

DESCRIPTION

TITLE OF INVENTION: CARBON NANOTUBE DISPERSION LIQUID,
METHOD FOR PREPARING SAME, ELECTRODE SLURRY COMPOSITION
5 COMPRISING SAME, ELECTRODE COMPRISING SAME, AND LITHIUM
SECONDARY BATTERY COMPRISING SAME

Technical Field

[1] The present specification claims priority to Korean
10 Patent Application No. 10-2021-0185214, filed December 22,
2021, and Korean Patent Application No. 10-2022-0171427, filed
December 9, 2022, the entire contents of which are
incorporated herein for all purposes by this reference.

[2] The present specification relates to a carbon nanotube
15 dispersion liquid, a method of preparing the same, an
electrode slurry composition including the same, an electrode
including the same, and a lithium secondary battery including
the same.

20 Background Art

[3] Secondary batteries are types of batteries capable of
being repeatedly used through discharging processes in which
chemical energy is converted to electrical energy and charging
processes, that is, the reverse of the discharging processes.
25 A secondary battery is composed of a positive electrode, a
negative electrode, an electrolyte, and a separator. Each of
the positive and negative electrodes typically includes an
electrode current collector and an electrode active material
layer formed on the electrode current collector. The

electrode active material layer is formed in such a manner that an electrode slurry composition containing an electrode active material, a conductive additive, a binder, and the like is applied on an electrode current collector, dried, and then
5 rolled.

[4] In the related art, point-type conductive additives such as carbon black have been mainly used as conductive additives to improve the conductivity of electrode active materials. However, point-type conductive additives are insignificantly
10 effective in improving electrical conductivity, so excessive amounts thereof thus must be used to obtain sufficient effects. As a result, there is a problem that the amount of electrode active materials included decreases, leading to a decrease in battery capacity.

[5] To solve such problems, attempts to apply highly conductive carbon nanotubes (CNTs) as conductive additives have been actively made. Carbon nanotubes can achieve high conductivity even in small amounts. For this reason, using carbon nanotubes is advantageous in significantly reducing
20 the amount of conductive additives included compared to using carbon black, which may lead to an increase in electric capacity.

[6] On the other hand, with a demand for high-capacity materials to overcome the limitations of graphite (low
25 theoretical capacity), silicon-based negative electrode materials are in the limelight. However, when silicon reacts with lithium, volume expansion at a level of about 100% to 400% results in not only a large initial irreversible capacity but also the collapse of an active material structure and

detachment from a current collector during charging and discharging, leading to loss of electrical contact. As a result, the lifespan characteristics of an electrode deteriorate.

5 [7] Therefore, there is an urgent need to introduce linear carbon nanotubes (single-walled or multi-walled carbon nanotubes) so that the volume expansion of silicon is buffered, and electrical contact is maintained.

[8] However, due to the nature of the material itself, which
10 grows in a bundle type or entangle type, carbon nanotubes have poor dispersibility in a slurry, leading to deterioration in coating properties and processability, and are not evenly distributed in an electrode active material layer, which is problematic. To solve these problems, a method of first
15 mixing carbon nanotubes with a dispersant and a solvent to prepare a carbon nanotube dispersion liquid and then applying the carbon nanotube dispersion liquid to an electrode slurry composition is being used.

[9] Additionally, battery efficiency may be affected
20 depending on the types of dispersants, purity of SWCNTs, degree of water dispersion, and the like.

[10] [Document of related art]

[11] [Patent Document]

[12] JP 2010-251293 A

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Detailed Description of the Invention

Technical Problem

[13] Proposed are a carbon nanotube dispersion liquid having improved dispersion stability, a method of preparing the same,

an electrode slurry composition including the same, an electrode including the same, and a lithium secondary battery including the same.

5 **Technical Solution**

[14] A first embodiment of the present disclosure provides a carbon nanotube dispersion liquid including single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more and [15] a cellulose-based dispersant,

10 [16] wherein the cellulose-based dispersant has a value of 7 or more and 13 or less calculated by Mathematical Formula 1.

[17] [Mathematical Formula 1]

[18] Degree of substitution (DS) of cellulose-based dispersant/(weight average molecular weight of cellulose-
15 based dispersant) * 10^6

[19] Additionally, a second embodiment of the present disclosure provides a method of preparing the carbon nanotube dispersion liquid described above, the method including mixing single-walled carbon nanotubes (SWCNTs) having a purity of
20 95% or more and a cellulose-based dispersant.

[20] Additionally, a third embodiment of the present disclosure provides an electrode slurry composition including the carbon nanotube dispersion liquid described above, a silicon-based electrode active material, and a binder.

25 [21] Additionally, a fourth embodiment of the present disclosure provides an electrode including an electrode active material layer formed by the electrode slurry composition described above.

[22] Additionally, a fifth embodiment of the present

disclosure provides a lithium secondary battery including the electrode described above.

Advantageous Effects

5 [23] A carbon nanotube dispersion liquid, according to one embodiment of the present disclosure, can improve dispersion stability.

Best Mode for Carrying Out the Invention

10 [24] Hereinafter, the present disclosure will be described in detail.

[25] As used herein, "carbon nanotube dispersion liquid" refers to a dispersion liquid containing carbon nanotubes, specifically meaning that carbon nanotubes are dispersed in
15 the dispersion liquid and do not aggregate with each other.

