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(71) Applicant: **TOYOTA JIDOSHA KABUSHIKI KAISHA** [JP/JP]; 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

(72) Inventor: **ISHII, Kenta**; c/o TOYOTA JIDOSHA KABUSHIKI KAISHA, of 1, Toyota-cho, Toyota-shi, Aichi-ken, 471-8571 (JP).

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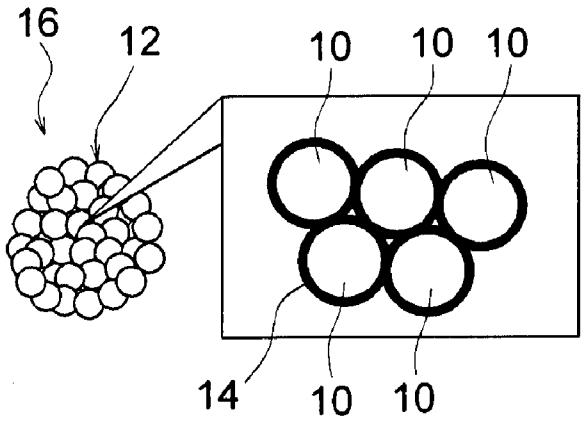
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FIG. 4



(57) Abstract: A method of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer is held on a current collector includes: preparing conductive binder-impregnated active material particles in which a conductive binder is impregnated into gaps between primary particles by mixing and stirring secondary particles, which are aggregates of plural primary particles of an active material, with the conductive binder; isotropically consolidating the conductive binder-impregnated active material particles; mixing the consolidated conductive binder-impregnated active material particles with a solvent to obtain a paste and forming an active material layer on a current collector by coating the current collector with the obtained paste; and rolling the active material layer.

SECONDARY BATTERY AND METHOD OF MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a secondary battery and a method of manufacturing a secondary battery and specifically relates to a secondary battery and a method of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer is held on a current collector.

2. Description of Related Art

[0002] Recently, the importance of secondary batteries such as a lithium ion secondary battery or a nickel metal hydride battery has increased as a power supply, for example, a vehicle-mounted power supply or a power supply for a PC or a portable device. In particular, a lithium ion secondary battery is preferably used as a vehicle-mounted power supply with high output because it is light-weight and has high energy density.

[0003] In one typical configuration, a lithium ion secondary battery includes an electrode having a configuration in which a material (active material) capable of reversibly storing and releasing lithium ions is formed on a conductive member (current collector). As a negative electrode active material which is used in a negative electrode, recently, lithium titanate has attracted attention because it can store and release lithium ions without any change in the structure and size of crystal lattices. For example, Japanese Patent Application Publication No. 2012-197187 (JP 2012-197187 A) discloses a secondary battery in which carbon composite lithium titanate is used as a negative electrode active material, the carbon composite lithium titanate being obtained by combining carbon with substantially spherical secondary particles (porous particles) of lithium titanate. In JP 2012-197187 A, a negative electrode active material layer is formed by mixing the carbon composite lithium titanate with a solvent to obtain a paste, coating a current collector with the obtained paste, and drying the current collector.

[0004] During the formation of the active material layer, the current collector is coated with the paste containing secondary particles of an active material, is dried, and is pressed (rolled). During the pressing, the thickness and density of the active material layer is adjusted. During the pressing step, primary particles of the active material may be peeled off from each other. In particular, when the active material layer is filled to have a high density, it is necessary that the pressing pressure be set to be high. Therefore, during the pressing step, the primary particles are likely to be peeled off from each other. When the primary particles are peeled off from each other during the pressing step, a conductive path between the primary particles is disconnected, which may cause deterioration in battery performance.

SUMMARY OF THE INVENTION

[0005] The invention has been made in consideration of the above-described points, and a main object is to provide a secondary battery and a method of manufacturing the secondary battery, in which the peeling of primary particles is prevented during the rolling of an active material layer so as to prevent deterioration in battery performance.

[0006] According to an aspect of the present invention, there is provided a method of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer is held on a current collector, the method including: preparing conductive binder-impregnated active material particles in which a conductive binder is impregnated into gaps between primary particles by mixing and stirring secondary particles, which are aggregates of plural primary particles of an active material, with the conductive binder (a stirring step); isotropically consolidating the conductive binder-impregnated active material particles (an isotropic consolidation step); mixing the consolidated conductive binder-impregnated active material particles with a solvent to obtain a paste and forming an active material layer on a current collector by coating the current collector with the obtained paste (a coating step); and rolling the active material layer (a rolling step).

[0007] According to the manufacturing method, the primary particles of the

active material are bonded to each other through the conductive binder and are further isotropically consolidated. Therefore, the bonding strength between the primary particle can be sufficiently secured, and the peeling of the primary particles which may occur during rolling can be prevented. Accordingly, according to this configuration, the optimum secondary battery, in which deterioration in performance caused by the peeling of the primary particles is suppressed, can be manufactured. This secondary battery may have, for example, superior cycle characteristics.

[0008] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, a consolidation pressure in the isotropic consolidation step is higher than a rolling pressure of the rolling step. By setting the consolidation pressure in the isotropic consolidation step to be higher than the rolling pressure in the rolling step, the peeling of the primary particles during the rolling step can be efficiently prevented.

[0009] In the manufacturing method of the second battery according to above aspect, the consolidation pressure in the isotropic consolidation step may be higher than the rolling pressure of the rolling step by 93 MPa or higher. By setting the consolidation pressure in the isotropic consolidation step to be higher than the rolling pressure in the rolling step by 93 MPa or higher, the peeling of the primary particles caused by the pressure applied in the rolling step can be more reliably prevented.

[0010] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, a ratio of the conductive binder is at least 4 mass% with respect to 100 mass% of the total mass of the conductive binder-impregnated active material particles. When the ratio of the conductive binder is as described above, the peeling of the primary particles in the rolling step can be efficiently prevented, and an increase in battery resistance or a decrease in battery capacity caused by the peeling of the primary particles can be more reliably suppressed.

[0011] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, as the conductive binder, polypyrrole is used. Polypyrrole has a low melting point and exhibits relatively high conductivity. Therefore,

polypyrrole can be preferably used as the conductive binder suitable for the object of the invention.

[0012] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, as the active material, lithium titanate is used. Lithium titanate is useful as an active material contributing to improvement of battery characteristics (for example, cycle characteristics or input and output characteristics), but accelerates the peeling of the primary particles during rolling. However, in the manufacturing method according to the invention, even when such lithium titanate is used, the peeling of the primary particles during rolling can be efficiently prevented, and a conductive path between the primary particles can be appropriately secured.

[0013] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, a density of the active material layer after the rolling step is at least 2 g/cm^3. In such a high-density active material layer, the pressure applied to the individual primary particles during rolling is high, and the primary particles are likely to be peeled off from each other. However, in the manufacturing method according to the invention, even when such a high-density active material layer is used, the peeling of the primary particles during rolling can be efficiently prevented, and a conductive path between the primary particles can be appropriately secured.

[0014] According to another aspect of the invention, there is provided a second battery including; an electrode having a configuration in which an active material layer is held on a current collector. Wherein the active material layer includes conductive binder-impregnated active material particles including secondary particles, which are aggregates of plural primary particles of an active material, and a conductive binder which are impregnated into gaps between the primary particles, and a DBP absorption number of the conductive binder-impregnated active material particles is 45 ($g/100\ cm^3$) or less. In this secondary battery, the bonding between the primary particles in the conductive binder-impregnated active material particles is strong, and a conductive path is suitably secured. Therefore, the secondary battery may have superior cycle characteristics.

[0015] In the preferred embodiment of the manufacturing method of the second

battery according to above aspect, the active material is formed of lithium titanate. By using such lithium titanate as the active material, in particular, input and output characteristics and cycle characteristics can be secured at a high level.

