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(71) Applicant 000006013
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo
(72) Inventor
Daigo TAKEMURA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo
(72) Inventor
Hiroaki URUSHIBATA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo
(74) Agent 100102439
Attorney Kaneo MIYATA (and 2 others)

Continued on Last Page

(54) [Title of the Invention] Electrode Structure and Battery Using the Same

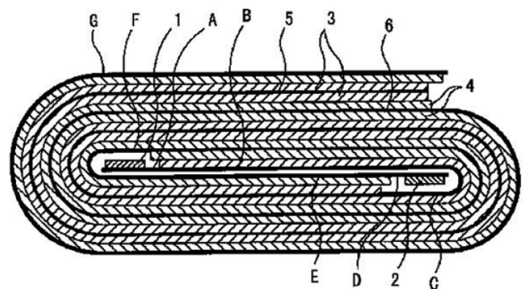
(57) [Abstract]

[Problem]

To provide a lightweight, compact, and highly reliable electrode structure with improved energy density and high reliability by preventing lithium metal deposition, and a battery using this structure.

[Solution]

Provided is an electrode structure composed of a positive electrode and a negative electrode with electrode active materials 3, 4 on the front and back surfaces of electrode current collectors 5, 6, and current collector terminals 1, 2 on one portion of a surface of the electrode current collectors, the positive electrode and negative electrode arranged opposite each other via an electron-insulating separator and wound in a spiral shape. In this electrode structure, no electrode active material is formed on the positive electrode portion opposite the current collection terminal formed on the current collector of the negative electrode. In this electrode structure, no electrode active material is formed to the inside of the innermost electrode current collector or to the outside of the outermost electrode current collector. Also provided is a battery with such an electrode structure.



1: Positive electrode current collector terminal
2: Negative electrode current collector terminal
3: Positive electrode active material layer
4: Negative electrode active material layer
5: Positive electrode current collector
6: Negative electrode current collector
A-G: Active material uncoated portions

[Claims]

[Claim 1]

An electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed on the positive electrode portion opposite the current collection terminal formed on the current collector of the negative electrode.

[Claim 2]

An electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the inside of the electrode current collector in the innermost layer.

[Claim 3]

An electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the outside of the electrode current collector in the outermost layer.

[Claim 4]

The electrode structure according to any of claims 1 to 3, wherein the electrode structure is flattened.

[Claim 5]

The electrode structure according to any of claims 1 to 4, wherein the separator is bonded to at least one of the positive electrode and the negative electrode.

[Claim 6]

A battery comprising the electrode structure according to any of claims 1 to 5.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an arrangement of electrode active material layers in a battery and the structure of the battery, especially to those that improve the performance of a spiral wound battery.

[0002]

[Background Art]

As the performance of electronic devices has improved in recent years, there has been demand for improved performance of batteries used as power sources in these devices, especially secondary batteries that can be recharged repeatedly. Lithium-ion secondary batteries are attracting attention as lightweight, portable, high-capacity batteries that can power electronic devices for longer periods of time. Therefore, in the explanation of the present invention, a lithium-ion secondary battery is used as the example.

[0003]

FIG. 9 is a cross-sectional view of the electrode structure portion of a conventional lithium-ion secondary battery. In this figure, 1 is a positive electrode collection terminal, 2 is a negative electrode collection terminal, 3 is a positive electrode active material, 4 is a negative electrode active material, 5 is a positive electrode current collector, and 6 is a negative electrode current collector. An electrolyte layer such as a separator (not shown) is provided between the positive electrode active material 3 and the negative electrode active material 4, and the electrolyte layer is made of a separator impregnated with a non-aqueous electrolyte solution in which an electrolyte has been dissolved. Here, 7 is insulating tape.

[0004]

For the lithium-ion secondary battery shown in FIG. 9, there has been demand for improvements to electrode active material layers, such as positive electrode active materials 3 and negative electrode active material 4, and a desire for new active materials, especially in order to make batteries smaller and thinner. Equally important is the development of electrode structures that can provide higher energy densities, that is, electrode structures composed of a positive electrode current collection terminal 1, a negative electrode current collection terminal 2, a positive electrode active material 3, a negative electrode active material 4, a positive electrode current collector 5, and a negative electrode current collector 6.

[0005]

[Technical Problem]

Among electrode structures, electrodes with electrode active material layers 3, 4 coated and formed on both sides of the electrode current collectors 5, 6 as shown in FIG. 9 ("double-sided coating" below) have electrode current collectors 5, 6 accounting for a smaller percentage of the battery and better volumetric energy density than electrodes with electrode active material layers 3, 4 coated and formed on one side of electrode current collectors 5, 6 ("single-sided coating" below). When the electrodes have a wound structure, there are unnecessary electrode active material layers 3, 4 on the innermost and outermost layers of the electrode structure because there are no opposing electrodes, and this leads to an increase in thickness and weight. Also, when electrodes with electrode active material layers 3, 4 on the innermost layer are pressed flat, the electrode current collectors 5, 6 may rupture due to significant elongation of the folded portion of the innermost layer. Here, the innermost layer of a spiral structure refers to the innermost electrode active material layer from the position where the electrodes start to be wound until one or one-half lap has been completed, while the outermost layer refers to the outermost electrode active material layer without an opposing electrode.

[0006]

A battery requires current collector terminals 1, 2 that are connected to the outside, and the

current collector terminals 1, 2 are located on a portion of the electrode current collectors 5, 6 that is not covered by electrode active material layers 3, 4 in the electrode. However, when flattening to make a thin battery, the current collector terminals 1, 2 have to be arranged so as not to increase the thickness of the battery.

[0007]

In addition, the electrode active material layers 3, 4 in the portions where the current collector terminals 1, 2 of the positive and negative electrodes are placed are removed to weld the electrode current collectors 5, 6 to the current collector terminals 1, 2. However, the electrode active material layers 3, 4 that are present in the electrode portions opposite those in which the current collector terminals 1, 2 are placed do not function as a battery and become useless active material, causing an increase in thickness and weight.

[0008]

If there is excess positive electrode active material 3, if some of the negative electrode active material 4 opposite the positive electrode active material 3 is not present, or if the negative electrode active material 4 opposite the positive electrode does not work as a battery, problems occur such as short circuiting caused by lithium metal deposition and ignition caused by this short circuiting if the current is concentrated in one portion of the negative electrode. Therefore, if there is no positive electrode active material 3 opposite the negative electrode active material 4, there is no problem with lithium metal deposition, etc. as described above. However, if there is no opposing negative electrode active material 4, such as the positive electrode active material 3 arranged around the negative electrode current collector terminal 2 in FIG. 9, the surface of the positive electrode active material 3 has to be covered with masking tape 7 or the positive electrode active material 3 has to be shaved off so that there is virtually no positive electrode active material 3 facing the negative electrode active material 4. This leads to problems such as an increased number of production steps and higher costs.

[0009]

When the ends of both positive and negative electrodes with electrode active material layers 3, 4 coated on both sides of the electrode current collectors 5, 6, as shown in FIG. 10, are

wound together, the innermost electrode active material layer 4 does not function as a battery because it has no opposing electrode. The positive and negative electrode active material layers 3, 4 face each other in the innermost layer once the terminals of the positive and negative electrodes are wound a half-lap as shown in FIG. 9. However, a gap tends to occur between the positive electrode and the electrolyte layer and the negative electrode and the electrolyte layer, and a sufficient electrode reaction cannot be expected. Also, when electrodes with double-sided coating are wound, the outermost layer contains a positive electrode active material or negative electrode active material without an opposing electrode, leading to an unnecessary increase in weight and volume.

[0010]

The presence of extra active material and masking tape in positions where the positive electrode active material 3 and negative electrode active material 4 do not face each other leads to a decrease in energy density, an increase in the overall thickness of the battery, and an increase in cost due to an increase in production steps.

[0011]

A first object of the present invention is to provide a lightweight, compact electrode structure with improved energy density, and a battery using the same. A second object of the present invention is to provide an electrode structure with high reliability by preventing lithium metal deposition, and a battery using the same. A third object of the present invention is to provide an electrode structure with improved battery life, and a battery using the same.

[0012]

[Solution to Problem]

A first aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode

structure characterized in that no electrode active material is formed on the positive electrode portion opposite the current collection terminal formed on the current collector of the negative electrode.

[0013]

A second aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the inside of the electrode current collector in the innermost layer.

[0014]

A third aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the outside of the electrode current collector in the outermost layer.

[0015]

A fourth aspect of the present invention is the electrode structure according to any of the first to third aspects, wherein the electrode structure is flattened.

[0016]

A fifth aspect of the present invention is the electrode structure according to any of the first to fourth aspects, wherein the separator is bonded to at least one of the positive electrode and the negative electrode.

[0017]

A sixth aspect of the present invention is a battery comprising the electrode structure according to any of the first to fifth aspects.

[0018]

[Embodiments of the Invention]

First Embodiment.

FIG. 1 is a cross-sectional view of the electrode structure in the first embodiment of the present invention, in which the beginning of the winding of the negative electrode and the positive electrode is shifted by half a lap. In order to avoid complicating the figure, the separator located between the positive electrode active material layer and the negative electrode active material layer 4 and on the outermost layer has been omitted in FIG. 1. In this figure, 1 is a positive electrode collection terminal, 2 is a negative electrode collection terminal, 3 is a positive electrode active material layer, 4 is a negative electrode active material layer, 5 is a positive electrode current collector, 6 is a negative electrode current collector, and A to G are active material uncoated portions.

