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Natalia Lehmann

Natalia Lehmann

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(21) Application number	Japanese Patent Application 2001-238662 (P2001-238662)	(71) Applicants	000001203 Shin-kobe Electric Machinery Co., Ltd.
(22) Application date	August 7, 2001 (2001.8.7)		2-8-7 Nihonbashimoto-cho, Chuo-ku, Tokyo
		(72) Inventor	Kenji Doihara 2-8-7 Nihonbashimoto-cho, Chuo-ku, Tokyo Within Shin-kobe Electric Machinery Co., Ltd.
		(72) Inventor	Katsunori Suzuki 2-8-7 Nihonbashimoto-cho, Chuo-ku, Tokyo Within Shin-kobe Electric Machinery Co., Ltd.
		(72) Representatives	100104721 Patent attorney Toshiaki Igarashi

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

(57) [Abstract]

[Challenges] Provides lithium secondary batteries with small variations in battery capacity and long life.

[Solution means] Cylindrical lithium-ion secondary batteries comprise a positive electrode formed on an aluminum foil with a positive electrode mixture layer containing lithium *manganate* and a negative electrode formed on an electrolytic copper foil with a negative electrode mixture layer containing

amorphous carbon. Electrolytic copper foil was used for the negative electrode current collector with a variation in weight per unit area of 2% or less and an elongation rate of 5% or less when pressing the negative electrode mixture layer. The variation in the thickness of the negative electrode current collector is suppressed, and the distortion of the electrolytic copper foil is small, preventing the occurrence of micro-short circuits.

[Scope of patent claims]

[Claim 1] A lithium secondary battery, comprising a positive electrode containing a lithium composite oxide, a negative electrode in which a negative electrode mixture layer containing a carbon material capable of doping and dedoping lithium ions by charging and discharging is formed on a negative electrode current collector, and an organic electrolyte solution that allows the movement of the lithium ions, wherein the negative electrode current collector is characterized by an electrolytic copper foil having a weight variation of 2% or less per unit area and an elongation of 5% or less before pressing the negative electrode mixture layer to a predetermined bulk density.

[Claim 2] The lithium secondary battery according to Claim 1, characterized in that the respective negative electrode current collector has a thickness of 7 μm to 25 μm and a surface roughness R_z of 2.0 μm or less.

[Detailed Description of the Invention]

[0001]

[Technical field to which the invention belongs]

The invention relates to lithium secondary batteries, in particular, lithium secondary batteries comprising a positive electrode containing lithium composite oxide, a negative electrode mixture layer containing carbon material that can dope and dedope lithium ions by charge and discharge, a negative electrode formed on a negative electrode current collector, and an organic electrolyte solution that allows movement of said lithium ions.

[0002]

[Prior Art] Lithium secondary batteries are mainly used for power supplies for portable devices such as VTR cameras, notebook personal computers, and cell phones, taking advantage of the benefits of high energy density. The internal structure of this battery is typically wound as shown below. Both the positive and negative electrodes are in the form of strips in which active material is applied to metal foil, and the cross section of the electrodes is wound in a spiral shape with a separator sandwiched between them so that the positive and negative electrodes do not come into direct contact with each other, forming a wound group. The wound group is then housed in a cylindrical can that

serves as a battery container, and after an electrolyte is injected, the opening is sealed.

[0003] A typical cylindrical lithium secondary battery has dimensions of 18 mm in diameter and 65 mm in height, which is called the 18650 type, and is widely used as a small lithium secondary battery for consumer use. The positive electrode active material of the 18650 lithium secondary battery is mainly lithium cobalt oxide, which is characterized by high capacity and long life, and the battery capacity is approximately 1.3 Ah to 1.7 Ah, the output is about 10 W.

[0004] On the other hand, in order to address environmental problems, the development of electric vehicles (EVs) that are completely battery-free and powered, and hybrid (electric) vehicles (HEVs) that are powered by both internal combustion engines and batteries, have been accelerated, and are entering the stage of some practical application.

[0005] Batteries that serve as power sources for EVs, etc. naturally require high capacity and high output characteristics, and lithium secondary batteries are attracting attention as batteries that meet this requirement. Electrode dimensions have been devised to obtain high capacity, high power batteries.

[0006] For the negative electrode current collector of lithium secondary batteries, rolled copper foil is often used. This material has high tensile strength, is resistant to stretching, has excellent stress resistance during the pressing process in electrode production, and has almost the same surface roughness on both sides, making it possible to produce negative electrodes with almost equal adhesion strength of the negative electrode mixture layer.