[0016] In the preferred embodiment of the manufacturing method of the second battery according to above aspect, a density of the active material layer is at least 2 g/cm^3. Due to an increase in the density of the active material layer, the number of contact points between the conductive binder-impregnated active material particles increases. Therefore, input and output characteristics and cycle characteristics can be further improved.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] Features, advantages, and technical and industrial significance of exemplary embodiments of the invention will be described below with reference to the accompanying drawings, in which like numerals denote like elements, and wherein:

FIG. 1 is a flowchart showing manufacturing steps of an electrode for a secondary battery according to an embodiment of the invention;

FIG. 2 is a diagram schematically showing an active material particle according to an embodiment of the invention;

FIG. 3 is a diagram schematically showing an active material particle according to an embodiment of the invention;

FIG. 4 is a diagram schematically showing an active material particle according to an embodiment of the invention;

FIG. 5 is a diagram schematically showing a battery configuration according to an embodiment of the invention; and

FIG. 6 is a diagram showing a wound electrode body according to an embodiment of the invention.

DETAILED DESCRIPTION OF EMBODIMENTS

[0018] Hereinafter, a secondary battery according to an embodiment of the invention will be described in detail. Matters necessary to implement the embodiments of

the invention other than those specifically referred to in this description may be understood as design matters based on the related art in the pertinent field for a person of ordinary skills in the art. The invention can be practiced based on the contents disclosed in this description and common technical knowledge in the subject field.

[0019] A method of manufacturing a secondary battery disclosed herein (hereinafter, also appropriately referred to as "manufacturing method") is a method of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer containing an active material is held on a current collector. "Secondary batteries" described in this specification refers to all the batteries that can be repeatedly charged, including so-called storage batteries such as a lithium ion secondary battery or a nickel metal hydride battery. "Active material" described in this specification refers to a material which can reversibly store and release (typically, intercalate and deintercalate) chemical species (lithium ions in a lithium ion secondary battery) as charge carriers in a secondary battery.

[0020] Hereinafter, the procedure of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer containing an active material is held on a current collector will be described with reference to FIG. 1. FIG. 1 is a flowchart showing steps of manufacturing the secondary battery. The manufacturing method according to the embodiment includes a stirring step (Step S10), an isotropic consolidation step (Step S20), a coating step (Step S30), and a rolling step (Step S40). In the stirring step Step S10, secondary particles, which are aggregates of plural primary particles of an active material, are mixed with a conductive binder to obtain a mixture, and the obtained mixture is stirred such that conductive binder-impregnated active material particles in which the conductive binder is impregnated into gaps between the primary particles are obtained. In the isotropic consolidation step Step S20, the conductive binder-impregnated active material particles are isotropically consolidated. In the coating step Step S30, the consolidated conductive binder-impregnated active material particles are mixed with a solvent to obtain a paste, and a current collector is coated with the obtained paste to form an active material layer on the current collector. In the rolling

step Step S40, the active material layer is rolled.

[0021] The method of manufacturing a secondary battery (in particular, an electrode for a secondary battery) according to the embodiment will be mainly described using a negative electrode (negative electrode sheet) for a lithium ion secondary battery including an aluminum foil-shaped negative electrode current collector (aluminum foil) as an example. However, the invention is not limited to this example. For example, the invention can be applied a positive electrode (positive electrode sheet) as well as a negative electrode. Hereinafter, the respective steps will be described in detail.

<Stirring Step>

[0022]

In the stirring step Step S10, as shown in FIG. 2, secondary particles 12 which are aggregates of plural primary particles 10 of a negative electrode active material are prepared. The secondary particles 12 and a conductive binder 14 are mixed with each other and stirred. As a result, as shown in FIG. 3, conductive binder-impregnated active material particles 16 in which the conductive binder 14 is impregnated into gaps between the primary particles 10 are obtained.

[0023] As the negative electrode active material, any material can be used without any particular limitation as long as it is one material or two or more materials, which can be used in a lithium ion secondary battery of the related art, and can be in the form of a secondary particle which is an aggregate of plural primary particles. Preferable examples of the negative electrode active material include a negative electrode active material which contains, as a major component, an oxide (lithium titanate) containing lithium and titanium as constituent metal elements, for example, $Li_4Ti_5O_{12}$, $LiTi_2O_4$, or Li_2TiO_3. The charge-discharge reaction potential of lithium titanate is higher than the reduction decomposition potential of an electrolytic solution. Therefore, lithium titanate is preferable from the viewpoints of suppressing the reaction decomposition of the electrolytic solution and improving cycle characteristics. In addition, the calorific value of lithium titanate at a high temperature is relatively small. Therefore, lithium titanate is also preferable from the viewpoint of suppressing a temperature increase, for example,

during overcharge. Alternatively, a negative electrode active material which contains a material containing at least one of silicon and tin as a major component may also be used.

[0024] As such a material, for example, material powder which can be prepared using a well-known method of the related art can be used as it is. For example, material powder can be preferably used which is substantially formed of secondary particles having an average secondary particle size of about 1 μm to 10 μm (preferably 3 μm to 6 μm) based on a laser diffraction scattering method. In addition, the average primary particle size of the material powder is preferably 300 nm or less, more preferably 200 nm or less, and still more preferably 100 nm or less. Due to a decrease in the average primary particle size, the diffusion length of lithium ions in the primary particles decreases, which enables a high-performance battery to be realized. From the viewpoint of promoting the impregnation of the conductive binder, the average primary particle size is preferably 10 nm or more, more preferably 20 nm or more, and still more preferably 30 nm or more. The manufacturing method disclosed herein can be more preferably applied to active material particles having an average secondary particle size and an average primary particle size in the above-described ranges. The average primary particle size of the material powder can be obtained by electron microscopy. As a specific procedure, for example, a predetermined number (for example, 100) of primary particles contained in the material powder as a measurement object are observed using a scanning electron microscope (SEM), and half ((I+d)/2) of the sum of the length I and the thickness d of each particle image is calculated as a primary particle size. The average of primary particle sizes of the predetermined number of primary particles can be calculated as an average primary particle size.

[0025] It is preferable that the conductive binder used in the stirring step has superior electron conductivity and can be melted at a relatively low temperature. For example, the melting point of the conductive binder is suitably about 300°C or lower, preferably 250°C or lower, and more preferably 200°C or lower (for example, 180°C or lower). In addition, it is preferable that the conductive binder can allow the primary particles of the active material to be bonded with a high bonding strength. Further, it is

preferable that the conductive binder can be easily impregnated into the gaps between the primary particles of the active material in a molten state. A conductive binder satisfying the above-described conditions can be used without any particular limitation. As the conductive binder, for example, a conductive polymer material such as polypyrrole, polyaniline, polyacetylene, polythiophene, polyparaphenylene, polyphenylene vinylene, polyacrylonitrile, or polyoxadiazole can be used. Among these conductive binders, one kind may be used alone, or two or more kinds may be used in combination. Among these, polypyrrole, polyaniline, or polyacetylene is preferable, and polypyrrole is more preferable. Polypyrrole has a relatively low melting point (melting point: 175°C) and exhibits high electron conductivity. Therefore, polypyrrole can be preferably used as the conductive binder suitable for the object of the invention.

[0026] Regarding the addition amount of the conductive binder, a ratio of the conductive binder is preferably 4 mass% or more with respect to 100 mass% of the total mass of the conductive binder-impregnated active material particles. When the ratio of the conductive binder is excessively low, the effect (the effect of suppressing the peeling of the primary particles) obtained by impregnation of the conductive binder may be insufficiently obtained. On the other hand, when the ratio of the conductive binder is excessively high, the amount of the active material contributing to the charge-discharge reaction is relatively decreased. Therefore, it may be difficult to realize a secondary battery having a high energy density. From the viewpoint of realizing a secondary battery having a high energy density, the ratio of the conductive binder is suitably about 10 mass% or less, preferably 8 mass% or less, and more preferably 6 mass% or less.

[0027] In the stirring step of the manufacturing method disclosed herein, the secondary particles of the active material and the conductive binder are mixed with each other and are stirred while being heated such that the conductive binder is in a molten state. As a result, the conductive binder in a molten state can be impregnated into the gaps between the primary particles. The heating temperature is not particularly limited as long as it is higher than the melting point of the conductive binder, and varies depending on the kind of the conductive binder. For example, the heating temperature can be set to be

substantially 150°C to 300°C (preferably 150°C to 200°C).

