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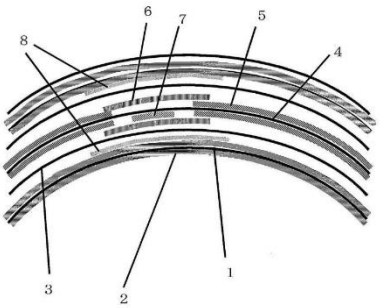
(54) [Title of the Invention] Non-Aqueous Electrolyte Secondary Battery

(57) [Abstract]

[Problem] If an internal short circuit occurs between an uncoated portion of a positive electrode current collector and a negative electrode plate coated with a negative electrode active material, a large current may flow, causing a large drop in open circuit voltage and heat generation.

[Solution] A non-aqueous electrolyte secondary battery having a group of electrodes composed of a positive electrode plate obtained by coating a positive electrode active material on a positive electrode current collector and a negative electrode plate obtained by coating a negative electrode active material on a negative electrode current collector, the positive electrode plate and the negative electrode plate being wound together via a barrier membrane, wherein the positive electrode plate has an uncoated portion somewhere other than the end portions in the length direction, a positive electrode lead is connected to the uncoated portion of the positive electrode plate, the positive electrode lead is covered with tape, and a heat-resistant protective film is formed on the surface of the negative electrode plate opposite the uncoated portion of the positive electrode plate.

[Selected Drawing] FIG. 4



Zhuhai CosMX Battery Co. EX1013
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[Claims]

[Claim 1]

A non-aqueous electrolyte secondary battery having a group of electrodes including a positive electrode plate composed of a positive electrode current collector to which a positive electrode active material has been applied and a negative electrode plate composed of a negative electrode current collector to which a negative electrode active material has been applied, the positive electrode and the negative electrode being wound together via an isolation membrane, the non-aqueous electrolyte secondary battery characterized in that an uncoated portion is provided other than at the end of the positive electrode plate in the length direction, a positive electrode lead is connected to the uncoated portion, the positive electrode lead is covered with tape, and a heat-resistant protective film is formed on the surface of the negative electrode plate facing the uncoated portion.

[Claim 2]

A non-aqueous electrolyte secondary battery having a group of electrodes including a positive electrode plate composed of a positive electrode current collector to which a positive electrode active material has been applied and a negative electrode plate composed of a negative electrode current collector to which a negative electrode active material has been applied, the positive electrode and the negative electrode being wound together via an isolation membrane, the non-aqueous electrolyte secondary battery characterized in that an uncoated portion is provided other than at the end of the positive electrode plate in the length direction, a positive electrode lead is connected to the uncoated portion, and a heat-resistant protective film is formed on the surface of the negative electrode plate facing the uncoated portion.

[Claim 3]

The non-aqueous electrolyte secondary battery according to claim 1 or 2, wherein the positive electrode active material is represented by general formula $Li_xNi_{(1-y-z)}Co_yM_zO_2$ (where x is a variable that changes during charging and discharging, $0 < x < 1.1$, $0 < y \leq 0.5$, $0 \leq z < 0.5$, and M is at least one element selected from the group consisting of Al, Mn, Mg, Ca, Fe, Ti, Zn, Sr, Ba, Zr, Y, B, and Ta).

[Detailed Description of the Invention]

[Technical Field]

[0001]

The present invention relates to a non-aqueous electrolyte secondary battery, and specifically to the structure of the positive electrode plate and negative electrode plate.

[Background Art]

[0002]

In recent years, there has been a rapid increase in the portability and cordlessness of electronic devices such as AV equipment and computers, and there is a growing demand for non-aqueous electrolyte secondary batteries that are compact, lightweight, and have a high energy density as a power source for these devices. Lithium-ion secondary batteries, of which non-aqueous electrolyte secondary batteries are one type, are widely expected to have especially high voltage and high energy density, and the race to increase capacitance, output, and reliability is intensifying. A non-aqueous electrolyte secondary battery has a group of electrodes including a positive electrode plate composed of a positive electrode current collector to which a positive electrode active material has been applied on both sides and a negative electrode plate composed of a negative electrode current collector to which a negative electrode active material has been applied to both sides, the positive electrode and the negative electrode being wound together via a separator serving as an isolation membrane. There is a possibility that the uncoated portions of the positive electrode current collector and the negative electrode plate would

short-circuit and generate heat by penetrating the separator in the portion where the uncoated part of the positive electrode current collector and the negative electrode plate face each other via the separator.

[0003]

In order to prevent the generation of heat, providing a heat-resistant protective film on some or all of the uncoated portion of a current collector facing the other electrode on the positive electrode plate and negative plate located at the winding beginning end and the winding terminating end of the electrode group has been proposed (see, for example, Patent Example 1).

[Patent Document 1] JP 2004-63343 A

[Summary of the Invention]

[Technical Problem]

[0004]

An internal short-circuit test using foreign substances was adopted as a test to confirm the safety of non-aqueous electrolyte secondary batteries. In order to intentionally cause internal short circuits when making groups of electrodes, for example, this test embeds foreign metal substances such as iron in the negative electrode plate in advance. The test involves repeating the charging and discharging process many times to cause an internal short circuit. The test result is determined by attaching a thermocouple to the battery in advance and determining that the battery is "generating heat" when the temperature reaches 100°C or more. If an internal short circuit occurs between the uncoated portion of the positive electrode current collector and the negative electrode plate coated with active material, a large current flows, and there is a possibility of a significant drop in open circuit voltage and abnormal heat generation.

[0005]

The following problems have been found with Patent Document 1. If a heat-resistant protective film is to be applied to some or all of an uncoated portion of a current collector facing the other electrode, the heat-resistant protective film must be formed on the surface of the current collector. As a result, adhesion between the heat-resistant protective film and the current collector becomes poor, and the heat-resistant protective film delaminates when the electrode group is created. The uncoated portion is recessed compared to the electrode portion where the active material has been applied, and so it is difficult to apply a heat-resistant protective film only to the uncoated portion in the manufacturing process (so that the heat-resistant protective film does not cover the portion coated with the active material).

[0006]

For the same reason, it is difficult to precisely form a heat-resistant protective film in the manufacturing process when a lead is connected to the uncoated portion. In a cylindrical non-aqueous electrolyte secondary battery with the positive electrode lead attached to the uncoated portion of a current collector at the winding beginning end of the electrode group, the positive electrode lead is connected by welding to the innermost surface, where the radius of curvature is smallest. As a result, the edge of the positive electrode lead damages the positive electrode plate on the outer circumference, causing the positive electrode plate to break.

[0007]

It is an object of the present invention to solve these problems by providing a non-aqueous electrolyte secondary battery that can form a negative electrode active material layer with very little unevenness and a dense, heat-resistant protective film with high adhesiveness to suppress heat generated during internal short-circuiting, without forming a heat-resistant protective film on the uncoated portion of the positive electrode current collector, by forming a negative electrode mix portion facing the uncoated portion.

[Solution to Problem]

[0008]

In order to solve this problem, the present invention is a non-aqueous electrolyte secondary battery having a group of electrodes including a positive electrode plate composed of a positive electrode current collector to which a positive electrode active material has been applied and a negative electrode plate composed of a negative electrode current collector to which a negative electrode active material has been applied, the positive electrode and the negative electrode being wound together via an isolation membrane, wherein an uncoated portion is provided other than at the end of the positive electrode plate in the length direction, a positive electrode lead is connected to the uncoated portion, the positive electrode lead is covered with tape, and a heat-resistant protective film is formed on the surface of the negative electrode plate facing the uncoated portion.

[0009]

Another aspect of the present invention is a non-aqueous electrolyte secondary battery, wherein an uncoated portion is provided other than at the end of the positive electrode plate in the length direction, a positive electrode lead is connected to the uncoated portion, and a heat-resistant protective film is formed on the surface of the negative electrode plate facing the uncoated portion.

[0010]

By doing this, the generated heat is suppressed when an internal short circuit occurs between the uncoated portion of the positive electrode current collector, which is the component with the highest risk of overheating, and the negative electrode plate coated with negative electrode active material.