[0019]

The characteristics of the electrode structure shown in FIG. 1 include the following: positions B and E of the first layer, that is, the innermost electrode active material layers 3, 4, where the positive electrode and negative electrode adhere poorly via the separator, and the outermost electrode active material layer (negative active material layer 4 in the figure) G, where there is no opposing electrode, are not coated; the electrode active material layer sites C and F that face the electrode current collection terminals 1, 2 attached to the innermost end that do not react as a battery are active material uncoated portions; and the electrode current collector terminals 1, 2, which are almost the same thickness as the electrode active material layers 3, 4, are efficiently placed in uncoated portions A and D of the electrode active material layer in the unwound portion of the first layer so as to hold down the increase in electrode thickness. This configuration results in a lightweight, compact electrode structure with improved energy density. In addition, the positive electrode portion facing the current collection terminal 2 formed on the negative electrode current collector 6 is an active material uncoated portion, which prevents lithium metal deposition. Also, by forming the negative electrode active material layer 4 larger

than the opposing positive electrode active material layer 3, lithium metal deposition is more reliably prevented. This is also true for each of the following embodiments. In FIG. 1, the electrode current collectors 5 and 6 are shown in bold lines, and the uncoated portions of the electrode active material layers in the electrode current collectors are shown in extra bold lines. The first layer of the spiral electrode structure refers to the starting point from which the winding begins to the point where the electrodes have been wound to this starting point.

[0020]

FIG. 2 (a) and FIG. 2 (b) are examples of electrodes with electrode active material layers 3, 4 pattern-coated to provide uncoated portions on one or both sides of electrode current collectors 5, 6 as shown in FIG. 1. In this figure, A to G are portions in which the electrode active material layer has not been uncoated. These correspond to A to G in FIG. 1. In FIG. 1 (a) and FIG. 1 (b), A and D are portions uncoated with the active material layer for attaching the positive electrode current collection terminal 1 and the negative electrode current collection terminal 2, respectively, B and E are portions corresponding to the innermost layer, C and F are portions uncoated with a positive electrode active material layer 3 and negative electrode active material layer 4 where the negative electrode current collector terminal 2 and the positive electrode current collector terminal 1 face each other, respectively, and G is a portion uncoated with the negative electrode active material layer 4 to the outside of the electrode current collector 6 of the outermost layer. The uncoated portions may be created by pattern coating when forming the electrode active material layers 3, 4, or by scraping off a portion of the uncoated portions after coating the entire surface.

[0021]

Second Embodiment.

FIG. 3 is a cross-sectional view of the electrode structure in the second embodiment of the present invention. In order to avoid complicating the figure, the separator located between the positive electrode active material layer and the negative electrode active material layer 4 and on the outermost layer has been omitted. In this example, the beginning of the winding of the negative electrode and the positive electrode is shifted by half a lap, and

the current collector terminals 1, 2 are placed at the outer ends of the wound electrodes. Unlike FIG. 1, the active material layers 3, 4 are also formed to the inside the electrode current collectors 5, 6 in the innermost layer, because this structure does not have much space for current collector terminals 1, 2 inside the electrode unit, so excess space is less likely to exist in the innermost layer. Also, active material layers 3, 4 are not formed to the outside of the electrode current collectors 5, 6 in the outermost layer because there is no active material on the opposing counter electrode. Therefore, there is no active material layer facing the current collector terminals 1, 2, and lithium metal deposition due to excess positive electrode active material can be prevented. The positive electrode active material layer 3 opposite the beginning of the winding end of the negative electrode is covered with insulating tape 7 to prevent lithium metal deposition, but instead of covering it with insulating tape 7, the active material in this portion may be removed. If the innermost layer adheres poorly, a structure in which the active material in the innermost layer has been removed is also effective.

[0022]

Third Embodiment.

FIG. 4 is a cross-sectional view of the electrode structure in the third embodiment of the present invention. In order to avoid complicating the figure, the separator located between the positive electrode active material layer and the negative electrode active material layer 4 and on the outermost layer has been omitted. In this example, the beginning of the winding of the negative electrode and the positive electrode is shifted by half a lap, and the current collector terminals 1, 2 are placed in the central portion of the electrodes. In this structure, as in FIG. 3, active material layers 3 and 4 are also formed to the inside the electrode current collectors 5, 6 in the innermost layer because, as in FIG. 3, there are no current collector terminals 1, 2 inside the electrode unit, so excess space is unlikely to exist in the innermost layer. Also, active material layers 3, 4 are not formed to the outside of the electrode current collectors 5, 6 in the outermost layer because there is no active material on the opposing counter electrode. In addition, active material layers facing the current collector terminals 1, 2 are not formed, eliminating excess space due to the thickness of the current collector terminals 1, 2, and preventing lithium metal deposition due to

excess positive electrode active material. The positive electrode active material layer 3 opposite the beginning of the winding end of the negative electrode is covered with insulating tape 7 to prevent lithium metal deposition, but instead of covering it with insulating tape 7, the active material in this portion may be removed. If the innermost layer adheres poorly, a structure in which the active material in the innermost layer has been removed is also effective.

[0023]

Fourth Embodiment.

FIG. 5 is a cross-sectional view of the electrode structure in the fourth embodiment of the present invention. In order to avoid complicating the figure, the separator located between the positive electrode active material layer and the negative electrode active material layer 4 and on the outermost layer has been omitted. In this example, the beginning of the winding of the negative electrode and the positive electrode is the same, and the current collector terminals 1, 2 are placed at the outer ends of the wound electrodes. Here, unlike in the first to third embodiments, the starting position of the winding of the positive electrode and the negative electrode is the same, so that the same poles, such as a negative electrode and negative electrode, face each other at the innermost part due to the initial folding, and no battery reaction can be expected if active material is present at the innermost layer. Therefore, no electrode active material is formed to the inside of the electrode current collector (the negative electrode current collector 6 in this figure) on the innermost layer.

[0024]

Fifth Embodiment.

FIG. 6 is a cross-sectional view of the electrode structure in the fifth embodiment of the present invention. In order to avoid complicating the figure, the separator located between the positive electrode active material layer and the negative electrode active material layer 4 and on the outermost layer has been omitted. In this example, the beginning of the winding of the negative electrode and the positive electrode is the same, and one current collector terminal 1 is placed at the inner end of the wound electrodes and the other current collector terminal 2 is placed in the central portion. In this case also, no electrode active material is formed

to the inside of the innermost electrode current collector 6. Also, active material is not formed on the positive electrode current collector 5 opposite the negative electrode current collector terminal 2 formed on the negative electrode current collector 6 at the inner end in order to prevent lithium metal deposition. However, active material is formed on the negative electrode portion opposite the positive electrode current collector terminal 1 formed on the positive electrode current collector 5 because there are no concerns about lithium metal deposition. Of course, the active material in this portion may be removed.

[0025]

[Examples]

Example 1.

(Fabrication of the Positive Electrode)

A positive electrode active material paste was prepared by dispersing 91 parts by weight of positive electrode active material consisting of LiCoO_2 , 6 parts by weight of artificial graphite serving as a conductive material, and 3 parts by weight of polyvinylidene fluoride (PVDF) serving as a binding material in N-methylpyrrolidone (NMP). This positive electrode active material paste was pattern-coated on 20 μm thick aluminum foil serving as the positive electrode current collector using the doctor-blade method as shown in FIG. 2 (A) to form a positive electrode active material layer with coated and uncoated portions, and then the layer was dried. The same positive electrode active material paste was pattern-coated on the back side using the doctor blade method to form a positive electrode active material layer on both sides of the aluminum foil. This was dried and pressed to produce a positive electrode with a thickness of 200 μm . Electrode dimensions were 49 mm long x 150 mm wide, uncoated portion A was 10 mm wide, portions B and C were 30 mm wide, and the positive electrode active material film on one side was 90 μm . A 0.1 mm thick x 3 mm wide aluminum current collector terminal was attached to the edge of an uncoated portion of the aluminum foil of the positive electrode by ultrasonic welding to serve as a lead. The current collector is not limited to foil, but can also be a mesh.

[0026]

(Creation of the Negative Electrode)

A negative electrode active material paste was prepared by dispersing 90 parts by weight of negative electrode active material consisting of mesophase carbon microbeads and 10 parts by weight of PVDF in NMP. The negative electrode active material paste was pattern-coated on 12 μm thick Cu foil serving as the negative electrode current collector using the doctor blade method as shown in FIG. 2 (b) to form a negative electrode active material film with coated and uncoated negative electrode active material portions, and the film was then dried. The negative electrode active material paste was pattern-coated on the back side as well, and dried to form negative electrode active material films on both sides of the Cu foil. This was then pressed to create the negative electrode. The electrode dimensions were 50 mm long x 180 mm wide, uncoated portion D was 5 mm wide, uncoated portions E and F were 30 mm wide, portion G was 55 mm wide, and the negative electrode active material film on one side was 90 μm . A Cu current collector terminal with a thickness of 0.1 mm and a width of 3 mm was attached to the edge of an uncoated portion of the Cu foil of the negative electrode by ultrasonic welding to serve as a lead. The current collector can be a mesh instead of foil, and the current collector terminal can be Ni instead of Cu.

