

(19) Japanese Patent Office (JP)

(12) Unexamined Patent Gazette (A)

(11) Unexamined Patent Application (Kokai) No.:

Unexamined Patent Application Publication No. 2018-6046
(P2018-6046A)

(43) Publication Date: January 11, 2018

(51) Int. Cl.		F1		Theme Code (Reference)
H01M 10/0569	(2010.01)	H01M 10/0569		5H011
H01M 10/052	(2010.01)	H01M 10/052		5H021
H01M 2/16	(2006.01)	H01M 2/16	L	5H029
H01M 2/02	(2006.01)	H01M 2/02	K	5H050
H01M 4/525	(2010.01)	H01M 4/525		

Request for Examination: Not Requested Number of Claims: 9 OL (Total of 19 pages)
Continued on the past page

(21) Application No.:	Unexamined Patent Application Publication No. 2016-128117 (P2016-128117)	(71) Applicant	590002817 SAMSUNG SDI Co., LTD. 150-20 Gongse-ro, Giheung-gu, Yongin-si, Gyeonggi-do, 446-9 Republic of Korea
(22) Filing Date:	June 28, 2016	(74) Agent	110000981 IPD International Patent Professional Corporation

Continued on the last page

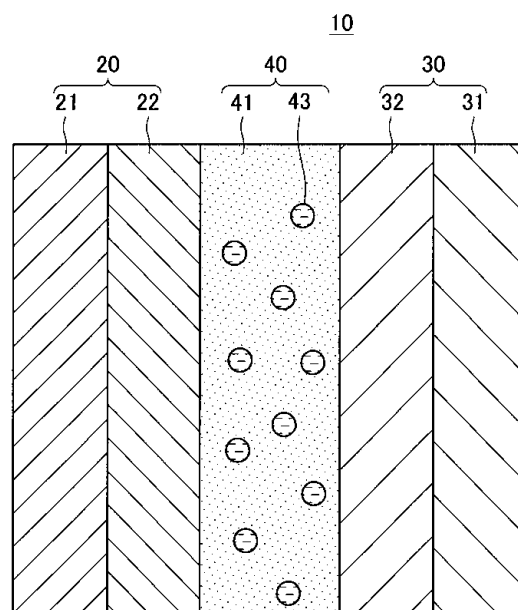
(54) [Title of the Invention] Lithium ion secondary battery

(57) [Abstract] (with correction)

[Problem] To provide a lithium ion secondary battery in which swelling during high-temperature storage is suppressed.

[Solution Means] A Lithium ion secondary battery 10, equipped with a positive electrode 20 comprising lithium cobalt oxide at 75% by mass or more relative to the total mass of the positive electrode active material, two types of carboxylate esters, and an electrolyte 43 comprising a nitrile compound having a molecular weight of 110 or more; wherein of the two types of carboxylate esters, the content of one carboxylate ester with a lower viscosity is greater than the content of the other carboxylate ester with a higher viscosity, and the viscosity of the electrolyte 43 at 20°C is 4.0 mPa·s or more.

[Selected Drawing] FIG. 1



[Claims]

[Claim 1]

A lithium ion secondary battery, equipped with a positive electrode comprising lithium cobalt oxide at 75% by mass or more relative to the total mass of the positive electrode active material, and an electrolyte comprising two types of carboxylate esters and a nitrile compound having a molecular weight of 110 or more; wherein a content of one of the two types of carboxylate esters having a lower viscosity is greater than a content of the other carboxylate ester having a higher viscosity, and the viscosity of the electrolyte at 20°C is 4.0 mPa·s or more.

[Claim 2]

The lithium ion secondary battery according to claim 1, wherein the two types of carboxylate esters are both chain carboxylate esters.

[Claim 3]

The lithium ion secondary battery according to claim 1 or 2, wherein the viscosity of the one of the carboxylate esters at 20°C is 0.50 mPa·s or more and 0.64 mPa·s or less.

[Claim 4]

The lithium ion secondary battery according to any one of claims 1 to 3, wherein the viscosity of the other carboxylic acid ester at 20°C is 0.65 mPa·s or more and 0.75 mPa·s or less.

[Claim 5]

The lithium ion secondary battery according to any one of claims 1 to 4, wherein the density of the positive electrode active material layer after rolling of the positive electrode is 4.0 g/cm³ or more and 4.3 g/cm³ or less.

[Claim 6]

The lithium ion secondary battery according to claim 5, wherein the density of the positive electrode active material layer after rolling of the positive electrode is 4.2 g/cm³ or more and 4.3 g/cm³ or less.

[Claim 7]

The lithium ion secondary battery according to any one of claims 1 to 6, wherein the potential of the positive electrode when fully charged is 4.4 V or more relative to lithium.

[Claim 8]

The lithium ion secondary battery according to any one of claims 1 to 6, further equipped with a negative electrode facing the positive electrode, and a separator layer sandwiched between the positive electrode and the negative electrode; wherein a polymer layer is provided between at least one of the positive electrode or the negative electrode and the separator layer.

[Claim 9]

The lithium ion secondary battery according to any one of claims 1 to 8, wherein the exterior material of the lithium ion secondary battery is a resin film having a laminate structure.

[0001]

The present invention relates to a lithium ion secondary battery.

[Background Art]

[0002]

In recent years, lithium ion secondary batteries have become widespread.

[0003]

Lithium ion secondary batteries have high voltage and capacity, and are therefore expected to be used as power sources for laptop computers, tablet terminals, mobile phones, and the like.

[0004]

In particular, laminated lithium ion secondary batteries, which use a resin film made by laminating resin to aluminum foil as the exterior body, are expected to be used as power sources for portable devices due to their freedom of shape and light weight.

[0005]

However, laminated lithium ion secondary batteries are more susceptible to deformation than lithium ion secondary batteries that use cylindrical or rectangular metal cans as their exteriors. As a result, when gas is generated inside a lithium ion secondary battery during charging and discharging, the exterior of a laminated lithium ion secondary battery can expand significantly.

[0006]

For example, the following Patent Document 1 discloses a technology that suppresses the swelling of a lithium ion secondary battery during charging and discharging and improves discharge characteristics by incorporating a chain propionic acid ester and a cyclic carbonate into the electrolyte.