[26] As used herein, "carbon nanotube" refers to "single-walled carbon nanotube", unless otherwise specified.

[27] As used herein, single-walled carbon nanotubes refer to carbon nanotubes in which the number of bonds forming the wall
20 is 1.

[28] As used herein, the carbon nanotubes may have a two-dimensional structure in which a plurality of carbon nanotubes is aggregated or arranged, which may be, for example, bundle-type carbon nanotubes, in which a plurality of carbon
25 nanotubes is arranged or aligned side by side in a uniform direction in a bundle-like or rope-like shape, or entangled-type carbon nanotubes, in which a plurality of carbon nanotubes is tangled without a uniform direction in a spherical or potato shape.

[29] A first embodiment of the present disclosure provides a carbon nanotube dispersion liquid including single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more and [30] a cellulose-based dispersant,

5 [31] wherein the cellulose-based dispersant has a value of 7 or more and 13 or less calculated by Mathematical Formula 1.

[32] [Mathematical Formula 1]

[33] Degree of substitution (DS) of cellulose-based dispersant/(weight average molecular weight of cellulose-
10 based dispersant) * 10^6

[34] The carbon nanotube dispersion liquid, according to the embodiment of the present disclosure, is characterized in that despite containing the single-walled carbon nanotubes having excellent conductivity, the dispersibility of the carbon
15 nanotubes is improved, thereby minimizing the interaction between the carbon nanotubes. Such characteristics may be verifiable by the significantly low viscosity of the dispersion liquid.

[35] The carbon nanotube dispersion liquid, according to the
20 embodiment of the present disclosure, contains the cellulose-based dispersant. The cellulose-based dispersant is characterized by having high dispersibility and lithium-ion conductivity. In other words, a high-performance lithium-ion battery may be manufactured when manufacturing a lithium-ion
25 battery using the carbon nanotube dispersion liquid containing the cellulose-based dispersant.

[36] In the embodiment of the present disclosure, the cellulose-based dispersant is characterized in that the value calculated by Mathematical Formula 1 is 7 or more and 13 or

less. Preferably, the value calculated by Mathematical Formula 1 is 8 or more and 10 or less, or 9 or more and 11 or less. When the above numerical range is satisfied, there may be the following advantages in improving the structural
5 stability of the dispersant, improving the dispersibility of the dispersion liquid, stabilizing the viscosity of the dispersion liquid, and evenly distributing the carbon nanotubes contained in the dispersion liquid. The application of such a dispersion liquid characterized as described above
10 to a battery is effective in improving the efficiency and capacity of the battery.

[37] In the embodiment of the present disclosure, the degree of substitution of the cellulose-based dispersant may be 0.3 or more and 2 or less and, preferably, is 0.5 or more and 1.2
15 or less, or 0.7 or more and 1 or less. When the above numerical range is satisfied, the solubility of the dispersant in the dispersion liquid is excellent, and the dispersibility of the carbon nanotubes may be improved.

[38] In the embodiment of the present disclosure, the degree
20 of substitution of the cellulose-based dispersant refers to the average number of substituent groups substituted for cellulose per cellulose repeat unit. In this case, the substituent group may be a methyl group, an ethyl group, a hydroxy group, a benzyl group, a trityl group, a cyano group,
25 a carboxymethyl group, a carboxyethyl group, a hydroxyethyl group, an aminoethyl group, a nitro group, and the like.

[39] In the embodiment of the present disclosure, the cellulose-based dispersant may have a weight average molecular weight in a range of 30,000 to 1,000,000, which is preferably

in the range of 50,000 to 800,000 or 60,000 to 200,000. When the above numerical range is satisfied, the solubility of the dispersant in the dispersion liquid is excellent. Additionally, there may be the following advantages in
5 improving the dispersibility of the carbon nanotubes and the dispersion stability. The unit of the weight average molecular weight may be g/mol.

[40] In the embodiment of the present disclosure, the cellulose-based dispersant may be methyl cellulose, ethyl
10 cellulose, hydroxyethyl cellulose, benzyl cellulose, trityl cellulose, cyanoethyl cellulose, carboxymethyl cellulose (CMC), carboxyethyl cellulose, aminoethyl cellulose, nitrocellulose, cellulose ether, a carboxymethyl cellulose sodium (CMCNa) salt, or a combination thereof.

15 [41] In the embodiment of the present disclosure, the cellulose-based dispersant may be carboxymethyl cellulose (CMC), a carboxymethyl cellulose sodium (CMCNa) salt, or a combination thereof. These materials have good solubility in water, high viscosity, and excellent coating properties. When
20 the dispersion liquid containing such a material described above is applied to a battery, battery performance may be improved.

[42] In the embodiment of the present disclosure, the single-walled carbon nanotubes may have a specific surface area (BET)
25 of 750 m²/g or larger. Preferably, the specific surface area is 900 m²/g or larger, or 1,000 m²/g or larger. The upper limit is not particularly limited but may be 2,000 m²/g or smaller, 1,800 m²/g or smaller, or 1,500 m²/g or smaller. Within the above numerical range, the aggregation of the

single-walled carbon nanotubes may be controlled, and electrical conductivity may be improved.

[43] In the embodiment of the present disclosure, the carbon nanotube dispersion liquid contains the single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more.