[0007]

[Challenges to Be Solved by the Invention]

However, large lithium secondary batteries for EVs and the like are repeatedly charged and discharged at a large current, and in order to ensure high capacity and high output, it is necessary to make the positive and negative electrodes thin to increase the opposing area, or to increase the bulk density of the negative electrode mixture layer to make the conductive network stronger and reduce resistance. Therefore, the positive and negative electrodes are long and wound many times. As the

thickness of the rolled copper foil becomes thinner, the number of times of rolling increases, and the variation in thickness in the rolling direction and distortion of the rolled copper foil also increase. This can make it difficult to accommodate the foil in a battery container, cause variation in battery capacity, cause uneven electrode reactions leading to premature battery life, or cause heat generation due to current concentration, compromising the safety of the battery. Therefore, it is important to produce a uniform and smooth electrode.

[0008] In addition, by applying a mixture (slurry) to the negative electrode and then pressing it, it is possible to contain more active material in a given volume, increasing the bulk density of the negative electrode mixture layer and thereby increasing capacity, and to strengthen the conductive network within the negative electrode, thereby achieving higher output and a longer life; however, at the same time, the negative electrode is stretched during the pressing process. If the negative electrode stretches too much, it will undulate in the width direction, causing problems such as wrinkles during the winding process and misalignment of the opposing positive and negative electrodes. [0009] Furthermore, if the charge and discharge are repeated, the negative electrode mixture layer will expand and contract, so the adhesion strength between the negative electrode current collector and the negative electrode mixture layer will be uneven due to the difference in the surface roughness of the negative electrode current collector, and if there is a difference between the length of the negative electrode current collector and the length of the negative electrode mixture layer during pressing, peeling will occur at the interface between the negative electrode collector and the negative electrode mixture layer, leading to a premature end of life. In particular, in the case of overcharging, the expansion of the negative electrode mixture layer increases, which may not only cause peeling at the interface between the negative electrode current collector and the negative electrode mixture layer, but also cause the negative electrode current collector to break, thereby compromising the safety of the battery. Furthermore, when a plurality of batteries are connected for use, if there is a large variation in

the capacity of each battery, the load on each battery will be uneven, resulting in a shortened lifespan. An example of a foil with little distortion is electrolytic copper foil, but it has a smaller tensile strength and is inferior in stress resistance compared to rolled copper foil.

[0010] In view of the above case, the present invention is challenged to provide a battery with a small variation in battery capacity and a long life.

[0011]

[Means for Solving the Problem] To solve the above problem, the present invention features a lithium secondary battery, comprising a positive electrode containing a lithium composite oxide, a negative electrode in which a negative electrode mixture layer containing a carbon material capable of doping and dedoping lithium ions by charging and discharging is formed on a negative electrode current collector, and an organic electrolyte solution that allows the movement of the lithium ions, wherein the negative electrode current collector is characterized by an electrolytic copper foil having a weight variation of 2% or less per unit area and an elongation of 5% or less before pressing the negative electrode mixture layer to a predetermined bulk density.

[0012] In the present invention, since an electrolytic copper foil with a weight variation per unit area of 2% or less is used for the negative electrode current collector, the variation in thickness of the negative electrode current collector can be suppressed and the electrode reaction can be made uniform. In addition, since an electrolytic copper foil with an elongation of 5% or less of the length before pressing when the negative electrode mixture layer is pressed to a predetermined bulk density is used, the distortion when pressed to a predetermined bulk density is small, preventing the occurrence of spontaneous short circuits, and a battery with small variation in battery capacity and long life can be obtained.

[0013] In this case, it is preferable that the negative electrode current collector has a thickness of 7 μm to 25 μm and a surface roughness R_z of 2.0 μm or less.

[0014]

[Embodiment of the invention] Below, an

embodiment of the present invention applied to a cylindrical lithium-ion secondary battery for HEVs will be described with reference to the drawings.

[0015] (Positive electrode) Lithium manganese oxide (LiMn_2O_4) powder as lithium composite oxide of active material, flaky graphite (average particle size: $20\text{ }\mu\text{m}$) as conductive material, acetylene black, and polyvinylidene fluoride as bonding agent were mixed in a ratio of 80:8:2:10 (wt%) to which N-methyl-2-pyrrolidone, a dispersion solvent, was added, and mixed to obtain a slurry. This slurry is applied to both sides of the aluminum foil of a $20\text{ }\mu\text{m}$ thick positive electrode collector, dried, and pressed using a roll press machine set to a surface temperature of 120°C to form a positive electrode mixture layer, cut to a width of 300 mm, a predetermined length, and a thickness of the positive electrode mixture layer (active substance application portion) (not including the thickness of the current collector) to obtain a positive electrode of $260\text{ }\mu\text{m}$. At this time, a 50 mm wide uncoated part was left on one side of the longitudinal direction of the positive electrode, and a notch was made in the uncoated part. The remainder of the cutout was used as a lead piece. Adjacent lead pieces were placed at 20 mm intervals. In addition, the width of the lead piece was set to 10 mm. The bulk density of the positive electrode mixture layer was 2.65 g/cm^3 .