[0007]

In addition, the following Patent Document 2 discloses a technology for improving the charge/discharge cycle characteristics and storage characteristics in a charged state of a lithium ion secondary battery by incorporating a nitrile compound having a chain-like saturated hydrocarbon group with two or more carbon atoms into the electrolyte.

[Prior Art Documents]

[Patent Documents]

[0008]

[Patent document 1] International Publication No. 2009/084928

[Patent document 2] Japanese Unexamined Patent Application Publication No. 2009-231261

[Summary of the Invention]

[Problem to be Solved by the Invention]

[0009]

However, with the technologies disclosed in the above Patent Documents 1 and 2, it has been difficult to sufficiently suppress the swelling of the lithium ion secondary battery. In addition, even if the swelling of the lithium ion secondary battery have been suppressed, it is possible for the battery characteristics such as the cycle characteristics to be deteriorated.

[0010]

The present invention has been made in view of the above problems; an object of the present invention is to provide a new and improved lithium ion secondary battery that is capable of suppressing swelling during high-temperature storage while maintaining the same or better cycle characteristics.

[Means for solving the problem]

[0011]

In order to solve the above problems, according to one aspect of the present invention, a secondary lithium ion secondary battery is provided, equipped with a positive electrode comprising lithium cobalt oxide at 75% by mass or more relative to the total mass of the positive electrode active material, and an electrolyte comprising two types of carboxylate esters and a nitrile compound having a molecular weight of 110 or more; wherein of the two types of carboxylate esters, the content of one carboxylate ester having a lower viscosity is greater than the content of the other carboxylate ester having a higher viscosity, and the viscosity of the electrolyte at 20°C is 4.0 mPa·s or more.

[0012]

The lithium ion secondary battery according to the present embodiment is able to suppress swelling during high-temperature storage while maintaining the same or better cycle characteristics.

[0013]

The two types of carboxylate esters may both be chain carboxylate esters.

[0014]

By using such a carboxylate ester, the lithium ion secondary battery according to the present embodiment is able to suppress swelling during high-temperature storage.

[0015]

The viscosity of one of the carboxylate esters at 20°C may be 0.50 mPa·s or more and 0.64 mPa·s or less.

[0016]

By setting the viscosity of the low-viscosity carboxylate ester at 20°C within the above range, the lithium ion secondary battery according to the present embodiment can prevent deterioration of cycle characteristics.

[0017]

The viscosity of the other carboxylate ester at 20°C may be 0.65 mPa·s or more and 0.75 mPa·s or less.

[0018]

By setting the viscosity of the high-viscosity carboxylate ester at 20°C within the above range, the lithium ion secondary battery according to the present embodiment is able to suppress swelling during high-temperature storage.

[0019]

The density of the positive electrode active material layer after rolling of the positive electrode may be 4.0 g/cm³ or more and 4.3 g/cm³ or less.

[0020]

The lithium ion secondary battery according to the present embodiment can more suitably suppress swelling during high-temperature storage when the design capacity is large and the energy density is high as described above.

[0021]

The density of the positive electrode active material layer after rolling of the positive electrode may be 4.2 g/cm³ or more and 4.3 g/cm³ or less.

[0022]

The lithium ion secondary battery according to the present embodiment can more effectively suppress swelling during high-temperature storage when the design capacity is even larger as described above.

[0023]

The potential of the positive electrode when fully charged may be 4.4 V or more relative to lithium.

[0024]

The lithium ion secondary battery according to the present embodiment can more effectively suppress swelling during high-temperature storage when the potential of the positive electrode is high and the energy density is high as described above.

[0025]

The battery may be further equipped with a negative electrode facing the positive electrode, and a separator layer sandwiched between the positive electrode and the negative electrode, and a polymer layer may be provided between at least one of the positive electrode or the negative electrode and the separator layer.

[0026]

The lithium ion secondary battery according to the present embodiment can more effectively prevent deterioration of cycle characteristics by providing a polymer layer between the electrode and the separator layer.

[0027]

The exterior material of the lithium ion secondary battery may be a resin film having a laminate structure.

[0028]

When the exterior material of the lithium ion secondary battery according to the present embodiment is formed of a resin film having a laminate structure, it is possible to more effectively suppress swelling during high-temperature storage.

[Effects of the Invention]

[0029]

As described above, according to the present invention, it is possible to suppress swelling during high-temperature storage while maintaining the same or higher cycle characteristics.

[Brief Description of the Drawings]

[0030]

[FIG. 1] A schematic diagram showing the internal structure of a lithium ion secondary battery according to one embodiment of the present invention.

[Best Form for Carrying Out the Invention]

[0031]

A preferred embodiment of the present invention will be described in detail below with reference to the attached drawings. In this specification and drawings, components having substantially the same functional configuration are denoted by the same reference numerals, and redundant description thereof will be omitted.

[0032]

<1. Structure of Lithium Ion Secondary Battery

First, the structure of a lithium ion secondary battery 10 according to one embodiment of the present invention will be described with reference to FIG. 1.

[0033]

The lithium ion secondary battery according to the present embodiment comprises lithium cobalt oxide in the positive electrode at 75% by mass or more relative to the total mass of the positive electrode active material, and comprises two types of carboxylate esters and a nitrile compound having a molecular weight of 110 or more in the electrolyte. In addition, in the lithium ion secondary battery 10 according to the present embodiment, the content of the carboxylate ester with a low viscosity among the two types of carboxylate esters comprised in the electrolyte is greater than the content of the carboxylate ester with a high viscosity, and the viscosity of the electrolyte at 20°C is 4.0 mPa·s or more.

[0034]

Below, the lithium ion secondary battery 10 according to the present embodiment will be described in detail with reference to FIG. 1.

[0035]

As shown in FIG. 1, the lithium ion secondary battery 10 is equipped with a positive electrode 20, a negative electrode 30, and a separator layer 40 impregnated with an electrolyte 43. The shape of the lithium ion secondary battery 10 is not particularly limited, and may be, for example, a cylindrical type, a rectangular type, a laminate type, or a button type.

[0036]

However, it is preferable for the lithium ion secondary battery 10 to be a laminate type lithium ion secondary battery having a resin film having a laminate structure as an exterior body. The resin film having a laminate structure is, for example, a film in which both sides of an aluminum foil are laminated with resin.