[44] In the embodiment of the present disclosure, the single-walled carbon nanotubes (SWCNTs) may have a purity of 96% or more, or 97% or more, which is preferably 99% or more. The purity may refer to the weight ratio of a carbon element (C) to the mass of the carbon nanotubes. When the above numerical range is satisfied, the electrical conductivity of the carbon nanotubes is improved.

[45] In the embodiment of the present disclosure, the single-walled carbon nanotubes may be contained in an amount in a range of 0.1 to 5 wt% based on the total weight of the carbon nanotube dispersion liquid. Additionally, the amount thereof contained may be in a range of 0.4 to 4 wt% or 1 to 2 wt%. When the amount thereof contained exceeds the above numerical range, the loading amount is reduced when manufacturing an electrode, resulting in an increase in process costs. Additionally, there may be a problem of binder migration when drying an electrode, leading to a decrease in adhesive strength, an increase in the viscosity of the carbon nanotube dispersion liquid, or the like. In other words, when the above numerical range is satisfied, the high-rate retention capacity and initial efficiency of an electrode to be manufactured may be improved.

[46] In the embodiment of the present disclosure, the single-walled carbon nanotubes may include two or more carbon

nanotube monomers. The carbon nanotube monomers may have a cylindrical form in which a graphite sheet has a nano-sized diameter while having a sp^2 -bonded structure.

[47] In the embodiment of the present disclosure, the carbon
5 nanotube monomers may have a diameter of 1 nm or larger and 200 nm or smaller, 1 nm or larger and 150 nm or smaller, or 1 nm or larger and 100 nm or smaller. Within the above numerical range, the dispersibility of the carbon nanotubes may be improved, and resistance may be prevented from increasing when
10 applied to an electrode.

[48] In the embodiment of the present disclosure, the carbon nanotube monomers may have a length in a range of 0.1 μm or greater and 200 μm or smaller, 0.1 μm or greater and 150 μm or smaller, or 0.5 μm or greater and 100 μm or smaller. Within
15 the above numerical range, the dispersibility of the carbon nanotubes may be improved, and resistance may be prevented from increasing when applied to an electrode.

[49] In the embodiment of the present disclosure, the carbon nanotubes may have an aspect ratio (length/diameter) in a
20 range of 5 to 50,000 or 10 to 15,000. Within the above numerical range, the dispersibility of the carbon nanotubes may be improved, and resistance may be prevented from increasing when applied to an electrode.

[50] In the embodiment of the present disclosure, the carbon
25 nanotubes may have a median particle size (D50) in a range of 0.1 to 10 μm , 0.5 to 1 μm , 1 to 5 μm , or 2 to 4 μm . The median particle size (D50) refers to a particle size corresponding to 50% of the cumulative number in the particle size distribution curve of the carbon nanotubes. The median

particle size (D50) may be measured, for example, using a laser diffraction method. Within the above numerical range, the carbon nanotubes may not aggregate with each other while improving dispersibility. In the embodiment of the present disclosure, the carbon nanotubes may have a specific surface area (BET) in a range of 10 to 5,000 m²/g, which is preferably in the range of 30 to 3,000 m²/g and more preferably in the range of 500 to 2,000 m²/g. When the specific surface area of the carbon nanotubes satisfies the above numerical range, the effect of improving conductivity is excellent.

[51] In the embodiment of the present disclosure, the single-walled carbon nanotubes may have an average particle size (D10) of 0.1 μm or larger and 10 μm or smaller, which is preferably 0.3 μm or larger and 8 μm or smaller, or 0.5 μm or larger and 5 μm or smaller.

[52] In the embodiment of the present disclosure, the single-walled carbon nanotubes may have an average particle size (D90) of 0.1 μm or larger and 20 μm or smaller, which is preferably 1 μm or larger and 20 μm or smaller, or 5 μm or larger and 20 μm or smaller.

[53] In the particle size distribution curve of the carbon nanotubes, the average particle size (D10) refers to a particle size corresponding to 10% of the cumulative number, the median particle size (D50) refers to a particle size corresponding to 50% of the cumulative number, and the average particle size (D90) refers to a particle size corresponding to 90% of the cumulative number.

[54] When one or more of the average particle size conditions described above are satisfied, the carbon nanotubes may not

aggregate with each other while improving dispersibility.

[55] In the embodiment of the present disclosure, the carbon nanotube dispersion liquid may further contain multi-walled carbon nanotubes in addition to the single-walled carbon
5 nanotubes described above.

[56] In the embodiment of the present disclosure, an aqueous solvent may be included.

[57] In the embodiment of the present disclosure, one or more selected from the group consisting of water, alcohol, and
10 ether may be used as the aqueous solvent.

[58] In the embodiment of the present disclosure, the aqueous solvent used may be ethers (such as dioxane, tetrahydrofuran, and methyl cellosolve), ether alcohols (such as ethoxy ethanol and methoxy ethoxy ethanol), esters (such as methyl acetate
15 and ethyl acetate), ketones (such as cyclohexanone and methyl ethyl ketone), alcohols (such as ethanol, isopropanol, and phenol), lower carboxylic acids (such as acetic acid), amines (such as triethylamine and new methanol amine), nitrogen-containing polar solvents (such as N,N-dimethylformamide,
20 nitromethane, N-methylpyrrolidone, and acetonitrile), sulfur compounds (such as dimethyl sulfoxide), and the like.

