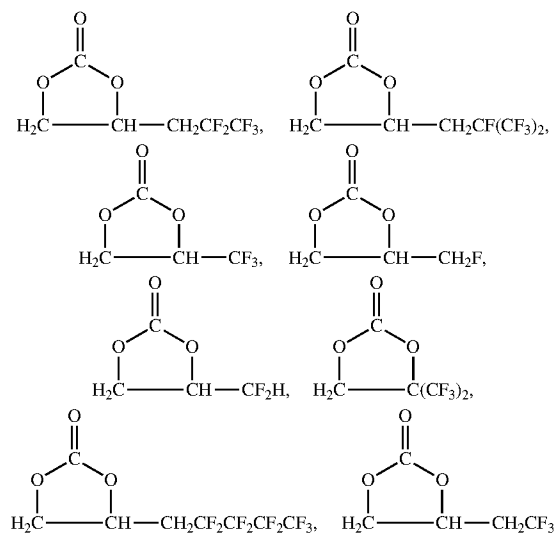
[Chem. 19]



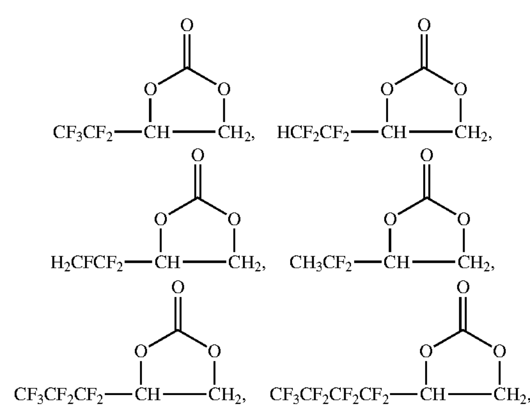
may also be used.

[0083] Those represented by the following formulas:

[Chem. 20]



[Chem. 21]



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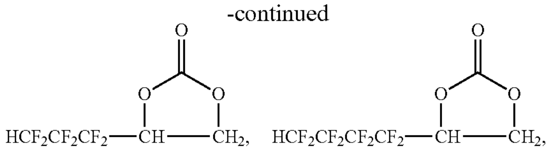
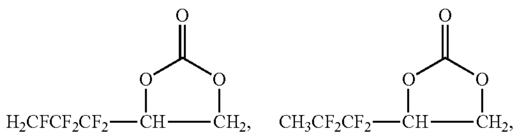


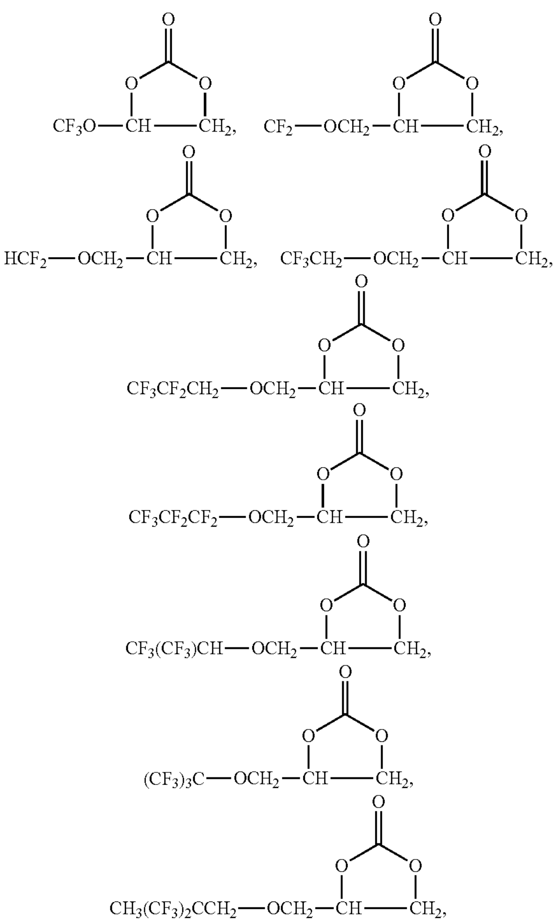
[Chem. 22]



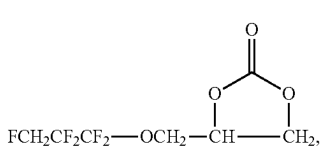
may be mentioned as specific examples of the fluorinated saturated cyclic carbonate in which at least one selected from X^1 to X^4 is a fluorinated alkyl group (a) and the others are —H.

[0084] Those represented by the following formulas:

[Chem. 23]



[Chem. 24]



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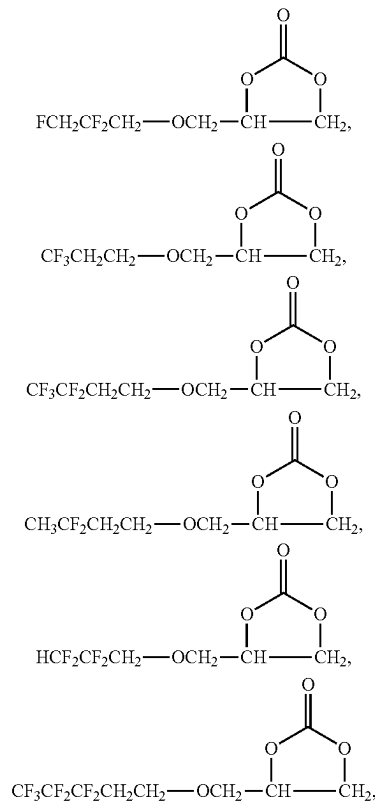
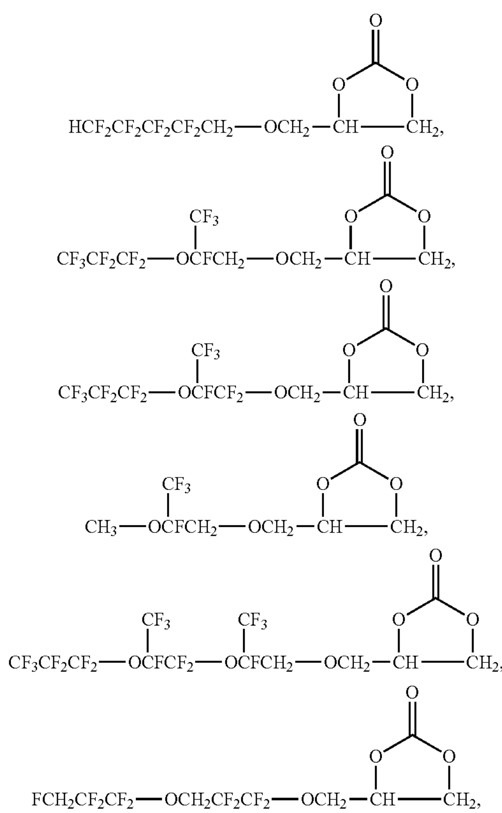


[Chem. 25]



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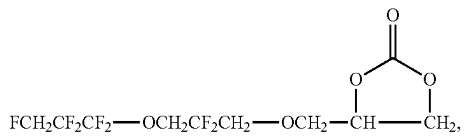
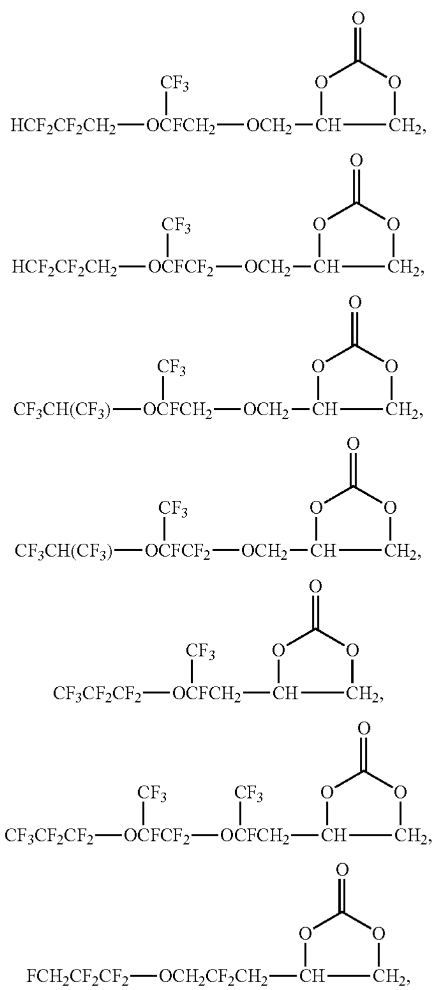
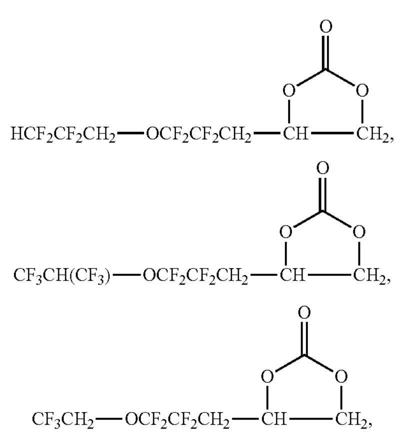


[Chem. 26]



[Chem. 27]



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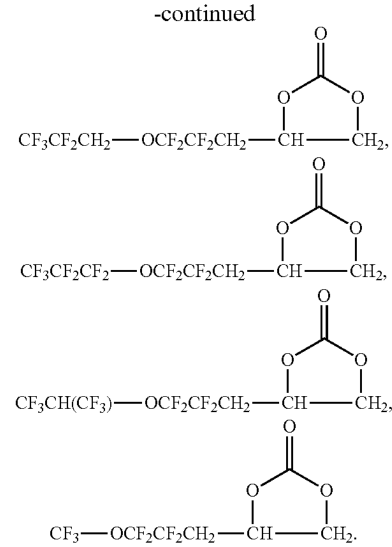
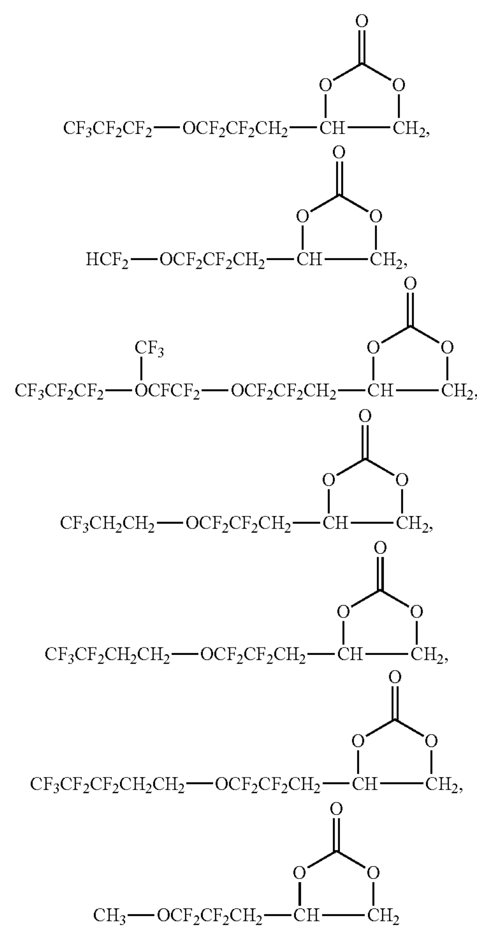


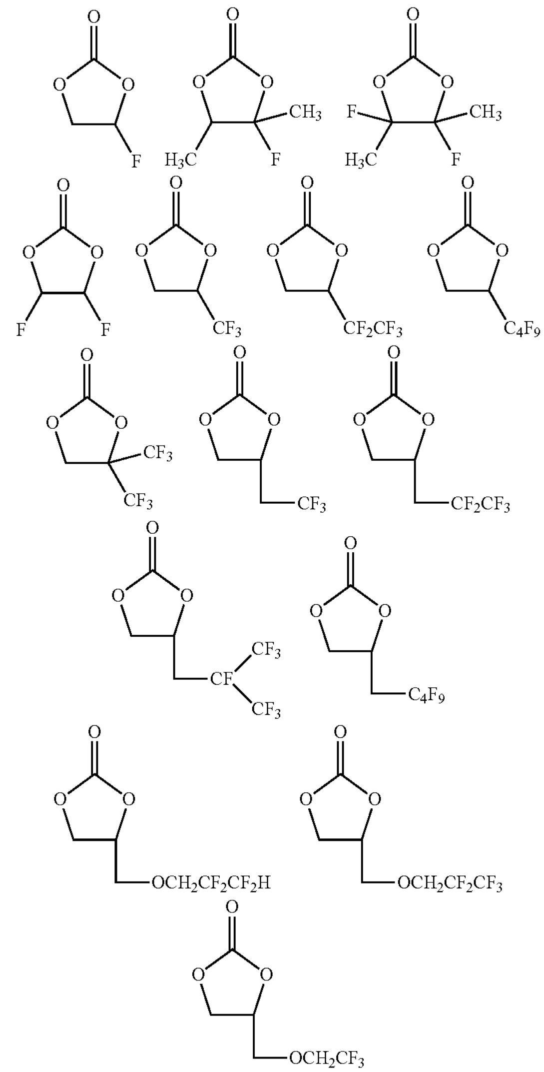
[Chem. 28]



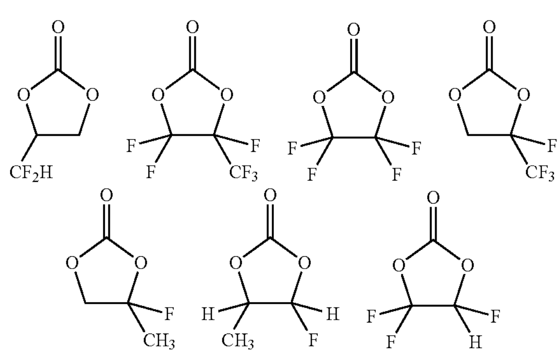
may be mentioned as specific examples of the fluorinated saturated cyclic carbonate in which at least one selected from X^1 to X^4 is a fluorinated alkyl group (b) containing an ether bond or a fluorinated alkoxy group (c) and the others are —H.

[0085] In particular, the fluorinated saturated cyclic carbonate is preferably any of the following compounds.

[Chem. 29]



[Chem. 30]



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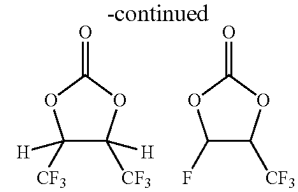


[0086] Examples of the fluorinated saturated cyclic carbonate also include trans-4,5-difluoro-1,3-dioxolan-2-one, 5-(1,1-difluoroethyl)-4,4-difluoro-1,3-dioxolan-2-one, 4-methylene-1,3-dioxolan-2-one, 4-methyl-5-trifluoromethyl-1,3-dioxolan-2-one, 4-ethyl-5-fluoro-1,3-dioxolan-2-one, 4-ethyl-5,5-difluoro-1,3-dioxolan-2-one, 4-ethyl-4,5-difluoro-1,3-dioxolan-2-one, 4-ethyl-4,5,5-trifluoro-1,3-dioxolan-2-one, 4,4-difluoro-5-methyl-1,3-dioxolan-2-one, 4-fluoro-5-methyl-1,3-dioxolan-2-one, 4-fluoro-5-trifluoromethyl-1,3-dioxolan-2-one, and 4,4-difluoro-1,3-dioxolan-2-one.

[0087] More preferred among these as the fluorinated saturated cyclic carbonate are fluoroethylene carbonate, difluoroethylene carbonate, trifluoromethylethylene carbonate, (3,3,3-trifluoropropylene carbonate), and 2,2,3,3,3-pentafluoropropylethylene carbonate.

[0088] The fluorinated unsaturated cyclic carbonate is a cyclic carbonate containing an unsaturated bond and a fluorine atom, and is preferably a fluorinated ethylene carbonate derivative substituted with a substituent containing an aromatic ring or a carbon-carbon double bond. Specific examples thereof include 4,4-difluoro-5-phenyl ethylene carbonate, 4,5-difluoro-4-phenyl ethylene carbonate, 4-fluoro-5-phenyl ethylene carbonate, 4-fluoro-5-vinyl ethylene carbonate, 4-fluoro-4-phenyl ethylene carbonate, 4,4-difluoro-4-vinyl ethylene carbonate, 4,4-difluoro-4-allyl ethylene carbonate, 4-fluoro-4-vinyl ethylene carbonate, 4-fluoro-4,5-diallyl ethylene carbonate, 4,5-difluoro-4-vinyl ethylene carbonate, 4,5-difluoro-4,5-divinyl ethylene carbonate, and 4,5-difluoro-4,5-diallyl ethylene carbonate.

[0089] One fluorinated cyclic carbonate may be used alone or two or more thereof may be used in any combination at any ratio.

[0090] The fluorinated cyclic carbonate, when contained, is preferably present in an amount of 5 to 90% by volume, more preferably 10 to 60% by volume, still more preferably 15 to 45% by volume, relative to the solvent.

[0091] The acyclic carbonate may be either a non-fluorinated acyclic carbonate or a fluorinated acyclic carbonate.

[0092] Examples of the non-fluorinated acyclic carbonate include hydrocarbon-based acyclic carbonates such as $CH_3OCOOCH_3$ (dimethyl carbonate, DMC), $CH_3CH_2OCOOCH_2CH_3$ (diethyl carbonate, DEC), $CH_3CH_2OCOOCH_3$ (ethyl methyl carbonate, EMC), $CH_3OCOOCH_2CH_2CH_3$ (methyl propyl carbonate), methyl butyl carbonate, ethyl propyl carbonate, ethyl butyl carbonate, dipropyl carbonate, dibutyl carbonate, methyl isopropyl carbonate, methyl-2-phenyl phenyl carbonate, phenyl-2-phenyl phenyl carbonate, trans-2,3-pentylene carbonate, trans-2,3-butylene carbonate, and ethyl phenyl carbonate. Preferred among these is at least one selected from the group consisting of ethyl methyl carbonate, diethyl carbonate, and dimethyl carbonate.

[0093] One non-fluorinated acyclic carbonate may be used alone or two or more thereof may be used in any combination at any ratio.

[0094] The non-fluorinated acyclic carbonate, when contained, is preferably present in an amount of 10 to 90% by volume, more preferably 40 to 85% by volume, still more preferably 50 to 80% by volume, relative to the solvent.

[0095] The fluorinated acyclic carbonate is an acyclic carbonate containing a fluorine atom. A solvent containing a fluorinated acyclic carbonate can suitably be used at high voltage.

[0096] An example of the fluorinated acyclic carbonate is a compound represented by the following formula (B):

$$Rf^2OCOOR^7 \tag{B}$$

wherein Rf^2 is a C1-C7 fluorinated alkyl group; and R^7 is a C1-C7 alkyl group optionally containing a fluorine atom.

[0097] Rf^2 is a C1-C7 fluorinated alkyl group and R^7 is a C1-C7 alkyl group optionally containing a fluorine atom.

[0098] The fluorinated alkyl group is a group obtainable by replacing at least one hydrogen atom of an alkyl group by a fluorine atom. When R^7 is an alkyl group containing a fluorine atom, it is a fluorinated alkyl group.

[0099] In order to give low viscosity, Rf^2 and R^7 each preferably have a carbon number of 1 to 7, more preferably 1 to 2.

[0100] Too large a carbon number may cause poor low-temperature characteristics and low solubility of an electrolyte salt. Too small a carbon number may cause low solubility of an electrolyte salt, low discharge efficiency, and increased viscosity, for example.

[0101] Examples of the fluorinated alkyl group having a carbon number of 1 include CFH_2—, CF_2H—, and CF_3—. In order to give high-temperature storage characteristics, particularly preferred is CFH_2— or CF_3—.

[0102] In order to give good solubility of an electrolyte salt, preferred examples of the fluorinated alkyl group having a carbon number of 2 or greater include fluorinated alkyl groups represented by the following formula (d-1):

$$R^{d1}—R^{d2}— \tag{d-1}$$

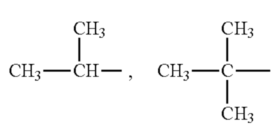
wherein R^{d1} is an alkyl group having a carbon number of 1 or greater and optionally containing a fluorine atom; R^{d2} is a C1-C3 alkylene group optionally containing a fluorine atom; and at least one of R^{d1} or R^{d2} contains a fluorine atom.

[0103] R^{d1} and R^{d2} each may further contain an atom other than carbon, hydrogen, and fluorine atoms.

[0104] R^{d1} is an alkyl group having a carbon number of 1 or greater and optionally containing a fluorine atom. R^{d1} is preferably a C1-C6 linear or branched alkyl group. The carbon number of R^{d1} is more preferably 1 to 3.

[0105] Specifically, for example, CH_3—, CF_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, $CH_3CH_2CH_2CH_2$—, and groups represented by the following formulas:

[Chem. 31]

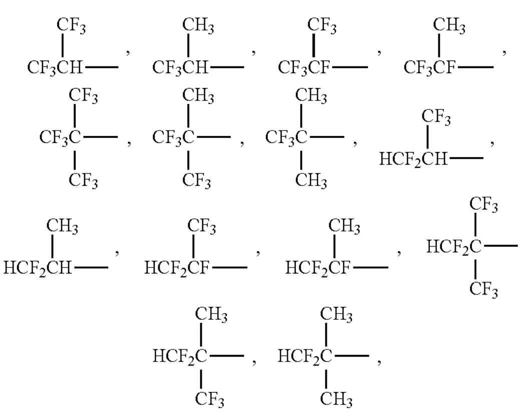


may be mentioned as linear or branched alkyl groups for R^{d1}.

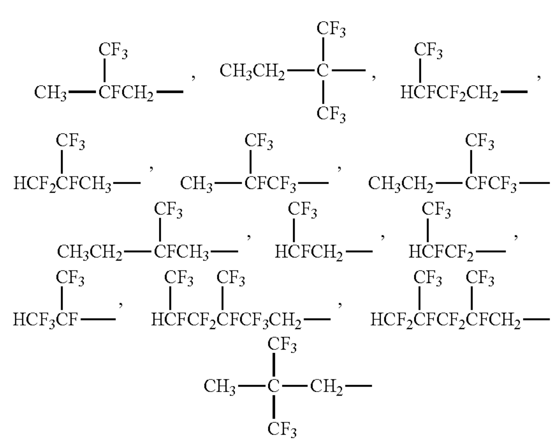
[0106] Examples of R^{d1} which is a linear alkyl group containing a fluorine atom include CF_3—, CF_3CH_2—, CF_3CF_2—, $CF_3CH_2CH_2$—, $CF_3CF_2CH_2$—, $CF_3CF_2CF_2$—, $CF_3CH_2CF_2$—, $CF_3CH_2CH_2CH_2$—, $CF_3CF_2CH_2CH_2$—, $CF_3CH_2CF_2CH_2$—, $CF_3CF_2CF_2CH_2$—, $CF_3CF_2CF_2CF_2$—, $CF_3CF_2CH_2CF_2$—, $CF_3CH_2CH_2CH_2CH_2$—, $CF_3CF_2CH_2CH_2CH_2$—, $CF_3CH_2CF_2CH_2CH_2$—, $CF_3CF_2CF_2CH_2CH_2$—, $CF_3CF_2CF_2CF_2CH_2$—, $CF_3CF_2CH_2CF_2CH_2$—, $CF_3CF_2CH_2CH_2CH_2CH_2$—, $CF_3CF_2CF_2CF_2CH_2CH_2$—, $CF_3CF_2CH_2CF_2CH_2CH_2$—, HCF_2—, HCF_2CH_2—, HCF_2CF_2—, $HCF_2CH_2CH_2$—, $HCF_2CF_2CH_2$—, $HCF_2CH_2CF_2$—, $HCF_2CF_2CH_2CH_2$—, $HCF_2CH_2CF_2CH_2$—, $HCF_2CF_2CF_2CF_2$—, $HCF_2CF_2CH_2CH_2CH_2$—, $HCF_2CH_2CF_2CH_2CH_2$—, $HCF_2CF_2CF_2CF_2CH_2$—, $HCF_2CF_2CF_2CF_2CH_2CH_2$—, FCH_2—, FCH_2CH_2—, FCH_2CF_2—, $FCH_2CF_2CH_2$—, $FCH_2CF_2CF_2$—, $CH_3CF_2CH_2$—, $CH_3CF_2CF_2$—, $CH_3CF_2CH_2CF_2$—, $CH_3CF_2CF_2CF_2$—, $CH_3CH_2CF_2CF_2$—, $CH_3CF_2CH_2CF_2CH_2$—, $CH_3CF_2CF_2CF_2CH_2$—, $CH_3CF_2CF_2CH_2CH_2$—, $CH_3CH_2CF_2CF_2CH_2$—, $CH_3CF_2CH_2CF_2CH_2CH_2$—, $CH_3CF_2CH_2CF_2CH_2CH_2$—, $HCFClCF_2CH_2$—, $HCF_2CFClCH_2$—, $HCF_2CFClCF_2CFClCH_2$—, and $HCFClCF_2CFClCF_2CH_2$—.

[0107] Examples of R^{d1} which is a branched alkyl group containing a fluorine atom include those represented by the following formulas.

[Chem. 32]



[Chem. 33]



[0108] The presence of a branch such as CH_3— or CF_3— may easily cause high viscosity. Thus, the number of such branches is more preferably small (one) or zero.

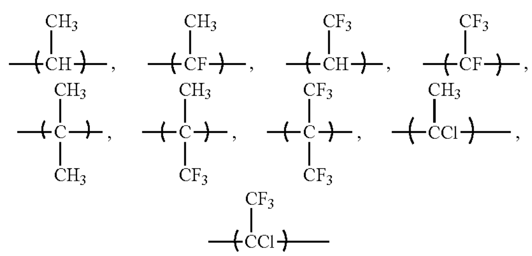
[0109] R^{d2} is a C1-C3 alkylene group optionally containing a fluorine atom. R^{d2} may be either linear or branched. Examples of a minimum structural unit constituting such a linear or branched alkylene group are shown below. R^{d2} is constituted by one or combination of these units.

(i) Linear Minimum Structural Units

[0110] —CH_2—, —CHF—, —CF_2—, —CHCl—, —CFCl—, —CCl_2—

(ii) Branched Minimum Structural Units

[Chem. 34]



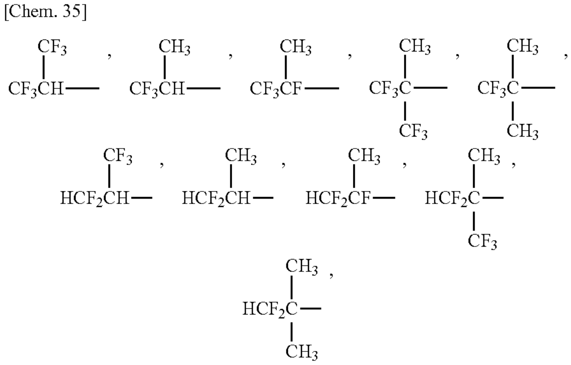
[0111] Preferred among these exemplified units are Cl-free structural units because such units may not be dehydrochlorinated by a base, and thus may be more stable.

[0112] R^{d2} which is a linear group consists only of any of the above linear minimum structural units, and is preferably —CH_2—, —CH_2CH_2—, or —CF_2—. In order to further improve the solubility of an electrolyte salt, —CH_2— or —CH_2CH_2— is more preferred.

[0113] R^{d2} which is a branched group includes at least one of the above branched minimum structural units. A preferred example thereof is a group represented by —(CX^aX^b)— (wherein X^a is H, F, CH_3, or CF_3; X^b is CH_3 or CF_3; when X^b is CF_3, X^a is H or CH_3). Such a group can much further improve the solubility of an electrolyte salt.

[0114] For example, CF_3CF_2—, HCF_2CF_2—, H_2CFCF_2—, CH_3CF_2—, CF_3CH_2—, $CF_3CF_2CF_2$—, $HCF_2CF_2CF_2$—, $H_2CFCF_2CF_2$—, $CH_3CF_2CF_2$—, and those represented by the following formulas:

[Chem. 35]



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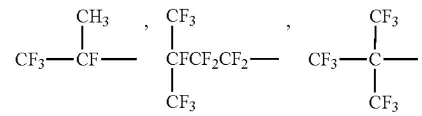
[Chem. 36]



may be specifically mentioned as preferred examples of the fluorinated alkyl group.

[0115] The fluorinated alkyl group for Rf^2 and R^7 is preferably CF_3—, CF_3CF_2—, $(CF_3)_2CH$—, CF_3CH_2—, $C_2F_5CH_2$—, $CF_3CF_2CH_2$—, $HCF_2CF_2CH_2$—, $CF_3CFHCF_2CH_2$—, CFH_2—, and CF_2H—. In order to give high incombustibility and good rate characteristics and oxidation resistance, more preferred are CF_3CH_2—, $CF_3CF_2CH_2$—, $HCF_2CF_2CH_2$—, CFH_2—, and CF_2H—.

[0116] R^7, when it is an alkyl group free from a fluorine atom, is a C1-C7 alkyl group. In order to give low viscosity, R^7 preferably has a carbon number of 1 to 4, more preferably 1 to 3.

[0117] Examples of the alkyl group free from a fluorine atom include CH_3—, CH_3CH_2—, $(CH_3)_2CH$—, and $C3H_7$—. In order to give low viscosity and good rate characteristics, preferred are CH_3— and CH_3CH_2—.

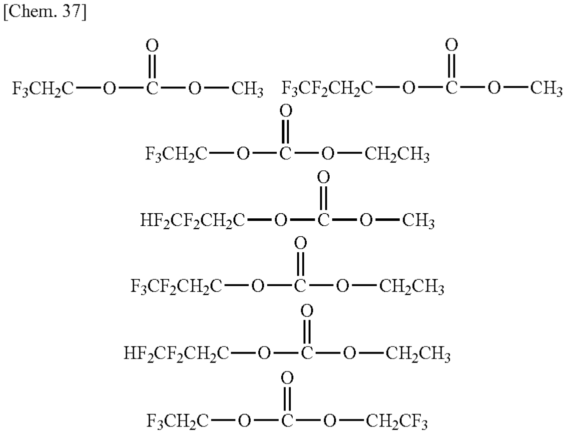
[0118] The fluorinated acyclic carbonate preferably has a fluorine content of 15 to 70% by mass. The fluorinated acyclic carbonate having a fluorine content within the above range can maintain the miscibility with a solvent and the solubility of a salt. The fluorine content is more preferably 20% by mass or more, still more preferably 30% by mass or more, particularly preferably 35% by mass or more, while more preferably 60% by mass or less, still more preferably 50% by mass or less.

