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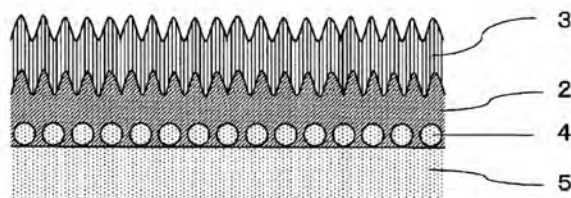
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(54) Method for manufacturing secondary battery negative electrode, copper foil for electrode, secondary battery and negative electrode for secondary battery

(57) Abstract

The purpose of the present invention is to provide a negative electrode for a non-aqueous solvent electrolyte secondary battery that can achieve high capacity during charging and discharging and suppress decline in capacity even through repeated cycles. This is a negative electrode for a secondary battery in which a Si-based negative electrode active material film of a predetermined thickness containing hydrogenated silicone with a predetermined hydrogen concentration is formed on a current collector substrate having a predetermined surface. In addition, it is a negative electrode for a secondary battery in which a Si-based negative electrode active material film with a predetermined surface shape is formed on a current collector substrate with a predetermined surface shape by a predetermined method. Furthermore, it is a negative electrode for a secondary battery in which a Si-based negative electrode active material film with a predetermined reciprocal electric double layer capacity is formed on a current collector substrate by a predetermined method.

Representative Figure - Figure 3



(30)	Priority Claim		
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Scope of Patent Claim

Claim 1

A negative electrode for a non-aqueous electrolyte secondary battery characterized by a negative electrode for non-aqueous electrolyte secondary batteries in which a silicone-based active material film is formed on the rough surface of a current collector substrate using copper foil having a rough surface with a surface roughness (Rz) (JIS B0601-1994 ten-point average roughness) specified in Japanese Industrial Standards of 1 μm or more,

a silicone-based active material film of 1 to 18 g/m² is formed on the rough surface of one or both sides of the current collector substrate, and the active material film includes hydrogenated silicone,

and the hydrogen content of the entire active material film is 0.1 atomic % or more and 30 atomic % or less.

Claim 2

A negative electrode for a non-aqueous electrolyte secondary battery characterized by a negative electrode for a non-aqueous electrolyte secondary battery in which a silicone-based active material film is formed on one or both sides of a current collector substrate using copper foil with a rough surface,

the thickness of the silicone-based active material film is 0.5 μm or more and 6 μm or less,

the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the surface of the silicone-based active material film is 2 μm or more and 20 μm or less,

the 3-point average value of S (JIS B0601-1994 average spacing of local calculations) on the surface of the silicone-based active material film is 0.005 mm or more and 0.014 mm or less,

and the 3-point average value of Sm (JIS B0601-1994 average spacing of unevenness) of the surface of the silicone-based active material film is 0.015 mm or more and 0.040 mm or less.

Claim 3

According to Claim 2, a negative electrode for a secondary battery characterized wherein the current collector substrate has at least a non-smooth or non-glossy surface on which the active material film is formed,

the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the surface on which the active material film is formed of the current collector substrate is 2 μm or more and 20 μm or less,

the S (average spacing of JIS B0601-1994 local calculations) of the active material film formation surface of the current collector substrate is 0.004 mm or more and 0.015 mm or less,

and the Sm (JIS B0601-1994 average spacing of irregularities) of the active material film formation surface of the current collector substrate is 0.015 mm or more and 0.035 mm or less.

Claim 4

A negative electrode for a non-aqueous electrolyte secondary battery characterized by a negative electrode for a non-aqueous electrolyte secondary battery in which a silicone-based active material film is formed on one or both sides of a current collector substrate using copper foil,

a silicone-based active material film of 1 to 14 g/m² is formed on the current collector substrate,

and the reciprocal of the electric double layer capacity of the negative electrode surface on which the silicone-based active material film is formed is 0.1 to 3 cm²/μF.