[Effects of the Invention]

[0011]

In the present invention, if an internal short circuit occurs between the uncoated portion of the positive electrode current collector and the negative electrode plate coated with negative electrode active material, heat generation does not become high. By protecting only the uncoated portion of the positive electrode current collector and the negative electrode plate coated with negative electrode active material with heat-resistant protective film, the energy density per unit volume of the non-aqueous electrolyte secondary battery can be increased compared to when the entire negative electrode plate is coated with a heat-resistant protective film. Also, by arranging the uncoated portion of the positive electrode current collector in a position other than the edge of the positive electrode plate, for example, by placing the welded part of the positive electrode lead in the center of the positive electrode plate, when the electrode group is created, the winding diameter at the positive electrode lead welding point does not become small, and the damage to the electrode plates due to the lead edge can be greatly alleviated.

[Best Mode of Carrying Out the Invention]

[0012]

An embodiment of the present invention is a non-aqueous electrolyte secondary battery having a group of electrodes including a positive electrode plate composed of a positive electrode current collector to which a positive electrode active material has been applied and a negative electrode plate composed of a negative electrode current collector to which a negative electrode active material has been applied, the positive electrode and the negative electrode being wound together via an isolation membrane, wherein an uncoated portion is provided other than at the end of the positive electrode plate in the length direction, a positive electrode lead is connected to the uncoated portion, the positive electrode lead is covered with tape, and a heat-resistant protective film is formed on the surface of the negative electrode plate facing the uncoated portion.

[0013]

By doing this, a heat-resistant protective film with good adhesion can be densely formed, and the heat generated during internal short-circuiting between the uncoated portion of the positive electrode current collector, which is the portion with the highest risk of heat generation, and the negative electrode plate coated with negative electrode active material, can be suppressed.

[0014]

In another embodiment of the present invention, the non-aqueous electrolyte secondary battery has an uncoated portion somewhere other than the end of the positive electrode plate in the length direction, the positive electrode lead is connected to the uncoated portion of the positive electrode plate, and a heat-resistant protective film is formed on the surface of the negative electrode plate opposite the uncoated portion of the positive electrode.

[0015]

By doing this, a heat-resistant protective film with good adhesion can be densely formed, and the heat generated during internal short-circuiting between the uncoated portion of the positive electrode current collector, which is the portion with the highest risk of heat generation, and the negative electrode plate coated with negative electrode active material, can be suppressed. Also, the risk of overheating is eliminated even if there is no tape affixed to prevent internal short circuits caused by "burrs" generated on the positive electrode lead, so the energy density per unit volume can be increased even further. In a preferred embodiment of the present invention, the positive electrode active material of the non-aqueous electrolyte secondary battery is represented by general formula $Li_xNi_{(1-y-z)}Co_yM_zO_2$ (where x is a variable that changes during charging and discharging, $0 < x < 1.1$, $0 < y \leq 0.5$, $0 \leq z < 0.5$, and M is at least one element selected from the group consisting of Al, Mn, Mg, Ca, Fe, Ti, Zn, Sr, Ba, Zr, Y, B, and Ta).

[0016]

By doing this, a heat-resistant protective film with good adhesion can be densely formed, and the heat generated during internal short-circuiting between the uncoated portion of the positive electrode current collector, which is the portion with the highest risk of heat generation, and the negative electrode plate coated with negative electrode active material, can be suppressed.

[0017]

The positive electrode will now be described in detail.

[0018]

The positive electrode active material can be a lithium-containing transition metal oxide such as lithium cobaltate ($LiCoO_2$) or lithium nickelate ($LiNiO_2$). Spinel-type composite oxides with manganese, which is a relatively inexpensive raw material, such as lithium manganese oxide ($LiMn_2O_4$), can also be used.

[0019]

Thickening agents that can be used in the positive electrode include carboxymethyl cellulose (CMC), methyl cellulose (MC), hydroxy methyl cellulose (HMC), ethyl cellulose, polyvinyl alcohol (PVA), oxidized starch, phosphorylated starch, and casein.

[0020]

There are no particular restrictions on the conductive agent, as long as it is an electrically conductive material. Examples include graphite such as natural graphite (flaky graphite, etc.), artificial graphite, and expanded graphite; carbon blacks such as acetylene black, channel black, furnace black, and thermal black; conductive fibers such as carbon fibers and metal fibers; metal powders such as copper and nickel; and organic conductive materials such as polyphenylene derivatives. These can be used

alone or in a mixture of two or more. Among these conductive agents, artificial graphite, acetylene black, and carbon fibers are especially preferred. The amount of conductive agent added is not particularly limited, but 1 to 30 wt% is preferred relative to the weight of the negative electrode active material, and 1 to 10 wt% by weight is even more preferred.

[0021]

The material in the positive electrode current collector can be aluminum (Al), titanium (Ti), tantalum (Ta), and other metals and their alloys, but aluminum (Al) and its alloys are preferred because they are lightweight and have a high energy density.

[0022]

The negative electrode will now be described in detail.

[0023]

Negative electrode active materials include graphite-based and amorphous carbon materials, as well as mixtures of these, in addition to alloys and metal compounds. These can be used alone or in mixtures of two or more. Alloys are preferably composed of at least one element selected from the group consisting of silicon, tin, aluminum, zinc, magnesium, titanium, and nickel. In addition, metal compounds include at least one selected from the group consisting of oxides and carbides of silicon, tin, aluminum, zinc, magnesium, titanium, and nickel. The average particle size of the negative electrode active material is not particularly limited, but 1 to 30 μm is preferred.

[0024]

The negative electrode current collector can be any electrochemically stable electronic conductor, and metals such as copper, nickel, and stainless steel can be used. Among these, copper foil is preferred because it is inexpensive and easy to process into a thin film. There are no particular restrictions on thickness, but 5 to 25 μm is preferred.

[0025]

There are no particular restrictions on the binder used in the manufacture of the positive and negative electrode plate, as long as it is a material that is stable in relation to the solvents and electrolytes used in the manufacture of the electrodes. For example, polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), styrene-butadiene rubber (SBR), isoprene rubber, butadiene rubber, and ethylene-propylene-diene polymer (EPDM) can be used.

[0026]

The non-aqueous electrolytes will now be described in detail.

[0027]

The non-aqueous solvent is preferably a carbonate. Both cyclic and linear carbonates can be used. Suitable cyclic carbonates include propylene carbonate (PC), ethylene carbonate (EC), and butylene carbonate (BC). These high dielectric constant solvents may be used alone or in combinations of two or more. Examples of aliphatic carbonates include dimethyl carbonate (DMC), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), di-n-propyl carbonate, methyl-n-propyl carbonate, and ethyl-i-propyl carbonate. These low-viscosity solvents may be used alone or in combinations of two or more. Cyclic carbonates and linear carbonates can be used in any combination.

[0028]

Electrolyte salts include inorganic lithium salts selected from lithium perchlorate ($LiClO_4$), lithium hexafluorophosphate ($LiPF_6$), and lithium tetrafluoroborate ($LiBF_4$), as well as fluorine-containing organic lithium salts, such as $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(CF_3CF_2SO_2)_2$, $LiN(CF_3SO_2)(C_4F_9SO_2)$, and

$LiC(CF_3SO_2)_3$. Among these electrolyte salts, $LiPF_6$ or $LiBF_4$ is preferred. These electrolyte salts can be used alone or in a combination of two or more. These electrolyte salts are preferably prepared and used at a concentration of 0.1 to 3.0 mol/L, preferably 0.5 to 2.0 mol/L, in the non-aqueous solvent.

[0029]

The non-aqueous electrolyte may also contain additives that increase resistance to overcharging. A benzene derivative consisting of a phenyl group or adjacent cyclic compound group is preferably used as an additive. Examples of such benzene derivatives include biphenyl, cyclohexylbenzene, diphenyl ether, and phenyl lactone.

[0030]

There are no particular restrictions on the shape of the non-aqueous electrolyte secondary battery, which may be a cylinder with spiral-wound sheet electrodes and a separator, a cylinder with an inside-out structure combining pellet electrodes and a separator, or a coin with layered pellet electrodes and a separator.

[0031]

There are no particular restrictions on the method used to manufacture the non-aqueous electrolyte secondary battery, and the method can be selected from among those that are commonly used.

[Examples]

[0032]

An embodiment of the present invention will now be described.