[0027]

(Creation of the Spiral Wound Electrode Structure)

A 25 μm porous polypropylene sheet (trade name Celgard from Hoechst) was used as the separator. Winding of this negative electrode and positive electrode were shifted by half a lap, the collector terminal was located inside, the active material uncoated portions of the positive electrode and negative electrode were placed opposite each other via the separator, the electrodes were wound into an oblong shape, and the ends of the winding were secured with polyimide tape to create a spiral wound electrode structure.

[0028]

Example 2.

(Flattening of the Electrode Structure)

The electrode structure wound in an oblong shape in Example 1 was interposed between flat plates such as metal plates and subjected to a load to create the flat spiral wound electrode

unit shown in FIG. 1. At this time, the electrode unit was dried under pressure at 60 to 120°C to obtain an electrode unit with a flat spiral wound structure. Flattening eliminates excess space for compactness and improves adhesion between the electrodes and the separator.

[0029]

Example 3.

(Bonded Flat Spiral Wound Electrode Structure)

A positive electrode and a negative electrode were prepared as in Example 1. An NMP solution obtained by dissolving 7 parts by weight of PVDF and dispersing 9 parts by weight of aluminum oxide powder was applied to one side of two separators as an adhesive. An adhesive layer using this adhesive retains the electrolyte when the electrolyte is poured, forming an adhesive layer with ion conductivity. Before the adhesive dried, this layer was affixed and bonded to both sides of the negative electrode to form a negative electrode with separators. The adhesive is an example and is not limited to PVDF. It can be a polymer such as polyvinyl alcohol, polyvinyl butyrate, polymethacrylate, or polymethacrylate-methyl, for example. Also, the concentration is not limited to 7 parts by weight. Aluminum oxide powder is added so that the adhesive layer readily become porous, and fine powders such as graphite and silica gel may also be added. The solvent is not limited to NMP, and can also be dimethylformamide (DMF), for example.

[0030]

A DMF solution obtained by dissolving 7 parts by weight of PVDF and dispersing 9 parts by weight of aluminum oxide powder was applied to the negative electrode with separators as an adhesive. The active material uncoated portions of the negative electrode and the active material uncoated portions of the positive electrode overlapped when bonded together and wound into an oblong shape. Before the adhesive dried, vacuum drying was performed while applying load to form an adhesive flat spiral wound electrode unit as shown in FIG. 1. The bonding process may be performed by bonding the negative electrode to a separator bonded to the positive electrode, or by bonding the positive electrode, separator, and negative electrode at the same time. Just one of the positive electrode and negative electrode may be bonded to the separator, and bonding the electrodes to the separator provides a highly reliable electrode

structure that is difficult to shift. Manufacturing is made easier by bonding one of the electrodes to the separator and then laminating the other electrode while wrapping it around the separator.

[0031]

Comparative Example 1.

In Comparative Example 1, the electrode structure shown in FIG. 9 was prepared with the same manufacturing method as in Example 3, using electrode made of the same material as in Example 1, with an electrode active material formed on one or both sides of the electrode current collector but without pattern coating. The dimensions of the electrode structure were 3.0 mm in thickness (the vertical dimension in the drawing), 25 mm in width (the horizontal dimension in the drawing), and 50 mm in height (the dimension orthogonal to the drawing) in both Example 3 and Comparative Example 1.

[0032]

(Sealing of the Electrode Unit)

The electrode structures prepared in Example 3 and Comparative Example 1 were immersed in an electrolyte obtained by dissolving lithium hexafluorophosphate in a mixed solvent of ethylene carbonate and diethyl carbonate (1:1 molar ratio) at a concentration of 1 mol/dm³ and allowed to soak sufficiently. The electrode structures were then sealed by heat fusion in a pouch made of a 110 µm thick aluminum laminate sheet. The current collecting tab portion was sealed by interposing the metal and heat fusible polyethylene portion between aluminum laminate sheets and performing heat fusing. The aluminum laminate sheet closed portions were 5 mm, which were thermally sealed in three directions (top, left, and right) to make a battery.

[0033]

Table 1 shows the results when each of the batteries was charged at a current of 100 mA until it reached 4.1 V and then discharged 10 minutes later at the same current value until it reached 2.5 V.

The battery created in Example 3 had a discharge capacity of 340 mAh, while the battery created in Comparative Example 1 had a discharge capacity of only 280 mAh. The external dimensions of the battery were the same, but in Example 3, the active materials not involved in the battery reaction were removed,

because the electrode active material layers were placed only where the positive electrode and negative electrode active materials face each other. As a result, the amount of electrode active material layer that functions as a battery is greater in Example 3 than in Comparative Example 1.

[0034]

[Table 1]

	Example 3	Comparative Example 1
Discharge Capacity (mAh)	340	280

[0035]

In Comparative Example 1, as shown in the enlarged central portion of the electrode structure in FIG. 8, extra space readily occurs in the innermost portion due to the thickness of current collector terminals 1, 2 and the insulating tape 7. However, in Example 3, as shown in the enlarged central portion of the electrode structure in FIG. 7, extra space is less likely to exist. Also, in Example 3, the electrode active material layer to the inside of the innermost layer, where space is easily created and battery reactions are unlikely to occur, is eliminated to reduce excess thickness. The resulting difference in discharge capacity with Comparative Example 1 indicates that a higher discharge capacity was obtained and the volumetric energy density was improved.

[0036]

A cycle test was conducted to compare the degradation in discharge capacity after 100 cycles by repeating charge-discharge cycles in which the batteries from Example 3 and Comparative Example 1 were charged at a current value of 100 mA until they reached 4.1 V and then discharged at the same current value 10 minutes later. The results are shown in Table 2. The battery in Example 3 maintained more than 90% of its initial discharge capacity after 100 cycles, while the battery in Comparative Example 1 had approximately 86% of its initial discharge capacity. In Comparative Example 1, extra negative electrode active material exists in the innermost and outermost layers, and when the charge-discharge cycle is repeated, lithium ions are taken in by the extra negative active material portions during charging. The extra degradation may be due to the fact that those lithium ions were not released during

discharge. Therefore, removing excess active material from the outermost and innermost layers improves cycle characteristics, suppresses battery degradation with respect to repeated use, and has the effect of extending battery life.

[0037]

[Table 2]

	Example 3	Comparative Example 1
Initial Discharge Capacity (mAh)	340	280
Discharge Capacity After 100 Cycles (mAh)	308	240
Deterioration (%) After 100 Cycles	90.6	85.7

[0038]

Example 4.

Using electrodes that differed only in terms of the active material coating patterns from the electrodes created in Example 1, an electrode structure with the same winding starting positions for the positive and negative electrodes in the fourth embodiment shown in FIG. 5 was created using the same production method as in Example 3, and this became Example 4.

[0039]

Comparative Example 2.

In Comparative Example 2, the electrode structure shown in Figure 10 was prepared using the same production method as in Example 3, using electrodes made of the same materials as in Example 1, with the electrode active material formed on one side or both sides of the electrode current collector without pattern coating. The dimensions of the electrode structures in Example 4 and Comparative Example 2 were the same as those of Example 3 and Comparative Example 1.

[0040]

The electrode structure created in this manner was soaked in an electrolyte as in Example 3 and Comparative Example 1, and sealed with aluminum laminate sheets to form a battery. Table 2 shows the results these batteries were charged at a current of 100 mA until they reached 4.1 V and then discharged 10 minutes later at the same current value until they

reached 2.5 V. The battery created in Example 4 had a discharge capacity of 340 mAh, while the battery created in Comparative Example 2 had a discharge capacity of only 300 mAh. The external dimensions of the battery were the same, but in Example 4, the active materials not involved in the battery reaction were removed, because the electrode active material layers were placed only where the positive electrode and negative electrode active materials face each other. As a result, the amount of electrode active material layer that functions as a battery is greater in Example 4 than in Comparative Example 2.

[0041]

[Table 3]

	Example 4	Comparative Example 2
Discharge Capacity (mAh)	340	300

[0042]

When the electrode unit in Comparative Example 2 was pressed and flattened, the current collector in the innermost fold of the electrode unit sometimes cracked, but this was not observed in the electrode unit of Example 4. This is because the electrode unit in Comparative Example 2 has an electrode active material layer in the innermost layer as shown in FIG. 10, and the elongation rate of the current collector in the innermost folded portion is large. Here, the metal electrode current collector, especially the positive electrode current collector, could not withstand elongation of the metal due to folding. In contrast, the electrode unit in Example 4 does not have an electrode active material layer in the innermost layer, so the elongation rate of the metal electrode current collector was smaller than in Comparative Example 2, and tearing of the electrode current collector was suppressed. Thus, the absence of electrode active material in the innermost layer was found to be effective in controlling the tearing of the electrode current collector when pressed and flattened.

[0043]

The electrode structures shown in the first through fourth embodiments are discussed in the examples, but electrode structures in the other embodiments can also be made in the same way as in Examples 1 to 4 using the

electrodes in Example 1, and differing only in terms of the active material coating pattern.

[0044]

[Effects of the Invention]

As mentioned above, the first aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed on the positive electrode portion opposite the current collection terminal formed on the current collector of the negative electrode. As a result, a lightweight and compact electrode structure with improved energy density and high reliability can be obtained by preventing lithium metal precipitation.