Claim 5

According to Claim 4, a negative electrode for a secondary battery characterized wherein the surface on which the active material film is formed of the current collector substrate is a non-flat surface or a non-glossy surface,

the active material film-forming surface of the current collector substrate has a rough surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of 1.5 μm or more,

and the reciprocal of the electric double layer capacity of the active material film formation surface of the current collector substrate is 0.03 to 0.1 cm²/μF.

Claim 6

According to any one of Claims 1, 2, and 4, a negative electrode for a secondary battery, characterized in that one or more silicone layers containing phosphorus or boron are formed between the current collector substrate

and the silicone-based active material film or on at least one upper layer of the silicone-based active material film.

Claim 7

According to any one of Claims 1, 2, and 4, a negative electrode for a secondary battery, characterized in that the silicone-based active material film contains phosphorus, and the phosphorus content of the entire active material film is 0.1 atomic % or more and 30 atomic % or less.

Claim 8

According to Claim 7, a negative electrode for a secondary battery characterized in that the silicone-based active material film further contains oxygen, and the oxygen content of the entire active material film is 1 atomic % or more and 50 atomic % or less.

Claim 9

According to any one of Claims 1, 2, and 4, a negative electrode for a secondary battery characterized in that a heat-resistant layer or a heat-resistant barrier film is formed on the surface of the current collector substrate on which the active material film is formed, at least one of a layer containing 0.01 to 0.5 g/m² of nickel or a layer containing 0.001 to 0.1 g/m² of zinc.

Claim 10

According to Claim 9, a negative electrode for a secondary battery, characterized in that a rust-prevention layer and/or a silane coupling treatment layer are further formed on the heat-resistant layer or the upper layer of the heat-resistant barrier film.

Claim 11

According to Claim 9, a negative electrode for a secondary battery, characterized in that the zinc in the heat-resistant layer or the heat-resistant barrier film exists as single-layer zinc.

Claim 12

According to Claim 9, a negative electrode for a secondary battery, characterized in that the zinc in the heat-resistant layer or the heat-resistant barrier film is diffused into a current collector substrate or a nickel layer.

Claim 13

A copper foil for electrodes characterized in that it is used in the negative electrode for a secondary battery according to any one of Claims 1, 2, and 4, and has a rough surface with a surface roughness (Rz) of 1 μm or more and 20 μm or less as specified in the Japanese Industrial Standards (JIS B0601-1994 10-point average roughness).

Claim 14

A secondary battery using a non-aqueous electrolyte solution, characterized in that it uses the negative electrode according to any one of Claims 1, 2, and 4.

Claim 15

According to Claim 14, a secondary battery, characterized in that the non-aqueous electrolyte solution contains a non-aqueous solvent containing fluorine.

Claim 16

A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized in that copper foil having a rough surface roughness (Rz) (JIS B0601-1994 ten-point average roughness) specified in Japanese Industrial Standards of 1 μm or more is used, with a process of continuously introducing a current collector substrate with an elongation of 5% or more at a temperature of 180°C into a film production room where silane gas and hydrogen gas are supplied within a supply concentration ratio [H₂]/[SiH₄] of 0 to 100,

and by the CVD method maintaining the temperature of the current collector substrate within the range of 100°C to 350°C, provides a process of continuously forming a silicone-based active material layer containing 0.1 atomic % or more and 30 atomic % or less hydrogen on one or both sides of the continuously introduced current collector substrate.

Claim 17

A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized in that there is a process of forming a silicone-based active material film by CVD (chemical vapor growth) or EB (electron beam) deposition on one or both sides of a current collector substrate using copper foil having a rough surface,

the thickness of the silicone-based active material film is 0.5 μm or more and 6 μm or less,

the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the surface of the silicone-based active material film

is 2 μm or more and 20 μm or less,

the 3-point average value of S (JIS B0601-1994 average spacing of local calculations) on the surface of the silicone-based active material film is 0.005 mm or more and 0.014 mm or less,

and the 3-point average value of S_m (JIS B0601-1994 average spacing of unevenness) of the surface of the silicone-based active material film is 0.015 mm or more and 0.040 mm or less.

