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(54) **NON-AQUEOUS ELECTROLYTE FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY COMPRISING SAME**

(57) The present invention relates to: a non-aqueous electrolyte solution for a lithium secondary battery, which includes a compound represented by Formula 1, a lithium salt, and an organic solvent; and a lithium secondary battery including the same.

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Description**TECHNICAL FIELD**

- 5 **[0001]** This application claims the benefit of Korean Patent Application No. 10-2021-0110204, filed on August 20, 2021, in the Korean Intellectual Property Office, the disclosures of which are incorporated herein in its entirety by reference.
- [0002]** The present invention relates to a non-aqueous electrolyte solution for a lithium secondary battery and a lithium secondary battery including the same.

10 **BACKGROUND ART**

[0003] A lithium secondary battery is generally prepared by a method in which, after an electrode assembly is formed by interposing a separator between a positive electrode including a positive electrode active material formed of a transition metal oxide containing lithium, and a negative electrode including a negative electrode active material capable of storing lithium ions, the electrode assembly is inserted into a battery case, a non-aqueous electrolyte solution, which becomes a medium for transferring the lithium ions, is injected thereinto, and the battery case is then sealed.

15 **[0004]** Lithium secondary batteries can be miniaturized and have high energy density and operating voltage, and thus have been applied to various fields such as mobile devices, electronic products, and electric vehicles. As the application fields of lithium secondary batteries are diversified, physical property requirements are gradually increasing, and in particular, development of lithium secondary batteries capable of being stably driven and having long life characteristics even under high temperature conditions is being required.

[0005] Meanwhile, when the lithium secondary battery is driven under high voltage and/or high temperature conditions, PF_6^- anions may be thermally decomposed from a lithium salt such as LiPF_6 contained in the electrolyte solution to generate a Lewis acid such as PF_5 , which reacts with moisture to generate HF. The decomposition products such as PF_5 and HF may not only destroy the film formed on the surface of the electrode, but may also cause decomposition reaction of the organic solvent, may react with the decomposition product of the positive electrode active material to elute transition metal ions, and the eluted transition metal ions may be electrodeposited on the negative electrode to destroy the film formed on the surface of the negative electrode.

25 **[0006]** If the electrolyte decomposition reaction is continued on the destroyed film as described above, the performance of the battery is further deteriorated, and thus the development of a secondary battery capable of maintaining excellent performance even under high voltage and high temperature conditions is being required.

DISCLOSURE OF THE INVENTION35 **TECHNICAL PROBLEM**

[0007] An aspect of the present invention provides a non-aqueous electrolyte solution, which can effectively remove decomposition products generated due to a lithium salt by including an aminopyrazole-based compound, and a lithium secondary battery including the same.

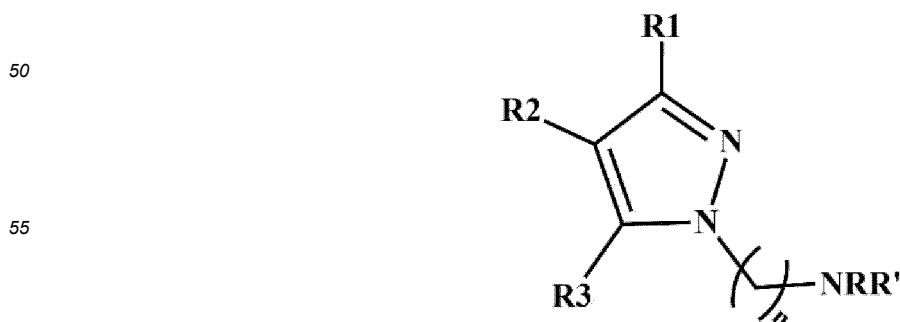
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TECHNICAL SOLUTION

[0008] According to an aspect of the present invention, there is provided a non-aqueous electrolyte solution including: a lithium salt; an organic solvent; and a compound represented by Formula 1 following.

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[Formula 1]



[0009] In Formula 1,

R and R' are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms,
 R1 to R3 are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms, and
 n is an integer of 1 to 10.

[0010] According to another aspect of the present invention, there is provided a lithium secondary battery including: a positive electrode including a positive electrode active material; a negative electrode including a negative electrode active material; a separator disposed between the negative electrode and the positive electrode; and the non-aqueous electrolyte solution for a lithium secondary battery.

ADVANTAGEOUS EFFECTS

[0011] The non-aqueous electrolyte solution according to the present invention includes an aminopyrazole-based compound, which can effectively suppress the generation of decomposition products by suppressing a decomposition reaction of lithium salts, thereby preventing the destruction of an electrode film and the elution of transition metals due to the decomposition products. In addition, through this, ultimately, there may be provided a lithium secondary battery having improved electrochemical properties.

BEST MODE FOR CARRYING OUT THE INVENTION

[0012] Hereinafter, the present invention will be described in more detail.

[0013] In general, an anion included in a lithium salt such as LiPF_6 , which is widely used in an electrolyte solution for a lithium secondary battery, forms decomposition products such as hydrogen fluoride (HF) and PF_5 by thermal decomposition or moisture. These decomposition products have acidic properties and deteriorate the film or electrode surface in the battery.

[0014] Transition metals in the positive electrode are easily eluted into the electrolyte solution due to decomposition products of the electrolyte solution, structural changes of the positive electrode due to repeated charging and discharging, or the like, and the eluted transition metals are re-deposited on the positive electrode to increase the resistance of the positive electrode. In addition, when the eluted transition metals move to the negative electrode through the electrolyte solution, the eluted transition metals are electrodeposited on the negative electrode, causing destruction of a solid electrolyte interphase (SEI) film and additional electrolyte decomposition reaction, thereby causing limitations such as consumption of lithium ions and increase of resistance.

[0015] In addition, when the battery is initially activated, a protective film is formed on each of the positive electrode and the negative electrode by a reaction of the electrolyte solution, and when the film becomes unstable due to the above-described reason, additional electrolyte decomposition occurs during charging and discharging or high-temperature exposure, thereby promoting degradation of the battery and generating gas.

