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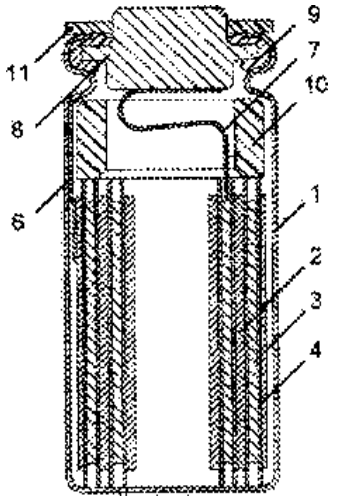
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(54) Title of the Invention

Cylindrical Battery

(57) Abstract

The present invention provides a small cylindrical battery that achieves both improved battery characteristics and enhanced long-term reliability and safety. The cylindrical battery has a bottomed cylindrical battery case (1), an electrode assembly (5) housed in the battery case (1) together with an electrolyte, a sealing member (8) embedded in an opening of the battery case (1), and a gasket (9) sandwiched between the sealing member (8) and the battery case (1), wherein the opening of the battery case (1) is sealed by drawing process applied to the open end portion of the battery case (1). Furthermore, the battery case (1) is made of stainless steel. In addition, the outer diameter of the battery case (1) is 10 mm or less, and the thickness of the battery case (1) is 0.05 mm or more and 0.2 mm or less.



CN 103797607 B

1. A cylindrical battery, comprising a bottomed cylindrical battery case, an electrode assembly housed in the battery case together with an electrolyte, a sealing member embedded in an opening of the battery case, and a gasket sandwiched between the sealing member and the battery case, the opening of the battery case is sealed by a drawing process applied to the open end portion of the battery case, wherein

the battery case is made of stainless steel with a carbon content of 0.03% by mass or less,

the outer diameter of the battery case is 10 mm or less,

the thickness of the battery case is 0.05 mm or more and 0.2 mm or less.

2. The cylindrical battery according to claim 1, wherein the stainless steel forming the battery case is austenitic stainless steel.

3. The cylindrical battery according to claim 1 or 2, wherein the stainless steel forming the battery case is stainless steel with a copper content of 1.0% by mass or more and 6.0% by mass or less.

4. The cylindrical battery according to claim 1 or 2, wherein the outer diameter of the battery case is 6 mm or less.

Cylindrical Battery

Technical Field

[0001] The present invention relates to cylindrical batteries with a battery case, such as lithium-ion secondary batteries.

Background Art

[0002] In recent years, lithium-ion secondary batteries have been widely used as a power source to drive electronic devices such as mobile digital devices. In particular, in multifunctional and high-load portable devices such as smartphones, there has been a continuous demand for improved battery characteristics, such as energy density and load characteristics, as well as lightweight design, for the batteries used as their power sources. Moreover, there has been a constant demand for improved long-term reliability and safety.

[0003] Lithium-ion secondary batteries typically have a metal battery case. By reducing the thickness of the battery case, increasing the internal volume, and filling the battery case with power generation elements at a high density, the energy density can be improved. Reducing the thickness of the battery case is particularly effective for increasing the internal volume of small batteries. As another example, there are lithium-ion batteries that use metal-resin laminated sheets instead of battery cases. In this case, by encapsulating battery components such as positive and negative electrodes, separators, and electrolytes within such thin sheets, weight reduction can be achieved along with increased energy density.

[0004] Prior Art Documents

[0005] Patent Documents

[0006] Patent Document 1: Japanese Patent Application Laid-Open Publication No. 2009-181754

[0007] Patent Document 2: Japanese Patent Application Laid-Open Publication No. 2008-223087

[0008] Patent Document 3: Japanese Patent Application Laid-Open Publication No. 2007-227339

Summary of the Invention

[0009] Problem to be Solved by the Invention

[0010] However, in batteries such as lithium-ion secondary batteries, it is difficult to simultaneously improve battery characteristics and improve long-term reliability and safety. For example, in lithium-ion secondary batteries, iron or aluminum are generally used as the battery case material. Therefore, if the thickness of the metal plate that forms the battery case is reduced in order to increase energy density, the strength of the battery case decreases. A decrease in the strength of the battery case will lead to a decrease in sealing performance and a decrease in the tolerance for expansion of the electrode plates due to repeated charge-discharge cycles or an increase in internal pressure due to gases. As a result, the battery case is prone to deformation or the battery characteristics deteriorate, making it difficult to achieve long-term reliability.

[0011] Furthermore, when metal-resin laminated sheets are used instead of battery cases, although energy density can be improved, problems caused by the decrease in battery case strength become significant. For example, if only the usual charge-discharge cycles are repeated, gases are generated due to the decomposition of the electrolyte, which causes the battery to expand significantly due to the increase in internal pressure. In addition, moisture can easily intrude from the outside of the battery into the interior due to weak sealing performance in the vicinity of the lead portion. Therefore, gases are generated due to the moisture, which causes the internal pressure to increase and the battery to expand. There are concerns that the aforementioned expansion may compromise the sealing of the laminated sheets.

[0012] Thus, in order to balance the improvement of battery characteristics with the improvement of long-term reliability and safety, when a battery case is used, it is very important to reduce the thickness of the battery case while achieving high strength and high sealing performance.

[0013] Therefore, in order to achieve high sealing performance when the opening of the battery case is sealed by crimp sealing, technologies have been proposed to improve the strength of the opening of a battery case by increasing only the thickness of the opening in the battery case (for example, see Patent Document 1). However, such battery cases are

difficult to mold and process due to their complex shape, and are not suitable for mass production.

[0014] In addition, technologies have been proposed to use aluminum alloy materials, whose strength has been improved by adding dissimilar metals and heat treatment, as battery case materials (for example, see Patent Document 2). However, if only the strength of a battery case is increased, the processability of the battery case decreases, making it difficult to achieve high sealing performance.

[0015] Therefore, an objective of the present invention is to provide a small cylindrical battery that achieves both improved battery characteristics and enhanced long-term reliability and safety.

[0016] Means for solving the problem

[0017] Through in-depth research, the inventors have discovered the conditions under which the improvement of battery characteristics and the enhancement of long-term reliability and safety can be achieved in small cylindrical batteries.

[0018] A cylindrical battery according to the present invention comprises a bottomed cylindrical battery case, an electrode assembly housed in the battery case together with an electrolyte, a sealing member embedded in an opening of the battery case, and a gasket sandwiched between the sealing member and the battery case, wherein the opening of the battery case is sealed by drawing process applied to the open end portion of the battery case. Moreover, the battery case is made of stainless steel. The outer diameter of the battery case is 10 mm or less, and the thickness of the battery case is 0.05 mm or more and 0.2 mm or less.

[0019] Effects of the Invention

[0020] The cylindrical battery according to the present invention can achieve both improved battery characteristics and enhanced long-term reliability and safety.

[0021] Although novel features of the present invention are described in the appended claims, both aspects of the structure and content of the present invention, as well as other objects and features of the present invention, will be better understood from the following detailed description in conjunction with the accompanying drawings.

Brief Description of the Accompanying Drawings

[0022] FIG. 1 is a longitudinal cross-sectional view schematically illustrating a cylindrical battery according to an embodiment of the present invention.

Detailed Description of the Embodiments

[0023] First, the cylindrical battery of the present invention will be described.

[0024] The cylindrical battery according to the present invention comprises a bottomed cylindrical battery case, an electrode assembly housed in the battery case together with an electrolyte, a sealing member embedded in an opening of the battery case, and a gasket sandwiched between the sealing member and the battery case, wherein the opening of the battery case is sealed by drawing process applied to the open end portion of the battery case. Moreover, the battery case is made of stainless steel. In addition, the outer diameter of the battery case is 10 mm or less, and the thickness of the battery case is 0.05 mm or more and 0.2 mm or less.

[0025] As shown in Table 1, stainless steel has a very high tensile breaking strength compared with iron (Fe) or aluminum (Al). Furthermore, Table 1 lists SUS316L (austenitic stainless steel) as an example of stainless steel. Therefore, as the present invention uses stainless steel as the material for the battery case, high strength can be maintained in the battery case even when the thickness of the battery case is reduced in a uniform manner. In addition, stainless steel, despite its high strength, has excellent machinability. Therefore, a high degree of sealing can be achieved in the battery case.

[0026] Table 1

[0027]

	Density (g/cm)	Tensile breaking strength (MPa)	Elongation (%)
SUS316L	8.03	481	40
Fe	7.78	196	60
Al	2.70	55	30

[0028] Moreover, the inventors have discovered that high sealing performance can be achieved in small cylindrical batteries with an outer diameter of 10 mm or less, especially when the thickness of the battery case is 0.05 mm or more and 0.2 mm or less. In addition, the inventors have found that these conditions are particularly preferred for small cylindrical batteries with an outer diameter of 6 mm or less. Therefore, in small cylindrical batteries, when sealing the opening of the battery case by applying drawing process to the open end of the battery case, the thickness of the battery case is very important as a condition for improving the sealing performance.

[0029] If drawing process is applied to the open end of the battery case, the drawn portion of the battery case shrinks (i.e., the diameter of the battery case decreases). When the diameter of the battery case before drawing process is 15 mm or more, the shrinkage rate of the battery case 1 caused by the drawing process is small and hardly affects the sealing performance. However, when the diameter of the battery case 1 before the drawing process is 10 mm or less, the shrinkage rate of the battery case 1 increases due to the drawing process, and abnormal deformations such as a decrease in roundness or wrinkles are easily generated at the open end of the battery case. Such problems are significant when the diameter of the battery case before the drawing process is 6 mm or less, which reduces the sealing performance. Thus, in small cylindrical batteries where the shrinkage rate of the battery case 1 is large due to the drawing process, the inventors have found that high sealing performance can be achieved when the battery case 1 is made of stainless steel and the thickness of the battery case 1 is 0.05 mm or more and 0.2 mm or less.

[0030] When the cylindrical battery is a lithium-ion battery, it is preferable that the battery case is made of a material with a broad potential window and high acid corrosion resistance. Regarding this point, stainless steels such as SUS316L have a very strong potential relative to the reduction side, and although not as strong as aluminum on the oxidation side, they have a broader potential window than that of iron or copper. Furthermore, regarding aluminum, if a reduction potential is applied in the presence of lithium ions, surface lithium plating occurs, and an alloy with lithium is formed. Because such alloying reactions are accompanied by volume expansion, the battery case becomes brittle and its strength decreases when it is made of aluminum, making it difficult to achieve long-term battery reliability.

[0031] In addition, stainless steel has higher acid corrosion resistance than iron, copper, and aluminum. This is because stainless steel has a protective layer on its surface. In lithium-ion batteries, lithium hexafluorophosphate ($LiPF_6$) is generally used as a supporting electrolyte. Such a supporting electrolyte can achieve excellent load characteristics while forming an electrolyte with high ionic conductivity. On the other hand, if moisture is present, lithium hexafluorophosphate produces, via hydrolysis, hydrofluoric acid (HF), which is a strong acid. Therefore, in lithium-ion batteries, in addition to improving the sealing to prevent moisture from entering from the outside, improving the acid corrosion resistance of the battery case is also important for achieving long-term reliability. This is because corrosion of the battery case allows moisture to penetrate, which accelerates the corrosion process.

[0032] Therefore, the cylindrical battery according to the present invention can achieve both improved battery characteristics and enhanced long-term reliability and safety. In addition, the thickness of the battery case can be made uniform, so the molding and quality management of the battery case is easy.

[0033] In the preferred specific configuration of the above-mentioned cylindrical battery, the stainless steel forming the battery case is austenitic stainless steel with a low carbon content. Furthermore, the stainless steel forming the battery case is preferably stainless steel with a carbon content of 0.08% by mass or less. Furthermore, the carbon content in the stainless steel is more preferably 0.05% by mass or less, and particularly preferably 0.03% by mass or less.

[0034] As shown in Table 1, stainless steel with such a low carbon content has high elongation and high tensile breaking strength. Therefore, stainless steel with a low carbon content has high machinability. In other words, when forming the battery case 1, it is easy to stretch the stainless steel for thinning, and the processing accuracy is also high.

For example, in slender cylindrical batteries, a battery case with a high height-to-diameter ratio can be easily and precisely formed, for instance, through deep drawing process. Therefore, it is possible to easily form with high precision a battery case 1 with a thickness of 0.05 mm or more and 0.2 mm or less, resulting in the stable manufacture of cylindrical batteries with high sealing performance.

[0035] In other preferred specific configurations of the above-described cylindrical battery, the stainless steel forming the battery case 1 is stainless steel with a copper content of 1.0% by mass or more and 6.0% by mass or less. More preferably, the copper content is 1.5% by mass or more and 5.0% by mass or less. Thus, copper-containing stainless steel has high tensile breaking strength, elongation, and acid corrosion resistance, and as shown in Table 2, the contact resistance on the surface of stainless steel is small. Furthermore, a protective layer that enhances acid corrosion resistance is usually formed on the surface of stainless steel. In the case of stainless steel that does not contain copper, this protective layer becomes the cause of increased contact resistance. On the other hand, by including copper in stainless steel, the resistance of the protective layer is reduced, which in turn reduces the contact resistance.

[0036] Table 2

[0037]

	Contact resistance (load 40g) (mΩ)
Austenitic stainless steel (including copper)	40
Austenitic stainless steel (no copper included)	8000

[0038] According to copper-containing stainless steel, electrical contact with a device can be easily obtained without forming a new surface layer or terminal. Furthermore, by increasing the contact area with the electrodes inside the battery, the internal resistance of the battery is reduced even without joining the battery case and electrodes by welding or other means, resulting in good load characteristics.

[0039] As mentioned above, stainless steel has high strength. Therefore, a large force is required when processing stainless steel into a desired shape. Therefore, the battery case is preferably a bottomed cylindrical battery case formed by applying deep drawing to a thin stainless steel sheet. By means of deep drawing, battery cases that are thin and uniform in thickness, and have minimal deviations in shape and thickness can be produced. Furthermore, if deep drawing is applied, the material loss is small. Therefore, a balance between improving battery characteristics and enhancing long-term reliability and safety can be achieved in cylindrical batteries.

