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(54) **CYLINDRICAL NON-AQUEOUS ELECTROLYTE SECONDARY CELL**

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(57) **ABSTRACT**

Provided is a secondary battery in which corrosion of an exterior body is stably suppressed. A non-aqueous electrolyte secondary battery according to an embodiment of the present disclosure comprises: an exterior body having a bottomed cylindrical shape and having a grooving portion in an opening portion; an electrode body and a non-aqueous electrolyte housed in the exterior body; and a sealing body caulked and fixed between the grooving portion and an opening end in the opening, wherein in a portion from the grooving portion of the inner surface of the exterior body to the open end portion, a powder of at least one among compounds selected from the group consisting of hydroxides, oxides, and carbonates is present.

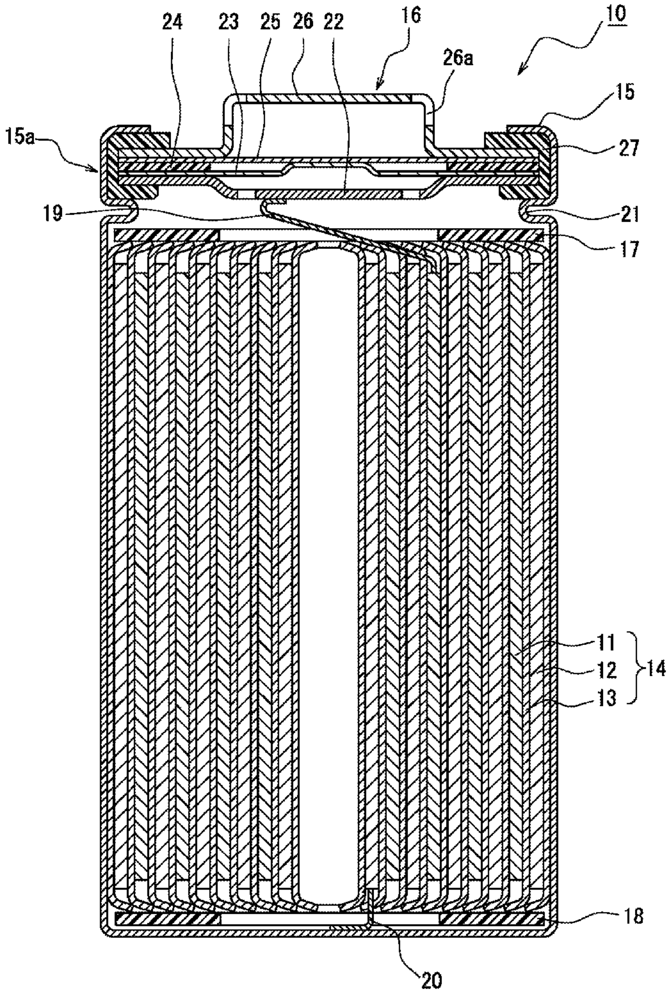


Figure 1

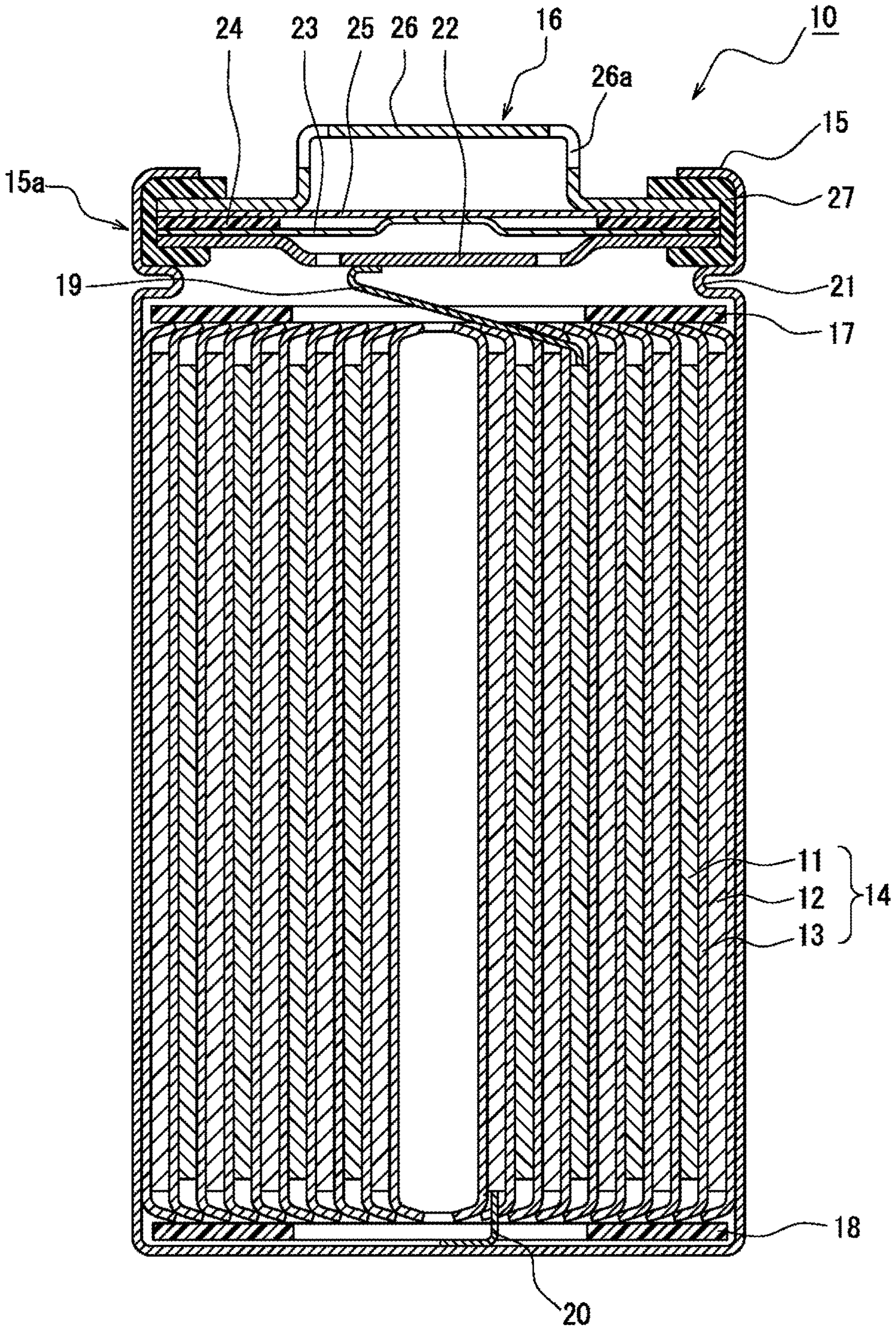
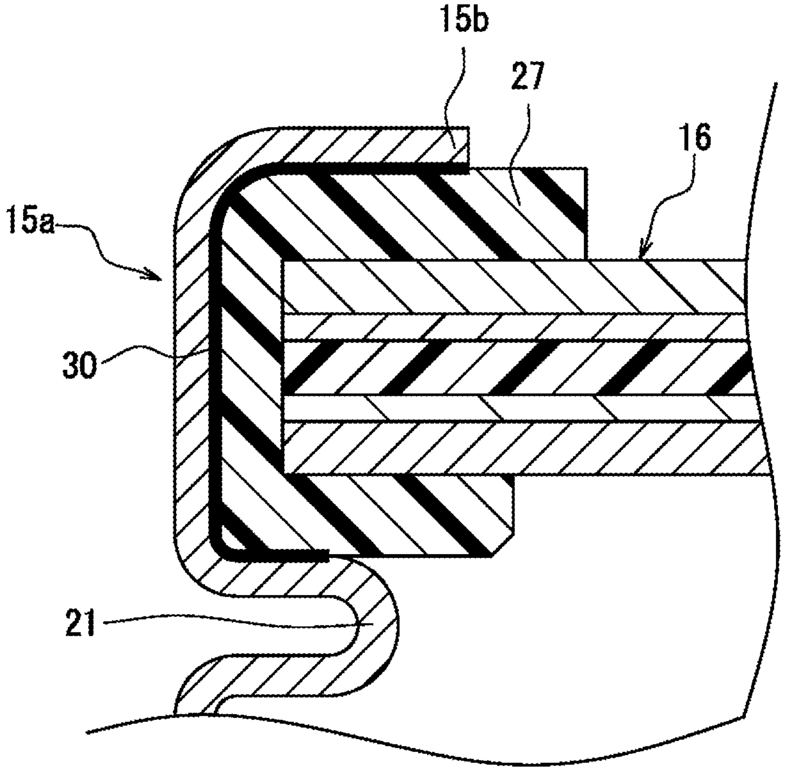