[0016] In order to solve the above limitations, the present inventors have found that the compound represented by Formula 1 is included in the non-aqueous electrolyte solution, and thus it is possible to reduce the decomposition reaction of the electrolyte solution and suppress elution of transition metals and gas generation. In particular, when the silicon-based negative electrode active material is used to secure high capacity, the decomposition reaction of the SEI film by the Lewis acid material generated by the decomposition of the electrolyte solution may be intensified, and when the high-Ni-based positive electrode active material is introduced, the thermal stability may be rapidly deteriorated, and the present inventors have confirmed that this limitation may be solved through the compound represented by Formula 1.

[0017] Hereinafter, each component constituting the present invention will be described in more detail.

Non-aqueous Electrolyte Solution

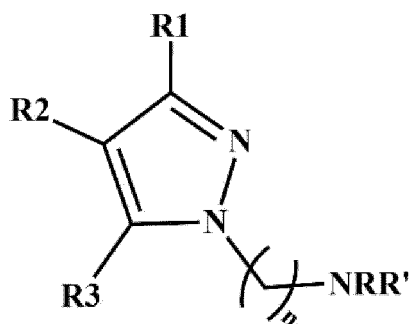
[0018] The present invention provides a non-aqueous electrolyte solution for a lithium secondary battery, the non-aqueous electrolyte solution including a lithium salt, an organic solvent, and a compound represented by Formula 1 following.

[0019] Hereinafter, each component will be described in detail.

(1) Compound Represented by Formula 1

[0020] The non-aqueous electrolyte solution of the present invention includes a compound represented by Formula 1 following:

[Formula 1]



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15 **[0021]** In Formula 1,

R and R' are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms,
 R1 to R3 are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms, and
 n is an integer of 1 to 10.

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[0022] The compound represented by Formula 1 may act as a Lewis base because nitrogen elements included in pyrazole and amine groups have non-covalent electron pairs and do not participate in the delocalization. Therefore, the reaction between PF₅ and moisture may be suppressed through a combination reaction with PF₅ which is the decomposition product of the lithium salt, and thus there is an effect of suppressing the formation of HF.

25 **[0023]** Pyrazolium, which is a cation of an ionic liquid conventionally used as an electrolyte additive, has already formed an additional bond to exhibit a cationic property, and thus there is no functional group capable of being bonded to PF₅, and thus it is not possible to have the same effect as the compound represented by Formula 1 of the present application, but there is a difference in that the compound represented by Formula 1 has a non-covalent electron pair and thus can be bonded to PF₅.

30 **[0024]** In an embodiment of the present invention, at least one among R1 to R3 in Formula 1 may be an alkyl group having 1 to 10 carbon atoms, preferably, a methyl group.

[0025] In an embodiment of the present invention, R2 in Formula 1 may be an alkyl group having 1 to 10 carbon atoms, preferably a methyl group.

[0026] In an embodiment of the present invention, each of R1 and R3 in Formula 1 may be hydrogen.

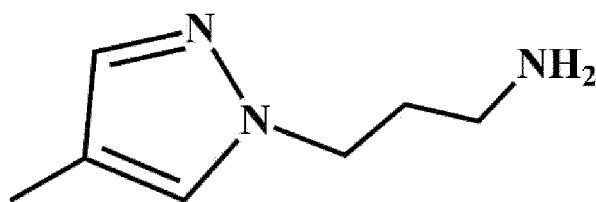
35 **[0027]** In an embodiment of the present invention, each of R and R' in Formula 1 may be hydrogen.

[0028] In an embodiment of the present invention, n in Formula 1 may be an integer of 1 to 8, specifically, an integer of 1 to 5, and more specifically, an integer of 2 to 4.

[0029] In an embodiment of the present invention, Formula 1 may be Formula 1a below.

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[Formula 1a]



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50 **[0030]** In an embodiment of the present invention, the compound represented by Formula 1a has a shape in which an amine group is substituted at N in the ring, and thus has an advantage of higher stability compared to the structure in which an NH functional group is present in the ring.

[0031] In an embodiment of the present invention, an amount of the compound represented by Formula 1 may be in a range of 0.1 wt% to 5 wt%, preferably 0.1 wt% to 1 wt%, and more preferably 0.1 wt% to 0.5 wt% based on the total weight of the non-aqueous electrolyte solution.

55 **[0032]** When the amount of the compound represented by Formula 1 is 0.1 wt% or more, the decomposition of PF₅ is suppressed, and thus the effect of reducing HF may be sufficiently exhibited, when the amount is 5 wt% or less, it is preferable in terms of preventing the initial resistance increases when the battery is driven.

(2) Additive

[0033] The non-aqueous electrolyte solution of the present invention may optionally further include the following additives as necessary in order to prevent the electrolyte solution from being decomposed to cause collapse of an electrode in a high-voltage environment, or further improve low-temperature high-rate discharge characteristics, high-temperature stability, overcharge protection, and a battery swelling suppression effect at high temperatures.

[0034] The additive may be at least any one selected from the group consisting of a cyclic carbonate-based compound, a halogen-substituted carbonate-based compound, a sultone-based compound, a sulfate-based compound, a phosphate-based or phosphite-based compound, a borate-based compound, a nitrile-based compound, an amine-based compound, a silane-based compound, a benzene-based compound, and a lithium salt-based compound.

[0035] The cyclic carbonate-based compound may be at least any one selected from the group consisting of vinylene carbonate (VC) and vinyl ethylene carbonate (VEC), and specifically may be vinylene carbonate.

[0036] The halogen-substituted carbonate-based compound may be fluoroethylene carbonate (FEC).

[0037] The sultone-based compound is a material capable of forming a stable solid electrolyte interphase (SEI) film on the surface of a negative electrode by a reduction reaction, and may be at least any one compound selected from the group consisting of 1,3-propane sultone (PS), 1,4-butane sultone, ethene sultone, 1,3-propene sultone (PRS), 1,4-butene sultone, and 1-methyl-1,3-propene sultone, and specifically may be 1,3-propane sultone (PS).

[0038] The sulfate-based compound is a material capable of forming a stable SEI film that does not crack even during high-temperature storage by being electrically decomposed on the surface of a negative electrode, and may be at least any one selected from the group consisting of ethylene sulfate (ESa), trimethylene sulfate (TMS), or methyl trimethylene sulfate (MTMS).