[0040] Furthermore, methods for processing stainless steel into a bottomed cylindrical shape include stamping processing method, DI (Drawing & Ironing) processing method, etc. However, these processing methods require the application of large forces evenly and continuously during the forming process, which is difficult to control, thus the shape and thickness of battery cases are prone to deviation. Especially when reducing the thickness of the battery case, holes are sometimes made or rupture occurs. In addition, methods for processing stainless steel into a bottomed cylindrical shape include a method of cutting cylindrical materials. However, in this method, although the shape of battery cases is not easily deviated, the material loss is large and the efficiency is low.

[0041] Next, the embodiments of the present invention will be described in detail with reference to the accompanying drawings. Furthermore, various components of the present invention are not limited to the embodiments, and various modifications can be made within the technical scope described in the claims.

[0042] FIG. 1 is a longitudinal cross-sectional view schematically illustrating a cylindrical battery according to an embodiment of the present invention. As shown in FIG. 1, the cylindrical battery has a bottomed cylindrical battery case 1, an electrode assembly 5 housed in the battery case 1 together with an electrolyte, a sealing member 8 embedded in the opening of the battery case 1, and a gasket 9 sandwiched between the sealing member 8 and the battery case 1.

[0043] Battery Case

[0044] The battery case 1 is formed by applying deep drawing processing to stainless steel with uniform thickness. The outer diameter of the battery case 1 is preferably 10 mm or less, more preferably 6 mm or less. The thickness of the battery case 1 is 0.05 mm or more and 0.2 mm or less. Furthermore, the ratio of the thickness of the sidewall (side thickness) to the thickness of the bottom (bottom thickness) of the battery case 1 is 0.20 or more and 1.20 or less,

preferably 0.33 or more and 1.05 or less.

[0045] The stainless steel forming the battery case 1 is preferably austenitic stainless steel with a low carbon content. In addition, the stainless steel forming the battery case 1 is preferably stainless steel with a low carbon content of 0.08% by mass or less. Furthermore, the carbon content in the stainless steel is more preferably 0.05% by mass or less, and particularly preferably 0.03% by mass or less.

[0046] Preferably, the stainless steel forming the battery case 1 contains copper. In such a battery case 1, the copper content is preferably 1.0% by mass or more and 6.0% by mass or less, more preferably 1.5% by mass or more and 5.0% by mass or less.

[0047] Sealing member and gasket

[0048] The sealing member 8 and the gasket 9 are components used to seal the opening of the battery case 1. Specifically, the sealing member 8 and the gasket 9 are inserted into the opening of the battery case 1, such that the gasket 9 is sandwiched between the sealing member 8 and the battery case 1. Then, drawing processing is applied to the open end of the battery case 1, and its open end is crimped onto the sealing member 8. Therefore, the gasket 9 is sealed tightly to the side of the sealing member 8 and the inner surface of the battery case 1 in a compressed state. In this way, the opening of the battery case 1 is sealed. Furthermore, a perforated circular plate 11 made of an electrically insulating material is embedded in the protrusion exposed to the outside of the battery case 1 in the sealing member 8. The circular plate 11 is used to prevent electrical short circuits between the sealing member 8 and the battery case 1.

[0049] Regarding the gasket 9, its material can use polypropylene (PP), polyethylene (PE), polyphenylene sulfide (PPS), perfluoroalkyl ethylene-hexafluoropropylene copolymer (PFA), cross-linked rubber, etc. In particular, PFA is preferred because of its low moisture permeability, which can suppress the intrusion of moisture into the battery, thus preventing the degradation of lithium-ion batteries.

[0050] Electrode assembly

[0051] The electrode assembly 5 has a negative electrode plate 2, a positive electrode plate 3, and a separator 4. In the electrode assembly 5, the negative electrode plate 2 and the positive electrode plate 3 are wound together while overlapping each other with a separator 4 sandwiched there between. In order to prevent winding slippage in the electrode assembly 5, the winding end portion of at least one of the negative electrode plate 2 and the positive electrode plate 3 is fixed to the outer peripheral surface of the electrode assembly 5 with fixing tape. Then, the electrode assembly 5 and a non-aqueous electrolyte (not shown) are accommodated together in the battery case 1. With such an electrode assembly 5 , the reaction area is increased, which can achieve strong load characteristics.

[0052] The negative electrode plate 2 and the positive electrode plate 3 are, as respectively described later, composed of a current collector, i.e., a core material, and a mixture layer (containing an active material) formed on the surface of the core material. Moreover, in order to increase battery capacity, the mixture layer is formed on the surface of the core material in a compressed state. Therefore, in the electrode assembly 5, if the radius of the winding heads of the negative electrode plate 2 and the positive electrode plate 3 is too small, there is a concern that the mixture layer may peel off from the core material, thus causing an electrical short circuit (internal short circuit) in the battery case 1. On the other hand, if the radius of a winding head is too large, the amount of the active material accommodated in the battery case 1 decreases, and the battery capacity decreases. Therefore, it is necessary to start winding the negative electrode plate 2 and the positive electrode plate 3 with an appropriate radius. For example, when a core is used to wind the negative electrode plate 2 and the positive electrode plate 3, the diameter R of the core is preferably 0.6 mm or more and less than 3.0 mm, more preferably 0.8 mm or more and less than 1.5 mm. A space with no active material exists near the central axis of the electrode assembly 5, and this space is preferably 3.0 mm or less in diameter, and more preferably less than 1.5 mm in diameter.

[0053] A negative electrode lead 6 is electrically connected to the negative electrode plate 2 (specifically, the negative electrode core material described later), and the end of the negative electrode lead 6 is joined to the inner surface of the side wall of the battery case 1 by spot welding or the like. Furthermore, if the stainless steel forming the battery case 1 contains copper, it is also possible to make the negative electrode lead 6 only contact the inner surface of the side wall of the battery case 1. Thus, the negative electrode plate 2 is electrically connected to the battery case 1, and the battery case 1 functions as the negative electrode terminal. Regarding the negative electrode lead 6, its material can use, for example, nickel, iron, stainless steel, copper, etc. The negative electrode lead 6 has the characteristic of bending with small pressure, and its shape is not particularly limited, which may be, for example, a rectangular shape with a welding allowance to the negative electrode core material and a welding allowance to the battery case 1, or an ellipse or polygon inscribed in the rectangular shape. In addition, the thickness of the negative electrode lead 6 is preferably 10 μm or more and 120 μm or less, more preferably 20 μm or more and 80 μm or less.

[0054] A positive electrode lead 7 is electrically connected to the positive electrode plate 3 (specifically, the positive electrode core material described later), and the end of the positive electrode lead 7 is joined to the sealing member 8 by spot welding or the like. Thus, the positive electrode plate 3 is electrically connected to the sealing member 8, and the sealing member 8 functions as the positive electrode terminal. Regarding the positive electrode lead 7, its material can use, for example, aluminum. The positive electrode lead 7 has the characteristic of bending with small pressure, and its shape is not particularly limited, which may be, for example, a rectangular shape. In addition, the thickness of the positive electrode lead 7 is preferably 40 μm or more and 150 μm or less, and even more preferably 50 μm or more and 100 μm or less.

[0055] Furthermore, an annular intermediate member 10 made of an electrical insulating material is disposed between the electrode assembly 5 and the sealing member 8, and the positive electrode lead 7 passes through the inner side of the intermediate member 10 and is connected to the positive electrode plate 3 and the sealing member 8. Thus, the intermediate member 10 prevents electrical short circuits between the negative and positive electrodes.

[0056] <Negative electrode plate>

[0057] The negative electrode plate 2 is composed of a negative electrode current collector, i.e., a negative electrode core material, and a negative electrode mixture layer formed on the surface of the negative electrode core material. The negative electrode plate 2 is formed, for example, by depositing a negative electrode active material in a thin film on the surface of the negative electrode core material. The negative electrode core material is a metal foil. For example, a long conductive substrate with a porous or non-porous structure can be used for the negative electrode core material. Materials used as negative electrode core materials can include, for example, stainless steel, nickel, or copper. The thickness of the negative electrode core material is not particularly limited, but it is preferably 1 μm or more and 500 μm or less, more preferably 5 μm or more and 20 μm or less. According to the negative electrode core material with such a thickness, the strength of the negative electrode plate 2 can be maintained, while the negative electrode plate 2 can be made lighter.

[0058] The negative electrode mixture layer contains a negative electrode active material. Therefore, the negative electrode active material will be described in detail below. Furthermore, it is preferable that the negative electrode mixture layer contains a binder and other materials in addition to the negative electrode active material.

[0059] (Negative electrode active material)

[0060] A lithium-ion intercalation/deintercalation material can be used as the negative electrode active material. Examples of such negative electrode active materials can include metals, metal fibers, carbon materials, oxides, nitrides, silicon compounds, tin compounds, or various alloy materials. Specific examples of carbon materials can include various types of natural graphite, coke, incompletely graphitized carbon, carbon fibers, spherical carbon, various types of artificial graphite, or amorphous carbon.

[0061] Here, the capacity density of elemental substances, such as silicon (Si)or tin (Sn), or silicon compounds and tin compounds is high. Therefore, silicon, tin, silicon compounds, or tin compounds are preferably used as negative electrode active materials. Specific examples of silicon compounds can include SiO_X (wherein $0.05 < x < 1.95$) or silicon alloys, silicon solid solutions, or the like formed by using at least one or more elements selected from B, Mg, Ni, Ti, Mo, Co, Ca, Cr, Cu, Fe, Mn, Nb, Ta, V, W, Zn, C, N, Sn, and other elements to substitute part of Si. In addition, specific examples of tin compounds can include Ni_2Sn_4, Mg_2Sn, SnO_x (wherein $0<x<2$), SnO_2, or $SnSiO_3$. Furthermore, the negative electrode active material can separately use one of the negative electrode active materials listed above, or can use two or more in combination.

[0062] <Positive electrode plate>

[0063] The positive electrode plate 3 is composed of a positive electrode current collector, i.e., a positive electrode core material, and a positive electrode mixture layer formed on the surface of the positive electrode core material. The positive electrode core material is a metal foil. For example, a long conductive substrate with a porous or non-porous structure can be used for the positive electrode core material. Materials used as positive electrode core materials can include, for example, aluminum. The thickness of the positive electrode core material is not particularly limited, but it is preferably 8 μm or more and 25 μm or less, more preferably 10 μm or more and 15 μm or less. According to the positive electrode core material with such a thickness, it is possible to form a smoothly curved electrode assembly 5 with a small diameter.

[0064] The positive electrode mixture layer contains a positive electrode active material, a binder, and a conductive agent. Therefore, the positive electrode active material, binder, and conductive agent are described in detail below.

[0065] (Positive electrode active material)

[0066] Lithium-containing composite oxides are preferably used as the positive electrode active material, and

examples can include $LiCoO_2$, $LiNiO_2$, $LiMnO_2$, $LiCo_xNi_{1x}O_2$, $LiCo_xM_{1x}O_2$, $LiNixM_{1x}O_2$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiMn_2O_4$, $LiMnMO_4$, $LiMePO_4$, $LiMePO_4F$ (wherein M is at least one of Na, Mg, Sc, Y, Mn, Fe, Co, Ni, Cu, Zn, Al, Cr, Pb, Sb, and B. x is $0<x<1$. Me is at least one metallic element selected from Fe, Mn, Co, and Ni), and compounds formed by substituting a portion of the elements in these lithium-containing compounds with a different element. In addition, positive electrode active materials that have undergone surface treatment with metal oxides, lithium oxides, or conductive agents can also be used as the positive electrode active material. Examples of surface treatment can include hydrophobic treatment.

[0067] The average particle size of the positive electrode active material is preferably 5 μm or more and 20 μm or less. If the average particle size of the positive electrode active material is less than 5 μm, the surface area of the active material particles is increased significantly. Therefore, the amount of a binder used to obtain the bonding strength that can be processed on the positive electrode plate 3 is increased to an extreme degree. Therefore, the mass of the active material in each electrode plate decreases, resulting in a reduction in capacity. On the other hand, if exceeding 20 μm, coating streaks can easily occur when coating the positive electrode core material with the positive electrode mixture slurry.

[0068] (Binder)

[0069] The binder can use, for example, PVDF, polytetrafluoroethylene, polyethylene, polypropylene, aromatic polyamide resin, polyamide, polyimide, polyamideimide, polyacrylonitrile, polyacrylic acid, polymethylacrylate, polyethylacrylate, polyhexylacrylate, polymethacrylic acid, poly(methyl methacrylate), poly(ethyl methacrylate), poly(hexyl methacrylate), polyvinyl acetate, polyvinylpyrrolidone, polyether, polyethersulfone, polyhexafluoropropylene, styrene-butadiene rubber, or carboxymethyl cellulose, etc. In addition, copolymers made by copolymerization of two or more materials selected from tetrafluoroethylene, hexafluoroethylene, hexafluoropropylene, perfluoroalkyl vinyl ether, vinylidene fluoride, trifluorochloroethylene, ethylene, propylene, pentafluoropropylene, fluoromethyl vinyl ether, acrylic acid, and hexadiene, or mixtures made by mixing two or more selected materials can be listed.

[0070] Among the binders listed above, particularly PVDF and its derivatives are chemically stable in non-aqueous electrolyte secondary batteries, and can fully bond the positive electrode mixture layer and the positive electrode core material, and at the same time fully bond the positive electrode active material, the binder, and the conductive agent forming the positive electrode mixture layer. Therefore, good charge and discharge cycle characteristics and discharge performance can be achieved. Therefore, PVDF or its derivatives are preferably used as the binder in this embodiment. In addition, PVDF and its derivatives are inexpensive, and thus become a preferred choice in terms of cost. Furthermore, to fabricate a positive electrode using PVDF as a binder, examples of using PVDF dissolved in N-methylpyrrolidone or using powdered PVDF dissolved in a positive electrode mixture slurry can be listed.

[0071] (Conductive agent)

[0072] The conductive agent can use, for example, graphite such as natural graphite or artificial graphite, carbon black such as acetylene black (AB), Ketjen black, channel black, furnace black, lamp black, or thermal black, conductive fibers such as carbon fiber or metal fibers, fluorinated carbon, metal powders such as aluminum, conductive whiskers such as zinc oxide or potassium titanate, conductive metal oxides such as titanium oxide, or organic conductive materials such as phenylene derivatives.