[0028] A stirrer for the stirring is not particularly limited, and examples thereof include a planetary mixer, a homogenizer, a disperser, a ball mill, a kneader, and a mixer. In the stirring step, it is preferable that the stirring is sufficiently performed until the conductive binder is uniformly impregnated into the gaps between the primary particles. For example, the stirring time can be set to be typically 10 minutes to 120 minutes (preferably 30 minutes to 60 minutes). In addition, in the stirring step, it is preferable that the stirring is performed in a reduced-pressure atmosphere in order to promote the impregnation of the conductive binder. For example, the reduced-pressure atmosphere (gauge pressure) is set to be typically -80 kPa or lower (preferably -90 kPa or lower).

<Isotropic Consolidation Step>

[0029]

In the isotropic consolidation step Step S20, the conductive binder-impregnated active material particles obtained in the stirring step are isotropically consolidated. That is, the conductive binder-impregnated active material particles are put into a rubber container and sealed. Next, the same pressure is applied to the conductive binder-impregnated active material particles through the rubber container in three directions including an up-down direction, a right-left direction, and a front-back direction. The conductive binder-impregnated active material particles are isotropically pressed to be consolidated. Due to the consolidation treatment, as shown in FIG. 4, the gaps between the primary particles 10 are decreased, and the primary particles 10 can be strongly bonded to each other through the conductive binder 14 impregnated between the primary particle 10. As a pressing device used in the isotropic consolidation step, any well-known pressing device of the related art which is used for isotropic pressing can be used without any particular limitation. For example, commercially available cold isostatic pressing (CIP) equipment can be appropriately adopted.

[0030] In the isotropic consolidation step, it is preferable that the pressing is sufficiently performed such that the gaps between the primary particles of the active material are decreased so as to prevent the peeling of the primary particles in the rolling

step. For example, it is preferable that the consolidation pressure in the isotropic consolidation step is higher than the rolling pressure in the rolling step described below. For example, the consolidation pressure in the isotropic consolidation step can set to be higher than the rolling pressure in the rolling step by 93 MPa or higher (for example, 93 MPa to 200 MPa), preferably 100 MPa or higher, and more preferably 110 MPa or higher. When the consolidation pressure value in the isotropic consolidation step is as described above, the peeling of the primary particles in the rolling step described below can be efficiently prevented. In a preferred embodiment, the consolidation pressure in the isotropic consolidation step can be set in a range, for example, 250 MPa to 400 MPa (preferably 280 MPa to 350 Mpa).

[0031] In addition, the pressing time in the isostatic consolidation step is suitably in a range of 5 minutes to 60 minutes and preferably in a range of 10 minutes to 30 minutes. When the pressing time is in the above-described range, the gaps between the primary particles of the active material can be efficiently decreased. In addition, in the isotropic consolidation step, it is preferable that the consolidation treatment is performed in a reduced-pressure atmosphere. For example, the reduced-pressure atmosphere (gauge pressure) is set to be typically -80 kPa or lower (preferably -90 kPa or lower). After the isotropic consolidation step, optionally, an appropriate cracking treatment may be performed. As a result, the conductive binder-impregnated active material particles (secondary particles) can be cracked into a desired size.

<Coating Step>

[0032]

In the coating step Step S30, the conductive binder-impregnated active material particles which are consolidated in the isotropic consolidation step are mixed with a solvent to prepare a paste for forming a negative electrode active material layer. A negative electrode current collector is coated with the paste to form a negative electrode active material layer on the negative electrode current collector.

[0033] Examples of the solvent used in the paste for forming a negative electrode active material layer include an organic solvent such as N-methylpyrrolidone (NMP),

pyrrolidone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, toluene, dimethylformamide, or dimethylacetamide; and a combination of two or more of the above-described organic solvents. Alternatively, an aqueous solvent may be used from various points of view such as a reduction in environmental burden, a reduction in material cost, the simplification of facilities, a reduction in the amount of a waste, and the improvement of handleability. As the aqueous solvent, water or a mixed solvent containing water as a major component is preferably used. As a solvent component constituting the mixed solvent other than water, one kind or two or more kinds of organic solvents (for example, lower alcohols or lower ketones) which can be uniformly mixed with water can be used.

[0034] In addition to the conductive binder-impregnated active material particles (negative electrode active material) and the solvent, the paste for forming a negative electrode active material layer contains a material which may be used as a component of a negative electrode active material layer in a general lithium ion secondary battery. Examples of the material include a conductive material and a binder.

[0035] Examples of the conductive material include carbon materials such as carbon powder and carbon fiber. One material alone or a combination of two or more materials selected from among the above exemplary conductive materials may be used. As the carbon powder, for example, powders of various carbon blacks (for example, acetylene black, oil furnace black, graphitized carbon black, carbon black, graphite, and ketjen black) and graphite powder may be used.

[0036] The binder allows the conductive binder-impregnated active material particles (negative electrode active material) contained in the negative electrode active material layer to be bonded to particles of the conductive material or allows these particles to be bonded to the negative electrode current collector. As such a binder, a polymer which can be dissolved or dispersed in a solvent to be used may be used. For example, in a paste for forming a negative electrode active material layer in which a nonaqueous solvent is used, a polymer such as polyvinylidene fluoride (PVDF), polyvinylidene chloride (PVDC), or polyacrylonitrile (PAN) can be preferably adopted. In a positive

electrode mixture composition in which an aqueous solvent is used, a water-soluble or water-dispersible polymer can be preferably adopted as the binder, the water-soluble or water-dispersible polymers including: cellulose-based polymers (for example, carboxymethyl cellulose (CMC) and hydroxypropyl methylcellulose (HPMC)); and rubbers (for example, a vinyl acetate copolymer, a styrene butadiene copolymer (SBR), and an acrylic acid-modified SBR resin (for example, SBR latex)). In addition, examples of the material which can be used as a component of the negative electrode active material layer include various polymer materials which can be used as a thickener of the paste for forming a negative electrode active material layer.

[0037] The mixing (kneading) operation of mixing the conductive binder-impregnated active material particles with the conductive material and the binder in the solvent can be performed using, for example, an appropriate stirrer (for example, a planetary mixer, a homogenizer, CLEAR MIX, or FILL MIX). During the preparation of the paste for forming a negative electrode active material layer, the conductive binder-impregnated active material particles, the conductive material, the binder, and a small amount of a solvent are kneaded into a thick paste. Next, the obtained kneaded material may be diluted with an appropriate amount of solvent.

[0038] The operation (step) of coating the negative electrode current collector with the paste for forming a negative electrode active material layer can be performed using the same method as that of preparing a negative electrode for a general lithium ion secondary battery of the related art. For example, for the coating, an appropriate well-known coater of the related art such as a slit coater, a die coater, a comma coater, or a gravure coater can be used. In this case, by using an elongated belt-shaped current collector sheet, the negative electrode current collector can be continuously coated with the paste for forming a negative electrode active material layer. The paste for forming a negative electrode active material layer with which the negative electrode current collector is coated is dried using appropriate drying means (for example, a hot air drying furnace in which gas heated by an appropriate heat source is blown). As a result, the solvent is removed from the paste for forming a negative electrode active material layer. By

removing the solvent from the paste for forming a negative electrode active material layer, a negative electrode active material layer can be formed.

[0039] The coating weight (in terms of solid content) of the negative electrode active material layer in the coating step is suitably about 22 mg/cm^2 or more, preferably 25 mg/cm^2 or more, and more preferably 27 mg/cm^2 or more. Along with an increase in the coating weight of the negative electrode active material layer, a secondary battery having a high energy density can be realized. In addition, from the viewpoint of reducing battery resistance, the coating weight of the negative electrode active material layer is suitably about 44 mg/cm^2 or less, preferably 40 mg/cm^2 or less, more preferably 35 mg/cm^2 or less, and still more preferably 30 mg/cm^2 or less. For example, it is preferable that the coating weight of the negative electrode active material layer is 22 mg/cm^2 to 44 mg/cm^2 from the viewpoint of realizing a secondary battery having a high energy density and reducing resistance.

[0040] Although not particularly limited, a ratio of the mass of the conductive binder-impregnated active material particles to the total mass of the negative electrode active material layer is preferably about 50 mass% or more (typically 50 mass% to 99 mass%) and more preferably about 70 mass% to 95 mass% (for example, 75 mass% to 95 mass%). The ratio of the mass of the conductive material to the total mass of the negative electrode active material layer is, for example, about 1 mass% to 10 mass% and is usually preferably about 2 mass% to 5 mass%. When the binder is used, the ratio of the mass of the binder to the total mass of the negative electrode active material layer is, for example, about 1 mass% to 10 mass% and is usually preferably about 2 mass% to 5 mass%.