Figure 2



CYLINDRICAL NON-AQUEOUS ELECTROLYTE SECONDARY CELL

TECHNICAL FIELD

[0001] The present disclosure relates to a cylindrical non-aqueous electrolyte secondary battery.

BACKGROUND

[0002] A cylindrical non-aqueous electrolyte secondary battery includes a cylindrical outer housing having a bottom, which contains an electrode assembly and a non-aqueous electrolyte. The interior of the battery is sealed with a sealing structure caulked and fixed between a groove portion and an open end in an opening portion of the outer housing. During production of such batteries, the non-aqueous electrolyte injected into the outer housing may remain adhered to the opening portion of the outer housing. The non-aqueous electrolyte remaining in a region of the outer housing above the groove portion where the sealing structure is to be caulked and fixed may react with water entering externally to generate hydrogen fluoride, resulting in corrosion of the outer housing. Patent Document 1 discloses a technique of enhancing airtightness of a battery by applying a sealant including an alkaline compound having an amino group in pitches to a region of an inner surface of the outer housing located above the groove portion.

CITATION LIST

Patent Literature

SUMMARY

Technical Problem

[0003] The technique disclosed in Patent Document 1, however, has a problem in that an alkaline compound such as butylamine is likely to volatilize and would not provide stable advantages, leaving plenty of room for improvement.

[0004] The present disclosures is therefore aimed toward providing a secondary battery that enables reliable inhibition of corrosion of the outer housing.

Solution to Problem

[0005] In accordance with one aspect of the present disclosure, a non-aqueous electrolyte secondary battery includes a cylindrical outer housing having a bottom, the outer housing including an opening portion having a groove portion, an electrode assembly and a non-aqueous electrolyte contained in the outer housing, and a sealing structure caulked and fixed between the groove portion and an opening end in the opening portion. A region of an inner surface of the outer housing between the groove portion and the opening end includes powder of one or more compounds selected from a group consisting of hydroxide, oxide, and carbonate.

Advantageous Effects

[0006] The non-aqueous electrolyte secondary battery according to the present disclosure enables stable inhibition of corrosion of the outer housing.

BRIEF DESCRIPTION OF DRAWINGS

[0007] FIG. **1** is a vertical cross sectional view of an example cylindrical non-aqueous electrolyte secondary battery of an embodiment.

[0008] FIG. **2** is an enlarged view of a region in the vicinity of an opening portion of the outer housing in FIG. **1**.

DESCRIPTION OF EMBODIMENTS

[0009] A cylindrical secondary battery according to an example embodiment of the present disclosure will be described by reference to the drawings. In the following description, specific shapes, materials, numerical values, directions, and the like are examples for facilitating understanding of the present invention, and may be modified as appropriate in accordance with specifications of the cylindrical secondary battery. It is further assumed that features of a plurality of embodiments and modification examples included in the following description may be used in appropriate combinations.

[0010] FIG. **1** is a vertical cross sectional view of a secondary battery **10** according to an example embodiment. The secondary battery **10** illustrated in FIG. **1** includes an outer housing **15** containing an electrode assembly **14** and a non-aqueous electrolyte (not shown). In the following, for convenience of explanation, a direction toward a sealing structure **16** indicates “upward” directed to a top and a direction toward the bottom of the outer housing **15** indicates “downward” directed to a bottom.