[0073] <Separator>

[0074] The separator 4 can use a microporous membrane, woven fabric, or nonwoven fabric with high ion permeability and specified mechanical strength and electrical insulation. In particular, polyolefins such as polypropylene and polyethylene are preferred materials for the separator 4. Polyolefins have excellent durability and a shut-off function, thus improving the safety of lithium-ion secondary batteries.

[0075] The thickness of the separator 4 is generally 10 μm or more and 300 μm or less, preferably 10 μm or more and 40 μm or less. In addition, the thickness of the separator 4 is more preferably 15 μm or more and 30 μm or less, and even more preferably 10 μm or more and 25 μm or less. Furthermore, when using a microporous membrane as the separator 4, the microporous membrane can be a single-layer membrane made of one material, or a composite membrane or multilayer membrane made of one or more materials. Furthermore, the porosity of the separator 4 is preferably 30% or

more and 70% or less, more preferably 35% or more and 60% or less. The so-called porosity here refers to the ratio of the total volume of the pores to the total volume of the separator 4.

[0076] <Non-aqueous electrolyte>

[0077] A liquid, gel, or solid non-aqueous electrolyte can be used as the non-aqueous electrolyte accommodated in the battery case 1. The liquid non-aqueous electrolyte contains an electrolyte salt (e.g., lithium salt) and a non-aqueous solvent that dissolves the electrolyte salt. The gel non-aqueous electrolyte contains a non-aqueous electrolyte and a polymeric material that retains the non-aqueous electrolyte. Examples of such polymer materials can include polyvinylidene fluoride, polyacrylonitrile, polyoxyethylene, polyvinyl chloride, polyacrylate, or polyvinylidene fluoride hexafluoropropylene. The solid non-aqueous electrolyte contains polymer solid electrolytes.

[0078] Non-aqueous solvents and electrolyte salts contained in the liquid non-aqueous electrolyte are described in detail below.

[0079] (Non-aqueous solvent)

[0080] Known non-aqueous solvents can be used as a non-aqueous solvent to dissolve electrolyte salts. There are no particular limitations on the type of the non-aqueous solvents. For example, cyclic carbonates, chain carbonates, or cyclic carboxylic acid esters can be used. Specific examples of cyclic carbonates herein can include propylene carbonate (PC) and ethylene carbonate (EC). In addition, specific examples of chain carbonates can include diethyl carbonate (DEC), ethylmethyl carbonate (EMC), or dimethyl carbonate (DMC). In addition, specific examples of cyclic carboxylic acid esters can include γ-butyrolactone (GBL) or γ-valerolactone (GVL). The non-aqueous solvent can separately use only one of the non-aqueous solvents listed above, or can use two or more in combination.

[0081] (Electrolyte salt)

[0082] Examples of electrolytes that dissolve in the non-aqueous solvent can include $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiAlCl_4$, $LiSbF_6$, LiSCN, $LiCF_3SO_3$, $LiCF_3CO_2$, $LiAsF_6$, $LiB_{10}Cl_{10}$, lithium salts of lower aliphatic carboxylic acids, LiCl, LiBr, Lil, lithium chloroborane, borate salts, or imide salts. Specific examples of borate salts here can include lithium bis[1,2-benzenediol(2-)-O,O']borate, lithium bis[2,3-naphthodiol(2-)-O,O']borate, lithium bis[2,2'-biphenyldiol(2-)-O,O']borate, or lithium bis(5-fluoro-2-hydroxy-benzenesulfonic acid-O,O')borate. In addition, specific examples of imide salts can include lithium bis(trifluoromethanesulfonyl)imide ($(CF_3S_2NLi$), lithium trifluoromethanesulfonyl nonafluorobutanesulfonyl imide ($LiN(CF_3SO_2)(C_4F_9SO_2)$), or lithium bis(pentafluoroethanesulfonyl)imide $(C_2F_5SO_2)_2NLi$). The electrolyte salt can separately use only one of the electrolytes listed above, or can use two or more in combination

[0083] Relative to the non-aqueous solvent, the solubility of the electrolyte salt is preferably 0.5 mol/m^3 or more and 2 mol/m^3 or less.

[0084] The liquid non-aqueous electrolyte may further contain, in addition to electrolyte salts and non-aqueous solvents, additives such as those that form, by decomposition, a film with high lithium-ion conductivity on the negative electrode, thereby improving the charge-discharge efficiency of the battery. Examples of additives with such functions can include vinylene carbonate (VC), 4-methyl vinylene carbonate, 4,5-dimethyl vinylene carbonate, 4-ethyl vinylene carbonate, 4,5-diethyl vinylene carbonate, 4-propyl vinylene carbonate, 4,5-dipropyl vinylene carbonate, 4-phenylvinylene carbonate, 4,5-diphenyl vinylene carbonate, vinyl ethylene carbonate (VEC), or divinyl ethylene carbonate. The additive can separately use only one of the additives listed above, or can use two or more in combination. In particular, it is preferred to select at least one of vinylene carbonate, vinyl ethylene carbonate, and divinyl ethylene carbonate from the additives listed above. Furthermore, the additive may also be an additive made by replacing some of the hydrogen atoms of the additives listed above with fluorine atoms.

[0085] In addition, the liquid non-aqueous electrolyte may further contain, in addition to electrolyte salts and non-aqueous solvents, well-known benzene derivatives that decompose on electrodes during overcharging to form a film to deactivate the battery. The benzene derivative with such function is preferably a substance that contains a phenyl group and a cyclic compound group adjacent to the phenyl group. Specific examples of the benzene derivatives here can include cyclohexylbenzene, biphenyl, or diphenyl ether. Furthermore, specific examples of the cyclic compound group contained in the benzene derivatives can include phenyl groups, cyclic ether groups, cyclic ester groups, cycloalkyl groups, or phenoxy groups. The benzene derivative can separately use only one of the benzene derivatives listed above, or can use two or more in combination. However, the content of the benzene derivatives relative to the non-aqueous solvent is preferably 10 vol% or less of the total non-aqueous solvent.

[0086] Embodiments

[0087] The embodiments of the present invention will be specifically described below.

[0088] <Embodiment 1>

[0089] (Fabrication of the positive electrode plate)

[0090] $LiNi_{0.82}Co_{0.15}Al_{0.03}O_2$ with an average particle size of 10 μm is prepared as the positive electrode active material. 4.7 vol% PVDF relative to 100 vol% of the positive electrode active material is prepared as the binder. 4.5 vol% acetylene black relative to 100 vol% of the positive electrode active material is prepared as the conductive agent. In addition, N-methylpyrrolidone (NMP) is prepared as the solvent, and a solution is prepared by dissolving the prepared binder in the solvent. Then, the prepared positive electrode active material, conductive agent, and solution are mixed to prepare a positive electrode mixture slurry.

[0091] Next, an aluminum foil with a thickness of 15 μm is prepared as the positive electrode core material, and the positive electrode mixture slurry is coated on both sides of the aluminum foil and then dried. Then, the positive electrode core material coated with the positive electrode mixture slurry on both sides and dried is rolled to produce a plate-shaped positive electrode plate with a thickness of 0.12 mm. Then, by cutting the positive electrode plate into pieces with a width of 30.5 mm and a length of 19.0 mm, to fabricate a positive electrode plate 3 with a thickness of 0.12 mm, a width of 30.5 mm, and a length of 19.0 mm.

[0092] (Fabrication of the negative electrode plate)

[0093] Flake graphite with an average particle size of 20 μm is prepared as the negative electrode active material. 4.7 vol% SBR relative to 100 vol% of the negative electrode active material is prepared as the binder. 4.5 vol% acetylene black relative to 100 vol% of the negative electrode active material is prepared as the conductive agent. In addition, pure water is prepared as the solvent, and a solution is prepared by dissolving the prepared binder in the solvent. Then, the prepared negative electrode active material, conductive agent, and solution are mixed to prepare a negative electrode mixture slurry.

[0094] Next, a copper foil with a thickness of 8 μm is prepared as the negative electrode core material, and the negative electrode mixture slurry is coated on both sides of the copper foil and then dried. Then, the negative electrode core material coated with the negative electrode mixture slurry on both sides and dried is rolled to produce a plate-shaped negative electrode plate with a thickness of 0.15 mm. Then, by cutting the negative electrode plate into pieces with a width of 29.5 mm and a length of 37.0 mm, to fabricate a negative electrode plate 2 with a thickness of 0.15 mm, a width of 29.5 mm, and a length of 37.0 mm.

[0095] (Preparation of the non-aqueous electrolyte)

[0096] A mixed solvent is prepared, as the non-aqueous solvent, by mixing ethylene carbonate and dimethyl carbonate at a volume ratio of 1:3. $LiPF_6$is prepared as the electrolyte salt. Then, 5 wt% of vinylene carbonate is added to the prepared non-aqueous solvent as an additive to improve the charge-discharge efficiency of the battery, while the electrolyte salt, $LiPF_6$, is dissolved in such a manner that the molar concentration relative to the non-aqueous solvent reaches 1.4 mol/m^3, thereby preparing the non-aqueous electrolyte.

[0097] (Fabrication of the cylindrical battery)

[0098] First, an aluminum positive electrode lead 7 is installed on the positive electrode core material of the prepared positive electrode plate 3. In addition, a nickel negative electrode lead 6 is installed on the negative electrode core

material of the prepared negative electrode plate 2. Then, the negative electrode plate 2 and the positive electrode plate 3 are wound together with a polyethylene separator 4 (16 μm thick) sandwiched therebetween, thereby fabricating the electrode assembly 5. In addition, a battery case 1 with a thickness of 0.1 mm and an outer diameter of 3.5 mm is made of SUS316L (copper-free, austenitic stainless steel with a carbon content of 0.03% by mass or less).

[0099] Next, an intermediate member 10 is disposed at the upper end of the electrode assembly 5. Then, the negative electrode lead 6 is soldered to the battery case 1, and the positive electrode lead 7 is soldered to the sealing member 8. Then, the electrode assembly 5 is accommodated inside the battery case 1. Then, the non-aqueous electrolyte is injected into the battery case 1 using a depressurization method. Then, the sealing member 8 and the gasket 9 made of PFA are inserted into the opening of the battery case 1 by clamping the gasket 9 between the battery case 1 and the sealing member 8. Then, a cylindrical battery with a diameter of 3.5 mm and a height of 35 mm is made by crimping the open end of the battery case 1 to the sealing member 8. The cylindrical battery is used as Embodiment 1.

[0100] <Embodiment 2>

[0101] Austenitic stainless steel with a copper content of 3.80% by mass is used as the stainless steel forming the battery case 1. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 2.

[0102] <Embodiment 3>

[0103] SUS316L is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 (outer diameter 3.5 mm) is specified as 0.15 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 3.

[0104] <Embodiment 4>

[0105] SUS316L is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 (outer diameter 3.5 mm) is specified as 0.20 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 4.

[0106] <Comparative Example 1>

[0107] SUS316L is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 (outer diameter 3.5 mm) is specified as 0.25 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 1.

[0108] <Comparative Example 2>

[0109] iron (Fe) is used as the material forming the battery case 1 (thickness 0.1 mm, outer diameter 3.5 mm). Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 2.

[0110] <Comparative Example 3>

[0111] iron (Fe) is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 (outer diameter 3.5 mm) is specified as 0.2 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 3.

[0112] Five cylindrical batteries are fabricated for each of Embodiments 1 to 4 and Comparative Examples 1 to 3. The average energy density, leakage rate, and internal short circuit rate of these cylindrical batteries are calculated. The results are shown in Table 3. Furthermore, the internal short circuit rate is the short circuit rate when the top of a 1.0 mm diameter rod is in contact with the side of a cylindrical battery and a stress of 1.5 kgf is applied under this condition.

[0113] Table 3

[0114]

	Battery case					Characteristic		
	Material	Cu (mass%)	C (mass%)	Thickness (mm)	Outer diameter (mm)	Energy density (Wh/L)	Leakage rate (%)	Internal short circuit rate (%)
Embodiment 1	SUS316L	0	<0.03	0.10	3.5	385	0	0
Embodiment 2	SUS	3.80	<0.03	0.10	3.5	385	0	0
Embodiment 3	SUS316L	0	<0.03	0.15	3.5	362	0	0
Embodiment 4	SUS316L	0	<0.03	0.20	3.5	340	0	0
Comparative Example 1	SUS316L	0	<0.03	0.25	3.5	318	80	0
Comparative Example 2	Fe	-	-	0.10	3.5	385	20	80
Comparative Example 3	Fe	-	-	0.20	3.5	339	80	0

[0115] Furthermore, long-term reliability tests are conducted on the cylindrical batteries of Embodiments 1 to 4 and the cylindrical batteries of Comparative Examples 1 to 3. Specifically, after storing these cylindrical batteries in an atmosphere of 85℃-90% RH for 20 days, the expansion rate of the battery case 1 and the capacity retention rate of the batteries are calculated. Furthermore, as the expansion rate of battery case 1, the proportion of the increase in the outer diameter of the battery case1 is calculated. In addition, the battery capacity retention rate is calculated based on the initial battery capacity. The results are shown in Table 4.

[0116] Table 4

[0117]

	Battery case					Characteristic	
	Material	Cu (mass%)	C (mass%)	Thickness (mm)	Outer diameter (mm)	Expansion rate (%)	Capacity retention rate (%)
Embodiment 1	SUS316L	0	<0.03	0.10	3.5	0	75
Embodiment 2	SUS	3.80	<0.03	0.10	3.5	0	75
Embodiment 3	SUS316L	0	<0.03	0.15	3.5	0	75
Embodiment 4	SUS316L	0	<0.03	0.20	3.5	0	50
Comparative Example 1	SUS316L	0	<0.03	0.25	3.5	0	8
Comparative Example 2	Fe	-	-	0.10	3.5	18	10
Comparative Example 3	Fe	-	-	0.20	3.5	4	30

[0118] By comparing Embodiments 1 to 4 and Comparative Example 1 in Table 3, it can be seen that in Comparative Example 1, where the thickness of the battery case 1 is large, the energy density is small, and the smaller the thickness of the battery case 1, the greater the energy density is. This is because as the thickness of the battery case 1 decreases, the internal volume of the battery case 1 (which accommodates the power generation elements) increases.