[0045]

The second aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the inside of the electrode current collector in the innermost layer. By omitting the active material to the inside of the innermost layer, which is not involved in the battery reaction, a lightweight, compact electrode structure with improved energy density can be obtained. In addition, cycle characteristics during repeated use are improved, and the battery life can be expected to increase. Tearing of the electrode current collector can also be prevented.

[0046]

The third aspect of the present invention is an electrode structure comprising a positive electrode and a negative electrode having an

electrode active material formed on the front and back surfaces of an electrode current collector and current collector terminals formed in one portion of one side of the electrode current collector, the positive electrode and a negative electrode arranged opposite each other via an electron-insulating separator and spirally wound around each other, the electrode structure characterized in that no electrode active material is formed to the outside of the electrode current collector in the outermost layer. By omitting the active material to the outside of the outermost layer, which has no counter electrode and is not involved in the battery reaction, a lightweight, compact electrode structure with improved energy density can be obtained. In addition, cycle characteristics during repeated use are improved, and the battery life can be expected to increase.

[0047]

Because flattening is performed in the fourth aspect of the present invention, the elimination of excess space allows for better adhesion between the electrodes and the separator, resulting in a higher energy density.

[0048]

Because the separator is bonded to at least one of the positive electrode and negative electrode in the fifth aspect of the present invention, the electrodes and the separator are less likely to shift, improving reliability.

[0049]

Because the battery in the sixth aspect of the present invention has the electrode structure according to any of the first to fifth aspects of the invention, a lightweight and compact battery with improved energy density and high reliability can be obtained by preventing lithium metal precipitation.

[Brief Description of the Drawings]

[FIG. 1]

FIG. 1 is a cross-sectional view of the configuration of the spiral electrode structure in the first embodiment of the present invention.

[FIG. 2]

FIG. 2 is a pair of cross-sectional views showing an example of the electrode pattern coating

process for the first embodiment of the present invention.

[FIG. 3]

FIG. 3 is a cross-sectional view of the configuration of the spiral electrode structure in the second embodiment of the present invention.

[FIG. 4]

FIG. 4 is a cross-sectional view of the configuration of the spiral electrode structure in the third embodiment of the present invention.

[FIG. 5]

FIG. 5 is a cross-sectional view of the configuration of the spiral electrode structure in the fourth embodiment of the present invention.

[FIG. 6]

FIG. 6 is a cross-sectional view of the configuration of the spiral electrode structure in the fifth embodiment of the present invention.

[FIG. 7]

FIG. 7 is an enlarged cross-sectional view of the center of the flat spiral electrode structure in the third embodiment of the present invention.

[FIG. 8]

FIG. 8 is an enlarged cross-sectional view of the center of the flat spiral electrode structure in the first comparative example.

[FIG. 9]

FIG. 9 is a cross-sectional view of the configuration of a conventional spiral electrode structure.

[FIG. 10]

FIG. 10 is a cross-sectional view of the configuration of another conventional spiral electrode structure.

[Reference Numbers]

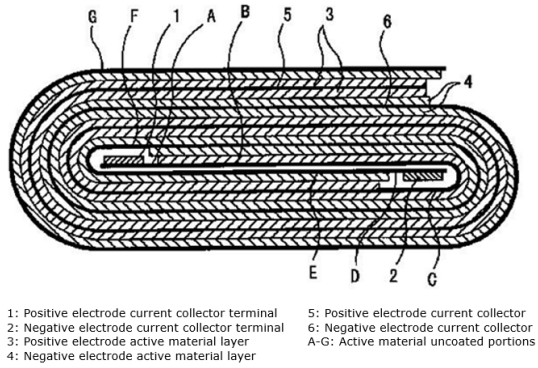
- 1: Positive electrode current collector terminal
- 2: Negative electrode current collector terminal
- 3: Positive electrode active material layer
- 4: Negative electrode active material layer
- 5: Positive electrode current collector
- 6: Negative electrode current collector

7: Insulating tape

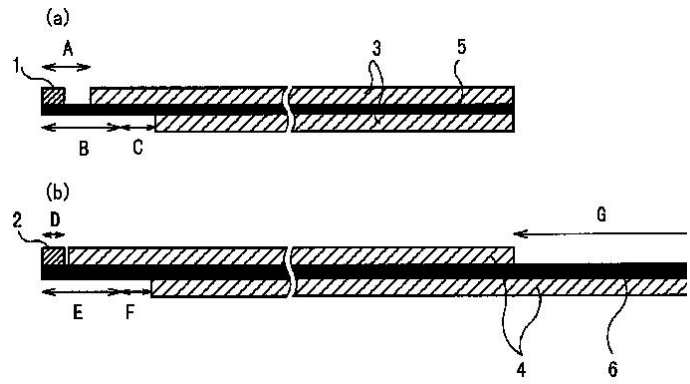
8: Separator

A-G: Active material uncoated portions

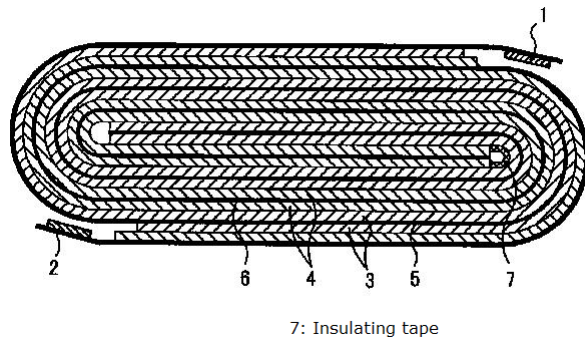
[FIG. 1]



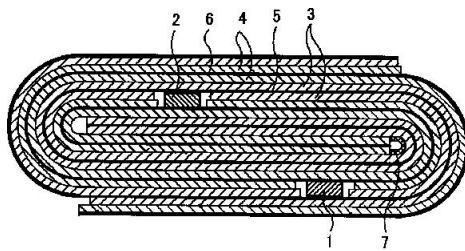
[FIG. 2]



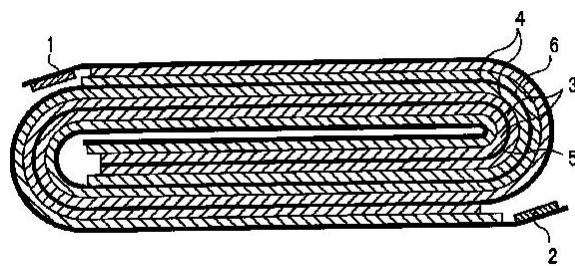
[FIG. 3]



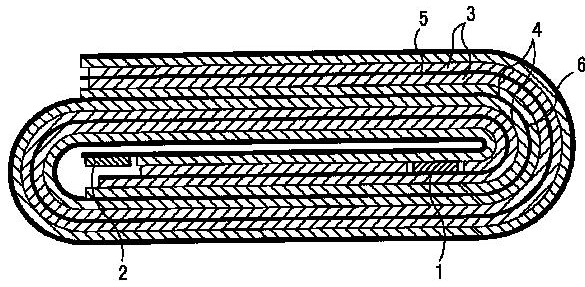
[FIG. 4]



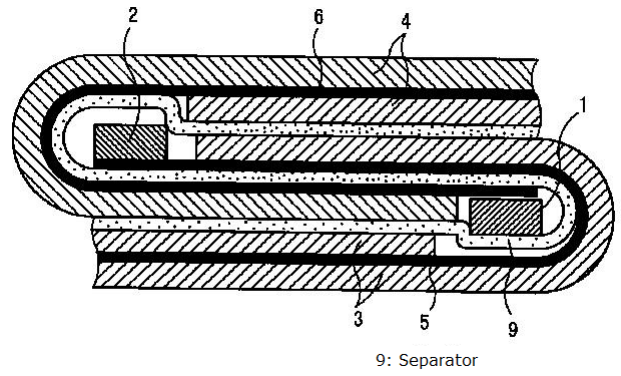
[FIG. 5]



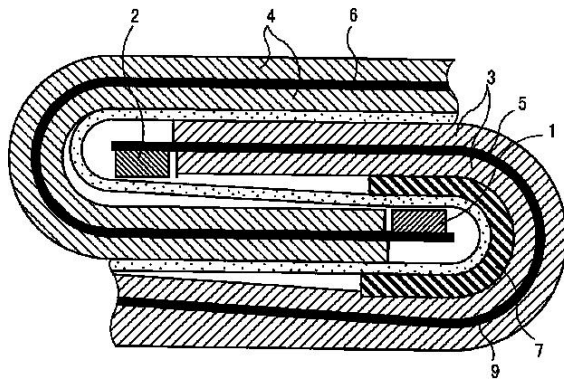
[FIG. 6]



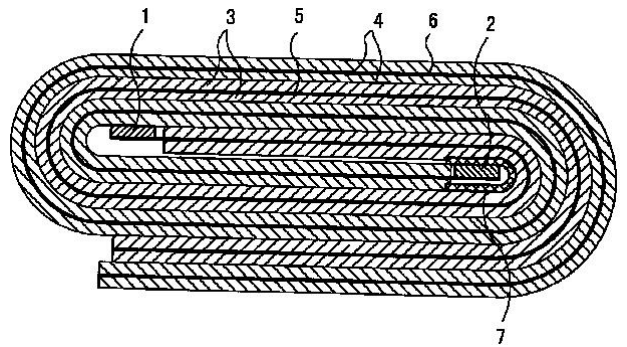
[FIG. 7]