<Rolling Step>

[0041]

In the rolling step Step S40, the negative electrode active material layer obtained in the coating step is rolled (pressed) in a thickness direction. A rolling device can be arbitrarily selected among rolling devices which are commonly used in a step of preparing a negative electrode for a general lithium ion secondary battery. For example, a roll pressing machine or a flat pressing machine can be used. In the rolling step, the thickness

and density of the negative electrode active material layer obtained in the coating step can be appropriately adjusted. It is preferable that the rolling pressure in the rolling step is lower than the consolidation pressure in the isotropic consolidation step as described above. In a preferred embodiment, the rolling pressure in the rolling step can be set in a range, for example, 100 MPa to 240 MPa (preferably 150 MPa to 210 MPa).

[0042] According to this configuration, as shown in FIG. 3, in the stirring step, the conductive binder 14 is impregnated into the gaps between the primary particles 10 of the active material such that the primary particles 10 are bonded to each other through the conductive binder 14. Further, as shown in FIG. 4, in the isotropic consolidation step, the gaps between the primary particles 10 are decreased, and the primary particles 10 are strongly bonded to each other through the conductive binder 14. Therefore, the peeling of the primary particles 10 which may occur in the rolling step can be prevented.

[0043] Although not particularly limited, the density of the negative electrode active material layer after the rolling step is suitably about 2 g/cm^3 or more (for example, 2 g/cm^3 to 2.2 g/cm^3) and preferably 2.1 g/cm^3 or more. Due to an increase in the density of the negative electrode active material layer, the number of contact points between the conductive binder-impregnated active material particles 16 increases. Therefore,battery resistance can be reduced, and cycle characteristics can be further improved. In such a high-density negative electrode active material layer, the pressure applied to the individual primary particles 10 during rolling is high, and the primary particles 10 are likely to be peeled off from each other. However, according to this configuration, even when such a high-density negative electrode active material layer is used, the peeling of the primary particles 10 during rolling can be efficiently prevented, and a conductive path between the primary particles 10 can be appropriately secured.

[0044] In this way, a negative electrode (negative electrode sheet) having a configuration in which the negative electrode active material layer containing the negative electrode active material is held on the negative electrode current collector can be obtained.

<Conductive Binder-Impregnated Active Material Particles>

[0045]

As shown in FIGS. 1 to 4, the negative electrode disclosed herein can be prepared through the following steps including: a stirring step of mixing secondary particles 12, which are aggregates of plural primary particles 10 of a negative active material, with a conductive binder 14 to obtain a mixture and stirring the obtained mixture such that conductive binder-impregnated active material particles 16 in which the conductive binder 14 is impregnated into gaps between the primary particles 10 are obtained; an isotropic consolidation step of isotropically consolidating the conductive binder-impregnated active material particles 16; a coating step of mixing the consolidated conductive binder-impregnated active material particles 16 with a solvent to obtain a paste and coating a negative electrode current collector with the obtained paste to form a negative electrode active material layer on the negative electrode current collector; and a rolling step of rolling the negative electrode active material layer. Therefore, in the conductive binder-impregnated active material particles 16 contained in the obtained negative electrode active material layer, the gaps between the primary particles 10 is small, and the DBP absorption number tends to decrease. Typically, the DBP absorption number of the conductive binder-impregnated active material particles 16 is about 45 (g/100 cm^3) or less (for example, 20 (g/100 cm^3) to 45 (g/100 cm^3)), and may be preferably 34 (g/100 cm^3) or less, and more preferably 30 (g/100 cm^3) or less. In the conductive binder-impregnated active material particles 16 having a DBP absorption number in the above-described range, the gaps between the primary particles 10 is small, and the primary particles 10 are strongly bonded to each other through the conductive binder 14. Therefore, the peeling of the primary particles 10 which may occur in the rolling step can be prevented. The DBP absorption number (g/100 cm^3) can be obtained according to JIS K 6217-4 "Carbon black for rubber industry, -Fundamental characteristics- Fourth Part: Determination of DBP".

[0046] In the negative electrode obtained as above, the peeling of the primary particles which may occur in the rolling step can be efficiently prevented, and higher performance can be obtained. Therefore, the negative electrode can be preferably used as a component of batteries having various configurations or a component (for example, a negative electrode) of an electrode body equipped in the batteries.

[0047] For example, the negative electrode can be preferably used as a component of a lithium ion secondary battery, the lithium ion secondary battery including: a negative electrode that is obtained using any one of methods disclosed herein; a positive electrode (which may be a positive electrode manufactured by applying the invention thereto); an electrolyte that is interposed between the positive and negative electrodes; and a separator that typically separates the positive and negative electrodes from each other (the separator is not necessarily provided in a battery in which a solid or gel electrolyte is used). For example, the structure (for example, a metal case or a laminate film structure) and size of an external case constituting the battery, or the structure (for example, a wound structure or a laminate structure) of an electrode body including positive and negative electrode current collectors as major components is not particularly limited.

<Lithium Ion Secondary Battery>

[0048]

Hereinafter, an embodiment of a lithium ion secondary battery including the negative electrode (negative electrode sheet) which is manufactured using the above-described method will be described with reference to schematic diagrams shown in FIGS. 5 and 6. FIG. 5 is a cross-sectional view showing a lithium ion secondary battery 100 according to an embodiment of the invention. FIG. 6 is a diagram showing an electrode body 40 included in the lithium ion secondary battery 100. In the lithium ion secondary battery 100, a negative electrode (negative electrode sheet) 60 is manufactured using the above-described method in which the conductive binder-impregnated active material particles are used.

[0049] In the lithium ion secondary battery 100 according to the embodiment of the invention, as shown in FIG. 5, a battery case (that is, an external case) 20 is formed in a flat square shape. In the lithium ion secondary battery 100, as shown in FIGS. 5 and 6, the flat wound electrode body 40 and a liquid electrolyte (electrolyte) 80 are accommodated in the battery case 20.

<Battery Case>

[0050]

The battery case 20 includes: a box-shaped (that is, a bottomed rectangular parallelepiped-shaped) case main body 21 having an opening at an end (corresponding to an upper end in a normal operating state of the battery 100); and a lid (sealing plate) 22 formed of a rectangular plate member that is attached to the opening to block the opening. A material of the battery case 20 is not particularly limited as long as it is the same material as that used in a lithium ion secondary battery of the related art. It is preferable that the battery case 20 is mainly formed of a light-weight metal material having high thermal conductivity, and examples of the metal material include aluminum.

[0051] As shown in FIG. 5, a positive electrode terminal 23 and a negative electrode terminal 24 for external connection are formed on the lid 22. A thin safety valve 30 and a liquid injection port 32 are formed between both the terminals 23, 24 of the lid 22. The safety valve 30 is configured to release an internal pressure of the battery case 20 when the internal pressure increases to be a predetermined level or higher. In FIG. 5, after liquid injection, the liquid injection port 32 is sealed with a sealing material 33.

<Wound Electrode Body>

[0052]

As shown in FIG. 6, the wound electrode body 40 includes: a positive electrode (positive electrode sheet 50) having an elongated sheet shape; a negative electrode (negative electrode sheet 60) having an elongated sheet shape as in the case of the positive electrode sheet 50; and two separators (separators 72, 74) having an elongated sheet shape.

<Positive Electrode Sheet>

[0053]

The positive electrode sheet 50 includes a belt-shaped positive electrode current collector 52 and a positive electrode active material layer 53. As the positive electrode current collector 52, for example, a metal foil suitable for the positive electrode may be suitably used. In this embodiment, aluminum foil is used as the positive electrode current collector 52. An uncoated portion 51 is set along one edge of the positive electrode current collector 52 in the width direction. In the example shown in the drawing, the positive electrode active material layer 53 is held on both surfaces of the positive electrode

current collector 52 other than the uncoated portion 51 set on the positive electrode current collector 52. The positive electrode active material layer 53 contains positive electrode active material particles, a conductive material, and a binder. As the conductive material and the binder, the same conductive material and binder as those of the above-described negative electrode can be used.