[0011] The electrode assembly **14** has a rolled structure including a positive electrode **11** and a negative electrode **12** wound with a separator **13** between the positive electrode **11** and the negative electrode **12**. The positive electrode **11** includes a belt-shape positive electrode current collector and positive electrode mixture layers disposed on respective opposite sides of the positive electrode current collector. The positive electrode current collector may be a metal foil such as aluminum or a film having such a metal disposed on a top layer, for example.

[0012] The positive electrode mixture layer is produced by, for example, applying a positive electrode mixture slurry including a positive electrode active material, a conductive agent, a binder material, and a solvent such as N-methyl-2-pyrrolidone (NMP), on the respective opposite sides of the positive electrode current collector and thereafter drying and compressing the applied membranes. Examples of the positive electrode active material include a lithium transition metal composite oxide containing a transition metal element such as Co, Mn, or Ni. Examples of the conductive agent include a carbon material, such as carbon black (CB), acetylene black (AB), Ketjenblack, and graphite. Examples of the binding material include a fluorine-containing resin, such as polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVdF), a polyacrylonitrile (PAN), polyimide (PI), acrylic resin, and polyolefin, for example.

[0013] The negative electrode **12** includes a belt-shape negative electrode current collector and negative electrode mixture layers disposed on respective opposite sides of the negative electrode current collector. The negative electrode current collector may be a metal foil such as copper or a film having such a metal disposed on a top layer, for example.

[0014] The negative electrode mixture layer is produced by applying a negative electrode mixture slurry including a negative electrode active material, a binder material, and water, for example, on the respective opposite sides of the negative electrode current collector and thereafter drying and compressing the applied membranes. Examples of the negative electrode active material include a carbon material such as natural graphite or artificial graphite, a metal such as Si or Sn which forms an alloy with Li, and an alloy or oxide containing these metals. Examples of the binder include styrene-butadiene rubber (SBR), CMC or its salt, polyacrylic acid or its salt, and polyvinyl alcohol, for example.

[0015] The separator **13** may be an ion-permeable and insulating porous sheet, for example. Specific examples of the porous sheet include a microporous thin film, woven fabric, and non-woven fabric. Suitable examples of the material for the separator **13** include an olefin resin such as polyethylene and polypropylene.

[0016] A non-aqueous solvent (organic solvent) of the non-aqueous electrolyte contained in the outer housing **15** may be carbonates, lactones, ethers, or ketones, for example, and may be mixtures of two or more of these solvents. The mixtures of two or more solvents preferably include mixture solvents of cyclic carbonates and chain carbonates. For example, the cyclic carbonate may include ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC). The chain carbonate may include dimethyl carbonate (DMC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC), for example. An electrolyte salt of the non-aqueous electrolyte may be $LiPF_6$, $LiBF_4$, or $LiCF_3SO_3$, for example, and mixtures thereof. The dissolution amount of the electrolyte salt with respect to the non-aqueous solvent is 0.5 to 2.0 mol/L, for example.

[0017] The sealing structure **16** seals the opening portion of the outer housing **15** to thereby hermetically seal the interior of the secondary battery **10**. Insulating plates **17** and **18** are disposed on top and bottom of the electrode assembly **14**, respectively. A positive electrode lead **19** extends upward through a through hole of the insulating plate **17** and is welded to an undersurface of a filter **22** that is a bottom plate of the sealing structure **16**. The secondary battery **10** includes, as a positive electrode terminal, a cap **26** that is a top plate of the sealing structure **16** electrically connected with the filter **22**. A negative electrode lead **20** extends toward the bottom of the outer housing **15** thorough a through hole of the insulating plate **18** and is welded to a bottom inner face of the outer housing **15**. The outer housing **15** in the secondary battery **10** functions as a negative electrode terminal.

[0018] The outer housing **15** is cylindrical with a bottom, and has an opening portion **15*a*** having a groove portion **21**. The outer housing **15** is made of a metal, for example. The groove portion **21** supports the sealing structure **16** with its top face. The outer housing **15** contains the electrode assembly **14** and the non-aqueous electrolyte in a region under the groove portion **21**. The groove portion **21** is preferably present annularly along the circumference of the outer housing **15**. The groove portion **21** may be formed by externally pressing side faces of the outer housing **15**, for example.