Claim 18

A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized in that there is a process of forming a silicone-based active material film of 1 to 14 g/m² by CVD (chemical vapor growth) or EB (electron beam) deposition on one or both sides of a current collector substrate using copper foil having a rough surface,

and the reciprocal of the electric double layer capacity of the negative electrode surface on which the silicone-based active material film is formed is 0.1 to 3 cm²/μF.

Claim 19

According to any one of Claims 16 to 18, a method of manufacturing a negative electrode for a secondary battery characterized in that in the CVD method, phosphine gas is further continuously supplied

and a silicone-based active material film containing phosphorus is formed in the above-described process of forming a silicone-based active material film.

Claim 20

According to any one of Claims 16 to 18, a method of manufacturing a negative electrode for a secondary battery characterized in that after the process of forming the silicone-based active material film, further comprising a step of introducing oxygen into the silicone-based active material film by atmospheric oxidation or heat treatment.

Specification

Technical Field

[0001]

The present invention relates to secondary batteries, and in particular to lithium ion secondary batteries using a non-aqueous electrolyte solution, a negative electrode used therein, a method of manufacturing the same, and copper foil for a negative electrode.

Background of Technology

[0002]

Recently, with the mobility and high functionality of electronic devices, secondary batteries, which are the driving power source, are becoming one of the most important components. In particular, lithium (Li) ion secondary batteries are occupying the mainstream position of secondary batteries, replacing conventional NiCd batteries and Ni hydrogen batteries, due to the high energy density obtained from the high voltage of the positive and negative electrode active materials used. However, Li-ion secondary batteries based on a combination of lithium cobalt oxide (LiCoO₂)-based positive electrode active material and graphite-based carbon negative electrode active material, which are standard in current Li-ion batteries, are unable to supply enough power for a long time to meet the power consumption of today's high-performance, high-load electronic components, and therefore do not meet the performance requirements for mobile power sources. The theoretical electrochemical specific capacity of negative electrode active materials is generally small, and even if it is a material intended for future practical use, it remains at a value smaller than the theoretical specific capacity of current carbon-based positive electrode active materials.

[0003]

In addition, carbon-based negative electrodes, whose performance has been improved every year, are also reaching the limit of their theoretical specific capacity, and a significant improvement in power capacity can no longer be expected with the combination of negative and positive active materials currently used. That is why, in the future, there will be limits to the demand for additional electronic devices to be highly functional and portable for a long time, and to be installed in industrial applications such as power tools, uninterruptible power supplies, power storage devices, and electric vehicles.

[0004] In such a situation, as a method that can dramatically increase electric capacity compared to current conditions, studies are being conducted to apply metal-based negative electrode active materials instead of carbon (C)-based negative electrode active materials. This uses germanium (Ge), tin (Sn), or silicone (Si)-based materials as the negative electrode active material, which have a theoretical specific capacity several to ten times that of the current C-based negative electrode, and in particular, Si is the focus of studies because it has a specific capacity comparable to that of metal Li, which is known to be difficult to put into practical use.

[0005] However, the basic performance required for a secondary battery is to have a large electric capacity that can be held by charging, and to maintain the size of this electric capacity as much as possible even through a use cycle of repeated charging and discharging. Even if the initial charge capacity is large, if the chargeable capacity or dischargeable capacity immediately decreases due to repeated charging and discharging, the lifespan is shortened and the value of use as a secondary battery is low. However, the problem with metal negative electrodes including Si is that the charge/discharge cycle life is short. The reason for this is that the adhesion between the current collector and the active material is low, and as a countermeasure against this, the shape of the surface of the current collector is defined, or a configuration in which the current collector components are diffused or alloyed in the active material film is used (For example, refer to Japanese Patent Publication No. 2002-319408, Patent No. 3733068, Patent No. 3733069, and Patent No. 3935067).