[0054] As the positive electrode active material, a material capable of storing and releasing lithium ions is used. For example, one kind or two or more kinds of materials (for example, an oxide having a layered structure or an oxide having a spinel structure) which are used in a lithium ion secondary battery of the related art are used without any particular limitation. Examples of the positive electrode active material include a lithium-containing transition metal oxide such as a lithium-nickel composite oxide, a lithium-cobalt composite oxide, or a lithium-manganese composite oxide. Since these materials (typically, particulate) can be in the form of a secondary particle which is an aggregate of plural primary particles, the manufacturing method according to the invention can be preferably applied thereto.

[0055] In a preferred embodiment, the calorific value of the positive electrode active material per 1 g in a safety evaluation test is 1.5 kJ/g or less (for example, 0.5 kJ/g to 1.5 kJ/g). Here, the safety evaluation test is performed as follows. First, an electrolytic solution is added to a predetermined amount of positive electrode active material, and the obtained solution is sealed in a measurement container. Next, using a differential scanning calorimeter (DSC), exothermic behavior in a range from room temperature to 450°C at a temperature increase rate of 15°C/min is measured. In this case, the calorific value of the positive electrode active material per 1 g can be calculated from the peak area of the obtained exothermic behavior. The calorific value of the positive electrode active material per 1 g is suitably about 1.5 kJ/g or less and preferably 1.2 kJ/g or less. By using the positive electrode active material having a small calorific value, a temperature increase, for example, during overcharge can be suppressed.

[0056] The positive electrode active material layer 53 is formed, for example, by mixing the positive electrode active material particles, the conductive material, and the

binder described above with each other in a solvent to prepare a paste (slurry) for forming a positive electrode active material layer, coating (coating and drying) the positive electrode current collector 52 with the paste, and rolling the positive electrode active material layer. At this time, as a solvent used in the paste for forming a positive electrode active material layer, both an aqueous solvent and a nonaqueous solvent can be used. For example, the same solvents as those used in the paste for forming a negative electrode active material layer can be used.

<Negative Electrode Sheet>

[0057]

As shown in FIG. 6, the negative electrode sheet 60 includes a belt-shaped negative electrode current collector 62 and a negative electrode active material layer 63. As the negative electrode current collector 62, for example, a metal foil suitable for the negative electrode may be suitably used. In this embodiment, as described above, belt-shaped aluminum foil is used as the negative electrode current collector 62. An uncoated portion 61 is set along one edge of the negative electrode current collector 62 in the width direction. The negative electrode active material layer 63 is held on both surfaces of the negative electrode current collector 62 other than the uncoated portion 61 set on the negative electrode current collector 62. As described above, the negative electrode active material layer 63 contains the conductive binder-impregnated active material particles as the negative electrode active material. Since the method of manufacturing the negative electrode sheet is as described above, the description thereof will not be repeated.

<Separators>

[0058]

As shown in FIG. 6, the separators 72,74 are members which separate the positive electrode sheet 50 and the negative electrode sheet 60 from each other. In this example, the separators 72, 74 are configured of a band-shaped sheet material having a predetermined width which has plural fine holes. As the separators 72, 74, a separator having a single-layer structure or a laminated structure which is formed of a porous polyolefin resin may be used. In addition, a layer containing insulating particles is further

formed on a surface of the sheet material formed of the above-described resin. Here, examples of the insulating particles include insulating inorganic particles (for example, a filler such as a metal oxide or a metal hydroxide) and insulating resin particles (for example, particles of polyethylene, polypropylene, or the like). In this example, as shown in FIG. 6, a width b1 of the negative electrode active material layer 63 is slightly wider than a width a1 of the positive electrode active material layer 53. Further, widths c1, c2 of the separators 72, 74 are slightly wider than the width b1 of the negative electrode active material layer 63 (c1, c2>b1>a1).

<Installation of Wound Electrode Body>

[0059]

In the embodiment, as shown in FIG. 6, the wound electrode body 40 is pressed to be bent flat in one direction perpendicular to a winding axis WL. In the example shown in FIG. 6, the uncoated portion 51 of the positive electrode current collector 52 and the uncoated portion 61 of the negative electrode current collector 62 are spirally exposed on both sides of the separators 72, 74, respectively. In this embodiment, as shown in FIG. 5, the center portion of the uncoated portion 51 is welded to current collector tabs 25, 26 of the electrode terminals (internal terminals), in which the current collector tabs 25, 26 are collectively disposed inside the battery case 20. In FIG. 5, reference numerals 25a, 26a represent the welded portions.

[0060] The wound electrode body 40 is accommodated in the case main body 21 in order from an upper end opening of the case main body 21, and this opening is sealed, for example, by welding with the lid 22. In addition, the electrolytic solution 80 is disposed (injected) into the case main body 21 through the liquid injection port 32.

<Electrolytic Solution (Nonaqueous Electrolytic Solution)>

[0061]

As the electrolytic solution (nonaqueous electrolytic solution) 80, the same nonaqueous electrolytic solution as that used for a lithium ion secondary battery in the related art may be used without any particular limitation. Typically, such a nonaqueous electrolytic solution has a composition in which an appropriate nonaqueous solvent

contains a supporting electrolyte. As the nonaqueous solvent, one kind or two or more kinds selected from the group consisting of ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, and 1,3-dioxolane may be used. In addition, as the supporting electrolyte, for example, a lithium salt such as $LiPF_6$, $LiBF_4$, $LiAsF_6$, $LiCF_3SO_3$, $LiC_4F_9SO_3$, $LiN(CF_3SO_2)_2$, or $LIC(CF_3SO_2)_3$ may be used. For example, a nonaqueous electrolytic solution in which a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) (for example, volume ratio=3:4:3) contains $LiPF_6$ in a concentration of about 1 mol/L may be used.

[0062] The nonaqueous electrolytic solution may contain a gas producing agent which reacts to produce gas when the battery voltage reaches a predetermined voltage or higher. As the gas producing agent, for example, cyclohexylbenzene (CHB) or biphenyl (BP) can be used. For example, during overcharge, cyclohexylbenzene (CHB) and biphenyl (BP) cause a polymerization reaction to produce gas (here, hydrogen gas). The addition amount of the gas producing agent with respect to the nonaqueous electrolytic solution may be, for example, 0.05 mass% to 10 mass%.

[0063] Next, the liquid injection port 32 is sealed with the sealing material 33. As a result, the assembly of the lithium secondary battery 100 according to the embodiment is completed. The sealing process of the battery case 20 and the injection process of the electrolytic solution may be the same as those which are performed when a lithium ion secondary battery of the related art is manufactured. These processes are not characteristics of the invention. In this way, the construction of the lithium ion secondary battery 100 according to the embodiment is completed.

[0064] In the lithium secondary battery 100 constructed in this way, as described above, the bonding strength between the primary particles in the conductive binder-impregnated active material particles (negative electrode active material) is sufficiently secured, and the peeling of the primary particles in the rolling step can be suitably suppressed. Therefore, superior battery performance can be exhibited. For example, by constructing a battery (for example, a lithium ion secondary battery) using the

above-described conductive binder-impregnated active material particles, a secondary battery can be provided which satisfies at least one (preferably all) of the following advantageous effects including: superior cycle characteristics; high energy density; superior input and output characteristics; and superior thermal stability.

[0065] As a preferable application target of the technique disclosed herein, for example, a secondary battery may be used which has a high volume energy density of 220 Wh/L or more (for example, 220 Wh/L to 400 Wh/L), 240 Wh/L or more (for example, 240 Wh/L to 300 Wh/L), or 250 Wh/L or more (for example, 250 Wh/L to 280 Wh/L) and which is assumed to be used in charging-discharging cycles including high-rate charging and discharging at, for example, 10 C or higher (for example, 10 C to 50 C) or 20 C or higher (for example, 20 C to 40 C).

[0066] In a preferred embodiment of the secondary battery, when the facing area between the positive electrode active material layer 53 of the positive electrode 50 and the negative electrode active material layer 63 of the negative electrode 60 is represented by S (m^2), and when the battery capacity is represented by X (Ah), it is preferable that a ratio S/X (that is, the facing area between the positive and negative electrodes per 1 Ah of the battery capacity) satisfies about 0.015 m^2/Ah to 0.03 m^2/Ah. When the ratio S/X is in the above-described range, the optimum secondary battery which satisfies both high energy density and high input and out performance at high levels can be constructed.