[0033]

(Example 1)

The method used to create the positive electrode plate will be described first. A positive electrode active material consisting of lithium cobaltate ($LiCoO_2$) was made by mixing lithium carbonate (Li_2CO_3) and cobalt(III) oxide (Co_3O_4) and then calcining the mixture at 900°C in air. This positive electrode active material was then mixed with a conductive material consisting of acetylene black (AB), and a binder consisting of polyvinylidene fluoride (PVDF) at a weight ratio of 100:2:3. The mixed materials were then kneaded and dispersed using N-methyl-2-pyrrolidone (NMP) serving as the dispersant to produce a positive electrode paste. The positive electrode paste was applied to the 15μm-thick aluminum foil serving as the current collector and then dried. The composite layer containing the positive electrode active material was then rolled to a density of 3.5 to 3.6 g/cm^3, and the total thickness of the positive electrode plate was adjusted to 0.17mm. This was cut to a total length of 612 mm, including a 6.5 mm uncoated portion, and a width of 57 mm. At this time, the uncoated portion was positioned so that it was 40 to 46.5 mm from the edge of the electrode plate in the longitudinal direction.

[0034]

Next, the positive electrode plates 1 and 2 were prepared a described below.

[0035]

First, the uncoated portion of the electrode plate, which consists of coated and uncoated portions, was connected to the positive electrode lead 7 using ultrasonic welding to create positive electrode plate α.

[0036]

Next, a positive electrode plate β was prepared with 9 mm wide polypropylene (PP) tape affixed to protect the lead of the positive electrode plate α.

[0037]

At this time, the positive electrode leads 7 to positive electrode plates α and β were both made to have a 50 to 200 μm burr in the direction opposite to the positive electrode plate.

[0038]

Cross-sectional views of positive electrode plates α and β are shown in FIG. 1 and FIG. 2, respectively.

[0039]

The method used to create the negative electrode plate will now be described. A negative electrode active material consisting of artificial graphite and a binder consisting of PVDF were mixed together at a weight ratio of 100:6, and then kneaded and dispersed using NMP as the dispersant to prepare a negative electrode paste. The negative electrode paste was applied to 10 μm thick copper foil serving as the current collector and dried. The composite layer containing the negative electrode active material was then rolled to a density of 1.57 g/cm^3.

[0040]

The total thickness of the negative electrode plate was set at 0.17 mm. Afterward, the negative electrode plate α was cut to 59 mm in width and 645 mm in length, the negative electrode lead was welded to the outermost surface, and PP tape was affixed only on the peripheral portion of the negative electrode lead.

[0041]

Then, when the electrode group was created on negative electrode plate α, a heat-resistant protective film was formed at a "location opposite the positive electrode lead 7," as explained below.

[0042]

Here, the "location opposite the positive electrode lead" refers to a location opposite a 15mm long section of positive electrode plate α or β, including the 6.5 mm uncoated portion.

[0043]

The heat-resistant protective film was prepared as follows. First, 960 g of alumina with a median diameter of 0.3 μm serving as an inorganic oxide filler, 500 g of modified acrylonitrile rubber serving as a binder, and a suitable amount of NMP were placed into a twin-arm kneader and stirred together to produce a heat-resistant protective film precursor paste. The heat-resistant protective film precursor paste was applied to the negative electrode plate 1, which is opposite the positive electrode lead 7. After drying, the heat-resistant protective film was formed to a thickness of 6 μm, and the negative electrode plate β was complete.

[0044]

Next, negative electrode plate γ was produced in the same way as the negative electrode plate α except that titania was used as the inorganic oxide filler instead of alumina.

[0045]

Positive electrode plates α and β and negative electrode plates α, β, and γ produced in this way were combined to make non-aqueous electrolyte secondary batteries. The combinations are shown in Table 1. Electrode groups a to f were produced by winding positive and negative electrode plates together via an interposed separator made of microporous polyethylene resin with a thickness of 16 μm. Cross-sectional views of the region around the positive electrode lead 7 in electrode groups c and f are shown in FIG. 3 and FIG. 4, respectively.

[0046]

Electrode groups a to f prepared in the manner described above were each placed in a cylindrical nickel-plated iron battery case 1, and polypropylene (PP) insulating plates were placed on the upper and lower surfaces of the electrode group. In order to collect the current from the positive and negative electrode plates, positive and negative electrode plate leads were led out from the current collectors of the positive and negative electrode plates, and the negative plate lead was connected to the battery case 1 by resistance welding.

[0047]

Next, ethylene carbonate (EC) and diethyl carbonate (DEC) were mixed together at a 1:1 volume ratio and lithium hexafluorophosphate ($LiPF_6$) was dissolved at 1 mol/L to produce the non-aqueous electrolyte solution that was injected into the battery case 1 containing the electrode groups. The positive electrode lead 7 drawn from the electrode group, was welded to a sealing plate with a pre-installed gasket. Afterward, the sealing plates were attached to the battery cases 1 and sealed by crimping to obtain non-aqueous electrolyte secondary batteries A to F. The electrode groups used in each battery are shown in Table 1.

[0048]

[Table 1]

Non-Aqueous Electrolyte Secondary Battery	Electrode Group	Positive Electrode Plate	Negative Electrode Plate	Remarks
A	a	α	α	Conventional Battery
B	b	α	β	Battery of the Present Invention
C	c	α	γ	Battery of the Present Invention
D	d	β	α	Conventional Battery
E	e	β	β	Battery of the Present Invention
F	f	β	γ	Battery of the Present Invention

One-hundred cells each for batteries A to F were prepared and charging and discharging was repeatedly performed 100 times at 25°C. As for the charging conditions, the constant-current/constant voltage method was used at 4.2V, with a maximum current of 1500mA and a cut-off current of 100mA. As for the discharge conditions, the constant current method was used, with a current of 400mA and a terminating voltage of 3.0V. These batteries had "burrs" intentionally attached to the positive electrode lead, so there was an ever-present possibility of overheating due to an internal short circuit caused by the "burr" on the positive electrode lead during charging and discharging. Table 2 shows the heat generation rate that occurred during the repetition of 100 cycles.

[0049]

[Table 2]

Non-Aqueous Electrolyte Secondary Battery	Heat Generation Rate
A	27/100
B	0/100
C	0/100
D	2/100
E	0/100
F	0/100

From the results in Table 2, which compare batteries B, C, E, and F to batteries A and D, it was clear that batteries A and D had a higher heat generation rate. From this, it can be seen that batteries B, C, E and F, which had a porous insulator applied to the surface of the negative electrode plate, were not generating heat. When the batteries A and D that had overheated were disassembled to check for short

circuits, it was found that the separator in the position opposite the positive electrode lead had turned black, and that the cause of the overheating was the “burr” on the positive electrode lead.

[0050]

(Example 2)

In the following example, a positive electrode active material other than lithium cobaltate was used.

[0051]

A nickel-cobalt mixed solution was prepared by dissolving nickel sulfate and cobalt sulfate in water at a cobalt to nickel molar ratio of 20%. Nickel-cobalt hydroxide was obtained by adding sodium hydroxide to the nickel-cobalt mixed solution and allowing it to coprecipitate. The resulting nickel-cobalt hydroxide was washed, dried at 80°C to make a nickel-cobalt hydroxide ($Ni_{0.8}Co_{0.2}(OH)_2$) powder.

[0052]

The nickel-cobalt hydroxide prepared in this way was mixed with lithium hydroxide hydrate at a Li/(Ni + Co) molar ratio of 1/1. This was sintered at 700°C for 20 hours in an oxygen atmosphere and pulverized to obtain $LiNi_{0.8}Co_{0.2}O_2$.

[0053]

The $LiNi_{0.8}Co_{0.2}O_2$ positive electrode active material obtained in this way was mixed with AB serving as the conductive material and PVDF serving as the binding agent at a weight ratio of 100:2:3. The positive electrode paste prepared by kneading and dispersing the components using NMP as the dispersant was applied, rolled, and cut in the same manner as in Example 1. Then, positive electrode plates γ and δ were prepared by connecting positive electrode leads 7 by ultrasonic welding in the same manner as positive electrode plates α and β in Example 1.

[0054]

Here, too, the positive electrode leads 7 of positive electrode plates γ and δ had 50 to 100 μm “burrs” in the opposite direction of the positive electrode plates.