[0039] The phosphate-based compound or the phosphite-based compound may be at least any one selected from the group consisting of lithium difluoro (bisoxalato)phosphate, lithium difluoro phosphate, tris(trimethylsilyl)phosphate, tris(trimethylsilyl)phosphite, tris(2,2,2-trifluoroethyl)phosphate, and tris(trifluoroethyl)phosphite.

[0040] The borate-based compound may be lithium tetraphenylborate.

[0041] The nitrile-based compound may be at least any one selected from the group consisting of succinonitrile (SN), adiponitrile (ADN), acetonitrile, propionitrile, butyronitrile, valeronitrile, caprylonitrile, heptanenitrile, cyclopentane carbonitrile, cyclohexane carbonitrile, 2-fluorobenzonitrile, 4-fluorobenzonitrile, difluorobenzonitrile, trifluorobenzonitrile, phenylacetonitrile, 2-fluorophenylacetonitrile, 4-fluorophenylacetonitrile, ethylene glycol bis(2-cyanoethyl)ether (ASA3), 1,3,6-hexanetricarbonitrile (HTCN), 1,4-dicyano-2-butene (DCB), and 1,2,3-tris(2-cyanoethyl)propane (TCEP).

[0042] The amine-based compound may be at least any one selected group consisting of triethanolamine and ethylenediamine, and the silane-based compound may be tetravinylsilane.

[0043] The benzene-based compound may be at least any one selected from the group consisting of monofluorobenzene, difluorobenzene, trifluorobenzene, and tetrafluorobenzene.

[0044] The lithium salt-based compound is a compound different from the lithium salt included in the non-aqueous electrolyte solution, and may be at least any one compound selected from the group consisting of lithium difluoro phosphite (LiDFP; LiPO_2F_2), lithium bisoxalato borate (LiBOB; $\text{Li}(\text{C}_2\text{O}_4)_2$), lithium tetrafluoroborate (LiBF_4), and lithium difluoro (bisoxalato)phosphate (LiDFOP).

[0045] Preferably, the non-aqueous electrolyte solution according to an embodiment of the present invention may further include at least any one additive selected from the group consisting of vinylene carbonate (VC), vinyl ethylene carbonate (VEC), fluoroethylene carbonate (FEC), 1,3-propane sultone (PS), 1,3-propene sultone (PRS), ethylene sulfate (ESa), succinonitrile (SN), adiponitrile (ADN), ethylene glycol bis(2-cyanoethyl)ether (ASA3), 1,3,6-hexanetricarbonitrile (HTCN), 1,4-dicyano-2-butene (DCB), 1,2,3-tris(2-cyanoethyl)propane (TCEP), lithium difluoro oxalato borate (LiODFB), lithium tetrafluoroborate (LiBF_4), lithium difluoro(bisoxalato)phosphate (LiDFOP), and lithium difluorophosphate (LiDFP).

[0046] More preferably, the non-aqueous electrolyte solution according to an embodiment of the present invention may further include at least any one additive selected from the group consisting of vinylene carbonate (VC), 1,3-propane sultone (PS), ethylene sulfate (ESa), and lithium difluorophosphate (LiDFP). In this case, films are rapidly formed on the positive electrode and the negative electrode to suppress the decomposition of the compound represented by Formula 1 of the present invention, and thus there is an effect of increasing the residual amount of the compound capable of being bonded to PF_5 .

[0047] Meanwhile, an amount of the additive may be in a range of 0.1 wt% to 10 wt%, preferably, 0.3 wt% to 5 wt% based on the total weight of the non-aqueous electrolyte solution. When the additive content is within the above range, there is an effect of suppressing side reactions through the formation of the films on the positive electrode and the negative electrode.

(3) Organic Solvent

[0048] The non-aqueous electrolyte solution of the present invention includes an organic solvent.

[0049] Various organic solvents typically used in a lithium electrolyte may be used as the organic solvent without limitation. For example, the organic solvent may be a cyclic carbonate-based solvent, a linear carbonate-based solvent, a linear ester-based solvent, a cyclic ester-based solvent, a nitrile-based solvent, or a mixture thereof, and may preferably include a mixture of a cyclic carbonate-based solvent and a linear carbonate-based solvent.

[0050] The cyclic carbonate-based solvent is a highly viscous organic solvent which may well dissociate the lithium salt in the electrolyte due to high permittivity, and may be at least any one selected from the group consisting of ethylene carbonate (EC), propylene carbonate (PC), 1,2-butylene carbonate, 2,3-butylene carbonate, 1,2-pentylene carbonate, 2,3-pentylene carbonate, and vinylene carbonate, and may preferably include ethylene carbonate (EC) or propylene carbonate (PC).

[0051] In addition, the linear carbonate-based solvent is an organic solvent having low viscosity and low permittivity, and may be at least any one selected from the group consisting of dimethyl carbonate (DMC), diethyl carbonate (DEC), dipropyl carbonate, ethyl methyl carbonate (EMC), methylpropyl carbonate, and ethylpropyl carbonate, and may preferably include ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), or diethyl carbonate (DEC).

[0052] In order to prepare an electrolyte having high ionic conductivity, it is desirable to use a mixture of the cyclic carbonate-based solvent and the linear carbonate-based solvent as the organic solvent.

[0053] The linear ester-based solvent may include at any one selected from the group consisting of methyl acetate, ethyl acetate, propyl acetate, methyl propionate, ethyl propionate, propyl propionate, and butyl propionate, and may preferably be methyl propionate, ethyl propionate, or propyl propionate.

[0054] The cyclic ester-based solvent may be at least any one selected from the group consisting of γ -butyrolactone, γ -valerolactone, γ -caprolactone, σ -valerolactone, and ϵ -caprolactone.