[0119] In the disclosure, the fluorine content is a value calculated based on the structural formula of the fluorinated acyclic carbonate by the following formula:

{(Number of fluorine atoms×19)/(Molecular weight of fluorinated acyclic carbonate)}×100(%).

[0120] In order to give low viscosity, the fluorinated acyclic carbonate is preferably any of the following compounds.

[Chem. 37]



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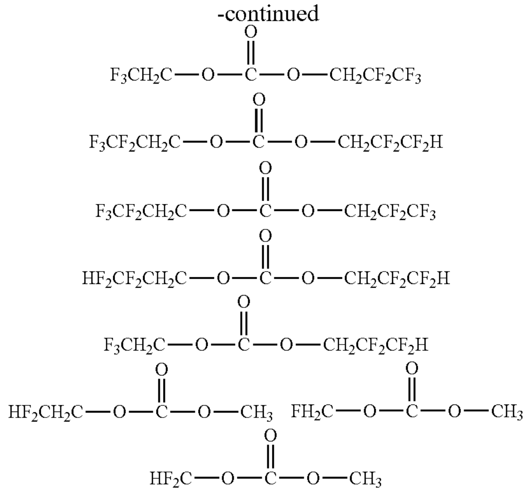


[0121] The fluorinated acyclic carbonate is particularly preferably methyl 2,2,2-trifluoroethyl carbonate ($F_2CH_2COC(=O)OCH$).

[0122] One fluorinated acyclic carbonate may be used alone, or two or more thereof may be used in any combination at any ratio.

[0123] The fluorinated acyclic carbonate, when contained, is preferably present in an amount of 10 to 90% by volume, more preferably 40 to 85% by volume, still more preferably 50 to 80% by volume, relative to the solvent.

[0124] The carboxylate may be either a cyclic carboxylate or an acyclic carboxylate.

[0125] The cyclic carboxylate may be either a non-fluorinated cyclic carboxylate or a fluorinated cyclic carboxylate.

[0126] Examples of the non-fluorinated cyclic carboxylate include a non-fluorinated saturated cyclic carboxylate, and preferred is a non-fluorinated saturated cyclic carboxylate containing a C2-C4 alkylene group.

[0127] Specific examples of the non-fluorinated saturated cyclic carboxylate containing a C2-C4 alkylene group include β-propiolactone, γ-butyrolactone, ε-caprolactone, 5-valerolactone, and α-methyl-γ-butyrolactone. In order to improve the degree of dissociation of lithium ions and to improve the load characteristics, particularly preferred among these are γ-butyrolactone and δ-valerolactone.

[0128] One non-fluorinated saturated cyclic carboxylate may be used alone or two or more thereof may be used in any combination at any ratio.

[0129] The non-fluorinated saturated cyclic carboxylate, when contained, is preferably present in an amount of 0 to 90% by volume, more preferably 0.001 to 90% by volume, still more preferably 1 to 60% by volume, particularly preferably 5 to 40% by volume, relative to the solvent.

[0130] The acyclic carboxylate may be either a non-fluorinated acyclic carboxylate or a fluorinated acyclic carboxylate. The solvent containing the acyclic carboxylate enables further reduction of an increase in resistance after high-temperature storage of the electrolytic solution.

[0131] Examples of the non-fluorinated acyclic carboxylate include methyl acetate, ethyl acetate, propyl acetate, butyl acetate, methyl propionate, ethyl propionate, propyl propionate, butyl propionate, tert-butyl propionate, tert-butyl butyrate, sec-butyl propionate, sec-butyl butyrate, n-butyl butyrate, methyl pyrophosphate, ethyl pyrophosphate, tert-butyl formate, tert-butyl acetate, sec-butyl formate, sec-butyl acetate, n-hexyl pivalate, n-propyl formate, n-propyl acetate, n-butyl formate, n-butyl pivalate, n-octyl pivalate, ethyl 2-(dimethoxyphosphoryl)acetate, ethyl 2-(dimethylphosphoryl)acetate, ethyl 2-(diethoxyphosphoryl)acetate, ethyl 2-(diethylphosphoryl)acetate, isopropyl propionate, isopropyl acetate, ethyl formate, ethyl 2-propynyl oxalate, isopropyl formate, isopropyl butyrate, isobutyl formate, isobutyl propionate, isobutyl butyrate, and isobutyl acetate.

[0132] Preferred among these are butyl acetate, methyl propionate, ethyl propionate, propyl propionate, and butyl propionate, particularly preferred are ethyl propionate and propyl propionate.

[0133] One non-fluorinated acyclic carboxylate may be used alone or two or more thereof may be used in any combination at any ratio.

[0134] The non-fluorinated acyclic carboxylate, when contained, is preferably present in an amount of 0 to 90% by volume, more preferably 0.001 to 90% by volume, still more preferably 1 to 60% by volume, particularly preferably 5 to 40% by volume, relative to the solvent.

[0135] The fluorinated acyclic carboxylate is an acyclic carboxylate containing a fluorine atom. A solvent containing a fluorinated acyclic carboxylate can be suitably used at high voltage.

[0136] In order to achieve good miscibility with other solvents and to give good oxidation resistance, preferred examples of the fluorinated acyclic carboxylate include a fluorinated acyclic carboxylate represented by the following formula:

$$R^{31}COOR^{32}$$

(wherein R^{31} and R^{32} are each independently a C1-C4 alkyl group optionally containing a fluorine atom, and at least one of R^{31} or R^{32} contains a fluorine atom).

[0137] Examples of R^{31} and R^{32} include non-fluorinated alkyl groups such as a methyl group ($—CH_3$), an ethyl group ($—CH_2CH_3$), a propyl group ($—CH_2CH_2CH_3$), an isopropyl group ($—CH(CH_3)_2$), a normal butyl group ($—CH_2CH_2CH_2CH_3$), and a tertiary butyl group ($—C(CH_3)_3$); and fluorinated alkyl groups such as $—CF_3$, $—CF_2H$, $—CFH_2$, $—CF_2CF_3$, $—CF_2CF_2H$, $—CF_2CFH_2$, $—CH_2CF_3$, $—CH_2CF_2H$, $—CH_2CFH_2$, $—CF_2CF_2CF_3$, $—CF_2CF_2CF_2H$, $—CF_2CF_2CFH_2$, $—CH_2CF_2CF_3$, $—CH_2CF_2CF_2H$, $—CH_2CF_2CFH_2$, $—CH_2CH_2CF_3$, $—CH_2CH_2CF_2H$, $—CH_2CH_2CFH_2$, $—CF(CF_3)_2$, $—CF(CF_2H)_2$, $—CF(CFH_2)_2$, $—CH(CF_3)_2$, $—CH(CF_2H)_2$, $—CH(CFH_2)_2$, $—CF(OCH_3)\ CF_3$, $—CF_2CF_2CF_2CF_3$, $—CF_2CF_2CF_2CF_2H$, $—CF_2CF_2CF_2CFH_2$, $—CH_2CF_2CF_2CF_3$, $—CH_2CF_2CF_2CF_2H$, $—CH_2CF_2CF_2CFH_2$, $—CH_2CH_2CF_2CF_3$, $—CH_2CH_2CF_2CF_2H$, $—CH_2CH_2CF_2CFH_2$, $—CH_2CH_2CH_2CF_3$, $—CH_2CH_2CH_2CF_2H$, $—CH_2CH_2CH_2CFH_2$, $—CF(CF_3)\ CF_2CF_3$, $—CF(CF_2H)\ CF_2CF_3$, $—CF(CFH_2)\ CF_2CF_3$, $—CF(CF_3)\ CF_2CF_2H$, $—CF(CF_3)\ CF_2CFH_2$, $—CF(CF_3)\ CH_2CF_3$, $—CF(CF_3)\ CH_2CF_2H$, $—CF(CF_3)\ CH_2CFH_2$, $—CH(CF_3)\ CF_2CF_3$, $—CH(CF_2H)\ CF_2CF_3$, $—CH(CFH_2)\ CF_2CF_3$, $—CH(CF_3)\ CF_2CF_2H$, $—CH(CF_3)\ CF_2CFH_2$, $—CH(CF_3)\ CH_2CF_3$, $—CH(CF_3)\ CH_2CF_2H$, $—CH(CF_3)\ CH_2CFH_2$, $—CF_2CF(CF_3)\ CF_3$, $—CF_2CF(CF_2H)\ CF_3$, $—CF_2CF(CFH_2)\ CF_3$, $—CF_2CF(CF_3)\ CF_2H$, $—CF_2CF(CF_3)\ CFH_2$, $—CH_2CF$

$(CF_3)\ CF_3$, $—CH_2CF(CF_2H)\ CF_3$, $—CH_2CF(CFH_2)\ CF_3$, $—CH_2CF(CF_3)\ CF_2H$, $—CH_2CF(CF_3)\ CFH_2$, $—CH_2CH(CF_3)\ CF_3$, $—CH_2CH(CF_2H)\ CF_3$, $—CH_2CH(CFH_2)\ CF_3$, $—CH_2CH(CF_3)\ CF_2H$, $—CH_2CH(CF_3)\ CFH_2$, $—CF_2CH(CF_3)\ CF_3$, $—CF_2CH(CF_2H)\ CF_3$, $—CF_2CH(CFH_2)\ CF_3$, $—CF_2CH(CF_3)\ CF_2H$, $—CF_2CH(CF_3)\ CFH_2$, $—C(CF_3)_3$, $—C(CF_2H)_3$, and $—C(CFH_2)_3$. In order to improve the miscibility with other solvents, viscosity, and oxidation resistance, particularly preferred among these are a methyl group, an ethyl group, $—CF_3$, $—CF_2H$, $—CF_2CF_3$, $—CH_2CF_3$, $—CH_2CF_2H$, $—CH_2CFH_2$, $—CH_2CH_2CF_3$, $—CH_2CF_2CF_3$, $—CH_2CF_2CF_2H$, and $—CH_2CF_2CFH_2$.

[0138] Specific examples of the fluorinated acyclic carboxylate include one or two or more of $CF_3CH_2C(=O)OCH_3$ (methyl 3,3,3-trifluoropropionate), $HCF_2C(=O)OCH_3$ (methyl difluoroacetate), $HCF_2C(=O)OC_2H_5$ (ethyl difluoroacetate), $CF_3C(=O)OCH_2CH_2CF_3$, $CF_3C(=O)OCH_2C_2F_5$, $CF_3C(=O)OCH_2CF_2CF_2H$ (2,2,3,3-tetrafluoropropyl trifluoroacetate), $CF_3C(=O)OCH_2CF_3$, $CF_3C(=O)OCH(CF_3)_2$, ethyl pentafluorobutyrate, methyl pentafluoropropionate, ethyl pentafluoropropionate, methyl heptafluoroisobutyrate, isopropyl trifluorobutyrate, ethyl trifluoroacetate, tert-butyl trifluoroacetate, n-butyl trifluoroacetate, methyl tetrafluoro-2-(methoxy)propionate, 2,2-difluoroethyl acetate, 2,2,3,3-tetrafluoropropyl acetate, $CH_3C(=O)OCH_2CF_3$ (2,2,2-trifluoroethyl acetate), 1H,1H-heptafluorobutyl acetate, methyl 4,4,4-trifluorobutyrate, ethyl 4,4,4-trifluorobutyrate, ethyl 3,3,3-trifluoropropionate, 3,3,3-trifluoropropyl 3,3,3-trifluoropropionate, ethyl 3-(trifluoromethyl)butyrate, methyl 2,3,3,3-tetrafluoropropionate, butyl 2,2-difluoroacetate, methyl 2,2,3,3-tetrafluoropropionate, methyl 2-(trifluoromethyl)-3,3,3-trifluoropropionate, and methyl heptafluorobutyrate.

[0139] In order to achieve good miscibility with other solvents and good rate characteristics, preferred among these are $CF_3CH_2C(=O)OCH_3$, $HCF_2C(=O)OCH_3$, $HCF_2C(=O)OC_2H_5$, $CF_3C(=O)OCH_2C_2F_5$, $CF_3C(=O)OCH_2CF_2CF_2H$, $CF_3C(=O)OCH_2CF_3$, $CF_3C(=O)OCH(CF_3)_2$, ethyl pentafluorobutyrate, methyl pentafluoropropionate, ethyl pentafluoropropionate, methyl heptafluoroisobutyrate, isopropyl trifluorobutyrate, ethyl trifluoroacetate, tert-butyl trifluoroacetate, n-butyl trifluoroacetate, methyl tetrafluoro-2-(methoxy)propionate, 2,2-difluoroethyl acetate, 2,2,3,3-tetrafluoropropyl acetate, $CH_3C(=O)OCH_2CF_3$, 1H, 1H-heptafluorobutyl acetate, methyl 4,4,4-trifluorobutyrate, ethyl 4,4,4-trifluorobutyrate, ethyl 3,3,3-trifluoropropionate, 3,3,3-trifluoropropyl 3,3,3-trifluoropropionate, ethyl 3-(trifluoromethyl)butyrate, methyl 2,3,3,3-tetrafluoropropionate, butyl 2,2-difluoroacetate, methyl 2,2,3,3-tetrafluoropropionate, methyl 2-(trifluoromethyl)-3,3-trifluoropropionate, and methyl heptafluorobutyrate, more preferred are $CF_3CH_2C(=O)OCH_3$, $HCF_2C(=O)OCH_3$, $HCF_2C(=O)OC_2H_5$, and $CH_3C(=O)OCH_2CF_3$, and particularly preferred are $HCF_2C(=O)OCH_3$, $HCF_2C(=O)OC_2H_5$, and $CH_3C(=O)OCH_2CF_3$.

[0140] One fluorinated acyclic carboxylate may be used alone or two or more thereof may be used in any combination at any ratio.

[0141] The fluorinated acyclic carboxylate, when contained, is preferably present in an amount of 10 to 90% by volume, more preferably 40 to 85% by volume, still more preferably 50 to 80% by volume, relative to the solvent.

[0142] The solvent preferably contains at least one selected from the group consisting of the cyclic carbonate, the acyclic carbonate, and the acyclic carboxylate, and more preferably contains the cyclic carbonate and at least one selected from the group consisting of the acyclic carbonate and the acyclic carboxylate. The cyclic carbonate is preferably a saturated cyclic carbonate.

[0143] An electrolytic solution containing a solvent of such a composition allows an electrochemical device to have further improved high-temperature storage characteristics and cycle characteristics.

[0144] For the solvent containing the cyclic carbonate and at least one selected from the group consisting of the acyclic carbonate and the acyclic carboxylate, the total amount of the cyclic carbonate and at least one selected from the group consisting of the acyclic carbonate and the acyclic carboxylate ester is preferably 10 to 100% by volume, more preferably 30 to 100% by volume, still more preferably 50 to 100% by volume.

[0145] For the solvent containing the cyclic carbonate and at least one selected from the group consisting of the acyclic carbonate and the acyclic carboxylate, the cyclic carbonate and at least one selected from the group consisting of the acyclic carbonate and the acyclic carboxylate preferably give a volume ratio of 5/95 to 95/5, more preferably 10/90 or more, still more preferably 15/85 or more, particularly preferably 20/80 or more, while more preferably 90/10 or less, still more preferably 60/40 or less, particularly preferably 50/50 or less.

[0146] The solvent also preferably contains at least one selected from the group consisting of the non-fluorinated saturated cyclic carbonate, the non-fluorinated acyclic carbonate, and the non-fluorinated acyclic carboxylate, more preferably contains the non-fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the non-fluorinated acyclic carbonate and the non-fluorinated acyclic carboxylate. An electrolytic solution containing a solvent of such a composition can suitably be used for electrochemical devices used at relatively low voltage.

[0147] For the solvent containing the non-fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the non-fluorinated acyclic carbonate and the non-fluorinated acyclic carboxylate, the total amount of the non-fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the non-fluorinated acyclic carbonate and the non-fluorinated acyclic carboxylate ester is preferably 5 to 100% by volume, more preferably 20 to 100% by volume, still more preferably 30 to 100% by volume.

[0148] For the electrolytic solution containing the non-fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the non-fluorinated acyclic carbonate and the non-fluorinated acyclic carboxylate, the non-fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the non-fluorinated acyclic carbonate and the non-fluorinated acyclic carboxylate ester preferably give a volume ratio of 5/95 to 95/5, more preferably 10/90 or more, still more preferably 15/85 or more, particularly preferably 20/80 or more, while more preferably 90/10 or less, still more preferably 60/40 or less, particularly preferably 50/50 or less.

[0149] The solvent preferably contains at least one selected from the group consisting of the fluorinated saturated cyclic carbonate, the fluorinated acyclic carbonate, and the fluorinated acyclic carboxylate, and more preferably contains the fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the fluorinated acyclic carbonate and the fluorinated acyclic carboxylate. An electrolytic solution containing a solvent of such a composition can suitably be used for not only electrochemical devices used at relatively high voltage but also electrochemical devices used at relatively low voltage.

[0150] For the solvent containing the fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the fluorinated acyclic carbonate and the fluorinated acyclic carboxylate, the total amount of the fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the fluorinated acyclic carbonate and the fluorinated acyclic carboxylate ester is preferably 5 to 100% by volume, more preferably 10 to 100% by volume, still more preferably 30 to 100% by volume.

[0151] For the solvent containing the fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the fluorinated acyclic carbonate and the fluorinated acyclic carboxylate, the fluorinated saturated cyclic carbonate and at least one selected from the group consisting of the fluorinated acyclic carbonate and the fluorinated acyclic carboxylate ester preferably give a volume ratio of 5/95 to 95/5, more preferably 10/90 or more, still more preferably 15/85 or more, particularly preferably 20/80 or more, while more preferably 90/10 or less, still more preferably 60/40 or less, particularly preferably 50/50 or less.

[0152] The solvent used may be an ionic liquid. The "ionic liquid" means a liquid containing an ion that is a combination of an organic cation and an anion.

[0153] Examples of the organic cation include, but are not limited to, imidazolium ions such as dialkyl imidazolium cations and trialkyl imidazolium cations; tetraalkyl ammonium ions; alkyl pyridinium ions; dialkyl pyrrolidinium ions; and dialkyl piperidinium ions.

[0154] Examples of the anion to be used as a counterion of any of these organic cations include, but are not limited to, a PF_6 anion, a $PF_3(C_2F_5)_3$ anion, a $PF_3(CF_3)_3$ anion, a BF_4 anion, a $BF_2(CF_3)_2$ anion, a $BF_3(CF_3)$ anion, a bis(oxalato) boric acid anion, a $P(C_2O_4)F_2$ anion, a Tf (trifluoromethanesulfonyl) anion, a Nf (nonafluorobutanesulfonyl) anion, a bis(fluorosulfonyl)imide anion, a bis(trifluoromethanesulfonyl)imide anion, a bis(pentafluoroethanesulfonyl)imide anion, a dicyanoamine anion, and halide anions.

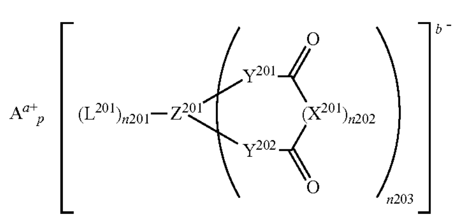
[0155] The solvent is preferably a non-aqueous solvent and the electrolytic solution of the disclosure is preferably a non-aqueous electrolytic solution.

[0156] The solvent is preferably present in an amount of 70 to 99.999% by mass, more preferably 80% by mass or more, while more preferably 92% by mass or less, of the electrolytic solution.

[0157] The electrolytic solution of the disclosure may further contain a compound (2) represented by the following formula (2).

Formula (2):

[Chem. 38]



[0158] In the formula, A^{a+} is a metal ion, a hydrogen ion, or an onium ion; a is an integer of 1 to 3; b is an integer of 1 to 3; p is b/a; n203 is an integer of 1 to 4; n201 is an integer of 0 to 8; n202 is 0 or 1; and Z^{201} is a transition metal or an element of group III, IV, or V of the periodic table.

[0159] X^{201} is O, S, a C1-C10 alkylene group, a C1-C10 halogenated alkylene group, a C6-C20 arylene group, or a C6-C20 halogenated arylene group (the alkylene, halogenated alkylene, arylene, and halogenated arylene groups may have a substituent or a hetero atom in the structure, and when n202 is 1 and n203 is 2 to 4, n203 X^{201}s may be bonded to each other).

[0160] L^{201} is a halogen atom, a cyano group, a C1-C10 alkyl group, a C1-C10 halogenated alkyl group, a C6-C20 aryl group, a C6-C20 halogenated aryl group (the alkylene, halogenated alkylene, arylene, and halogenated arylene groups may have a substituent or a hetero atom in the structure, and when n201 is 2 to 8, n201 L^{201}s may be bonded to form a ring), or —$Z^{203}Y^{203}$.

[0161] Y^{201}, Y^{202}, and Z^{203} are each independently O, S, NY^{204}, a hydrocarbon group, or a fluorinated hydrocarbon group. Y^{203} and Y^{204} are each independently H, F, a C1-C10 alkyl group, a C1-C10 halogenated alkyl group, a C6-C20 aryl group, or a C6-C20 halogenated aryl group (the alkyl, halogenated alkyl, aryl, and halogenated aryl groups may have a substituent or a hetero atom in the structure, and when multiple Y^{203}s or Y^{204}s are present, they may be bonded to form a ring).

[0162] Examples of A^{a+} include a lithium ion, a sodium ion, a potassium ion, a magnesium ion, a calcium ion, a barium ion, a cesium ion, a silver ion, a zinc ion, a copper ion, a cobalt ion, an iron ion, a nickel ion, a manganese ion, a titanium ion, a lead ion, a chromium ion, a vanadium ion, a ruthenium ion, a yttrium ion, a lanthanoid ion, an actinoid ion, a tetrabutylammonium ion, a tetraethylammonium ion, a tetramethylammonium ion, a triethylmethylammonium ion, a triethylammonium ion, a pyridinium ion, an imidazolium ion, a hydrogen ion, a tetraethylphosphonium ion, a tetramethylphosphonium ion, a tetraphenylphosphonium ion, a triphenylsulfonium ion, and a triethylsulfonium ion.

[0163] For applications such as electrochemical devices, A^{a+} is preferably a lithium ion, a sodium ion, a magnesium ion, a tetraalkylammonium ion, or a hydrogen ion, particularly preferably a lithium ion. The valence a of an A^{a+} cation is an integer of 1 to 3. When the valence a is larger than 3, the crystal lattice energy becomes larger, which problematically makes it difficult to dissolve the electrolytic solution of the disclosure in a solvent. The valence is therefore more preferably 1 when the solubility is required. The valence b of an anion is similarly an integer of 1 to 3, particularly preferably 1. The constant p which represents a ratio between the cation and the anion is necessarily determined by the ratio b/a of their valence values.

[0164] Next, a ligand portion of the formula (2) is described. Herein, the organic or inorganic moiety bonded to Z^{201} in the formula (2) is referred to as a ligand.

[0165] Z^{201} is preferably Al, B, V, Ti, Si, Zr, Ge, Sn, Cu, Y, Zn, Ga, Nb, Ta, Bi, P, As, Sc, Hf, or Sb, more preferably Al, B, or P.

[0166] X^{201} represents O, S, a C1-C10 alkylene group, a C1-C10 halogenated alkylene group, a C6-C20 arylene group, or a C6-C20 halogenated arylene group. These alkylene and arylene groups may have a substituent or a hetero atom in the structure. Specifically, they may have a halogen atom or a linear or cyclic alkyl group, an aryl group, an alkenyl group, an alkoxy group, an aryloxy group, a sulfonyl group, an amino group, a cyano group, a carbonyl group, an acyl group, an amide group, or a hydroxy group as a substituent in place of hydrogen on the alkylene or arylene group. They also may have a structure where nitrogen, sulfur, or oxygen is introduced in place of carbon on the alkylene or arylene group. When n202 is 1 and n203 is 2 to

4, n203 X^{201}s may be bonded to each other. Examples of such a structure include ligands such as ethylenediaminetetraacetic acid.

[0167] L^{201} represents a halogen atom, a cyano group, a C1-C10 alkyl group, a C1-C10 halogenated alkyl group, a C6-C20 aryl group, a C6-C20 halogenated aryl group, or —$Z^{203}Y^{203}$ (Z^{203} and Y^{203} are described later). As in the case of X^{201}, the alkyl and aryl groups here may have a substituent or a hetero atom in the structure, and when n201 is 2 to 8, n201 L^{201}s may be bonded to form a ring. L^{201} is preferably a fluorine atom or a cyano group. When L^{201} is a fluorine atom, solubility and dissociation of anionic compound salts are increased, which in turn favorably increases ionic conductivity. In addition, oxidation resistance is improved to reduce or inhibit occurrence of side reactions.

[0168] Y^{201}, Y^{202}, and Z^{203} each independently represent O, S, NY^{204}, a hydrocarbon group, or a fluorinated hydrocarbon group. Y^{201} and Y^{202} each are preferably O, S, or NY^{204}, more preferably 0. The compound (2) is characterized in that a bond of Y^{201} with Z^{201} and a bond of Y^{202} with Z^{201} are present within the same ligand and such ligands form a chelate structure with Z^{201}. Owing to this chelate, the compound has higher heat resistance, higher chemical stability, and higher hydrolysis resistance. The constant n202 in this ligand is 0 or 1. When the constant n202 is 0, in particular, the chelate ring is a 5-membered ring, which favorably allows strongest exertion of the chelate effect to increase the stability.

[0169] The fluorinated hydrocarbon group herein is a group obtainable by replacing at least one hydrogen atom of a hydrocarbon group with a fluorine atom.

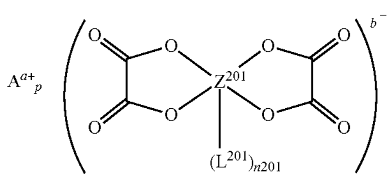
[0170] Y^{203} and Y^{204} are each independently H, F, a C1-C10 alkyl group, a C1-C10 halogenated alkyl group, a C6-C20 aryl group, or a C6-C20 halogenated aryl group. These alkyl and aryl groups may have a substituent or a hetero atom in the structure. When multiple Y^{203}s or Y^{204}s are present, they may be bonded to form a ring.

[0171] The constant n203 related to the number of ligands described above is an integer of 1 to 4, preferably 1 or 2, more preferably 2. The constant n201 related to the number of ligands described above is an integer of 0 to 8, preferably an integer of 0 to 4, more preferably 0, 2, or 4. Preferably, n201 is 2 when n203 is 1 and n201 is 0 when n203 is 2.

[0172] In the formula (2), the alkyl, halogenated alkyl, aryl, and halogenated aryl groups may be those with a different functional group such as a branch, a hydroxy group, or an ether bond.

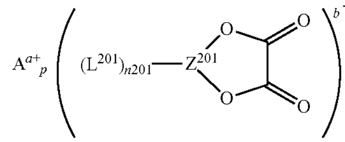
[0173] The compound (2) is preferably a compound represented by the following formula:

[Chem. 39]



(wherein A^{a+}, a, b, p, n201, Z^{201}, and L^{201} are as described above), or a compound represented by the following formula:

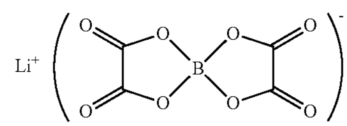
[Chem. 40]



(wherein A^{a+}, a, b, p, n201, Z^{201}, and L^{201} are as described above).

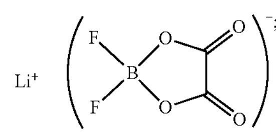
[0174] Examples of the compound (2) include lithium (oxalate)borate salts including lithium bis(oxalate)borate (LIBOB) represented by the following formula:

[Chem. 41]



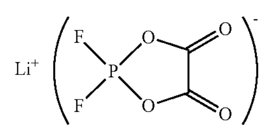
lithium difluorooxalatoborate (LiDFOB) represented by the following formula:

[Chem. 42]



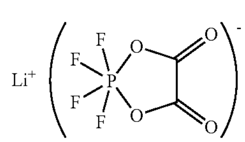
lithium difluorooxaratophosphanite (LiDFOP) represented by the following formula:

[Chem. 43]



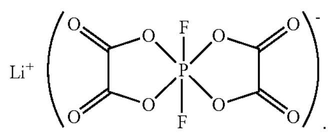
lithium tetrafluorooxalatophosphanite (LiTFOP) represented by the following formula:

[Chem. 44]



and lithium bis(oxalato)difluorophosphanite represented by the following formula:

[Chem. 45]



[0175] Examples of the compound (2) also include dicarboxylic acid complex salts in which the complex center element is boron, such as lithium bis(malonato)borate, lithium difluoro(malonato)borate, lithium bis(methylmalonato)borate, lithium difluoro(methylmalonato)borate, lithium bis(dimethylmalonato)borate, and lithium difluoro (dimethylmalonato)borate.

[0176] Examples of the compound (2) also include dicarboxylic acid complex salts in which the complex center element is phosphorus, such as lithium tris(oxalato)phosphate, lithium tris(malonato)phosphate, lithium difluorobis (malonato)phosphate, lithium tetrafluoro(malonato)phosphate, lithium tris(methylmalonato)phosphate, lithium difluorobis(methylmalonato)phosphate, lithium tetrafluoro (methylmalonato)phosphate, lithium tris(dimethylmalonato) phosphate, lithium difluorobis(dimethylmalonato)phosphate, and lithium tetrafluoro(dimethylmalonato)phosphate.

[0177] Examples of the compound (2) also include dicarboxylic acid complex salts in which the complex center element is aluminum, such as $LiAl(C_2O_4)_2$ and $LiAlF_2(C_2O_4)$.