[0055]

Then, negative electrode plates α, β, and γ in Example 1 were combined with positive electrode plates γ and δ to create electrode groups g to l using the same production method as in Example 1. Non-aqueous electrolyte secondary batteries G to L were prepared using electrode groups g to l. The positive electrode plates, negative electrode plates, and electrode groups used in batteries G to L are listed in Table 3.

[0056]

[Table 3]

Non-Aqueous Electrolyte Secondary Battery	Electrode Group	Positive Electrode Plate	Negative Electrode Plate	Remarks
G	g	γ	α	Conventional Battery
H	h	γ	β	Battery of the Present Invention
I	i	γ	γ	Battery of the Present Invention
J	j	δ	α	Conventional Battery
K	k	δ	β	Battery of the Present Invention
L	l	δ	γ	Battery of the Present Invention

One hundred cells each of batteries G to L were prepared and charging/discharging was performed repeatedly at 25°C for 100 cycles. The charging and discharging conditions were the same as those in Example 1. These batteries had "burrs" intentionally attached to the positive electrode lead, so there was an ever-present possibility of overheating. Table 4 shows the heat generation rate that occurred during the repetition of 100 cycles.

[0057]

[Table 4]

Non-Aqueous Electrolyte Secondary Battery	Heat Generation Rate
G	25/100
H	0/100
I	0/100
J	3/100
K	0/100
L	0/100

The results in Table 4 comparing batteries H, I, K, and L with batteries G and J clearly show that batteries G and J had higher heat generation rates. Therefore, batteries with porous insulators applied to the surface of the negative electrode plate, such as batteries H, I, K, and L, do not generate heat. Disassembling batteries G and J and checking the short-circuit locations revealed that the separator opposite the positive electrode lead had turned black, indicating that the heat was generated by the "burr" in the positive electrode lead.

[0058]

These results show that even if the "burr" on the positive electrode lead is as large as 100 μm, an internal short circuit caused by the "burr" on the positive electrode lead does not generate heat, and a safe non-aqueous electrolyte secondary battery can be provided.

[0059]

While the present invention was described above using lithium secondary batteries as the non-aqueous electrolyte secondary batteries, the same effect can be obtained in non-aqueous electrolyte secondary batteries other than lithium secondary batteries, such as magnesium secondary batteries.

[Industrial Applicability]

[0060]

The non-aqueous electrolyte secondary battery of the present invention is useful as a main power source for electronic devices. For example, it is suitable for use as the main power supply for portable consumer products such as mobile phones and notebook PCs, the main power supply for power tools such as electric screwdrivers, and main power supply in industrial applications such as EV vehicles.

[Brief Description of the Drawings]

[0061]

[FIG. 1]

FIG. 1 is a schematic cross-sectional view of positive electrode plate α used in an example of the present invention.

[FIG. 2]

FIG. 2 is a schematic cross-sectional view of positive electrode plate β used in an example of the present invention.

[FIG. 3]

FIG. 3 is a schematic cross-sectional view of electrode group c used in an example of the present invention near the position of the positive electrode lead.

[FIG. 4]

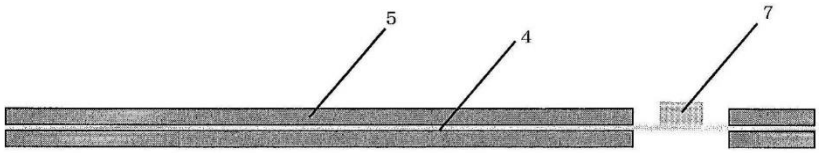
FIG. 4 is a schematic cross-sectional view of electrode group f used in an example of the present invention near the position of the positive electrode lead.

[Reference Numbers]

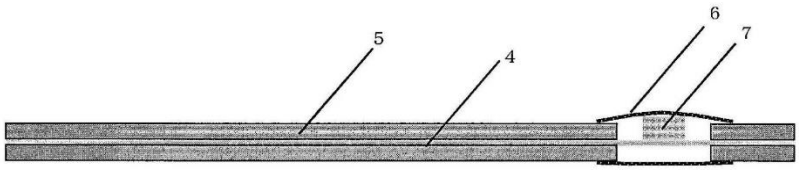
[0062]

1: Negative electrode current collector
2: Negative electrode active material
3: Separator
4: Positive electrode current collector
5: Positive electrode active material
6: PP tape
7: Positive electrode lead
8: Porous insulating film

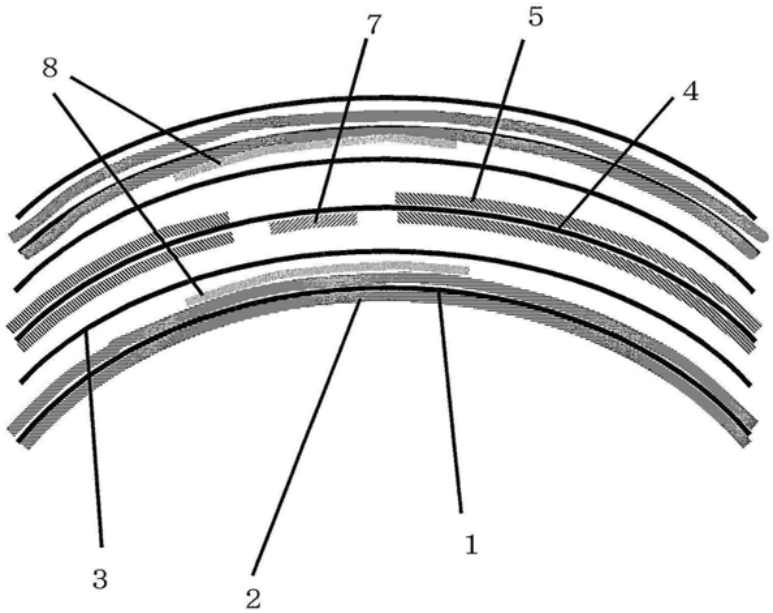
[FIG. 1]



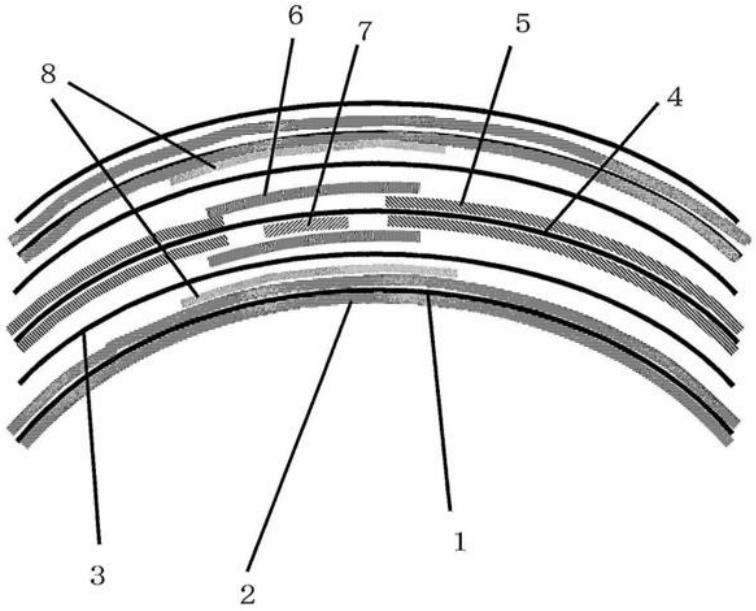
[FIG. 2]



[FIG. 3]



[FIG. 4]



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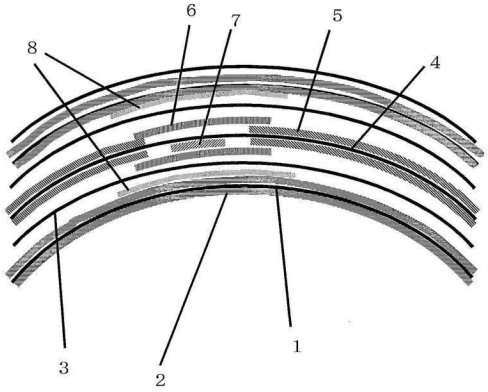
(54)【発明の名称】非水電解液二次電池