[0119] By comparing Embodiment 1and Comparative Example 2 in Table 3 and Table 4, it can be seen that although the thickness of the battery case 1 is the same at 0.10 mm, there are also the following differences. In other words, in Comparative Example 2, where the battery casing 1 is made of iron, it is easy for an internal short circuit to occur and it is easy for the battery case 1 to expand, while in Embodiment 1, where the battery case 1 is made of SUS316L, no internal short circuit occurs and the battery case 1 does not expand. This is believed that the strength of SUS316L is higher than that of iron (Fe), and thus the strength of the battery case 1 made of SUS316L is increased. Furthermore, it is believed that the expansion of the battery case 1 in Comparative Example 2 is due to the generation of hydrogen gas caused by the moisture that has penetrated into the battery case.

[0120] By comparing Embodiments 1 to 4 and Comparative Example 1 in Table 3, it can be seen that: although the material of the battery case 1 is the same SUS316L, and the outer diameter is the same 3.5 mm, leakage tends to occur in Comparative Example 1, where the thickness of the battery case 1 is 0.25 mm, while no leakage occurs in Embodiments 1 to 4, where the thickness is 0.20 mm or less. In other words, it can be seen that high sealing performance can be achieved in Embodiments 1 to 4. This is because, in Embodiments 1 to 4, no abnormal shapes such as decreased roundness or wrinkles are produced, and thus no path for leakage is formed.

[0121] By comparing Embodiments 1 to 4 and Comparative Example 1 in Table 4, it can be seen that: although the material of the battery case 1 is the same SUS316L, the capacity retention rate is very low in Comparative Example 1, where the thickness of the battery case 1 is 0.25 mm, while the capacity retention rate is as high as 50% or more in Embodiments 1 to 4, where the thickness is 0.20 mm or less. This is because, in Embodiments 1 to 4, no abnormal shapes such as decreased roundness or wrinkles are produced, thereby suppressing the evaporation of the electrolyte and the intrusion of moisture from the outside.

[0122] On the other hand, in Comparative Examples 2 and 3 where the battery case 1 is made of iron (Fe), the capacity retention rate is very low. This is because the battery case 1 has low strength, and thus the battery case 1 is prone to expansion along with the generation of hydrogen gas, which deteriorates the sealing performance (refer to the leakage rate in Table 3) and degrades the battery characteristics. Furthermore, the battery case is corroded by the production of strong acid, i.e., hydrofluoric acid. This corrosion leads to the intrusion of moisture, which accelerates the corrosion process. Therefore, it is believed that high battery capacity cannot be maintained.

[0123] By comparing Embodiment 1and Embodiment 2 in Table 3 and Table 4, it can be seen that even if the stainless steel forming the battery case 1 contains copper, the copper does not have an adverse effect on the battery characteristics and long-term reliability. Furthermore, the copper contained in the stainless steel reduces the contact resistance of the stainless steel surface.

[0124] These results show that stainless steel is the preferred material for the battery case 1 in order to improve the strength of the battery case 1. Therefore, it is not easy for internal short circuits to occur. In addition, by further specifying the thickness of the battery case 1 to be 0.2 mm or less, the energy density is increased, while the sealing performance and the capacity retention rate are improved. As a result, the improvement of battery characteristics and the enhancement of long-term reliability and safety can be achieved at the same time.

[0125] <Embodiment 5>

[0126] SUS316L is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 6 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 5.

[0127] <Embodiment 6>

[0128] SUS316L is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 10 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 6.

[0129] <Comparative Example 4>

[0130] SUS316L is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 15 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 4.

[0131] <Comparative Example 5>

[0132] SUS316L is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 is specified as 0.2 mm, and the outer diameter is specified as 15 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 5.

[0133] <Comparative Example 6>

[0134] Iron (Fe) is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 6 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 6.

[0135] <Comparative Example 7>

[0136] Iron (Fe) is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 10 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 7.

[0137] <Comparative Example 8>

[0138] Iron (Fe) is used as the material forming the battery case 1. In addition, the outer diameter of the battery case 1 (thickness 0.1 mm) is specified as 15 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 8.

[0139] <Comparative Example 9>

[0140] Iron (Fe) is used as the material forming the battery case 1. In addition, the thickness of the battery case 1 is specified as 0.2 mm, and the outer diameter is specified as 15 mm. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Comparative Example 9.

[0141] Five cylindrical batteries are fabricated for each of Embodiments 1, 5, and 6 and Comparative Examples 2 and 4 to 9. The leakage rate, internal short circuit rate, and battery capacity retention rate of these cylindrical batteries are calculated. The results are shown in Table 5. Furthermore, the internal short circuit rate is the short circuit rate when the top of a 1.0 mm diameter rod is in contact with the side of a cylindrical battery and a stress of 1.5 kgf is applied under this condition. The capacity retention rate of a cylindrical battery is determined after it has been stored in an atmosphere of 85℃ -90% RH for 20 days. In addition, the battery capacity retention rate is calculated based on the initial battery capacity.

[0142] Table 5

[0143]

	Battery case					Characteristic		
	Material	Cu (mass%)	C (mass%)	Thickness (mm)	Outer diameter (mm)	Leakage rate (%)	Internal short circuit rate (%)	Capacity retention rate (%)
Embodiment 1	SUS316L	0	<0.03	0.10	3.5	0	0	75
Embodiment 5	SUS316L	0	<0.03	0.10	6	0	0	75
Embodiment 6	SUS316L	0	<0.03	0.10	10	20	0	75
Comparative Example 4	SUS316L	0	<0.03	0.10	15	60	20	60
Comparative Example 5	SUS316L	0	<0.03	0.20	15	0	0	75
Comparative Example 2	Fe	-	-	0.10	3.5	20	80	10
Comparative Example 6	Fe	-	-	0.10	6	20	80	10
Comparative Example 7	Fe	-	-	0.10	10	40	80	5
Comparative Example 8	Fe	-	-	0.10	15	40	80	5
Comparative Example 9	Fe	-	-	0.20	15	0	0	75

[0144] In Table 5, by comparing Embodiments 1, 5, and 6 with Comparative Example 4, it can be seen that although the material of the battery case 1 is the same SUS316L and the thickness is the same 0.10 mm, there are still the following differences. In other words, in Comparative Example 4, where the outer diameter of the battery case 1 is 15 mm, it is easy for an internal short circuit to occur, while in Embodiments 1, 5, and 6, where the outer diameter thereof is 10 mm or less, no internal short circuit occurs. This is based on the following reasons. In other words, even when the battery case 1 is made of high-strength SUS316L, the curvature of the side of the battery case 1 is reduced when the outer diameter of the battery case 1 is large. As a result, the battery case 1 is easily deformed relative to external forces. In contrast, if the outer diameter of the battery case 1 decreases, the curvature of the side of the battery case 1 increases, resulting in that the battery case 1 is difficult to deform relative to external forces.

[0145] On the other hand, in Comparative Examples 2 and 6 to 8, where the battery case 1 is made of iron (Fe), the internal short circuit rate is very high. This is because the battery case 1 has low strength, so the battery case 1 is easy to deform relative to external forces. Furthermore, in Comparative Examples 2 and 6 to 8, leakage is prone to occur due to the low strength of the battery case 1. In addition, in Comparative Examples 2 and 6 to 8, the capacity retention rate is very low. This is because the battery case 1 has low strength, and thus the battery case 1 is prone to expansion along with the generation of hydrogen gas, which deteriorates the sealing performance and degrades the battery characteristics. Furthermore, the battery case is corroded by the production of strong acid, i.e., hydrofluoric acid. This corrosion leads to the intrusion of moisture, which accelerates the corrosion process. Therefore, it is believed that high battery capacity cannot be maintained.

[0146] These results show that stainless steel is the preferred material for the battery case 1 in order to improve the strength of the battery case 1. Therefore, it is not easy for internal short circuits to occur. In addition, by further specifying the outer diameter of the battery case 1 to be 10 mm or less, the sealing performance and the capacity retention rate are

improved. As a result, the improvement of battery characteristics and the enhancement of long-term reliability and safety can be achieved at the same time. Furthermore, the results from Comparative Examples 5 and 9 show that when the outer diameter of the battery case 1 is large (greater than 10 mm), regardless of the material of the battery case 1, the long-term reliability and safety can be enhanced by increasing the thickness of the battery case 1. However, when the outer diameter of the battery case 1 is small (10 mm or less), if the thickness of the battery case 1 is increased, the internal volume decreases significantly. In addition, sealing by the drawing process becomes difficult, and the sealing performance deteriorates.

[0147] <Embodiment 7>

[0148] The material used to form the battery case 1 is SUS316 (austenitic stainless steel with a carbon content of 0.08% by mass or less). Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 7.

[0149] Five cylindrical batteries are fabricated for each of Embodiments 1 and 7, and the leakage rate and capacity retention rate of these cylindrical batteries are calculated. The results are shown in Table 6. Furthermore, the capacity retention rate of a cylindrical battery is determined after it has been stored in an atmosphere of 85℃ -90% RH for 20 days. In addition, the battery capacity retention rate is calculated based on the initial battery capacity.

[0150] Table 6

[0151]

	Battery case					Characteristic	
	Material	Cu (mass%)	C (mass%)	Thickness (mm)	Outer diameter (mm)	Leakage rate (%)	Capacity retention rate (%)
Embodiment 1	SUS316L	0	<0.03	0.10	3.5	0	75
Embodiment 7	SUS316	0	<0.08	0.10	3.5	2.0	55

[0152] From the results shown in Table 6, it can be seen that in Embodiments 1 and 7, where the carbon content is 0.08% by mass or less, leakage is not easy to occur, and the capacity retention rate is also high. Furthermore, it can be seen that the carbon content is more preferably 0.03% by mass or less.

[0153] As shown in Table 1, stainless steel with a low carbon content has high elongation and high tensile breaking strength. Therefore, stainless steel with low carbon content has high machinability. In other words, when forming the battery case 1, it is easy to stretch the stainless steel for thinning, and the processing accuracy is also high. Therefore, it is possible to easily form with high precision a battery case 1 with small thickness, resulting in the stable manufacture of cylindrical batteries with high sealing performance.

[0154] The results show that the stainless steel forming the battery case is preferably stainless steel with a carbon content of 0.08% by mass or less, and more preferably stainless steel with a carbon content of 0.03% by mass or less. Consequently, the sealing performance and the capacity retention rate are improved. As a result, the improvement of battery characteristics and the enhancement of long-term reliability and safety can be achieved at the same time.

[0155] <Embodiment 8>

[0156] In Embodiment 2, a cylindrical battery is fabricated without soldering the negative electrode lead 6 to the battery case 1, but only making them contact each other. Other fabrication conditions are the same as in Embodiment 2. The cylindrical battery made in this way is used as Embodiment 8.

[0157] <Embodiment 9>

[0158] In Embodiment 1, a cylindrical battery is fabricated without soldering the negative electrode lead 6 to the battery case 1, but only making them contact each other. Other fabrication conditions are the same as in Embodiment 1. The cylindrical battery made in this way is used as Embodiment 9.

[0159] The internal resistance of the cylindrical battery in Embodiments 8 and 9 is determined. The results are shown in Table 7.

[0160] Table 7

[0161]

	Battery case					Characteristic
	Material	Cu (mass%)	C (mass%)	Thickness (mm)	Outer diameter (mm)	Internal resistance (Ω)
Embodiment 8	SUS	3.80	<0.03	0.10	3.5	1
Embodiment 9	SUS316L	0	<0.03	0.10	3.5	20

[0162] As can be seen from the results shown in Table 7, when the negative lead 6 is only in contact with the battery case 1, the internal resistance is significantly increased in Embodiment 9 that does not contain copper, while in Embodiment 8 that contains copper, the internal resistance is significantly decreased. In other words, by mixing copper into austenitic stainless steel, the contact resistance of the stainless steel surface decreases.

[0163] This is based on the following reasons. In other words, a protective layer that enhances acid corrosion resistance is usually formed on the surface of stainless steel. In the case of stainless steel that does not contain copper, this protective layer becomes the cause of increased contact resistance. On the other hand, by including copper in stainless steel, the resistance of the protective layer is reduced, which consequently reduces the contact resistance.

[0164] Therefore, by mixing copper into the stainless steel forming the battery case 1, the welding of the battery case 1 and the negative electrode lead 6 can be omitted. In addition, in a cylindrical battery (Embodiment 2) where the negative electrode lead 6 is welded to the battery case 1, for example, even in the event that the welded portion fractures during use, the internal resistance remains low as long as the negative electrode lead 6 is in contact with the battery case 1.

[0165] Although the present invention has been described based on the currently preferred embodiments, it should be understood that these contents are not to be construed as limiting. Undoubtedly, various changes and improvements will be obvious to those skilled in the art after reading the content above. Therefore, it is intended that the appended claims be interpreted to cover all changes and modifications that fall within the true spirit and scope of the present invention.

[0166] Potential for industrial applications

[0167] The cylindrical battery according to the present invention can be used as a power source in a variety of electronic devices such as mobile digital devices.

[0168] Description of symbols

[0169] 1-battery case, 2-negative electrode plate, 3-positive electrode plate, 4-separator, 5-electrode assembly, 6-negative electrode lead, 7-positive electrode lead, 8-sealing member, 9-gasket, 10-intermediate member, 11-circular plate.