[0037]

In the laminated lithium ion secondary battery 10, the surfaces of the exterior body that come into contact with the positive electrode 20, the negative electrode 30, and the separator layer 40 are covered with resin. Therefore, in the lithium ion secondary battery 10, compared to a cylindrical or rectangular lithium ion secondary battery whose exterior body is made of metal, the nitrile compound with a molecular weight of 110 or more comprised in the electrolyte 43 can be prevented from reacting with the metal of the exterior body.

[0038] The positive electrode 20 is equipped with an electrode collector 21 and a positive electrode active material layer 22. The electrode collector 21 may be any conductive material, such as aluminum, stainless steel, or nickel-plated steel.

[0039] The positive electrode active material layer 22 comprises at least a positive electrode active material and a conductive agent, and may further comprise a binder. The ratio of the content of the positive electrode active material, the conductive agent, and the binder is not particularly limited, and the content applied in the conventional lithium ion secondary battery can be used.

[0040]

The positive electrode active material comprises lithium cobalt oxide. The content of lithium cobalt oxide is 75 mass% or more with respect to the total mass of the positive electrode active material.

[0041]

The lithium ion secondary battery 10 according to the present embodiment comprises 75 mass% or more of lithium cobalt oxide as the positive electrode active material, and as shown in the examples described below, the cycle characteristics can be improved. On the other hand, if the content of lithium cobalt oxide is less than 75 mass%, the nitrile compound with a molecular weight of 110 or more in the electrolyte 43 is excessively adsorbed to the positive electrode 20, preventing the absorption and release of lithium ions on the positive electrode 20, which is undesirable as it reduces the cycle characteristics.

[0042]

The positive electrode active material may comprise one or more active materials other than lithium cobalt oxide in the range of 0% to 25% by mass of the total mass. The active material comprised in the positive electrode active material is, for example, a transition metal oxide or solid solution oxide comprising lithium, or a material capable of electrochemically absorbing and

releasing lithium ions. For example, examples of transition metal oxides comprising lithium include Li/Ni/Co/Mn-based composite oxides such as $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, Li/Ni-based composite oxides such as LiNiO_2 , and Li/Mn-based composite oxides such as LiMn_2O_4 . Examples of solid solution oxides comprising lithium include $\text{Li}_a\text{Mn}_x\text{Co}_y\text{Ni}_z\text{O}_2$ ($1.150 \leq a \leq 1.430$, $0.45 \leq x \leq 0.6$, $0.10 \leq y \leq 0.15$, $0.20 \leq z \leq 0.28$), $\text{LiMn}_x\text{Co}_y\text{Ni}_z\text{O}_2$ ($0.3 \leq x \leq 0.85$, $0.10 \leq y \leq 0.3$, $0.10 \leq z \leq 0.3$), and $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$.

[0043]

The conductive agent may be, for example, carbon black such as ketjen black and acetylene black, natural graphite, artificial graphite, fibrous carbon such as carbon nanotubes, graphene, and carbon nanofibers, or a composite of these fibrous carbons and carbon black. However, the conductive agent is not limited to the above substances as long as it is capable of increasing the conductivity of the positive electrode.

[0044]

For example, polyvinylidene difluoride, ethylene-propylene-diene terpolymer, styrene-butadiene rubber, acrylonitrile-butadiene rubber, fluoroelastomer, polyvinyl acetate, polymethylmethacrylate, polyethylene, or nitrocellulose can be used as the binder. However, the binder is not particularly limited as long as it can bind the positive electrode active material and conductive agent to the electrode collector 21, and has oxidation resistance to withstand the high potential of the positive electrode and stability against the electrolyte 43.

[0045]

The positive electrode active material layer 22 can be formed, for example, by dispersing the positive electrode active material, conductive agent, and binder in an appropriate organic solvent (e.g., N-methyl-2-pyrrolidone, etc.) to form a positive electrode slurry, applying the positive electrode slurry to the electrode collector 21, and then drying and rolling.

[0046]

In the lithium ion secondary battery 10 according to the present embodiment, the density of the positive electrode active material layer 22 after rolling is preferably 4.0 g/cm^3 or more and 4.3 g/cm^3 or less, and more preferably 4.2 g/cm^3 or more and 4.3 g/cm^3 or less. In addition, in such a case, the potential of the positive electrode 20 when fully charged is preferably 4.4 V or more relative to lithium. As shown in the examples described later, the lithium ion secondary battery 10 according to the present embodiment can more effectively maintain cycle characteristics and suppress swelling during high-temperature storage, particularly when the density of the positive electrode active material layer 22 after rolling is high and the energy density of the positive electrode 20 is high.

[0047]

The negative electrode 30 is equipped with an electrode collector 31 and a negative electrode active material layer 32. The electrode collector 31 may be any conductive material, such as copper, copper alloy, aluminum, stainless steel, or nickel-plated steel.

[0048]

The negative electrode active material layer 32 comprises at least a negative electrode active material, and may further comprise a conductive agent and a binder. The ratio of the content of the negative electrode active material, conductive agent, and binder is not particularly limited, and it is possible to use the content applied in conventional lithium ion secondary batteries.

[0049]

The negative electrode active material may be, for example, artificial graphite, natural graphite, a mixture of artificial graphite and natural graphite, natural graphite coated with artificial graphite, silicon (Si) or tin (Sn) fine particles, silicon (Si) or tin (Sn) oxide fine particles, an alloy based on silicon or tin, and titanium oxide (TiO_x) compounds such as $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Mixtures thereof may also be used. Silicon oxide is represented as SiO_x ($0 \leq x \leq 2$). In addition to these, metallic lithium may also be used as the negative electrode active material.

[0050]

The conductive agent may be the same as that used in the positive electrode active material layer 22. The binder may also be the same as that used in the positive electrode active material layer 22.

[0051]

The negative electrode active material layer 32 can be formed, for example, by dispersing the negative electrode active material and binder in a suitable solvent (e.g., water, etc.) to form a negative electrode slurry, applying the negative electrode slurry to the electrode collector 31, and then drying and rolling. The density of the negative electrode active material layer 32 after rolling is not particularly limited, and it may be any density that is applicable to the negative electrode active material layer of a lithium ion secondary battery.

[0052]

The separator layer 40 comprises a separator 41 and an electrolyte 43.