[0055] The nitrile-based solvent may be at least any one selected from the group consisting of succinonitrile, acetonitrile, propionitrile, butyronitrile, valeronitrile, caprylonitrile, heptanenitrile, cyclopentane carbonitrile, cyclohexane carbonitrile, 2-fluorobenzonitrile, 4-fluorobenzonitrile, difluorobenzonitrile, trifluorobenzonitrile, phenylacetonitrile, 2-fluorophenylacetonitrile and 4-fluorophenylacetonitrile, and may preferably be succinonitrile.

[0056] Remainders except for the amounts of the other components except for the organic solvent, for example, the compound represented by Formula 1, the additive, and the lithium salt in the total weight of the non-aqueous electrolyte solution may all be organic solvents unless otherwise stated.

(4) Lithium Salt

[0057] The non-aqueous electrolyte solution of the present invention includes a lithium salt.

[0058] Any lithium salt typically used in an electrolyte for a lithium secondary battery may be used as the lithium salt without limitation, and specifically, the lithium salt may include Li^+ as a cation, and may include at least one selected from the group consisting of F^- , Cl^- , Br^- , I^- , NO_3^- , $\text{N}(\text{CN})_2^-$, BF_4^- , ClO_4^- , $\text{B}_{10}\text{Cl}_{10}^-$, AlCl_4^- , AlO_4^- , PF_6^- , CF_3SO_3^- , CH_3CO_2^- , CF_3CO_2^- , AsF_6^- , SbF_6^- , CH_3SO_3^- , $(\text{CF}_3\text{CF}_2\text{SO}_2)_2\text{N}^-$, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, $(\text{FSO}_2)_2\text{N}^-$, $\text{BF}_2\text{C}_2\text{O}_4^-$, BC_4O_8^- , $\text{BF}_2\text{C}_2\text{O}_4\text{CHF}^-$, $\text{PF}_4\text{C}_2\text{O}_4^-$, $\text{PF}_2\text{C}_4\text{O}_8^-$, PO_2F_2^- , $(\text{CF}_3)_2\text{PF}_4^-$, $(\text{CF}_3)_3\text{PF}_3^-$, $(\text{CF}_3)_4\text{PF}_2^-$, $(\text{CF}_3)_5\text{PF}^-$, $(\text{CF}_3)_6\text{P}^-$, $\text{C}_4\text{F}_9\text{SO}_3^-$, $\text{CF}_3\text{CF}_2\text{SO}_3^-$, $\text{CF}_3\text{CF}_2(\text{CF}_3)_2\text{CO}^-$, $(\text{CF}_3\text{SO}_2)_2\text{CH}^-$, $\text{CF}_3(\text{CF}_2)_7\text{SO}_3^-$, and SCN^- as an anion.

[0059] Specifically, the lithium salt may be at least any one selected from the group consisting of LiPF_6 , LiClO_4 , LiBF_4 , $\text{LiN}(\text{FSO}_2)_2(\text{LiFSI})$, LiTFSI , lithium bis (pentafluoroethanesulfonyl) imide (LiBETI), LiSO_3CF_3 , LiPO_2F_2 , lithium bis(oxalate)borate (LiBOB), lithium difluoro(oxalate)borate (LiFOB), lithium difluoro(bisoxalato) phosphate (LiDFOP), lithium tetrafluoro(oxalate) phosphate (LiTFOP), and lithium fluoromalonato(difluoro) borate (LiFMDFB), and may preferably be LiPF_6 .

[0060] In an embodiment of the present invention, a concentration of the lithium salt in the non-aqueous organic solution containing the lithium salt and the organic solvent may be in a range of 0.5 M to 4.0 M, preferably, 0.5 M to 3.0 M, and more preferably, 0.8 M to 2.0 M. When the concentration of the lithium salt is within the above range, the effect of improving low-temperature output and cycle characteristics is sufficiently secured, and the viscosity and surface tension are prevented from being excessively increased, thereby obtaining appropriate electrolyte impregnability.

Lithium Secondary Battery

[0061] Next, a lithium secondary battery according to the present invention will be described.

[0062] The lithium secondary battery according to the present invention includes a positive electrode including a positive electrode active material, a negative electrode including a negative electrode active material, a separator disposed between the positive electrode and the negative electrode, and a non-aqueous electrolyte solution, and, in this case, the non-aqueous electrolyte is the non-aqueous electrolyte solution according to the present invention. Since the non-aqueous electrolyte solution has been described above, a description thereof will be omitted and other components will be described below.

(1) Positive Electrode

[0063] The positive electrode according to the present invention may include a positive electrode active material and be prepared by coating a positive electrode collector with a positive electrode slurry containing the positive electrode active material, a binder, a conductive agent, a solvent, etc., and then drying and rolling the coated positive electrode collector.

[0064] The positive electrode collector is not particularly limited so long as it has conductivity without causing adverse chemical changes in the battery, and, for example, stainless steel; aluminum; nickel; titanium; sintered carbon; or aluminum or stainless steel of which the surface is treated with carbon, nickel, titanium, silver, or the like may be used.

[0065] The positive electrode active material is a compound capable of reversibly intercalating and deintercalating lithium, and may be at least any one selected from the group consisting of LCO (LiCoO₂); LNO (LiNiO₂); LMO (LiMnO₂); LiMn₂O₄; LiCoPO₄; LFP (LiFePO₄); and a lithium composite transition metal oxide including nickel (Ni), cobalt (Co), and manganese (Mn).

[0066] In an embodiment of the present invention, the positive electrode active material may have a molar ratio of nickel in the transition metal of 70 mol% or more, preferably 80 mol% or more, and more preferably 85 mol% or more.

[0067] In an embodiment of the present invention, the lithium composite transition metal oxide may be any one selected from the group consisting of LiNiCoMnO₂; LiNi_{1-x-y-z}Co_xM¹_yM²_zO₂ (M¹ and M² are each independently any one selected from the group consisting of Al, Ni, Co, Fe, Mn, V, Cr, Ti, W, Ta, Mg, and Mo, and x, y, and z are each independently an atomic fraction of oxide composition elements, and 0 ≤ x < 0.5, 0 ≤ y < 0.5, 0 ≤ z < 0.5, and x + y + z = 1); and a compound represented by Formula 2 following.