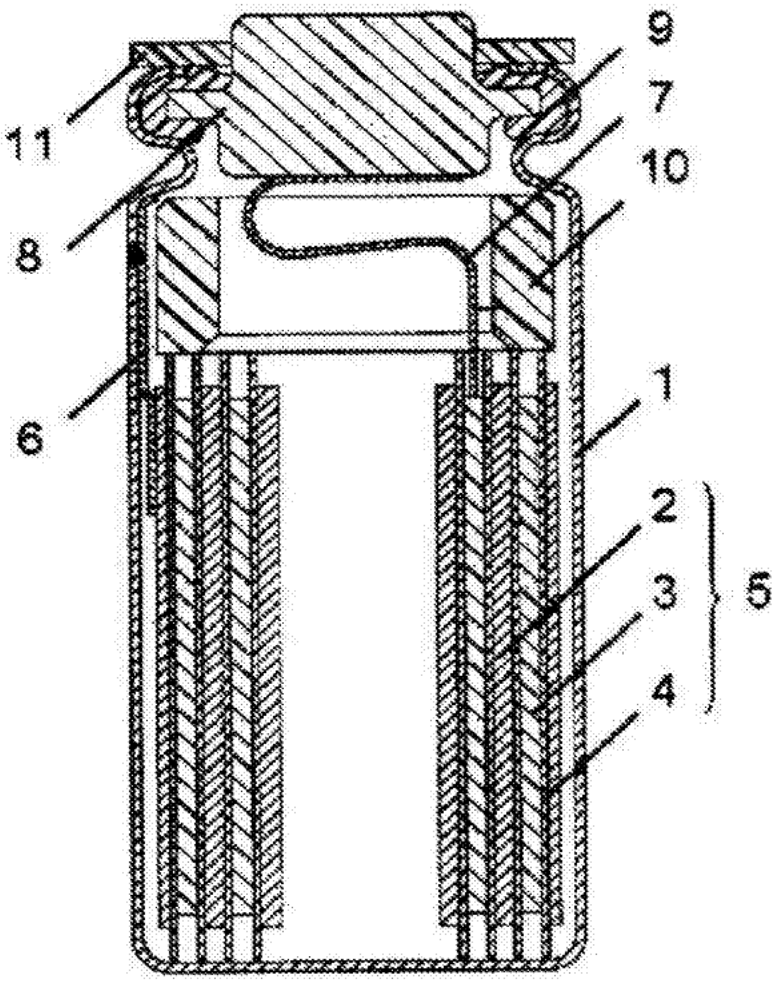


FIG. 1

welocalize

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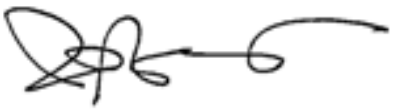
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Dated: May 20, 2026



(Bibliographic information, abstract, specifications)

(Claims, drawings)

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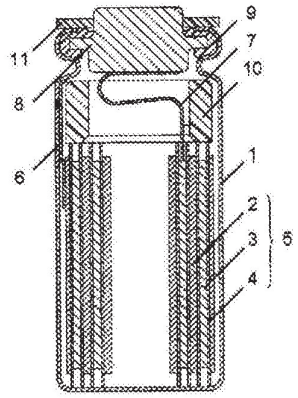
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(54)发明名称

圆筒型电池

(57)摘要

本发明提供一种实现了使电池特性的提高和长期可靠性及安全性的提高得以兼顾的小型的圆筒型电池。圆筒型电池具备有底圆筒状的电池壳(1)、与电解质一同收纳在电池壳(1)中的电极组(5)、嵌入电池壳(1)的开口部中的封口部件(8)、夹在封口部件(8)与电池壳(1)之间的垫圈(9),通过对电池壳(1)的开口端部实施拉深加工而密封电池壳1的开口部。而且,电池壳(1)由不锈钢构成。此外,电池壳(1)的外径为10mm以下,电池壳(1)的厚度为0.05mm以上且0.2mm以下。



CN 103797607 B

1. 一种圆筒型电池，其具备有底圆筒状的电池壳、与电解质一同收纳在所述电池壳中的电极组、嵌入所述电池壳的开口部中的封口部件、和夹在所述封口部件与所述电池壳之间的垫圈，通过对所述电池壳的开口端部实施拉深加工而密封所述电池壳的开口部，其中，

所述电池壳由碳含量为 0.03 质量％以下的不锈钢构成，

所述电池壳的外径为 10mm 以下，

所述电池壳的厚度为 0.05mm 以上且 0.2mm 以下。

2. 根据权利要求 1 所述的圆筒型电池，其中，构成所述电池壳的所述不锈钢为奥氏体系不锈钢。

3. 根据权利要求 1 或 2 所述的圆筒型电池，其中，构成所述电池壳的所述不锈钢是铜含量为 1.0 质量％以上且 6.0 质量％以下的不锈钢。

4. 根据权利要求 1 或 2 所述的圆筒型电池，其中，所述电池壳的外径为 6mm 以下。

圆筒型电池

技术领域

[0001] 本发明涉及锂离子二次电池等具备电池壳的圆筒型电池。

背景技术

[0002] 近年来，在移动式数字设备等电子设备中，作为驱动该电子设备的电源而广泛使用锂离子二次电池。特别是，在智能手机等多功能且要求强负载的便携式设备中，对于用作其电源的电池，一直要求能量密度及负载特性等电池特性的提高以及轻量化。而且，一直要求提高长期可靠性及安全性。

[0003] 锂离子二次电池通常具备金属制的电池壳，通过减小电池壳的厚度、增大内容积，同时在电池壳中高密度地填充发电要素，能够提高能量密度。减小电池壳的厚度在增大内容积这点上，对于小型的电池是特别有效的。作为其它的例子，有取代电池壳而使用金属－树脂层叠薄板的锂离子电池。在此种情况下，通过用该薄的薄板内包正负极、隔膜、电解液等电池构成要素，可与能量密度的提高一同实现轻量化。

[0004] 现有技术文献

[0005] 专利文献

[0006] 专利文献 1 :日本特开 2009-181754 号公报

[0007] 专利文献 2 :日本特开 2008-223087 号公报

[0008] 专利文献 3 :日本特开 2007-227339 号公报

发明内容

[0009] 发明要解决的问题

[0010] 可是，在锂离子二次电池等电池中，使电池特性的提高和长期可靠性及安全性的提高得以兼顾是困难的。例如，在锂离子二次电池中，一般采用铁或铝等作为电池壳材料。因此，如果为提高能量密度而减小构成电池壳的金属板的厚度，则电池壳的强度下降。电池壳的强度的下降会招致密封性的下降及相对于因重复充放电循环而产生的电极板的膨胀或因气体原因而产生的内压上升的容许度的下降。其结果是，容易产生电池壳的变形或电池特性的劣化，难实现长期可靠性。

[0011] 此外，在取代电池壳而采用金属－树脂层叠薄板时，尽管能提高能量密度，但是因电池壳强度的下降而产生的问题显著化。例如，如果仅重复通常的充放电循环，则因电解液的分解而产生气体，由此因内压上升而使电池显著膨胀。此外，因引线部附近的密封性脆弱而容易从电池外部向内部侵入水分。所以，因该水分而产生气体，由此使内压上升，电池膨胀。有上述膨胀会破坏层叠薄板的密封的顾虑。

[0012] 如此，为了兼顾电池特性的提高和长期可靠性及安全性的提高，在采用电池壳的同时，在电池壳中一边减小其厚度一边实现高强度和高密封性是非常重要的。

[0013] 因此，为了在对电池壳的开口部实施敛缝封口时得到高的密封性，提出了通过只增大电池壳中的开口部的厚度来提高电池壳的开口部的强度的技术（例如参照专利文献

1)。可是,如此的电池壳因形状复杂而难以进行成型加工及品质管理,不太适合大批量生产。

[0014] 此外,提出了采用通过添加异种金属和热处理而提高了强度的铝合金材料作为电池壳材料的技术(例如参照专利文献2)。可是,如果光提高电池壳的强度,则电池壳的加工性下降,实现高密封性变得困难。

[0015] 因此,本发明的目的是,提供一种实现了使电池特性的提高和长期可靠性及安全性的提高得以兼顾的小型的圆筒型电池。

[0016] 用于解决课题的手段

[0017] 本发明者们通过深入研究,发现了在小型的圆筒型电池中使电池特性的提高和长期可靠性及安全性的提高得以兼顾的条件。

[0018] 本发明的圆筒型电池具备有底圆筒状的电池壳、与电解质一同收纳在电池壳中的电极组、嵌入电池壳的开口部中的封口部件、夹在封口部件与电池壳之间的垫圈,通过对电池壳的开口端部实施拉深(しぼり)加工而密封电池壳的开口部。而且,电池壳由不锈钢构成。电池壳的外径为10mm以下,电池壳的厚度为0.05mm以上且0.2mm以下。

[0019] 发明效果

[0020] 根据本发明的圆筒型电池,可实现使电池特性的提高和长期可靠性及安全性的提高得以兼顾。

[0021] 尽管在附加权利要求书中描述了本发明的新特征,但是从下面结合附图的详细描述,将更好地理解本发明的构成和内容的两方面,以及本发明的其它目的和特征。

附图说明

[0022] 图1是概念地表示本发明的实施方式的圆筒型电池的纵向剖视图。

具体实施方式

[0023] 首先,对本发明的圆筒型电池进行说明。

[0024] 本发明的圆筒型电池具备有底圆筒状的电池壳、与电解质一同收纳在电池壳中的电极组、嵌入电池壳的开口部中的封口部件、夹在封口部件与电池壳之间的垫圈,通过对电池壳的开口端部实施拉深加工而密封电池壳的开口部。而且,电池壳由不锈钢构成。此外,电池壳的外径为10mm以下,电池壳的厚度为0.05mm以上且0.2mm以下。

[0025] 如表1所示,不锈钢与铁(Fe)或铝(Al)相比,具有非常高的拉伸断裂强度。再有,表1中作为不锈钢的一例子列举了SUS316L(奥氏体系不锈钢)。所以,如本发明通过采用不锈钢作为电池壳的材料,即使在整体以均匀的状态减小电池壳厚度时,也可在电池壳中维持高的强度。此外,不锈钢尽管强度高,但其加工性优良。所以,在电池壳中能够实现高的密封性。

[0026] 表1

[0027]

	比重（g/cm）	拉伸断裂强度（MPa）	延伸率（%）
SUS316L	8.03	481	40
Fe	7.78	196	60
Al	2.70	55	30

[0028] 而且，本发明者们发现：在电池壳的外径为10mm以下的小型的圆筒型电池中，特别是在电池壳的厚度为0.05mm以上且0.2mm以下的情况下，可实现高的密封性。此外，本发明者们发现：这些条件在电池壳的外径为6mm以下的小型的圆筒型电池中是特别优选的。如此，在小型的圆筒型电池中，在通过对电池壳的开口端部实施拉深加工而密封电池壳的开口部时，作为提高密封性的条件，电池壳的厚度是非常重要的。

[0029] 如果对电池壳的开口端部实施拉深加工，则在电池壳中的被拉深的部分，电池壳收缩（即电池壳的直径减小）。在拉深加工前的电池壳的直径为15mm以上时，因拉深加工导致的电池壳1的收缩变化率小，几乎不影响密封性等。可是，在拉深加工前的电池壳1的直径为10mm以下时，因拉深加工导致的电池壳1的收缩变化率增大，在电池壳的开口端部容易产生正圆度的下降或折皱等异常的变形。如此的问题在拉深加工前的电池壳的直径为6mm以下时显著，使密封性降低。如此，在因拉深加工导致的电池壳1的收缩变化率大的小型的圆筒型电池中，本发明者们发现：在电池壳1由不锈钢构成、且电池壳1的厚度在0.05mm以上且0.2mm以下的情况下，可实现高的密封性。

[0030] 在圆筒型电池为锂离子电池时，优选电池壳由具有宽的电位窗和高的耐酸腐蚀性的材料构成。在此点上，SUS316L等不锈钢相对于还原侧的电位非常强，关于氧化侧，虽不及铝的程度，但具有比铁或铜宽的电位窗。再有，关于铝，如果在锂离子的存在下施加还原电位则表面析出锂，生成与锂的合金。因如此的合金化反应伴随有体积的膨胀，因此在电池壳由铝构成时，电池壳脆化，其强度降低，因此实施电池的长期可靠性是困难的。

[0031] 此外，不锈钢具有比铁、铜、铝高的耐酸腐蚀性。这是因为不锈钢在其表面具有保护层。在锂离子电池中，一般采用六氟磷酸锂（$LiPF_6$）作为支持电解质。这样的支持电解质能够在构成具有高的离子传导性的电解液的同时，实现优良的负载特性。其另一方面，如果存在水分则六氟磷酸锂通过水解而生成强酸的氢氟酸（HF）。因此，在锂离子电池中，除了通过提高密封性而抑制水分从外部侵入以外，提高电池壳的耐酸腐蚀性对于实现长期可靠性也是重要的。因为，电池壳的腐蚀招致水分的侵入，使腐蚀的进展加速。

[0032] 如此，根据本发明的圆筒型电池，可实现电池特性的提高和长期可靠性及安全性的提高的兼顾。此外，能够使电池壳的厚度均匀，因此电池壳的成型加工及品质管理是容易的。

[0033] 在上述圆筒型电池的优选的具体的构成中，构成电池壳的不锈钢为碳含量低的奥氏体系不锈钢。此外，优选构成电池壳的不锈钢是碳含量为0.08质量%以下的不锈钢。另外，不锈钢中的碳含量更优选为0.05质量%以下，特别优选为0.03质量%以下。

[0034] 如此碳含量低的不锈钢如表1所示，延伸率大且拉伸断裂强度高。所以，碳含量低的不锈钢具有高的加工性。也就是说，在形成电池壳1时，容易拉伸不锈钢进行减薄加工，此外，加工精度也高。例如，在细长的圆筒型电池中，例如通过深拉深加工，能够容易且高精

度地形成高度与直径的比例大的电池壳。因此，能够容易且高精度地形成厚度为0.05mm以上且0.2mm以下的电池壳1，其结果是，可稳定地制造具有高密封性的圆筒型电池。

[0035] 在上述圆筒型电池的优选的其它的具体构成中，构成电池壳1的不锈钢是铜含量为1.0质量％以上且6.0质量％以下的不锈钢。更优选铜含量为1.5质量％以上且5.0质量％以下。如此，含铜的不锈钢的拉伸断裂强度、延伸率及耐酸腐蚀性都高，且如表2所示，不锈钢表面上的接触电阻小。再有，在不锈钢表面，通常形成有提高耐酸腐蚀性的保护层，在不锈钢不含铜的情况下，该保护层成为接触电阻增大的原因。另一方面，通过在不锈钢中含有铜，保护层的电阻减小，其结果是接触电阻减小。