[59] In the embodiment of the present disclosure, the carbon nanotube dispersion liquid may have a viscosity of 10,000 cPs or less at a temperature of 25°C and a shear rate of 15 sec⁻¹, which is preferably 5,000 cPs or less, 3,000 cPs or less,
25 or 2,000 cPs or less. Considering the purpose of the present disclosure, the lower the viscosity, the more it is beneficial. Thus, the lower limit is not particularly limited, but the viscosity may be 10 cPs or more, 30 cPs or

more, or 50 cPs or more. When the above numerical range of the viscosity is satisfied, the carbon nanotubes in the carbon nanotube dispersion liquid may not aggregate with each other, whereby processability thereof may be improved when used to
5 manufacture an electrode.

[60] The viscosity of the carbon nanotube dispersion liquid may be measured by methods commonly used in the field to which this technology pertains. For example, the measurement may be performed using a DVNext CP rheometer manufactured by
10 Brookfield at a measurement temperature of 25°C and a shear rate of 15 sec⁻¹. To further accurately measure the viscosity, the measurement may be performed after storing the prepared carbon nanotube dispersion liquid for one week at a temperature of 25°C.

[61] A second embodiment of the present disclosure provides a method of preparing the carbon nanotube dispersion liquid described above, the method including a step of mixing single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more and a cellulose-based dispersant.

[62] In the embodiment of the present disclosure, the mixing step of the single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more and the cellulose-based dispersant may be performed under a temperature condition where the physical properties do not change. For example, this step may be
20 performed at a temperature of 50°C or lower and, more specifically, at a temperature in the range of 5°C to 50°C.

[63] In the embodiment of the present disclosure, the method of preparing the carbon nanotube dispersion liquid may include a step of dispersing the single-walled carbon nanotubes

(SWCNTs) having a purity of 95% or more.

[64] In the embodiment of the present disclosure, the dispersing step of the single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more may be performed by methods
5 using a ball mill, a bead mill, a disc mill, a basket mill, a high-pressure homogenizer, or the like and, more specifically, may be performed by milling methods using a disc mill or a high-pressure homogenizer.

[65] During milling using the disc mill, the size of beads
10 may be appropriately determined depending on the type and amount of carbon nanotubes and the type of dispersant. Specifically, the diameter of the beads may be in a range of 0.1 to 5 mm and, more specifically, in the range of 0.5 to 4 mm. Additionally, this bead milling process may be performed
15 at a speed in a range of 2,000 to 10,000 rpm, which may be more specifically in the range of 5,000 to 9,000 rpm.

[66] Milling using the high-pressure homogenizer, for example, is performed by forces such as cavitation, shear, impact, and explosion when allowed to pass through the gap by
20 compressing the resulting mixture with a plunger pump of the high-pressure homogenizer and pushing the same through the gap of the homogenization valve.

[67] In the embodiment of the present disclosure, the dispersing step of the single-walled carbon nanotubes (SWCNTs)
25 having a purity of 95% or more may be performed for 10 to 120 minutes and, more specifically, for 20 to 90 minutes so that the carbon nanotubes are sufficiently dispersed.

[68] A third embodiment of the present disclosure provides an electrode slurry composition including the carbon nanotube

dispersion liquid described above, an electrode active material, and a binder.

[69] In the embodiment of the present disclosure, the electrode active material includes a silicon-based electrode active material. The silicon-based electrode active material may include one or more types selected from the group consisting of metal silicon (Si), a silicon oxide (SiO_x , where $0 < x < 2$), silicon carbide (SiC), and a Si-Y alloy (where Y is an element selected from the group consisting of an alkali metal, an alkaline earth metal, an element of group 13, an element of group 14, a transition metal, a rare-earth element, and a combination thereof, but not Si). The element Y may be selected from the group consisting of Mg, Ca, Sr, Ba, Ra, Sc, Y, Ti, Zr, Hf, Rf, V, Nb, Ta, Db, 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, Tl, Ge, P, As, Sb, Bi, S, Se, Te, Po, and a combination thereof.

[70] In the embodiment of the present disclosure, the silicon-based electrode active material exhibits higher capacity characteristics than carbon-based electrode active materials. Therefore, when the silicon-based electrode active material is additionally included, further excellent capacity characteristics may be obtained. Still, the volume of the silicon-based electrode active material greatly changes during charging and discharging. For this reason, when being repeatedly charged and discharged, battery characteristics rapidly deteriorate, so cycle characteristics are insufficient, making the silicon-based electrode active material challenging to commercialize. However, in the case

of using carbon nanotubes as a conductive additive, as in the present disclosure, cycle characteristics may be improved when applying the silicon-based electrode active material. As a result, when using the electrode slurry composition of the present disclosure, including the carbon nanotube dispersion liquid of the present disclosure and the silicon-based electrode active material, a secondary battery having excellent capacity characteristics and cycle characteristics may be implemented.