[0178] In order to enable easy availability and contribute to formation of a stable film-shaped structure, more preferred among these are lithium bis(oxalato)borate, lithium difluoro(oxalato)borate, lithium tris(oxalato)phosphate, lithium difluorobis(oxalato)phosphate, and lithium tetrafluoro(oxalato)phosphate.

[0179] The compound (2) is particularly preferably lithium bis(oxalato)borate.

[0180] In order to give much better cycle characteristics, the compound (2) is preferably in an amount of 0.001% by mass or more, more preferably 0.01% by mass or more, while preferably 10% by mass or less, more preferably 3% by mass or less, relative to the solvent.

[0181] The electrolytic solution of the disclosure may be substantially free from the compound (2). The phrase "substantially free from the compound (2)" means that the amount of the compound (2) is less than 0.01% by mass relative to the solvent. The amount of the compound (2) may be less than 0.001% by mass relative to the solvent.

[0182] The electrolytic solution of the disclosure preferably further contains an electrolyte salt other than the compound (2). Examples of the electrolyte salt used include alkali metal salts, ammonium salts, and metal salts other than alkali metal salts (such as light metal salts other than alkali metal salts), as well as any of those to be used for electrolytic solutions such as liquid salts (ionic liquids), inorganic polymer salts, and organic polymer salts.

[0183] Examples of electrolyte salts of electrolytic solutions for electrochemical devices include the following compounds: MPF_6, MBF_4, $MClO_4$, $MAsF_6$, MB(C6H$_5$)$_4$, MCH_3SO_3, MCF_3SO_3, $MAlCl_4$, M_2SiF_6, MCl, and MBr. In the formulas, M is at least one metal selected from the group consisting of Li, Na, and K, preferably one selected from the group consisting of Li, Na, and K, more preferably Li or Na. The use of any of these alkali metal salts gives excellent properties including battery capacity, cycle characteristics, and storage characteristics. In particular, preferred is at least one selected from MPF_6, MBF_4, $MClO_4$, and $MAsF_6$, more preferably MPF_6. The use of any of these alkali metal salts further lowers the internal resistance, resulting in higher effects.

[0184] The electrolyte salt of the electrolytic solution for a lithium-ion secondary battery is preferably a lithium salt.

[0185] Any lithium salt may be used. Specific examples thereof include the following:

[0186] inorganic lithium salts such as $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAlF_4$, $LiSbF_6$, $LiTaF_6$, $LiWF_7$, $LiAsF_6$, $LiAlCl_4$, LiI, LiBr, LiCl, $LiB_{10}Cl_{10}$, Li_2SiF_6, Li_2PFO_3, and $LiPO_2F_2$;

[0187] lithium tungstate salts such as $LiWOF_5$;

[0188] lithium carboxylates such as HCO_2Li, CH_3CO_2Li, CH_2FCO_2Li, CHF_2CO_2Li, CF_3CO_2Li, $CF_3CH_2CO_2Li$, $CF_3CF_2CO_2Li$, $CF_3CF_2CF_2CO_2Li$, and $CF_3CF_2CF_2CF_2CO_2Li$;

[0189] lithium salts containing an S=O group such as FSO_3Li, CH_3SO_3Li, CH_2FSO_3Li, CHF_2SO_3Li, CF_3SO_3Li, $CF_3CF_2SO_3Li$, $CF_3CF_2CF_2SO_3Li$, $CF_3CF_2CF_2CF_2SO_3Li$, lithium methylsulfate, lithium ethylsulfate ($C_2H_5OSO_3Li$), and lithium 2,2,2-trifluoroethylsulfate;

[0190] lithium imide salts such as $LiN(FCO)_2$, LiN (FCO) (FSO_2), $LiN(FSO_2)_2$, $LiN(FSO_2)$ (CF_3SO_2), $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, lithium bis-perfluoroethanesulfonyl imide, lithium cyclic 1,2-perfluoroethanedisulfonyl imide, lithium cyclic 1,3-perfluoropropanedisulfonyl imide, lithium cyclic 1,2-ethanedisulfonyl imide, lithium cyclic 1,3-propanedisulfonyl imide, lithium cyclic 1,4-perfluorobutanedisulfonyl imide, $LiN(CF_3SO_2)(FSO_2)$, $LiN(CF_3SO_2)$ $(C_3F_7SO_2)$, $LiN(CF_3SO_2)(C_4F_9SO_2)$, and $LiN(POF_2)_2$;

[0191] lithium methide salts such as $LiC(FSO_2)_3$, $LiC(CF_3SO_2)_3$, and $LiC(C_2F_5SO_2)_3$; and fluorine-containing organic lithium salts such as salts represented by the formula: $LiPF_a(C_nF_{2n+1})_{6-a}$ (wherein a is an integer of 0 to 5; and n is an integer of 1 to 6) such as $LiPF_3(C_2F)_3$, $LiPF_3(CF_3)_3$, $LiPF_3(iso\text{-}C_3F_7)_3$, $LiPF_5(iso\text{-}C_3F_7)$, $LiPF_4(CF_3)_2$, and $LiPF_4(C_2F)_2$, as well as $LiPF_4(CF_3SO_2)_2$, $LiPF_4(C_2FSO_2)_2$, $LiBF_3CF_3$, $LiBF_3C_2F_5$, $LiBF_3C_3F_7$, $LiBF_2(CF_3)_2$, $LiBF_2(C_2F)_2$, $LiBF_2(CF_3SO_2)_2$, and $LiBF_2(C_2FSO_2)_2$, and LiSCN, $LiB(CN)_4$, $LiB(C_6H)_4$, $Li_2(C_2O_4)$, $LiP(C_2O_4)$, and $Li_2B_{12}FbH_{12\text{-}b}$ (wherein b is an integer of 0 to 3).

[0192] In order to achieve an effect of improving properties such as output characteristics, high-rate charge and discharge characteristics, high-temperature storage characteristics, and cycle characteristics, particularly preferred among these are $LiPF_6$, $LiBF_4$, $LiSbF_6$, $LiTaF_6$, $LiPO_2F_2$, FSO_3Li, CF_3SO_3Li, $LiN(FSO_2)_2$, $LiN(FSO_2)$ (CF_3SO_2), $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, lithium cyclic 1,2-perfluoroethanedisulfonyl imide, lithium cyclic 1,3-perfluoropropanedisulfonyl imide, $LiC(FSO_2)_3$, $LiC(CF_3SO_2)_3$, $LiC(C_2FSO_2)_3$, $LiBF_3CF_3$, $LiBF_3C_2F_5$, $LiPF_3(CF_3)_3$, $LiPF_3$

$(C_2F_5)_3$, and the like. Most preferred is at least one lithium salt selected from the group consisting of $LiPF_6$, $LiN(FSO_2)_2$, and $LiBF_4$.

[0193] One of these electrolyte salts may be used alone or two or more thereof may be used in any combination. In combination use of two or more thereof, preferred examples thereof include a combination of $LiPF_6$ and $LiBF_4$ and a combination of $LiPF_6$ and $LiPO_2F_2$, $C_2H_5OSO_3Li$, or FSO_3Li, each of which have an effect of improving the high-temperature storage characteristics, the load characteristics, and the cycle characteristics.

[0194] In this case, $LiBF_4$, $LiPO_2F_2$, $C_2H_5OSO_3Li$, or FSO_3Li may be present in any amount that does not significantly impair the effects of the disclosure in 100% by mass of the whole electrolytic solution. The amount thereof is usually 0.01% by mass or more, preferably 0.1% by mass or more, while the upper limit thereof is usually 30% by mass or less, preferably 20% by mass or less, more preferably 10% by mass or less, still more preferably 5% by mass or less, relative to the electrolytic solution of the disclosure.

[0195] In another example, an inorganic lithium salt and an organic lithium salt are used in combination. Such a combination has an effect of reducing deterioration due to high-temperature storage. The organic lithium salt is preferably CF_3SO_3Li, $LiN(FSO_2)_2$, $LiN(FSO_2)(CF_3SO_2)$, $LiN(CF_3SO_2)_2$, $LiN(C_2F_5SO_2)_2$, lithium cyclic 1,2-perfluoroethanedisulfonyl imide, lithium cyclic 1,3-perfluoropropanedisulfonyl imide, $LiC(FSO_2)_3$, $LiC(CF_3SO_2)_3$, $LiC(C_2F_5SO_2)_3$, $LiBF_3CF_3$, $LiBF_3C_2F_5$, $LiPF_3(CF_3)_3$, $LiPF_3(C_2F_5)_3$, or the like. In this case, the proportion of the organic lithium salt is preferably 0.1% by mass or more, particularly preferably 0.5% by mass or more, while preferably 30% by mass or less, particularly preferably 20% by mass or less, of 100% by mass of the whole electrolytic solution.

[0196] The electrolyte salt of the electrolytic solution for a sodium-ion secondary battery is preferably a sodium salt.

[0197] Any sodium salt may be used. Specific examples thereof include the following:

- **[0198]** inorganic sodium salts such as $NaPF_6$, $NaBF_4$, $NaClO_4$, $NaAlF_4$, $NaSbF_6$, $NaTaF_6$, $NaWF_7$, $NaAsF_6$, $NaAlCl_4$, NaI, NaBr, NaCl, $NaB_{10}Cl_{10}$, Na_2SiF_6, Na_2PFO_3, and $NaPO_2F_2$;
- **[0199]** sodium tungstate salts such as $NaWOF_5$;
- **[0200]** sodium carboxylates such as HCO_2Na, CH_3CO_2Na, CH_2FCO_2Na, CHF_2CO_2Na, CF_3CO_2Na, $CF_3CH_2CO_2Na$, $CF_3CF_2CO_2Na$, $CF_3CF_2CF_2CO_2Na$, and $CF_3CF_2CF_2CF_2CO_2Na$;
- **[0201]** sodium salts containing an S═O group such as FSO_3Na, CH_3SO_3Na, CH_2FSO_3Na, CHF_2SO_3Na, CF_3SO_3Na, $CF_3CF_2SO_3Na$, $CF_3CF_2CF_2SO_3Na$, $CF_3CF_2CF_2CF_2SO_3Na$, sodium methylsulfate, sodium ethylsulfate ($C_2H_5OSO_3Na$), and sodium 2,2,2-trifluoroethylsulfate;
- **[0202]** sodium imide salts such as $NaN(FCO)_2$, $NaN(FCO)(FSO_2)$, $NaN(FSO_2)_2$, $NaN(FSO_2)(CF_3SO_2)$, $NaN(CF_3SO_2)_2$, $NaN(C_2F_5SO_2)_2$, sodium bis-perfluoroethanesulfonyl imide, sodium cyclic 1,2-perfluoroethanedisulfonyl imide, sodium cyclic 1,3-perfluoropropanedisulfonyl imide, sodium cyclic 1,2-ethanedisulfonyl imide, sodium cyclic 1,3-propanedisulfonyl imide, sodium cyclic 1,4-perfluorobutanedisulfonyl imide, $NaN(CF_3SO_2)(FSO_2)$, $NaN(CF_3SO_2)(C_3F_7SO_2)$, $NaN(CF_3SO_2)(C_4F_9SO_2)$, and $NaN(POF_2)_2$;
- **[0203]** sodium methide salts such as $NaC(FSO_2)_3$, $NaC(CF_3SO_2)_3$, and $NaC(C_2F_5SO_2)_3$; and fluorine-containing organic sodium salts such as salts represented by the formula: $NaPF_a(C_nF_{2n+1})_{6-a}$ (wherein a is an integer of 0 to 5; and n is an integer of 1 to 6) such as $NaPF_3(C_2F_5)_3$, $NaPF_3(CF_3)_3$, $NaPF_3(iso\text{-}C_3F_7)_3$, $NaPF_5(iso\text{-}C_3F_7)$, $NaPF_4(CF_3)_2$, and $NaPF_4(C_2F_5)_2$, as well as $NaPF_4(CF_3SO_2)_2$, $NaPF_4(C_2F_5SO_2)_2$, $NaBF_3CF_3$, $NaBF_3C_2F_5$, $NaBF_3C_3F_7$, $NaBF_2(CF_3)_2$, $NaBF_2(C_2F_5)_2$, $NaBF_2(CF_3SO_2)_2$, and $NaBF_2(C_2F_5SO_2)_2$, and NaSCN, $LiB(CN)_4$, $NaB(C6H_5)_4$, $Na_2(C_2O_4)$, $NaP(C_2O_4)_3$, and $Na_2B_{12}F_bH_{12-b}$ (wherein b is an integer of 0 to 3).

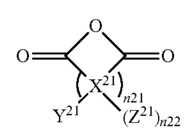
[0204] In order to achieve an effect of improving properties such as output characteristics, high-rate charge and discharge characteristics, high-temperature storage characteristics, and cycle characteristics, particularly preferred among these are $NaPF_6$, $NaBF_4$, $NaSbF_6$, $NaTaF_6$, $NaPO_2F_2$, FSO_3Na, CF_3SO_3Na, $NaN(FSO_2)_2$, $NaN(FSO_2)(CF_3SO_2)$, $NaN(CF_3SO_2)_2$, $NaN(C_2F_5SO_2)_2$, sodium cyclic 1,2-perfluoroethanedisulfonyl imide, sodium cyclic 1,3-perfluoropropanedisulfonyl imide, $NaC(FSO_2)_3$, $NaC(CF_3SO_2)_3$, $NaC(C_2F_5SO_2)_3$, $NaBF_3CF_3$, $NaBF_3C_2F_5$, $NaPF_3(CF_3)_3$, $NaPF_3(C_2F_5)_3$, and the like. Most preferred is at least one sodium salt selected from the group consisting of $NaPF_6$, $NaN(FSO_2)_2$, and $NaBF_4$.

[0205] The electrolyte salt in the electrolytic solution may have any concentration that does not impair the effects of the disclosure. In order to make the electric conductivity of the electrolytic solution within a favorable range and to ensure good battery performance, the lithium or sodium in the electrolytic solution preferably has a total mole concentration of 0.3 mol/L or higher, more preferably 0.4 mol/L or higher, still more preferably 0.5 mol/L or higher, while preferably 3 mol/L or lower, more preferably 2.5 mol/L or lower, still more preferably 2.0 mol/L or lower.

[0206] Too low a total mole concentration of lithium or sodium may cause insufficient electric conductivity of the electrolytic solution, while too high a concentration may cause an increase in viscosity and then reduction in electric conductivity, impairing the battery performance.

[0207] The electrolytic solution of the disclosure preferably further contains a compound (3) represented by the following formula (3):

[Chem. 46]



(wherein X^{21} is a group containing at least H or C; n^{21} is an integer of 1 to 3; Y^{21} and Z^{21} are the same as or different from each other, and are each a group containing at least H, C, O, or F; n^{22} is 0 or 1; and Y^{21} and Z^{21} optionally bind to each other to form a ring). The electrolytic solution containing the compound (3) can cause much less reduction in capacity retention and can cause a much less increase in amount of gas generated even when stored at high temperature.

[0208] When n^{21} is 2 or 3, the two or three X^{21}s may be the same as or different from each other.

[0209] When multiple Y^{21}s and multiple Z^{21}s are present, the multiple Y^{21}s may be the same as or different from each other and the multiple Z^{21}s may be the same as or different from each other.

[0210] X^{21} is preferably a group represented by —$CY^{21}Z^{21}$— (wherein Y^{21} and Z^{21} are defined as described above) or a group represented by —CY^{21}═CZ^{21}— (wherein Y^{21} and Z^{21} are defined as described above).

[0211] Y^{21} preferably includes at least one selected from the group consisting of H—, F—, CH_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, CF_3—, CF_3CF_2—, CH_2FCH_2—, and $CF_3CF_2CF_2$—.

[0212] Z^{21} preferably includes at least one selected from the group consisting of H—, F—, CH_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, CF_3—, CF_3CF_2—, CH_2FCH_2—, and $CF_3CF_2CF_2$—.

[0213] Alternatively, Y^{21} and Z^{21} may bind to each other to form a carbon ring or a heterocyclic ring that may contain an unsaturated bond and may have aromaticity. The ring preferably has a carbon number of 3 to 20.

[0214] Next, specific examples of the compound (3) are described. In the following examples, the term "analog" means an acid anhydride obtainable by replacing part of the structure of an acid anhydride mentioned as an example by another structure within the scope of the disclosure. Examples thereof include dimers, trimers, and tetramers each composed of a plurality of acid anhydrides, those having respective substituents which are structural isomers having the same carbon number but having different branch structures, and those having the same substituent but at different sites in an acid anhydride.

[0215] Specific examples of an acid anhydride having a 5-membered cyclic structure include succinic anhydride, methylsuccinic anhydride (4-methylsuccinic anhydride), dimethylsuccinic anhydride (e.g., 4,4-dimethylsuccinic anhydride, 4,5-dimethylsuccinic anhydride), 4,4,5-trimethylsuccinic anhydride, 4,4,5,5-tetramethylsuccinic anhydride, 4-vinylsuccinic anhydride, 4,5-divinylsuccinic anhydride, phenylsuccinic anhydride (4-phenylsuccinic anhydride), 4,5-diphenylsuccinic anhydride, 4,4-diphenylsuccinic anhydride, citraconic anhydride, maleic anhydride, methylmaleic anhydride (4-methylmaleic anhydride), 4,5-dimethylmaleic anhydride, phenylmaleic anhydride (4-phenylmaleic anhydride), 4,5-diphenylmaleic anhydride, itaconic anhydride, 5-methylitaconic anhydride, 5,5-dimethylitaconic anhydride, phthalic anhydride, and 3,4,5,6-tetrahydrophthalic anhydride, and analogs thereof.

[0216] Specific examples of an acid anhydride having a 6-membered cyclic structure include cyclohexanedicarboxylic anhydride (e.g., cyclohexane-1,2-dicarboxylic anhydride), 4-cyclohexene-1,2-dicarboxylic anhydride, glutaric anhydride, glutaconic anhydride, and 2-phenylglutaric anhydride, and analogs thereof.

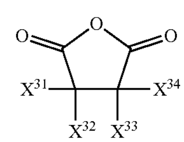
[0217] Specific examples of an acid anhydride having a different cyclic structure include 5-norbornene-2,3-dicarboxylic anhydride, cyclopentanetetracarboxylic dianhydride, pyromellitic anhydride, and diglycolic anhydride, and analogs thereof.

[0218] Specific examples of an acid anhydride having a cyclic structure and substituted with a halogen atom include monofluorosuccinic anhydride (e.g., 4-fluorosuccinic anhydride), 4,4-difluorosuccinic anhydride, 4,5-difluorosuccinic anhydride, 4,4,5-trifluorosuccinic anhydride, trifluoromethylsuccinic anhydride, tetrafluorosuccinic anhydride (4,4,5,5-tetrafluorosuccinic anhydride), 4-fluoromaleic anhydride, 4,5-difluoromaleic anhydride, trifluoromethylmaleic anhydride, 5-fluoroitaconic anhydride, and 5,5-difluoroitaconic anhydride, and analogs thereof.

[0219] Preferred among these as the compound (3) are glutaric anhydride, citraconic anhydride, glutaconic anhydride, itaconic anhydride, diglycolic anhydride, cyclohexanedicarboxylic anhydride, cyclopentanetetracarboxylic dianhydride, 4-cyclohexene-1,2-dicarboxylic anhydride, 3,4,5,6-tetrahydrophthalic anhydride, 5-norbornene-2,3-dicarboxylic anhydride, phenylsuccinic anhydride, 2-phenylglutaric anhydride, maleic anhydride, methylmaleic anhydride, trifluoromethylmaleic anhydride, phenylmaleic anhydride, succinic anhydride, methylsuccinic anhydride, dimethylsuccinic anhydride, trifluoromethylsuccinic anhydride, monofluorosuccinic anhydride, and tetrafluorosuccinic anhydride. More preferred are maleic anhydride, methylmaleic anhydride, trifluoromethylmaleic anhydride, succinic anhydride, methylsuccinic anhydride, trifluoromethylsuccinic anhydride, and tetrafluorosuccinic anhydride, and still more preferred are maleic anhydride and succinic anhydride.

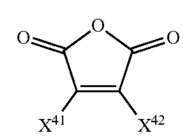
[0220] The compound (3) preferably includes at least one selected from the group consisting of: a compound (4 represented by the following formula (4):

[Chem. 47]



(wherein X^{31} to X^{34} are the same as or different from each other, and are each a group containing at least H, C, O, or F); and a compound (5) represented by the following formula (5):

[Chem. 48]



(wherein X^{41} and X^{42} are the same as or different from each other, and are each a group containing at least H, C, O, or F).

[0221] X^{31} to X^{34} are the same as or different from each other, and preferably include at least one selected from the group consisting of an alkyl group, a fluorinated alkyl group, an alkenyl group, and a fluorinated alkenyl group. X^{31} to X^{34} each preferably have a carbon number of 1 to 10, more preferably 1 to 3.

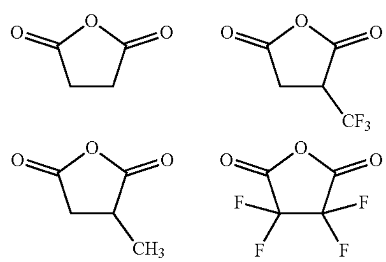
[0222] X^{31} to X^{34} are the same as or different from each other, and more preferably include at least one selected from the group consisting of H—, F—, CH_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, CF_3—, CF_3CF_2—, CH_2FCH_2—, and $CF_3CF_2CF_2$—.

[0223] X^{41} and X^{42} are the same as or different from each other, and preferably include at least one selected from the group consisting of an alkyl group, a fluorinated alkyl group, an alkenyl group, and a fluorinated alkenyl group. X^{41} and X^{42} each preferably have a carbon number of 1 to 10, more preferably 1 to 3.

[0224] X^{41} and X^{42} are the same as or different from each other, and more preferably include at least one selected from the group consisting of H—, F—, CH_3—, CH_3CH_2—, $CH_3CH_2CH_2$—, CF_3—, CF_3CF_2—, CH_2FCH_2—, and $CF_3CF_2CF_2$—.

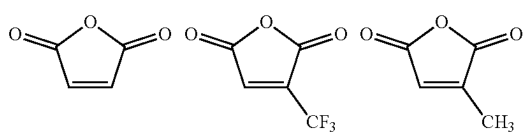
[0225] The compound (4) is preferably any of the following compounds.

[Chem. 49]



[0226] The compound (5) is preferably any of the following compounds.

[Formula 50]

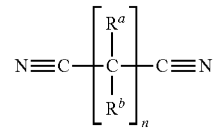


[0227] In order to cause much less reduction in capacity retention and a much less increase in amount of gas generated even when stored at high temperature, the electrolytic solution preferably contains 0.0001 to 15% by mass of the compound (3) relative to the electrolytic solution. The amount of the compound (3) is more preferably 0.01 to 10% by mass, still more preferably 0.1 to 3% by mass, particularly preferably 0.1 to 1.0% by mass.

[0228] In order to cause much less reduction in capacity retention and a much less increase in amount of gas generated even when stored at high temperature, the electrolytic solution, when containing both the compounds (4) and (5), preferably contains 0.08 to 2.50% by mass of the compound (4) and 0.02 to 1.50% by mass of the compound (5), more preferably 0.80 to 2.50% by mass of the compound (4) and 0.08 to 1.50% by mass of the compound (5), relative to the electrolytic solution.

[0229] The electrolytic solution of the disclosure may contain at least one selected from the group consisting of nitrile compounds represented by the following formulas (1a), (1b), and (1c):

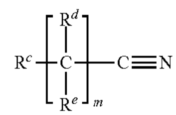
[Chem. 51]



(1a)

(wherein R^a and R^b are each independently a hydrogen atom, a cyano group (CN), a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom; and n is an integer of 1 to 10);

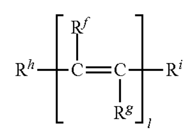
[Chem. 52]



(1b)

(wherein R^c is a hydrogen atom, a halogen atom, an alkyl group, a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom, or a group represented by NC—R^{c1}—X^{c1}— (wherein R^{c1} is an alkylene group, X^{c1} is an oxygen atom or a sulfur atom); R^d and R^e are each independently a hydrogen atom, a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom; and m is an integer of 1 to 10);

[Chem. 53]



(1c)

(wherein R^f, R^g, R^h, and R^i are each independently a group containing a cyano group (CN), a hydrogen atom (H), a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom; at least one selected from the group consisting of R^f, R^g, R^h, and R^i is a group containing a cyano group; and 1 is an integer of 1 to 3).

[0230] This can improve the high-temperature storage characteristics of an electrochemical device. One nitrile compound may be used alone, or two or more thereof may be used in any combination at any ratio.

[0231] In the formula (1a), R^a and R^b are each independently a hydrogen atom, a cyano group (CN), a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom.

[0232] Examples of the halogen atom include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Preferred among these is a fluorine atom.

[0233] The alkyl group is preferably a C1-C5 alkyl group. Specific examples of the alkyl group include a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, and a tert-butyl group.

[0234] An example of the group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom is a group obtainable by replacing at least one hydrogen atom of the aforementioned alkyl group by the aforementioned halogen atom.

[0235] When R^a and R^b are alkyl groups or groups each obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom, R^a and R^b may bind to each other to form a cyclic structure (e.g., a cyclohexane ring).

[0236] R^a and R^b are each preferably a hydrogen atom or an alkyl group.

[0237] In the formula (1a), n is an integer of 1 to 10. When n is 2 or greater, all of n R^as may be the same as each other, or at least part of them may be different from the others. The same applies to R^b. In the formula, n is preferably an integer of 1 to 7, more preferably an integer of 2 to 5.

[0238] Preferred as the nitrile compound represented by the formula (1a) are dinitriles and tricarbonitriles.

[0239] Specific examples of the dinitriles include malononitrile, succinonitrile, glutaronitrile, adiponitrile, pimelonitrile, suberonitrile, azelanitrile, sebaconitrile, undecanedinitrile, dodecanedinitrile, methylmalononitrile, ethylmalononitrile, isopropylmalononitrile, tert-butylmalononitrile, methylsuccinonitrile, 2,2-dimethylsuccinonitrile, 2,3-dimethylsuccinonitrile, 2,3,3-trimethylsuccinonitrile, 2,2,3,3-tetramethylsuccinonitrile, 2,3-diethyl-2,3-dimethylsuccinonitrile, 2,2-diethyl-3,3-dimethylsuccinonitrile, bicyclohexyl-1,1-dicarbonitrile, bicyclohexyl-2,2-dicarbonitrile, bicyclohexyl-3,3-dicarbonitrile, 2,5-dimethyl-2,5-hexanedicarbonitrile, 2,3-diisobutyl-2,3-dimethylsuccinonitrile, 2,2-diisobutyl-3,3-dimethylsuccinonitrile, 2-methylglutaronitrile, 2,3-dimethylglutaronitrile, 2,4-dimethylglutaronitrile, 2,2,3,3-tetramethylglutaronitrile, 2,2,4,4-tetramethylglutaronitrile, 2,2,3,4-tetramethylglutaronitrile, 2,3,3,4-tetramethylglutaronitrile, 1,4-dicyanopentane, 2,6-dicyanoheptane, 2,7-dicyanooctane, 2,8-dicyanononane, 1,6-dicyanodecane, 1,2-dicyanobenzene, 1,3-dicyanobenzene, 1,4-dicyanobenzene, 3,3'-(ethylenedioxy)dipropionitrile, 3,3'-(ethylenedithio)dipropionitrile, 3,9-bis(2-cyanoethyl)-2,4,8,10-tetraoxaspiro[5,5]undecane, butanenitrile, and phthalonitrile. Particularly preferred among these are succinonitrile, glutaronitrile, and adiponitrile.

[0240] Specific examples of the tricarbonitriles include pentanetricarbonitrile, propanetricarbonitrile, 1,3,5-hexanetricarbonitrile, 1,3,6-hexanetricarbonitrile, heptanetricarbonitrile, 1,2,3-propanetricarbonitrile, 1,3,5-pentanetricarbonitrile, cyclohexanetricarbonitrile, triscyanoethylamine, triscyanoethoxypropane, tricyanoethylene, and tris(2-cyanoethyl)amine. Particularly preferred are 1,3,6-hexanetricarbonitrile and cyclohexanetricarbonitrile, and most preferred is cyclohexanetricarbonitrile.

[0241] In the formula (1b), R^c is a hydrogen atom, a halogen atom, an alkyl group, a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom, or a group represented by NC—R^{c1}—X^{c1}— (wherein R^{c1} is an alkylene group; and X^{c1} is an oxygen atom or a sulfur atom); R^d and R^e are each independently a hydrogen atom, a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom.

[0242] Examples of the halogen atom, the alkyl group, and the group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom include those mentioned as examples thereof for the formula (1a).

[0243] R^{c1} in NC—R^{c1}—X^{c1}— is an alkylene group. The alkylene group is preferably a C1-C3 alkylene group.

[0244] R^c, R^d, and R^e are each preferably independently a hydrogen atom, a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom.

[0245] At least one selected from R^c, R^d, and R^e is preferably a halogen atom or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom, more preferably a fluorine atom or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a fluorine atom.

[0246] When R^d and R^e are each an alkyl group or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom, R^d and R^e may bind to each other to form a cyclic structure (e.g., a cyclohexane ring).

[0247] In the formula (1b), m is an integer of 1 to 10. When m is 2 or greater, all of m R^ds may be the same as each other, or at least part of them may be different from the others. The same applies to R^e. In the formula, m is preferably an integer of 2 to 7, more preferably an integer of 2 to 5.

[0248] Examples of the nitrile compound represented by the formula (1b) include acetonitrile, propionitrile, butyronitrile, isobutyronitrile, valeronitrile, isovaleronitrile, lauronitrile, 3-methoxypropionitrile, 2-methylbutyronitrile, trimethylacetonitrile, hexanenitrile, cyclopentanecarbonitrile, cyclohexanecarbonitrile, fluoroacetonitrile, difluoroacetonitrile, trifluoroacetonitrile, 2-fluoropropionitrile, 3-fluoropropionitrile, 2,2-difluoropropionitrile, 2,3-difluoropropionitrile, 3,3-difluoropropionitrile, 2,2,3-trifluoropropionitrile, 3,3,3-trifluoropropionitrile, 3,3'-oxydipropionitrile, 3,3'-thiodipropionitrile, pentafluoropropionitrile, methoxyacetonitrile, and benzonitrile. Particularly preferred among these is 3,3,3-trifluoropropionitrile.