[0036] 表2

[0037]

	接触电阻（载荷40g）（mΩ）
奥氏体系不锈钢（含铜）	40
奥氏体系不锈钢（不含铜）	8000

[0038] 根据含铜的不锈钢，能够容易在不形成新的表面层或端子的情况下得到与设备的电接触。此外，通过在电池内部增大与电极的接触面积，即使不通过焊接等接合电池壳和电极，电池的内部电阻也降低，其结果是，可得到良好的负载特性。

[0039] 如上所述，不锈钢具有高的强度。因此，在将不锈钢加工成所希望的形状时需要大的力。因此，优选电池壳为通过对厚度薄的不锈钢板进行深拉深而形成为有底圆筒状的电池壳。通过深拉深，能够得到厚度薄且均匀、而且形状及厚度的偏差小的电池壳。此外，如果采用深拉深则材料的损失小。因而，在圆筒型电池中，能够使电池特性的提高和长期可靠性及安全性的提高得以兼顾。

[0040] 再有，作为将不锈钢加工成有底圆筒状的方法，有冲压加工法及DI(Drawing & Ironing)加工法等加工法。可是，在这些加工法中，加工成型时需要均等地持续施加大的力，难以对其进行控制，因此电池壳的形状及厚度容易产生偏差。特别是在减小电池壳厚度时，有时开孔或断裂。此外，作为将不锈钢加工成有底圆筒状的方法，有对圆柱状的材料进行切削的方法。可是，在该方法中，尽管电池壳的形状不易产生偏差，但是材料的损失大，效率低。

[0041] 接着，参照附图对本发明的实施方式进行具体的说明。再有，本发明的各部构成并不局限于实施方式，可在权利要求所述的技术范围内进行种种变更。

[0042] 图1是概念地表示本发明的实施方式的圆筒型电池的纵剖视图。如图1所示，圆筒型电池具备有底圆筒状的电池壳1、与电解质一同收纳在电池壳1中的电极组5、嵌入电池壳1的开口部中的封口部件8、夹在封口部件8与电池壳1之间的垫圈9。

[0043] 《电池壳》

[0044] 电池壳1通过对具有均匀厚度的不锈钢材实施深拉深加工而形成。电池壳1的外径优选为10mm以下，更优选为6mm以下。电池壳1的厚度为0.05mm以上且0.2mm以下。再有，电池壳1的侧壁的厚度（侧厚）与底部的厚度（底厚）的比值为0.20以上且1.20以

下，优选为 0.33 以上且 1.05 以下。

[0045] 构成电池壳 1 的不锈钢优选为碳含量低的奥氏体系不锈钢。此外，构成电池壳 1 的不锈钢优选是碳含量为 0.08 质量％以下的不锈钢。另外，不锈钢中的碳含量更优选为 0.05 质量％以下，特别优选为 0.03 质量％以下。

[0046] 优选在构成电池壳 1 的不锈钢中含有铜。在如此的电池壳 1 中，铜含量优选为 1.0 质量％以上且 6.0 质量％以下，更优选为 1.5 质量％以上且 5.0 质量％以下。

[0047] 《封口部件及垫圈》

[0048] 封口部件 8 及垫圈 9 是用于密封电池壳 1 的开口部的部件。具体地讲，将封口部件 8 及垫圈 9 以在封口部件 8 与电池壳 1 之间夹着垫圈 9 的方式插入电池壳 1 的开口部。然后，对电池壳 1 的开口端部实施拉深加工，将其开口端部敛缝在封口部件 8 上。所以，垫圈 9 以被压缩的状态密合在封口部件 8 的侧面及电池壳 1 的内表面。如此，将电池壳 1 的开口部密封。此外，在封口部件 8 中的朝电池壳 1 的外部露出的突起部上，嵌入由电绝缘材料构成的有孔的圆板 11。该圆板 11 用于防止在封口部件 8 与电池壳 1 之间产生电短路。

[0049] 关于垫圈 9，作为其材料，可使用聚丙烯 (PP)、聚乙烯 (PE)、聚苯硫醚 (PPS)、全氟烷基乙烯 - 六氟丙烯共聚物 (PFA)、交联型橡胶等。特别是 PFA 在透湿度低、能够抑制使锂离子电池的劣化扩展的水分向电池内部的侵入这点上是优选的。

[0050] 《电极组》

[0051] 电极组 5 具有负极板 2、正极板 3 和隔膜 4。在电极组 5 中，以中间夹着隔膜 4 的状态相互重叠地一起卷绕负极板 2 及正极板 3。为了不在电极组 5 中产生卷滑动，用固定胶带将负极板 2 及正极板 3 中的至少任一方的卷尾的部分固定在电极组 5 的外周面上。然后，将电极组 5 与非水电解质（未图示）一同收纳在电池壳 1 中。根据如此的电极组 5，反应面积增大，可实现强负载特性。

[0052] 负极板 2 及正极板 3 分别如后述，由集电体即芯材和形成于芯材表面上的合剂层（含活性物质）构成。而且，为了增大电池容量，合剂层以压缩的状态形成在芯材表面上。因此，在电极组 5 中，如果负极板 2 及正极板 3 的卷头的半径过小，则有合剂层从芯材上剥离、因此为原因在电池壳 1 内产生电短路（内部短路）的顾虑。另一方面，如果卷头的半径过大，则收纳在电池壳 1 内的活性物质的量减少，电池容量减小。因而，需要以适度的半径开始卷绕负极板 2 及正极板 3。例如，在采用卷芯卷绕负极板 2 及正极板 3 的情况下，卷芯的直径 R 优选为 0.6mm 以上且 3.0mm 以下，更优选为 0.8mm 以上且低于 1.5mm。在电极组 5 的中心轴附近，存在有不存在活性物质的空间，该空间优选直径为 3.0mm 以下，更优选直径低于 1.5mm。

[0053] 在负极板 2（具体地讲，是后述的负极芯材）上电连接有负极引线 6，负极引线 6 的端部通过点焊等被接合在电池壳 1 的侧壁内表面上。再有，在构成电池壳 1 的不锈钢含有铜的情况下，也可以只使负极引线 6 与电池壳 1 的侧壁内表面接触。如此，负极板 2 被电连接在电池壳 1 上，电池壳 1 作为负极端子发挥功能。关于负极引线 6，作为其材料，例如可使用镍、铁、不锈钢、铜等。负极引线 6 具有用小的压力就弯曲的特性，作为其形状没有特别的限定，可列举出具有与负极芯材的焊接余量及与电池壳 1 的焊接余量的长方形状、或与该长方形状内切的椭圆或多边形等。此外，负极引线 6 的厚度优选为 10μm 以上且 120μm 以下，更优选为 20μm 以上且 80μm 以下。

[0054] 在正极板3(具体地讲,是后述的正极芯材)上电连接有正极引线7,正极引线7的端部通过点焊等被接合在封口部件8上。如此,正极板3被电连接在封口部件8上,封口部件8作为正极端子发挥功能。关于正极引线7,作为其材料,例如可使用铝。正极引线7具有用小的压力就弯曲的特性,作为其形状没有特别的限定,可列举出长方形状等。此外,正极引线7的厚度优选为40μm以上且150μm以下,更优选为50μm以上且100μm以下。

[0055] 再有,在电极组5与封口部件8之间配置有由电绝缘材构成的环状的中间部件10,正极引线7通过中间部件10的内侧,与正极板3和封口部件8连接。由此,通过中间部件10防止在负极与正极之间发生电短路。

[0056] <负极板>

[0057] 负极板2由负极集电体即负极芯材和形成于负极芯材表面上的负极合剂层构成。负极板2例如通过在负极芯材表面上薄膜状地沉积负极活性物质而形成。负极芯材为金属箔,关于负极芯材,例如可使用具有多孔性结构或无孔性结构的长尺寸的导电性基板。作为负极芯材的材料,例如可使用不锈钢、镍或铜等。负极芯材的厚度没有特别的限定,但优选为1μm以上且500μm以下,更优选为5μm以上且20μm以下。根据如此厚度的负极芯材,能够保持负极板2的强度,同时使负极板2轻量化。

[0058] 负极合剂层含有负极活性物质。因此,以下对负极活性物质进行详细说明。再有,优选在负极合剂层中除负极活性物质以外还含有粘结剂等。

[0059] (负极活性物质)

[0060] 作为负极活性物质,可使用可嵌入及脱嵌锂离子的物质。作为如此的负极活性物质,例如可列举出金属、金属纤维、碳材料、氧化物、氮化物、硅化合物、锡化合物或各种合金材料等。作为碳材料的具体例子,例如可列举出各种天然石墨、焦炭、不完全石墨化碳、碳纤维、球状碳、各种人造石墨或非晶质碳等。

[0061] 这里,硅(Si)或锡(Sn)等单质、或硅化合物及锡化合物的容量密度大。因此,作为负极活性物质,优选使用硅、锡、硅化合物或锡化合物。作为硅化合物的具体例子,例如,可列举出SiO_x(其中$0.05 < x < 1.95$)或用选自B、Mg、Ni、Ti、Mo、Co、Ca、Cr、Cu、Fe、Mn、Nb、Ta、V、W、Zn、C、N及Sn等元素中的至少1种以上的元素置换Si的一部分而成的硅合金、或硅固溶体等。此外,作为锡化合物的具体例子,例如可列举出Ni_2Sn_4、Mg_2Sn、SnO_x(其中$0 < x < 2$)、SnO_2或$SnSiO_3$等。再有,负极活性物质可以单独使用上述列举的负极活性物质中的1种,也可以组合使用2种以上。

[0062] <正极板>

[0063] 正极板3由正极集电体即正极芯材和形成于正极芯材的表面上的正极合剂层构成。正极芯材为金属箔,作为正极芯材,例如可使用具有多孔性结构或无孔性结构的长尺寸的导电性基板。作为正极芯材的材料,例如可使用铝等。正极芯材的厚度没有特别的限定,但优选为8μm以上且25μm以下,更优选为10μm以上且15μm以下。根据如此厚度的正极芯材,能够构成流畅弯曲的直径小的电极组5。

[0064] 正极合剂层含有正极活性物质、粘结剂及导电剂。因此,下面对正极活性物质、粘结剂及导电剂进行详细说明。

[0065] (正极活性物质)

[0066] 作为正极活性物质,优选含锂复合氧化物,可列举出例如$LiCoO_2$、$LiNiO_2$、$LiMnO_2$、

$LiCo_xNi_{1-x}O_2$、$LiCo_xM_{1-x}O_2$、$LiNixM_{1-x}O_2$、$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$、$LiMn_2O_4$、$LiMnMO_4$、$LiMePO_4$、$Li_2MePO_4F$（其中是 M 为 Na、Mg、Sc、Y、Mn、Fe、Co、Ni、Cu、Zn、Al、Cr、Pb、Sb 及 B 中的至少 1 种。x 为 0 ＜ x ＜ 1。Me 为含有选自 Fe、Mn、Co、Ni 中的至少 1 种的金属元素）、以及用异种元素置换这些含锂化合物的一部分元素而成的化合物。此外，作为正极活性物质，也可以采用通过金属氧化物、锂氧化物或导电剂等进行了表面处理的正极活性物质。作为表面处理，例如可列举疏水化处理。

[0067] 正极活性物质的平均粒径优选为 5μm 以上且 20μm 以下。如果正极活性物质的平均粒径低于 5μm，则活性物质粒子的表面积极大地增大。因此，用于得到可对正极板 3 进行处理的粘接强度的粘结剂量极端地增加。因此，每个极板的活性物质量减少，容量下降。另一方面，如果超过 20μm，则在正极芯材上涂布正极合剂料浆时容易发生涂布条纹。

[0068] （粘结剂）

[0069] 作为粘结剂，可使用例如 PVDF、聚四氟乙烯、聚乙烯、聚丙烯、芳香族聚酰胺树脂、聚酰胺、聚酰亚胺、聚酰胺亚胺、聚丙烯腈、聚丙烯酸、聚丙烯酸甲酯、聚丙烯酸乙酯、聚丙烯酸己酯、聚甲基丙烯酸、聚甲基丙烯酸甲酯、聚甲基丙烯酸乙酯、聚甲基丙烯酸己酯、聚醋酸乙烯酯、聚乙烯基吡咯烷酮、聚醚、聚醚砜、聚六氟丙烯、丁苯橡胶或羧甲基纤维素等。此外，可列举出使选自四氟乙烯、六氟乙烯、六氟丙烯、全氟烷基乙烯基醚、偏氟乙烯、三氟氯乙烯、乙烯、丙烯、五氟丙烯、氟代甲基乙烯基醚、丙烯酸及己二烯中的 2 种以上的材料共聚而成的共聚物、或将选择的 2 种以上材料混合而成的混合物。

[0070] 在上述列举的粘结剂中，特别是 PVDF 及其衍生物由于在非水电解质二次电池内化学上稳定，可充分粘结正极合剂层和正极芯材，同时充分粘结构成正极合剂层的正极活性物质、粘结剂和导电剂，因此可得到良好的充放电循环特性及放电性能。因此，作为本实施方式的粘结剂，优选使用 PVDF 或其衍生物。加之，PVDF 及其衍生物廉价，因此在成本方面也是优选的。再有，要制作使用 PVDF 作为粘结剂的正极，在制作正极时，可列举出例如将 PVDF 溶解于 N- 甲基吡咯烷酮中使用的情况、或将粉末状的 PVDF 溶解于正极合剂料浆中使用的情况。

[0071] （导电剂）

[0072] 作为导电剂，例如，可采用天然石墨或人造石墨等石墨类，乙炔黑（AB：acetylene black）、科琴黑、槽炭黑、炉黑、灯黑或热炭黑等炭黑类，碳纤维或金属纤维等导电性纤维类、氟化碳、铝等金属粉末类、氧化锌或钛酸钾等导电性晶须类、氧化钛等导电性金属氧化物、或苯撑衍生物等有机导电性材料等。