[0053]

The separator 41 is not particularly limited, and any material can be used as long as it is used as a separator for a lithium ion secondary battery. As the separator 41, it is preferable to use a porous film or nonwoven fabric that exhibits excellent high-rate discharge performance, either alone or in combination. The separator 41 may be coated with an inorganic material such as Al_2O_3 or SiO_2 , or a polymer such as polyvinylidene fluoride. The separator 41 may comprise an inorganic material such as Al_2O_3 or SiO_2 as a filler.

[0054]

In the lithium ion secondary battery 10 according to the present embodiment, it is preferable to provide a polymer layer between the separator 41 and at least one of the positive electrode 20 or the negative electrode 30 by coating the separator 41 with a polymer, or by coating either the positive electrode 20 or the negative electrode 30 with a polymer. The polymer layer provided

between the separator 41 and at least one of the positive electrode 20 or the negative electrode 30 increases the adhesion between the separator 41 and the positive electrode 20 or the negative electrode 30, thereby reducing distortion of the lithium ion secondary battery 10 and making it easier to maintain its shape.

[0055]

However, because the polymer layer has low conductivity, providing a polymer layer may result in an increase in resistance between the positive electrode 20 and the negative electrode 30. In the lithium ion secondary battery 10 according to the present embodiment, by using two types of carboxylic acid esters for the electrolyte 43 and increasing the content of the carboxylic acid ester with low viscosity, the fluidity of the electrolyte 43 can be improved, and the conductivity can be improved. Therefore, even if a polymer layer is provided between at least either the positive electrode 20 or the negative electrode 30 and the separator 41, the lithium ion secondary battery 10 can be used more suitably without increasing the resistance between the positive electrode 20 and the negative electrode 30.

[0056]

Examples of materials constituting the separator 41 that can be used include, for example, polyolefin resins such as polyethylene and polypropylene; polyester resins such as polyethylene terephthalate and polybutylene terephthalate; and polyvinylidene difluoride, vinylidene fluoride-hexafluoropropylene copolymer, vinylidene fluoride-perfluorovinyl ether, difluoride-perfluorovinylether copolymer, vinylidene difluoride-tetrafluoroethylene copolymer, vinylidene difluoride-trifluoroethylene copolymer, vinylidene difluoride-fluoroethylene copolymer, vinylidene difluoride-hexafluoroacetone copolymer, vinylidene fluoride-ethylene difluoride-ethylene copolymer, vinylidene difluoride-propylene copolymer, vinylidene fluoride-trifluoropropylene copolymer, vinylidene difluoride-tetrafluoroethylene-hexafluoropropylene copolymer, vinylidene difluoride-ethylene-tetrafluoroethylene copolymer difluoride-ethylene-tetrafluoroethylene copolymer, and the like. The porosity of the separator is not particularly limited, and the porosity of the separator of a conventional lithium ion secondary battery can be arbitrarily applied.

[0057]

When the separator 41 is coated with a polymer, for example, polyvinylidene fluoride (PVDF) can be used for the coating. When at least one of the positive electrode 20 and the negative electrode 30 is coated with a polymer, a similar polymer can be used.

[0058]

The electrolyte 43 comprises a lithium salt, at least two kinds of carboxylate esters, and a nitrile compound having a molecular weight of 110 or more. The viscosity of the electrolyte 43 at 20°C is 4.0 mPa·s or more. The above-mentioned viscosity is a value measured by using a rotational viscometer at 60 rpm in an environment of 20°C (hereinafter the same).

[0059]

The lithium salt is an electrolyte of electrolyte 43. The lithium salt may be LiPF₆, LiClO₄, LiBF₄, LiAsF₆, LiSbF₆, LiSO₃CF₃, LiC(SO₂CF₃)₃, LiC(SO₂CF₃)₃, LiI, LiCl, LiF, LiPF₅(SO₂CF₃), LiPF₄(SO₂CF₃)₂, and the like. These lithium salts may be used alone or in a mixture of two or more kinds. The concentration of the lithium salt is not particularly limited, but may be, for example, about 0.5 to 2.0 mol/L.

[0060]

The two types of carboxylate esters are non-aqueous solvents that dissolve the lithium salt and various additives. The two types of carboxylate esters have different viscosities, and the electrolyte 43 comprises more of the low-viscosity carboxylate ester than the high-viscosity carboxylate ester.

[0061]

In the lithium ion secondary battery 10 according to the present embodiment, the electrolyte 43 comprises two types of carboxylate esters, so that the electrolyte 43 can have both electrochemical stability and fluidity. Specifically, the low-viscosity carboxylate ester alone is not preferred because it cannot suppress side reactions at each electrode. The high-viscosity carboxylate ester alone is also not preferred because it reduces the fluidity of the electrolyte 43.

[0062]

Furthermore, by making the content of the carboxylate ester having a lower viscosity greater than the content of the carboxylate ester having a higher viscosity among the two types of carboxylate esters, the fluidity of the electrolyte 43 is ensured, and as shown in the examples described later, a decrease in the cycle characteristics of the lithium ion secondary battery 10 can be prevented.

[0063]

Here, of the two types of carboxylate esters, the viscosity of the carboxylate ester with the lower viscosity at 20°C may be, for example, 0.50 mPa·s or more and 0.64 mPa·s or less. The viscosity of the carboxylate ester with the higher viscosity at 20°C may be, for example, 0.65 mPa·s or more and 0.75 mPa·s or less.

[0064]

By setting the viscosities of the two types of carboxylate esters at 20°C to values within the above-mentioned range, the viscosity of the electrolyte 43 at 20°C can be set to 4.0 mPa·s or more. As a result, in the lithium ion secondary battery 10 according to the present embodiment, swelling during high-temperature storage can be suppressed, as shown in the examples described later. The upper limit of the viscosity of the electrolyte 43 at 20°C is, for example, 4.5 mPa·s.

[0065]

In the lithium ion secondary battery 10 according to the present embodiment, examples of the carboxylate ester comprised in the electrolyte 43 include chain carboxylic acid esters such as methyl acetate (MA), ethyl acetate (EA), propyl acetate (PA), butyl acetate (EB), methyl propionate (MP), ethyl propionate (EP), propyl propionate (PP), butyl propionate (BP), methyl

butyrate (MB), ethyl butyrate (EB), propyl butyrate (PB) and butyl butyrate (butyl butyrate (BB); γ -butyrolactone (GBL), γ -valerolactone (GVL), α -acetyl-butylolactone, α -methyl- γ -butyrolactone, β -methyl- γ -butyrolactone, α -angelica lactone, Examples of the carboxylic acid esters include α -methylene- γ -butyrolactone, γ -hexanolactone, γ -nonanolactone, γ -octanolactone, and γ -methyl- γ -decanolactone. The carboxylic acid esters comprised in the electrolyte 43 are preferably chain carboxylic acid esters.