[0068] Specifically, the positive electrode active material may include a lithium composite transition metal oxide represented by Formula 2 following:



[0069] In Formula 2,

M is at least any one selected from the group consisting of W, Cu, Fe, V, Cr, Ti, Zr, Zn, Al, In, Ta, Y, La, Sr, Ga, Sc, Gd, Sm, Ca, Ce, Nb, Mg, B, and Mo,

1 + x, a, b, c, and d are each independently an atomic fraction of elements, and -0.2 ≤ x ≤ 0.2, 0.50 ≤ a < 1, 0 < b ≤ 0.3, 0 < c ≤ 0.3, 0 ≤ d ≤ 0.1, and a + b + c + d = 1.

[0070] 1 + x above represents a molar ratio of lithium in a lithium composite transition metal oxide, and x may satisfy -0.1 ≤ x ≤ 0.2, or 0 ≤ x ≤ 0.2. When the molar ratio of lithium satisfies the above range, the crystal structure of the lithium composite transition metal oxide may be stably formed.

[0071] a above represents a molar ratio of nickel among all metals excluding lithium in the lithium composite transition metal oxide, and may satisfy 0.60 ≤ a < 1, 0.70 ≤ a < 1, 0.80 ≤ a < 1, or 0.85 ≤ a < 1. When the molar ratio of nickel satisfies the above range, high energy density may be exhibited and high capacity may be achieved.

[0072] b above represents a molar ratio of cobalt among all metals excluding lithium in the lithium composite transition metal oxide, and may satisfy 0 < b ≤ 0.25, 0 < b ≤ 0.20, 0 < b ≤ 0.15, or 0 < b ≤ 0.10. When the molar ratio of cobalt satisfies the above range, good resistance characteristics and output characteristics may be achieved.

[0073] c above represents a molar ratio of manganese among all metals excluding lithium in the lithium composite transition metal oxide, and may satisfy 0 ≤ c ≤ 0.25, 0 < c ≤ 0.20, 0 < c ≤ 0.15, or 0 < c ≤ 0.10. When the molar ratio of manganese satisfies the above range, the structural stability of the positive electrode active material is exhibited excellent.

[0074] In an embodiment of the present invention, the lithium composite transition metal oxide may include at least one doping element selected from the group consisting of W, Cu, Fe, V, Cr, Ti, Zr, Zn, Al, In, Ta, Y, La, Sr, Ga, Sc, Gd, Sm, Ca, Ce, Nb, Mg, B, and Mo. In other words, d above representing the molar ratio of the doping element in all metals excluding lithium in the lithium composite transition metal oxide may satisfy 0 < d ≤ 0.10, 0 < d ≤ 0.08, 0 < d ≤ 0.05, or 0 < d ≤ 0.03.

[0075] More specifically, the lithium composite transition metal oxide may be at least any one selected from the group consisting of Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O₂, Li(Ni_{0.7}Mn_{0.15}Co_{0.15})O₂, Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂, and Li(Ni_{0.9}Mn_{0.03}Co_{0.06}Al_{0.01})O₂.

[0076] The positive electrode active material may be included in an amount of 80 wt% to 99 wt%, specifically, 90 wt% to 99 wt% based on the total weight of the solid content in the positive electrode slurry. In this case, when the amount of the positive electrode active material is 80 wt% or less, since energy density is reduced, capacity may be reduced.

[0077] The binder is a component that assists in the binding between the active material and the conductive agent and in the binding with the current collector, and may be commonly added in an amount of 1 wt% to 30 wt% based on the total weight of the solid content in the positive electrode slurry. Examples of the binder may be polyvinylidene fluoride, polyvinyl alcohol, carboxymethylcellulose (CMC), starch, hydroxypropylcellulose, regenerated cellulose, polyvinylpyrrolidone, polytetrafluoroethylene, polyethylene, polypropylene, an ethylene-propylene-diene monomer, a sulfonated eth-

ylene-propylene-diene monomer, a styrene-butadiene rubber, a fluoro rubber, or various copolymers thereof.

[0078] In addition, the conductive agent is a material providing conductivity without causing adverse chemical changes in the battery, and may be added in an amount of 0.5 wt% to 20 wt% based on the total weight of the solid content in the positive electrode slurry.

[0079] For example, the conductive agent may be at least any one selected from the group consisting of carbon black such as acetylene black, Ketjen black, channel black, furnace black, lamp black, or thermal black; graphite powder such as natural graphite, artificial graphite, or graphite; conductive fibers such as carbon fibers or metal fibers; conductive powder such as fluorocarbon powder, aluminum powder, or nickel powder; conductive whiskers such as zinc oxide whiskers or potassium titanate whiskers; conductive metal oxide such as titanium oxide; or a conductive material such as polyphenylene derivatives.

[0080] Furthermore, the solvent of the positive electrode slurry may include an organic solvent, such as N-methyl-2-pyrrolidone (NMP), and may be used in an amount such that desirable viscosity is obtained when the positive electrode active material, the binder, and the conductive agent are included. For example, the solvent may be included in an amount such that a concentration of the solid content in the positive electrode slurry containing the positive electrode active material, the binder, and the conductive agent is 40 wt% to 90 wt%, preferably, 50 wt% to 80 wt%.

(2) Negative Electrode

[0081] The negative electrode according to the present invention may include a negative electrode active material and be prepared by coating a negative electrode collector with a negative electrode slurry containing the negative electrode active material, a binder, a conductive agent, a solvent, etc., and then drying and rolling the coated negative electrode collector.

[0082] The negative electrode collector generally has a thickness of 3 μm to 500 μm . The negative electrode collector is not particularly limited so long as it has high conductivity without causing adverse chemical changes in the battery, and, for example, copper; stainless steel; aluminum; nickel; titanium; sintered carbon; copper or stainless steel that is surface-treated with one of carbon, nickel, titanium, silver, or the like; an aluminum-cadmium alloy, or the like may be used. Also, similar to the positive electrode collector, the negative electrode collector may have fine surface roughness to improve bonding strength with the negative electrode active material, and the negative electrode collector may be used in various shapes such as a film, a sheet, a foil, a net, a porous body, a foam body, and a non-woven fabric body.