[0073] ＜隔膜＞

[0074] 关于隔膜 4，可使用具有大的离子透过度、且兼备规定的机械强度和电绝缘性的微多孔薄膜、纺织布或无纺布等。特别是，关于隔膜 4，作为其材料，例如优选使用聚丙烯、聚乙烯等聚烯烃。聚烯烃的耐久性优良且具有关闭功能，因而能够提高锂离子二次电池的安全性。

[0075] 隔膜 4 的厚度一般为 10μm 以上且 300μm 以下，优选为 10μm 以上且 40μm 以下。此外，隔膜 4 的厚度更优选为 15μm 以上且 30μm 以下，进一步优选为 10μm 以上且 25μm 以下。此外，在使用微多孔薄膜作为隔膜 4 的情况下，微多孔薄膜可以是由 1 种材料构成的单层膜，也可以是由 1 种或 2 种以上的材料构成的复合膜或多层膜。此外，隔膜 4 的空穴率

优选为30％以上且70％以下，更优选为35％以上且60％以下。这里所谓的空穴率，表示孔全体的容积相对于隔膜4的总体积的比率。

[0076] ＜非水电解质＞

[0077] 作为收纳在电池壳1中的非水电解质，能够使用液状、凝胶状或固体状的非水电解质。液状的非水电解质含有电解质盐（例如锂盐）和使该电解质盐溶解的非水溶剂。凝胶状的非水电解质含有非水电解质和保持该非水电解质的高分子材料。作为该高分子材料，可列举出例如聚偏氟乙烯、聚丙烯腈、聚氧乙烯、聚氯乙烯、聚丙烯酸酯或聚偏氟乙烯六氟丙烯等。固体状的非水电解质含有高分子固体电解质。

[0078] 以下对液状的非水电解质所含的非水溶剂及电解质盐进行详细说明。

[0079] （非水溶剂）

[0080] 作为使电解质盐溶解的非水溶剂，能够使用公知的非水溶剂。该非水溶剂的种类没有特别的限定，例如，可使用环状碳酸酯、链状碳酸酯或环状羧酸酯等。这里作为环状碳酸酯的具体例子，可列举出例如碳酸亚丙酯（PC：propylene carbonate）或碳酸亚乙酯（EC：ethylene carbonate）等。此外，作为链状碳酸酯的具体例子，可列举出例如碳酸二乙酯（DEC：diethyl carbonate）、碳酸甲乙酯（EMC：ethylmethyl carbonate）或碳酸二甲酯（DMC：dimethyl carbonate）等。此外，作为环状羧酸酯的具体例子，可列举出例如γ-丁内酯（GBL：gamma-butyrolactone）或γ-戊内酯（GVL：gamma-valerolactone）等。非水溶剂可以单独使用上述列举的非水溶剂中的1种，也可以组合使用2种以上。

[0081] （电解质盐）

[0082] 作为溶解于非水溶剂中的电解质，可列举出例如$LiClO_4$、$LiBF_4$、$LiPF_6$、$LiAlCl_4$、$LiSbF_6$、LiSCN、$LiCF_3SO_3$、$LiCF_3CO_2$、$LiAsF_6$、$LiB_{10}Cl_{10}$、低级脂肪族羧酸锂、LiCl、LiBr、LiI、氯硼烷锂、硼酸盐类或酰亚胺盐类等。这里作为硼酸盐类的具体例子，可列举出例如二[1,2-苯二酚根合(2-)-O,O']硼酸锂、二[2,3-萘二酚根合(2-)-O,O']硼酸锂、二[2,2'-联苯二酚合根(2-)-O,O']硼酸锂或二(5-氟-2-羟基-1-苯磺酸-O,O')硼酸锂等。此外，作为酰亚胺盐类的具体例例子，可列举出例如双三氟甲磺酰亚胺锂（(CF_3S_2NLi)、三氟甲烷磺酰壬氟丁烷磺酰亚胺锂（$LiN(CF_3SO_2)(C_4F_9SO_2)$）、或双五氟乙烷磺酰亚胺锂（$(C_2F_5SO_2)_2NLi$）等。作为电解质盐，可以单独使用上述列举的电解质中的1种，也可以组合使用2种以上。

[0083] 电解质盐相对于非水溶剂的溶解量优选为0.5mol/m^3以上且2mol/m^3以下。

[0084] 液状的非水电解液，除了电解质盐及非水溶剂以外，也可以含有例如在负极上通过分解形成锂离子传导性高的被膜、提高电池的充放电效率的添加剂。作为具有如此功能的添加剂，可列举出例如碳酸亚乙烯酯（VC：vinylene carbonate）、4-甲基碳酸亚乙烯酯、4,5-二甲基碳酸亚乙烯酯、4-乙基碳酸亚乙烯酯、4,5-二乙基碳酸亚乙烯酯、4-丙基碳酸亚乙烯酯、4,5-二丙基碳酸亚乙烯酯、4-苯基碳酸亚乙烯酯、4,5-二苯基碳酸亚乙烯酯、碳酸乙烯基亚乙酯（VEC：vinyl ethylene carbonate）、或碳酸二乙烯基亚乙酯等。作为添加剂，可以单独使用上述列举的添加剂中的1种，也可以组合使用2种以上。特别是，优选选自上述列举的添加剂中的碳酸亚乙烯酯、碳酸乙烯基亚乙酯及碳酸二乙烯基亚乙酯中的至少1种。再有，作为添加剂，也可以是用氟原子置换了上述列举的添加剂的一部分氢原子而成的添加剂。

[0085] 另外，液状的非水电解质中，除了电解质盐及非水溶剂以外，也可以含有例如在过充电时在电极上分解而形成被膜、使电池不活性化的公知的苯衍生物。作为具有如此功能的苯衍生物，优选含有苯基及与该苯基邻接的环状化合物基的物质。这里，作为苯衍生物的具体例子，可列举出例如环己基苯、联苯或二苯醚等。此外，作为苯衍生物中所含的环状化合物基的具体例子，可列举出例如苯基、环状醚基、环状酯基、环烷基或苯氧基等。作为苯衍生物，可以单独使用上述列举的苯衍生物中的 1 种，也可以组合使用 2 种以上。但是，苯衍生物的相对于非水溶剂的含量优选为非水溶剂总体的 10vol％以下。

[0086] 实施例

[0087] 以下，对本发明的实施例进行具体的说明。

[0088] ＜实施例 1 ＞

[0089] （正极板的制作）

[0090] 作为正极活性物质，准备平均粒径为 10μm 的 $LiNi_{0.82}Co_{0.15}Al_{0.03}O_2$。作为粘结剂，相对于正极活性物质 100vol％准备 4.7vol％的 PVDF。作为导电剂，相对于正极活性物质 100vol％准备 4.5vol％的乙炔黑。此外，作为溶剂，准备 N- 甲基吡咯烷酮 (NMP)，通过在该溶剂中溶解准备好的粘结剂，调制溶液。然后，通过将准备的正极活性物质和导电剂及溶液混合，调制正极合剂料浆。

[0091] 接着，作为正极芯材，准备厚度为 15μm 的铝箔，在该铝箔的两面涂布正极合剂料浆，然后使其干燥。再然后，对两面涂布有正极合剂料浆并被干燥的正极芯材进行轧制，制作厚 0.12mm 的板状的正极用板。然后，通过将该正极用板裁断成宽 30.5mm、长 19.0mm，制作厚 0.12mm、宽 30.5mm、长 19.0mm 的正极板 3。

[0092] （负极板的制作）

[0093] 作为负极活性物质，准备平均粒径为 20μm 的鳞片状石墨。作为粘结剂，相对于负极活性物质 100vol％准备 4.7vol％的 SBR。作为导电剂，相对于负极活性物质 100vol％准备 4.5vol％的乙炔黑。此外，作为溶剂准备纯水，通过将准备好的粘结剂溶解在该溶剂中而调制溶液。然后，将准备的负极活性物质和导电剂及溶液混合，调制负极合剂料浆。

[0094] 接着，作为负极芯材，准备厚度为 8μm 的铜箔，在该铜箔的两面上涂布负极合剂料浆，然后使其干燥。再然后，对两面涂布有负极合剂料浆且被干燥的负极芯材进行轧制，制作厚 0.15mm 的板状的负极用板。然后，通过将该负极用板裁断成宽 29.5mm、长 37.0mm，制作厚 0.15mm、宽 29.5mm、长 37.0mm 的负极板 2。

[0095] （非水电解质的调制）

[0096] 作为非水溶剂，准备了以体积比 1 ： 3 混合了碳酸亚乙酯和碳酸二甲酯而成的混合溶剂。作为电解质盐，准备了 $LiPF_6$。然后，在准备的非水溶剂中添加 5wt％的碳酸亚乙烯酯作为提高电池的充放电效率的添加剂，同时以相对于非水溶剂的摩尔浓度达到 1.4mol/m^3的方式使电解质盐即 $LiPF_6$溶解，由此调制非水电解质。

[0097] （圆筒型电池的制作）

[0098] 首先，在准备好的正极板 3 的正极芯材上安装铝制的正极引线 7，此外，在准备好的负极板 2 的负极芯材上安装镍制的负极引线 6。然后，将负极板 2 和正极板 3 以它们之间夹着聚乙烯制的隔膜 4（厚度 16μm）的状态卷绕，由此制作电极组 5。另外，采用 SUS316L（不含铜，碳含量为 0.03 质量％以下的奥氏体系不锈钢），制作厚度为 0.1mm 且外

径为 3.5mm 的电池壳 1。

[0099] 接着，在电极组 5 的上端配置中间部件 10。然后，将负极引线 6 焊接在电池壳 1 上，同时将正极引线 7 焊接在封口部件 8 上。然后，将电极组 5 收纳在电池壳 1 内。然后，利用减压方式向电池壳 1 内注入非水电解质。再然后，以将垫圈 9 夹在电池壳 1 与封口部件 8 之间的方式，将封口部件 8 及由 PFA 构成的垫圈 9 插入电池壳 1 的开口部。然后，通过将电池壳 1 的开口端部敛缝在封口部件 8 上，制作了直径 3.5mm、高 35mm 的圆筒型电池。将该圆筒型电池作为实施例 1。

[0100] ＜实施例 2 ＞

[0101] 作为构成电池壳 1 的不锈钢，使用铜含量为 3.80 质量％的奥氏体系不锈钢。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 2。

[0102] ＜实施例 3 ＞

[0103] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（外径 3.5mm）的厚度规定为 0.15mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 3。

[0104] ＜实施例 4 ＞

[0105] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（外径 3.5mm）的厚度规定为 0.20mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 4。

[0106] ＜比较例 1 ＞

[0107] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（外径 3.5mm）的厚度规定为 0.25mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 1。

[0108] ＜比较例 2 ＞

[0109] 作为构成电池壳 1（厚度 0.1mm、外径 3.5mm）的材料，使用铁 (Fe)。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 2。

[0110] ＜比较例 3 ＞

[0111] 作为构成电池壳 1 的材料，采用铁 (Fe)，此外，将电池壳 1（外径 3.5mm）的厚度规定为 0.2mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 3。

[0112] 将实施例 1 ～ 4 的圆筒型电池以及比较例 1 ～ 3 的圆筒型电池分别各制作 5 个，对这些圆筒型电池，求出能量密度的平均值、漏液发生率及内部短路发生率。其结果见表 3。再有，内部短路发生率为使直径 1.0mm 的圆棒的顶端与圆筒型电池的侧面接触，以此状态负载 1.5kgf 的应力时的短路发生率。

[0113] 表 3

[0114]

	电池壳					特性		
	材料	Cu (质量%)	C (质量%)	厚度 (mm)	外径 (mm)	能量密度 (Wh/L)	漏液发生率(%)	内部短路发生率(%)
实施例 1	SUS316L	0	<0.03	0.10	3.5	385	0	0
实施例 2	SUS	3.80	<0.03	0.10	3.5	385	0	0
实施例 3	SUS316L	0	<0.03	0.15	3.5	362	0	0
实施例 4	SUS316L	0	<0.03	0.20	3.5	340	0	0
比较例 1	SUS316L	0	<0.03	0.25	3.5	318	80	0
比较例 2	Fe	-	-	0.10	3.5	385	20	80
比较例 3	Fe	-	-	0.20	3.5	339	80	0

[0115] 进而对实施例 1 ～ 4 的圆筒型电池以及比较例 1 ～ 3 的圆筒型电池进行长期可靠性试验。具体地讲，在将这些圆筒型电池在 85℃ -90％ RH 气氛下保存 20 天后，求出电池壳 1 的膨胀率和电池容量的维持率。再有，作为电池壳 1 的膨胀率，求出电池壳 1 的外径的增加量的比例。此外，以初期的电池容量为基准求出电池容量的维持率。其结果见表 4。

[0116] 表 4

[0117]

	电池壳					特性	
	材料	Cu (质量%)	C (质量%)	厚度 (mm)	外径 (mm)	膨胀率 (%)	容量维持率 (%)
实施例 1	SUS316L	0	<0.03	0.10	3.5	0	75
实施例 2	SUS	3.80	<0.03	0.10	3.5	0	75
实施例 3	SUS316L	0	<0.03	0.15	3.5	0	75
实施例 4	SUS316L	0	<0.03	0.20	3.5	0	50
比较例 1	SUS316L	0	<0.03	0.25	3.5	0	8
比较例 2	Fe	-	-	0.10	3.5	18	10
比较例 3	Fe	-	-	0.20	3.5	4	30

[0118] 在表 3 中通过对实施例 1 ～ 4 和比较例 1 进行比较，得知 :在电池壳 1 的厚度大的比较例 1 中，能量密度小，电池壳 1 的厚度越减小，能量密度越增大。这是因为伴随着电池壳 1 的厚度的减小，（收纳发电要素的）电池壳 1 的内容积增大。

[0119] 在表 3 及表 4 中通过对实施例 1 和比较例 2 进行比较，发现尽管电池壳 1 的厚度同为 0.10mm，但也有以下差异。也就是说，在电池壳 1 的材料为铁的比较例 2 中，容易发生内部短路，且电池壳 1 容易膨胀，而在电池壳 1 的材料为 SUS316L 的实施例 1 中，没有发生内部短路，且电池壳 1 没有膨胀。认为这是因为，SUS316L 的强度高于铁 (Fe) 的强度，所以由 SUS316L 构成的电池壳 1 的强度提高。再有，认为比较例 2 中的电池壳 1 的膨胀是由于因侵入电池壳内的水分的影响而产生了氢气。