[71] In the embodiment of the present disclosure, the electrode active material may further include other types of electrode active materials along with the silicon-based electrode active material. Examples of the other types of electrode active materials used may include: carbonaceous materials, such as artificial graphite, natural graphite, graphitized carbon fibers, and amorphous carbon; metallic compounds capable of forming an alloy with lithium, such as Al, Sn, Pb, Zn, Bi, In, Mg, Ga, Cd, Si alloys, Sn alloys, or Al alloys; metal oxides capable of doping and undoping lithium, such as SnO₂, vanadium oxide, and lithium vanadium oxide; composites containing the metallic compound and the carbonaceous material described above, such as Sn-C composites; or the like. Among these materials, carbonaceous materials are particularly preferable.

[72] In the embodiment of the present disclosure, the total amount of the electrode active material, which is a combination of the silicon-based electrode active material and the other types of electrode active materials, may be in a range of 70 to 99 wt% and is preferably in the range of 80

to 98 wt%, based on the total amount of solid content in the electrode slurry composition. When the amount of the electrode active material included satisfies the above numerical range, excellent capacity characteristics may be
5 achieved.

[73] In the embodiment of the present disclosure, as the binder configured to obtain adhesive strength between the active materials or between the active material and a current collector, any binders commonly used in the field to which
10 this technology pertains may be usable, and the types thereof are not particularly limited. Examples of the binder used may include polyvinylidene fluoride (PVDF), vinylidene fluoride-hexafluoropropylene copolymers (PVDF-co-HFP), polyvinyl alcohol, polyacrylonitrile, carboxymethyl cellulose
15 (CMC), starch, hydroxypropyl cellulose, regenerated cellulose, polyvinylpyrrolidone, tetrafluoroethylene, polyethylene, polypropylene, ethylene-propylene-diene polymers (EPDMs), sulfonated-EPDMs, styrene-butadiene rubber (SBR), fluorine rubber, or various copolymers thereof. Among
20 these examples, a single type or a mixture of two or more types may be used.

[74] In the embodiment of the present disclosure, the binder may be included in an amount of 5 wt% or less based on the total amount of the solid content, which is preferably in the
25 range of 1 to 3 wt%. When the amount of the binder included satisfies the above numerical range, excellent adhesive strength to electrodes may be achieved while minimizing an increase in electrode resistance.

[75] In the embodiment of the present disclosure, the

electrode slurry composition may further contain a solvent, if necessary, to adjust the viscosity and the like. In this case, the solvent may be water, an organic solvent, or a mixture thereof. Examples of the organic solvent may include:

5 amide-based polar organic solvents, such as dimethylformamide (DMF), diethylformamide, dimethylacetamide (DMAc), and N-methylpyrrolidone (NMP); alcohols, such as methanol, ethanol, 1-propanol, 2-propanol (isopropyl alcohol), 1-butanol (n-butanol), 2-methyl-1-propanol (isobutanol), 2-butanol (sec-

10 butanol), 1-methyl-2-propanol (tert-butanol), pentanol, hexanol, heptanol, or octanol; glycols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,3-propanediol, 1,3-butanediol, 1,5-pentanediol, or hexylene glycol; polyhydric alcohols, such as glycerin,

15 trimethylolpropane, pentaerythritol, or sorbitol; glycol ethers, such as ethylene glycol monomethyl ether, diethylene glycol monomethyl ether, triethylene glycol monomethyl ether, tetraethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monoethyl ether,

20 triethylene glycol monoethyl ether, tetraethylene glycol monoethyl ether, ethylene glycol monobutyl ether, diethylene glycol monobutyl ether, triethylene glycol monobutyl ether, or tetraethylene glycol monobutyl ether; ketones, such as acetone, methyl ethyl ketone, methyl propyl ketone, or

25 cyclopentanone; esters such as ethyl acetate, γ -butyl lactone, and ϵ -propiolactone; and the like. Among these examples, a single type or a mixture of two or more types may be used, but the organic solvent is not limited thereto.

[76] In the embodiment of the present disclosure, the

electrode slurry composition may further contain additives such as a viscosity modifier and a filler, if necessary.

[77] A fourth embodiment of the present disclosure provides an electrode including an electrode active material layer
5 formed by the electrode slurry composition described above. Specifically, the electrode may be manufactured by applying the electrode slurry composition of the present disclosure described above and then drying the resulting product to form the electrode active material layer. More specifically, the
10 electrode active material layer may be formed by a method of applying the electrode slurry composition on an electrode current collector and then drying the resulting product, or by a method of applying the electrode slurry composition on a separate support and then laminating a film obtainable by
15 being detached from the support, on the electrode current collector. If necessary, the electrode active material layer may be formed in such a manner and then subjected to an additional rolling process. In this case, the drying and rolling processes may be performed under appropriate
20 conditions considering the physical properties of an electrode to be ultimately manufactured, but are not particularly limited.

[78] In the embodiment of the present disclosure, the electrode current collector is not particularly limited as
25 long as it is made of a conductive material that does not cause chemical changes in batteries. Examples thereof used may include copper, stainless steel, aluminum, nickel, titanium, and alloys thereof, these metals whose surface is treated with carbon, nickel, titanium, silver, and the like,

or sintered carbon.

[79] In the embodiment of the present disclosure, the electrode current collector may typically have a thickness in a range of 3 to 500 μm . Additionally, the bonding strength of the electrode active material may be strengthened by forming fine protrusions and depressions on the surface of the current collector. Furthermore, the electrode current collector used may have various forms, such as a film, sheet, foil, net, porous material, foam, and non-woven material.