[0006] In addition to this, the present inventors discovered the relationship between the dielectric layer on the surface of copper foil for current collectors and the reciprocal of the electric double layer capacity, and invented copper foil for secondary battery negative electrode current collectors (Refer to Japanese Patent No. 3581784).

Prior art literature

Patent literature

[0007] (Patent Document 0001) Publication No. 2002-319408
(Patent Document 0002) Patent No. 3733068 Publication
(Patent Document 0003) Patent No. 3733069 Publication
(Patent Document 0004) Patent No. 3935067 Publication
(Patent Document 0005) Patent No. 3581784 Publication

Content of Invention

Task to Resolve

[0008] However, in the inventions described in the above patent literature 1 to 4, the improvement in charge/discharge cycle characteristics is insufficient and does not achieve the purpose of practical use. In addition, the diffusion alloy phase of the substrate current collector and the metal film did not contribute to the charging capacity in Li-ion batteries, and had the drawback of deteriorating the characteristics of the high-capacity active material.

[0009] The present invention relates to a negative electrode in which a negative electrode active material such as Si is directly formed on a negative electrode current collector, which is being considered for use in Li-ion secondary batteries, and a secondary battery using the same, and the purpose is to provide a negative electrode and secondary battery that can achieve high capacity through charging and discharging, and can suppress decline in capacity even through repeated cycles compared to before.

Means to Resolve Task

[0010] The present inventors, without being limited by prior knowledge, have carefully studied, in particular, the number and capacity of charging and discharging cycles of the negative electrode for Li-ion batteries and the configuration of the negative electrode material, and as a result, the present invention was discovered by finding that when a conventional silicone-based active material is used, the decrease in charge and discharge capacity due to repeated charge and discharge cycles is large and the short lifespan of the battery is related to the silicone-based film quality. By using a negative electrode having a predetermined Si-based negative electrode active material of the present invention, it was discovered that the original high charge/discharge capacity was reliably obtained, that the flexibility could easily respond to volume changes due to expansion/contraction during charge/discharge due to good adhesion between the current collector and the active material, and that the cycle characteristics could be improved.