[0019] The sealing structure **16** includes a filter **22**, a lower vent member **23**, an insulating member **24**, an upper vent member **25**, and the cap **26** stacked in sequence from the side of the sealing structure **16** close to the electrode assembly **14**. These members forming the sealing structure **16** each have a disc shape or an annular shape and the members other than the insulating member **24** are electrically connected with each other. The lower vent member **23** and the upper vent member **25** are connected with each other at their center portions, and the insulating member **24** is disposed between the lower vent member **23** and the upper vent member **25** at their edge portions. An increase in the internal pressure of the battery caused by abnormal heating, for example, ruptures the lower vent member **23**. This causes the upper vent member **25** to expand toward the cap **26** and separate from the lower vent member **23**, thereby interrupting electrical connection between the upper vent member **25** and the lower vent member **23**. Further increase in the internal pressure causes the upper vent member **25** to rupture to allow a gas to discharge from an opening **26*a*** of the cap **26**.

[0020] Referring now to FIG. **2**, hermetical sealing in the opening portion **15*a*** of the secondary battery **10** will be described. FIG. **2** is an enlarged view of a region near the opening portion **15*a*** of the outer housing **15**.

[0021] The sealing structure **16** is fixed, by caulking, between the groove portion **21** and an opening end **15*b*** in the opening portion **15*a*** of the outer housing **15**. More specifically, the sealing structure **16** is compressed and fixed between the groove portion **21** and the opening end **15*b*** that is an inwardly-bent upper end of the outer housing **15**, via a gasket **27**. The gasket **27** is a flexible insulating member, and electrically isolates the sealing structure **16** that is a positive electrode terminal and the outer housing **15** that is a negative electrode terminal from each other. The gasket **27** is compressed vertically to secure airtightness or hermetical sealing within the secondary battery **10**. Any compressible insulating material, such as polypropylene (PP), polyphenylene sulfide (PPS), a polyethylene (PE), polybutylene terephthalate (PBT), perfluoroalkoxyalkane (PFA), polytetrafluoroethylene (PTFE), and polyamide (PA), may be used as a material for the gasket **27**.

[0022] Powder of one or more compounds selected from a group consisting of hydroxide, oxide, and carbonate (hereinafter referred to as a "compound" or "compounds") is present in a region of the inner face of the outer housing **15** between the groove portion **21** and the opening end **15*b*** (hereinafter referred to as an "opening upper region" **30**). This allows hydrogen fluoride generated by reaction of a non-aqueous electrolyte adhered to the inner face of the opening portion **15*a*** with water entering from the opening end **15*b***, to be neutralized with the compounds present in the opening upper region **30**, thereby inhibiting corrosion of the outer housing **15**. Also, the compounds, which do not volatilize for a long preservation period, can reliably inhibit corrosion of the outer housing.

[0023] The ratio of (molecular weight)/(sum of the number of valences of cation) in the compound is preferably 60 or less. This can reduce the required amount (mass) of the compounds present in the opening upper region **30**. Here, the sum of the number of valences of cation refers to summation of the number of valences of all cations forming the compound. For example, the sum of the number of valences of cations in Al_2O_3, which includes two Al^{3+}'s, equals to six.

[0024] The compound preferably includes any of aluminum hydroxide ($Al(OH)_3$), magnesium hydroxide ($Mg(OH)_2$), aluminum oxide (Al_2O_3), magnesium oxide (MgO). lithium carbonate (Li_2CO_3), or sodium carbonate (Na_2CO_3). These have low volatility and low toxicity, and are therefore suitable for use in the secondary battery **10**. In particular, the compound preferably includes $Al(OH)_3$ or $Mg(OH)_2$, which has a small specific gravity and, as will be described below, does not cause sedimentation during production of a coating solution including the compound and is easy to handle.