10 [80] In the embodiment of the present disclosure, the electrode may be a negative electrode.

[81] A fifth embodiment of the present disclosure provides a lithium secondary battery including the electrode described above.

15 [82] In the embodiment of the present disclosure, provided is a lithium secondary battery including a positive electrode, a negative electrode, a separator positioned between the positive and negative electrodes, and an electrolyte, in which one or more of the positive and negative electrodes is the electrode described above.

20 [83] In the embodiment of the present disclosure, the separator is configured to separate the negative and positive electrodes and provide a passage for lithium ions to move. Any separators commonly used in secondary batteries may be usable without particular limitations. Specifically, as the separator, a porous polymer film, for example, a porous polymer film formed using polyolefin-based polymers, such as ethylene homopolymers, propylene homopolymers, ethylene/butene copolymers, ethylene/hexene copolymers, and

ethylene/methacrylate copolymers, or a laminated structure thereof consisting of two or more layers may be used. Additionally, common porous non-woven fabrics, for example, non-woven fabrics made of polyethylene terephthalate fibers, 5 glass fibers having high melting points, and the like, may be used. Furthermore, a coated separator containing ceramic components or polymeric materials may be used to obtain heat resistance or mechanical strength, which may be optionally used in a structure consisting of a single layer or multiple 10 layers.

[84] In the embodiment of the present disclosure, examples of the electrolyte may include an organic liquid electrolyte, an inorganic liquid electrolyte, a solid polymer electrolyte, a gel-type polymer electrolyte, a solid inorganic electrolyte, 15 and a molten inorganic electrolyte, which may be usable when manufacturing lithium secondary batteries, but are not limited thereto.

Mode for Invention

20 [85] Hereinafter, the present disclosure will be described in more detail through examples.

[86] <Example 1>

[87] Single-walled carbon nanotube (TUBALL 01RW03, prepared by OCSiAl, specific surface area: 1,160 m²/g) having a purity 25 of 99%, carboxymethyl cellulose {degree of substitution (DS): 0.87, Product number: 419273, prepared by Sigma Aldrich, weight average molecular weight: 90,000} as a cellulose-based dispersant, and water as a solvent were mixed to prepare 1 kg of a mixture, which was then mixed using a high-shear force

in-line mixer (manufactured by IM001 K&S) and subjected to high-pressure treatment using a high-pressure homogenizer to prepare a carbon nanotube dispersion liquid. In this case, the single-walled carbon nanotubes had a D10 of 0.88 um, a D50 of 4.72 um, and a D90 of 18.5 um.

[88] In this case, the carboxymethyl cellulose had a value of 9.67 calculated by Mathematical Formula 1.

[89] [Mathematical Formula 1]

[90] Degree of substitution (DS) of cellulose-based dispersant/(weight average molecular weight of cellulose-based dispersant) * 10⁶

[91] **<Comparative Example 1>**

[92] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using single-walled carbon nanotubes (TUBALL 01RW02, prepared by OCSiAl) having a purity of 80% instead of the single-walled carbon nanotubes having a purity of 99%.

[93] **<Comparative Example 2>**

[94] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using single-walled carbon nanotubes (TUBALL 01RW01, prepared by OCSiAl) having a purity of 75% instead of the single-walled carbon nanotubes having a purity of 99%.

[95] **<Comparative Example 3>**

[96] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using single-walled carbon nanotubes having particle size characteristics as in Table 1 below and using polyvinylpyrrolidone and tannic acid as the dispersant instead of carboxymethyl cellulose.

[97] **<Comparative Example 4>**

[98] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using polyvinylpyrrolidone and HP20 (Sokalan HP20, prepared by BASF) as the dispersant instead of carboxymethyl cellulose.

[99] **<Comparative Example 5>**

[100] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using polyvinylpyrrolidone alone as the dispersant instead of carboxymethyl cellulose.

[101] **<Comparative Example 6>**

[102] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using carboxymethyl cellulose {degree of substitution (DS): 1.2, weight average molecular weight: 90,000} instead of carboxymethyl cellulose used in Example 1. In this case, the carboxymethyl cellulose used herein had a value of 13.33 calculated by Mathematical Formula 1.

[103] **<Comparative Example 7>**

[104] A carbon nanotube dispersion liquid was prepared in the same manner as in Example 1, except for using carboxymethyl cellulose {degree of substitution (DS): 0.6, Catalog number: 332601000, prepared by Thermo Scientific, weight average molecular weight: 90,000} instead of carboxymethyl cellulose used in Example 1. In this case, the carboxymethyl cellulose used herein had a value of 6.67 calculated by Mathematical Formula 1.

[105] **<Comparative Example 8>**

[106] A carbon nanotube dispersion liquid was prepared in the

same manner as in Example 1, except for using carboxymethyl cellulose {degree of substitution (DS): 0.87, Product number: 419303, prepared by Sigma-Aldrich, weight average molecular weight: 250,000} instead of carboxymethyl cellulose used in
5 Example 1. In this case, the carboxymethyl cellulose used herein had a value of 3.48 calculated by Mathematical Formula 1.

[107] **<Evaluation of physical properties>**

[108] **Measurement of purity of single-walled carbon nanotubes**

10 [109] Purity was measured and calculated by the method of the calculation equation below.