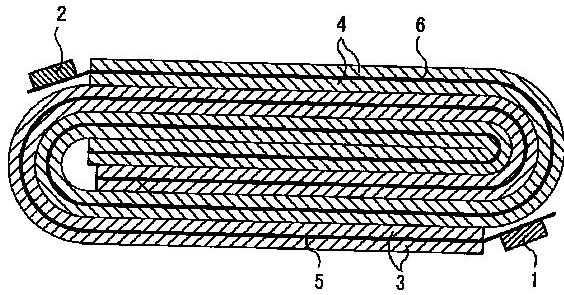
[FIG. 8]



[FIG. 9]



[FIG. 10]



Continued From Front Page

(72) Inventor Hisashi SHIODA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Atsushi ARAKANE
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Seiji YOSHIOKA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Shigeru AIHARA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Makiko KICHISE
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(72) Inventor Takashi NISHIMURA
Mitsubishi Electric Corporation
2-2-3, Marunouchi, Chiyoda-ku, Tokyo

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(21)出願番号	特願平10-235673	(71)出願人	000006013 三菱電機株式会社 東京都千代田区丸の内二丁目2番3号
(22)出願日	平成10年8月21日(1998.8.21)	(72)発明者	竹村 大吾 東京都千代田区丸の内二丁目2番3号 三 菱電機株式会社内
		(72)発明者	漆畑 広明 東京都千代田区丸の内二丁目2番3号 三 菱電機株式会社内
		(74)代理人	100102439 弁理士 宮田 金雄 (外2名)

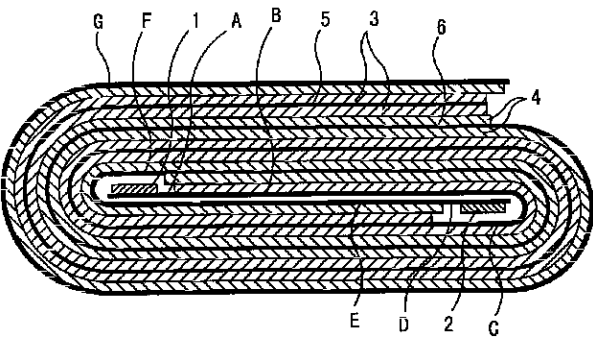
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(54)【発明の名称】 電極構造体およびそれを用いた電池

(57)【要約】

【課題】 軽量・小型でエネルギー密度の向上した、さらにリチウム金属の析出を防止して信頼性の高い電極構造体およびそれを用いた電池を提供する。

【解決手段】 電極集電体5、6の表裏両面に電極活物質3、4を、電極集電体の片面の1部に集電端子1、2をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、負極の集電体に形成された集電端子に対向する正極部分には電極活物質が形成されていない電極構造体。さらに、最内層の電極集電体の内側または最外層の電極集電体の外側には電極活物質が形成されていない電極構造体。このような電極構造体を備えた電池。



- | | |
|------------|---------------|
| 1 : 正極集電端子 | 5 : 正極集電体 |
| 2 : 負極集電端子 | 6 : 負極集電体 |
| 3 : 正極活物質層 | A~G : 活物質未塗工部 |
| 4 : 負極活物質層 | |

【特許請求の範囲】

【請求項1】 電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、上記負極の集電体に形成された集電端子に対向する正極部分には電極活物質が形成されていないことを特徴とする電極構造体。

【請求項2】 電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最内層の電極集電体の内側には電極活物質が形成されていないことを特徴とする電極構造体。

【請求項3】 電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最外層の電極集電体の外側には電極活物質が形成されていないことを特徴とする電極構造体。

【請求項4】 平板化したことを特徴とする請求項1ないし3の何れかに記載の電極構造体。

【請求項5】 正極および負極の少なくとも一方とセパレータを接着したことを特徴とする請求項1ないし4の何れかに記載の電極構造体。

【請求項6】 上記請求項1ないし5の何れかに記載された電極構造体を備えた電池。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】この発明は、電池に用いる電極活物質層の配置形状および電池の構造に関するもので、特に渦巻型電池の性能を向上させるものである。

【0002】

【従来の技術】近年における電子機器性能の向上に伴って、この電子機器の電源として用いる電池、特に繰り返し充電可能な二次電池に対して性能向上が求められてきた。電子機器をより長時間駆動することができ、軽量で持ち運びが容易でかつ高容量な電池としてリチウムイオン二次電池が注目されている。そこで本発明ではリチウムイオン二次電池を例として説明する。

【0003】図9は、従来のリチウムイオン二次電池の電極構造体部分の構成を示す断面図である。図において、1は正極集電端子、2は負極集電端子、3は正極活物質、4は負極活物質、5は正極集電体、6は負極集電体であり、正極活物質3と負極活物質4との間には図示していないセパレータなどの電解質層が設けられ、この電解質層にはセパレータに電解質を溶解した非水系の電解液を含浸したものが用いられる。7は絶縁テープである。

【0004】図9に示したリチウムイオン二次電池にお

いて、特に電池の小型、薄膜化のために、正極活物質3および負極活物質4といった電極活物質層の改良や新たな活物質の探求がなされているが、それと同様に、より高いエネルギー密度が得られる電極構造の開発、すなわち正極集電端子1、負極集電端子2、正極活物質3、負極活物質4、正極集電体5および負極集電体6が構成する電極構造が重要となっている。

【0005】

【発明が解決しようとする課題】電極構造体としては、電極集電体5、6の片面に電極活物質層3、4を塗布・成形（以下、片面塗工という）した電極より、図9に示したような電極集電体5、6の両面に電極活物質層3、4を塗布・成形（以下、両面塗工という）した電極の方が、電池全体のうち電極集電体5、6の占める割合は小さく、体積エネルギー密度は向上する。また、電極を巻回させた構造をもつ場合、電極構造体の最内層や最外層には対向する電極が存在しないために不要な電極活物質層3、4が存在し、厚みや重量の増加につながる。さらに、最内層に電極活物質層3、4を有する電極をプレスして平板状にした場合には、最内層の折り曲げ部分の伸び率が大きいので、電極集電体5、6が破裂する可能性がある。ここで渦巻型構造の最内層とは電極を巻回し始めた位置から1周もしくは半周するまでの一番内側の電極活物質層を示し、最外層とは一番外側の対向する電極のない電極活物質層を示す。

【0006】電池には前述のように外部との導通をとる集電端子1、2が必要であり、集電端子1、2は、電極中の電極活物質層3、4で覆われていない電極集電体5、6の一部に配置されるが、特に平板化して薄型の電池を作製する場合には電池の厚みが厚くならないよう考慮して集電端子1、2を配置する必要がある。

【0007】また、正極および負極の集電端子1、2を配置する部分の電極活物質層3、4は電極集電体5、6と集電端子1、2との溶接を行うために除去されるが、このために集電端子1、2の配置された部分と対向する電極部分に存在する電極活物質層3、4は電池として働かず、無駄な活物質となり厚みや重量の増加の原因となる。

【0008】また、正極活物質3が過剰に存在したり、正極活物質3に対向する負極活物質4の一部が存在しなかったり、正極に対向している負極活物質4が電池として働かないと、負極の一部分に電流が集中してリチウム金属の析出による短絡およびこの短絡に起因する発火等の問題が生じてくる。そこで、負極活物質4に対向する正極活物質3が存在しない場合には上記リチウム金属の析出等の問題はないが、例えば図9の負極集電端子2の周囲に配置された正極活物質3のように対向する負極活物質4のない場合は、正極活物質3の表面をマスク用テープ7等で覆ったり、正極活物質3を削り取るなどして、実質的に負極活物質4に対向しない正極活物質3が

ないようにする必要が生じる。これにより生産工程の増加やコスト上昇などの課題が存在した。

【0009】また、図10に示すような電極集電体5、6の両面に電極活物質層3、4をそれぞれ両面塗工した正負両電極の端部を合わせて巻回した場合、最内層の電極活物質層4は対向する電極がないため電池として機能しない。図9のように正極と負極の端子を半周ずらして巻回した場合では最内層は正負の電極活物質層3、4が対向するようになるが、正極と電解質層および負極と電解質層の間に空間が生じやすく、十分な電極反応は期待できない。更に、両面塗工した電極を巻回した場合の最外層には対向する電極を持たない正極活物質もしくは負極活物質が存在し重量増加および体積増加につながっていた。

【0010】このように正極活物質3と負極活物質4が対向していない部分に余分な活物質や、マスク用テープが存在することで、エネルギー密度の減少や電池全体の厚み増加、また生産工程の増加によるコスト増加に至るという問題があった。

【0011】本発明の第1の目的は、軽量・小型でエネルギー密度の向上した電極構造体およびそれを用いた電池を提供するものである。また、第2の目的は、リチウム金属の析出を防止して信頼性の高い電極構造体およびそれを用いた電池を提供するものである。さらに、第3の目的は、電池寿命の向上した電極構造体およびそれを用いた電池を提供するものである。

【0012】

【課題を解決するための手段】第1の発明に係る電極構造体は、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、上記負極の集電体に形成された集電端子に対向する正極部分には電極活物質が形成されていないものである。

【0013】第2の発明に係る電極構造体は、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最内層の電極集電体の内側には電極活物質が形成されていないものである。