[0066]

A nitrile compound having a molecular weight of 110 or more improves the electrochemical stability of the carboxylate ester comprised in the electrolyte 43. Specifically, a nitrile compound having a molecular weight of 110 or more is able to suppress side reactions on the surface of the positive electrode 20 by adsorbing to the positive electrode 20. As a result, the lithium ion secondary battery 10 according to the present embodiment is able to suppress swelling during high-temperature storage. Further, if the molecular weight of the nitrile compound is less than 110, as shown in the examples described below, the effect of suppressing side reactions on the surface of the positive electrode 20 decreases, and swelling during high-temperature storage cannot be sufficiently suppressed. However, it goes without saying that the electrolyte 43 may comprise a nitrile compound having a molecular weight of less than 110 (for example, succinonitrile, etc.) in addition to a nitrile compound having a molecular weight of 110 or more.

[0067]

In the lithium ion secondary battery 10 according to the present embodiment, the nitrile compound comprised in the electrolyte 43 has a nitrile group (for example, a CN group); as long as the molecular weight is 110 or more, the molecular weight is not particularly limited. Examples include compounds having three or more nitrile groups like mononitrile compounds such as heptanenitrile, octanenitrile, nonanenitrile, decanenitrile, dodecanenitrile (lauronitrile), tridecanenitrile, tetradecanenitrile (myristoylnitrile), Hexadecanenitrile, pentadecanenitrile, heptadecanenitrile, octadecanenitrile (stearoxynitrile), nonadecanenitrile, icosanenitrile, and cinnamonitrile; dinitrile compounds such as pimelonitrile, suberonitrile, azelanitrile, sebaconitrile, undecanedinitrile, dodecanedinitrile, tert-butylmalononitrile, trimethylsuccinonitrile, tetramethylsuccinonitrile, tetramethylsuccinonitrile, 3,3'-oxydipropionitrile, 3,3'-thiodipropionitrile, 3,3'-(ethylenedioxy)dipropionitrile, and 3,3'-(ethylenedithio)dipropionitrile; and 1,2,3-propanetricarbonitrile, 1,3,5-pentanetricarbonitrile, 1,3,6-hexanetricarbonitrile, 1,2,3-tris(2-cyanoethoxy)propane, tris(2-cyanoethyl)amine. As the nitrile compound comprised in the electrolyte 43, a dinitrile compound or a trinitrile compound is more preferable.

[0068]

The electrolyte 43 may comprise a nonaqueous solvent other than the carboxylic acid ester. For example, the electrolyte 43 may comprise, as a solvent, cyclic carbonates such as propylene carbonate, ethylene carbonate, butylene carbonate, or chloroethylene carbonate; linear carbonates such as dimethyl carbonate, diethyl carbonate, or ethylmethyl carbonate; tetrahydrofuran or its derivatives; ethers such as 1,3-dioxane, 1,4-dioxane, 1,2-dimethoxyethane, 1,4-dibutoxyethane, or methyl diglyme; dioxolane or its derivatives; ethylene sulfide, sulfolane, sultone, or derivatives thereof and the like, alone or in combination of two or more thereof.

[0069]

Furthermore, various additives such as a negative electrode SEI (Solid Electrolyte Interface) forming agent or a surfactant may be added to the electrolyte 43.

[0070]

Examples of such additives that may be used include succinic anhydride, lithium bis(oxalate)borate, lithium tetrafluoroborate, propane sultone, butane sultone, propene sultone, 3-sulfolene, fluorinated arylether, and fluorinated acrylate. The content of the additives may be the same as that of a typical lithium ion secondary battery.

[0071]

<2. Manufacturing method of lithium ion secondary battery>

Next, a manufacturing method of the lithium ion secondary battery 10 will be described. However, the manufacturing method of the lithium ion secondary battery 10 is not limited to the following method, and other known manufacturing methods can be applied.

[0072]

The positive electrode 20 is manufactured as follows. First, a mixture of a positive electrode active material, a conductive agent, and a binder in a desired ratio is dispersed in an organic solvent (e.g., N-methyl-2-pyrrolidone) to form a positive electrode slurry. Next, the positive electrode slurry is formed (e.g., coated) on the electrode collector 21 and dried to form a positive electrode active material layer 22.

[0073]

The coating method is not particularly limited, but may be, for example, a knife coater method or a gravure coater method. The following coating steps are also performed in the same manner.

[0074]

The positive electrode active material layer 22 is then compressed to the desired density by a compressor. This results in the manufacture of the positive electrode 20. The density of the positive electrode active material layer 22 may be the density of the positive electrode active material layer of a conventional lithium ion secondary battery, or may be the preferred density described above.

[0075]

The negative electrode 30 is manufactured in the same manner as the positive electrode 20. First, a negative electrode active material and a binder are mixed in a desired ratio and dispersed in a solvent (e.g., water) to form a negative electrode slurry.

Next, the negative electrode slurry is formed (e.g., coated) on the electrode collector 31 and dried to form the negative electrode active material layer 32.

[0076]

The negative electrode active material layer 32 is then compressed to a desired density by a compressor. As a result, the negative electrode 30 is manufactured. There are no particular limitations on the density of the negative electrode active material layer 32, and it may be the same density as the negative electrode active material layer of a conventional lithium ion secondary battery. When metallic lithium is used as the negative electrode active material layer 32, the negative electrode 30 can be manufactured by laminating metallic lithium foil to the electrode collector 31.

[0077]

Then, the separator 41 is sandwiched between the positive electrode 20 and the negative electrode 30 to manufacture the electrode structure. The manufactured electrode structure is then processed into a desired shape (e.g., cylindrical, square, laminated, button, etc.) and inserted into a container of that shape. Furthermore, electrolyte 43 comprising the above-mentioned components is injected into the container, so that the electrolyte 43 permeates the pores in the separator 41. This produces the lithium ion secondary battery 10.