[0025] The required amount of the compound present in the opening upper region **30** is computable by estimation of the amount of hydrogen fluoride to be generated based on the amount of the non-aqueous electrolyte assumed to be adhered to the opening portion **15***a* of the outer housing **15**. In the outer housing **15** having a cylindrical shape with a bottom, with a diameter φ of 18 mm and a height of 65 mm, for example, presence of 0.5 mg to 40 mg of the compound, more preferably 1 mg to 20 mg of the compound, and particularly preferably 3 mg to 14 mg of the compound, in the opening portion can neutralize hydrogen fluoride to thereby inhibit corrosion of the outer housing **15**.

[0026] To allow the compound to be present in the opening upper region **30**, a coating solution including the compound may be applied to the opening upper region **30**. The coating solution is produced by mixing the compound in a solvent which may be xylene, ethylbenzene, or toluene, for example. Further, as an additive to the coating solution, rubber-based polymer represented by 1,2-polybutadiene that is conventionally used as a sealant, pitch, asphalt, or vinyl polymer, silicon-based polymer, acrylic polymer, urethane polymer, and fluorocarbon polymer or combinations of two or more of these substances may be used. The ratio of the compound in the coating solution is preferably 0.5 mass % to 20 mass %, more preferably 1 mass % to 10 mass %, and particularly preferably 3 mass % to 7 mass %, for example. These ranges enable appropriate application of the coating solution to the opening upper region **30**. A particularly preferable ratio of the compound in the coating solution is approximately 5 weight % in terms of viscosity, sedimentation, and an application amount, and also in view of enhancement of operability. After application of the coating solution, a heating treatment may be applied to dry the coating solution. The heating treatment can be performed at 100° C. to 200° C. for 30 to 300 minutes.

[0027] An example method of producing the secondary battery **10** will be described. First, the insulating plates **17** and **18** are respectively placed on top and bottom of the electrode assembly **14** and the assembly is housed in the outer housing **15**. The negative electrode lead **20** is then welded to the bottom of the outer housing **15**. The groove portion **21** is formed in the opening portion **15***a* of the outer housing **15** by pressing, and thereafter, a coating solution is applied to a region of the opening portion **15***a* above the groove portion **21**. After leaving the assembly in this state for 30 minutes at room temperatures, the gasket **27** is placed above the groove portion **21**. Thereafter, the sealing structure **16** is welded to the positive electrode lead **19** and heating treatment is performed at 110° C. for 150 minutes. An appropriate amount of non-aqueous electrolyte is further injected into the outer housing **15**. Then, the sealing structure **16** is caulked and fixed between the opening end **15***b* of the outer housing **15** and the groove portion **21**, via the gasket **27**, thereby producing a cylindrical non-aqueous electrolyte secondary battery.

EXAMPLES

[0028] Examples of the present disclosure will be described below; however, the present disclosure is not limited to these examples.

Example 1

[Production of Positive Electrode]

[0029] Lithium cobalt oxide expressed as $LiCoO_2$ was used as a positive electrode active material. First, 100 parts by mass of the positive electrode active material, 1 part by mass of acetylene black (AB) or a conductive agent, and 1 part by mass of polyvinylidene fluoride (PVDF) or a binder were mixed. An appropriate amount of N-methyl-2-pyrrolidone (NMP) was further added to the mixture to prepare a positive electrode mixture slurry. Then, the positive electrode mixture slurry was applied to the opposite sides of a positive electrode current collector made of an aluminum foil. The resulting positive electrode current collector was then dried in a drier, and thereafter cut into a predetermined electrode size and rolled with a roller to form a positive electrode in a belt shape. Further, a blank portion free of an active material was formed at one end of the positive electrode in the longitudinal direction and an aluminum positive electrode lead was fixed to the blank portion by ultrasonic welding.