(57)【要約】
【課題】　部短絡が、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった場合、大きな電流が流れ、大幅な開回路電　の低下や、　熱を引き起こす可能性があるという問題があった。
【解決手段】正極集電　に正極活物質を塗布した正極板と、負極集電　に負極活物質を塗布した負極板とを、隔離膜を介して捲回された電極群を有する非水電解液二次電池において、前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記正極板未塗工部に正極リードを接　し、前記正極リードをテープで被覆し、かつ前記正極板未塗工部と　向する負極板表面に耐熱性保護膜が形成されている非水電解液二次電池。
【選　】　4



【特許請求の範　】
【請求項１】
正極集電　に正極活物質を塗布した正極板と、負極集電　に負極活物質を塗布した負極板とを、隔離膜を介して捲回された電極群を有する非水電解液二次電池において、
前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記未塗工部に正極リードを接　し、前記正極リードをテープで被覆し、かつ前記未塗工部と　向する負極板表面に耐熱性保護膜が形成されている非水電解液二次電池。
【請求項２】
正極集電　に正極活物質を塗布した正極板と、負極集電　に負極活物質を塗布した負極板とを、隔離膜を介して捲回された電極群を有する非水電解液二次電池において、
前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記未塗工部に正極リードを接　し、かつ前記未塗工部と　向する負極板表面に耐熱性保護膜が形成されている非水電解液二次電池。
【請求項３】
前記正極活物質は、一般式$Li_xNi_{(1-y-z)}Co_yM_zO_2$（ｘは充放電で　化するであり、０＜ｘ＜１．１，　０＜ｙ≦０．５，　０≦ｚ＜０．５，　ＭはＡｌ，Ｍｎ，Ｍｇ，Ｃａ，Ｆｅ，Ｔｉ，Ｚｎ，Ｓｒ，Ｂａ，Ｚｒ，Ｙ，Ｂ，Ｔａからなる群から選ばれる少なくとも１種類の元素）からなる請求項１または２に記載の非水電解液二次電池。
【　明の詳細な　明】
【技術分野】
【０００１】
本　明は非水電解液二次電池に　し、特に正極板と負極板の構造に　するものである。
【背景技術】
【０００２】
近年、ＡＶ機器あるいはパソコン等の電子機器のポータブル化、コードレス化が急速に進んでおり、これらの　動用電源として小型、　量で高エネルギー密度を有する非水電解液二次電池への要求が高まっている。非水電解液二次電池の代表であるリチウムイオン二次電池は、特に高電　、高エネルギー密度を有する電池として期待が大きく、高容量化、高出力化、高信　性の開　競　が激化してきている。非水電解液二次電池では、通常、正極集電　の　面に正極活物質を塗布した正極板と、負極集電　の　面に負極活物質を塗布した負極板の間に、隔離膜としてセパレータを介して渦　き　に捲回した電極群を備えている。正極集電　の未塗工部と負極板がセパレータを介して　向する部分において、セパレータを貫通して、正極集電　の未塗工部と負極板が短絡し　熱する可能性があった。
【０００３】
この　熱を防止するため、電極群の　き始め端部および　き終わり端部に位置する正極板と負極板において、少なくとも一方の集電　における他方の電極に　向する未塗工部の一部または全部に耐熱性保護膜を設けることが提案されている（例えば、特許文　１　照）。
【特許文　１】特開２００４－６３３４３　公報
【　明の開示】
【　明が解決しようとする課題】
【０００４】
非水電解液二次電池の安全性を確認する試　として異物による　部短絡試　を採用した。この試　は、電極群を作製する際、　部短絡を故意的に起こすために、例えば、負極板上に　などの金　異物を予め埋め　んで作製する。その後、充放電を　回繰り返すことで　部短絡を　生させるという試　である。試　結果については、予め電池に熱電　を取り付け、電池の　度が１００℃以上に達したら「　熱した」と判　する方法である。この部短絡が、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった場合、大きな電流が流れ、大幅な開回路電　の低下や、異常に　熱する可能性があるという問題があった。

【０００５】

特許文　１には次のような問題があった。一方の集電　における他方の電極に　向する未塗工部の一部または全部に耐熱性保護膜を設ける場合、耐熱性保護膜を集電　表面に形成する必要があり、耐熱性保護膜と集電　の密着性が低くなり、電極群作製時に耐熱性保護膜が　がれ落ちるという問題があった。未塗工部は、活物質が塗布された電極部分に比べて窪んでおり、未塗工部のみに（活物質の塗工部に耐熱性保護膜がかからないように）耐熱性保護膜を塗布することが、製造工程上困難であるという問題があった。

【０００６】

さらに、未塗工部にリードを接　した場合も同　な理由で、耐熱性保護膜を緻密に形成することは製造工程上難しい。電極群の　き始め端部の未塗工部の集電　に正極リードを設けた円筒形の非水電解液二次電池の場合、曲率半　が最も小さくなる最　周側に正極リードを溶接により接　しているため、正極リードのエッジ部が外周側の正極板にダメージを　え、正極板が切れるという新たな問題があった。

【０００７】

本　明はこのような　　の課題を解決するものであり、正極集電　の未塗工部に耐熱性保護膜を形成するのではなく、未塗工部と　向する負極合　部に設けることにより、凹凸のきわめて少ない負極合　層と、密着性の高い緻密な耐熱性保護膜を形成でき、　部短絡時の　熱を抑制できる非水電解液二次電池を提供することができる。

【課題を解決するための手段】

【０００８】

上記課題を解決するために、本　明の非水電解液二次電池は、
正極集電　に正極活物質を塗布した正極板と、負極集電　に負極活物質を塗布した負極板とを、隔離膜を介して捲回された電極群を有しており、前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記未塗工部に正極リードを接　し、前記正極リードをテープで被覆し、かつ前記未塗工部と　向する負極板表面に耐熱性保護膜が形成されている。

【０００９】

また、別の本　明の非水電解液二次電池は、前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記未塗工部に正極リードを接　し、かつ前記未塗工部と　向する負極板表面に耐熱性保護膜が形成されている。

【００１０】

こうすることにより、最も　熱の危　性の高い、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった　部短絡時の　熱を抑制することができる。

【　明の　果】

【００１１】

本　明によると、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こる　部短絡が　生した場合、　熱が高　になることはなくなる。正極集電　の未塗工部と負極活物質が塗布された負極板の間のみを耐熱性保護膜で保護することによって、負極板全　を耐熱性保護膜で被覆した場合に比べ、非水電解液二次電池の　積　りのエネルギー密度を大きくすることができるという利点もある。また、正極集電　の未塗工部を正極板端部以外の部分に配置することにより、例えば、正極リードの溶着部を正極板の中央部にすることにより、電極群作製時に正極リード溶着箇所の捲回　が小さくならず、リードエッジ部による極板ダメージを大きく緩和することができる。

【　明を　施するための最良の形態】

【００１２】

本　明の　施の形態における非水電解液二次電池は、正極集電　に正極活物質を塗布した正極板と、負極集電　に負極活物質を塗布した負極板とを、隔離膜を介して捲回された電極群を有する非水電解液二次電池において、前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記正極板未塗工部に正極リードを接　し、前記正極リードをテープで被覆し、かつ前記正極板未塗工部と　向する負極板表面に耐熱性保護膜が形成されている。