【0014】第3の発明に係る電極構造体は、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最外層の電極集電体の外側には電極活物質が形成されていないものである。

【0015】第4の発明に係る電極構造体は、上記第1ないし第3の何れかの発明において、平板化したもので

ある。

【0016】第5の発明に係る電極構造体は、上記第1ないし第4の何れかの発明において、正極および負極の少なくとも一方とセパレータを接着したものである。

【0017】第6の発明に係る電池は、上記第1ないし5の発明の何れかに記載された電極構造体を備えたものである。

【0018】

【発明の実施の形態】実施の形態1. 図1は本発明の実施の形態1による電極構造体を示す断面図であり、負極と正極の巻き始めを半周ずらして巻かれている例である。なお、図1は図の複雑化を避けるために、正極活物質層と負極活物質層との間および最外層に配置されているセパレータを省略している。図において、1は正極集電端子、2は負極集電端子、3は正極活物質層、4は負極活物質層、5は正極集電体、6は負極集電体、A～Gは活物質未塗工部である。

【0019】図1に示した電極構造体の特徴は、正極と負極がセパレータを介して密着しにくい第一層すなわち最内層の電極活物質層3および4の一部B、Eと、対向する対極の存在しない最外層の電極活物質層（図では負極活物質層4）Gを塗工していない点と、最内端部に取り付けられた電極集電端子1、2に対向する電極活物質層部位C、Fは電池として反応しないので、活物質の未塗工部となっている点と、電極活物質層3、4とほぼ同厚みの電極集電端子1、2を第一層の巻き出し部分の電極活物質層の未塗工の部分A、Dに電極厚みの増大を抑えるように効率よく配置している点の特徴である。このような構成により、軽量、かつコンパクトでエネルギー密度の向上した電極構造体を得られる。さらに、負極集電体6に形成された集電端子2に対向する正極部分は活物質の未塗工部となっているので、リチウム金属の析出を防止することができる。またさらに、負極活物質層4を対向する正極活物質層3より大きく形成することにより、リチウム金属の析出をより確実に防止している。これは以下の各実施の形態においても同様である。図1では電極集電体5、6は太線で示し、この電極集電体のうちの電極活物質層の未塗工の部分Aを極太線で示している。この渦巻型の電極構造体の第一層とは巻回し始めた位置を出発点として、この出発点まで巻かれた部位までをさす。

【0020】図2(a)および(b)は、図1に示したような電極集電体5、6の片面または両面に未塗工の部分をつけるために電極活物質層3、4をパターン塗工した電極の例で、図中A～Gは電極活物質層が未塗工となっている部分であり、図1のA～Gに対応している。図1(a)および(b)で、AおよびDはそれぞれ正極集電端子1および負極集電端子2を取り付けるための活物質層が未塗工の部分であり、BおよびEは最内層に対応する部分であり、CおよびFはそれぞれ負極集電端子2

および正極集電端子1が対向する正極活物質層3および負極活物質層4が未塗工となる部分に対応する。また、Gは最外層の電極集電体6の外側の負極活物質層4が未塗工となる部分に対応する。なお、未塗工の部分の形成は、電極活物質層3、4の形成時にパターン塗工して作製してもよいし、全面塗工後その一部を削り取るなどして作製してもよい。

【0021】実施の形態2．図3は本発明の実施の形態2による電極構造体を示す断面図であり、図の複雑化を避けるために、正極活物質層3と負極活物質層4との間および最外層に配置されているセパレータを省略している。負極と正極の巻き始めを半周ずらして巻かれている例であり、巻回した電極の外側の端部に集電端子1、2を配置した場合を示す。この構造は電極体内部に集電端子1、2を持たないため余剰空間が存在しにくく、最内層にも余分な空間が生じにくいので、図1と異なり最内層の電極集電体5、6の内側にも活物質層3、4を形成している。また、最外層の電極集電体5、6の外側には対向する対極の活物質がないので活物質層3、4は形成していない。よって、集電端子1、2に対向する活物質層は無く、余剰な正極活物質によるリチウム金属の析出も防止できる。なお、負極の巻始め端部に対向する正極活物質層3は絶縁テープ7で覆ってリチウム金属の析出を防止しているが、絶縁テープ7で覆う代わりにこの部分の活物質を除去してもよい。また、最内層が密着しにくい場合は最内層の活物質を除去した構造も有効である。

【0022】実施の形態3．図4は本発明の実施の形態3による電極構造体を示す断面図であり、図の複雑化を避けるために、正極活物質層3と負極活物質層4との間および最外層に配置されているセパレータを省略している。負極と正極の巻き始めを半周ずらして巻かれている例であり、電極の中央部に集電端子1、2を配置した場合を示す。この構造の場合も図3の場合と同様に電極体内部に集電端子1、2を持たないため余剰空間が存在しにくく、最内層にも余分な空間が生じにくいので、最内層の電極集電体5、6の内側にも活物質層3、4を形成している。また、最外層の電極集電体5、6の外側には対向する対極の活物質がないので活物質層3、4は形成していない。また、集電端子1、2に対向する活物質層は形成せず、集電端子1、2の厚みによる余分な空間を排除し、さらに余剰な正極活物質によるリチウム金属の析出も防止している。なお、負極の巻始め端部に対向する正極活物質層3は絶縁テープ7で覆ってリチウム金属の析出を防止しているが、絶縁テープ7で覆う代わりにこの部分の活物質を除去してもよい。また、最内層が密着しにくい場合は最内層の活物質を除去した構造も有効である。

【0023】実施の形態4．図5は本発明の実施の形態4による電極構造体を示す断面図であり、図の複雑化を

避けるために、正極活物質層3と負極活物質層4との間および最外層に配置されているセパレータを省略している。負極と正極の巻き始め位置を同じにして巻かれている例であり、巻回した電極の外側端部に集電端子1、2を配置した場合を示す。この場合、実施の形態1～3の場合と異なり、正極と負極の巻き始め位置が同じであるため、初回の折り返しにより最内部において、負極と負極のように同じ極が対向するようになり、最内層に活物質が存在しても電池反応は期待できない。よって、最内層の電極集電体（この図では負極集電体6）の内側には電極活物質は形成していない。

【0024】実施の形態5．図6は本発明の実施の形態5による電極構造体を示す断面図であり、図の複雑化を避けるために、正極活物質層3と負極活物質層4との間および最外層に配置されているセパレータを省略している。負極と正極の巻き始め位置を同じにして巻かれている例であり、巻回した電極の内側端部に一方の集電端子1を、中央部に他方の集電端子2を配置した場合を示す。この場合も最内周の電極集電体6の内側には電極活物質は形成していない。また、内側端部の負極集電体6に形成された負極集電端子2に対向する正極集電体5には活物質を形成しないでリチウム金属の析出を防止しているが、正極集電体5に形成された正極集電端子1に対向する負極部分にはリチウム金属析出の心配がないので活物質を形成している。勿論、この部分の活物質を除去してもよい。

【0025】

【実施例】実施例1．

（正極の作製） LiCoO_2 からなる正極活物質9重量部と、導電材としての人造黒鉛6重量部と、結着材としてのポリフッ化ビニリデン（以下、PVDFと略す）3重量部をN-メチルピロリドン（以下、NMPと略す）に分散することにより調整した正極活物質ペーストを、正極集電体となる厚み $20\mu\text{m}$ のアルミ箔上にドクターブレード法により、図2(a)のようにパターン塗工して正極活物質層の塗工の部分と未塗工の部分を持つ正極活物質層を形成した後、乾燥した。更に、裏面にもドクターブレード法により、同じ正極活物質ペーストをパターン塗工してアルミ箔の両面に正極活物質層を形成し乾燥した後、プレスして厚さ $200\mu\text{m}$ の正極を作製した。電極寸法は長さ 49mm ×幅 150mm 、未塗工部Aは幅 10mm 、B+Cは幅 30mm 、片面の正極活物質膜は $90\mu\text{m}$ とした。正極のアルミ箔の未塗工部分の端部にはリードとしての厚み 0.1mm 、幅 3mm のアルミ集電端子を超音波溶接により取り付けた。なお、集電体は箔に限らずメッシュでもよい。

【0026】（負極の作成）メソフェーズカーボンマイクロビーズからなる負極活物質90重量部とPVDF10重量部をNMPに分散することにより調整した負極活物質ペーストを、負極集電体となる厚み $12\mu\text{m}$ のCu

箔上にドクターブレード法により図2(b)のようにパターン塗工して負極活物質塗工部と未塗工部を持つ負極活物質膜を形成した後乾燥した。更に、裏面にも負極活物質ペーストをパターン塗工して乾燥してCu箔の両面に負極活物質膜を形成した後、プレスして負極を作成した。電極寸法は長さ50mm×幅180mm、未塗工部Dは幅5mm、未塗工部E+Fは幅30mm、G55mm、片面の負極活物質膜は90 μ mとした。負極のCu箔の未塗工部分の端部にはリードとして厚み0.1mm、幅3mmのCu集電端子を超音波溶接により取り付けた。なお、集電体は箔に限らずメッシュでもよく、集電端子はCuに限らずNiでよい。