[0249] In the formula (1c), R^f, R^g, R^h, and R^i are each independently a group containing a cyano group (CN), a hydrogen atom, a halogen atom, an alkyl group, or a group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom.

[0250] Examples of the halogen atom, the alkyl group, and the group obtainable by replacing at least one hydrogen atom of an alkyl group by a halogen atom include those mentioned as examples thereof for the formula (1a).

[0251] Examples of the group containing a cyano group include a cyano group and a group obtainable by replacing at least one hydrogen atom of an alkyl group by a cyano group. Examples of the alkyl group in this case include those mentioned as examples for the formula (1a).

[0252] At least one selected from R^f, R^g, R^h, and R^i is a group containing a cyano group. Preferably, at least two selected from R^f, R^g, R^h, and R^i are each a group containing a cyano group. More preferably, R^h and R^i are each a group containing a cyano group. When R^h and R^i are each a group containing a cyano group, R^f and R^g are preferably hydrogen atoms.

[0253] In the formula (1c), 1 is an integer of 1 to 3. When 1 is 2 or greater, all of 1 R^fs may be the same as each other, or at least part of them may be different from the others. The same applies to R^g. In the formula, 1 is preferably an integer of 1 or 2.

[0254] Examples of the nitrile compound represented by the formula (1c) include 3-hexenedinitrile, mucononitrile, maleonitrile, fumaronitrile, acrylonitrile, methacrylonitrile, crotononitrile, 3-methylcrotononitrile, 2-methyl-2-butenenitrile, 2-pentenenitrile, 2-methyl-2-pentenenitrile, 3-methyl-2-pentenenitrile, and 2-hexenenitrile. Preferred are 3-hexenedinitrile and mucononitrile, and particularly preferred is 3-hexenedinitrile.

[0255] The nitrile compounds are preferably present in an amount of 0.2 to 7% by mass relative to the electrolytic solution. This can further improve the high-temperature storage characteristics and safety of an electrochemical device at high voltage. The lower limit of the total amount of the nitrile compounds is more preferably 0.3% by mass, still more preferably 0.5% by mass. The upper limit thereof is more preferably 5% by mass, still more preferably 2% by mass, particularly preferably 0.5% by mass.

[0256] The electrolytic solution of the disclosure may contain a compound containing an isocyanate group (hereinafter, also abbreviated as "isocyanate"). The isocyanate used may be any isocyanate. Examples of the isocyanate include monoisocyanates, diisocyanates, and triisocyanates.

[0257] Specific examples of the monoisocyanates include isocyanatomethane, isocyanatoethane, 1-isocyanatopropane, 1-isocyanatobutane, 1-isocyanatopentane, 1-isocyanatohexane, 1-isocyanatoheptane, 1-isocyanatooctane, 1-isocyanatononane, 1-isocyanatodecane, isocyanatocyclohexane, methoxycarbonyl isocyanate, ethoxycarbonyl isocyanate, propoxycarbonyl isocyanate, butoxycarbonyl isocyanate, methoxysulfonyl isocyanate, ethoxysulfonyl isocyanate, propoxysulfonyl isocyanate, butoxysulfonyl isocyanate, fluorosulfonyl isocyanate, methyl isocyanate, butyl isocyanate, phenyl isocyanate, 2-isocyanatoethyl acrylate, 2-isocyanatoethyl methacrylate, and ethyl isocyanate.

[0258] Specific examples of the diisocyanates include 1,4-diisocyanatobutane, 1,5-diisocyanatopentane, 1,6-diisocyanatohexane, 1,7-diisocyanatoheptane, 1,8-diisocyanatooctane, 1,9-diisocyanatononane, 1,10-diisocyanatodecane, 1,3-diisocyanatopropene, 1,4-diisocyanato-2-butene, 1,4-diisocyanato-2-fluorobutane, 1,4-diisocyanato-2,3-difluorobutane, 1,5-diisocyanato-2-pentene, 1,5-diisocyanato-2-methylpentane, 1,6-diisocyanato-2-hexene, 1,6-diisocyanato-3-hexene, 1,6-diisocyanato-3-fluorohexane, 1,6-diisocyanato-3,4-difluorohexane, toluene diisocyanate, xylene diisocyanate, tolylene diisocyanate, 1,2-bis(isocyanatomethyl)cyclohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,4-bis(isocyanatomethyl)cyclohexane, 1,2-diisocyanatocyclohexane, 1,3-diisocyanatocyclohexane, 1,4-diisocyanatocyclohexane, dicyclohexylmethane-1,1'-diisocyanate, dicyclohexylmethane-2,2'-diisocyanate, dicyclohexylmethane-3,3'-diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, isophorone diisocyanate, bicyclo[2.2.1]heptane-2,5-diylbis(methyl=isocyanate), bicyclo[2.2.1]heptane-2,6-diylbis(methyl=isocyanate), 2,4,4-trimethylhexamethylene diisocyanate, 2,2,4-trimethylhexamethylene diisocyanate, hexamethylene diisocyanate, 1,4-phenylene diisocyanate, octamethylene diisocyanate, and tetramethylene diisocyanate.

[0259] Specific examples of the triisocyanates include 1,6,11-triisocyanatoundecane, 4-isocyanatomethyl-1,8-octamethylene diisocyanate, 1,3,5-triisocyanatomethylbenzene, 1,3,5-tris(6-isocyanatohex-1-yl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, and 4-(isocyanatomethyl)octamethylene=diisocyanate.

[0260] In order to enable industrially easy availability and cause low cost in production of an electrolytic solution, preferred among these are 1,6-diisocyanatohexane, 1,3-bis(isocyanatomethyl)cyclohexane, 1,3,5-tris(6-isocyanatohex-1-yl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione, 2,4,4-trimethylhexamethylene diisocyanate, and 2,2,4-trimethylhexamethylene diisocyanate. From the technical viewpoint, they can contribute to formation of a stable film-shaped structure and can therefore more suitably be used.

[0261] The isocyanate may be present in any amount that does not significantly impair the effects of the disclosure. The amount is preferably, but not limited to, 0.001% by mass or more and 1.0% by mass or less relative to the electrolytic solution. The isocyanate in an amount of not smaller than this lower limit can give a sufficient effect of improving the cycle characteristics to a non-aqueous electrolyte secondary battery. The isocyanate in an amount of not larger than this upper limit can eliminate an initial increase in resistance of a non-aqueous electrolyte secondary battery. The amount of the isocyanate is more preferably 0.01% by mass or more, still more preferably 0.1% by mass or more, particularly preferably 0.2% by mass or more, while more preferably 0.8% by mass or less, still more preferably 0.7% by mass or less, particularly preferably 0.6% by mass or less.

[0262] The electrolytic solution of the disclosure may contain a cyclic sulfonate. The cyclic sulfonate may be any cyclic sulfonate. Examples of the cyclic sulfonate include a saturated cyclic sulfonate, an unsaturated cyclic sulfonate, a saturated cyclic disulfonate, and an unsaturated cyclic disulfonate.

[0263] Specific examples of the saturated cyclic sulfonate include 1,3-propanesultone, 1-fluoro-1,3-propanesultone, 2-fluoro-1,3-propanesultone, 3-fluoro-1,3-propanesultone, 1-methyl-1,3-propanesultone, 2-methyl-1,3-propanesultone, 3-methyl-1,3-propanesultone, 1,3-butanesultone, 1,4-butanesultone, 1-fluoro-1,4-butanesultone, 2-fluoro-1,4-butanesultone, 3-fluoro-1,4-butanesultone, 4-fluoro-1,4-butanesultone, 1-methyl-1,4-butanesultone, 2-methyl-1,4-butanesultone, 3-methyl-1,4-butanesultone, 4-methyl-1,4-butanesultone, and 2,4-butanesultone.

[0264] Specific examples of the unsaturated cyclic sulfonate include 1-propene-1,3-sultone, 2-propene-1,3-sultone, 1-fluoro-1-propene-1,3-sultone, 2-fluoro-1-propene-1,3-sultone, 3-fluoro-1-propene-1,3-sultone, 1-fluoro-2-propene-1,3-sultone, 2-fluoro-2-propene-1,3-sultone, 3-fluoro-2-propene-1,3-sultone, 1-methyl-1-propene-1,3-sultone, 2-methyl-1-propene-1,3-sultone, 3-methyl-1-propene-1,3-sultone, 1-methyl-2-propene-1,3-sultone, 2-methyl-2-propene-1,3-sultone, 3-methyl-2-propene-1,3-sultone, 1-butene-1,4-sultone, 2-butene-1,4-sultone, 3-butene-1,4-sultone, 1-fluoro-1-butene-1,4-sultone, 2-fluoro-1-butene-1,4-sultone, 3-fluoro-1-butene-1,4-sultone, 4-fluoro-1-butene-1,4-sultone, 1-fluoro-2-butene-1,4-sultone, 2-fluoro-2-butene-1,4-sultone, 3-fluoro-2-butene-1,4-sultone, 4-fluoro-2-butene-1,4-sultone, 1,3-propenesultone, 1-fluoro-3-butene-1,4-sultone, 2-fluoro-3-butene-1,4-sultone, 3-fluoro-3-butene-1,4-sultone, 4-fluoro-3-butene-1,4-sultone, 1-methyl-1-butene-1,4-sultone, 2-methyl-1-butene-1,4-sultone, 3-methyl-1-butene-1,4-sultone, 4-methyl-1-butene-1,4-sultone, 1-methyl-2-butene-1,4-sultone, 2-methyl-2-butene-1,4-sultone, 3-methyl-2-butene-1,4-sultone, 4-methyl-2-butene-1,4-sultone, 1-methyl-3-butene-1,4-sultone, 2-methyl-3-butene-1,4-sultone, 3-methyl-3-butene-1,4-sultone, and 4-methyl-3-butene-14-sultone.

[0265] In order to enable easy availability and contribute to formation of a stable film-shaped structure, more preferred among these are 1,3-propanesultone, 1-fluoro-1,3-propanesultone, 2-fluoro-1,3-propanesultone, 3-fluoro-1,3-propanesultone, and 1-propene-1,3-sultone. The cyclic sulfonate may be in any amount that does not significantly impair the effects of the disclosure. The amount is preferably, but not limited to, 0.001% by mass or more and 3.0% by mass or less relative to the electrolytic solution.

[0266] The cyclic sulfonate in an amount of not smaller than this lower limit can give a sufficient effect of improving the cycle characteristics to a non-aqueous electrolyte secondary battery. The cyclic sulfonate in an amount of not larger than this upper limit can eliminate an increase in the cost of producing a non-aqueous electrolyte secondary battery. The amount of the cyclic sulfonate is more preferably 0.01% by mass or more, still more preferably 0.1% by mass or more, particularly preferably 0.2% by mass or more, while more preferably 2.5% by mass or less, still more preferably 2.0% by mass or less, particularly preferably 1.8% by mass or less.

[0267] The electrolytic solution of the disclosure may further contain a polyethylene oxide that has a weight average molecular weight of 2000 to 4000 and has —OH, —OCOOH, or —COOH at an end.

[0268] The presence of such a compound can improve the stability at the interfaces with the respective electrodes, improving the characteristics of an electrochemical device.

[0269] Examples of the polyethylene oxide include polyethylene oxide monool, polyethylene oxide carboxylic acid, polyethylene oxide diol, polyethylene oxide dicarboxylic acid, polyethylene oxide triol, and polyethylene oxide tricarboxylate. One of these may be used alone or two or more thereof may be used in any combination.

[0270] In order to give better characteristics of an electrochemical device, preferred are a mixture of polyethylene oxide monool and polyethylene oxide diol and a mixture of polyethylene carboxylic acid and polyethylene dicarboxylic acid.

[0271] The polyethylene oxide having too small a weight average molecular weight may be easily oxidatively decomposed. The weight average molecular weight is more preferably 3000 to 4000.

[0272] The weight average molecular weight can be determined by gel permeation chromatography (GPC) in polystyrene equivalent.

[0273] The polyethylene oxide is preferably present in an amount of 1×10^{-6} to 1×10^{-2} mol/kg in the electrolytic solution. Too large an amount of the polyethylene oxide may cause poor characteristics of an electrochemical device.

[0274] The amount of the polyethylene oxide is more preferably 5×10^{-6} mol/kg or more.

[0275] The electrolytic solution of the disclosure may further contain as an additive any of other components such as a fluorinated saturated cyclic carbonate, an unsaturated cyclic carbonate, an overcharge inhibitor, and a known different aid. This can reduce impairment of the characteristics of an electrochemical device.

[0276] Examples of the fluorinated saturated cyclic carbonate include compounds represented by the aforementioned formula (A). Preferred among these are fluoroethylene carbonate, difluoroethylene carbonate, monofluoromethyl ethylene carbonate, trifluoromethyl ethylene carbonate, and 2,2,3,3,3-pentafluoropropylethylene carbonate (4-(2,2,3,3,3-pentafluoro-propyl)-[1,3]dioxolan-2-one). One fluorinated saturated cyclic carbonate may be used alone, or two or more thereof may be used in any combination at any ratio.

[0277] The fluorinated saturated cyclic carbonate is preferably present in an amount of 0.001 to 10% by mass, more preferably 0.01 to 5% by mass, still more preferably 0.1 to 3% by mass, relative to the electrolytic solution.

[0278] Examples of the unsaturated cyclic carbonate include vinylene carbonate compounds, ethylene carbonate compounds substituted with a substituent that contains an aromatic ring, a carbon-carbon double bond, or a carbon-carbon triple bond, phenyl carbonate compounds, vinyl carbonate compounds, allyl carbonate compounds, and catechol carbonate compounds.

[0279] Examples of the vinylene carbonate compounds include vinylene carbonate, methylvinylene carbonate, 4,5-dimethylvinylene carbonate, phenylvinylene carbonate, 4,5-diphenylvinylene carbonate, vinylvinylene carbonate, 4,5-divinylvinylene carbonate, allylvinylene carbonate, 4,5-diallylvinylene carbonate, 4-fluorovinylene carbonate, 4-fluoro-5-methylvinylene carbonate, 4-fluoro-5-phenylvinylene carbonate, 4-fluoro-5-vinylvinylene carbonate, 4-allyl-5-fluorovinylene carbonate, ethynylethylene carbonate, propargylethylene carbonate, methylvinylene carbonate, and dimethylvinylene carbonate.

[0280] Specific examples of the ethylene carbonate compounds substituted with a substituent that contains an aromatic ring, a carbon-carbon double bond, or a carbon-carbon triple bond include vinylethylene carbonate, 4,5-divinylethylene carbonate, 4-methyl-5-vinylethylene carbonate, 4-allyl-5-vinylethylene carbonate, ethynylethylene carbonate, 4,5-diethynylethylene carbonate, 4-methyl-5-ethynylethylene carbonate, 4-vinyl-5-ethynylethylene carbonate, 4-allyl-5-ethynylethylene carbonate, phenylethylene carbonate, 4,5-diphenylethylene carbonate, 4-phenyl-5-vinylethylene carbonate, 4-allyl-5-phenylethylene carbonate, allylethylene carbonate, 4,5-diallylethylene carbonate, 4-methyl-5-allylethylene carbonate, 4-methylene-1,3-dioxolan-2-one, 4,5-di methylene-1,3-dioxolan-2-one, and 4-methyl-5-allylethylene carbonate.

[0281] The unsaturated cyclic carbonate is preferably vinylene carbonate, methylvinylene carbonate, 4,5-dimethylvinylene carbonate, vinylvinylene carbonate, 4,5-vinylvinylene carbonate, allylvinylene carbonate, 4,5-diallylvinylene carbonate, vinylethylene carbonate, 4,5-divinylethylene carbonate, 4-methyl-5-vinylethylene carbonate, allylethylene carbonate, 4,5-diallylethylene carbonate, 4-methyl-5-allylethylene carbonate, 4-allyl-5-vinylethylene carbonate, ethynylethylene carbonate, 4,5-diethynylethylene carbonate, 4-methyl-5-ethynylethylene carbonate, and 4-vinyl-5-ethynylethylene carbonate. In order to form a more stable interface protecting film, particularly preferred are vinylene carbonate, vinylethylene carbonate, and ethynylethylene carbonate, and most preferred is vinylene carbonate.

[0282] The unsaturated cyclic carbonate may have any molecular weight that does not significantly impair the effects of the disclosure. The molecular weight is preferably 50 or higher and 250 or lower. The unsaturated cyclic carbonate having a molecular weight within this range can easily ensure its solubility in the electrolytic solution and can easily lead to sufficient achievement of the effects of the disclosure. The molecular weight of the unsaturated cyclic carbonate is more preferably 80 or higher and 150 or lower.

[0283] The unsaturated cyclic carbonate may be produced by any production method, and may be produced by a known method selected as appropriate.

[0284] One unsaturated cyclic carbonate may be used alone or two or more thereof may be used in any combination at any ratio.

[0285] The unsaturated cyclic carbonate may be present in any amount that does not significantly impair the effects of the disclosure. The amount of the unsaturated cyclic carbonate is preferably 0.001% by mass or more, more preferably 0.01% by mass or more, still more preferably 0.1% by mass or more, of 100% by mass of the electrolytic solution. The amount is preferably 5% by mass or less, more preferably 4% by mass or less, still more preferably 3% by mass or less. The unsaturated cyclic carbonate in an amount within the above range allows an electrochemical device containing the electrolytic solution to easily exhibit a sufficient effect of improving the cycle characteristics, and can easily avoid a situation with impaired high-temperature storage characteristics, generation of a large amount of gas, and a reduced discharge capacity retention.

[0286] In addition to the aforementioned non-fluorinated unsaturated cyclic carbonates, a fluorinated unsaturated cyclic carbonate may also suitably be used as an unsaturated cyclic carbonate.

[0287] The fluorinated unsaturated cyclic carbonate is a cyclic carbonate containing an unsaturated bond and a fluorine atom. The number of fluorine atoms in the fluorinated unsaturated cyclic carbonate may be any number that is 1 or greater. The number of fluorine atoms is usually 6 or smaller, preferably 4 or smaller, most preferably 1 or 2.

[0288] Examples of the fluorinated unsaturated cyclic carbonate include fluorinated vinylene carbonate derivatives and fluorinated ethylene carbonate derivatives substituted with a substituent that contains an aromatic ring or a carbon-carbon double bond.

[0289] Examples of the fluorinated vinylene carbonate derivatives include 4-fluorovinylene carbonate, 4-fluoro-5-methylvinylene carbonate, 4-fluoro-5-phenylvinylene carbonate, 4-allyl-5-fluorovinylene carbonate, and 4-fluoro-5-vinylvinylene carbonate.

[0290] Examples of the fluorinated ethylene carbonate derivatives substituted with a substituent that contains an aromatic ring or a carbon-carbon double bond include 4-fluoro-4-vinylethylene carbonate, 4-fluoro-4-allylethylene carbonate, 4-fluoro-5-vinylethylene carbonate, 4-fluoro-5-allylethylene carbonate, 4,4-difluoro-4-vinylethylene carbonate, 4,4-difluoro-4-allylethylene carbonate, 4,5-difluoro-4-vinylethylene carbonate, 4,5-difluoro-4-allylethylene carbonate, 4-fluoro-4,5-divinylethylene carbonate, 4-fluoro-4,5-diallylethylene carbonate, 4,5-difluoro-4,5-divinylethylene carbonate, 4,5-difluoro-4,5-diallylethylene carbonate, 4-fluoro-4-phenylethylene carbonate, 4-fluoro-5-phenylethylene carbonate, 4,4-difluoro-5-phenylethylene carbonate, and 4,5-difluoro-4-phenylethylene carbonate.

[0291] In order to form a stable interface protecting film, more preferably used as the fluorinated unsaturated cyclic carbonate are 4-fluorovinylene carbonate, 4-fluoro-5-methylvinylene carbonate, 4-fluoro-5-vinylvinylene carbonate, 4-allyl-5-fluorovinylene carbonate, 4-fluoro-4-vinylethylene carbonate, 4-fluoro-4-allylethylene carbonate, 4-fluoro-5-vinylethylene carbonate, 4-fluoro-5-allylethylene carbonate, 4,4-difluoro-4-vinylethylene carbonate, 4,4-difluoro-4-allylethylene carbonate, 4,5-difluoro-4-vinylethylene carbonate, 4,5-difluoro-4-allylethylene carbonate, 4-fluoro-4,5-divinylethylene carbonate, 4-fluoro-4,5-diallylethylene carbonate, 4,5-difluoro-4,5-divinylethylene carbonate, and 4,5-difluoro-4,5-diallylethylene carbonate.

[0292] The fluorinated unsaturated cyclic carbonate may have any molecular weight that does not significantly impair the effects of the disclosure. The molecular weight is preferably 50 or higher and 500 or lower. The fluorinated unsaturated cyclic carbonate having a molecular weight within this range can easily ensure the solubility of the fluorinated unsaturated cyclic carbonate in the electrolytic solution.

[0293] The fluorinated unsaturated cyclic carbonate may be produced by any method, and may be produced by any known method selected as appropriate. The molecular weight is more preferably 100 or higher and 200 or lower.

[0294] One fluorinated unsaturated cyclic carbonate may be used alone or two or more thereof may be used in any combination at any ratio. The fluorinated unsaturated cyclic carbonate may be contained in any amount that does not significantly impair the effects of the disclosure. The amount of the fluorinated unsaturated cyclic carbonate is usually preferably 0.001% by mass or more, more preferably 0.01% by mass or more, still more preferably 0.1% by mass or more, while preferably 5% by mass or less, more preferably 4% by mass or less, still more preferably 3% by mass or less, of 100% by mass of the electrolytic solution. The fluorinated unsaturated cyclic carbonate in an amount within this range allows an electrochemical device containing the electrolytic solution to exhibit an effect of sufficiently improving the cycle characteristics and can easily avoid a situation with reduced high-temperature storage characteristics, generation of a large amount of gas, and a reduced discharge capacity retention.

[0295] The electrolytic solution of the disclosure may contain a compound containing a triple bond. This compound may be of any type as long as it contains one or more triple bonds in the molecule.

[0296] Specific examples of the compound containing a triple bond include the following compounds:

- **[0297]** hydrocarbon compounds such as 1-penthyne, 2-penthyne, 1-hexyne, 2-hexyne, 3-hexyne, 1-heptyne, 2-heptyne, 3-heptyne, 1-octyne, 2-octyne, 3-octyne, 4-octyne, 1-nonyne, 2-nonyne, 3-nonyne, 4-nonyne, 1-dodecyne, 2-dodecyne, 3-dodecyne, 4-dodecyne, 5-dodecyne, phenyl acetylene, 1-phenyl-1-propyne, 1-phenyl-2-propyne, 1-phenyl-1-butyne, 4-phenyl-1-butyne, 4-phenyl-1-butyne, 1-phenyl-1-penthyne, 5-phenyl-1-penthyne, 1-phenyl-1-hexyne, 6-phenyl-1-hexyne, diphenyl acetylene, 4-ethynyl toluene, and dicyclohexyl acetylene;
- **[0298]** monocarbonates such as 2-propynylmethyl carbonate, 2-propynylethyl carbonate, 2-propynylpropyl carbonate, 2-propynylbutyl carbonate, 2-propynylphenyl carbonate, 2-propynylcyclohexyl carbonate, di-2-propynylcarbonate, 1-methyl-2-propynylmethyl carbonate, 1,1-dimethyl-2-propynylmethyl carbonate,

2-butynylmethyl carbonate, 3-butynylmethyl carbonate, 2-pentynylmethyl carbonate, 3-pentynylmethyl carbonate, and 4-pentynylmethyl carbonate; dicarbonates such as 2-butyne-1,4-diol dimethyl dicarbonate, 2-butyne-1,4-diol diethyl dicarbonate, 2-butyne-1,4-diol dipropyl dicarbonate, 2-butyne-1,4-diol dibutyl dicarbonate, 2-butyne-1,4-diol diphenyl dicarbonate, and 2-butyne-1,4-diol dicyclohexyl dicarbonate;

[0299] monocarboxylates such as 2-propynyl acetate, 2-propynyl propionate, 2-propynyl butyrate, 2-propynyl benzoate, 2-propynyl cyclohexylcarboxylate, 1,1-dimethyl-2-propynyl acetate, 1,1-dimethyl-2-propynyl propionate, 1,1-dimethyl-2-propynyl butyrate, 1,1-dimethyl-2-propynyl benzoate, 1,1-dimethyl-2-propynyl cyclohexylcarboxylate, 2-butynyl acetate, 3-butynyl acetate, 2-pentynyl acetate, 3-pentynyl acetate, 4-pentynyl acetate, methyl acrylate, ethyl acrylate, propyl acrylate, vinyl acrylate, 2-propenyl acrylate, 2-butenyl acrylate, 3-butenyl acrylate, methyl methacrylate, ethyl methacrylate, propyl methacrylate, vinyl methacrylate, 2-propenyl methacrylate, 2-butenyl methacrylate, 3-butenyl methacrylate, methyl 2-propynoate, ethyl 2-propynoate, propyl 2-propynoate, vinyl 2-propynoate, 2-propenyl 2-propynoate, 2-butenyl 2-propynoate, 3-butenyl 2-propynoate, methyl 2-butynoate, ethyl 2-butynoate, propyl 2-butynoate, vinyl 2-butynoate, 2-propenyl 2-butynoate, 2-butenyl 2-butynoate, 3-butenyl 2-butynoate, methyl 3-butynoate, ethyl 3-butynoate, propyl 3-butynoate, vinyl 3-butynoate, 2-propenyl 3-butynoate, 2-butenyl 3-butynoate, 3-butenyl 3-butynoate, methyl 2-penthynoate, ethyl 2-penthynoate, propyl 2-penthynoate, vinyl 2-penthynoate, 2-propenyl 2-penthynoate, 2-butenyl 2-penthynoate, 3-butenyl 2-penthynoate, methyl 3-penthynoate, ethyl 3-penthynoate, propyl 3-penthynoate, vinyl 3-penthynoate, 2-propenyl 3-penthynoate, 2-butenyl 3-penthynoate, 3-butenyl 3-penthynoate, methyl 4-penthynoate, ethyl 4-penthynoate, propyl 4-penthynoate, vinyl 4-penthynoate, 2-propenyl 4-penthynoate, 2-butenyl 4-penthynoate, and 3-butenyl 4-penthynoate, fumarates, methyl trimethylacetate, and ethyl trimethylacetate;

[0300] dicarboxylates such as 2-butyne-1,4-diol diacetate, 2-butyne-1,4-diol dipropionate, 2-butyne-1,4-diol dibutyrate, 2-butyne-1,4-diol dibenzoate, 2-butyne-1,4-diol dicyclohexanecarboxylate, hexahydrobenzo[1,3,2]dioxathiolane-2-oxide (1,2-cyclohexane diol), 2,2-dioxide-1,2-oxathiolan-4-yl acetate, and 2,2-dioxide-1,2-oxathiolan-4-yl acetate;

[0301] oxalic acid diesters such as methyl 2-propynyl oxalate, ethyl 2-propynyl oxalate, propyl 2-propynyl oxalate, 2-propynyl vinyl oxalate, allyl 2-propynyl oxalate, di-2-propynyl oxalate, 2-butynyl methyl oxalate, 2-butynyl ethyl oxalate, 2-butynyl propyl oxalate, 2-butynyl vinyl oxalate, allyl 2-butynyl oxalate, di-2-butynyl oxalate, 3-butynyl methyl oxalate, 3-butynyl ethyl oxalate, 3-butynyl propyl oxalate, 3-butynyl vinyl oxalate, allyl 3-butynyl oxalate, and di-3-butynyl oxalate;

[0302] phosphine oxides such as methyl(2-propynyl) (vinyl)phosphine oxide, divinyl(2-propynyl)phosphine oxide, di(2-propynyl) (vinyl)phosphine oxide, di(2-propenyl)2(-propynyl)phosphine oxide, di(2-propynyl) (2-propenyl)phosphine oxide, di(3-butenyl) (2-propynyl)phosphine oxide, and di(2-propynyl) (3-butenyl) phosphine oxide;

[0303] phosphinates such as 2-propynyl methyl(2-propenyl)phosphinate, 2-propynyl 2-butenyl(methyl)phosphinate, 2-propynyl di(2-propenyl)phosphinate, 2-propynyl di(3-butenyl)phosphinate, 1,1-dimethyl-2-propynyl methyl(2-propenyl)phosphinate, 1,1-dimethyl-2-propynyl 2-butenyl(methyl)phosphinate, 1,1-dimethyl-2-propynyl di(2-propenyl)phosphinate, 1,1-dimethyl-2-propynyl di(3-butenyl)phosphinate, 2-propenyl methyl(2-propynyl)phosphinate, 3-butenyl methyl(2-propynyl)phosphinate, 2-propenyl di(2-propynyl)phosphinate, 3-butenyl di(2-propynyl)phosphinate, 2-propenyl 2-propynyl(2-propenyl)phosphinate, and 3-butenyl 2-propynyl(2-propenyl)phosphinate;

[0304] phosphonates such as methyl 2-propynyl 2-propenylphosphonate, methyl(2-propynyl) 2-butenylphosphonate, (2-propynyl) (2-propenyl) 2-propenylphosphonate, (3-butenyl) (2-propynyl) 3-butenylphosphonate, (1,1-dimethyl-2-propynyl) (methyl) 2-propenylphosphonate, (1,1-dimethyl-2-propynyl)(methyl) 2-butenylphosphonate, (1,1-dimethyl-2-propynyl) (2-propenyl) 2-propenylphosphonate, (3-butenyl) (1,1-dimethyl-2-propynyl) 3-butenylphosphonate, (2-propynyl) (2-propenyl) methylphosphonate, (3-butenyl) (2-propynyl) methylphosphonate, (1,1-dimethyl-2-propynyl) (2-propenyl) methylphosphonate, (3-butenyl) (1,1-dimethyl-2-propynyl) methylphosphonate, (2-propynyl) (2-propenyl) ethylphosphonate, (3-butenyl) (2-propynyl) ethylphosphonate, (1,1-dimethyl-2-propynyl) (2-propenyl) ethylphosphonate, and (3-butenyl) (1,1-dimethyl-2-propynyl) ethylphosphonate; and

[0305] phosphates such as (methyl) (2-propenyl) (2-propynyl) phosphate, (ethyl) (2-propenyl) (2-propynyl) phosphate, (2-butenyl)(methyl) (2-propynyl) phosphate, (2-butenyl) (ethyl) (2-propynyl) phosphate, (1,1-dimethyl-2-propynyl)(methyl) (2-propenyl) phosphate, (1,1-dimethyl-2-propynyl) (ethyl) (2-propenyl) phosphate, (2-butenyl) (1,1-dimethyl-2-propynyl)(methyl) phosphate, and (2-butenyl) (ethyl) (1,1-dimethyl-2-propynyl) phosphate.