【００１３】
こうすることにより、耐熱性保護膜を密着性よく、緻密に形成することができ、最も熱の危　性の高い、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった　部短絡時の　熱を抑制することができる。
【００１４】
本　明の別の　施の形態における非水電解液二次電池は、前記正極板の長さ方向の端部以外に未塗工部が設けてあり、前記正極板未塗工部に正極リードを接　し、かつ前記正極未塗工部と　向する負極板表面に耐熱性保護膜が形成されている。
【００１５】
こうすることにより、耐熱性保護膜を密着性よく、緻密に形成することができ、最も熱の危　性の高い、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった　部短絡時の　熱を抑制することができる。さらに、正極リードで　生した“ばり”による　部短絡を防止するために貼付しているテープがなくても、　熱の危　性はなくなるため、　積　りのエネルギー密度をさらに大きくすることができる
本　明の好ましい　施の形態における非水電解液二次電池は、正極活物質が一般式$Li_xNi_{(1-y-z)}Co_yM_zO_2$（ｘは充放電で　化する　　であり、０＜ｘ＜１．１，　０＜ｙ≦０．５，　０≦ｚ＜０．５，　ＭはＡｌ，Ｍｎ，Ｍｇ，Ｃａ，Ｆｅ，Ｔｉ，Ｚｎ，Ｓｒ，Ｂａ，Ｚｒ，Ｙ，Ｂ，Ｔａからなる群から選ばれる少なくとも１種類の元素）からなる。
【００１６】
こうすることにより、耐熱性保護膜を密着性よく、緻密に形成することができ、最も熱の危　性の高い、正極集電　の未塗工部と負極活物質が塗布された負極板の間で起こった　部短絡時の　熱を抑制することができる。
【００１７】
以下、正極について詳述する。
【００１８】
正極活物質は、コバルト酸リチウム（$LiCoO_2$）やニッケル酸リチウム（以下、$LiNiO_2$と略す）などのリチウム含有遷移金　酸化物を用いることができる。また、原料が比較的安　なマンガンを用いたマンガン酸リチウム（$LiMn_2O_4$）のようなスピネル型複合酸化物を用いることもできる。
【００１９】
正極の　粘　としては、カルボシキメチルセルロース（以下、ＣＭＣと略す）、メチルセルロース（ＭＣ）、ヒドロキシメチルセルロース（ＨＭＣ）、エチルセルロース、ポリビニルアルコール（ＰＶＡ）、酸化スターチ、リン酸化スターチ、およびガゼイン等を用いるとよい。
【００２０】
導電　は電子　導性材料であれば何でもよい。例えば、天然　鉛（鱗片　　鉛など）、人造　鉛、膨張　鉛などのグラファイト類、アセチレンブラック、チャンネルブラック、ファーネスブラック、およびサーマルブラック等のカ－ボンブラック類、炭素　維、金　維などの導電性　維類、銅、ニッケル等の金　粉末類およびポリフェニレン誘導　などの有機導電性材料などを　　又はこれらの混合物として含ませることができる。これらの導電　のなかで、人造　鉛、アセチレンブラック、炭素　維が特に好ましい。導電　の添加量は特に限定されないが、負極活物質に　して１～３０重量％が好ましく、さらには１～１０重量％が好ましい。
【００２１】
正極の集電　の材質は、アルミニウム（Ａｌ）、チタン（Ｔｉ）、およびタンタル（Ｔａ）等の金　またはその合金が使用できるが、　量でエネルギー密度が有利であることから、特に、アルミニウム（Ａｌ）またはその合金を使用するのが望ましい。
【００２２】
以下、負極について詳述する。

【００２３】
負極活物質は、　鉛系、非晶質系等の炭素材料あるいはその混合　、合金や金　化合物などが　げられ、これらを　　もしくは２種以上を混合して用いることができる。合金は、ケイ素、スズ、アルミニウム、　鉛、マグネシウム、チタン、およびニッケルよりなる群から選　される少なくとも一種の元素からなるのが好ましい。また、金　化合物はケイ素、スズ、アルミニウム、　鉛、マグネシウム、チタン、およびニッケルの酸化物や炭化物よりなる群から選　される少なくとも一種である。負極活物質の平均粒　は特に限定されないが、１～３０μｍが好ましい。

【００２４】
負極板の集電　は電　化　的に安定な電子　導　であれば何でもよく、銅、ニッケル、ステンレス等の金　が使用できるが、これらの中で薄膜に加工しやすく、低コストであることから銅箔が好ましい。厚みは特に限定されないが、５～２５μｍが好ましい。

【００２５】
正極板および負極板の製造に用いられる結着　については、電極製造時に使用する溶媒や電解質に　して安定な材料であれば、特に限定されない。例えば、ポリフッ化ビニリデン（ＰＶＤＦ）、ポリテトラフルオロエチレン（ＰＴＦＥ）、スチレン・ブタジエンゴム（ＳＢＲ）、イソプロピレンゴム、ブタジエンゴム、およびエチレンプロピレンジエタンポリマー（ＥＰＤＭ）等を用いるとよい。

【００２６】
以下、非水電解質について詳述する。

【００２７】
非水溶媒は炭酸エステルが好ましい。炭酸エステルは、環　、鎖　のいずれも使用することができる。環　炭酸エステルとしては、プロピレンカーボネート（以下、ＰＣと略す）、エチレンカーボネート（ＥＣ）、ブチレンカーボネート（ＢＣ）等が好適に　げられる。これらの高誘電率溶媒は、１種類、または２種類以上を組み合わせて使用してもよい。鎖　炭酸エステルとしては、例えばジメチルカーボネート（以下、ＤＭＣと略す）、ジエチルカーボネート（ＤＥＣ）、エチルメチルカーボネート（ＥＭＣ）、ジ－ｎ－プロピルカーボネート、メチル－ｎ－プロピルカーボネート、エチル－ｉ－プロピルカーボネート等が　げられる。これらの低粘度溶媒は、１種類、または２種類以上を組み合わせて使用してもよい。環　炭酸エステルと鎖　炭酸エステルはそれぞれ任意に選　して組み合わせて使用することもできる。

【００２８】
電解質　としては、過　素酸リチウム（$LiClO_4$）、六フッ化リン酸リチウム（$LiPF_6$）、および四フッ化ホウ酸リチウム（$LiBF_4$）から選ばれる無機リチウム　や、$LiCF_3SO_3$、$LiN(CF_3SO_2)_2$、$LiN(CF_3CF_2SO_2)_2$、$LiN(CF_3SO_2)(C_4F_9SO_2)$、および$LiC(CF_3SO_2)_3$などの含フッ素有機リチウム　等が　げられる。それら電解質　の中でも、$LiPF_6$、もしくは$LiBF_4$が好ましい。これらの電解質　は１種類、または２種類以上を組み合わせて用いることができる。これらの電解質　は、上述した非水溶媒に、通常０．１～３．０ｍｏｌ／Ｌ、好ましくは０．５～２．０ｍｏｌ／Ｌの濃度になるように調製して使用するのが好ましい。

【００２９】
非水電解質には、過充電に　する耐性を高める添加　を含ませてもよい。添加　には、フェニル基およびそれに隣接する環　化合物基からなるベンゼン誘導　を用いることが好ましい。このようなベンゼン誘導　として、ビフェニル、シクロヘキシルベンゼン、ジフェニルエーテル、フェニルラクトンなどが　げられる。

【００３０】
非水電解質二次電池の形　については特に限定されず、シート電極およびセパレータをスパイラル　にしたシリンダータイプ、ペレット電極およびセパレータを組み合わせたインサイドアウト構造のシリンダータイプ、ペレット電極およびセパレータを積層したコインタイプ等が使用可能である。