[0016] (Negative electrode) To the 92 parts by weight of Carbotron P powder manufactured by Kureha Co., Ltd., which is an amorphous carbon, as a carbon material of active material, 8 parts by weight of polyvinylidene fluoride was added as a bonding agent to make a negative electrode mixture, and N-methyl-2-pyrrolidone, a dispersion solvent, was added to this, and kneading was performed to obtain a slurry. This slurry is applied to both sides of the electrolytic copper foil (negative electrode current collector) of a predetermined thickness with a weight variation of 2% or less per unit area, dried, and pressed at a predetermined pressure using a roll press machine set to a surface temperature of 120°C to form a negative electrode mixture layer, and cut to obtain a negative electrode having a width of 305 mm, a predetermined length, a predetermined bulk

density, and a negative electrode mixture layer (active material coated portion) of a predetermined thickness (not including the thickness of the current collector). At this time, an uncoated part with a width of 50 mm was left on one side of the longitudinal direction of the negative electrode. Subsequently, the uncoated part was notched in the same way as the positive electrode. The remainder of the cutout was used as a lead piece. Adjacent lead pieces were placed at 20 mm intervals. In addition, the width of the lead piece was set to 10 mm.

[0017] In order to form a negative electrode mixture layer with a predetermined bulk density in this electrolytic copper foil, the longitudinal elongation s of the electrolytic copper foil when pressing the negative electrode surface is 5% or less of the longitudinal length L of the electrolytic copper foil before pressing ($s \leq 0.05L$) was used. Percentage of elongation s to length L (hereinafter referred to as elongation rate) The length L , $L+s$ of the electrolytic copper foil before and after pressing was measured and calculated at $s/L \times 100$ (%). Before and after pressing, the lengths of the electrolytic copper foil were marked on both ends so that the lengths were known, and the length between the marks was measured with a stainless steel ruler to determine the lengths L , $L+s$.

[0018] In addition, the amount of active material loaded into the positive and negative electrodes was set so that the chargeable capacity up to the charge end potential of the positive electrode of 4.5 V (Li/Li + standard) and the chargeable capacity up to the charge end voltage of the negative electrode of 0 V (Li/Li + standard) were the same per unit area facing each other via the separator. Incidentally, for positive electrode active materials, the rechargeable capacity of lithium manganate per unit active material weight was 105 mAh/g and the rechargeable capacity of negative electrode active materials was 450 mAh/g.

[0019] (Battery creation) The positive electrode and the negative electrode thus prepared were wound together with a $40\text{ }\mu\text{m}$ thick polyethylene separator interposed therebetween so as not to come into direct contact with each other. At this time, as shown in FIG. 1, the lead pieces 9 of the positive electrode and the

negative electrode were positioned on both end faces of the wound group 6 on the opposite sides to each other. The length of the positive electrode, negative electrode, and separator was adjusted to have an outer diameter of 65 ± 0.1 mm in the wound group 6. In addition, the length of the negative electrode was made 18 cm longer than the length of the positive electrode, so that when the positive electrode and negative electrode were wound, the positive electrode would not protrude from the negative electrode in the winding direction at the innermost circumference, and the positive electrode would not protrude from the negative electrode in the winding direction at the outermost circumference. The width of the negative electrode mixture layer was 5 mm longer than the width of the positive electrode mixture layer so that the positive electrode mixture layer does not protrude from the negative electrode mixture layer even in the direction perpendicular to the winding direction. [0020] The lead pieces 9 extending from the positive electrode are deformed, and all of them are brought into contact with the periphery of the flange 7, which protrudes integrally from the pole (positive electrode external terminal 1) that is approximately on an extension of the shaft core 11. Then, the lead pieces 9 and the periphery of the flange 7 are ultrasonically welded together to connect and fix the lead pieces 9 to the periphery of the flange 7. In addition, the connection operation of the negative electrode external terminal 1' and the lead piece 9 extending from the negative electrode was performed in the same manner as the connection operation of the positive electrode external terminal 1 and the lead piece 9 extending from the positive electrode.