<Example 1>

[0067]

Hereinafter, several examples relating to the invention will be described, but the examples are not intended to limit the invention.

<Preparation of Conductive Binder-Impregnated Active Material Particles>

[0068]

Lithium titanate (here, $Li_4Ti_5O_{12}$ was used) as a negative electrode active material; and polypyrrole as a conductive binder were mixed with each other at a mass ratio of 96:4. The mixture was put into a stirrer (a planetary mixer was used) and then was stirred for 30 minutes while heating it at 180°C under a reduced pressure of -90 kPa (gauge pressure)

(stirring step). The obtained mixed powder was put into a rubber container and sealed under a reduced pressure of -90 kPa. Next, using CIP equipment (piston CIP equipment manufactured by Kobe Steel Ltd. was used), the mixed powder was isotropically consolidated under 300 MPa (isotropic consolidation step). After the consolidation treatment, the powder extracted from the rubber container was crushed. In this way, conductive binder-impregnated active material particles according to Example 1 were obtained. The DBP absorption number of the conductive binder-impregnated active material particles was 31 (g/100 cm^3).

<Negative Electrode Sheet>

[0069]

A negative electrode sheet was prepared as follows. The obtained conductive binder-impregnated active material particles; acetylene black (AB) as a conductive material; polyvinylidene fluoride (PVDF) as a binder were kneaded in N-methylpyrrolidone (NMP) such that a mass ratio of the materials was 92.8:3.5:3.7. As a result, a paste for forming a negative electrode active material layer was prepared. Aluminum foil (negative electrode current collector) having a thickness of 12 μm was coated with the paste such that the coating weight thereof (the coating amount in terms of solid content, that is, the dry mass of the negative electrode active material layer) was 40.7 mg/cm^2 and was dried. As a result, a negative electrode active material layer was formed on the aluminum foil (coating step). Next, the negative electrode active material layer was rolled under a pressing pressure of 188 MPa such that the density of the negative electrode active material layer was 2.0 g/cm^3 (rolling step). In this way, a negative electrode sheet according to Example 1 was prepared.

<Positive Electrode Sheet>

[0070]

A positive electrode sheet was prepared as follows. $LiNi_{0.85}Co_{0.15}Mn_{0.05}O_2$ powder as a positive electrode active material; AB as a conductive material; and PVDF as a binder were kneaded in N-methylpyrrolidone (NMP) such that a mass ratio of the materials was 93.55:3.75:2.7. As a result, a paste for forming a positive electrode active material layer

was prepared. Aluminum foil (positive electrode current collector) having a thickness of 12 μm was coated with the paste and dried. As a result, a positive electrode active material layer was formed on the aluminum foil. Next, the positive electrode active material layer was rolled. As a result, a positive electrode sheet was prepared.

[0071] In addition, the calorific value of the positive electrode active material per 1 g was measured. Specifically, an electrolytic solution was added to a predetermined amount of positive electrode active material, and the obtained solution was sealed in a measurement container. Next, using differential scanning calorimeter (DSC), exothermic behavior in a range from room temperature to 450°C at a temperature increase rate of 15°C/min was measured. The calorific value of the positive electrode active material per 1 g was calculated from the peak area of the obtained exothermic behavior. In Example 1, the calorific value of the positive electrode active material per 1 g was 1.2 kJ/g.

<Preparation of Lithium Ion Secondary Battery>

[0072]

The positive electrode sheet and the negative electrode sheet were laminated with two separators interposed therebetween, and the laminate was wound in an elliptical shape to prepare a wound body. This wound body was pressed to be flattened from the horizontal direction. As a result, a flat wound electrode body was prepared. This wound electrode body and a nonaqueous electrolytic solution were accommodated in a battery case (here, a square case was used), and an opening of the battery case was air-tightly sealed. Here, in order to prepare the separator, a porous layer (thickness: 4 μm) containing insulating alumina particles was formed on a porous sheet (thickness: 16 μm) having a three-layer structure of polypropylene (PP)/polyethylene (PE)/polypropylene (PP). In addition, in order to prepare the electrolytic solution, ethylene carbonate, dimethyl carbonate, and ethyl methyl carbonate were mixed with each other at a volume ratio of 3:4:3, and 1.1 mol of $LiPF_6$ was dissolved in the mixed solution. 4 mass% of CHB and 1 mass% of BP were added to the electrolytic solution. In this way, a battery for an evaluation test was prepared.

<Measurement of Initial Capacity>

[0073]

The obtained battery was put into a thermostatic chamber at 25°C, was charged to 2.7 V at a constant current and a constant voltage. Next, the battery was put into a thermostatic chamber at 60°C and was left to stand in for 24 hours so as to be activated. After the activation step, the initial capacity of the battery for an evaluation test was measured at a temperature of 25°C in a voltage range of 1.5 V to 2.7 V according to the following Steps 1 to 3. Step 1: The battery was discharged at a constant current of 0.1 C until the voltage reached 1.5 V. Next, the battery was discharged at a constant voltage for 2 hours, and the operation was stopped for 10 seconds. Step 2: After Step 1, the battery was charged at a constant current of 0.1 C until the voltage reached 2.7 V. Next, the battery was charged at a constant voltage for 2 hours, and the operation was stopped for 10 seconds. Step 3: After Step 2, the battery was discharged at a constant current of 0.1 C until the voltage reached 1.5 V. Here, the discharge capacity during the discharge at the constant current in Step 3 was set as the initial capacity (battery rated capacity).

[0074] Here, the initial capacity of the battery of Example 1 was 39 Ah. In addition, the volume energy density was 240 Wh/L. In addition, the S/X ratio (area/capacity) was 0.017 (m^2/Ah) which was obtained by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Example 2>

[0075]

A battery for an evaluation test of Example 2 was prepared by the same procedure as that of Example 1, except that the coating weight of the negative electrode active material layer was changed to 44 mg/cm^2, the density of the negative electrode active material layer was changed to 2.2 g/cm^3, the pressing pressure in the rolling step was changed to 207 MPa, and the calorific value of the positive electrode active material per 1 g was changed to 1.5 kJ/g. The DBP absorption number of the conductive binder-impregnated active material particles was 32 (g/100 cm^3). In addition, the volume energy density was 255 Wh/L. In addition, the S/X ratio (area/capacity) was 0.015 (m^2/Ah) which was obtained

by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Example 3>

[0076]

A battery for an evaluation test of Example 3 was prepared by the same procedure as that of Example 1, except that the coating weight of the negative electrode active material layer was changed to 27.2 mg/cm^2. The DBP absorption number of the conductive binder-impregnated active material particles was 30 (g/100 cm^3). In addition, the volume energy density was 220 Wh/L. In addition, the S/X ratio (area/capacity) was 0.025 (m^2/Ah) which was obtained by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Example 4>

[0077]

A battery for an evaluation test of Example 4 was prepared by the same procedure as that of Example 1, except that the coating weight of the negative electrode active material layer was changed to 22 mg/cm^2, the density of the negative electrode active material layer was changed to 2.2 g/cm^3, and the pressing pressure in the rolling step was changed to 207 MPa. The DBP absorption number of the conductive binder-impregnated active material particles was 34 (g/100 cm^3). In addition, the volume energy density was 224 Wh/L. In addition, the S/X ratio (area/capacity) was 0.03 (m^2/Ah) which was obtained by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Example 5>

[0078]

A battery for an evaluation test of Example 5 was prepared by the same procedure as that of Example 1, except that the pressure in the isotropic consolidation step was changed to 100 MPa. The DBP absorption number of the conductive binder-impregnated active material particles was 45 (g/100 cm^3). In addition, the volume energy density was 240

Wh/L. In addition, the S/X ratio (area/capacity) was 0.017 (m^2/Ah) which was obtained by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Comparative Example>

[0079]

A battery for an evaluation test of Comparative Example was prepared by the same procedure as that of Example 1, except that a negative electrode active material (lithium titanate) into which a conductive binder was not impregnated was used; and the isotropic consolidation treatment was not performed. The DBP absorption number of the negative electrode active material into which a conductive binder was not impregnated was 52 (g/100 cm^3). In addition, the volume energy density was 240 Wh/L. In addition, the S/X ratio (area/capacity) was 0.017 (m^2/Ah) which was obtained by dividing the facing area S (m^2) between the positive electrode active material layer and the negative electrode active material layer by the initial capacity X (Ah).