[0120] 在表 3 中通过对实施例 1 ～ 4 和比较例 1 进行比较，得知 :尽管电池壳 1 的材料同为 SUS316L，外径同为 3.5mm，但是在电池壳 1 的厚度为 0.25mm 的比较例 1 中容易发生漏液，而在其厚度为 0.20mm 以下的实施例 1 ～ 4 中没有发生漏液。也就是说，得知 :在实施例 1 ～ 4 中，可实现高的密封性。这是因为，在实施例 1 ～ 4 中，没有产生正圆度的下降或折皱等异常的形状，所以没有形成产生漏液的路径。

[0121] 在表 4 中通过对实施例 1 ～ 4 和比较例 1 进行比较，得知：尽管电池壳 1 的材料同为 SUS316L，但是在电池壳 1 的厚度为 0.25mm 的比较例 1 中容量维持率非常低，而在其厚度为 0.20mm 以下的实施例 1 ～ 4 中容量维持率高达 50％以上。这是因为，在实施例 1 ～ 4 中没有产生正圆度的下降或折皱等异常的形状，所以抑制了电解液的蒸发及水分从外部的侵入。

[0122] 另一方面，在电池壳 1 的材料为铁 (Fe) 的比较例 2 及 3 中，容量维持率非常低。这是因为，因电池壳 1 的强度低，因此伴随着氢气的发生，电池壳 1 容易膨胀，所以密封性（参照表 3 的漏液发生率）下降，电池特性劣化。此外，因产生强酸即氢氟酸而使电池壳腐蚀，该腐蚀招致水分的侵入，使腐蚀的进展加速，因此认为不能维持高的电池容量。

[0123] 在表 3 及表 4 中通过对实施例 1 和实施例 2 进行比较，得知：即使构成电池壳 1 的不锈钢含有铜，该铜也不对电池特性及长期可靠性施加不良影响。再有，不锈钢所含的铜还使不锈钢表面的接触电阻下降。

[0124] 由这些结果得知：为了提高电池壳 1 的强度，作为电池壳 1 的材料优选采用不锈钢。由此，不易发生内部短路。另外，除此以外通过将电池壳 1 的厚度规定为 0.2mm 以下，能量密度提高，同时密封性及容量维持率提高，其结果是，可使电池特性的提高和长期可靠性及安全性的提高得以兼顾。

[0125] ＜实施例 5 ＞

[0126] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（厚度 0.1mm）的外径规定为 6mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 5。

[0127] ＜实施例 6 ＞

[0128] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（厚度 0.1mm）的外径规定为 10mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 6。

[0129] ＜比较例 4 ＞

[0130] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1（厚度 0.1mm）的外径规定为 15mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 4。

[0131] ＜比较例 5 ＞

[0132] 作为构成电池壳 1 的材料采用 SUS316L，此外，将电池壳 1 的厚度规定为 0.2mm，将外径规定为 15mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 5。

[0133] ＜比较例 6 ＞

[0134] 作为构成电池壳 1 的材料采用铁 (Fe)，此外，将电池壳 1（厚度 0.1mm）的外径规定为 6mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 6。

[0135] ＜比较例 7 ＞

[0136] 作为构成电池壳 1 的材料采用铁 (Fe)，此外，将电池壳 1（厚度 0.1mm）的外径规定为 10mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 7。

[0137] ＜比较例 8 ＞

[0138] 作为构成电池壳 1 的材料采用铁 (Fe)，此外，将电池壳 1（厚度 0.1mm）的外径规定为 15mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 8。

[0139] ＜比较例 9 ＞

[0140] 作为构成电池壳 1 的材料采用铁 (Fe)，此外，将电池壳 1 的厚度规定为 0.2mm，将外径规定为 15mm。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为比较例 9。

[0141] 将实施例 1、5 及 6 的圆筒型电池以及比较例 2 及 4 ～ 9 的圆筒型电池分别各制作 5 个，对这些圆筒型电池，求出了漏液发生率、内部短路发生率及电池容量的维持率。其结果见表 5。再有，内部短路发生率为使直径 1.0mm 的圆棒的顶端与圆筒型电池的侧面接触，以此状态负载 1.5kgf 的应力时的短路发生率。在将圆筒型电池在 85℃ -90％ RH 气氛下保存 20 天后求出电池容量的维持率。此外，以初期的电池容量为基准求出电池容量的维持率。

[0142] 表 5

[0143]

	电池壳					特性		
	材料	Cu (质量%)	C (质量%)	厚度 (mm)	外径 (mm)	漏液发生率(%)	内部短路发生率(%)	容量维持率(%)
实施例 1	SUS316L	0	<0.03	0.10	3.5	0	0	75
实施例 5	SUS316L	0	<0.03	0.10	6	0	0	75
实施例 6	SUS316L	0	<0.03	0.10	10	20	0	75
比较例 4	SUS316L	0	<0.03	0.10	15	60	20	60
比较例 5	SUS316L	0	<0.03	0.20	15	0	0	75
比较例 2	Fe	-	-	0.10	3.5	20	80	10
比较例 6	Fe	-	-	0.10	6	20	80	10
比较例 7	Fe	-	-	0.10	10	40	80	5
比较例 8	Fe	-	-	0.10	15	40	80	5
比较例 9	Fe	-	-	0.20	15	0	0	75

[0144] 在表 5 中通过对实施例 1、5 及 6 和比较例 4 进行比较，发现尽管电池壳 1 的材料同为 SUS316L，厚度同为 0.10mm，也有以下差别。也就是说，在电池壳 1 的外径为 15mm 的比较例 4 中，容易发生内部短路，而在其外径为 10mm 以下的实施例 1、5 及 6 中没有发生内部短路。这是基于以下的理由。也就是说，即使在电池壳 1 由强度高的 SUS316L 构成的情况下，在电池壳 1 的外径大的情况下，电池壳 1 的侧面的曲率减小，其结果是，相对于外力电池壳 1 容易变形。与此相对照，如果电池壳 1 的外径减小，则电池壳 1 的侧面的曲率增大，其结果是，相对于外力电池壳 1 难以变形。

[0145] 另一方面，在电池壳 1 的材料为铁 (Fe) 的比较例 2 及 6 ～ 8 中，内部短路发生率非常高。这是因为电池壳 1 的强度低，所以相对于外力电池壳 1 容易变形。此外，在比较例 2 及 6 ～ 8 中，由于电池壳 1 的强度低，所以容易发生漏液。另外，在比较例 2 及 6 ～ 8 中，容量维持率非常低。这是因为电池壳 1 的强度低，因而伴随着氢气的发生，电池壳 1 容易膨胀，所以密封性下降，电池特性劣化。此外，因产生了强酸即氢氟酸而使电池壳腐蚀，该腐蚀招致水分的侵入，使腐蚀的进展加速，因此认为不能维持高的电池容量。

[0146] 由这些结果得知 :为了提高电池壳 1 的强度，作为电池壳 1 的材料优选使用不锈钢。由此，不易发生内部短路。而且，除此以外，通过将电池壳 1 的外径规定为 10mm 以下，密封性及容量维持率提高，其结果是，可使电池特性的提高和长期可靠性及安全性的提高得以兼顾。再有，从比较例 5 及 9 的结果得知 :在电池壳 1 的外径大时 (大于 10mm 时)，不

管电池壳 1 的材料怎样，可以通过增加电池壳 1 的厚度来提高长期可靠性及安全性。可是，在电池壳 1 的外径小时（10mm 以下时），如果增加电池壳 1 的厚度，则内容积的下降显著，此外，利用拉深加工的密封变得困难，密封性下降。

[0147] ＜实施例 7 ＞

[0148] 作为构成电池壳 1 的材料采用 SUS316（碳含量为 0.08 质量％以下的奥氏体系不锈钢）。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 7。

[0149] 将实施例 1 及 7 的圆筒型电池分别各制作 5 个，求出这些圆筒型电池的漏液发生率及电池容量的维持率。其结果见表 6。再有，在将圆筒型电池在 85℃ -90％ RH 气氛下保存 20 天后求出电池容量的维持率。此外，以初期的电池容量为基准求出电池容量的维持率。

[0150] 表 6

[0151]

	电池壳					特性	
	材料	Cu (质量%)	C (质量%)	厚度 (mm)	外径 (mm)	漏液发生率 (%)	容量维持率 (%)
实施例 1	SUS316L	0	<0.03	0.10	3.5	0	75
实施例 7	SUS316	0	<0.08	0.10	3.5	20	55

[0152] 从表 6 所示的结果得知：在碳含量为 0.08 质量％以下的实施例 1 及 7 中，不易发生漏液，此外容量维持率也高。而且，得知碳含量更优选为 0.03 质量％以下。

[0153] 关于碳含量低的不锈钢，如表 1 所示，其延伸率高，且拉伸断裂强度高。所以，碳含量低的不锈钢具有高的加工性。也就是说，在形成电池壳 1 时，容易通过拉伸对不锈钢进行减薄加工，此外，加工精度也高。因而，能够容易且以高精度形成厚度薄的电池壳 1，其结果是，可稳定地制造具有高密封性的圆筒型电池。

[0154] 由该结果得知：构成电池壳的不锈钢优选为碳含量为 0.08 质量％以下的不锈钢，更优选为碳含量为 0.03 质量％以下的不锈钢。由此，密封性及容量维持率提高，其结果是，可使电池特性的提高和长期可靠性及安全性的提高得以兼顾。

[0155] ＜实施例 8 ＞

[0156] 在实施例 2 中，在不将负极引线 6 焊接在电池壳 1 上而仅使其接触的条件下制作圆筒型电池。其它的制作条件与实施例 2 相同。将如此制作的圆筒型电池作为实施例 8。

[0157] ＜实施例 9 ＞

[0158] 在实施例 1 中，在不将负极引线 6 焊接在电池壳 1 上而仅使其接触的条件下制作圆筒型电池。其它的制作条件与实施例 1 相同。将如此制作的圆筒型电池作为实施例 9。

[0159] 求出了实施例 8 及 9 的圆筒型电池的内部电阻。其结果见表 7。

[0160] 表 7

[0161]

	电池壳					特性
	材料	Cu (质量%)	C (质量%)	厚度 (mm)	外径 (mm)	内部电阻 (Ω)
实施例 8	SUS	3.80	<0.03	0.10	3.5	1
实施例 9	SUS316L	0	<0.03	0.10	3.5	20

[0162] 由表 7 所示的结果得知 :在只使负极引线 6 与电池壳 1 接触时,在不含铜的实施例 9 中内部电阻显著增高,而在含铜的实施例 8 中,内部电阻显著减小。也就是说,通过使铜混合在奥氏体系不锈钢中,不锈钢表面的接触电阻下降。

[0163] 这是依据以下的理由。也就是说,通常在不锈钢表面上形成用于提高耐酸腐蚀性的保护层,在不锈钢不含铜的情况下,该保护层成为接触电阻增大的原因。另一方面,通过在不锈钢中含铜,保护层的电阻减小,其结果是使接触电阻减小。

[0164] 因而,通过使铜混合在构成电池壳 1 的不锈钢中,可将电池壳 1 和负极引线 6 的焊接省略。此外,在将负极引线 6 焊接在电池壳 1 上的圆筒型电池 (实施例 2) 中,例如即使在使用中该焊接断裂的情况下,只要负极引线 6 与电池壳 1 接触,也能维持内部电阻低的状态。

[0165] 尽管基于目前优选的实施方式描述了本发明,但是应理解的是这些内容不解释为限制性的解释。毫无疑问,各种改变和改进对本发明所属技术领域的本领域技术人员来说在阅读了上面内容之后是显而易见的。因此,希望将所附的权利要求书解释为覆盖属于本发明的真正精神和范围内的所有改变和改进。

[0166] 产业上的利用可能性

[0167] 本发明的圆筒型电池能够在移动式数字设备等各式各样的电子设备中作为其电源使用。

[0168] 符号说明

[0169] 1－电池壳,2－负极板,3－正极板,4－隔膜,5－电极组,6－负极引线,7－正极引线,8－封口部件,9－垫圈,10－中间部件,11－圆板。

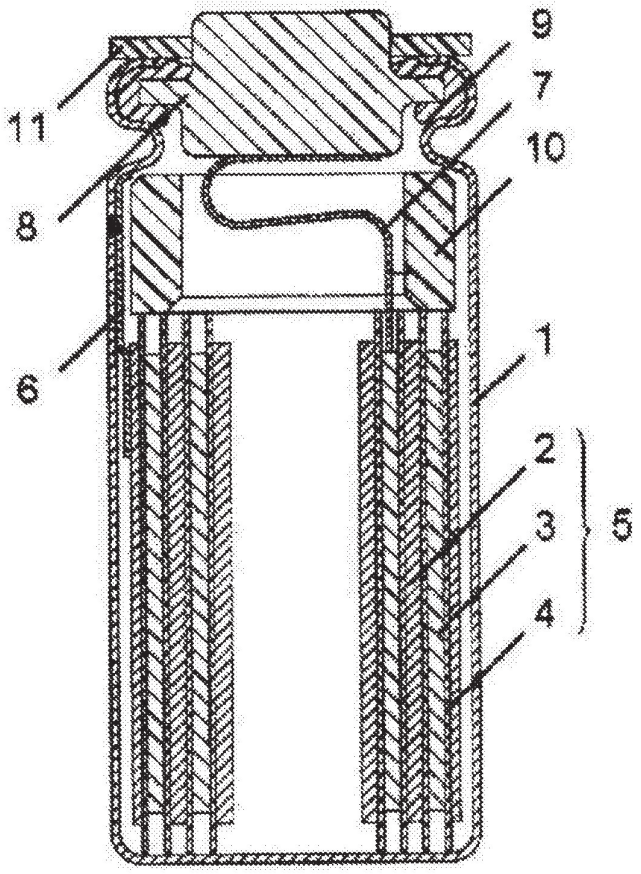


图 1