[0021] After that, an insulation coating 8 was applied to the entire periphery of the flange portion 7 of the positive electrode external terminal 1 and the negative electrode external terminal 1'. This insulation coating 8 also affected the entire circumference of the circumferential surface of the wound group 6. For the insulation coating 8, an adhesive tape was used, the base of which was polyimide and one side of which was coated with an adhesive made of hexamethacrylate. This adhesive tape was wound multiple times from the peripheral

surface of the flange portion 7 to the outer peripheral surface of the wound group 6 to form an insulation coating 8. The number of windings is adjusted so that the maximum diameter part of the wound group 6 is the part where the insulation coating 8 is present, and the maximum diameter is made slightly smaller than the inner diameter of the stainless steel battery container 5, and the wound group 6 is inserted into the battery container 5. The outer diameter of the battery container 5 is 67 mm and the inner diameter is 66 mm.

[0022] Then, a second ceramic washer 3' made of alumina and having a thickness of 2 mm at the part that abuts the back surface of the disk-shaped battery lid 4, an inner diameter of 16 mm and an outer diameter of 25 mm was fitted onto the electrode post whose tip constitutes the positive electrode external terminal 1' [sic.] and the electrode post whose tip constitutes the negative electrode external terminal 1'. In addition, a first ceramic washer 3 made of alumina and having a plate shape with a thickness of 2 mm, an inner diameter of 16 mm and an outer diameter of 28 mm was placed on the battery lid 4, and the positive electrode external terminal 1 and the negative electrode external terminal 1' were each passed through the first ceramic washer 3. The four peripheral end faces of the battery lid were then fitted to the opening of the battery container 5 and the entire contact area of both sides was laser welded. At this time, the positive electrode external terminal 1 and the negative electrode external terminal 1' penetrate a hole formed in the center of the battery lid 4 and protrude to the outside of the battery lid 4. The first ceramic washer 3, a metal washer 14 smoother than the bottom surface of the metal nut 2, were then fitted into the positive electrode external terminal 1 and the negative electrode external terminal 1' respectively in this order. The battery lid 4 is provided with a rupture valve 10 that ruptures in response to an increase in the internal pressure of the battery. The rupture pressure of the rupture valve 10 is 1.3×10^6 to 1.8×10^6 Pa.

[0023] Nut 2 was then threaded onto positive electrode external terminal 1 and negative electrode external terminal 1', respectively, and battery lid 4 was secured by tightening between

flange portion 7 and nut 2 via the second ceramic washer 3', the first ceramic washer 3 and the metal washer 14. The tightening torque value at this time was 7 N·m. The metal washer 14 did not rotate until the tightening work was completed. In this state, the compression of the rubber (EPDM) O-ring 16 interposed between the back surface of the battery lid 4 and the flange portion 7 blocks the power generation element inside the battery container 5 from the outside air.

[0024] Thereafter, a predetermined amount of organic electrolyte was injected into the battery container 5 through the injection port 15 provided in the battery lid 4, and then the injection port 15 was sealed to complete the cylindrical lithium ion secondary battery 20.

[0025] The organic electrolyte used was a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate in a volume ratio of 1:1:1, with 1 mol/L of lithium hexafluorophosphate (LiPF6) dissolved in it. The cylindrical lithium-ion battery 20 is not provided with a current interrupt mechanism that blocks current in response to an increase in the internal pressure of the battery container 5.

[0026]

[Examples] Next, the cylindrical lithium ion secondary battery 20 of the examples made according to the present embodiment described above will be described. The battery of the comparative example made for comparison will also be described.

[0027] (Example 1) As shown in Table 1 below, in Example 1, an electrolytic copper foil (e.g., WS foil manufactured by Furukawa Circuit Foil Co., Ltd.) with an average thickness of 10 μm (89 g/m²), and a weight variation per unit area of 1.0% was used as the negative electrode current collector. The surface of the negative electrode was pressed with a linear pressure of 3.9×10^5 N/m, and a vent pressure of 3.0×10^6 Pa to obtain a negative electrode with a negative electrode mixture layer thickness of 60 μm and a bulk density of 1.00 g/cm³. The variation in the capacity (A.h) of the three batteries in this example was 1%.

[0028]

(Table 1)

	Variations (%)
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	Collector weight	Capacity
Embodiment 1	1.0	1
Embodiment 2	2.0	3
Comparative Example 1	3.0	8
Comparative Example 2	4.0	12

[0029] (Example 2) As shown in Table 1, in Example 2, electrolytic copper foil with a weight variation per unit area of 2.0% was used for the negative electrode current collector, and a battery was fabricated in the same manner as in Example 1. The variation in the capacity (A.h) of the three batteries in this example was 3%.