[110] [Calculation Equation]

[111]
$$\text{Purity} = 100 * (\text{Mass of test container and ash} - \text{Mass of test container}) / (\text{Mass of test container and dried sample} -$$

15
$$\text{Mass of test container})$$

[112] Specifically, the amount of impurities capable of being incorporated during an electrode manufacturing process was analyzed using an electric furnace. The sample was dried according to a method, the test procedure KS L 3412, and
20 cooled to room temperature in a desiccator.

[113] With the use of a scale, the mass of dried test container A was measured to the nearest ± 0.002 g, and 25 to 50 g of sample B was placed into a crucible to measure the mass once the sample in the desiccator cooled to room temperature. The
25 mass of the sample and the test container was re-measured to the nearest ± 0.002 g.

[114] The test container containing the sample was positioned in the electric furnace, followed by injecting air thereinto at a slow rate, and the furnace was operated so that the

sample reached a temperature of 500°C within 1 hour or 750°C within 2 hours.

[115] The sample was periodically mixed to help oxidize the sample. When completely ashed (the black stain disappeared),
5 the electric furnace was heated to a temperature of up to 950°C, and the same temperature was maintained for 1 hour. The test container containing the ash was taken out of the electric furnace and cooled to room temperature in the desiccator, followed by measuring the mass of the test
10 container containing the ash. The sample was placed back into the electric furnace at a temperature of 950°C and heated for 30 minutes, followed by measuring mass C to the nearest $\pm$ 0.002 g.

[116] **Measurement of degree of substitution of cellulose-based
15 dispersant**

[117] Into 250 ml of a beaker, 4 g of the cellulose-based dispersant sample used in the example and comparative examples, 75 ml of a 95% ethanol solution, and phenolphthalein (1% ethanol solution) were introduced and stirred while adding
20 a standard sodium hydroxide solution (0.4 mol/L).

[118] Then, the resulting product was stirred using a magnetic heating stirrer and titrated using a standard hydrochloric acid solution (0.4 mol/L).

[119] The titration was completed when the color turned from
25 dark red to transparent.

[120] The degree of substitution of the cellulose-based dispersant was calculated using Equation 1 below.

[121] [Equation 1]

$$[122] \text{DS} = (0.162 * A) / (1 - 0.058 * A)$$

[123] The A is the number of millimoles (mmol/g) of sodium hydroxide used to neutralize 1 g of the cellulose-based dispersant, and the unit of the coefficients, 0.162 and 0.058, of A is g/mmol.

5 [124] The A was calculated using Equation 2 below.

[125] [Equation 2]

[126] $A = (B * C - D * E) / F$

[127] In Equation 2,

[128] B is the volume (mL) of the sodium hydroxide standard
10 solution added,

[129] C is the concentration (mol/L) of the sodium hydroxide standard solution added,

[130] D is the volume (mL) of the hydrochloric acid standard solution used during the titration,

15 [131] E is the concentration (mol/L) of the hydrochloric acid standard solution used during the titration, and

[132] F is the weight (g) of the cellulose-based dispersant sample.

[133] **Measurement of weight average molecular weight of
20 cellulose-based dispersant**

[134] Measurement was performed by gel permeation chromatography (GPC) using the following: a detector: RI-detector; a column: Agilent PL aquagel-OH30 8 um; an eluent: 0.2 M NaNO₃ + 0.01 M NaH₂PO₄ (pH 7); and a standard material:
25 PEF/PEO.

[135] **Measurement method of particle size of single-walled carbon nanotubes**

[136] A laser diffraction method was used, and a laser diffraction particle size measuring device (Malvern

Mastersizer3000) available at this time was used. The median particle size (D50) based on 50% of the particle size distribution was calculated using the measuring device. On the other hand, D10 and D90 mean the particle sizes corresponding to 10% and 90% of the particle size distribution, respectively.

[137] **Measurement method of viscosity of dispersion liquid**

[138] A DVNext CP rheometer manufactured by Brookfield was used, and the measurement was performed at a temperature of 25°C and a shear rate of 15 sec⁻¹.

[139] **Measurement of initial cell efficiency**

[140] A coin cell was manufactured as follows.

[141] An electrode slurry was prepared by mixing an electrode active material (including silicon microparticles and graphite in a 7:93 weight ratio) with water in each of the carbon nanotube dispersion liquids of the example and comparative examples and then mixing the resulting product for 30 minutes using a ball-milling method.

[142] The electrode slurry was applied onto a Cu foil current collector and dried for 4 hours at a temperature of 60°C under vacuum conditions.

[143] The dried electrode was punched to a diameter of 11 mm, and Li metal was used as the counter electrode, thereby manufacturing a coin half-cell. In this case, Celgard 2450 was used as a separator, and a composition of LiPF₆ (1.3 M) in ethylene carbonate (EC): diethylene carbonate (DEC) in a 30:70 volume ratio with 10 wt% of fluoroethylene carbonate (FEC) was prepared and injected as an electrolyte.

[144] The initial charge and discharge characteristics of the

coin cell were evaluated under the following conditions: 0.1 A/g, room temperature, and a voltage level in a range of 0.01 to 1.5 V.

[145] **Measurement of high-rate retention capacity of cell**

5 [146] The final charge and discharge characteristics of each coin cell manufactured above were evaluated at 2 A/g and 4 A/g.