<Evaluation of Battery for Evaluation Test>

[0080]

The performance of the battery for an evaluation test was evaluated based on the IV resistance as output characteristics, the capacity retention after cycles, and the temperature increase after a nail penetration test. Next, regarding the battery for an evaluation test constructed as above, the measurement of the IV resistance, the measurement of the capacity retention after cycles, and the nail penetration test will be described in this order.

<IV Resistance of Battery for Evaluation Test>

[0081]

Here, in order to evaluate output characteristics of the battery for an evaluation test, the IV resistance was measured. The IV resistance was measured as follows. Step 1: As SOC adjustment, the battery was charged to SOC 60%. Step 2: After Step 1, the battery was discharged at a current value of 0.8 C for 10 seconds. Here, the current value measured in Step 2 was divided by a voltage drop value ΔV which was obtained by subtracting the voltage value after the discharge for 10 seconds from the initial voltage

value in Step 2. The obtained value was obtained as an IV resistance value.

<Capacity Retention after Cycles>

[0082]

In a cycle test, the battery for an evaluation test underwent a charge-discharge pattern of repeatedly performing charging and discharging at 2C. Specifically, the battery was charged to SOC 85% at a constant current of 2 C, and then was discharged to SOC 20% at a constant current of 2 C. This charging-discharging cycle was continuously performed 2000 times. The capacity retention after cycles was calculated from the equation "(Discharge Capacity in 2000th Cycle/Initial Capacity)×100". The discharge capacity in 2000th cycle was measured by the same procedure as that of the measurement of the initial capacity.

<Nail Penetration Test>

[0083]

As SOC adjustment, the battery for an evaluation test was charged to SOC 100%. Next, an iron nail having a diameter of 6 mm was caused to penetrate into a region near the center of the battery at a speed of 20 mm/sec. At this time, a thermocouple was attached to the outermost surface of the battery case to check whether or not the temperature was continuously increased. Here, a battery where the temperature was not continuously increased was evaluated as "O", and a battery where the temperature was continuously increased was evaluated as "X"

[0084] Regarding each example, the results of the tests are shown in Table 1.

[Table 1]

	Conductive Binder	DBP Absorption Number	Consolidation Pressure	Pressing Pressure	IV Resistance	Capacity Resistance	Nail Penetration Test
		g/100 cm^3	MPa	MPa	mΩ	%	
Example 1	Polypyrrole	31	300	188	1.2	98	O
Example 2	Polypyrrole	32	300	207	1.2	98	O
Example 3	Polypyrrole	30	300	188	0.9	98	O
Example 4	Polypyrrole	34	300	207	0.8	98	O
Example 5	Polypyrrole	45	100	188	1.5	92	O
Comparative Example		52	-	188	1.5	91	O

[0085] As shown in Table 1, in the batteries according to Examples 1 to 5 in which the conductive binder was impregnated into the gaps between the primary particles and the isotropic consolidation treatment was performed, the capacity retention was higher and cycle durability was superior as compared to Comparative Example in which the conductive binder was not used and the isotropic consolidation treatment was not performed. It can be seen from the results that cycle characteristics can be improved by impregnating the conductive binder into the gaps between the primary particles and performing the isotropic consolidation treatment. In addition, in the batteries according to Examples 1 to 4 in which the consolidation pressure in the isotropic consolidation step was higher than the pressing pressure in the rolling step, the capacity retention was higher and the IV resistance was lower as compared to the battery according to Example 5. It can be seen from the above results that it is preferable that the consolidation pressure in the isotropic consolidation step is set to be higher than the pressing pressure in the rolling step. In the batteries provided for the nail penetration test, a continuous temperature increase was not observed. The results show that all the batteries were thermally stable.

[0086] Hereinabove, the invention has been described in detail, but the above-described embodiments and examples are merely exemplary. The invention disclosed herein includes various modifications and alternations of the above-described specific examples. For example, in the above-described example, the electrode body of the secondary battery is the wound electrode body. However, a so-called laminate electrode body may be adopted in which a positive electrode sheet and a negative electrode sheet are alternately laminated with a separator interposed therebetween. In addition,

here, the lithium ion secondary battery is described as an example. However the secondary battery disclosed herein may adopt a structure of a secondary battery other than a lithium ion secondary battery unless expressly stated otherwise.

[0087] In the secondary battery disclosed herein, as described above, the peeling of the primary particles in the rolling step can be preferably suppressed, and cycle durability is superior. Therefore, the secondary battery disclosed herein is preferable as a vehicle-mounted power supply for an automobile in which cycle durability is required at a high level. In this case, for example, the secondary battery disclosed herein can be preferably used as a power supply for driving a motor (electric motor) of a vehicle such as an automobile in the form of a battery pack where plural secondary batteries are connected.

CLAIMS:

1. A method of manufacturing a secondary battery which includes an electrode having a configuration in which an active material layer is held on a current collector, the method comprising:

preparing conductive binder-impregnated active material particles in which a conductive binder is impregnated into gaps between primary particles by mixing and stirring secondary particles, which are aggregates of plural primary particles of an active material, with the conductive binder;

isotropically consolidating the conductive binder-impregnated active material particles;

mixing the consolidated conductive binder-impregnated active material particles with a solvent to obtain a paste and forming an active material layer on a current collector by coating the current collector with the obtained paste; and

rolling the active material layer.

2. The method of manufacturing the secondary battery according to claim 1, wherein

when isotropically consolidating the conductive binder-impregnated active material particles, a consolidation pressure is higher than a rolling pressure when rolling the active material layer.

3. The method of manufacturing the secondary battery according to claim 2, wherein

when isotropically consolidating the conductive binder-impregnated active material particles, the consolidation pressure is higher than the rolling pressure by 93 MPa or higher.

4. The method of manufacturing the secondary battery according to any one of claims 1 to 3, wherein

a ratio of the conductive binder is at least 4 mass% with respect to 100 mass% of the

total mass of the conductive binder-impregnated active material particles.

5. The method of manufacturing the secondary battery according to any one of claims 1 to 4, wherein

as the conductive binder, polypyrrole is used.

6. The method of manufacturing the secondary battery according to any one of claims 1 to 5, wherein

as the active material, lithium titanate is used.

7. The method of manufacturing the secondary battery according to any one of claims 1 to 6, wherein

a density of the active material layer after the rolling step is at least 2 g/cm^3.

8. A secondary battery comprising:

an electrode having a configuration in which an active material layer is held on a current collector, wherein

the active material layer includes conductive binder-impregnated active material particles, the conductive binder-impregnated active material particles including secondary particles, which are aggregates of plural primary particles of an active material, and a conductive binder which are impregnated into gaps between the primary particles, and

a DBP absorption number of the conductive binder-impregnated active material particles is 45 ($g/100\ cm^3$) or less.

9. The secondary battery according to claim 8, wherein

the active material is formed of lithium titanate.

10. The secondary battery according to claim 8 or 9, wherein

a density of the active material layer is at least 2 g/cm^3.