[Embodiments]

[0078]

Below, the lithium ion secondary battery according to the present embodiment will be described in detail with reference to embodiments and comparative examples. Note that the embodiments shown below are merely examples, and the lithium ion secondary battery according to the present embodiment is not limited to the examples below.

[0079]

<Production of Lithium Ion Secondary Battery>

(Embodiment 1)

The lithium ion secondary battery according to Embodiment 1 was produced by the following method.

[0080]

First, lithium cobalt oxide represented by LiCoO_2 (average particle size 13 μm , BET specific surface area 0.35 m^2/g), a conductive agent made of a carbon material, and polyvinylidene fluoride were dispersed in N-methyl-2-pyrrolidone in a mass ratio of 97:1.5:1.5 to form a positive electrode slurry.

[0081]

Next, the positive electrode slurry was applied to an electrode collector made of aluminum foil with a thickness of 12 μm , a length of 269 mm, and a width of 27 mm, with an area of 253 mm x 27 mm (front side) and 206 mm x 27 mm (back side), and then dried and rolled. Furthermore, a current collecting tab made of an aluminum flat plate with a thickness of 70 μm , a length of 35 mm, and a width of 4 mm was attached to the uncoated part of the positive electrode slurry to manufacture a positive electrode. The total thickness of the manufactured positive electrode was 121 μm , and the density of the positive electrode active material layer after rolling was 4.1 g/cm^3 .

[0082]

Next, artificial graphite (average particle size 11 μm), carboxymethylcellulose (CMC), and styrene-butadiene copolymer (SBR) were dispersed in pure water in a mass ratio of 97.5:1:1.5 to form a negative electrode slurry. Next, the negative electrode slurry was applied to both sides of an electrode collector made of electrolytic copper foil with a thickness of 10 μm , a length of 336 mm, and a width of 30 mm, and then dried. Furthermore, a current collector tab made of a nickel flat plate with a thickness of 70 μm , a length of 35 mm, and a width of 4 mm was attached to the uncoated portion of the negative electrode slurry to manufacture a negative electrode. The total thickness of the manufactured negative electrode was 148 μm , and the density of the negative electrode active material layer was 1.7 g/cm^3 .

[0083]

Next, lithium hexafluorophosphate (LiPF_6) was dissolved at a concentration of 1.2 mol/L as an electrolyte in a solvent in which ethylene carbonate (EC), propylene carbonate (PC), ethyl propionate (EP), and propyl propionate (PP) were mixed in a volume ratio of 20:10:40:30, respectively, to manufacture an electrolyte.

[0084]

Ethyl propionate (EP) and propyl propionate (PP) are the two types of carboxylic acid esters in the present invention. Ethyl propionate has a lower viscosity than propyl propionate.

[0085]

In addition, the following additives were added to the produced electrolyte relative to the total mass of the electrolyte ($\text{EC}+\text{PC}+\text{EP}+\text{PP}+\text{LiPF}_6$): 5% by mass of fluoroethylene carbonate (FEC), 1% by mass of vinylene carbonate (VC), 2% by mass of 1,3-propanesultone (PS), and 3% by mass of succinonitrile, a nitrile compound with a molecular weight of 80; furthermore, 1,3,6-hexanetricarbonitrile having a molecular weight of 161 as a nitrile compound having a molecular weight of 110 or more was added in an amount of 2 mass % based on the total mass of the electrolyte solution.

[0086]

Furthermore, a coating layer made of PVDF and Al_2O_3 was formed to a thickness of 1.5 μm on both sides of a separator made of a 7 μm -thick microporous polypropylene film. The separator with the coating layer formed thereon was sandwiched between the positive electrode and negative electrode manufactured above, rolled up, and compressed to manufacture a flat electrode structure. The manufactured electrode structure was housed in a battery container made of an aluminum laminate film.

[0087]

The electrolyte of the above composition was injected into the battery container housing the electrode structure, and the electrolyte was impregnated into each pore in the separator. Furthermore, the current collecting tabs of the positive electrode and negative electrode were taken out to the outside to manufacture the lithium ion secondary battery according to Embodiment 1. The battery specifications of the lithium ion secondary battery according to Embodiment 1 are 3.8 cm long x 3.1 cm wide x 3.2 mm thick, and the design capacity is 450 mAh.

[0088]

(Embodiment 2)

A lithium ion secondary battery according to Embodiment 2 was manufactured in the same manner as Embodiment 1, except that a mixture of 80% by mass LiCoO_2 and 20% by mass $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ was used as the positive electrode active material instead of 100% by mass LiCoO_2 .

[0089]

(Embodiments 3-5)

A lithium ion secondary battery according to Embodiments 3-5 was manufactured in the same manner as Embodiment 1, except that the nitrile compounds with molecular weights of 110 or more were changed in the electrolyte. The nitrile compounds used are shown in Table 1.

[0090]

(Embodiment 6)

A lithium ion secondary battery according to Embodiment 6 was manufactured in the same manner as Embodiment 1, except that butyl acetate (EB) was used instead of propyl propionate (PP) in the electrolyte.

[0091] (Comparative Example 1)

A lithium ion secondary battery according to Comparative Example 1 was manufactured in the same manner as in Embodiment 1, except that a mixture of 60 mass% LiCoO_2 and 40 mass% $\text{LiNi}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ was used as the positive electrode active material instead of 100 mass% LiCoO_2 .

[0092] (Comparative Examples 2 to 4)

A lithium ion secondary battery according to Comparative Examples 2 to 4 was manufactured in the same manner as in Embodiment 1, except that the content ratios of ethyl propionate (EP) and propyl propionate (PP) in the electrolyte were changed. The content ratios of ethyl propionate (EP) and propyl propionate (PP) after the change are shown in Table 1.

[0093]

(Comparative Example 5)

A lithium ion secondary battery according to Comparative Example 5 was manufactured in the same manner as in Embodiment 1, except that in the electrolyte, a nitrile compound having a molecular weight of 110 or more was replaced with a nitrile compound having a molecular weight of less than 110. The nitrile compounds used are shown in Table 1.

[0094]

(Comparative Examples 6 to 8)

A lithium ion secondary battery according to Comparative Examples 6 to 8 was manufactured in the same manner as in Embodiment 1, except that in the electrolyte, instead of ethyl propionate (EP), other solvents were used. The solvents used are shown in Table 1.