[147] [Table 1]

Classification	Example 1	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8
SWCNT purity	99%	80%	75%	99%	99%	99%	99%	99%	99%
Degree of substitution of cellulose-based dispersant	0.87	0.87	0.87	Not included	Not included	Not included	1.2	0.6	0.87
Weight average molecular weight of cellulose-based dispersant	90,000	90,000	90,000	Not included	Not included	Not included	90,000	90,000	250,000
Mathematical Formula 1	9.67	9.67	9.67	—	—	—	13.33	6.67	3.48
D10 (um)	0.88	0.89	0.89	0.45	0.88	0.88	1.51	2.22	2.05
D50 (um)	4.72	4.73	4.74	1.59	4.72	4.72	5.1	8.11	22
D90 (um)	18.5	21.75	23.74	9.74	18.5	18.5	30	32.1	90.3
Viscosity (cPs)	1,411	4,500	7,196	79.8	More than 15,000	More than 15,000	4,060	5,044	More than 15,000
Initial efficiency (%)	78.5	71.4	70.6	71.5	71.1	63.4	72.5	72.3	72

High-rate retention capacity (mAh/g, at 2 A/g)	300	100	100	100	80	Not measurable	150	140	110
High-rate retention capacity (mAh/g, at 4 A/g)	200	50	50	60	40	Not measurable	90	80	60

[148] From the above results, it was confirmed that the carbon nanotube dispersion liquid, including the single-walled carbon nanotubes having a purity of 99% and the cellulose-based dispersant having a value of 7 or more and 13 or less calculated by Mathematical Formula 1, exhibited low viscosity and had high initial efficiency and high-rate retention capacity (Example 1). On the other hand, it was confirmed that when the single-walled carbon nanotubes had a purity of less than 95%, the viscosity was high, and the initial efficiency and high-rate retention capacity were low (Comparative Examples 1 and 2). Additionally, even when the single-walled carbon nanotubes had a purity of 95% or more, it was confirmed that the initial efficiency and high-rate retention capacity were low when not involving the cellulose-based dispersant (Comparative Examples 3 to 5).

[149] On the other hand, even when the single-walled carbon nanotubes had a purity of 95% or more, it was confirmed that the initial efficiency and high-rate retention capacity were low when the value calculated by Mathematical Formula 1 was less than 7 (Comparative Examples 7 and 8), or when the value calculated by Mathematical Formula 1 exceeded 13 (Comparative Example 6).

CLAIMS

1. A carbon nanotube dispersion liquid comprising:
single-walled carbon nanotubes (SWCNTs) having a purity
5 of 95% or more; and

a cellulose-based dispersant, wherein the cellulose-based dispersant has a value of 7 or more and 13 or less calculated by Mathematical Formula 1.

[Mathematical Formula 1]

10 Degree of substitution (DS) of cellulose-based dispersant/(weight average molecular weight of cellulose-based dispersant) * 10^6

2. The dispersion liquid of claim 1, wherein the degree
15 of substitution of the cellulose-based dispersant is 0.3 or more and 2 or less.

3. The dispersion liquid of claim 1, wherein the cellulose-based dispersant has a weight average molecular
20 weight in a range of 30,000 to 1,000,000.

4. The dispersion liquid of claim 1, wherein the cellulose-based dispersant is methyl cellulose, ethyl cellulose, hydroxyethyl cellulose, benzyl cellulose, trityl
25 cellulose, cyanoethyl cellulose, carboxymethyl cellulose (CMC), carboxyethyl cellulose, aminoethyl cellulose, nitrocellulose, cellulose ether, a carboxymethyl cellulose sodium (CMCNa) salt, or a combination thereof.

5. The dispersion liquid of claim 1, wherein the single-walled carbon nanotubes have a specific surface area (BET) of 750 m²/g or larger.

5 6. The dispersion liquid of claim 1, wherein the single-walled carbon nanotubes are comprised in an amount in a range of 0.1 to 5 wt% based on the total weight of the dispersion liquid.

10 7. The dispersion liquid of claim 1, wherein the single-walled carbon nanotubes have an average particle size (D50) of 0.1 um or larger and 10 um or smaller.

8. The dispersion liquid of claim 1, wherein the
15 dispersion liquid comprises an aqueous solvent.

9. The dispersion liquid of claim 1, wherein the single-walled carbon nanotubes have an average particle size (D10) of 0.1 um or larger and 10 um or smaller.

20

10. The dispersion liquid of claim 1, wherein the dispersion liquid has a viscosity of 10,000 cPs or less at a temperature of 25°C and a shear rate of 15 sec⁻¹.

25 11. A method of preparing the dispersion liquid of any one of claims 1 to 10, the method comprising mixing a cellulose-based dispersant and single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more.

12. The method of claim 11, wherein the method comprises dispersing the single-walled carbon nanotubes (SWCNTs) having a purity of 95% or more.

5 13. An electrode slurry composition comprising:
the dispersion liquid of any one of claims 1 to 10;
an electrode active material; and
a binder.

10 14. An electrode comprising an electrode active material layer formed by the electrode slurry composition of claim 13.

15 15. The electrode of claim 14, wherein the electrode is a negative electrode.

16. A lithium secondary battery comprising the electrode of claim 15.