FIG. 1

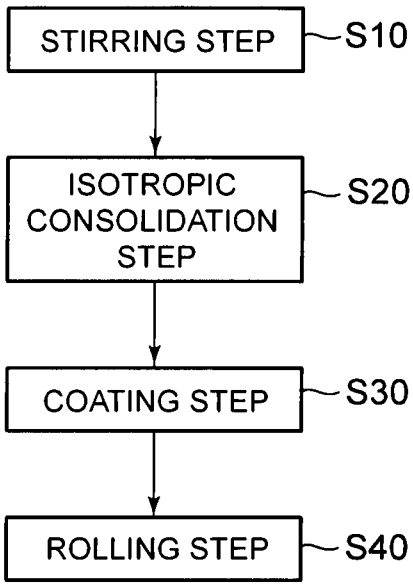

STIRRING STEP
S10
ISOTROPIC CONSOLIDATION STEP
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COATING STEP
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ROLLING STEP
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FIG. 2

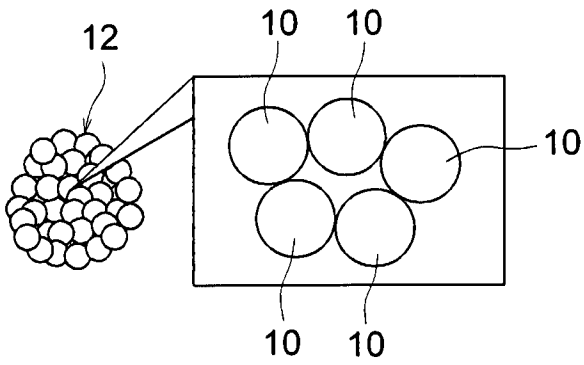


FIG. 3

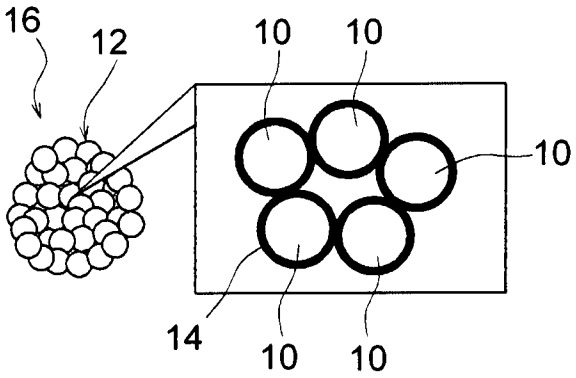


FIG. 4

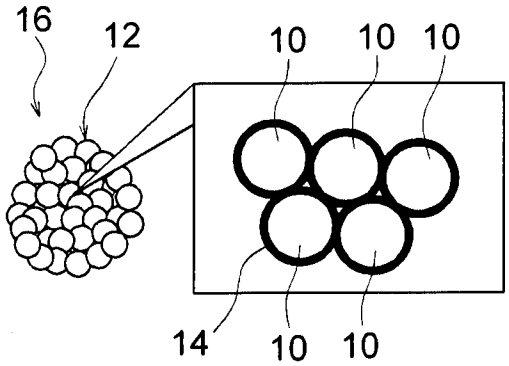


FIG. 5

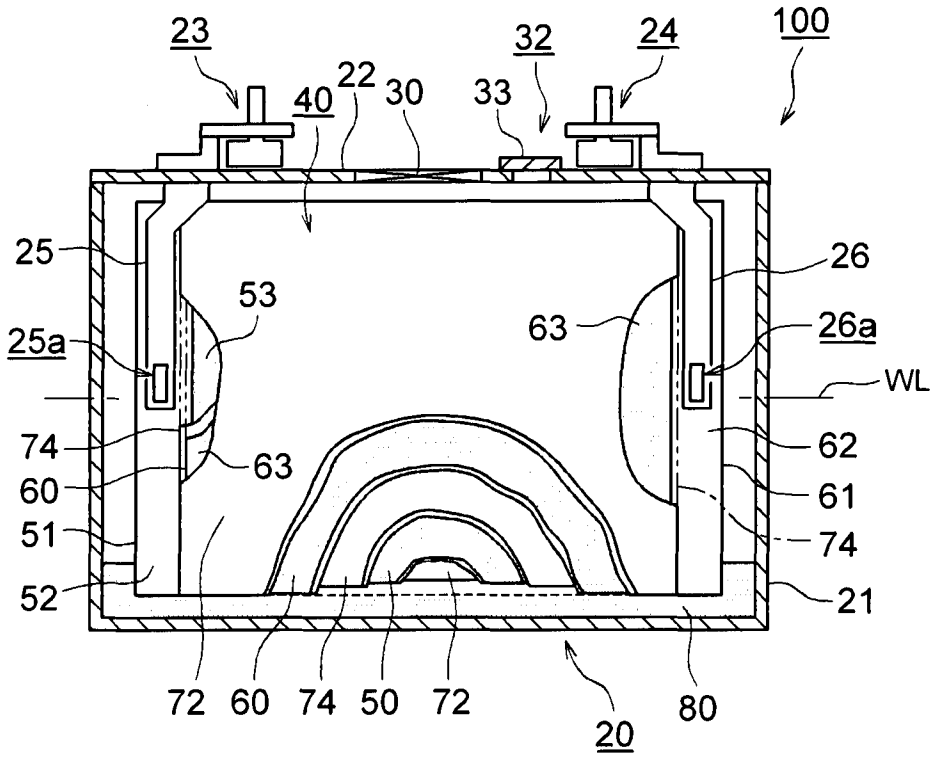
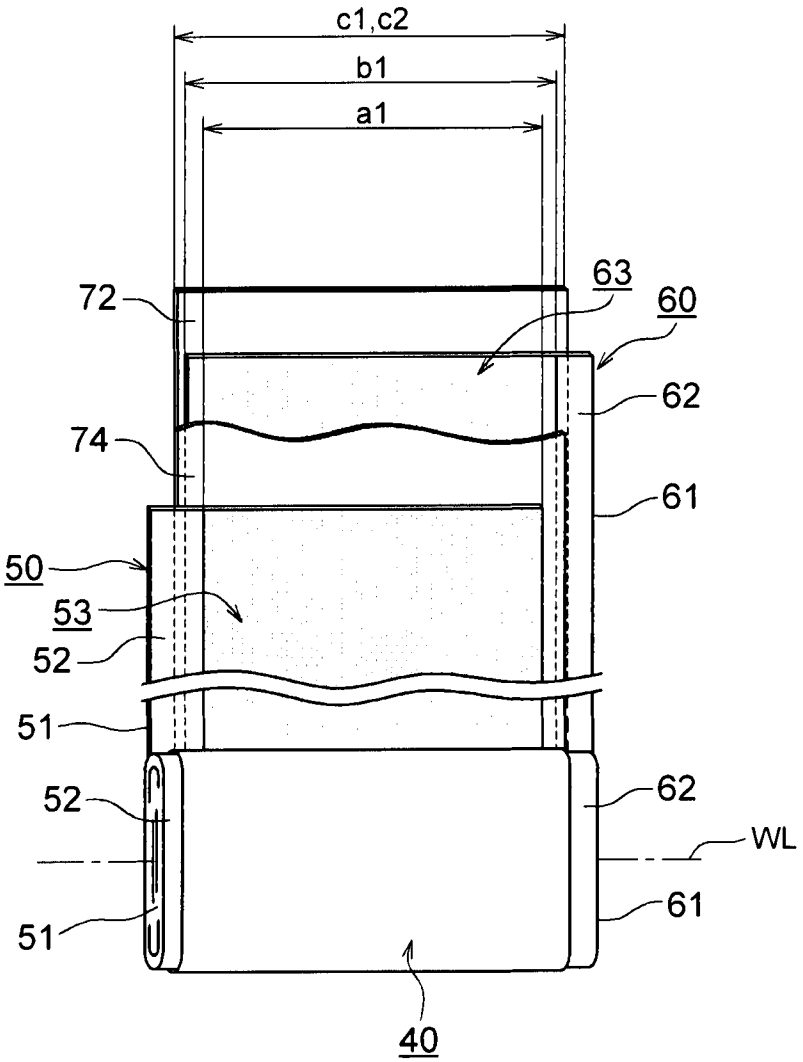

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FIG. 6



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/001647

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/04 H01M4/1391 H01M4/62 H01M4/66
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2001 351634 A (MITSUBISHI HEAVY IND LTD) 21 December 2001 (2001-12-21) abstract paragraphs [0014] - [0019] paragraphs [0035], [0057]	1-10
Y	US 2005/221182 A1 (FUJIWARA SHOZO [JP] ET AL) 6 October 2005 (2005-10-06) page 2, paragraph 0023 - page 3, paragraph 0043 page 9, paragraph 0144	1-10
Y	JP 2007 220324 A (KANSAI COKE & CHEMICALS) 30 August 2007 (2007-08-30)	1-7
A	abstract paragraph [0010] - paragraph [0016]	8-10

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 December 2015	17/12/2015

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Kelly, Michael

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2015/001647

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 2013/209888 A1 (NAGAI HIROKI [JP]) 15 August 2013 (2013-08-15) page 2, paragraph 0023-0034 -----	1-10

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INTERNATIONAL SEARCH REPORT

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