[0030] (Comparative Examples 1 and 2) As shown in Table 1, in Comparative Examples 1 and 2, electrolytic copper foil with a weight variation per unit area of 3.0% and 4.0%, respectively, was used for the negative electrode current collector, and batteries were fabricated in the same manner as in Example 1. The variation in the capacity of the three batteries (A.h.) in this comparative example was 8% and 12%, respectively.

[0031] (Example 3) As shown in Table 2 below, in Example 3, an electrolytic copper foil with a surface roughness R_z (a ten-point average surface roughness) = 1.5 μm and a thickness of 7 μm was used for the negative electrode current collector. The negative electrode surface was pressed with a linear pressure of 5.9×10^5 N/m and a vent pressure of 3.0×10^6 Pa, and a battery was fabricated using a negative electrode with a negative electrode mixture layer thickness of 55 μm , a bulk density of 1.05 g/cm³ and an elongation rate of 4.8%. In order to investigate the incidence of defects (short circuits) described below, multiple wound groups were prepared (the same applies to the following examples and comparative examples).

[0032]

(Table 2)

	Negative electrode current collector	
	Thickness (μm)	Growth rate (%)
Comparative Example 3	6	6.0
Embodiment 3	7	4.8
Embodiment 4	10	3.5
Embodiment 5	15	2.5
Embodiment 6	20	2.2
Embodiment 7	25	2.0

[0033] (Examples 4-7) As shown in Table 2, in Examples 4-7, batteries were fabricated in the same manner as in Example 3, except that electrolytic copper foils with thicknesses of 10, 15, 20, and 25 μm , respectively, and elongations of 3.5, 2.5, 2.2, and 2.0%, respectively, were used for the negative electrode current collector.

[0034] (Comparative Example 3) As shown in Table 2, in Comparative Example 3, a battery was fabricated in the same manner as in Example 3, except that an electrolytic copper foil with a thickness of 6 μm and an elongation rate of 6.0% was used for the negative electrode current collector.

[0035] (Example 8) As shown in Table 3 below, in Example 8, an electrolytic copper foil with a surface roughness R_z of 0.8 μm and an average thickness of 10 μm was used for the negative electrode current collector. The surface of the negative electrode was pressed with a linear pressure of $3.9 \times 10^5 \text{ N/m}$ and a vent pressure of $3.0 \times 10^6 \text{ Pa}$ to obtain a negative electrode with a negative electrode mixture layer having a thickness of 60 μm and a bulk density of 1.00 g/cm^3 . The electrodeposition conditions were changed to change the surface roughness R_z of the electrolytic copper foil. The surface roughness of the electrolytic copper foil was measured in accordance with JIS C 6511 10. A

plurality of negative electrodes were prepared in order to provide them for a peeling test described later (the same applies to the following Examples and Comparative Examples).

[0036]

(Table 3)

	R_z (μm)
Embodiment 8	0.8
Embodiment 9	1.2
Example 10	1.5
Example 11	2.0
Comparative Example 4	2.5

[0037] (Examples 9 to 11) As shown in Table 3, in Examples 9 to 11, batteries were fabricated in the same manner as in Example 8, except that electrolytic copper foils with surface roughnesses R_z of 1.2, 1.5, and 2.0 μm , respectively, were used for the negative electrode current collector.

[0038] (Comparative Example 4) As shown in Table 3, in Comparative Example 4, the battery was made in the same manner as in Example 8 except that electrolytic copper foils with surface roughnesses R_z was used for the negative electrode current collector and 2.5 μm of electrolytic copper foil was used.

[0039] (Test/Evaluation) Next, for each of the negative electrodes, wound groups, and batteries of the examples and comparative examples prepared as described above, a peeling test of the negative electrodes, calculation of the incidence rate of defects (short circuits) in the winding groups, and a cycle life test to determine the life of the batteries were performed in the following manner.

[0040] <Peeling test> In Examples 8 to 11 and Comparative Example 4, a 180° peeling test was also performed to measure the adhesion strength of the interface between the negative electrode mixture layer of each negative

electrode and the electrolytic copper foil.

[0041] <Calculation of the short circuit incidence rate> In Examples 3 to 11 and Comparative Examples 3 and 4, after the positive and negative electrodes were wound and assembled, the resistance of the wound group was measured using an alternating current resistance meter to investigate the incidence of the short circuit in the separator.