【００３１】
　非水電解質二次電池を製造する方法については、特に限定されず、通常採用されている方法の中から適宜選　することができる。
【　施例】
【００３２】
以下、本　明の一　施の形態について　明する。
【００３３】
（　施例１）
まず、正極板の作製方法について　明する。炭酸リチウム（Li_2CO_3）と四酸化三コバルト（Co_3O_4）を混合して空　中において９００℃で　成したコバルト酸リチウム（以下、$LiCoO_2$と略す）からなる正極活物質、アセチレンブラック（以下、ＡＢと略す）からなる導電材、およびポリフッ化ビニリデン（以下、ＰＶＤＦと略す）からなる結着　を重量比が１００：２：３となるように混合したものを、Ｎ－メチル－２－ピロリドン（以下、ＮＭＰと略す）を分散媒として用いて混練分散して正極ペーストを作製した。正極ペーストを、集電　として厚さ１５μｍのアルミニウム箔に塗着し、乾燥した。その後、正極活物質を含む合　層の密度が３．５～３．６ｇ／ｃm^3になるように　延し、正極板の　厚みを０．１７ｍｍとした。未塗工部が６．５ｍｍを含む全長が６１２ｍｍ、幅５７ｍｍとなるように裁　した。この時、未塗工部は極板の長手方向端部より４０～４６．５ｍｍの位置になるように配置した。
【００３４】
次に、以下に　明する正極板１と２を作製した。
【００３５】
まず、前述の塗工部および未塗工部からなる極板の未塗工部に正極リード７を超音波溶着により接　し正極板αを作製した。
【００３６】
次に、正極板αのリードを保護するために幅９ｍｍのポリプロピレン（以下、ＰＰと略す）テープを貼付けした正極板βを作製した。
【００３７】
このとき正極板αおよびβの正極リード７は、いずれも５０～２００μｍの”ばり”が正極板とは逆向きの方向に出るようにした。
【００３８】
正極板αおよびβの　略　面　をそれぞれ　１および２に示す。
【００３９】
次に、負極板の作製方法について　明する。人造　鉛からなる負極活物質、ＰＶＤＦからなる結着　を重量比が１００：６となるように混合したものを、ＮＭＰを分散媒として用いて混練分散して負極ペーストを作製した。負極ペーストを集電　として厚さ１０μｍの銅箔に塗着、乾燥した。その後、負極活物質を含む合　層の密度が１．５７ｇ／ｃm^3になるように　延した。
【００４０】
負極板の　厚みを０．１７ｍｍとした。その後、幅５９ｍｍ、全長６４５ｍｍに裁　した後、最外周部に負極リードを溶接し、負極リードの周　部のみにＰＰテープを貼付けした負極板αを作製した。
【００４１】
そして、負極板α上の電極群作製時に「正極リード７と　向する箇所」に、以下に　明する耐熱性保護膜を形成した。
【００４２】
ここで言う、「正極リードと　向する箇所」とは、正極板αまたはβの未塗工部６．５ｍｍを含む長手方向１５ｍｍの範　に　向する箇所のことを指す。
【００４３】
耐熱性保護膜は次のようにして作製した。無機酸化物フィラーとしてメディアン　０．

３μｍのアルミナ９６０ｇ、結着　として　性アクリロニトリルゴム５００ｇ、および適量のＮＭＰを　腕式練合機に入れ、攪拌し、耐熱性保護膜前　　ペーストを作製した。耐熱性保護膜前　　ペーストを正極リード７と　向する負極板１上に塗布した。その後、乾燥して、厚さが６μｍの耐熱性保護膜を形成し、負極板βを作製した。

【００４４】

次に、無機酸化物フィラーとして、アルミナの代わりにチタニアを用い、これ以外は負極板αと同　の方法で負極板γを作製した。

【００４５】

このようにして得られた正極板α、βと負極板α、β、およびγを組み合わせて非水電解液二次電池を作製し、その組み合わせを表１に示した。セパレータとして厚さ１６μｍの微多孔性ポリエチレン樹脂を用い、それを介して正極板と負極板を捲回し、電極群ａ～ｆを作製した。また、電極群ｃ、ｆにおいて、正極リード７を接　した付近の　略　　面　をそれぞれ　３、４に示した。

【００４６】

以上のようにして作製した電極群ａ～ｆを、ニッケル（Ｎｉ）メッキを施した　製の円筒形の電池ケース１に　納し、電極群上下　面にポリプロピレン（ＰＰ）製絶　板を配した。そして正負極板の各　から集電を行うために、正負極リードを正負極板の集電　からそれぞれ導出して、負極リードを電池ケース１に抵抗溶接で接　した。

【００４７】

次に、電極群が　納された電池ケース１　に、エチレンカーボネート（ＥＣ）とジエチルカーボネート（ＤＥＣ）を　積比で１：１で混合し、１モル／Ｌの六フッ化リン酸リチウム（$LiPF_6$）を溶解した非水電解液を注入した。そして、予めガスケットを組みんだ封口板に、電極群から導出させた正極リード７を溶接した。その後、封口板を電池ケース１に　着し、カシメにより封口して、非水電解液二次電池Ａ～Ｆを作製した。それぞれの電池に用いた電極群を表１に示した。

【００４８】

【表１】

非水電解液二次電池	電極群	正極板	負極板	備考
A	a	α	α	従来電池
B	b	α	β	本発明電池
C	c	α	γ	本発明電池
D	d	β	α	従来電池
E	e	β	β	本発明電池
F	f	β	γ	本発明電池

電池Ａ～Ｆをそれぞれ１００セルずつ用意し、２５℃で充放電を１００サイクル繰り返した。充電　件は電　４．２Ｖの定電流・定電　方式で行い、最大電流は１５００ｍＡ、終止電流は１００ｍＡとした。放電　件は定電流方式で行い、電流は４００ｍＡ、終止電　は３．０Ｖとした。今回作製した電池には、正極リードに意　的に“ばり”を設けているため、充放電中に正極リードの“ばり”による　部短絡で　熱する可能性がある。表２に、１００サイクル繰り返す最中に　生した　熱率を示す。

【００４９】

【表２】

非水電解液二次電池	発熱率
A	27/100
B	0/100
C	0/100
D	2/100
E	0/100
F	0/100

表２の結果から、電池Ｂ、Ｃ、Ｅ、およびＦは、電池Ａ、Ｄと比較すると、　熱率は電池Ａ、Ｄの方が多く、その違いは明らかであった。このことから、電池Ｂ、Ｃ、ＥおよびＦのように負極板表面に多孔性絶　物を塗布した電池は　熱していない。　熱が起こった電池Ａ、Ｄを分解して短絡箇所を確認すると、正極リードと　向する位置のセパレータが　色化しており、正極リードの“ばり”が原因で　熱していたことがわかった。

【００５０】

（　施例２）

次いで、正極活物質としてコバルト酸リチウム以外の正極活物質を使用した場合について　明する。

【００５１】

Ｎｉに　してＣｏのモル比が２０％になるように硫酸ニッケルと硫酸コバルトを水に溶解して硫酸ニッケル－コバルト混合溶液を作成した。この硫酸ニッケル－コバルト混合溶液に水酸化ナトリウムを投入して共沈させることにより、ニッケル－コバルト水酸化物を得た。得られたニッケル－コバルト水酸化物を水洗し、８０℃で乾燥して粉末　にし、ニッケル－コバルト水酸化物（$Ni_{0.8}Co_{0.2}(OH)_2$）を作製した。

【００５２】

このようにして作製したニッケル－コバルト水酸化物を、水酸化リチウム－水和物にＬｉ／（Ｎｉ＋Ｃｏ）のモル比が１／１になるように混合した。酸素雰　　下で７００℃の　度で２０時間　成し、粉　して$LiNi_{0.8}Co_{0.2}O_2$を得た。

【００５３】

このようにして作製した正極活物質$LiNi_{0.8}Co_{0.2}O_2$、導電材としてＡＢ、および結着　としてＰＶＤＦを、それぞれの重量比が１００：２：３となるように混合した。ＮＭＰを分散媒として用いて混練分散して作製した正極ペーストを、　施例１と同　にして塗着、　延、裁　を行った。そして　施例１で記載した正極板α、βと同　に正極リード７を超音波溶着により接　して正極板γ、δを作製した。

【００５４】

この場合も、正極板γ、δの正極リード７には、５０～１００μｍの”ばり”が正極板とは逆向きの方向に出るようにした。

【００５５】

そして、　施例１と同　の負極板α、β、およびγと、正極板γ、δを組み合わせ、施例１と同　の作製方法で電極群ｇ～ｌを作製した。電極群ｇ～ｌを用いて非水電解液二次電池Ｇ～Ｌを作製した。電池Ｇ～Ｌに用いた正極板、負極板、および電極群を表３に示した。

【００５６】

【表３】

非水電解液二次電池	電極群	正極板	負極板	備考
G	g	γ	α	従来電池
H	h	γ	β	本発明電池
I	I	γ	γ	本発明電池
J	j	δ	α	従来電池
K	k	δ	β	本発明電池
L	l	δ	γ	本発明電池

電池Ｇ～Ｌをそれぞれ１００セルずつ用意し、２５℃で充放電を１００サイクル　施した。充放電　件は　施例１と同じである。今回作製した電池には、正極リードに意　的に“ばり”を設けているため、充放電中に　熱する可能性がある。表４に、１００サイクル繰り返す最中に　生した　熱率を示す。