[0306] In order to more stably form a negative electrode film in the electrolytic solution, preferred among these are compounds containing an alkynyloxy group.

[0307] In order to improve the storage characteristics, particularly preferred are compounds such as 2-propynylmethyl carbonate, di-2-propynyl carbonate, 2-butyne-1,4-diol dimethyl dicarbonate, 2-propynyl acetate, 2-butyne-1,4-diol diacetate, methyl 2-propynyl oxalate, and di-2-propynyl oxalate.

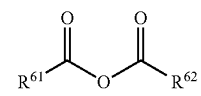
[0308] One compound containing a triple bond may be used alone or two or more thereof may be used in any combination at any ratio. The compound containing a triple bond may be present in any amount that does not significantly impair the effects of the disclosure relative to the whole electrolytic solution of the disclosure. The compound is usually contained at a concentration of 0.01% by mass or more, preferably 0.05% by mass or more, more preferably 0.1% by mass or more, while usually 5% by mass or less, preferably 3% by mass or less, more preferably 1% by mass or less, relative to the electrolytic solution of the disclosure. The compound satisfying the above range can further improve the effects such as output characteristics, load characteristics, cycle characteristics, and high-temperature storage characteristics.

[0309] In order to effectively reduce burst or combustion of a battery in case of overcharge, for example, of an electrochemical device containing the electrolytic solution, the electrolytic solution of the disclosure may contain an overcharge inhibitor.

[0310] Examples of the overcharge inhibitor include aromatic compounds, including unsubstituted or alkyl-substituted terphenyl derivatives such as biphenyl, o-terphenyl, m-terphenyl, and p-terphenyl, partially hydrogenated products of unsubstituted or alkyl-substituted terphenyl derivatives, cyclohexylbenzene, t-butylbenzene, t-amylbenzene, diphenyl ether, dibenzofuran, diphenyl cyclohexane, 1,1,3-trimethyl-3-phenylindan, cyclopentylbenzene, cyclohexylbenzene, cumene, 1,3-diisopropylbenzene, 1,4-diisopropylbenzene, t-butylbenzene, t-amylbenzene, t-hexylbenzene, and anisole; partially fluorinated products of the aromatic compounds such as 2-fluorobiphenyl, 4-fluorobiphenyl, o-cyclohexylfluorobenzene, p-cyclohexylfluorobenzene, fluorotoluene, and benzotrifluoride; fluorine-containing anisole compounds such as 2,4-difluoroanisole, 2,5-difluoroanisole, 1,6-difluoroanisole, 2,6-difluoroanisole, and 3,5-difluoroanisole; aromatic acetates such as 3-propylphenyl acetate, 2-ethylphenyl acetate, benzylphenyl acetate, methylphenyl acetate, benzyl acetate, and phenethylphenyl acetate; aromatic carbonates such as diphenyl carbonate and methylphenyl carbonate, toluene derivatives such as toluene and xylene, and unsubstituted or alkyl-substituted biphenyl derivatives such as 2-methylbiphenyl, 3-methylbiphenyl, 4-methylbiphenyl, and o-cyclohexylbiphenyl. Preferred among these are aromatic compounds such as biphenyl, alkylbiphenyl, terphenyl, partially hydrogenated terphenyl, cyclohexylbenzene, t-butylbenzene, t-amylbenzene, diphenyl ether, and dibenzofuran, diphenyl cyclohexane, 1,1,3-trimethyl-3-phenylindan, 3-propylphenyl acetate, 2-ethylphenyl acetate, benzylphenyl acetate, methylphenyl acetate, benzyl acetate, diphenyl carbonate, and methylphenyl carbonate. One of these compounds may be used alone or two or more thereof may be used in any combination. In order to achieve good balance between the overcharge inhibiting characteristics and the high-temperature storage characteristics with a combination use of two or more thereof, preferred is a combination of cyclohexylbenzene and t-butylbenzene or t-amylbenzene, or a combination of at least one oxygen-free aromatic compound selected from the group consisting of biphenyl, alkylbiphenyl, terphenyl, partially hydrogenated terphenyl, cyclohexylbenzene, t-butylbenzene, t-amylbenzene, and the like and at least one oxygen-containing aromatic compound selected from the group consisting of diphenyl ether, dibenzofuran, and the like.

[0311] The electrolytic solution used in the disclosure may contain a carboxylic anhydride other than the compound (3). The carboxylic anhydride is preferably a compound represented by the following formula (6). The carboxylic anhydride may be produced by any method which may be selected from known methods as appropriate.

[Chem. 54]



[0312] In the formula (6), R^{61} and R^{62} are each independently a hydrocarbon group having a carbon number of 1 or greater and 15 or smaller and optionally containing a substituent.

[0313] R^{61} and R^{62} each may be any monovalent hydrocarbon group. For example, each of them may be either an aliphatic hydrocarbon group or an aromatic hydrocarbon group, or may be a bond of an aliphatic hydrocarbon group and an aromatic hydrocarbon group. The aliphatic hydrocarbon group may be a saturated hydrocarbon group and may contain an unsaturated bond (carbon-carbon double bond or carbon-carbon triple bond). The aliphatic hydrocarbon group may be either acyclic or cyclic. In the case of an acyclic group, it may be either linear or branched. The group may be a bond of an acyclic group and a cyclic group. R^{61} and R^{62} may be the same as or different from each other.

[0314] When the hydrocarbon group for R^{61} and R^{62} contains a substituent, the substituent may be of any type as long as it is not beyond the scope of the disclosure. Examples thereof include halogen atoms such as a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom. Preferred is a fluorine atom. Examples of the substituent other than the halogen atoms include substituents containing a functional group such as an ester group, a cyano group, a carbonyl group, or an ether group. Preferred are a cyano group and a carbonyl group. The hydrocarbon group for R^{61} and R^{62} may contain only one of these substituents or may contain two or more thereof. When two or more substituents are contained, these substituents may be the same as or different from each other.

[0315] The hydrocarbon group for R^{61} and R^{62} has a carbon number of usually 1 or greater, while usually 15 or smaller, preferably 12 or smaller, more preferably 10 or smaller, still more preferably 9 or smaller. When R^{61} and R^{62} bind to each other to form a divalent hydrocarbon group, the divalent hydrocarbon group has a carbon number of usually 1 or greater, while usually 15 or smaller, preferably 13 or smaller, more preferably 10 or smaller, still more preferably 8 or smaller. When the hydrocarbon group for R^{61} and R^{62} contains a substituent that contains a carbon atom, the carbon number of the whole R^{61} or R^{62} including the substituent preferably satisfies the above range.

[0316] Next, specific examples of the acid anhydride represented by the formula (6) are described. In the following examples, the term "analog" means an acid anhydride obtainable by replacing part of the structure of an acid anhydride mentioned as an example by another structure within the scope of the disclosure. Examples thereof include dimers, trimers, and tetramers each composed of a plurality of acid anhydrides, those having respective substituents which are structural isomers having the same carbon number but having different branch structures, and those having the same substituent but at different sites in an acid anhydride.

[0317] First, specific examples of an acid anhydride in which R^{61} and R^{62} are the same as each other are described.

[0318] Specific examples of an acid anhydride in which R^{61} and R^{62} are acyclic alkyl groups include acetic anhydride, propionic anhydride, butanoic anhydride, 2-methylpropionic anhydride, 2,2-dimethylpropionic anhydride, 2-methylbutanoic anhydride, 3-methylbutanoic anhydride, 2,2-dimethylbutanoic anhydride, 2,3-dimethylbutanoic anhydride, 3,3-dimethylbutanoic anhydride, 2,2,3-trimethylbutanoic anhydride, 2,3,3-trimethylbutanoic anhydride, 2,2,3,3-tetramethylbutanoic anhydride, and 2-ethylbutanoic anhydride, and analogs thereof.

[0319] Specific examples of an acid anhydride in which R^{61} and R^{62} are cyclic alkyl groups include cyclopropanecarboxylic anhydride, cyclopentanecarboxylic anhydride, and cyclohexanecarboxylic anhydride, and analogs thereof.

[0320] Specific examples of an acid anhydride in which R^{61} and R^{62} are alkenyl groups include acrylic anhydride, 2-methylacrylic anhydride, 3-methylacrylic anhydride, 2,3-dimethylacrylic anhydride, 3,3-dimethylacrylic anhydride, 2,3,3-trimethylacrylic anhydride, 2-phenylacrylic anhydride, 3-phenylacrylic anhydride, 2,3-diphenylacrylic anhydride, 3,3-diphenylacrylic anhydride, 3-butenoic anhydride, 2-methyl-3-butenoic anhydride, 2,2-dimethyl-3-butenoic anhydride, 3-methyl-3-butenoic anhydride, 2-methyl-3-methyl-3-butenoic anhydride, 2,2-dimethyl-3-methyl-3-butenoic anhydride, 3-pentenoic anhydride, 4-pentenoic anhydride, 2-cyclopentenecarboxylic anhydride, 3-cyclopentenecarboxylic anhydride, and 4-cyclopentenecarboxylic anhydride, and analogs thereof.

[0321] Specific examples of an acid anhydride in which R^{61} and R^{62} are alkynyl groups include propynoic anhydride, 3-phenylpropynoic anhydride, 2-butynoic anhydride, 2-penthynoic anhydride, 3-butynoic anhydride, 3-penthynoic anhydride, and 4-penthynoic anhydride, and analogs thereof.

[0322] Specific examples of an acid anhydride in which R^{61} and R^{62} are aryl groups include benzoic anhydride, 4-methylbenzoic anhydride, 4-ethylbenzoic anhydride, 4-tert-butylbenzoic anhydride, 2-methylbenzoic anhydride, 2,4,6-trimethylbenzoic anhydride, 1-naphthalenecarboxylic anhydride, and 2-naphthalenecarboxylic anhydride, and analogs thereof.

[0323] Examples of an acid anhydride substituted with a fluorine atom are mainly listed below as examples of the acid anhydride in which R^{61} and R^{62} are substituted with a halogen atom. Acid anhydrides obtainable by replacing any or all of the fluorine atoms thereof with a chlorine atom, a bromine atom, or an iodine atom are also included in the exemplary compounds.

[0324] Examples of an acid anhydride in which R^{61} and R^{62} are halogen-substituted acyclic alkyl groups include fluoroacetic anhydride, difluoroacetic anhydride, trifluoroacetic anhydride, 2-fluoropropionic anhydride, 2,2-difluoropropionic anhydride, 2,3-difluoropropionic anhydride, 2,2,3-trifluoropropionic anhydride, 2,3,3-trifluoropropionic anhydride, 2,2,3,3-tetrapropionic anhydride, 2,3,3,3-tetrapropionic anhydride, 3-fluoropropionic anhydride, 3,3-difluoropropionic anhydride, 3,3,3-trifluoropropionic anhydride, and perfluoropropionic anhydride, and analogs thereof.

[0325] Examples of an acid anhydride in which R^{61} and R^{62} are halogen-substituted cyclic alkyl groups include 2-fluorocyclopentanecarboxylic anhydride, 3-fluorocyclopentanecarboxylic anhydride, and 4-fluorocyclopentanecarboxylic anhydride, and analogs thereof.

[0326] Examples of an acid anhydride in which R^{61} and R^{62} are halogen-substituted alkenyl groups include 2-fluoroacrylic anhydride, 3-fluoroacrylic anhydride, 2,3-difluoroacrylic anhydride, 3,3-difluoroacrylic anhydride, 2,3,3-trifluoroacrylic anhydride, 2-(trifluoromethyl)acrylic anhydride, 3-(trifluoromethyl)acrylic anhydride, 2,3-bis(trifluoromethyl)acrylic anhydride, 2,3,3-tris(trifluoromethyl) acrylic anhydride, 2-(4-fluorophenyl)acrylic anhydride, 3-(4-fluorophenyl)acrylic anhydride, 2,3-bis(4-fluorophenyl)acrylic anhydride, 3,3-bis(4-fluorophenyl)acrylic anhydride, 2-fluoro-3-butenoic anhydride, 2,2-difluoro-3-butenoic anhydride, 3-fluoro-2-butenoic anhydride, 4-fluoro-3-butenoic anhydride, 3,4-difluoro-3-butenoic anhydride, and 3,3,4-trifluoro-3-butenoic anhydride, and analogs thereof.

[0327] Examples of an acid anhydride in which R^{61} and R^{62} are halogen-substituted alkynyl groups include 3-fluoro-2-propynoic anhydride, 3-(4-fluorophenyl)-2-propynoic anhydride, 3-(2,3,4,5,6-pentafluorophenyl)-2-propynoic anhydride, 4-fluoro-2-butynoic anhydride, 4,4-difluoro-2-butynoic anhydride, and 4,4,4-trifluoro-2-butynoic anhydride, and analogs thereof.

[0328] Examples of an acid anhydride in which R^{61} and R^{62} are halogen-substituted aryl groups include 4-fluorobenzoic anhydride, 2,3,4,5,6-pentafluorobenzoic anhydride, and 4-trifluoromethylbenzoic anhydride, and analogs thereof.

[0329] Examples of an acid anhydride in which R^{61} and R^{62} each contain a substituent containing a functional group such as an ester, a nitrile, a ketone, an ether, or the like include methoxyformic anhydride, ethoxyformic anhydride, methyloxalic anhydride, ethyloxalic anhydride, 2-cyanoacetic anhydride, 2-oxopropionic anhydride, 3-oxobutanoic anhydride, 4-acetylbenzoic anhydride, methoxyacetic anhydride, and 4-methoxybenzoic anhydride, and analogs thereof.

[0330] Then, specific examples of an acid anhydride in which R^{61} and R^{62} are different from each other are described below.

[0331] R^{61} and R^{62} may be in any combination of those mentioned as examples above and analogs thereof. The following gives representative examples.

[0332] Examples of a combination of acyclic alkyl groups include acetic propionic anhydride, acetic butanoic anhydride, butanoic propionic anhydride, and acetic 2-methylpropionic anhydride.

[0333] Examples of a combination of an acyclic alkyl group and a cyclic alkyl group include acetic cyclopentanoic anhydride, acetic cyclohexanoic anhydride, and cyclopentanoic propionic anhydride.

[0334] Examples of a combination of an acyclic alkyl group and an alkenyl group include acetic acrylic anhydride, acetic 3-methylacrylic anhydride, acetic 3-butenoic anhydride, and acrylic propionic anhydride.

[0335] Examples of a combination of an acyclic alkyl group and an alkynyl group include acetic propynoic anhydride, acetic 2-butynoic anhydride, acetic 3-butynoic anhydride, acetic 3-phenyl propynoic anhydride, and propionic propynoic anhydride.

[0336] Examples of a combination of an acyclic alkyl group and an aryl group include acetic benzoic anhydride, acetic 4-methylbenzoic anhydride, acetic 1-naphthalenecarboxylic anhydride, and benzoic propionic anhydride.

[0337] Examples of a combination of an acyclic alkyl group and a hydrocarbon group containing a functional group include acetic fluoroacetic anhydride, acetic trifluoroacetic anhydride, acetic 4-fluorobenzoic anhydride, fluoroacetic propionic anhydride, acetic alkyloxalic anhydride, acetic 2-cyanoacetic anhydride, acetic 2-oxopropionic anhydride, acetic methoxyacetic anhydride, and methoxyacetic propionic anhydride.

[0338] Examples of a combination of cyclic alkyl groups include cyclopentanoic cyclohexanoic anhydride.

[0339] Examples of a combination of a cyclic alkyl group and an alkenyl group include acrylic cyclopentanoic anhydride, 3-methylacrylic cyclopentanoic anhydride, 3-butenoic cyclopentanoic anhydride, and acrylic cyclohexanoic anhydride.

[0340] Examples of a combination of a cyclic alkyl group and an alkynyl group include propynoic cyclopentanoic anhydride, 2-butynoic cyclopentanoic anhydride, and propynoic cyclohexanoic anhydride.

[0341] Examples of a combination of a cyclic alkyl group and an aryl group include benzoic cyclopentanoic anhydride, 4-methylbenzoic cyclopentanoic anhydride, and benzoic cyclohexanoic anhydride.

[0342] Examples of a combination of a cyclic alkyl group and a hydrocarbon group containing a functional group include fluoroacetic cyclopentanoic anhydride, cyclopentanoic trifluoroacetic anhydride, cyclopentanoic 2-cyanoacetic anhydride, cyclopentanoic methoxyacetic anhydride, and cyclohexanoic fluoroacetic anhydride.

[0343] Examples of a combination of alkenyl groups include acrylic 2-methylacrylic anhydride, acrylic 3-methylacrylic anhydride, acrylic 3-butenoic anhydride, and 2-methylacrylic 3-methylacrylic anhydride.

[0344] Examples of a combination of an alkenyl group and an alkynyl group include acrylic propynoic anhydride, acrylic 2-butynoic anhydride, and 2-methylacrylic propynoic anhydride.

[0345] Examples of a combination of an alkenyl group and an aryl group include acrylic benzoic anhydride, acrylic 4-methylbenzoic anhydride, and 2-methylacrylic benzoic anhydride.

[0346] Examples of a combination of an alkenyl group and a hydrocarbon group containing a functional group include acrylic fluoroacetic anhydride, acrylic trifluoroacetic anhydride, acrylic 2-cyanoacetic anhydride, acrylic methoxyacetic anhydride, and 2-methylacrylic fluoroacetic anhydride.

[0347] Examples of a combination of alkynyl groups include propynoic 2-butynoic anhydride, propynoic 3-butynoic anhydride, and 2-butynoic 3-butynoic anhydride.

[0348] Examples of a combination of an alkynyl group and an aryl group include benzoic propynoic anhydride, 4-methylbenzoic propynoic anhydride, and benzoic 2-butynoic anhydride.

[0349] Examples of a combination of an alkynyl group and a hydrocarbon group containing a functional group include propynoic fluoroacetic anhydride, propynoic trifluoroacetic anhydride, propynoic 2-cyanoacetic anhydride, propynoic methoxyacetic anhydride, and 2-butynoic fluoroacetic anhydride.

[0350] Examples of a combination of aryl groups include benzoic 4-methylbenzoic anhydride, benzoic 1-naphthalenecarboxylic anhydride, and 4-methylbenzoic 1-naphthalenecarboxylic anhydride.

[0351] Examples of a combination of an aryl group and a hydrocarbon group containing a functional group include benzoic fluoroacetic anhydride, benzoic trifluoroacetic anhydride, benzoic 2-cyanoacetic anhydride, benzoic methoxyacetic anhydride, and 4-methylbenzoic fluoroacetic anhydride.

[0352] Examples of a combination of hydrocarbon groups each containing a functional group include fluoroacetic trifluoroacetic anhydride, fluoroacetic 2-cyanoacetic anhydride, fluoroacetic methoxyacetic anhydride, and trifluoroacetic 2-cyanoacetic anhydride.

[0353] Preferred among the acid anhydrides having an acyclic structure are acetic anhydride, propionic anhydride, 2-methylpropionic anhydride, cyclopentanecarboxylic anhydride, cyclohexanecarboxylic anhydride, acrylic anhydride, 2-methylacrylic anhydride, 3-methylacrylic anhydride, 2,3-dimethylacrylic anhydride, 3,3-dimethylacrylic anhydride, 3-butenoic anhydride, 2-methyl-3-butenoic anhydride, propynoic anhydride, 2-butynoic anhydride, benzoic anhydride, 2-methylbenzoic anhydride, 4-methylbenzoic anhydride, 4-tert-butylbenzoic anhydride, trifluoroacetic anhydride, 3,3,3-trifluoropropionic anhydride, 2-(trifluoromethyl)acrylic anhydride, 2-(4-fluorophenyl) acrylic anhydride, 4-fluorobenzoic anhydride, 2,3,4,5,6-pentafluorobenzoic anhydride, methoxyformic anhydride, and ethoxyformic anhydride. More preferred are acrylic anhydride, 2-methylacrylic anhydride, 3-methylacrylic anhydride, benzoic anhydride, 2-methylbenzoic anhydride, 4-methylbenzoic anhydride, 4-tert-butylbenzoic anhydride, 4-fluorobenzoic anhydride, 2,3,4,5,6-pentafluorobenzoic anhydride, methoxyformic anhydride, and ethoxyformic anhydride.

[0354] These compounds are preferred because they can appropriately form a bond with lithium oxalate to provide a film having excellent durability, thereby improving especially the charge and discharge rate characteristics after a durability test, input and output characteristics, and impedance characteristics.

[0355] The carboxylic anhydride may have any molecular weight that does not significantly impair the effects of the disclosure. The molecular weight is usually 90 or higher, preferably 95 or higher, while usually 300 or lower, preferably 200 or lower. The carboxylic anhydride having a molecular weight within the above range can reduce an increase in viscosity of an electrolytic solution and can give a reasonable film density, appropriately improving the durability.

[0356] The carboxylic anhydride may be formed by any production method which may be selected from known methods. One of the carboxylic anhydrides described above alone may be contained in the non-aqueous electrolytic solution of the disclosure, or two or more thereof may be contained in any combination at any ratio.

[0357] The carboxylic anhydride may be contained in any amount that does not significantly impair the effects of the disclosure relative to the electrolytic solution of the disclosure. The carboxylic anhydride is usually contained at a concentration of 0.01% by mass or more, preferably 0.1% by mass or more, while usually 5% by mass or less, preferably 3% by mass or less, relative to the electrolytic solution of the disclosure. The carboxylic anhydride in an amount within the above range can easily achieve an effect of improving the cycle characteristics and have good reactivity, easily improving the battery characteristics.

[0358] The electrolytic solution of the disclosure may further contain a known different aid. Examples of the different aid include hydrocarbon compounds such as pentane, heptane, octane, nonane, decane, cycloheptane, benzene, furan, naphthalene, 2-phenyl bicyclohexyl, cyclohexane, 2,4,8,10-tetraoxaspiro[5.5]undecane, and 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane;

[0359] fluorine-containing aromatic compounds such as fluorobenzene, difluorobenzene, hexafluorobenzene, benzotrifluoride, monofluorobenzene, 1-fluoro-2-cyclohexylbenzene, 1-fluoro-4-tert-butylbenzene, 1-fluoro-3-cyclohexylbenzene, 1-fluoro-2-cyclohexylbenzene, and biphenyl fluoride;

[0360] carbonate compounds such as erythritan carbonate, spiro-bis-dimethylene carbonate, and methoxyethyl-methyl carbonate; ether compounds such as dioxolane, dioxane, 2,5,8,11-tetraoxadodecane, 2,5,8,11,14-pentaoxapentadecane, ethoxymethoxyethane, trimethoxymethane, glyme, and ethyl monoglyme;

[0361] ketone compounds such as dimethyl ketone, diethyl ketone, and 3-pentanone;

[0362] acid anhydrides such as 2-allylsuccinic anhydride;

[0363] ester compounds such as dimethyl oxalate, diethyl oxalate, ethylmethyl oxalate, di(2-propynyl) oxalate, methyl 2-propynyl oxalate, dimethyl succinate, di(2-propynyl) glutarate, methyl formate, ethyl formate, 2-propynyl formate, 2-butyne-1,4-diyl diformate, 2-propynyl methacrylate, and dimethyl malonate;

[0364] amide compounds such as acetamide, N-methyl formamide, N,N-dimethyl formamide, and N,N-dimethyl acetamide;

[0365] sulfur-containing compounds such as ethylene sulfate, vinylene sulfate, ethylene sulfite, methyl fluorosulfonate, ethyl fluorosulfonate, methyl methanesulfonate, ethyl methanesulfonate, busulfan, sulfolene, diphenyl sulfone, N,N-dimethylmethanesulfonamide, N,N-diethylmethanesulfonamide, methyl vinyl sulfonate, ethyl vinyl sulfonate, allyl vinyl sulfonate, propargyl vinyl sulfonate, methyl allyl sulfonate, ethyl allyl sulfonate, allyl sulfonate, propargyl allyl sulfonate, 1,2-bis(vinylsulfonyloxy)ethane, propanedisulfonic anhydride, sulfobutyric anhydride, sulfobenzoic anhydride, sulfopropionic anhydride, ethanedisulfonic anhydride, methylene methanedisulfonate, 2-propynyl methanesulfonate, pentene sulfite, pentafluorophenyl methanesulfonate, propylene sulfate, propylene sulfite, propane sultone, butylene sulfite, butane-2,3-diyl dimethanesulfonate, 2-butyne-1,4-diyl dimethanesulfonate, 2-propynyl vinyl sulfonate, bis(2-vinylsulfonylethyl)ether, 5-vinyl-hexahydro-1,3,2-benzodioxathiol-2-oxide, 2-propynyl 2-(methanesulfonyloxy)propionate, 5,5-dimethyl-1,2-oxathiolan-4-one 2,2-dioxide, 3-sulfo-propionic anhydride, trimethylene methanedisulfonate, 2-methyl tetrahydrofuran, trimethylene methanedisulfonate, tetramethylene sulfoxide, dimethylene methanedisulfonate, difluoroethyl methyl sulfone, divinyl sulfone, 1,2-bis(vinylsulfonyl)ethane, methyl ethylenebissulfonate, ethyl ethylenebissulfonate, ethylene sulfate, and thiophene 1-oxide;

[0366] nitrogen-containing compounds such as 1-methyl-2-pyrrolidinone, 1-methyl-2-piperidone, 3-methyl-2-oxazolidinone, 1,3-dimethyl-2-imidazolidinone, N-methylsuccinimide, nitromethane, nitroethane, and ethylene diamine;

[0367] phosphorus-containing compounds such as trimethyl phosphite, triethyl phosphite, triphenyl phosphite, trimethyl phosphate, triethyl phosphate, triphenyl phosphate, dimethyl methyl phosphonate, diethyl ethyl phosphonate, dimethyl vinyl phosphonate, diethyl vinyl phosphonate, ethyl diethyl phosphonoacetate, methyl dimethyl phosphinate, ethyl diethyl phosphinate, trimethylphosphine oxide, triethylphosphine oxide, bis(2,2-difluoroethyl)2,2,2-trifluoroethyl phosphate, bis(2,2,3,3-tetrafluoropropyl)2,2,2-trifluoroethyl phosphate, bis(2,2,2-trifluoroethyl)methyl phosphate, bis(2,2,2-trifluoroethyl)ethyl phosphate, bis(2,2,2-trifluoroethyl)2,2-difluoroethyl phosphate, bis(2,2,2-trifluoroethyl)2,2,3,3-tetrafluoropropyl phosphate, tributyl phosphate, tris(2,2,2-trifluoroethyl) phosphate, tris(1,1,1,3,3,3-hexafluoropropan-2-yl) phosphate, trioctyl phosphate, 2-phenylphenyldimethyl phosphate, 2-phenylphenyldiethyl phosphate, (2,2,2-trifluoroethyl) (2,2,3,3-tetrafluoropropyl)methyl phosphate, methyl 2-(dimethoxyphosphoryl) acetate, methyl 2-(dimethylphosphoryl) acetate, methyl 2-(diethoxyphosphoryl) acetate, methyl 2-(diethylphosphoryl) acetate, methyl methylenebisphosphonate, ethyl methylenebisphosphonte, methyl ethylenebisphosphonte, ethyl ethylenebisphosphonte, methyl butylenebisphosphonate, ethyl butylenebisphosphonate, 2-propynyl 2-(dimethoxyphosphoryl) acetate, 2-propynyl 2-(dimethylphosphoryl) acetate, 2-propynyl 2-(diethoxyphosphoryl) acetate, 2-propynyl 2-(diethylphosphoryl) acetate, tris(trimethylsilyl) phosphate, tris(triethylsilyl) phosphate, tris(trimethoxysilyl) phosphate, tris(trimethylsilyl) phosphite, tris(triethylsilyl) phosphite, tris (trimethoxysilyl) phosphite, and trimethylsilyl polyphosphate;

[0368] boron-containing compounds such as tris(trimethylsilyl) borate and tris(trimethoxysilyl) borate; and

[0369] silane compounds such as dimethoxyaluminoxytrimethoxysilane, diethoxyaluminoxytriethoxysilane, dipropoxyaluminoxytriethoxysilane, dibutoxyaluminoxytrimethoxysilane, dibutoxyaluminoxytriethoxysilane, titanium tetrakis(trimethylsiloxide), titanium tetrakis(triethylsiloxide), and tetramethylsilane.

[0370] One of these compounds may be used alone or two or more thereof may be used in any combination. These aids can improve the capacity retention characteristics and the cycle characteristics after high-temperature storage.

[0371] Preferred among these as the different aid are phosphorus-containing compounds, and preferred are tris (trimethylsilyl) phosphate and tris(trimethylsilyl) phosphite.

[0372] The different aid may be present in any amount that does not significantly impair the effects of the disclosure. The amount of the different aid is preferably 0.01% by mass or more and 5% by mass or less of 100% by mass of the electrolytic solution. The different aid in an amount within this range can easily sufficiently exhibit the effects thereof and can easily avoid a situation with impairment of battery characteristics such as high-load discharge characteristics. The amount of the different aid is more preferably 0.1% by mass or more, still more preferably 0.2% by mass or more, while more preferably 3% by mass or less, still more preferably 1% by mass or less.

[0373] The electrolytic solution of the disclosure may further contain as an additive any of a cyclic carboxylate, an acyclic carboxylate, an ether compound other than the compound (1), a nitrogen-containing compound, a boron-containing compound, an organosilicon-containing compound, a fireproof agent (flame retardant), a surfactant, an additive for increasing the permittivity, an improver for cycle characteristics and rate characteristics, and a sulfone-based compound to the extent that the effects of the disclosure are not impaired.