[0042] <Cycle life test> Each prepared battery was discharged after charging at room temperature, and the discharge capacity was measured. The charging conditions were a constant voltage of 4.2 V, a limited current of 80 A, and a time of 3.5 hours. The discharge conditions were a constant current of 20 A and a final voltage of 2.5 V. Thereafter, the fabricated battery was repeatedly charged and discharged in a thermostatic chamber set at 50°C in the same manner as above, and the time when the battery reached 70% of its initial capacity was determined to be the end of its life.

[0043] The test results of the cycle life test are shown in Tables 4 to 6 below, the calculation results of the short circuit incidence rate are shown in Tables 5 and 6 below, and the test results of the peeling test are shown in Table 6 below.

[0044]
(Table 4)

	Number of cycles
Embodiment 1	500
Embodiment 2	450
Comparative Example 1	200
Comparative Example 2	100

[0045]
(Table 5)

	Short circuit rate (%)	Number of cycles
Comparative	5	150

ive Example 3		
Embodiment 3	0	450
Embodiment 4	0	500
Embodiment 5	0	500
Embodiment 6	0	500
Embodiment 7	0	500

[0046]
(Table 6)

	Adhesion strength (9.8 N/m)	Short circuit incidence (%)	Number of cycles (time(s))
Embodiment 8	200	0	370
Embodiment 9	190	0	350
Example 10	180	0	350
Example 11	150	0	300
Comparative Example 4	100	2	200

[0047] As shown in Table 4, the battery of Comparative Examples 1 and 2 with a variation in the weight of the negative electrode current collector exceeding 2% has a variation in the battery capacity of 8% or more, and the battery with this battery connected in series has reached an early life. Investigation of the cause showed that the capacity of the smallest battery was significantly reduced, resulting in the battery life. When there is a large variation in the capacity of each battery, it is believed that a load is placed on the battery with the smaller capacity, causing it, for example, to go into an over-discharged or over-charged state, resulting in a significant decrease in capacity. This also results in a loss of safety and reliability of the battery pack.

[0048] On the other hand, the batteries of Examples 1 to 3, in which the variation in weight of the negative electrode collector was kept to 2% or less, had a battery capacity variation of 3% or less, and a battery pack in which these batteries were connected in series exhibited cycle life characteristics of more than 450 cycles. Therefore, by using electrolytic copper foil with a weight variation of 2% or less in the negative electrode current collector, a battery with excellent cycle life characteristics can be realized. For example, when a large number of batteries are connected, such as large batteries for electric vehicles, it is possible to maintain good cycle life characteristics by further reducing the variation in capacity of each battery.

[0049] In addition, as shown in Table 5, in the wound group of Comparative Example 3, where the longitudinal elongation of the negative electrode after the pressing process exceeds 5%, the distortion of the negative electrode becomes very large, and variations occur in the outer diameter of the wound group after the winding. When the wound group is measured with an AC resistance meter after the winding and assembly, the resistance of the wound group is low, and the waviness of the positive electrode caused the opposing position with the negative electrode to shift, and insulation with the separator is not sufficiently performed. In addition, the tension required for winding must be large, which results in tight winding and deformation of the wound group into a bumpy shape. The wound group is also sensitive to the unevenness of the electrode surface, causing frequent short-circuits through the separator, and the battery reaches an early end of life in cycle life tests.

[0050] On the other hand, the resistance of the wound group of Examples 3 to 7 using a negative electrode with a longitudinal elongation of 5% or less after the pressing process showed a value of 50 M Ω or more, it was confirmed that it was isolated by a separator, and the battery also showed cycle life characteristics of 450 cycles or more. Therefore, by using electrolytic copper foil with a weight variation of 2% or less, a thickness of 7 μm to 25 μm , a surface roughness of R_z of 1.5 μm , and an elongation of 5% or less in the negative

electrode current collector, a battery with excellent cycle life characteristics can be realized.

[0051] Furthermore, as shown in Table 6, when the surface roughness R_z of the negative electrode current collector increases, the contact area between the negative electrode current collector and the negative electrode mixture layer decreases, and as a result, the adhesion strength of the interface between the negative electrode current collector and the negative electrode mixture layer decreases, and the cycle characteristics decrease, suggesting that this is the cause of the above-mentioned early life. Therefore, by using electrolytic copper foil with a weight variation of 2% or less, a thickness of 10 μm , and a surface roughness of R_z of 2.0 μm or less in the negative electrode current collector, a battery with excellent cycle life characteristics can be realized.