[Production of Negative Electrode]

[0030] Natural graphite powder was used for a negative electrode active material. First, 100 parts by mass of the negative electrode active material, 1 part by mass of styrene-butadiene rubber (SBR) or a binder, and 1 part by mass of carboxymethylcellulose (CMC) or a thickener were mixed, and an appropriate amount of water was further added to the mixture to prepare a negative electrode mixture slurry. Then, the negative electrode mixture slurry was applied to the opposite sides of a negative electrode current collector made of a copper foil. The resulting negative electrode collector was then dried in a drier, and thereafter cut into a predetermined electrode size and rolled with a roller to form a positive electrode in a belt shape. Further, a blank portion free of an active material was formed at one end of the negative electrode in the longitudinal direction and an aluminum positive electrode lead was fixed to the blank portion by ultrasonic welding.

[Production of Electrode Assembly]

[0031] The positive electrode and the negative electrode that were produced were wound via a separator into a scroll to produce a wound electrode assembly. At this time, an end of the positive electrode to which a positive electrode lead is connected was positioned close to the inner circumference (winding start) and an end of the negative electrode to which a negative electrode lead is connected was positioned close to the outer circumference (wining end). The separator that was used includes a heat-resisting layer having a dispersed filler of polyamide and alumina disposed on one side of a polyethylene porous film.

[Preparation of Non-Aqueous Electrolytic Solution]

[0032] Ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) were mixed at a volume ratio of EC:EMC:DMC=3:3:4, to form a mixture solvent, and 1 mol/L of $LiPF_6$ was added to the mixture solvent to prepare a non-aqueous electrolytic solution.

[Preparation of Coating Solution]

[0033] A coating solution was prepared by mixing a solvent containing 90 g of xylene and 5 g of 1,2-polybutadiene with 5 g of aluminum hydroxide ($Al(OH)_3$) powder.

[Production of Secondary Battery]

[0034] A cylindrical metal can having a diameter φ 18 mm and a height of 65 mm was used as an outer housing. An electrode assembly having insulating plates on top and bottom respectively was stored in the outer housing, and thereafter the negative electrode lead was welded to the bottom of the outer housing. A groove portion was then formed in an opening portion of the outer housing by pressing and thereafter the coating solution was applied to a region of the opening portion above the groove portion. After leaving the coating solution for 30 minutes at room temperature, a gasket was placed above the groove portion. A sealing structure was then welded to the positive electrode lead, and a heating treatment was performed at 110° C. for 150 minutes, and 6.5 g of the non-aqueous electrolyte was injected into the outer housing. Thereafter, the opening portion of the outer housing was sealed with the sealing structure by caulking via the gasket, thereby producing the cylindrical non-aqueous electrolyte secondary battery. The produced secondary battery bad nominal voltage of 4.2 V and rated capacity of 1950 mAh. Five secondary batteries were produced in this manner.

Example 2

[0035] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using magnesium hydroxide ($Mg(OH)_2$) powder in place of $Al(OH)_3$ powder.

Example 3

[0036] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using aluminum oxide (Al_2O_3) powder in place of $Al(OH)_3$ powder.

Example 4

[0037] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using magnesium oxide (MgO) powder in place of $Al(OH)_3$ powder.

Example 5

[0038] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using lithium carbonate (Li_2CO_3) powder in place of $Al(OH)_3$ powder.

Example 6

[0039] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using sodium carbonate (Na_2CO_3) powder in place of $Al(OH)_3$ powder.

Comparative Example 1

[0040] A battery was produced in a manner similar to Example 1 except that, in applying a compound to the outer housing, the coating solution was prepared only with a mixture of 95 g of xylene and 5 g of polybutadiene, and without mixing $Al(OH)_3$ powder in the coating solution.

Comparative Example 2

[0041] A battery was produced in a manner similar to Example 1 except that, to apply a compound to the outer housing, the coating solution was prepared using a mixture 10 g of butylamine ($C_4H_{11}N$) liquid in place of the $Al(OH)_3$ powder, 85 g of xylene, and 5 g of polybutadiene.

[Evaluation of Corrosion Occurrence by Accelerated Test]

[0042] The batteries in Examples and Comparative Examples were charged with constant. current of 0.3 C at the temperature of 25° C. until the battery voltage reached 4.2 V, and then charged with constant voltage of 4.2 V until the current value reached 0.02 C. Thereafter, the batteries were left for 30 days at the temperature of 75° C. and the humidity of 90%, and then an accelerated fest for corrosion of the outer housing was performed. An X-ray Computed Tomography (CT) device was used to perform 360° tomographic observation of the batteries after the accelerated fest and occurrence of corrosion of the outer housing in a region above the groove portion was checked. Evaluation was based on the number of batteries in which corrosion occurred.