【0027】(渦巻電極構造体作成)セパレータとして25 μ mの多孔性ポリプロピレンシート(ヘキスト社製、商品名セルガード)を使用した。上記作成した正極および負極を、巻き始めを半周ずらし、集電端子が内部に位置し、正極および負極の活物質未塗工部がセパレータを介して対向するように配置して、長円状に巻き込んでいって巻き終わり端部をポリイミドテープで固定し渦巻電極構造体を作成した。

【0028】実施例2。

(電極構造体の平板化)実施例1で、長円状に巻いた電極構造体を金属板等の平板で挟み込み、荷重をかけて平板状にして図1のような平板状渦巻電極体を作成した。この時、60～120℃で長円状の電極体を加圧しながら乾燥し、平板状渦巻構造の電極体を得た。このように平板化することにより、余分な空間が排除されてコンパクト化が図れるとともに電極とセパレータとの密着性がよくなる。

【0029】実施例3。

(接着平板状渦巻電極構造体)正極および負極は実施例1と同様に作成した。2枚のセパレータの片面にPVDFを7重量部溶解させ、酸化アルミニウム粉末9重量部を分散させたNMP溶液を接着剤として塗布した。この接着剤による接着層は、電解液を注液した場合に電解液を保持し、イオン伝導性を有する接着層を形成する。その後、接着剤が乾燥する前に上記作成した負極の両面に密着させ、貼り合わせることでセパレータ付き負極を形成した。なお、接着剤は一例であり、PVDFに限らず、例えばポリビニルアルコール、ポリビニルブチラート、ポリメタクリルサンメチル等の高分子であってもよい。また濃度も7重量部に限らない。また、酸化アルミニウム粉末は接着層が多孔体になり易いように添加しており、黒鉛やシリカゲル等の微粉体を添加してもよい。また、溶剤もNMPに限らず、例えばジメチルホルムアミド(以下、DMFと略す)であってもよい。

【0030】上記セパレータ付き負極に、PVDFを7重量部溶解させ、酸化アルミニウム粉末9重量部を分散させたDMF溶液を接着剤として塗布して、負極の活物質未塗工部と正極の活物質未塗工部が重なり合うように

して貼りあわせ長円状に巻き、接着剤が乾燥する前に、荷重をかけながら真空乾燥を行って図1のような接着平板状渦巻電極体を作成した。なお、接着工程は正極にセパレータを接着したものに負極を接着したり、正極とセパレータと負極を同時に接着してもよい。また、正極と負極の一方のみをセパレータと接着してもよく、電極とセパレータを接着することにより、ずれ難く信頼性の高い電極構造体を得られる。また、電極の一方とセパレータを接着しておいてから他の電極を巻き込みながら張り合わせるにより製造が容易となる。

【0031】比較例1。比較例1として、実施例1と同じ材料からなり、電極活物質が電極集電体の両面に一面に形成された、パターン塗工を施していない電極を用いて実施例3と同様の作成方法で図9に示した電極構造体を作成した。なお、電極構造体の寸法は実施例3、比較例1ともに厚さ(図面に向かって上下方向の寸法)3.0mm、幅(左右方向の寸法)25mm、高さ(図面に垂直な方向の寸法)50mmとした。

【0032】(電極体の封口)上記作成した実施例3と比較例1による電極構造体をエチレンカーボネートとジエチルカーボネートの混合溶媒(モル比で1:1)に6フッ化リン酸リチウムを1mol/dm³の濃度で溶解させた電解液中に浸漬して十分にしみ込ませた後、厚さ110 μ mのアルミラミネートシートで作成した袋に熱融着で封入した。集電タブ部は金属と熱融着性のあるポリエチレンのついてある部分をアルミラミネートシートで挟んで熱融着して密閉した。アルミラミネートシートの閉じしろは5mmで、上と左右の3方向を熱融着によりシールして電池化した。

【0033】上記作成した各電池を100mAの電流で4.1Vになるまで充電させて、10分後に同様の電流値で2.5Vに達するまで放電を行った時の結果を表1に示す。実施例3で作成した電池は340mAhの放電容量が得られたが、比較例1で作成した電池は280mAhの放電容量しか得られなかった。電池の外寸寸法は同じであるが、実施例3では電池反応に関与しない活物質を取り除いて、正極と負極の活物質が対向する部分にのみ電極活物質層を配置しているため、電池として機能する電極活物質層の量が実施例3の方が比較例1よりも多いからである。

【0034】

【表1】

	実施例3	比較例1
放電容量 (mAh)	340	280

【0035】また、比較例1では図8に電極構造体の中心部を拡大して示すように、集電端子1、2および絶縁テープ7の厚みにより最内部に余分な空間が生じ易いが、実施例3では図7に電極構造体の中心部を拡大して

示すように、余分な空間が存在しにくい。更に実施例3では空間が生じ易く、電池反応の起こりにくい最内層内側の電極活物質層をなくして余分な厚みを減らしている。その結果、比較例1との放電容量の差異が生じ、より高い放電容量が得られ、体積エネルギー密度の向上が図られたことがわかる。

【0036】さらに、上記実施例3及び比較例1による電池を100mAの電流値で4.1Vになるまで充電させて10分後に同じ電流値で放電を行うという充放電を繰り返すサイクル試験を行い、100サイクル後の放電容量の劣化を比較した結果を表2に示す。実施例3による電池では100サイクル後の放電容量は初期放電容量の90%以上を維持していたが、比較例1による電池では約86%であった。これは、比較例1では最内層と最外層に余分な負極活物質が存在しているため、充放電サイクルを繰り返した時にその余分な負極活物質部分において充電時にリチウムイオンが取り込まれたが、放電時にはそのリチウムイオンが放出されなかったことが原因であると考えられる。このように、最外層と最内層の余剰活物質を取り除くことでサイクル特性が向上し、繰り返しの使用に対する電池の劣化が抑制され、電池の寿命延長の効果もある。

【0037】

【表2】

	実施例3	比較例1
初期放電容量(mAh)	340	280
100サイクル後放電容量(mAh)	308	240
100サイクル後劣化率(%)	90.6	85.7

【0038】実施例4. 実施例1で作成した電極と活物質の塗工パターンのみが異なる電極を用い、実施例3と同様の作成方法で、図5で示した実施の形態4の正極と負極の巻き始め位置が同じである電極構造体を作成して実施例4とした。

【0039】比較例2. 比較例2として、実施例1と同じ材料からなり、電極活物質が電極集電体の両面に一面に形成された、パターン塗工を施していない電極を用い、実施例3と同様の作成方法で図10に示した電極構造体を作成した。なお、電極構造体の寸法は実施例4、比較例2ともに実施例3、比較例1と同じとした。

【0040】上記のように作成された電極構造体に実施例3、比較例1と同様に電解液をしみ込ませてアルミラミネートシートでシールして電池化した。このようにして作成した各電池を100mAの電流で4.1Vになるまで充電させ、10分後に同様の電流値で2.5Vに達するまで放電を行った時の結果を表2に示す。実施例4で作成した電池は340mAhの放電容量が得られたが、比較例2で作成した電池は300mAhの放電容量しか得られなかった。電池の外形寸法は同じであるが、

実施例4では電池反応に関与しない活物質を取り除いて、正極と負極の活物質が対向する部分にのみ電極活物質層を配置しているため、電池として機能する電極活物質層の量が実施例4の方が比較例2よりも多いからである。

【0041】

【表3】

	実施例4	比較例2
放電容量 (mAh)	340	300

【0042】また、比較例2の電極体をプレスして平板化すると、電極体の最内部の折り曲げ部分の集電体に亀裂が入る場合があったが、実施例4の電極体においてはそのようなことはみられなかった。これは比較例2の電極体では図10のように最内層に電極活物質層を有しているため最内部の折り曲げ部分の集電体の伸び率が大きく、金属の電極集電体、特に正極集電体が折り曲げに対する金属の伸びに耐えきれなかったことが原因である。一方、実施例4の電極体では最内層に電極活物質層を有していないため金属の電極集電体の伸び率が比較例2に比べて小さくなり、電極集電体の断裂が抑制された。このように、最内層に電極活物質を設けないことで、プレスして平板化した場合に電極集電体の断裂制御の効果も見られた。

【0043】なお、上記実施例では実施の形態1および4で示した電極構造体を取り上げたが、他の実施の形態で示した電極構造体についても活物質塗布パターンのみが異なる実施例1と同様の電極を用いて実施例1～4と同様の方法で作成できる。

【0044】

【発明の効果】以上のように、第1の発明によれば、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、上記負極の集電体に形成された集電端子に対向する正極部分には電極活物質が形成されていないので、軽量・小型でエネルギー密度の向上した、しかもリチウム金属の析出を防止して信頼性の高い電極構造体を得られる。

【0045】また、第2の発明によれば、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最内層の電極集電体の内側には電極活物質が形成されていないので、電池反応が期待しにくい最内層内側の活物質を省いて軽量・小型でエネルギー密度の向上した電極構造体を得られる。また、繰り返し使用におけるサイクル特性の向上がみられ、電池寿命の向上が期待できる。さらに、電極集電体

の断裂が防止できる。

【0046】また、第3の発明によれば、電極集電体の表裏両面に電極活物質を、上記電極集電体の片面の1部に集電端子をそれぞれ形成した正極および負極を、電子絶縁性のセパレータを介して対向配置して渦巻状に巻回されてなる電極構造体であって、最外層の電極集電体の外側には電極活物質が形成されていないので、対極がなく電池反応に関与しない最外層外側の活物質を省いて軽量・小型でエネルギー密度の向上した電極構造体を得られる。また、繰り返し使用におけるサイクル特性の向上がみられ、電池寿命の向上が期待できる。