[0052] In the battery of this example, by using a negative electrode current collector that can withstand pressing stress to obtain the required negative electrode bulk density, the longitudinal elongation of the negative electrode can be suppressed to 5% or less, and a negative electrode with low distortion and a large bulk density of the combination agent can be obtained. Therefore, even electrolytic copper foil, which is inferior to tensile strength and stress resistance compared to rolled copper foil, can be used to obtain a battery with a small variation in capacity and a long life. Lithium secondary batteries with such high output and high rate discharge characteristics are particularly suitable for electric and hybrid electric vehicles.

[0053] In the above embodiments, while examples are given for large secondary batteries used for electric vehicle power supplies, etc., it goes without saying that the battery is not limited to its intended use, size, or capacity. Also, it is possible to apply the invention to cylindrical lithium ion batteries with a structure in which the battery top lid is sealed by a caulk in a bottom cylinder container (can). However, because electric vehicles require relatively high capacity, high power batteries, it is particularly preferred to mount the batteries of the above embodiments to which the invention has been applied.

[0054] In the above embodiment, a cylindrical lithium ion secondary battery not equipped with a current interruption mechanism is exemplified, but the present invention may be applied to a battery equipped with a current interruption mechanism. In this way, the mechanical split valve 10 operates even if the electrical current shut-off mechanism does not operate in the event of an abnormality such as a vehicle collision accident, ensuring higher safety of the vehicle-mounted battery.

[0055] Furthermore, in the above embodiment, an adhesive tape having a polyimide base material and an adhesive made of hexamethacrylate applied to one side thereof is used for the insulation coating 8, but this is not limited thereto. For example, it is possible to suitably use an adhesive tape having a polyolefin base material such as polypropylene or polyethylene and an acrylic adhesive such as hexamethacrylate or butyl acrylate applied to one or both sides thereof, or a tape made of polyolefin or polyimide without an adhesive applied thereto.

[0056] Also, in the above embodiments, lithium manganate was used as the positive electrode, amorphous carbon as the negative electrode for lithium ion batteries, and a mixture of ethylene carbonate, dimethyl carbonate, and diethyl carbonate in a volume ratio of 1:1:1, in which 1 mole/liter of lithium hexafluorophosphate was dissolved, was used as the electrolyte, but there is no particular limitation on the method for producing the battery of the present invention, and any of the commonly used negative electrode active materials and non-aqueous electrolytes can be used. In order to ensure the safety of high-capacity, high-power batteries for electric vehicle applications, it is more desirable to use lithium manganate, a lithium manganese compound oxide, rather than lithium-cobalt and lithium-nickel composite oxides as positive electrode active materials. Acetylene black was also illustrated as a conductive aid, but other conductive aids may be used, and no conductive aids may be used.

[0057] In addition, although polyvinylidene fluoride was used as a bonding agent in the above embodiments, polymers such as Teflon®, polyethylene, polystyrene, polybutadiene, butyl rubber, nitrile rubber, styrene/butadiene rubber,

polysulfide rubber, nitro cellulose, cyanoethyl cellulose, various latexes, acrylonitrile, vinylidene fluoride, propylene fluoride, chloroprene fluoride, and mixtures thereof can be used as the bonding agent for electrode plate active materials for lithium ion batteries. However, it is preferable to use a fluoropolymer as described above.

[0058] Furthermore, as a positive electrode active material for lithium secondary batteries other than those shown in the above embodiments, it is preferable to use a material into which lithium can be inserted and removed, and a lithium manganese double oxide into which a sufficient amount of lithium has been inserted in advance. It is also possible to use lithium manganate having a spinel structure or a material in which part of the manganese or lithium in the crystal is replaced or doped with other elements.

[0059] Also, the negative electrode active materials for lithium ion batteries other than those shown in the above embodiments include, for example, natural graphite, various graphite materials made by humans, carbonaceous materials such as coke, etc., but these may be used, and the present invention is not particularly limited in the particle shape, which may be scaly, spherical, fibrous, clumpy, etc.

[0060] Furthermore, as an electrolyte, an electrolyte dissolved in an organic solvent may be used using a common lithium salt as an electrolyte, and this is not particularly limited to lithium salts or organic solvents. For example, LiClO_4 , LiAsF_6 , LiPF_6 , LiBF_4 , $\text{LiB}(\text{C}_6\text{H}_5)_4$, $\text{CH}_3\text{SO}_3\text{Li}$, $\text{CF}_3\text{SO}_3\text{Li}$, and mixtures thereof can be used as the electrolyte.