[0095]

(Embodiment 7)

The effect of the present invention on a lithium ion secondary battery with a high energy density was examined by changing the design capacity of the lithium ion secondary battery to 520 mAh.

[0096]

In Embodiment 7, a lithium ion secondary battery was manufactured in the same manner as in Embodiment 1, except that the design capacity of the lithium ion secondary battery was changed to 520 mAh. Specifically, the amount of positive electrode slurry applied to the positive electrode and the strength of rolling were changed, so that the density of the positive electrode active material layer after rolling was 4.2 g/cm^3 and the total thickness of the positive electrode was $135 \text{ }\mu\text{m}$. In addition, the amount of negative electrode slurry applied to the negative electrode was changed, and the total thickness of the negative electrode was set to $163 \text{ }\mu\text{m}$. The other configurations were the same as those of Embodiment 1, and a lithium ion secondary battery according to Embodiment 7 was manufactured.

[0098]

<Method of evaluating lithium ion secondary batteries>

The lithium ion secondary batteries according to Embodiments 1 to 7 and Comparative Examples 1 to 9 manufactured as described above were evaluated for the viscosity of the electrolyte, cycle characteristics, and thickness increase due to high-temperature storage. The evaluation results of Embodiments 1 to 6 and Comparative Examples 1 to 8 are shown in Table 1, and the evaluation results of Embodiment 7 and Comparative Example 9 are shown in Table 2.

[0099]

(Viscosity of electrolyte)

The viscosity of the electrolyte of each lithium ion secondary battery was measured at 60 rpm in an environment of 20°C using a rotational viscometer (Brookfield Digital Viscometer LVDV-E). The measurement results are shown in Tables 1 and 2.

[0100]

(Cycle characteristics)

In an environment of 45°C, each lithium ion secondary battery was charged at a constant current of 90 mA until the voltage reached 4.4 V, and then constant-voltage charging was performed at a constant voltage of 4.4 V until the current value reached 11 mA. Then, the battery was discharged to 3.0 V at a constant current of 90 mA to perform initial charge and discharge.

[0101]

Next, the battery was charged to 4.4 V at a constant current of 450 mA at room temperature, and then constant-voltage charging was performed at a constant voltage of 4.4 V until the current value reached 11 mA. The battery was then discharged to 3.0 V at a constant current of 450 mA. This cycle of charge and discharge was repeated until 300 cycles were performed.

[0102]

The cycle characteristics were evaluated by calculating the capacity retention rate by dividing the discharge capacity at the 300th cycle by the discharge capacity at the first cycle. The results are shown in Tables 1 and 2. In Table 1, the cycle characteristics of each lithium ion secondary battery are shown as relative values with the lithium ion secondary battery of Embodiment 1 set to 100, and in Table 2, the cycle characteristics of each lithium ion secondary battery are shown as relative values with the lithium ion secondary battery of Embodiment 7 set to 100.

[0103]

(Thickness increase due to high-temperature storage)

First, after the first charge/discharge cycle was performed as described above, each lithium ion secondary battery was charged at a constant current of 450 mA until the voltage reached 4.4 V, and then constant-voltage charging was performed at a constant voltage of 4.4 V until the current value reached 11 mA. Then, the thickness (thickest point) of each lithium ion secondary battery after charging was measured with a caliper or the like to measure the battery thickness before storage. Next, each lithium ion secondary battery was left in a thermostatic chamber at 60°C for 20 days, and the thickness (thickest point) of each lithium ion secondary battery after leaving it was measured with a caliper or the like to measure the battery thickness after storage.

[0104]

Here, the thickness increase during high-temperature storage was evaluated by calculating the thickness increase by dividing the battery thickness after storage by the battery thickness before storage. The results are shown in Tables 1 and 2. In Table 1, the cycle characteristics of each lithium ion secondary battery are shown as relative values with the lithium ion secondary battery of Embodiment 1 set to 100, and in Table 2, the cycle characteristics of each lithium ion secondary battery are shown as relative values with the lithium ion secondary battery of Embodiment 7 set to 100.

[0105]

<Evaluation results of lithium ion secondary batteries>

The results of the evaluation above are shown in Tables 1 and 2 below.

[0106]

First, the evaluation results of a lithium ion secondary battery with a design capacity of 450 mAh are shown in Table 1.

[0107]

[Table 1]

(Table 1)

	Positive Electrode	Electrolyte							Battery characteristics			
	LiCoO ₂ content [mass%]	Carboxylic acid esters				Nitrile compounds		Viscosity [mPa · s]	Cycle Characteristics	Thickness Increase		
		Low viscosity material	Proportion [volume %]	High viscosity material	Proportion [volume %]	Material	Molecular weight					
Embodiment 1	100	EP	40	PP	30	HTCN	161	4.1	100	100		
Embodiment 2	80							4.1	99	99		
Embodiment 3	100							SBRN	136	4.0	104	99
Embodiment 4								SBCN	164	4.1	100	99
Embodiment 5						nPA		HTCN	161	4.2	101	99
Embodiment 6				EP		EB		4.1	99	99		
Comparative Example 1	60	EP	40	PP	30	HTCN	161	4.1	75	101		
Comparative Example 2	100		20		50			4.5	79	95		
Comparative Example 3			0		70			4.9	69	92		
Comparative Example 4			70		0			3.7	105	105		
Comparative Example 5						ADPN	108	3.9	102	111		
Comparative Example 6	MP		40		30	HTCN	161	3.7	110	105		
Comparative Example 7	EA							3.8	100	120		
Comparative Example 8	DMC							4.1	105	163		

[0108]

In Table 1, EP stands for ethyl propionate, nPA stands for n-propyl acetate, PP stands for propyl propionate, and EB stands for butyl acetate. MP stands for methyl propionate, EA stands for ethyl acetate, and DMC stands for dimethyl carbonate. Further, EP, nPA, MP, EA, and DMC have lower viscosities than PP and EB.

[0109]

In Table 1, HTC� stands for 1,3,6-hexanetricarbonitrile, SBRN stands for suberonitrile, SBCN stands for sebaconitrile, and ADPN stands for adiponitrile.

[0110]

With reference to the results in Table 1, it can be seen that the lithium ion secondary batteries according to Embodiments 1 to 6 can reduce the amount of thickness increase during high-temperature storage while maintaining cycle characteristics equal to or higher than those of Comparative Examples 1 to 8.