[0083] In an embodiment of the present invention, the negative electrode active material may include a silicon-based material, and the silicon-based material may be at least any one selected from the group consisting of Si, SiO_x ($0 < x < 2$), and a Si-Y alloy (Y is an element selected from among an alkali metal, an alkaline earth metal, a Group 13 element, a Group 14 element, a transition metal, a rare earth element, and a combination thereof, and cannot be Si), and preferably SiO .

[0084] The capacity of the silicon-based negative electrode active material is about 10 times higher than that of graphite, and thus mass loading ($\text{mg}\cdot\text{cm}^{-2}$) is lowered, thereby improving fast charging performance of the battery. However, there is a limitation in that the lithium ion loss rate due to the irreversible reaction is high and the volume change is large, thereby adversely affecting the life, and this limitation may be solved by applying the above-described non-aqueous electrolyte solution. However, a negative electrode containing the silicon-based negative electrode active material contains more oxygen-rich (O-rich) components in the SEI film than a graphite negative electrode, and the SEI film containing the O-rich components tends to be more easily decomposed when a Lewis acid, such as HF or PF_5 , is present in the electrolyte. Thus, with respect to the negative electrode containing the silicon-based negative electrode active material, there is a need to suppress the formation of the Lewis acid, such as HF and PF_5 , or scavenge the formed Lewis acid in order to stably maintain the SEI film. Since the non-aqueous electrolyte solution according to the present invention includes the compound represented by Formula 1, which can suppress the generation of Lewis acid or remove the generated Lewis acid, it is possible to effectively solve the limitation of the SEI film decomposition accompanying the use of the negative electrode containing the silicon-based active material.

[0085] In an embodiment of the present invention, the silicon-based material may be included in an amount of 1 wt% to 20 wt%, preferably, 5 wt% to 15 wt% based on the total weight of the negative electrode active material. When the silicon-based material is included in the above range, there is an effect of increasing the capacity of the negative electrode and improving the fast charging performance.

[0086] The negative electrode active material of the present invention may further include a carbon-based material; a metal or an alloy of lithium and the metal; a metal composite oxide; a material which may be doped and undoped with lithium; a lithium metal; and a transition metal oxide in addition to the silicon-based material.

[0087] As the carbon-based material, a carbon-based negative electrode active material generally used in a lithium ion secondary battery may be used without particular limitation, and as a typical example, crystalline carbon, amorphous carbon, or a mixture thereof may be used. Examples of the crystalline carbon may include graphite such as irregular, planar, flaky, spherical, or fibrous natural graphite or artificial graphite, and examples of the amorphous carbon may

include soft carbon (low-temperature sintered carbon) or hard carbon, mesophase pitch carbide, sintered cokes, or the like.

[0088] As the metal or the alloy of lithium and the metal, a metal selected from the group consisting of Cu, Ni, Na, K, Rb, Cs, Fr, Be, Mg, Ca, Sr, Si, Sb, Pb, In, Zn, Ba, Ra, Ge, Al, and Sn, or an alloy of lithium and the metal may be used.

[0089] As the metal composite oxide, at least any one selected from the group consisting of PbO , PbO_2 , Pb_2O_3 , Pb_3O_4 , Sb_3O_3 , Sb_2O_4 , Sb_2O_5 , GeO , GeO_2 , Bi_2O_3 , Bi_2O_4 , Bi_2O_5 , $Li_xFe_2O_3$ ($0 \leq x \leq 1$), Li_xWO_2 ($0 \leq x \leq 1$), and $Sn_xMe_{1-x}Me'_yO_z$ (where: Me is Mn, Fe, Pb, or Ge; Me' is Al, B, P, Si, Groups I, II and III elements of the periodic table, or halogen; $0 < x \leq 1$; $1 \leq y \leq 3$; and $1 \leq z \leq 8$) may be used.

[0090] The material which may be doped and undoped with lithium may include Sn, SnO_2 , Sn-Y (wherein Y above is an element selected from the group consisting of an alkali metal, an alkaline earth metal, a Group 13 element, a Group 14 element, a transition metal, a rare earth element, and a combination thereof, and is not Sn), or the like.

[0091] In Si-Y and Sn-Y above, the element Y may be at least any one selected from the group consisting of Mg, Ca, Sr, Ba, Ra, Sc, Y, Ti, Zr, Hf, Rf, V, Nb, Ta, Db (dubnium), Cr, Mo, W, Sg, Tc, Re, Bh, Fe, Pb, Ru, Os, Hs, Rh, Ir, Pd, Pt, Cu, Ag, Au, Zn, Cd, B, Al, Ga, Sn, In, Ge, P, As, Sb, Bi, S, Se, Te, and Po.

[0092] Examples of the transition metal oxide may include lithium-containing titanium composite oxide (LTO), vanadium oxide, lithium vanadium oxide, or the like.

[0093] The negative electrode active material may be included in an amount of 80 wt% to 99 wt% based on the total weight of solid content in the negative electrode slurry.

[0094] The binder is a component that assists in the binding among the conductive agent, the active material, and the current collector, and is commonly added in an amount of 1 wt% to 30 wt% based on the total weight of the solid content in the negative electrode slurry. Examples of the binder may include polyvinylidene fluoride, polyvinyl alcohol, carboxymethylcellulose (CMC), starch, hydroxypropylcellulose, regenerated cellulose, polyvinylpyrrolidone, polytetrafluoroethylene, polyethylene, polypropylene, an ethylene-propylene-diene monomer, a sulfonated ethylene-propylene-diene monomer, a styrene-butadiene rubber, a fluoro rubber, various copolymers thereof, or the like.

[0095] The conductive agent is a component for further improving the conductivity of the negative electrode active material, and may be added in an amount of 0.5 wt% to 20 wt% based on the total weight of the solid content in the negative electrode slurry. The conductive agent is not particularly limited as long as it has conductivity without causing adverse chemical changes in the battery, and, for example, may be at least any one selected from the group consisting of carbon black such as acetylene black, Ketjen black, channel black, furnace black, lamp black, or thermal black; graphite powder such as natural graphite, artificial graphite, or graphite; conductive fibers such as carbon fibers or metal fibers; conductive powder such as fluorocarbon powder, aluminum powder, or nickel powder; conductive whiskers such as zinc oxide whiskers or potassium titanate whiskers; conductive metal oxide such as titanium oxide; or a conductive material such as polyphenylene derivatives.