【００５７】

【表４】

非水電解液二次電池	発熱率
G	25/100
H	0/100
I	0/100
J	3/100
K	0/100
L	0/100

表４の結果から、電池Ｈ、Ｉ、Ｋ、およびＬは、電池Ｇ、Ｊと比較すると、　熱率は電池Ｇ、Ｊの方が多く、その違いは明らかであった。このことから、電池Ｈ、Ｉ、ＫおよびＬのように負極板表面に多孔性絶　物を塗布した電池は　熱していない。　熱が起こった電池Ｇ、Ｊを分解して短絡箇所を確認すると、正極リードと　向する位置のセパレータが　色化しており、正極リードの“バリ”が原因で　熱していたことがわかった。

【００５８】

以上のことから、正極リードの“ばり”が１００μｍのように大きくても、正極リードの“ばり”による　部短絡で　熱することなく、安全な非水電解液二次電池を提供することができる。

【００５９】

また、非水電解液二次電池として、リチウム二次電池について　明したが、リチウム二次電池以外のマグネシウム二次電池などの非水電解液二次電池においても、同　の　果が得られるものである。

【産業上の利用可能性】

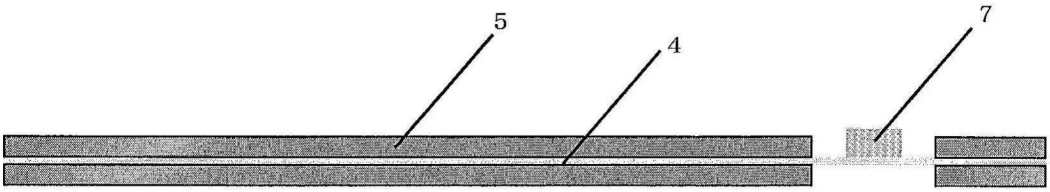
【００６０】

本　明の非水電解液二次電池は、電子機器等の主電源に有用である。例えば、携　電話やノート型パソコン等の民生用モバイルツールの主電源、電動ドライバー等のパワーツールの主電源、およびＥＶ自動車等の産業用主電源の用途に適している。

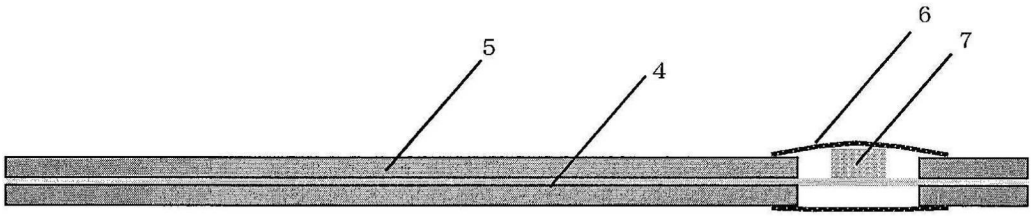
【　面の簡　な　明】

【００６１】
【　１】本　明の　施例で使用した正極板αの　略　面
【　２】本　明の　施例で使用した正極板βの　略　面
【　３】本　明の　施例で使用した電極群ｃの正極リード位置付近の　略　　面
【　４】本　明の　施例で使用した電極群ｆの正極リード位置付近の　略　　面
【符　の　明】
【００６２】
　１　　負極集電
　２　　負極活物質
　３　　セパレータ
　４　　正極集電
　５　　正極活物質
　６　　ＰＰテープ
　７　　正極リード
　８　　多孔性絶　膜

【　１】



【　２】



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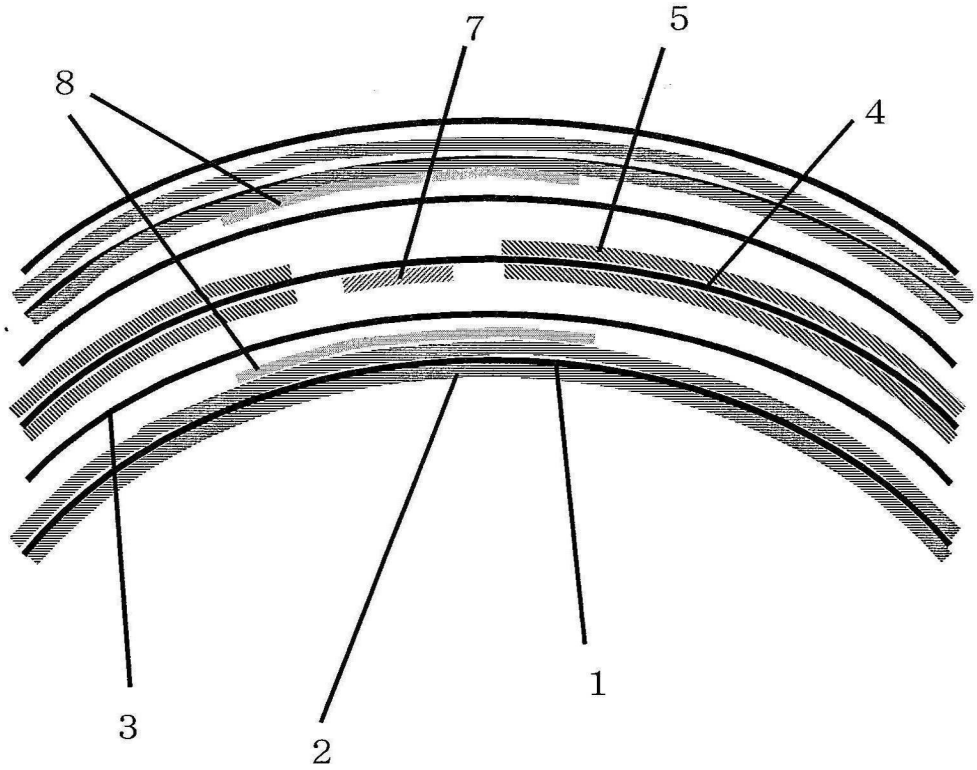

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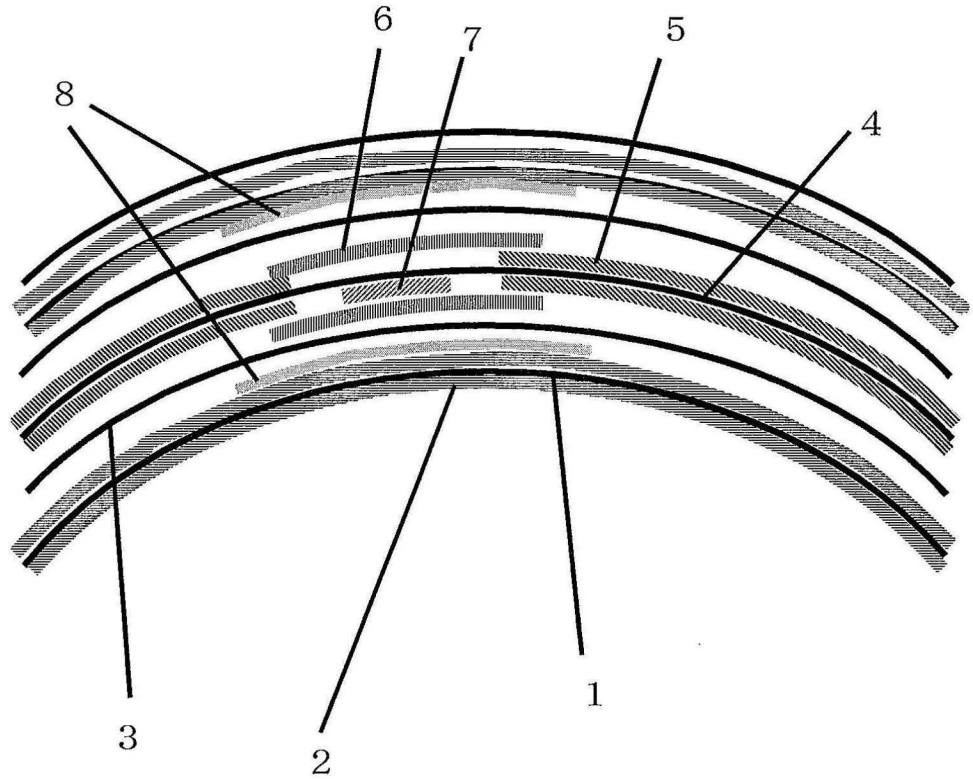

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KA45E LA21E
5H050 AA15　BA15　BA17　CA07　CA08　CB01　CB02　CB07　CB08　CB11
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Date: December 5, 2024

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Frank McGee