[0043] Evaluation results for Examples and Comparative Examples are shown in Table 1. Table 1 further shows the type of mixed compound, and the molecular weight, the total number of valences of cation, and the (molecular weight)/(total number of valences of cation) of the compound.

TABLE 1

	COMPOUND				
	TYPE	MOLECULAR WEIGHT	TOTAL NUMBER OF VALENCES OF CATION	MOLECULAR WEIGHT/TOTAL NUMBER OF VALENCES OF CATION	EVALUATION NUMBER OF OCCURRENCE OF CORROSION
EXAMPLE 1	$Al(OH)_3$	78	3	26	0/5
EXAMPLE 2	$Mg(OH)_2$	58.3	2	29.2	0/5
EXAMPLE 3	Al_2O_3	102	6	17	0/5
EXAMPLE 4	MgO	40.3	2	20.2	0/5
EXAMPLE 5	Li_2CO_3	73.8	2	36.9	0/5
EXAMPLE 6	Na_2CO_3	106	2	53	0/5
COMPARATIVE EXAMPLE 1	—	—	—	—	5/5

TABLE 1-continued

	COMPOUND				
	TYPE	MOLECULAR WEIGHT	TOTAL NUMBER OF VALENCES OF CATION	MOLECULAR WEIGHT/TOTAL NUMBER OF VALENCES OF CATION	EVALUATION NUMBER OF OCCURRENCE OF CORROSION
COMPARATIVE EXAMPLE 2	$C_4H_{11}N$	73	1	73	5/5

[0044] Corrosion occurred in all of the batteries in Comparative Examples 1 and 2, whereas no corrosion occurred in the batteries in Examples 1 to 6. In Comparative Example 2, 10 mass % of compound ($C_4H_{11}N$) in the coating solution had no advantageous effects, whereas in Examples 1 to 6, inclusion of 5 mass %, which is a half of 10 mass %, of a compound had advantageous effects. It is assumed that in Comparative Example 2, sufficient neutralization of hydrogen fluoride was not possible with this amount of $C_4H_{11}N$ for the following reason. In Comparative Example 2, $C_4H_{11}N$ indicates univalent alkaline property by coordinate bond of one proton to an amino group; however as $C_4H_{11}N$ has a large molecular weight, a greater amount of the compound was required for neutralization of hydrogen fluoride and its volatility also decreased the addition amount.

REFERENCE SIGNS LIST

[0045] **10** secondary battery, **11** positive electrode, **12** negative electrode, **13** separator, **14** electrode assembly, **15** outer housing, **15***a* opening portion, **15***b* opening end, **16** sealing structure, **17**, **18** insulating plate, **19** positive electrode lead, **20** negative electrode lead, **21** groove portion, **22** filter, **23** lower vent member, **24** insulating member, **25** upper vent member, **26** cap, **26***a* opening, **27** gasket, **30** opening upper region.

1. A cylindrical non-aqueous electrolyte secondary battery comprising:

a cylindrical outer housing having a bottom, the outer housing including an opening portion having a groove portion;

an electrode assembly and a non-aqueous electrolyte contained in the outer housing; and

a sealing structure caulked and fixed between the groove portion and an opening end in the opening portion, wherein

a region of an inner surface of the outer housing between the groove portion and the opening end includes powder of one or more compounds selected from a group consisting of hydroxide, oxide, and carbonate.

2. The cylindrical non-aqueous electrolyte secondary battery according to claim **1**, wherein

(molecular weight)/(total number of valences of cation) of the compounds is less than or equal to 60.

3. The cylindrical non-aqueous electrolyte secondary battery according to claim **1**, wherein

the compounds comprise any of aluminum hydroxide, magnesium hydroxide, aluminum oxide, magnesium oxide, lithium carbonate, or sodium carbonate.

* * * * *