[0096] The solvent of the negative electrode slurry may include water; or an organic solvent, such as NMP or alcohol, and may be used in an amount such that desirable viscosity is obtained when the negative electrode active material, the binder, the conductive agent, and the like are included. For example, the solvent may be included in an amount such that a concentration of the solid content in the slurry including the negative electrode active material, the binder, and the conductive agent is 30 wt% to 80 wt%, preferably, 40 wt% to 70 wt%.

(3) Separator

[0097] The lithium secondary battery according to the present invention includes a separator between the positive electrode and the negative electrode.

[0098] The separator separates the negative electrode and the positive electrode and provides a movement path of lithium ions, and any separator may be used as the separator without particular limitation as long as it is typically used in a lithium secondary battery, and particularly, a separator having excellent wettability of the electrolyte and excellent stability as well as low resistance to the transfer of electrolyte ions is preferable.

[0099] Specifically, a porous polymer film, for example, a porous polymer film prepared from a polyolefin-based polymer, such as an ethylene homopolymer, a propylene homopolymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, and an ethylene/methacrylate copolymer; or a laminated structure having two or more layers thereof may be used as the separator. Also, a typical porous nonwoven fabric, for example, a nonwoven fabric formed of high melting point glass fibers or polyethylene terephthalate fibers may be used. Furthermore, a coated separator including a ceramic component or a polymer material may be used to secure heat resistance or mechanical strength, and the separator having a single layer or multilayer structure may be used.

[0100] The lithium secondary battery according to the present invention as described above may be useful for portable devices, such as mobile phones, notebook computers, and digital cameras, electric cars such as hybrid electric vehicles (HEVs), and the like.

[0101] Thus, according to another embodiment of the present invention, a battery module including the lithium sec-

ondary battery as a unit cell and a battery pack including the battery module are provided.

[0102] The battery module or the battery pack may be used as a power source of at least one medium and large sized device of a power tool; electric cars including an electric vehicle (EV), a hybrid electric vehicle, and a plug-in hybrid electric vehicle (PHEV); and a power storage system.

[0103] A shape of the lithium secondary battery of the present invention is not particularly limited, but a cylindrical type using a can, a prismatic type, a pouch type, a coin type, or the like may be used.

[0104] The lithium secondary battery according to the present invention may not only be used in a battery cell that is used as a power source of a small device, but may also be preferably used as a unit cell in a medium-and-large-sized battery module including a plurality of battery cells.

[0105] Hereinafter, the present invention will be described in detail with reference to specific examples.

MODE FOR CARRYING OUT THE INVENTION

<Examples>

Example 1.

(Preparation of Non-aqueous Electrolyte Solution)

[0106] A non-aqueous organic solution was prepared by mixing ethylene carbonate (EC) and ethyl methyl carbonate (EMC) in a volume ratio of 30:70 and then dissolving LiPF_6 in the mixture so as to have a concentration of 1.0 M. A non-aqueous electrolyte solution (100 wt%) was prepared by mixing 0.5 wt% of the compound represented by Formula 1a and the non-aqueous organic solution as a remainder.

(Preparation of Lithium Secondary Battery)

[0107] $\text{Li}(\text{Ni}_{0.9}\text{Mn}_{0.03}\text{Co}_{0.06}\text{Al}_{0.01})\text{O}_2$ as a positive electrode active material, a conductive agent (carbon black), and a binder (polyvinylidene fluoride) were added to N-methyl-2-pyrrolidone (NMP) at a weight ratio of 97.6:0.8:1.6 to prepare a positive electrode slurry (solid content: 60 wt%). A 13.5 μm thick aluminum (Al) thin film, as a positive electrode collector, was coated with the positive electrode slurry, dried, and then roll-pressed to prepare a positive electrode.

[0108] A negative electrode active material (graphite:SiO=90.0:10.0 weight ratio), a binder (SBR-CMC), and a conductive agent (carbon black) were added in a weight ratio of 97.6:0.8:1.6 to water, which is a solvent, to prepare a negative electrode slurry (solid content: 60 wt%). A 6 μm thick copper (Cu) thin film, as a negative electrode collector, was coated with the negative electrode slurry, dried, and then roll-pressed to prepare a negative electrode.

[0109] An electrode assembly was prepared by sequentially stacking the positive electrode, a polyolefin-based porous separator coated with inorganic particles (Al_2O_3), and the negative electrode.

[0110] The electrode assembly was accommodated in a pouchtype battery case, and the prepared non-aqueous electrolyte solution was injected thereinto to prepare a lithium secondary battery.

Example 2.

[0111] A lithium secondary battery was prepared in the same manner as in Example 1 except that the amount of the compound represented by Formula 1a is changed to 0.3 wt% and 0.5 wt% of vinylene carbonate (VC) is further added in the preparation of the non-aqueous electrolyte solution.

Comparative Example 1.

[0112] A lithium secondary battery was prepared in the same manner as in Example 1 except that the compound represented by Formula 1a was not added in the preparation of the non-aqueous electrolyte solution.

Comparative Example 2.

[0113] A lithium secondary battery was prepared in the same manner as in Example 2 except that the compound represented by Formula 1a was not added in the preparation of the non-aqueous electrolyte solution.

<Experimental Example 1: HF Content Measurement After High-temperature Storage>

[0114] After the non-aqueous electrolyte solutions prepared in Example 1 and Comparative Example 1 were left at

60 °C for 4 weeks, the hydrogen fluoride (HF) content in the electrolyte solutions was measured in ppm by acid-base neutralization titration. Metrohm 785 DMP Titrino was used as measurement equipment, and 0.1 N of sodium hydroxide standard solution was used as the titration sample. Specifically, after about 100 mL of cold tertiary distilled water was injected into a 250-mL beaker having a magnetic bar, the beaker was placed in an ice bath, waited until it reached 3 °C, and then, when it reached 3 °C, an electrode and a dosing tube were immersed in the beaker and stirred. After each of the non-aqueous electrolyte solutions of Example 1 and Comparative Example 1 was added in the stirred state, the accurate weight of the sample was input to start titration, and the concentration of HF measured through titration was shown in Table 1 below.