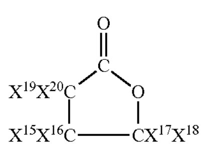
[0374] Examples of the cyclic carboxylate include those having a carbon number of 3 to 12 in total in the structural formula. Specific examples thereof include gamma-butyrolactone, gamma-valerolactone, gamma-caprolactone, epsilon-caprolactone, and 3-methyl-γ-butyrolactone. In order to improve the characteristics of an electrochemical device owing to improvement in the degree of dissociation of lithium ions, particularly preferred is gamma-butyrolactone.

[0375] In general, the cyclic carboxylate as an additive is preferably present in an amount of 0.1% by mass or more, more preferably 1% by mass or more, of 100% by mass of the solvent. The cyclic carboxylate in an amount within this range can easily improve the electric conductivity of the electrolytic solution, improving the large-current discharge characteristics of an electrochemical device. The amount of the cyclic carboxylate is also preferably 10% by mass or less, more preferably 5% by mass or less. Such an upper limit may allow the electrolytic solution to have a viscosity within an appropriate range, may make it possible to avoid a reduction in the electric conductivity, may reduce an increase in the resistance of the negative electrode, and may allow an electrochemical device to have large-current discharge characteristics within a favorable range.

[0376] The cyclic carboxylate to be suitably used may also be a fluorinated cyclic carboxylate (fluorine-containing lactone). Examples of the fluorine-containing lactone include fluorine-containing lactones represented by the following formula (C):

[Chem. 55]

(C)



[0377] wherein X^{15} to X^{20} are the same as or different from each other, and are each —H, —F, —C1, —CH_3, or a fluorinated alkyl group; and at least one selected from X^{15} to X^{20} is a fluorinated alkyl group.

[0378] Examples of the fluorinated alkyl group for X^{15} to X^{20} include —CFH_2, —CF_2H, —CF_3, —CH_2CF_3, —CF_2CF_3, —$CH_2CF_2CF_3$, and —$CF(CF_3)_2$. In order to achieve high oxidation resistance and an effect of improving the safety, —CH_2CF_3 and —$CH_2CF_2CF_3$ are preferred.

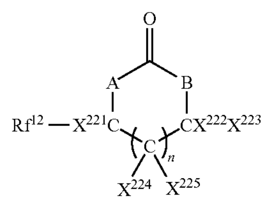
[0379] Only one of X^{15} to X^{20} or a plurality thereof may be replaced by —H, —F, —C1, —CH_3, or a fluorinated alkyl group as long as at least one selected from X^{15} to X^{20} is a fluorinated alkyl group. In order to give good solubility of an electrolyte salt, the number of substituents is preferably 1 to 3, more preferably 1 or 2.

[0380] The substitution of the fluorinated alkyl group may be at any of the above sites. In order to give a good synthesizing yield, the substitution site is preferably X^{17} and/or X^{18}. In particular, X^{17} or X^{18} is preferably a fluorinated alkyl group, especially —CH_2CF_3 or —$CH_2CF_2CF_3$. The substituent for X^{15} to X^{20} other than the fluorinated alkyl group is —H, —F, —C1, or CH_3. In order to give good solubility of an electrolyte salt, —H is preferred.

[0381] In addition to those represented by the above formula, the fluorine-containing lactone may also be a fluorine-containing lactone represented by the following formula (D):

[Chem. 56]

(D)

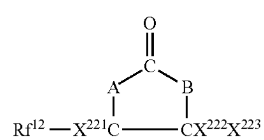


wherein one of A or B is $CX^{226}X^{227}$ (where X^{226} and X^{227} are the same as or different from each other, and are each —H, —F, —C1, —CF_3, —CH_3, or an alkylene group in which a hydrogen atom is optionally replaced by a halogen atom and which optionally contains a hetero atom in the chain) and the other is an oxygen atom; Rf^{12} is a fluorinated alkyl group optionally containing an ether bond or a fluorinated alkoxy group; $X^{22}1$ and X^{222} are the same as or different from each other, and are each —H, —F, —C1, —CF_3, or CH_3; X^{223} to X^{225} are the same as or different from each other, and are each —H, —F, —C1, or an alkyl group in which a hydrogen atom is optionally replaced by a halogen atom and which optionally contains a hetero atom in the chain; and n=0 or 1.

[0382] A preferred example of the fluorine-containing lactone represented by the formula (D) is a 5-membered ring structure represented by the following formula (E):

[Chem. 57]

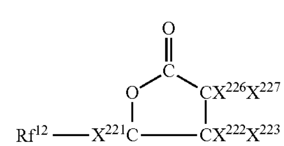
(E)



(wherein A, B, Rf^{12}, X^{221}, X^{222}, and X^{223} are defined as in the formula (D)) because it can be easily synthesized and can have good chemical stability. Further, in relation to the combination of A and B, fluorine-containing lactones represented by the following formula (F):

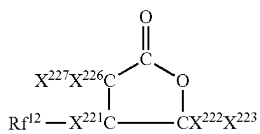
[Chem. 58]

(F)



(wherein Rf^{12}, X^{221}, X^{222}, X^{223}, X^{226}, and X^{227} are defined as in the formula (D)) and fluorine-containing lactones represented by the following formula (G):

[Chem. 59]

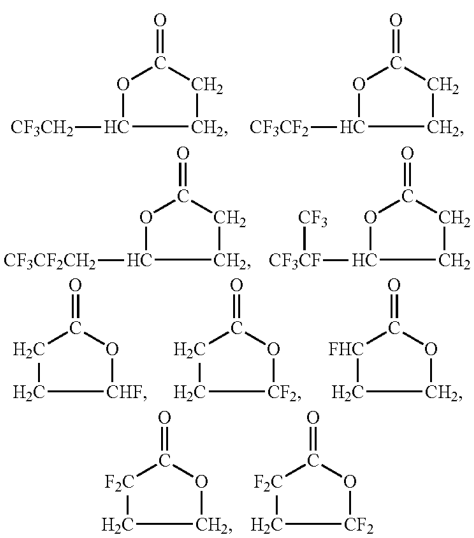


(G)

(wherein Rf^{12}, X^{221}, X^{222}, X^{223}, X^{226}, and X^{227} are defined as in the formula (D)) may be mentioned.

[0383] In order to particularly give excellent characteristics such as high permittivity and high withstand voltage, and to improve the characteristics of the electrolytic solution in the disclosure, for example, to give good solubility of an electrolyte salt and to reduce the internal resistance well, those represented by the following formulas:

[Chem. 60]



may be mentioned.

[0384] The presence of a fluorinated cyclic carboxylate can lead to, for example, effects of improving the ion conductivity, improving the safety, and improving the stability at high temperature.

[0385] Examples of the acyclic carboxylate include those having a carbon number of 3 to 7 in total in the structural formula thereof. Specific examples thereof include methyl acetate, ethyl acetate, n-propyl acetate, isopropyl acetate, n-butyl acetate, isobutyl acetate, t-butyl acetate, methyl propionate, ethyl propionate, n-propyl propionate, isobutyl propionate, n-butyl propionate, methyl butyrate, isobutyl propionate, t-butyl propionate, methyl butyrate, ethyl butyrate, n-propyl butyrate, isopropyl butyrate, methyl isobutyrate, ethyl isobutyrate, n-propyl isobutyrate, and isopropyl isobutyrate.

[0386] In order to improve the ion conductivity owing to viscosity reduction, preferred among these are methyl acetate, ethyl acetate, n-propyl acetate, n-butyl acetate, methyl propionate, ethyl propionate, n-propyl propionate, isopropyl propionate, methyl butyrate, and ethyl butyrate.

[0387] The ether compound is preferably a C2-C10 acyclic ether or a C3-C6 cyclic ether.

[0388] Examples of the C2-C10 acyclic ether include dimethyl ether, diethyl ether, di-n-butyl ether, dimethoxymethane, methoxyethoxymethane, diethoxymethane, dimethoxyethane, methoxyethoxyethane, diethoxyethane, ethylene glycol di-n-propyl ether, ethylene glycol di-n-butyl ether, diethylene glycol, diethylene glycol dimethyl ether, pentaethylene glycol, triethylene glycol dimethyl ether, triethylene glycol, tetraethylene glycol, tetraethylene glycol dimethyl ether, and diisopropyl ether.

[0389] Further, the ether compound may also suitably be a fluorinated ether.

[0390] An example of the fluorinated ether is a fluorinated ether (I) represented by the following formula (1):

$$Rf^3—O—Rf^4 \qquad (I)$$

(wherein Rf^3 and Rf^4 are the same as or different from each other, and are each a C1-C10 alkyl group or a C1-C10 fluorinated alkyl group; and at least one of Rf^3 or Rf^4 is a fluorinated alkyl group). The presence of the fluorinated ether (I) allows the electrolytic solution to have improved incombustibility as well as improved stability and safety at high temperature under high voltage.

[0391] In the formula (1), at least one of Rf^3 or Rf^4 is a C1-C10 fluorinated alkyl group. In order to allow the electrolytic solution to have further improved incombustibility and further improved stability and safety at high temperature under high voltage, both Rf^3 and Rf^4 are preferably C1-C10 fluorinated alkyl groups. In this case, Rf^3 and Rf^4 may be the same as or different from each other.

[0392] Particularly preferably, Rf^3 and Rf^4 are the same as or different from each other, and Rf^3 is a C3-C6 fluorinated alkyl group and Rf^4 is a C2-C6 fluorinated alkyl group.

[0393] If the sum of the carbon numbers of Rf^3 and Rf^4 is too small, the fluorinated ether may have too low a boiling point. Too large a carbon number of Rf^3 or Rf^4 may cause low solubility of an electrolyte salt, may start to adversely affect the miscibility with other solvents, and may cause high viscosity, resulting in poor rate characteristics. In order to achieve an excellent boiling point and rate characteristics, advantageously, the carbon number of Rf^3 is 3 or 4 and the carbon number of Rf^4 is 2 or 3.

[0394] The fluorinated ether (I) preferably has a fluorine content of 40 to 75% by mass. The fluorinated ether (I) having a fluorine content within this range may lead to particularly excellent balance between the non-flammability and the miscibility. The above range is also preferred for good oxidation resistance and safety.

[0395] The lower limit of the fluorine content is more preferably 45% by mass, still more preferably 50% by mass, particularly preferably 55% by mass. The upper limit thereof is more preferably 70% by mass, still more preferably 66% by mass.

[0396] The fluorine content of the fluorinated ether (I) is a value calculated based on the structural formula of the fluorinated ether (I) by the following formula:

{(Number of fluorine atoms×19)/

(Molecular weight of fluorinated ether (I))}×100 (%).

[0397] Examples of Rf^3 include $CF_3CF_2CH_2$—, CF_3CFHCF_2—, $HCF_2CF_2CF_2$—, $HCF_2CF_2CH_2$—, $CF_3CF_2CH_2CH_2$—, $CF_3CFHCF_2CH_2$—, $HCF_2CF_2CF_2CF_2$—, $HCF_2CF_2CF_2CH_2$—, $HCF_2CF_2CH_2CH_2$—, and $HCF_2CF(CF_3)$ CH_2—. Examples of R^f4 include —$CH_2CF_2CF_3$, —CF_2CFHCF_3, —$CF_2CF_2CF_2H$, —$CH_2CF_2CF_2H$, —$CH_2CH_2CF_2CF_3$, —$CH_2CF_2CFHCF_3$, —$CF_2CF_2CF_2CF_2H$, —$CH_2CF_2CF_2CF_2H$, —$CH_2CH_2CF_2CF_2H$, —$CH_2CF(CF_3)CF_2H$, —CF_2CF_2H, —CH_2CF_2H, and —CF_2CH_3.

[0398] Specific examples of the fluorinated ether (I) include $HCF_2CF_2CH_2OCF_2CF_2H$, $CF_3CF_2CH_2OCF_2CF_2H$, $HCF_2CF_2CH_2OCF_2CFHCF_3$, $CF_3CF_2CH_2OCF_2CFHCF_3$, $C6F_{13}OCH_3$, $C6F_{13}OC_2H_5$, $CBF_{17}OCH_3$, $C_8F_{17}OC_2H_5$, $CF_3CFHCF_2CH(CH_3)OCF_2CFHCF_3$, $HCF_2CF_2OCH(C_2H_5)_2$, $HCF_2CF_2OC_4Hg$, $HCF_2CF_2OCH_2CH(C_2H)_2$, and $HCF_2CF_2OCH_2CH(CH_3)_2$.

[0399] In particular, those having HCF_2— or CF_3CFH— at one or each end can provide a fluorinated ether (I) having excellent polarizability and a high boiling point. The boiling point of the fluorinated ether (I) is preferably 67° C. to 120° C., more preferably 80° C. or higher, still more preferably 90° C. or higher.

[0400] Such a fluorinated ether (I) may include one or two or more of $CF_3CH_2OCF_2CFHCF_3$, $CF_3CF_2CH_2OCF_2CFHCF_3$, $HCF_2CF_2CH_2OCF_2CFHCF_3$, $HCF_2CF_2CH_2OCH_2CF_2CF_2H$, $CF_3CFHCF_2CH_2OCF_2CFHCF_3$, $HCF_2CF_2CH_2OCF_2CF_2H$, $CF_3CF_2CH_2OCF_2CF_2H$, and the like.

[0401] Advantageously, in order to achieve a high boiling point and good miscibility with other solvents and to give good solubility of an electrolyte salt, the fluorinated ether (I) preferably includes at least one selected from the group consisting of $HCF_2CF_2CH_2OCF_2CFHCF_3$ (boiling point: 106° C.), $CF_3CF_2CH_2OCF_2CFHCF_3$ (boiling point: 82° C.), $HCF_2CF_2CH_2OCF_2CF_2H$ (boiling point: 92° C.), and $CF_3CF_2CH_2OCF_2CF_2H$ (boiling point: 68° C.), more preferably at least one selected from the group consisting of $HCF_2CF_2CH_2OCF_2CFHCF_3$ (boiling point: 106° C.), and $HCF_2CF_2CH_2OCF_2CF_2H$ (boiling point: 92° C.).

[0402] Examples of the C3-C6 cyclic ether include 1,2-dioxane, 1,3-dioxane, 2-methyl-1,3-dioxane, 4-methyl-1,3-dioxane, 1,4-dioxane, metaformaldehyde, 2-methyl-1,3-dioxolane, 1,3-dioxolane, 4-methyl-1,3-dioxolane, 2-(trifluoroethyl)dioxolane, 2,2,-bis(trifluoromethyl)-1,3-dioxolane, and fluorinated compounds thereof. In order to achieve a high ability to solvate with lithium ions and improve the degree of ion dissociation, preferred are dimethoxymethane, diethoxymethane, ethoxymethoxymethane, ethylene glycol n-propyl ether, ethylene glycol di-n-butyl ether, diethylene glycol dimethyl ether, and crown ethers. In order to achieve low viscosity and to give a high ion conductivity, particularly preferred are dimethoxymethane, diethoxymethane, and ethoxymethoxymethane.

[0403] Examples of the nitrogen-containing compound include nitrile, fluorine-containing nitrile, carboxylic acid amide, fluorine-containing carboxylic acid amide, sulfonic acid amide, fluorine-containing sulfonic acid amide, acetamide, and formamide. Also, 1-methyl-2-pyrrolidinone, 1-methyl-2-piperidone, 3-methyl-2-oxazolidinone, 1,3-dimethyl-2-imidazolidinone, and N-methylsuccinimide may be used. The nitrile compounds represented by the formulas (1a), (1b), and (1c) are not included in the above nitrogen-containing compounds.

[0404] Examples of the boron-containing compound include borates such as trimethyl borate and triethyl borate, boric acid ethers, and alkyl borates.

[0405] Examples of the organosilicon-containing compound include $(CH_3)_4$—Si, $(CH_3)_3$—Si—$Si(CH_3)_3$, and silicone oil.

[0406] Examples of the fireproof agent (flame retardant) include organophosphates and phosphazene-based compounds. Examples of the organophosphates include fluorine-containing alkyl phosphates, non-fluorine-containing alkyl phosphates, and aryl phosphates. In order to achieve a flame retardant effect even in a small amount, fluorine-containing alkyl phosphates are particularly preferred.

[0407] Examples of the phosphazene-based compounds include methoxypentafluorocyclotriphosphazene, phenoxypentafluorocyclotriphosphazene, dimethylaminopentafluorocyclotriphosphazene, diethylaminopentafluorocyclotriphosphazene, ethoxypentafluorocyclotriphosphazene, and ethoxyheptafluorocyclotetraphosphazene.

[0408] Specific examples of the fluorine-containing alkyl phosphates include fluorine-containing dialkyl phosphates disclosed in JP H11-233141 A, cyclic alkyl phosphates disclosed in JP H11-283669 A, and fluorine-containing trialkyl phosphates.

[0409] Preferred examples of the fireproof agent (flame retardant) include $(CH_3O)_3P{=}O$, $(CF_3CH_2O)_3P{=}O$, $(HCF_2CH_2O)_3P{=}O$, $(CF_3CF_2CH_2)_3P{=}O$, and $(HCF_2CF_2CH_2)_3P{=}O$.

[0410] The surfactant may be any of cationic surfactants, anionic surfactants, nonionic surfactants, and amphoteric surfactants. In order to give good cycle characteristics and rate characteristics, the surfactant is preferably one containing a fluorine atom.

[0411] Preferred examples of such a surfactant containing a fluorine atom include fluorine-containing carboxylic acid salts represented by the following formula (30):

$$Rf^5COO^-M^+ \tag{30}$$

(wherein Rf^5 is a C3-C10 fluorine-containing alkyl group optionally containing an ether bond; M^+ is Li^+, Na^+, K^+, or $NHR'_3{}^+$, wherein R's are the same as or different from each other, and are each H or a C1-C3 alkyl group), and fluorine-containing sulfonic acid salts represented by the following formula (40):

$$Rf^6SO_3^-M^+ \tag{40}$$

(wherein Rf^6 is a C3-C10 fluorine-containing alkyl group optionally containing an ether bond; M^+ is Li^+, Na^+, K^+, or $NHR'_3{}^+$, wherein R's are the same as or different from each other, and are each H or a C1-C3 alkyl group).

[0412] In order to reduce the surface tension of the electrolytic solution without impairing the charge and discharge cycle characteristics, the surfactant is preferably present in an amount of 0.01 to 2% by mass of the electrolytic solution.

[0413] Examples of the additive for increasing the permittivity include sulfolane, methylsulfolane, γ-butyrolactone, and γ-valerolactone.

[0414] Examples of the improver for cycle characteristics and rate characteristics include methyl acetate, ethyl acetate, tetrahydrofuran, and 1,4-dioxane.

[0415] The electrolytic solution of the disclosure may be combined with a polymer material and thereby formed into a gel-like (plasticized), gel electrolytic solution.

[0416] Examples of such a polymer material include conventionally known polyethylene oxide and polypropylene oxide, and modified products thereof (see JP H08-222270 A, JP 2002-100405 A); polyacrylate-based polymers, polyacrylonitrile, and fluororesins such as polyvinylidene fluoride and vinylidene fluoride-hexafluoropropylene copolymers (see JP H04-506726 T, JP H08-507407 T, JP H10-294131 A); and composites of any of these fluororesins and any hydrocarbon resin (see JP H11-35765 A, JP H11-86630 A). In particular, polyvinylidene fluoride or a vinylidene fluoride-hexafluoropropylene copolymer is preferably used as a polymer material for a gel electrolyte.

[0417] The electrolytic solution of the disclosure may also contain an ion conductive compound disclosed in Japanese Patent Application No. 2004-301934.

[0418] This ion conductive compound is an amorphous fluorine-containing polyether compound having a fluorine-containing group at a side chain and is represented by the following formula (101):

A-(D)-B (101)

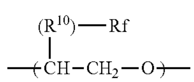
wherein D is represented by the following formula (201):

$-(D1)_n-(FAE)_m-(AE)_p-(Y)_q-$ (201)

[wherein D1 is an ether unit containing a fluorine-containing ether group at a side chain and is represented by the following formula (2a):

[Chem. 61]

(2a)

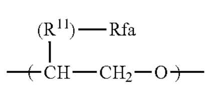


(wherein R^f is a fluorine-containing ether group optionally containing a crosslinkable functional group; and R^{10} is a group or a bond that links R^f and the main chain);

[0419] FAE is an ether unit containing a fluorinated alkyl group at a side chain and is represented by the following formula (2b):

[Chem. 62]

(2b)

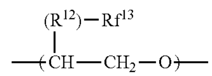


(wherein Rfa is a hydrogen atom or a fluorinated alkyl group optionally containing a crosslinkable functional group; and R^{11} is a group or a bond that links Rfa and the main chain);

[0420] AE is an ether unit represented by the following formula (2c):

[Chem. 63]

(2c)

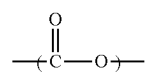


(wherein R^{13} is a hydrogen atom, an alkyl group optionally containing a crosslinkable functional group, an aliphatic cyclic hydrocarbon group optionally containing a crosslinkable functional group, or an aromatic hydrocarbon group optionally containing a crosslinkable functional group; and R^{12} is a group or a bond that links R^{13} and the main chain);

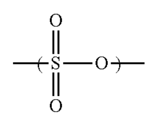
[0421] Y is a unit containing at least one selected from the following formulas (2d-1) to (2d-3):

[Chem. 64]

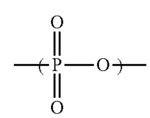
(2d-1)



(2d-2)



(2d-3)



[0422] n is an integer of 0 to 200;

[0423] m is an integer of 0 to 200;

[0424] p is an integer of 0 to 10000;

[0425] q is an integer of 1 to 100;

[0426] n+m is not 0; and

[0427] the bonding order of D1, FAE, AE, and Y is not specified]; and

[0428] A and B are the same as or different from each other, and are each a hydrogen atom, an alkyl group optionally containing a fluorine atom and/or a crosslinkable functional group, a phenyl group optionally containing a fluorine atom and/or a crosslinkable functional group, a —COOH group, —OR (where R is a hydrogen atom or an alkyl group optionally containing a fluorine atom and/or a crosslinkable functional group), an ester group, or a carbonate group, and when an end of D is an oxygen atom, A and B are each none of a —COOH group, —OR, an ester group, and a carbonate group.

[0429] The electrolytic solution of the disclosure may contain a sulfone-based compound. Preferred as the sulfone-based compound are a C3-C6 cyclic sulfone and a C2-C6 acyclic sulfone. The number of sulfonyl groups in one molecule is preferably 1 or 2.

[0430] Examples of the cyclic sulfone include monosulfone compounds such as trimethylene sulfones, tetramethylene sulfones, and hexamethylene sulfones; disulfone compounds such as trimethylene disulfones, tetramethylene disulfones, and hexamethylene disulfones. In order to give good permittivity and viscosity, more preferred among these are tetramethylene sulfones, tetramethylene disulfones, hexamethylene sulfones, and hexamethylene disulfones, and particularly preferred are tetramethylene sulfones (sulfolanes).

[0431] The sulfolanes are preferably sulfolane and/or sulfolane derivatives (hereinafter, also abbreviated as "sulfolanes" including sulfolane). The sulfolane derivatives are preferably those in which one or more hydrogen atoms binding to any carbon atom constituting the sulfolane ring is replaced by a fluorine atom or an alkyl group.

[0432] In order to achieve high ion conductivity and high input and output, preferred among these are 2-methylsulfolane, 3-methylsulfolane, 2-fluorosulfolane, 3-fluorosulfolane, 2,2-difluorosulfolane, 2,3-difluorosulfolane, 2,4-difluorosulfolane, 2,5-difluorosulfolane, 3,4-difluorosulfolane, 2-fluoro-3-methylsulfolane, 2-fluoro-2-methylsulfolane, 3-fluoro-3-methylsulfolane, 3-fluoro-2-methylsulfolane, 4-fluoro-3-methylsulfolane, 4-fluoro-2-methylsulfolane, 5-fluoro-3-methylsulfolane, 5-fluoro-2-methylsulfolane, 2-fluoromethylsulfolane, 3-fluoromethylsulfolane, 2-difluoromethylsulfolane, 3-difluoromethylsulfolane, 2-trifluoromethylsulfolane, 3-trifluoromethylsulfolane, 2-fluoro-3-(trifluoromethyl)sulfolane, 3-fluoro-3-(trifluoromethyl) sulfolane, 4-fluoro-3-(trifluoromethyl)sulfolane, 3-sulfolene, 5-fluoro-3-(trifluoromethyl)sulfolane, and the like.

[0433] Examples of the acyclic sulfone include dimethyl sulfone, ethyl methyl sulfone, diethyl sulfone, n-propyl methyl sulfone, n-propyl ethyl sulfone, di-n-propyl sulfone, isopropyl methyl sulfone, isopropyl ethyl sulfone, diisopropyl sulfone, n-butyl methyl sulfone, n-butyl ethyl sulfone, t-butyl methyl sulfone, t-butyl ethyl sulfone, monofluoromethyl methyl sulfone, difluoromethyl methyl sulfone, trifluoromethyl methyl sulfone, monofluoroethyl methyl sulfone, difluoroethyl methyl sulfone, trifluoroethyl methyl sulfone, pentafluoroethyl methyl sulfone, ethyl monofluoromethyl sulfone, ethyl difluoromethyl sulfone, ethyl trifluoromethyl sulfone, perfluoroethyl methyl sulfone, ethyl trifluoroethyl sulfone, ethyl pentafluoroethyl sulfone, di(trifluoroethyl)sulfone, perfluorodiethyl sulfone, fluoromethyl-n-propyl sulfone, difluoromethyl-n-propyl sulfone, trifluoromethyl-n-propyl sulfone, fluoromethyl isopropyl sulfone, difluoromethyl isopropyl sulfone, trifluoromethyl isopropyl sulfone, trifluoroethyl-n-propyl sulfone, trifluoroethyl isopropyl sulfone, pentafluoroethyl-n-propyl sulfone, pentafluoroethyl isopropyl sulfone, trifluoroethyl-n-butyl sulfone, trifluoroethyl-t-butyl sulfone, pentafluoroethyl-n-butyl sulfone, and pentafluoroethyl-t-butyl sulfone.

[0434] In order to achieve high ion conductivity and high input and output, preferred among these are dimethyl sulfone, ethyl methyl sulfone, diethyl sulfone, n-propyl methyl sulfone, isopropyl methyl sulfone, n-butyl methyl sulfone, t-butyl methyl sulfone, monofluoromethyl methyl sulfone, difluoromethyl methyl sulfone, trifluoromethyl methyl sulfone, monofluoroethyl methyl sulfone, difluoroethyl methyl sulfone, trifluoroethyl methyl sulfone, pentafluoroethyl methyl sulfone, ethyl monofluoromethyl sulfone, ethyl difluoromethyl sulfone, ethyl trifluoromethyl sulfone, ethyl trifluoroethyl sulfone, ethyl pentafluoroethyl sulfone, trifluoromethyl-n-propyl sulfone, trifluoromethyl isopropyl sulfone, trifluoroethyl-n-butyl sulfone, trifluoroethyl-t-butyl sulfone, trifluoromethyl-n-butyl sulfone, trifluoromethyl-t-butyl sulfone, and the like.

[0435] The sulfone-based compound may be present in any amount that does not significantly impair the effects of the disclosure. The amount is usually 0.3% by volume or more, preferably 0.5% by volume or more, more preferably 1% by volume or more, while usually 40% by volume or less, preferably 35% by volume or less, more preferably 30% by volume or less, in 100% by volume of the solvent. The sulfone-based compound in an amount within the above range can easily achieve an effect of improving the cycle characteristics and the durability such as storage characteristics, can lead to an appropriate range of the viscosity of a non-aqueous electrolytic solution, can eliminate a reduction in electric conductivity, and can lead to appropriate ranges of the input and output characteristics and charge and discharge rate characteristics of a non-aqueous electrolyte secondary battery.

[0436] In order to improve the output characteristics, the electrolytic solution of the disclosure also preferably contains as an additive a compound (7) that is at least one selected from the group consisting of lithium fluorophosphate salts (other than $LiPF_6$) and lithium salts containing a S═O group.

[0437] When the compound (7) is used as an additive, the above-described electrolyte salt is preferably a compound other than the compound (7).

[0438] Examples of the lithium fluorophosphate salts include lithium monofluorophosphate ($LiPO_3F$) and lithium difluorophosphate ($LiPO_2F_2$).

[0439] Examples of the lithium salts containing a S═O group include lithium monofluorosulfonate (FSO_3Li), lithium methyl sulfate (CH_3OSO_3Li), lithium ethyl sulfate ($C_2H_5OSO_3Li$), and lithium 2,2,2-trifluoroethyl sulfate.

[0440] Preferred among these as the compound (7) are $LiPO_2F_2$, FSO_3Li, and $C_2H_5OSO_3Li$.

[0441] The compound (7) is preferably present in an amount of 0.001 to 20% by mass, more preferably 0.01 to 15% by mass, still more preferably 0.1 to 10% by mass, particularly preferably 0.1 to 7% by mass, relative to the electrolytic solution.

[0442] The electrolytic solution of the disclosure may further contain a different additive, if necessary. Examples of the different additive include metal oxides and glass.

[0443] The electrolytic solution of the disclosure preferably contains 1 to 1000 ppm of hydrogen fluoride (HF). The presence of HF can promote formation of a film of the aforementioned additive. Too small an amount of HF tends to impair the ability to form a film on the negative electrode, impairing the characteristics of an electrochemical device. Too large an amount of HF tends to impair the oxidation resistance of the electrolytic solution due to the influence by HF. The electrolytic solution of the disclosure, even when containing HF in an amount within the above range, causes no reduction in capacity recovery of an electrochemical device after high-temperature storage.

[0444] The amount of HF is more preferably 5 ppm or more, still more preferably 10 ppm or more, particularly preferably 20 ppm or more. The amount of HF is also more preferably 200 ppm or less, still more preferably 100 ppm or less, still further more preferably 80 ppm or less, particularly preferably 50 ppm or less.