[0111]

For example, in Comparative Example 1, the content of LiCoO₂ in the positive electrode active material is less than 75 mass%, so the cycle characteristics are reduced. In Comparative Examples 2 and 3, the low-viscosity carboxylic acid ester is not comprised, or the content of the low-viscosity carboxylic acid ester is less than that of the high-viscosity carboxylic acid ester, so the cycle characteristics are reduced. In Comparative Example 4, the amount of thickness increase during high-temperature storage increases because the high-viscosity carboxylate ester is not comprised.

[0112]

In Comparative Example 5, the molecular weight of all nitrile compounds comprised is less than 110, so the amount of thickness increase during high-temperature storage increases. In Comparative Examples 6 and 7, the viscosity of the electrolyte at 20°C is less than 4.0 mPa·s, so the amount of thickness increase during high-temperature storage increases. In Comparative Example 8, one of the solvents is DMC, and two types of carboxylate esters are not comprised, so the amount of thickness increase during high-temperature storage increases.

[0113]

Next, the evaluation results of a lithium ion secondary battery with a design capacity of 520 mAh are shown in Table 2.

[0114]

[Table 2]

(Table 2)

	Positive Electrode	Electrolyte							Battery characteristics	
	LiCoO ₂ content [mass%]	Carboxylic acid esters				Nitrile compounds		Viscosity [mPa·s]	Cycle Characteristics	Thickness Increase
		Low viscosity material	Proportion [volume %]	High viscosity material	Proportion [volume %]	Material	Molecular weight			
Embodiment 7	100	EP	40	PP	30	HTCN	161	4.1	100	100
Comparative Example 9			20		50			4.5	65	95

[0115]

In Table 2, EP stands for ethyl propionate, and PP stands for propyl propionate. EP has a lower viscosity than PP. HTC� stands for 1,3,6-hexanetricarbonitrile.

[0116]

With reference to the results shown in Table 2, it can be seen that the lithium ion secondary battery of Embodiment 7 can reduce the amount of thickness increase during high-temperature storage while maintaining cycle characteristics equal to or better than those of Comparative Example 9.

[0117]

Furthermore, the difference in the evaluation results between Embodiment 7 and Comparative Example 9 is greater than the difference in the evaluation results between Embodiment 1 and Comparative Example 2, which have the same configuration except for the design capacity. Therefore, it is found that the lithium ion secondary battery according to the present embodiment can reduce the amount of thickness increase during high-temperature storage while maintaining cycle characteristics more favorably when the design capacity is large and the energy density is high.

[0118]

As can be seen from the above evaluation results, the lithium ion secondary battery according to the present embodiment is able to suppress swelling during high-temperature storage while maintaining cycle characteristics at or above the same level.

[0119]

The preferred embodiments of the present invention has been described in detail above with reference to the accompanying drawings, but the present invention is not limited to such examples. It is clear that a person with ordinary skill in the art pertaining to the present invention is able to conceive of various modified or revised examples within the scope of the technical ideas described in the claims, and it is understood that these naturally fall within the technical scope of the present invention.

[Explanation of Symbols]

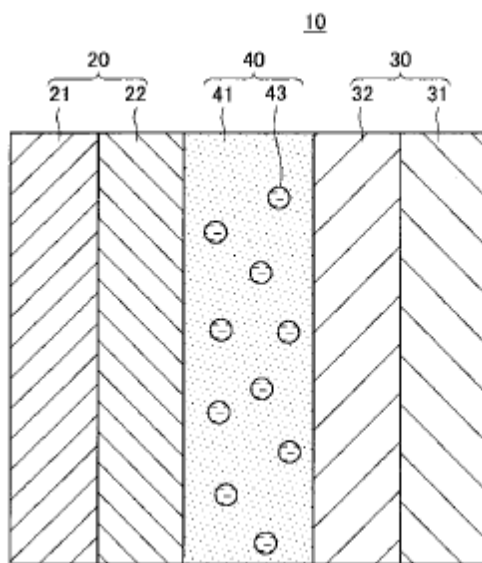
[0120]

- 10 lithium ion secondary battery
- 20 positive electrode
- 21 electrode collector
- 22 positive electrode active material layer
- 30 negative electrode
- 31 electrode collector
- 32 negative electrode active material layer
- 40 separator layer
- 41 separator
- 43 electrolyte

(13)

JP 2018-6046 A 2018.1.11

[FIG. 1]



Continued from the front page

Theme code (reference)

(51)Int.Cl.		F I
H O 1 M 4/131 (2010.01)		H O 1 M 4/131
H O 1 M 4/13 (2010.01)		H O 1 M 4/13

(72) Inventor Yamamoto Hidekazu
c/o SAMSUNG Japan Research Center 2-7 Sugasawa-cho, Tsurumi-ku, Yokohama-shi, Kanagawa-ken

[F terms (reference)] 5H011 AA01 BB04 CC02 KK00 KK02 KK04 KK05 KK06
5H021 AA01 CC04 EE02 HH00 HH01 HH05 HH06 HH07 HH10
5H029 AJ04 AJ05 AJ07 AK03 AL02 AL03 AL07 AL11 AL12 AM02
AM03 AM04 AM05 BJ12 DJ02 DJ04 DJ06 DJ09 DJ11 EJ12
HJ00 HJ01 HJ08 HJ10 HJ12 HJ14 HJ18
5H050 AA07 AA10 AA13 BA16 BA17 CA08 CA09 CB02 CB03 CB08
CB11 CB12 DA01 DA13 DA19 EA23 FA04 HA00 HA01 HA08
HA10 HA12 HA14 HA18



DECLARATION OF TRANSLATOR

I, Carl T. Sullivan, hereby declare as follows:

1. I personally performed the attached translation from Japanese into English of the patent number JP2018006046A that is entitled “リチウムイオン二次電池” in Japanese and “Lithium ion secondary battery” in English (also attached).

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

3. I am competent to perform this translation, because I have a **32 years of professional translation experience including patent translation, active ATA membership (prior Japanese Language Division Administrator), and Associate Professor of Japanese Language.**

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

A handwritten signature in black ink, appearing to read "C. T. Sullivan", written over a light grey rectangular background.

Dated: January 17, 2025

Carl T. Sullivan

136 Madison Avenue, 6th Floor
New York, NY 10016
212.581.8870