[Table 1]

	HF after high-temperature storage (ppm)
Example 1	4.43
Comparative Example 1	67.1

[0115] From the results of Table 1, it may be confirmed that the concentration of HF in the non-aqueous electrolyte solution in Example 1 including the compound represented by Formula 1a was lower than that in the non-aqueous electrolyte solution in Comparative Example 1 not including the compound represented by Formula 1a. That is, it may be seen that the compound represented by Formula 1a of the present application suppresses the decomposition reaction of the lithium salt in the electrolyte solution so that the concentration of HF, which is the decomposition product, is lowered.

<Experimental Example 2: High-temperature Storage Evaluation>

[0116] After each of the lithium secondary batteries prepared in Example 2 and Comparative Example 2 was activated at a CC of 0.1 C, degassing was performed.

[0117] Subsequently, each secondary battery was charged at a CC of 0.33 C to 4.20 V under a constant current-constant voltage (CC-CV) condition at 25°C, and then stored at 60 °C for 8 weeks. Thereafter, amounts of gases generated in the lithium secondary batteries were measured, and the results are shown in Table 2 below.

[Table 2]

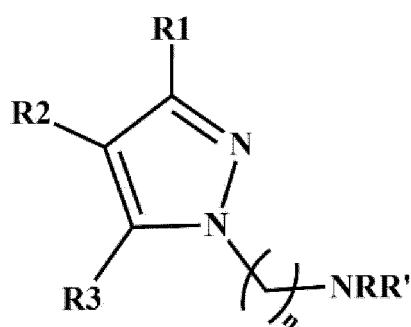
	Amount of CO ₂ generated (μL)	Amount of CO generated (μL)	Amount of hydrocarbon generated (μL)	Total (μL)
Example 2	945	71	605	1,621
Comparative Example 2	1,160	70	749	1,979

[0118] From the results of Table 2, it may be confirmed that the amounts of gases generated in the battery in Example 2 including the compound represented by Formula 1a was much less than that in the battery in Comparative Example 2 not including the compound represented by Formula 1a. That is, when the electrolyte solution including the compound represented by Formula 1a is used, it may be seen that the amounts of gases generated, which are factors that deteriorate the performance of the battery and the safety after high-temperature storage, are reduced.

Claims

1. A non-aqueous electrolyte solution for a lithium secondary battery, comprising a lithium salt, an organic solvent, and a compound represented by Formula 1 following:

[Formula 1]



wherein, in Formula 1,
 R and R' are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms,
 R1 to R3 are each independently hydrogen or an alkyl group having 1 to 10 carbon atoms, and
 n is an integer of 1 to 10.

2. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein at least one among R1 to R3 in Formula 1 is an alkyl group having 1 to 10 carbon atoms.
3. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein R2 in Formula 1 is an alkyl group having 1 to 10 carbon atoms.
4. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein each of R and R' in Formula 1 is hydrogen.
5. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein the amount of the compound represented by Formula 1 is in a range of 0.1 wt% to 5 wt% based on the total weight of the non-aqueous electrolyte solution.
6. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein the amount of the compound represented by Formula 1 is in a range of 0.1 wt% to 1 wt% based on the total weight of the non-aqueous electrolyte solution.
7. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, further comprising at least any one additive selected from the group consisting of vinylene carbonate, 1,3-propane sultone, ethylene sulfate, and lithium difluoro phosphate.
8. The non-aqueous electrolyte solution for a lithium secondary battery of claim 1, wherein the organic solvent comprises a mixture of a cyclic carbonate-based solvent and a linear carbonate-based solvent.
9. A lithium secondary battery comprising:
 - a positive electrode including a positive electrode active material;
 - a negative electrode including a negative electrode active material;
 - a separator disposed between the positive electrode and the negative electrode; and
 - the non-aqueous electrolyte solution of claim 1.
10. The lithium secondary battery of claim 9, wherein the positive electrode active material comprises a lithium composite transition metal oxide represented by Formula 2 following:



wherein, in Formula 2,
 M is at least any one selected from the group consisting of W, Cu, Fe, V, Cr, Ti, Zr, Zn, Al, In, Ta, Y, La, Sr, Ga, Sc, Gd, Sm, Ca, Ce, Nb, Mg, B, and Mo,

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1+x, a, b, c, and d are each independently an atomic fraction of elements, and
 $-0.2 \leq x \leq 0.2$, $0.50 \leq a < 1$, $0 < b \leq 0.3$, $0 < c \leq 0.3$, $0 \leq d \leq 0.1$, and $a+b+c+d=1$.

5 11. The lithium secondary battery of claim 9, wherein the positive electrode active material has a molar ratio of nickel among transition metals of 70 mol% or more.

10 12. The lithium secondary battery of claim 9, wherein the negative electrode active material comprises a silicon-based material.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2022/012370

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A. CLASSIFICATION OF SUBJECT MATTER		
H01M 10/0567(2010.01)i; H01M 10/052(2010.01)i; H01M 4/525(2010.01)i; H01M 4/505(2010.01)i; H01M 4/48(2010.01)i		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) H01M 10/0567(2010.01); H01G 9/038(2006.01); H01M 10/05(2010.01); H01M 10/052(2010.01); H01M 10/0525(2010.01); H01M 10/36(2006.01)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Korean utility models and applications for utility models: IPC as above Japanese utility models and applications for utility models: IPC as above		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) eKOMPASS (KIPO internal), STN (Registry, Caplus) & keywords: 비수 전해액(non-aqueous electrolyte), 리튬염(lithium salt), 유기용매(organic solvent), 첨가제(additive), 피라졸 유도체(pyrazole derivative)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "D" document cited by the applicant in the international application "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 18 November 2022		Date of mailing of the international search report 18 November 2022
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon Building 4, 189 Cheongsaro, Seo-gu, Daejeon 35208 Facsimile No. +82-42-481-8578		Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

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Form PCT/ISA/210 (patent family annex) (July 2022)

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