[0061] Also, examples of the nonaqueous electrolyte organic solvents other than those in the above embodiments include propylene carbonate, ethylene carbonate, 1,2-dimethoxyethane, 1,2-diethoxyethane, γ -butyrolactone, tetrahydrofuran, 1,3-dioxolane, 4-methyl-1,3-dioxolane, diethylether, sulfolane, methylsulfolane, acetonitrile, propionitrile, or the like, a mixed solvent of two or more of these may be used, and the mixture ratio is not limited.

[0062] In the above embodiments, while various dimensions, etc. have been illustrated, the present invention is not limited thereto, and various aspects can be adopted within the scope of the above claims.

[0063]

[Effects of the invention] As explained above, in accordance with the present invention, the following effect can be obtained: Since an electrolytic copper foil with a weight variation per unit area of 2% or less is used for the negative electrode current collector, the variation in thickness of the negative electrode current collector can be suppressed and the electrode reaction can be made uniform. In addition, since an electrolytic copper foil with an elongation of 5% or less of the length before pressing when the negative electrode mixture layer is pressed to a predetermined bulk density is used, the distortion when pressed to a predetermined bulk density is small, preventing the occurrence of spontaneous short circuits, and a battery with small variation in battery capacity and long life can be obtained.

[Brief description of the drawings]

[FIG. 1] A cross-sectional view of a cylindrical lithium ion secondary battery according to an embodiment to which the present invention can be applied.

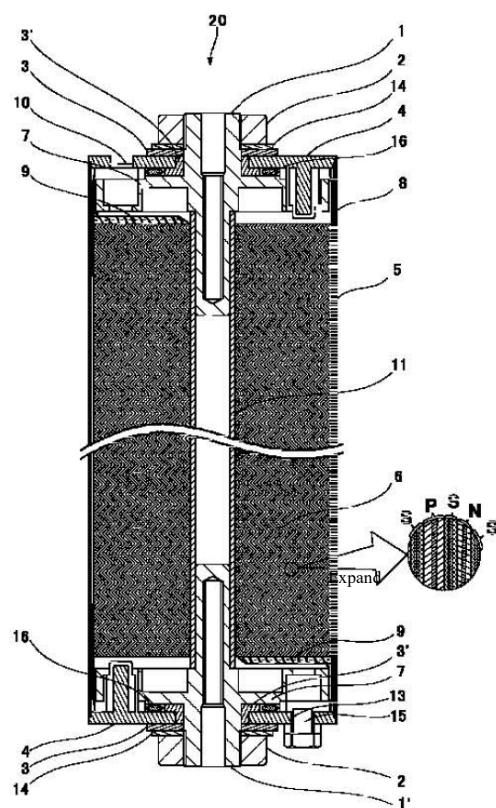
[Explanation of references]

P Positive electrode

N Negative electrode

20 Cylindrical Lithium-Ion Secondary Battery (Lithium Secondary Battery)

[FIG. 1]



- | | |
|---|----------------------------|
| 1 Positive electrode external terminal | 8 Insulation coating |
| 1' Negative electrode external terminal | 9 Lead pieces |
| 2 Nuts | 10 Rupture valve |
| 3 First ceramic washer | 11 Shaft core |
| 3' Second ceramic washer | 12 Solution injection port |
| 4 Battery lid | 13 Positive electrode |
| 5 Battery | 14 Metallic washer |
| | 15 Lids |
| | 16 Nuts |
| | 17 Nuts |
| | 18 Nuts |
| | 19 Nuts |
| | 20 Nuts |
| | S Separator |
| | P Positive electrode |
| | N Negative electrode |

containers	
6 Scales	16
	ORing
7 Steel part	20 Cylindrical Lithium-Ion Secondary Battery

Continued from front page

(72) Inventor: Kensuke Hironaka 2-8-7 Nihonbashimoto-cho, Chuo-ku, Tokyo Within Shin-kobe Electric Machinery Co., Ltd.	F Term	5H0	AA0	AS1	CC0	DD0	EE0
	(reference)	17	3	0	1	1	1
			HH0	HH0			
			1	3			
		5H0	AJ0	AJ1	AJ1	AK0	AL0
		29	1	2	4	3	6
			AM	AM	AM	AM	AM
			02	03	04	05	07
			BJ0	BJ1	DJ0	DJ1	EJ01
			2	4	7	4	
			HJ0	HJ0	HJ0		
			1	3	4		
		5H0	AA0	AA0	AA1	AA1	BA1
		50	7	8	5	9	7
			CA0	CB0	DA0	DA0	FA0
			9	7	3	7	5
			FA1	HA0	HA0	HA0	HA0
			1	0	1	3	4