[0445] The amount of HF can be determined by neutralization titration.

[0446] The electrolytic solution of the disclosure is preferably prepared by any method using the aforementioned components.

[0447] The electrolytic solution of the disclosure is used in a battery including a negative electrode containing an alkali metal-containing material. The alkali metal may be a single alkali metal. The alkali metal preferably includes at least one selected from the group consisting of lithium, sodium, and potassium, more preferably at least one selected from the group consisting of lithium and sodium, particularly preferably lithium.

[0448] Examples of the battery include secondary batteries such as lithium-ion secondary batteries, sodium-ion secondary batteries, and potassium-ion secondary batteries. The battery is preferably a lithium-ion secondary battery or a sodium-ion secondary battery, more preferably a lithium-ion secondary battery.

[0449] An electrochemical device including the electrolytic solution of the disclosure is also one aspect of the disclosure.

[0450] The secondary battery can have a known structure, typically including positive and negative electrodes that can occlude and release ions (e.g., lithium ions and sodium ions) and the electrolytic solution of the disclosure. A secondary battery including the electrolytic solution of the disclosure is also one aspect of the disclosure. A lithium-ion secondary battery including the electrolytic solution of the disclosure is also one aspect of the disclosure.

[0451] Hereinafter, a secondary battery including the electrolytic solution of the disclosure is described.

[0452] The secondary battery preferably includes a positive electrode, a negative electrode, and the above electrolytic solution.

<Positive Electrode>

[0453] The positive electrode preferably includes a positive electrode active material layer containing a positive electrode active material and a current collector.

[0454] The positive electrode active material may be any material that can electrochemically occlude and release alkali metal ions, and is preferably, for example, a substance containing an alkali metal and at least one transition metal. Specific examples thereof include alkali metal-containing transition metal complex oxides and alkali metal-containing transition metal phosphoric acid compounds. Preferred among these as the positive electrode active material is an alkali metal-containing transition metal complex oxide that generates high voltage. Examples of the alkali metal ions include lithium ions, sodium ions, and potassium ions. In a preferred embodiment, the alkali metal ions may be lithium ions or sodium ions. In other words, in this embodiment, the alkali-metal ion secondary battery may be a lithium-ion secondary battery or a sodium-ion secondary battery.

[0455] Examples of the alkali metal-containing transition metal complex oxide include

[0456] lithium-manganese spinel complex oxides represented by the formula (3-1): $M_aMn_{2-b}M^1{}_bO_4$ (wherein M is at least one metal selected from the group consisting of Li, Na, and K; 0.9≤a; 0≤b≤1.5; and M^1 is at least one metal selected from the group consisting of Fe, Co, Ni, Cu, Zn, Al, Sn, Cr, V, Ti, Mg, Ca, Sr, B, Ga, In, Si, and Ge),

[0457] lithium-nickel complex oxides represented by the formula (3-2): $MNi_{1-c}M^2{}_cO_2$ (wherein M is at least one metal selected from the group consisting of Li, Na, and K; 0≤c≤0.5; and M^2 is at least one metal selected from the group consisting of Fe, Co, Mn, Cu, Zn, Al, Sn, Cr, V, Ti, Mg, Ca, Sr, B, Ga, In, Si, and Ge), and

[0458] lithium-cobalt complex oxides represented by the formula (3-3): $MCo_{1-d}M^3{}_dO_2$ (wherein M is at least one metal selected from the group consisting of Li, Na, and K; 0≤d≤0.5; and M^3 is at least one metal selected from the group consisting of Fe, Ni, Mn, Cu, Zn, Al, Sn, Cr, V, Ti, Mg, Ca, Sr, B, Ga, In, Si, and Ge). In the formulas, M is preferably at least one metal selected from the group consisting of Li, Na, and K, more preferably Li or Na.

[0459] In order to provide a high-power secondary battery having a high energy density, preferred is $MCoO_2$, $MMnO_2$, $MNiO_2$, MMn_2O_4, $MNi_{0.8}Co_{0.15}Al_{0.05}O_2$, $MNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, or $MNi_{0.8}Mn_{0.1}Co_{0.1}O_2$, preferably a compound represented by the following formula (3-4):

$$MNi_hCo_iMn_jM^5{}_kO_2 \tag{3-4}$$

(wherein M is at least one metal selected from the group consisting of Li, Na, and K; M^5 is at least one selected from the group consisting of Fe, Cu, Zn, Al, Sn, Cr, V, Ti, Mg, Ca, Sr, B, Ga, In, Si, and Ge; (h+i+j+k)=1.0; 0≤h≤1.0; 0≤i≤1.0; 0≤j≤1.0; and 0≤k≤0.2).

[0460] Examples of the alkali metal-containing transition metal complex oxide include compounds represented by the following formula (70):

$$MeM^4{}_f(PO_4)_g$$

(wherein M is at least one metal selected from the group consisting of Li, Na, and K; M^4 is at least one selected from the group consisting of V, Ti, Cr, Mn, Fe, Co, Ni, and Cu; 0.5≤e≤3; 1≤f≤2; and 1≤g≤3). In the formulas, M is preferably at least one metal selected from the group consisting of Li, Na, and K, more preferably Li or Na.

[0461] The transition metal of the lithium-containing transition metal phosphoric acid compound is preferably V, Ti, Cr, Mn, Fe, Co, Ni, Cu, or the like. Specific examples thereof include iron phosphates such as $LiFePO_4$, $Li_3Fe_2(PO_4)_3$, and $LiFeP_2O_7$, cobalt phosphates such as $LiCoPO_4$, and those obtained by replacing one or more transition metal atoms as main components of these lithium transition metal phosphoric acid compounds with another element such as Al, Ti, V, Cr, Mn, Fe, Co, Li, Ni, Cu, Zn, Mg, Ga, Zr, Nb, or Si.

[0462] The lithium-containing transition metal phosphoric acid compound preferably has an olivine structure.

[0463] Other examples of the positive electrode active material include $MFePO_4$, $MNi_{0.7}Co_{0.2}O_2$, $M_{1.2}Fe_{0.4}Mn_{0.4}O_2$, $MNi_{0.5}Mn_{1.5}O_4$, MV_3O_6, and M_2MnO_3. In particular, a positive electrode material such as $Mni_{0.5}Mn_{1.5}O_4$ is preferred because its crystal structure does not collapse even when the secondary battery is driven at a voltage higher than 4.4 V or at a voltage of 4.6 V or higher. Thus, an electrochemical device such as a secondary battery including a positive electrode material containing any of the above-exemplified positive electrode active materials is preferred because the residual capacity thereof is less likely to decrease and the percentage increase in resistance thereof is less likely to change even after storage at high temperature and the battery performance thereof may not be impaired even when the battery is driven at high voltage.

[0464] Examples of other positive electrode active materials include solid solution materials of M_2MnO_3 and

MM^5O_2 (wherein M is at least one metal selected from the group consisting of Li, Na, and K; and M^5 is a transition metal such as Co, Ni, Mn, or Fe).

[0465] Examples of the solid solution materials include alkali metal manganese oxides represented by $Mx[Mn(1-y)M^7y]Oz$. In the formula, M is at least one selected from the group consisting of Li, Na, and K; M^7 includes at least one metal element other than M or Mn, and includes, for example, one or more selected from the group consisting of Co, Ni, Fe, Ti, Mo, W, Cr, Zr, and Sn. The values of x, y, and z in the formula fall within the ranges of $1<x<2$, $0\leq y$ 1, and $1.5<z<3$, respectively. In particular, a manganese-containing solid solution material such as $Li_{1.2}Mn_{0.5}Co_{0.14}Ni_{0.14}O_2$, which is a Li_2MnO_3-based solid solution of $LiNiO_2$ and $LiCoO_2$, is preferred because it can provide an alkali metal-ion secondary battery with a high energy density.

[0466] In order to improve the continuous charge characteristics, the positive electrode active material preferably contains lithium phosphate. Lithium phosphate may be used in any manner, and is preferably used in admixture with the positive electrode active material. The lower limit of the amount of lithium phosphate used is preferably 0.1% by mass or more, more preferably 0.3% by mass or more, still more preferably 0.5% by mass or more, relative to the sum of the amounts of the positive electrode active material and lithium phosphate. The upper limit thereof is preferably 10% by mass or less, more preferably 8% by mass or less, still more preferably 5% by mass or less.

[0467] To a surface of the positive electrode active material may be attached a substance having a composition different from the positive electrode active material. Examples of the substance attached to the surface include oxides such as aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, magnesium oxide, calcium oxide, boron oxide, antimony oxide, and bismuth oxide; sulfates such as lithium sulfate, sodium sulfate, potassium sulfate, magnesium sulfate, calcium sulfate, and aluminum sulfate; carbonates such as lithium carbonate, calcium carbonate, and magnesium carbonate; and carbon.

[0468] Such a substance may be attached to a surface of the positive electrode active material by, for example, a method of dissolving or suspending the substance in a solvent, impregnating the positive electrode active material with the solution or suspension, and drying the impregnated material; a method of dissolving or suspending a precursor of the substance in a solvent, impregnating the positive electrode active material with the solution or suspension, and heating the material and the precursor to cause a reaction therebetween; or a method of adding the substance to a precursor of the positive electrode active material and simultaneously sintering the materials. In the case of attaching carbon, for example, a carbonaceous material in the form of activated carbon may be mechanically attached to the surface afterward.

[0469] For the amount of the substance attached to the surface in terms of the mass relative to the amount of the positive electrode active material, the lower limit thereof is preferably 0.1 ppm or more, more preferably 1 ppm or more, still more preferably 10 ppm or more, while the upper limit thereof is preferably 20% or less, more preferably 10% or less, still more preferably 5% or less. The substance attached to the surface can reduce oxidation of the electrolytic solution on the surface of the positive electrode active material, improving the battery life. Too small an amount of the substance may fail to sufficiently provide this effect. Too large an amount thereof may hinder the entrance and exit of lithium ions, increasing the resistance.

[0470] Particles of the positive electrode active material may have any shape conventionally used, such as a bulky shape, a polyhedral shape, a spherical shape, an ellipsoidal shape, a plate shape, a needle shape, or a pillar shape. The primary particles may agglomerate to form secondary particles.

[0471] The positive electrode active material commonly has a tap density of preferably 0.5 g/cm^3 or higher, more preferably 0.8 g/cm^3 or higher, still more preferably 1.0 g/cm^3 or higher. The positive electrode active material having a tap density below the lower limit may cause an increased amount of a dispersion medium required and increased amounts of a conductive material and a binder required in formation of the positive electrode active material layer, as well as limitation on the packing fraction of the positive electrode active material in the positive electrode active material layer, resulting in limitation on the battery capacity. The use of a complex oxide powder having a high tap density enables formation of a positive electrode active material layer with a high density. A higher tap density is normally preferred, and there is no upper limit. Still, too high a tap density may be a rate-determining factor of diffusion of lithium ions in the positive electrode active material layer with the electrolytic solution serving as a diffusion medium, easily impairing the load characteristics. Thus, the upper limit of the tap density is preferably 4.0 g/cm^3 or lower, more preferably 3.7 g/cm^3 or lower, still more preferably 3.5 g/cm^3 or lower.

[0472] In the disclosure, the tap density is determined as a powder packing density (tap density) g/cm^3 when 5 to 10 g of the positive electrode active material powder is packed into a 10-ml glass graduated cylinder and the cylinder is tapped 200 times with a stroke of about 20 mm.

[0473] The particles of the positive electrode active material have a median size d50 (or a secondary particle size when the primary particles agglomerate to form secondary particles) of preferably 0.3 μm or greater, more preferably 0.5 μm or greater, still more preferably 0.8 μm or greater, most preferably 1.0 μm or greater, while preferably 30 μm or smaller, more preferably 27 μm or smaller, still more preferably 25 μm or smaller, most preferably 22 μm or smaller. The particles having a median size below the lower limit may fail to provide a product with a high tap density. The particles having a median size greater than the upper limit may cause prolonged diffusion of lithium in the particles, impairing the battery performance and generating streaks in formation of the positive electrode for a battery, i.e., when the active material and components such as a conductive material and a binder are formed into slurry by adding a solvent and the slurry is applied in the form of a thin film, for example. Mixing two or more positive electrode active materials having different median sizes d50 can further improve the easiness of packing in formation of the positive electrode.

[0474] In the disclosure, the median size d50 is determined using a known laser diffraction/scattering particle size distribution analyzer. In the case of using LA-920 (Horiba, Ltd.) as the particle size distribution analyzer, the dispersion medium used in the measurement is a 0.1% by mass sodium hexametaphosphate aqueous solution and the measurement refractive index is set to 1.24 after 5-minute ultrasonic dispersion.

[0475] When the primary particles agglomerate to form secondary particles, the average primary particle size of the positive electrode active material is preferably 0.05 μm or greater, more preferably 0.1 μm or greater, still more preferably 0.2 μm or greater. The upper limit thereof is preferably 5 μm or smaller, more preferably 4 μm or smaller, still more preferably 3 μm or smaller, most preferably 2 μm or smaller. The primary particles having an average primary particle size greater than the upper limit may have difficulty in forming spherical secondary particles, adversely affecting the powder packing. Further, such primary particles may have a greatly reduced specific surface area, highly possibly impairing the battery performance such as output characteristics. In contrast, the primary particles having an average primary particle size below the lower limit may usually be insufficiently grown crystals, causing poor charge and discharge reversibility, for example.

[0476] In the disclosure, the primary particle size is measured by scanning electron microscopic (SEM) observation. Specifically, the primary particle size is determined as follows. A photograph at a magnification of 10000× is first taken. Any 50 primary particles are selected and the maximum length between the left and right boundary lines of each primary particle is measured along the horizontal line. Then, the average value of the maximum lengths is calculated, which is defined as the primary particle size.

[0477] The positive electrode active material has a BET specific surface area of preferably 0.1 m^2/g or larger, more preferably 0.2 m^2/g or larger, still more preferably 0.3 m^2/g or larger. The upper limit thereof is preferably 50 m^2/g or smaller, more preferably 40 m^2/g or smaller, still more preferably 30 m^2/g or smaller. The positive electrode active material having a BET specific surface area smaller than the above range may easily impair the battery performance. The positive electrode active material having a BET specific surface area larger than the above range may less easily have an increased tap density, easily causing a difficulty in applying the material in formation of the positive electrode active material layer.

[0478] In the disclosure, the BET specific surface area is defined by a value determined by single point BET nitrogen adsorption utilizing a gas flow method using a surface area analyzer (e.g., fully automatic surface area measurement device, Ohkura Riken Co., Ltd.), a sample pre-dried in nitrogen stream at 150° C. for 30 minutes, and a nitrogen-helium gas mixture with the nitrogen pressure relative to the atmospheric pressure being accurately adjusted to 0.3.

[0479] When the secondary battery of the disclosure is used as a large-size lithium-ion secondary battery for hybrid vehicles or distributed generation, it needs to achieve high output. Thus, the particles of the positive electrode active material preferably mainly composed of secondary particles.

[0480] The particles of the positive electrode active material preferably include 0.5 to 7.0% by volume of fine particles having an average secondary particle size of 40 μm or smaller and having an average primary particle size of 1 μm or smaller. The presence of fine particles having an average primary particle size of 1 μm or smaller enlarges the contact area with the electrolytic solution and enables more rapid diffusion of lithium ions between the electrode and the electrolytic solution, improving the output performance of the battery.

[0481] The positive electrode active material may be produced by any usual method of producing an inorganic compound. In particular, a spherical or ellipsoidal active material can be produced by various methods. For example, a material substance of transition metal is dissolved or crushed and dispersed in a solvent such as water, and the pH of the solution or dispersion is adjusted under stirring to form a spherical precursor. The precursor is recovered and, if necessary, dried. Then, a Li source such as LiOH, Li_2CO_3, or $LiNO_3$ is added thereto and the mixture is sintered at high temperature, thereby providing an active material.

[0482] In production of the positive electrode, one of the aforementioned positive electrode active materials may be used alone or two or more thereof having different compositions may be used in any combination at any ratio. Preferred examples of the combination in this case include a combination of $LiCoO_2$ and $LiMn_2O_4$ in which part of Mn may optionally be replaced by a different transition metal (e.g., $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$), and a combination with $LiCoO_2$ in which part of Co may optionally be replaced by a different transition metal.

[0483] In order to achieve a high battery capacity, the amount of the positive electrode active material is preferably 50 to 99.5% by mass, more preferably 80 to 99% by mass, of the positive electrode mixture. The amount of the positive electrode active material in the positive electrode active material layer is preferably 80% by mass or more, more preferably 82% by mass or more, particularly preferably 84% by mass or more. The upper limit thereof is preferably 99% by mass or less, more preferably 98% by mass or less. Too small an amount of the positive electrode active material in the positive electrode active material layer may lead to an insufficient electric capacity. In contrast, too large an amount thereof may lead to insufficient strength of the positive electrode.

[0484] The positive electrode active material layer preferably further contains a binder, a thickening agent, and a conductive material.

[0485] The binder may be any material that is safe against a solvent to be used in production of the electrode and the electrolytic solution. Examples thereof include resin polymers such as polyethylene, polypropylene, polyethylene terephthalate, polymethyl methacrylate, aromatic polyamide, chitosan, alginic acid, polyacrylic acid, polyimide, cellulose, and nitro cellulose; rubbery polymers such as styrene-butadiene rubber (SBR), isoprene rubber, butadiene rubber, fluoroelastomers, acrylonitrile-butadiene rubber (NBR), and ethylene-propylene rubber; styrene-butadiene-styrene block copolymers and hydrogenated products thereof; thermoplastic elastomeric polymers such as ethylene-propylene-diene terpolymers (EPDM), styrene-ethylene-butadiene-styrene copolymers, and styrene-isoprene-styrene block copolymers and hydrogenated products thereof; soft resin polymers such as syndiotactic-1,2-polybutadiene, polyvinyl acetate, ethylene-vinyl acetate copolymers, and propylene-α-olefin copolymers; fluoropolymers such as polyvinylidene fluoride, polytetrafluoroethylene, vinylidene fluoride copolymers, and tetrafluoroethylene-ethylene copolymers; and polymer compositions having ion conductivity of alkali metal ions (especially, lithium ions and sodium ions). One of these may be used alone or two or more thereof may be used in any combination at any ratio.

[0486] The amount of the binder, which is expressed as the proportion of the binder in the positive electrode active material layer, is usually 0.1% by mass or more, preferably 1% by mass or more, more preferably 1.5% by mass or more. The proportion is also usually 80% by mass or less, preferably 60% by mass or less, still more preferably 40% by mass or less, most preferably 10% by mass or less. Too low a proportion of the binder may fail to sufficiently hold the positive electrode active material and cause insufficient mechanical strength of the positive electrode, impairing the battery performance such as cycle characteristics. In contrast, too high a proportion thereof may cause reduction in battery capacity and conductivity.

[0487] Examples of the thickening agent include carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidized starch, monostarch phosphate, casein, polyvinylpyrrolidone, and salts thereof. One of these agents may be used alone or two or more thereof may be used in any combination at any ratio.

[0488] The proportion of the thickening agent relative to the active material is usually 0.1% by mass or higher, preferably 0.2% by mass or higher, more preferably 0.3% by mass or higher, while usually 5% by mass or lower, preferably 3% by mass or lower, more preferably 2% by mass or lower. The thickening agent at a proportion lower than the above range may cause significantly poor easiness of application. The thickening agent at a proportion higher than the above range may cause a low proportion of the active material in the positive electrode active material layer, resulting in a low capacity of the battery and high resistance between the positive electrode active materials.

[0489] The conductive material may be any known conductive material. Specific examples thereof include metal materials such as copper and nickel, and carbon materials such as graphite, including natural graphite and artificial graphite, carbon black, including acetylene black, Ketjen black, channel black, furnace black, lamp black, and thermal black, and amorphous carbon, including needle coke, carbon nanotube, fullerene, and VGCF. One of these materials may be used alone or two or more thereof may be used in any combination at any ratio. The conductive material is used in an amount of usually 0.01% by mass or more, preferably 0.1% by mass or more, more preferably 1% by mass or more, while usually 50% by mass or less, preferably 30% by mass or less, more preferably 15% by mass or less, in the positive electrode active material layer. The conductive material in an amount less than the above range may cause insufficient conductivity. In contrast, conductive material in an amount more than the above range may cause a low battery capacity.

[0490] Examples of the material of the current collector for a positive electrode include metal materials such as aluminum, titanium, tantalum, stainless steel, and nickel, and alloys thereof; and carbon materials such as carbon cloth and carbon paper. Preferred is any metal material, especially aluminum or an alloy thereof.

[0491] In the case of a metal material, the current collector may be in the form of metal foil, metal cylinder, metal coil, metal plate, expanded metal, punched metal, metal foam, or the like. In the case of a carbon material, it may be in the form of carbon plate, carbon thin film, carbon cylinder, or the like. Preferred among these is metal foil. The thin film may be in the form of mesh, as appropriate. The thin film may have any thickness, and the thickness is usually 1 μm or greater, preferably 3 μm or greater, more preferably 5 μm or greater, while usually 1 mm or smaller, preferably 100 μm or smaller, more preferably 50 μm or smaller. The thin film having a thickness smaller than the above range may have insufficient strength as a current collector. In contrast, the thin film having a thickness greater than the above range may have poor handleability.

[0492] In order to reduce the electric contact resistance between the current collector and the positive electrode active material layer, the current collector also preferably has a conductive aid applied on the surface thereof. Examples of the conductive aid include carbon and noble metals such as gold, platinum, and silver.

[0493] The ratio between the thicknesses of the current collector and the positive electrode active material layer may be any value, and the ratio {(thickness of positive electrode active material layer on one side immediately before injection of electrolytic solution)/(thickness of current collector)} is preferably 20 or lower, more preferably 15 or lower, most preferably 10 or lower. The ratio is also preferably 0.5 or higher, more preferably 0.8 or higher, most preferably 1 or higher. The current collector and the positive electrode active material layer showing a ratio higher than the above range may cause the current collector to generate heat due to Joule heating during high-current-density charge and discharge. The current collector and the positive electrode active material layer showing a ratio lower than the above range may cause an increased ratio by volume of the current collector to the positive electrode active material, reducing the battery capacity.

[0494] The positive electrode may be produced by a usual method. An example of the production method is a method in which the positive electrode active material is mixed with the aforementioned binder, thickening agent, conductive material, solvent, and other components to form a slurry-like positive electrode mixture, and then this mixture is applied to a current collector, dried, and pressed so as to be densified.

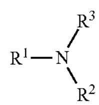
[0495] The densification may be achieved using a manual press or a roll press, for example. The density of the positive electrode active material layer is preferably 1.5 g/cm^3 or higher, more preferably 2 g/cm^3 or higher, still more preferably 2.2 g/cm^3 or higher, while preferably 5 g/cm^3 or lower, more preferably 4.5 g/cm^3 or lower, still more preferably 4 g/cm^3 or lower. The positive electrode active material layer having a density higher than the above range may cause low permeability of the electrolytic solution toward the vicinity of the interface between the current collector and the active material, and poor charge and discharge characteristics particularly at a high current density, failing to provide high output. The positive electrode active material layer having a density lower than the above range may cause poor conductivity between the active materials and increase the battery resistance, failing to provide high output.

[0496] The solvent for forming slurry may be any solvent that can dissolve or disperse therein the positive electrode active material, the conductive material, and the binder, as well as a thickening agent used as appropriate. The solvent may be either an aqueous solvent or an organic solvent. Examples of the aqueous solvent include water and solvent mixtures of an alcohol and water. Examples of the organic solvent include aliphatic hydrocarbons such as hexane; aromatic hydrocarbons such as benzene, toluene, xylene, and methyl naphthalene; heterocyclic compounds such as quinoline and pyridine; ketones such as acetone, methyl ethyl ketone, and cyclohexanone; esters such as methyl acetate and methyl acrylate; amines such as diethylene triamine and N,N-dimethylaminopropylamine; ethers such as diethyl ether, propylene oxide, and tetrahydrofuran (THF); amides such as N-methylpyrrolidone (NMP), dimethyl formamide, and dimethyl acetamide; and aprotic polar solvents such as hexamethyl phospharamide and dimethyl sulfoxide.

[0497] The organic solvent used may be a solvent represented by the formula (60).

Formula (60):

[Chem. 65]



[0498] In the formula, R^1, R^2, and R^3 are each independently H or a monovalent substituent; R^1, R^2, and R^3 have a total carbon number of 6 or greater; at least one selected from R^1, R^2, and R^3 is an organic group containing a carbonyl group; and any two of R^1, R^2, and R^3 may bind to each other to form a ring.

[0499] The solvent represented by the formula (60) preferably includes at least one selected from the group consisting of 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone (NEP), N-butyl-2-pyrrolidone (NBP), acryloylmorpholine, N-cyclohexyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 3-butoxy-N,N-dimethylpropaneamide, N,N,N',N'-tetraethylurea, N,N-dimethylacetoacetamide, N-octyl-2-pyrrolidone, and N,N-diethylacetamide.

[0500] In order to achieve excellent application properties, the solvent preferably includes water or at least one selected from the group consisting of N,N-dimetylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and solvents represented by the formula (60), more preferably at least one selected from the group consisting of N,N-dimetylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone (NEP), N-butyl-2-pyrrolidone (NBP), acryloylmorpholine, N-cyclohexyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 3-butoxy-N,N-dimethylpropaneamide, N,N,N',N'-tetraethylurea, N,N-dimethylacetoacetamide, N-octyl-2-pyrrolidone, and N,N-diethylacetamide, still more preferably at least one selected from the group consisting of N-methyl-2-pyrrolidone, N,N-dimethylacetamide, 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone, and N-butyl-2-pyrrolidone, particularly preferably at least one selected from the group consisting of N-methyl-2-pyrrolidone and N,N-dimethylacetamide.

[0501] In order to improve the stability at high output and high temperature in the case of using the electrolytic solution of the disclosure, the area of the positive electrode active material layer is preferably large relative to the outer surface area of an external case of the battery. Specifically, the total area of the positive electrode is preferably 15 times or more, more preferably 40 times or more, greater than the surface area of the external case of the secondary battery. For closed, square-shaped cases, the outer surface area of an external case of the battery herein means the total area calculated from the dimensions including the length, width, and thickness of the case portion into which a power-generating element is packed except for a protruding portion of a terminal. For closed, cylinder-like cases, the outer surface area of an external case of the battery herein means the geometric surface area of an approximated cylinder of the case portion into which a power-generating element is packed except for a protruding portion of a terminal. The total area of the positive electrode herein means the geometric surface area of the positive electrode mixture layer opposite to a mixture layer including the negative electrode active material. For structures including a current collector foil and positive electrode mixture layers on both sides of the current collector, the total area of the positive electrode is the sum of the areas calculated on the respective sides.

[0502] The positive electrode plate may have any thickness. In order to achieve a high capacity and high output, the lower limit of the thickness of the mixture layer on one side of the current collector excluding the thickness of the base metal foil is preferably 10 μm or greater, more preferably 20 μm or greater, while preferably 500 μm or smaller, more preferably 450 μm or smaller.

[0503] To a surface of the positive electrode plate may be attached a substance having a composition different from the positive electrode plate. Examples of the substance attached to the surface include oxides such as aluminum oxide, silicon oxide, titanium oxide, zirconium oxide, magnesium oxide, calcium oxide, boron oxide, antimony oxide, and bismuth oxide; sulfates such as lithium sulfate, sodium sulfate, potassium sulfate, magnesium sulfate, calcium sulfate, and aluminum sulfate; carbonates such as lithium carbonate, calcium carbonate, and magnesium carbonate; and carbon.

<Negative Electrode>

[0504] The negative electrode preferably includes a negative electrode active material layer containing a negative electrode active material and a current collector.

[0505] The negative electrode active material used is an alkali metal-containing material. The alkali metal may be a single alkali metal. The alkali metal preferably includes at least one selected from the group consisting of lithium, sodium, and potassium, more preferably at least one selected from the group consisting of lithium and sodium, particularly preferably lithium.

[0506] A different material that can electrochemically occlude and release alkali metal ions may be used together with the alkali metal. The different material may be any one selected from, for example, those containing carbonaceous materials such as artificial graphite, graphite carbon fiber, resin-baked carbon, pyrolytic vapor-grown carbon, coke, mesocarbon microbeads (MCMB), furfuryl alcohol resin-baked carbon, polyacene, pitch-based carbon fiber, vapor grown carbon fiber, natural graphite, and non-graphitizable carbon; silicon-containing compounds such as silicon and silicon alloys; and $Li_4Ti_5O_{12}$, or a mixture of two or more of these. Among these, a material at least partially containing a carbonaceous material and/or a silicon-containing compound can be particularly suitably used.

[0507] A negative electrode active material used in the disclosure suitably contains silicon as a constitutional element. With a negative electrode active material containing silicon as a constitutional element, a high-capacity battery can be produced.

[0508] As a material containing silicon, silicon particles, particles having a structure where silicon fine particles are dispersed in a silicon-based compound, silicon oxide particles represented by the formula: SiOx ($0.5 \le x \le 1.6$), or a mixture of these is/are preferred. The use of any of these can provide a negative electrode mixture for lithium-ion secondary batteries with higher initial charge-discharge efficiency, high capacity, and excellent cycle characteristics.

[0509] The term "silicon oxide" herein is a generic term for amorphous silicon oxides. Silicon oxides prior to disproportionation are represented by the formula: SiOx ($0.5 \le x \le 1.6$) where x preferably satisfies $0.8 \le x \le 1.6$, more preferably $0.8 \le x \le 1.3$. Such a silicon oxide can be obtained, for example, by heating a mixture of silicon dioxide and metallic silicon to generate silicon monoxide gas, followed by cooling the silicon monoxide gas for deposition.