【0047】また、第4の発明によれば、平板化したので、余分な空間をなくして電極とセパレータとの密着性が良好となり、よりエネルギー密度が向上する。

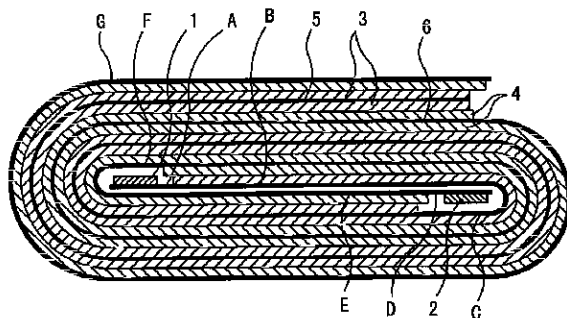
【0048】また、第5の発明によれば、正極および負極の少なくとも一方とセパレータを接着したので、電極とセパレータとがずれにくく、信頼性が向上する。

【0049】また、第6の発明によれば、上記第1ないし5の発明の何れかに記載された電極構造体を備えることにより、軽量・小型でエネルギー密度の向上した、しかもリチウム金属の析出を防止して信頼性の高い電池が得られる。

【図面の簡単な説明】

【図1】 本発明の実施の形態1による渦巻電極構造体

【図1】



- | | |
|-----------|--------------|
| 1: 正極集電端子 | 5: 正極集電体 |
| 2: 負極集電端子 | 6: 負極集電体 |
| 3: 正極活物質層 | A~G: 活物質未塗工部 |
| 4: 負極活物質層 | |

の構成を示す断面図である。

【図2】 本発明の実施の形態1に係る電極パターン塗工例を示す断面図である。

【図3】 本発明の実施の形態2による渦巻電極構造体の構成を示す断面図である。

【図4】 本発明の実施の形態3による渦巻電極構造体の構成を示す断面図である。

【図5】 本発明の実施の形態4による渦巻電極構造体の構成を示す断面図である。

【図6】 本発明の実施の形態5による渦巻電極構造体の構成を示す断面図である。

【図7】 本発明の実施例3による平板状渦巻電極構造体の中心部を拡大して示す断面図である。

【図8】 本発明の比較例1による平板状渦巻電極構造体の中心部を拡大して示す断面図である。

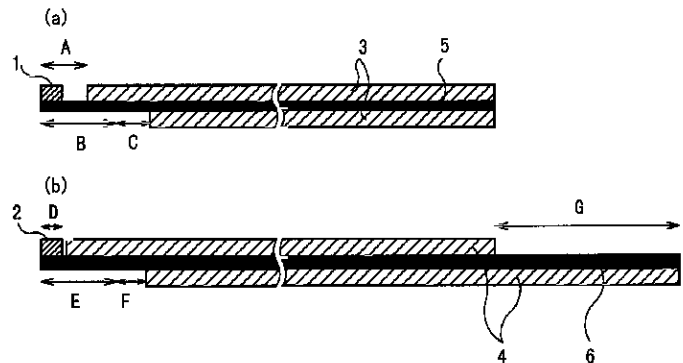
【図9】 従来の渦巻電極構造体の構成を示す断面図である。

【図10】 従来の渦巻電極構造体の別の構成を示す断面図である。

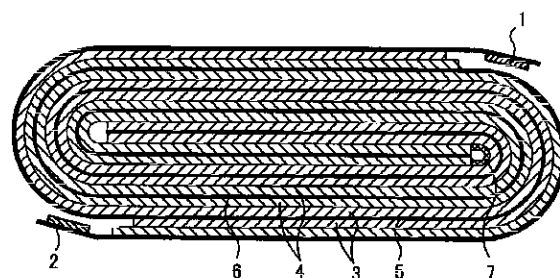
【符号の説明】

1 正極集電端子、2 負極集電端子、3 正極活物質層、4 負極活物質層、5 正極集電体、6 負極集電体、7 絶縁テープ、8 セパレータ、A~G活物質未塗工部。

【図2】

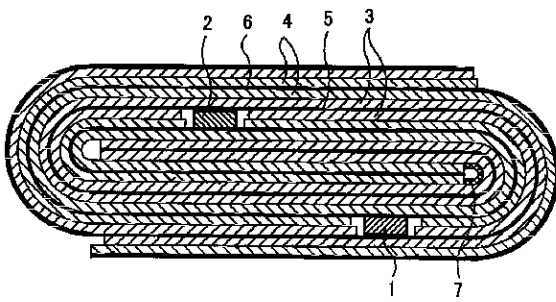


【図3】

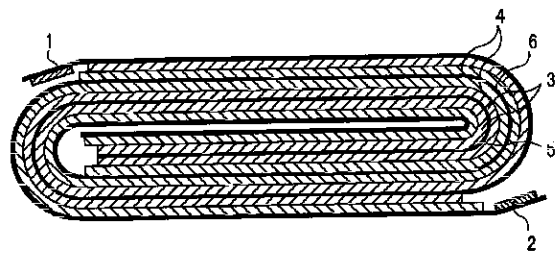


7: 絶縁テープ

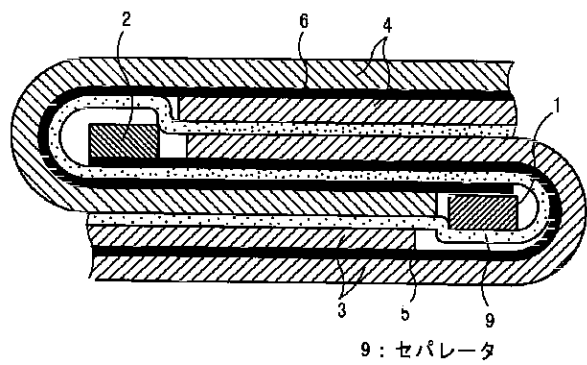
【図4】



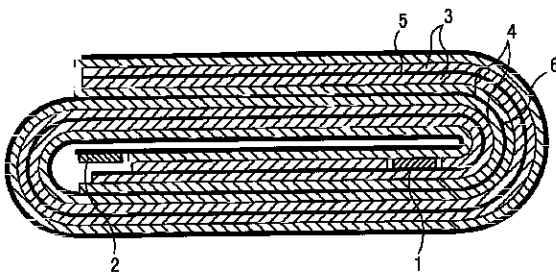
【図5】



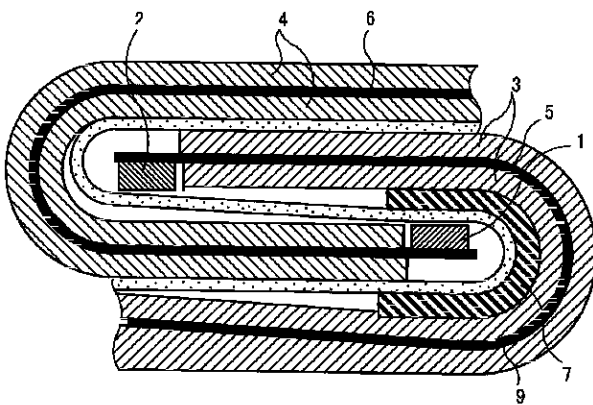
【図7】



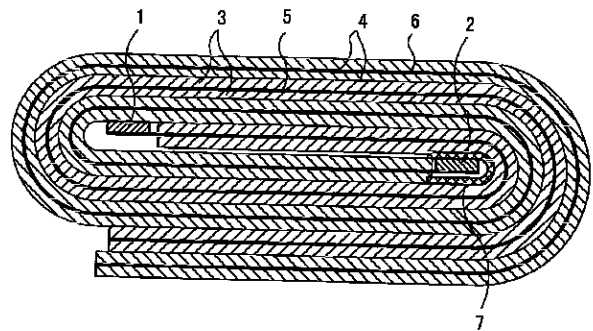
【図6】



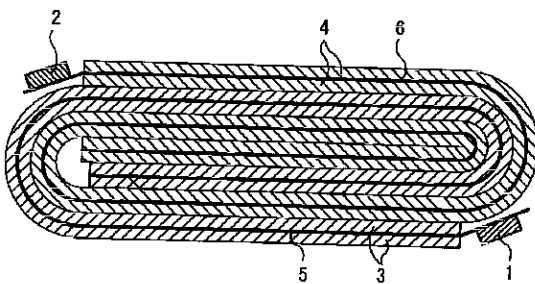
【図8】



【図9】



【図10】



フロントページの続き

(72)発明者 塩田 久
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内
(72)発明者 荒金 淳
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内
(72)発明者 吉岡 省二
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内
(72)発明者 相原 茂
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内

(72)発明者 吉瀬 万希子
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内
(72)発明者 西村 隆
東京都千代田区丸の内二丁目2番3号 三
菱電機株式会社内
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TRANSLATOR CERTIFICATION

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To whom it may concern:

I, Frank McGee, a translator fluent in the Japanese and English languages, on behalf of Morningside Translations, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the documents listed below in a form that reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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Frank McGee

QUESTEL CONFIDENTIAL

4001 S 700 East, Suite 500 #B17
Salt Lake City, UT 84107