[0510] The particles having a structure where silicon fine particles are dispersed in a silicon-based compound can be obtained, for example, by a method including sintering a mixture of silicon fine particles and a silicon-based compound or by a disproportionation reaction in which silicon oxide particles (SiOx) prior to disproportionation are heated in an inert non-oxidizing atmosphere such as an argon atmosphere at a temperature of 400° C. or higher, suitably 800° C. to 1100° C. The material obtained by the latter method is particularly suitable as silicon fine crystals are uniformly dispersed. Through the above disproportionation reaction, silicon nanoparticles can have a size of 1 to 100 nm. The silicon oxide in the particles having a structure where silicon nanoparticles are dispersed in a silicon-based compound is desirably silicon dioxide. Dispersion of silicon nanoparticles (crystals) in an amorphous silicon oxide can be confirmed by transmission electron microscopy.

[0511] The physical properties of the silicon-containing particles can be appropriately determined according to the aimed composite particles. The average particle size, for example, is preferably 0.1 to 50 μm. The lower limit is more preferably 0.2 μm or larger, still more preferably 0.5 μm or larger. The upper limit is more preferably 30 μm or smaller, more preferably 20 μm or smaller. The average particle size herein is expressed as the weight-average particle size in particle size distribution measurement by a laser diffraction method.

[0512] The BET specific surface area is preferably 0.5 to 100 m^2/g, more preferably 1 to 20 m^2/g. With the BET specific surface area of 0.5 m^2/g or larger, there is no risk that the adhesiveness of the negative electrode material when applied to the electrode decreases and the battery characteristics are impaired. With the BET specific surface area of 100 m^2/g or smaller, the silicon dioxide percentage on the particle surface increases, which eliminates a risk that the battery capacity is reduced when such particles are used as a negative electrode material for secondary batteries.

[0513] The silicon-containing particles are provided with conductivity when coated with carbon, which improves the battery characteristics. Examples of the method for imparting conductivity include a method including mixing the silicon-containing particles with conductive particles such as graphite particles, a method including coating the silicon-containing particle surface with a carbon film, and a method combining these two methods. Preferred is a method including coating with a carbon film, and more preferred is a method including chemical vapor deposition (CVD).

[0514] In order to increase the capacity of the resulting electrode mixture, the amount of the negative electrode active material in the electrode mixture is preferably 40% by mass or more, more preferably 50% by mass or more, particularly preferably 60% by mass or more. The upper limit thereof is preferably 99% by mass or less, more preferably 98% by mass or less.

[0515] The negative electrode active material layer may contain a conductive aid.

[0516] The conductive aid used may be any known conductive material. Specific examples thereof include metal materials such as copper and nickel, and carbon materials such as graphite, including natural graphite and artificial graphite, carbon black, including acetylene black, Ketjen black, channel black, furnace black, lamp black, and thermal black, and amorphous carbon, including needle coke, carbon nanotube, fullerene, and VGCF. One of these materials may be used alone or two or more thereof may be used in any combination at any ratio.

[0517] The conductive aid is used in an amount of usually 0.01% by mass or more, preferably 0.1% by mass or more, more preferably 1% by mass or more, while usually 50% by mass or less, preferably 30% by mass or less, more preferably 15% by mass or less, in the electrode mixture. The conductive aid in an amount less than the above range may cause insufficient conductivity. In contrast, the conductive aid in an amount more than the above range may cause a low battery capacity.

[0518] The negative electrode active material layer may further contain a thermoplastic resin. Examples of the thermoplastic resin include vinylidene fluoride, polypropylene, polyethylene, polystyrene, polyethylene terephthalate, and polyethylene oxide. One of these may be used alone or two or more thereof may be used in any combination at any ratio.

[0519] The proportion of the thermoplastic resin relative to the negative electrode active material is usually 0.01% by mass or higher, preferably 0.05% by mass or higher, more preferably 0.10% by mass or higher, while usually 3.0% by mass or lower, preferably 2.5% by mass or lower, more preferably 2.0% by mass or lower. The thermoplastic resin added can improve the mechanical strength of the electrode. The thermoplastic resin at a proportion higher than the above range may cause a low proportion of the electrode active material in the negative electrode active material layer, resulting in a low capacity of the battery and high resistance between the active materials.

[0520] The negative electrode active material layer suitably contains a binder.

[0521] Examples of the binder include the same binders as those mentioned for the positive electrode. The proportion of the binder is preferably 0.1% by mass or more, more preferably 0.5% by mass or more, particularly preferably 0.6% by mass or more, while preferably 20% by mass or less, more preferably 15% by mass or less, still more preferably 10% by mass or less, particularly preferably 8% by mass or less, relative to the negative electrode active material. The binder at a proportion relative to the negative electrode active material higher than the above range may lead to an increased proportion of the binder which fails to contribute to the battery capacity, causing a low battery capacity. The binder at a proportion lower than the above range may cause lowered strength of the negative electrode.

[0522] In particular, in the case of using a rubbery polymer typified by SBR as a main component, the proportion of the binder is usually 0.1% by mass or more, preferably 0.5% by mass or more, more preferably 0.6% by mass or more, while usually 5% by mass or less, preferably 3% by mass or less, more preferably 2% by mass or less, relative to the negative electrode active material. In the case of using a fluoropolymer typified by polyvinylidene fluoride as a main component, the proportion of the binder is usually 1% by mass or more, preferably 2% by mass or more, more preferably 3% by mass or more, while usually 15% by mass or less, preferably 10% by mass or less, more preferably 8% by mass or less, relative to the negative electrode active material.

[0523] The negative electrode active material layer may contain a thickening agent.

[0524] Examples of the thickening agent include the same thickening agents as those mentioned for the positive electrode. The proportion of the thickening agent is usually 0.1% by mass or more, preferably 0.5% by mass or more, still more preferably 0.6% by mass or more, while usually 5% by mass or less, preferably 3% by mass or less, still more preferably 2% by mass or less, relative to the negative electrode active material. The thickening agent at a proportion relative to the negative electrode active material lower than the above range may cause significantly poor easiness of application. The thickening agent at a proportion higher than the above range may cause a small proportion of the negative electrode active material in the negative electrode active material layer, resulting in a low capacity of the battery and high resistance between the negative electrode active materials.

[0525] The negative electrode mixture of the disclosure may further contain different components such as a leveling agent or a reinforcement material.

[0526] The negative electrode active material layer can be provided as follows, for example. A binder and a solvent are mixed, and to the resulting mixture are added other components such as a negative electrode active material, followed by further mixing, whereby a slurry negative electrode mixture is prepared. The resulting negative electrode mixture is uniformly applied to a current collector (e.g., metal foil, metal mesh), dried, and optionally pressed, whereby a thin negative electrode active material layer was formed as a thin film electrode. Alternatively, a negative electrode mixture may be prepared by mixing components such as a negative electrode active material and a binder, followed by addition of a solvent.

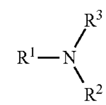
[0527] The solvent is preferably an organic solvent.

[0528] Examples of organic solvents include: nitrogen-containing organic solvents such as N-methyl-2-pyrrolidone, N,N-dimethylacetamide, and dimethylformamide; ketone solvents such as acetone, methyl ethyl ketone, cyclohexanone, and methyl isobutyl ketone; ester solvents such as ethyl acetate and butyl acetate; ether solvents such as tetrahydrofuran and dioxane; β-alkoxypropionamides such as β-methoxy-N,N-dimethylpropionamide, β-n-butoxy-N,N-dimethylpropionamide, and β-n-hexyloxy-N,N-dimethylpropionamide; and low-boiling-point general purpose organic solvents such as solvent mixtures of the above solvents.

[0529] The organic solvent used may be a solvent represented by the formula (60).

Formula (60):

[Chem. 66]



[0530] In the formula, R^1, R^2, and R^3 are each independently H or a monovalent substituent; R^1, R^2, and R^3 have a total carbon number of 6 or greater; at least one selected from R^1, R^2, and R^3 is an organic group containing a carbonyl group; and any two of R^1, R^2, and R^3 may bind to each other to form a ring.

[0531] The solvent represented by the formula (60) preferably includes at least one selected from the group consisting of 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone (NEP), N-butyl-2-pyrrolidone (NBP), acryloylmorpholine, N-cyclohexyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 3-butoxy-N,N-dimethylpropaneamide, N,N,N',N'-tetraethylurea, N,N-dimethylacetoacetamide, N-octyl-2-pyrrolidone, and N,N-diethylacetamide.

[0532] In order to achieve excellent application properties, the solvent preferably includes at least one selected from the group consisting of N,N-dimetylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and solvents represented by the formula (60), more preferably at least one selected from the group consisting of N,N-dimetylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone (NEP), N-butyl-2-pyrrolidone (NBP), acryloylmorpholine, N-cyclohexyl-2-pyrrolidone, N-vinyl-2-pyrrolidone, 3-butoxy-N,N-dimethylpropaneamide, N,N,N',N'-tetraethylurea, N,N-dimethylacetoacetamide, N-octyl-2-pyrrolidone, and N,N-diethylacetamide, still more preferably at least one selected from the group consisting of N-methyl-2-pyrrolidone, N,N-dimethylacetamide, 3-methoxy-N,N-dimethylpropaneamide, N-ethyl-2-pyrrolidone, and N-butyl-2-pyrrolidone, particularly preferably at least one selected from the group consisting of N-methyl-2-pyrrolidone and N,N-dimethylacetamide.

[0533] The amount of the solvent in the negative electrode mixture is determined in consideration of factors such as easiness of application to a current collector and thin film formability after drying. The ratio by mass of the binder and the solvent is typically 0.5:99.5 to 20:80.

[0534] The negative electrode includes a negative electrode active material layer and a current collector. The negative electrode active material layer is formed using the negative electrode mixture, and may be provided on one side or both sides of the current collector.

[0535] Examples of the current collector in the negative electrode of the disclosure include foils or meshes of metals such as iron, stainless steel, copper, aluminum, nickel, and titanium, and carbon materials such as carbon cloth and carbon paper. Preferred among these is copper foil.

[0536] The negative electrode can be suitably produced by a method including applying the negative electrode mixture to a current collector. After application of the negative electrode mixture, the coating is further dried and optionally heat-treated, and the resulting dry film may be pressed.

[0537] In the case of a metal material, the current collector may be in the form of metal foil, metal cylinder, metal coil, metal plate, expanded metal, punched metal, metal foam, or the like. In the case of a carbon material, it may be in the form of carbon plate, carbon thin film, carbon cylinder, or the like. Preferred among these is a metal foil. The thin film may be in the form of mesh, as appropriate. The thin film may have any thickness, and the thickness is usually 1 μm or greater, preferably 3 μm or greater, more preferably 5 μm or greater, while usually 1 mm or smaller, preferably 100 μm or smaller, more preferably 50 μm or smaller. The thin film having a thickness smaller than the above range may have insufficient strength as a current collector. In contrast, the thin film having a thickness greater than the above range may have poor handleability.

[0538] The thickness of the negative electrode plate is a design matter in accordance with the positive electrode plate to be used, and may be any value. The thickness of the mixture layer excluding the thickness of the base metal foil is usually 15 μm or greater, preferably 20 μm or greater, more preferably 30 μm or greater, while usually 300 μm or smaller, preferably 280 μm or smaller, more preferably 250 μm or smaller.

<Separator>

[0539] The secondary battery of the disclosure preferably further includes a separator.

[0540] The separator may be formed from any known material and may have any known shape as long as the resulting separator is stable to the electrolytic solution and is excellent in a liquid-retaining ability. The separator is preferably in the form of a porous sheet or a nonwoven fabric which is formed from a material stable to the electrolytic solution of the disclosure, such as resin, glass fiber, or inorganic matter, and which has an excellent liquid-retaining ability.

[0541] Examples of the material of a resin or glass-fiber separator include polyolefins such as polyethylene and polypropylene, aromatic polyamide, polytetrafluoroethylene, polyether sulfone, and glass filters. One of these materials may be used alone or two or more thereof may be used in any combination at any ratio, for example, in the form of a polypropylene/polyethylene bilayer film or a polypropylene/polyethylene/polypropylene trilayer film. In order to achieve good permeability of the electrolytic solution and a good shut-down effect, the separator is preferably a porous sheet or nonwoven fabric formed from a polyolefin such as polyethylene or polypropylene.

[0542] The separator may have any thickness, and the thickness is usually 1 μm or greater, preferably 5 μm or greater, more preferably 8 μm or greater, while usually 50 μm or smaller, preferably 40 μm or smaller, more preferably 30 μm or smaller. The separator thinner than the above range may have poor insulation and mechanical strength. The separator thicker than the above range may cause not only poor battery performance such as poor rate characteristics but also a low energy density of the whole electrolyte battery.

[0543] The separator which is a porous one such as a porous sheet or a nonwoven fabric may have any porosity. The porosity is usually 20% or higher, preferably 35% or higher, more preferably 45% or higher, while usually 90% or lower, preferably 85% or lower, more preferably 75% or lower. The separator having a porosity lower than the above range tends to have high film resistance, causing poor rate characteristics. The separator having a porosity higher than the above range tends to have low mechanical strength, causing poor insulation.

[0544] The separator may also have any average pore size. The average pore size is usually 0.5 μm or smaller, preferably 0.2 μm or smaller, while usually 0.05 μm or larger. The separator having an average pore size larger than the above range may easily cause short circuits. The separator having an average pore size smaller than the above range may have high film resistance, causing poor rate characteristics.

[0545] Examples of the inorganic matter include oxides such as alumina and silicon dioxide, nitrides such as aluminum nitride and silicon nitride, and sulfates such as barium sulfate and calcium sulfate, each in the form of particles or fibers.

[0546] The separator is in the form of a thin film such as a nonwoven fabric, a woven fabric, or a microporous film. The thin film favorably has a pore size of 0.01 to 1 μm and a thickness of 5 to 50 μm. Instead of the above separate thin film, the separator may have a structure in which a composite porous layer containing particles of the above inorganic matter is disposed on a surface of one or each of the positive and negative electrodes using a resin binder. For example, alumina particles having a 90% particle size of smaller than 1 μm may be applied to the respective surfaces of the positive electrode with fluororesin used as a binder to form a porous layer.

<Battery Design>

[0547] The electrode group may be either a laminate structure including the above positive and negative electrode plates with the above separator in between, or a wound structure including the above positive and negative electrode plates in spiral with the above separator in between. The proportion of the volume of the electrode group in the battery internal volume (hereinafter, referred to as an electrode group proportion) is usually 40% or higher, preferably 50% or higher, while usually 90% or lower, preferably 80% or lower.

[0548] The electrode group proportion lower than the above range may cause a low battery capacity. The electrode group proportion higher than the above range may cause small void space in the battery. Thus, if the battery temperature rises to high temperature and thereby the components swell and the liquid fraction of the electrolyte exhibits high vapor pressure to raise the internal pressure, the battery characteristics such as charge and discharge repeatability and high-temperature storageability may be impaired and a gas-releasing valve for releasing the internal pressure toward the outside may be actuated.

[0549] The current collecting structure may be any structure. In order to more effectively improve the high-current-density charge and discharge performance by the electrolytic solution of the disclosure, the current collecting structure is preferably a structure which reduces the resistances at wiring portions and jointing portions. Such reduction in internal resistance can particularly favorably lead to the effects achieved with the electrolytic solution of the disclosure.

[0550] In an electrode group having the laminate structure, the metal core portions of the respective electrode layers are preferably bundled and welded to a terminal. If an electrode has a large area, the internal resistance is high. Thus, multiple terminals may preferably be disposed in the electrode so as to reduce the resistance. In an electrode group having the wound structure, multiple lead structures may be disposed on each of the positive electrode and the negative electrode and bundled to a terminal. This can reduce the internal resistance.

[0551] The external case may be made of any material that is stable to an electrolytic solution to be used. Specific examples thereof include metals such as nickel-plated steel plates, stainless steel, aluminum and aluminum alloys, and magnesium alloys, and a layered film (laminate film) of resin and aluminum foil. In order to reduce the weight, a metal such as aluminum or an aluminum alloy or a laminate film is favorably used.

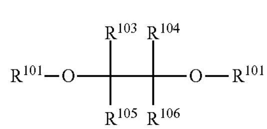
[0552] An external case made of metal may have a sealed-up structure formed by welding the metal by laser welding, resistance welding, or ultrasonic welding, or a caulking structure using the metal with a resin gasket in between. An external case made of a laminate film may have a sealed-up structure formed by hot-melting resin layers. In order to improve the sealability, a resin which is different from the resin of the laminate film may be disposed between the resin layers. Especially, in the case of forming a sealed-up structure by hot-melting the resin layers with current collecting terminals in between, metal and resin are to be bonded. Thus, the resin to be disposed between the resin layers is favorably a resin having a polar group or a modified resin having a polar group introduced therein.

[0553] The lithium-ion secondary battery of the disclosure may have any shape, such as a cylindrical shape, a square shape, a laminate shape, a coin shape, or a large-size shape. The shapes and the structures of the positive electrode, the negative electrode, and the separator may be changed in accordance with the shape of the battery.

[0554] The embodiments have been described above, and it will be understood that various changes in form or detail can be made without departing from the gist and scope of the claims.

[0555] The disclosure (1) relates to an electrolytic solution which is for use in a battery including a negative electrode containing an alkali metal-containing material, the electrolytic solution containing a solvent, the solvent including a compound (1) represented by the following formula (1):

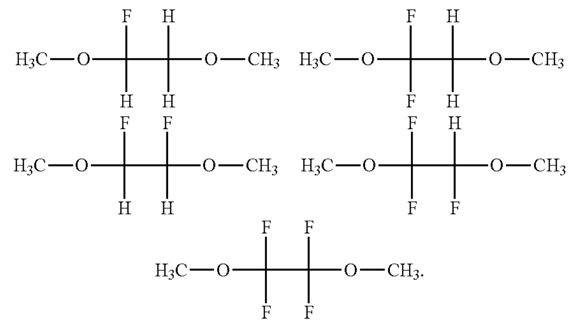
[Chem. 67]



wherein R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group, R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom.

[0556] The disclosure (2) relates to the electrolytic solution according to the disclosure (1), wherein the compound (1) includes at least one selected from the group consisting of compounds represented by the following formulas:

[Chem. 68]



[0557] The disclosure (3) relates to the electrolytic solution according to the disclosure (1) or (2), wherein the compound (1) is contained in an amount of 0.01 to 80% by volume relative to the solvent.

[0558] The disclosure (4) relates to the electrolytic solution in any combination with any one of the disclosures (1) to (3), wherein the alkali metal includes at least one selected from the group consisting of lithium, sodium, and potassium.

[0559] The disclosure (5) relates to an electrochemical device including the electrolytic solution in any combination with any one of the disclosures (1) to (4).

[0560] The disclosure (6) relates to a secondary battery including the electrolytic solution in any combination with any one of the disclosures (1) to (4).

[0561] The disclosure (7) relates to a lithium-ion secondary battery including the electrolytic solution in any combination with any one of the disclosures (1) to (4).

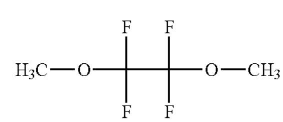
EXAMPLES

[0562] The disclosure is more specifically described with reference to examples, but the disclosure is not intended to be limited by these examples.

[0563] Compounds (A-1) to (A-5) used as solvent 1 are shown below.

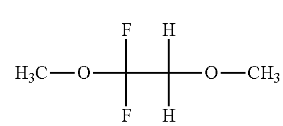
[Chem. 69]

(A-1)



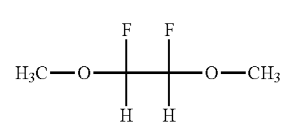
[Chem. 70]

(A-2)



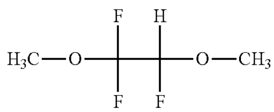
[Chem. 71]

(A-3)



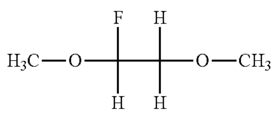
-continued

[Chem. 72]



(A-4)

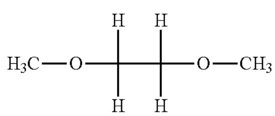
[Chem. 73]



(A-5)

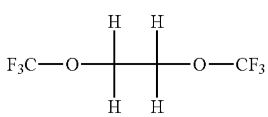
[0564] Compounds (B-1) to (B-4) used as the solvent 1 are shown below.

[Chem. 74]



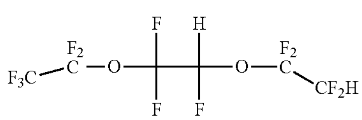
(B-1)

[Chem. 75]



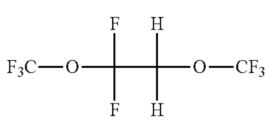
(B-2)

[Chem. 76]



(B-3)

[Chem. 77]



(B-4)

[0565] A compound used as solvent 2 is shown below.

[0566] EC: ethylene carbonate

[0567] A compound used as solvent 3 is shown below.

[0568] EMC: ethyl methyl carbonate

$CF_2CF_2CH_2OCF_2CHF_2$ (C-1):

Examples 1 to 12 and Comparative Examples 1 to 5

(Preparation of Electrolytic Solution)

[0569] The solvent 1, the solvent 2, and the solvent 3 were mixed at a ratio by volume as shown in Table 1. To the resulting mixture was added $LiN(FSO_2)_2$ (LiFSI) such that the concentration of LiFSI was 1.0 mol/L, whereby a non-aqueous electrolytic solution was prepared.

[Production of Positive Electrode]

[0570] First, 97 parts by mass of $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ serving as a positive electrode active material, 1.5 parts by mass of acetylene black serving as a conductive aid, and 1.5 parts by mass of polyvinylidene fluoride (8% by mass NMP solution) serving as a binder were mixed using a disperser to form slurry. The resulting slurry was applied to aluminum foil and dried. The workpiece was rolled using a press and cut to provide a piece in a predetermined shape. This piece was used as a positive electrode.

[Production of Negative Electrode]

[0571] Lithium metal foil serving as a negative electrode material was cut to provide a piece in a predetermined size, whereby a negative electrode was produced.

[Production of Battery]

[0572] The produced negative electrode was placed to face the above positive electrode with a porous polyethylene film (separator) in between, to which the non-aqueous electrolytic solution prepared above was injected such that it sufficiently permeates into the components such as the separator. The workpiece was then sealed, pre-charged, and aged, whereby a coin cell was produced.

(Analysis of Battery Characteristics)

[Storage Test]

[0573] The secondary battery produced above was subjected to a pre-cycling test at 25° C. In a pre-cycle, the cell was charged in a constant current/constant voltage mode to 4.3 V at a current equivalent to 0.2 C (the current value in the constant current mode was 0.01 C), and then discharged to 2.5 V at a constant current at a rate of 0.2 C. The above cycle was performed three times. Then, the cell was charged in a constant current/constant voltage mode to 4.3 V at a constant current of 0.1 C (the current value in the constant current mode was 0.01 C). The resulting cell was stored in an environment of 80° C. for 48 hours. The cell after 48-hour storage was discharged to 2.5 V at a constant current of 0.1 C. The capacity measured thereafter was determined as the residual capacity. The results in other examples were obtained with the capacity value obtained in Comparative Example 1 taken as 1. Here, 1 C means the current value at which the reference capacity of the battery is discharged in one hour. For example, 0.2 C means ⅕ of this current value.

[0574] Table 1 shows the results.

(Analysis of Performance of Lithium Dissolution/Deposition)

[Production of Battery]

[0575] The test was performed using, as a cell, a HS cell available from Hosen Corp. From lithium foil was punched out a φ13 piece, and a separator impregnated with the electrolytic solution was placed thereon. Further, from copper foil was punched out a φ15 piece, and placed on the separator. The cell was sealed to complete the cell. Assembly of the cell was performed in a glove box in an argon atmosphere.

[Dissolution/Deposition Test]

[0576] Ten coulombs of Li were electrodeposited on the copper foil so that lithium was deposited on the copper foil side. Then, 1 coulomb of Li on the copper foil was dissolved and deposited, and the dissolution/deposition performance was compared. Specifically, the cell was charged and discharged at a current density of 1.0 mA/cm^2 at a temperature of 35° C. such that the charge/discharge capacity was 0.2778 mAh (1 coulomb). The cycle in which the polarization of charge/discharge exceeded 0.2 V was determined as the condition for termination. A larger number of cycles means smoother lithium dissolution/deposition.

[0577] Table 1 shows the results.

[Production of Battery]

[0581] The produced negative electrode was placed to face the above positive electrode with a porous polyethylene film (separator) in between, to which the non-aqueous electrolytic solution prepared above was injected such that it sufficiently permeates into the components such as the separator. The workpiece was then sealed, pre-charged, and aged, whereby a coin cell was produced.

(Analysis of Battery Characteristics)

[Cycle Characteristics]

[0582] The resulting aluminum laminated cell was subjected to constant current/constant voltage charge (hereinafter, referred to as CC/CV charge) (0.1 C cut off) to 4.2 V at a current corresponding to 0.2 C and at 25° C., and then discharged to 3 V at a constant current of 0.2 C. This was counted as one cycle, and performed three times. Then, the cell was subjected to CC/CV charge (0.1 C cut off) to 3.8 V at a current corresponding to 1.0 C and at 45° C., and then discharged to 1.5 V at a constant current of 1.0 C. This was counted as one cycle, and the discharge capacity was used to determine the initial discharge capacity. The cycle was again performed, and the discharge capacity after the 300th cycle was determined. The ratio of the discharge capacity after the 300th cycle to the initial discharge capacity was determined. This value was defined as the cycle capacity retention (%). PGP-90

$$\text{Capacity retention (\%)} = (\text{Discharge capacity after 300th cycle}) / (\text{Initial discharge capacity at 1.0 C}) \times 100$$

[0583] The results are shown as relative values with the value of Comparative Example 6 taken as 1.

TABLE 1

	Solvent 1	Concentration (vol %)	Solvent 2	Concentration (vol %)	Solvent 3	Concentration (vol %)	Battery characteristics Residual capacity in storage test (relative value with Comparative Example 1 taken as 1)	Dissolution/ deposition test Number of cycles
Example 1	A-1	0.1	EC	20	EMC	79.9	1.40	143
Example 2	A-1	1	EC	20	EMC	79	1.45	150
Example 3	A-1	5	EC	20	EMC	75	1.50	156
Example 4	A-1	10	EC	20	EMC	70	1.52	182
Example 5	A-1	20	EC	20	EMC	60	1.60	195
Example 6	A-1	40	EC	20	EMC	40	1.62	218
Example 7	A-1	60	EC	20	EMC	20	1.53	234
Example 8	A-1	80	EC	10	EMC	10	1.52	260
Example 9	A-2	40	EC	20	EMC	40	1.59	211
Example 10	A-3	40	EC	20	EMC	40	1.59	208
Example 11	A-4	40	EC	20	EMC	40	1.58	234
Example 12	A-5	40	EC	20	EMC	40	1.57	182
Comparative Example 1	B-1	40	EC	20	EMC	40	1.00	130
Comparative Example 2	B-1	40	EC	30	C-1	30	1.01	133
Comparative Example 3	B-2	40	EC	20	EMC	40	1.13	134
Comparative Example 4	B-3	40	EC	20	EMC	40	1.18	133
Comparative Example 5	B-4	40	EC	20	EMC	40	1.13	133

Example 13 and Comparative Example 6

(Preparation of Electrolytic Solution)

[0578] The solvent 1, the solvent 2, and the solvent 3 were mixed at a ratio by volume as shown in Table 2. To the resulting mixture was added $NaN(FSO_2)_2$ (NaFSI) such that the concentration of NaFSI was 1.0 mol/L, whereby a non-aqueous electrolytic solution was prepared.

[Production of Positive Electrode]

[0579] First, 97 parts by mass of $NaCoO_2$ serving as a positive electrode active material and 1.5 parts by mass of polyvinylidene fluoride (8% by mass NMP solution) serving as a binder were mixed using a disperser to form slurry. The resulting slurry was applied to aluminum foil and dried. The workpiece was rolled using a press and cut to provide a piece in a predetermined size. This piece was used as a positive electrode.

[Production of Negative Electrode]

[0580] Sodium metal foil was cut to provide a piece in a predetermined size, whereby a negative electrode was produced.

[0584] Table 2 shows the results.

TABLE 2

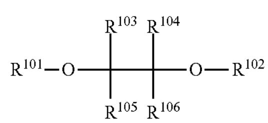
	Solvent 1	Concentration (vol %)	Solvent 2	Concentration (vol %)	Solvent 3	Concentration (vol %)	Battery characteristics Cycle characteristics (Relative value with Comparative Example 6 taken as 1)
Example 13	A-1	40	EC	20	EMC	40	1.55
Comparative Example 6	B-1	40	EC	20	EMC	40	1.00

1. An electrolytic solution which is for use in a battery comprising a negative electrode containing an alkali metal-containing material,

the electrolytic solution comprising a solvent,

the solvent comprising a compound (1) represented by the following formula (1):

[Chem. 1]

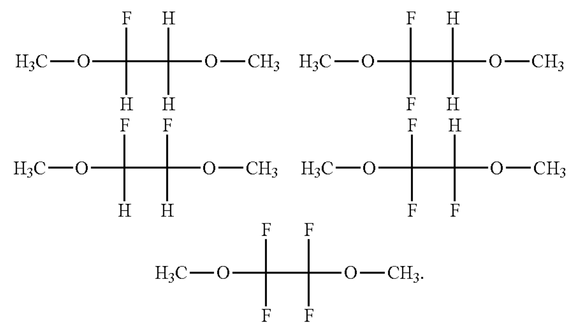


wherein R^{101} and R^{102} are each independently a C1-C3 non-fluorinated alkyl group, R^{103} to R^{106} are each independently a hydrogen atom or a halogen atom, and at least one selected from R^{103} to R^{106} is a halogen atom.

2. The electrolytic solution according to claim **1**,

wherein the compound (1) includes at least one selected from the group consisting of compounds represented by the following formulas:

[Chem. 2]



3. The electrolytic solution according to claim **1**,

wherein the compound (1) is contained in an amount of 0.01 to 80% by volume relative to the solvent.

4. The electrolytic solution according to claim **1**,

wherein the alkali metal includes at least one selected from the group consisting of lithium, sodium, and potassium.

5. An electrochemical device comprising the electrolytic solution according to claim **1**.

6. A secondary battery comprising the electrolytic solution according to claim **1**.

7. A lithium-ion secondary battery comprising the electrolytic solution according to claim **1**.

* * * * *