- [0011] In addition to this, the present inventors found that cycle characteristics are often not improved solely by knowledge (for example, see Patent No. 3733069) of the surface shape of a conventional current collector, and that the shape of the active material surface formed on the surface of the current collector greatly affects the cycle characteristics. By using a negative electrode having a predetermined Si-based negative electrode active material and a predetermined surface shape, the inherently high charge/discharge capacity can be reliably obtained. Also, based on the good adhesion between the current collector and the active material, the charge/discharge cycle life can also be maintained for a long time due to the countless microsites that enable insertion and extraction of Li ions into the active material, which can be secured from the shape of the negative electrode surface.
- [0012] In addition to this, the present inventors found that cycle characteristics are often not improved by knowledge of the surface shape of a conventional current collector, and that the shape of the active material surface formed on the surface of the current collector greatly affects the cycle characteristics. By using a negative electrode having a predetermined Si-based negative electrode active material and a predetermined surface shape, the inherently high charge/discharge capacity can be reliably obtained. Also, based on the good adhesion between the current collector and the active material, the charge/discharge cycle life can also be maintained for a long time due to the countless microsites that enable insertion and extraction of Li ions into the active material, which can be secured from the shape of the negative electrode surface. It is not the most important to define the surface shape of a conventional current collector, but the surface shape on which the active material is formed is important, and in particular, a large surface area and an appropriate roughness shape are desirable.
- [0013] On the surface of the current collector or the surface formed with the active material, etc., there is an inevitable dielectric layer mainly composed of an oxide film and a composite derivative layer composed of a passivation film such as a rust prevention layer constituted in the present invention. These thin layers are polarized, and the capacity (C:F farads) accumulated in the electric double layer generated by electrolyte immersion can generally be measured based on the relationship shown in the following equation.
- [0014] $1/C = A \cdot d + B \dots(1)$
- [0015] (d is the thickness of the polarizable layer formed on the copper foil surface, A and B are integers)
- [0016] The present inventors first used this relationship to understand the relationship between the dielectric layer on the surface of the copper foil for a current collector and the reciprocal of the electric double layer capacity, and then invented a copper foil for a secondary battery negative electrode current collector and put it into general use (Patent No. 3581784 Publication). However, the constant A in equation (1) includes a term of surface area, and as the electric double layer capacity is proportional to the surface area, it is evaluated as a value per unit area. It may be represented as follows:
- [0017] $1/C = A' \cdot d \cdot 1/S + B' \dots(2)$
- [0018] (d is the thickness of the polarizable layer formed on the surface of the copper foil, S is the actual surface area, and A' and B' are integers)
- [0019] Thus, the electric double layer capacity can be one of the indicators indicating the size of the actual surface area per unit area, which varies depending on the surface shape. On the other hand, as the value of the electric double layer capacitance due to the dielectric film also has an influence, a simple overall trend is not obtained. For example, it varies depending on whether it is a film component that easily creates a dielectric layer or a film component that makes it difficult to create a dielectric layer. As the dielectric layer becomes thicker, the capacity decreases and its reciprocal value increases, so even based on certain measurement conditions, the levels of these sizes can be considered to be different depending on the electrode or electrode surface. However, based on certain ingredients or samples, while the amount of natural oxide film formed also varies depending on the size of the surface area, as the apparent area of the measured sample is constant, the effect of the actual surface area and the resulting effect of the dielectric layer appear in the electric double layer capacity or its reciprocal.
- [0020] By identifying and examining the relationship between the actual surface area of the negative electrode, the electric double layer capacity, or the reciprocal of the electric double layer capacity, which represents the dielectric thickness, and the number of cycles by charge and discharge of the secondary battery and the charge and discharge capacity, it was discovered that the conventional problems with the above battery characteristics could be solved, and the present invention was made based on this knowledge. As a result of a detailed review, in the group of active material coating components that produce a certain degree of constant dielectric layer, it was found that the trend obtained from the effect of the size of the actual surface area of the electrode surface was captured, and the relationship between the indicator range expressed as the capacity C accumulated in the electric double layer, or its reciprocal $1/C$, and the negative electrode or negative electrode current collector with excellent charge and discharge characteristics was discovered.
- [0021] In other words, the present invention provides:
- [0022] (1) A negative electrode for a non-aqueous electrolyte secondary battery characterized by a negative electrode for a non-aqueous electrolyte secondary battery in which a silicone-based active material film is formed on the rough surface of a current collector substrate using copper foil having a surface roughness (Rz) (JIS B0601-1994 10-point average roughness) specified in Japanese Industrial Standards of 1 μm or more, a silicone-based active material film of 1 to 18 g/m² is formed on the rough surface of one or both sides of the current collector substrate, the active material film contains hydrogenated silicone, and the hydrogen content of the entire active material film is 0.1 atomic % or more and 30 atomic % or less.
- [0023] (2) A negative electrode for a non-aqueous electrolyte secondary battery characterized by a negative electrode for secondary transfer of a non-aqueous solvent electrolyte in which a silicone-based active material film is formed on one or both sides of a current collector substrate using copper foil with a rough surface, the thickness of the silicone-based active material film is 0.5 μm or more and 6 μm or less, the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the surface of the silicone-

based active material film is 2 μm or more and 20 μm or less, the 3-point average value of S (JIS B0601-1994 average spacing of local calculations) on the surface of the silicone-based active material film is 0.005 mm or more and 0.014 mm or less, and the 3-point average value of Sm (JIS B0601-1994 average spacing of unevenness) of the surface of the silicone-based active material film is 0.015 mm or more and 0.040 mm or less.

- [0024] (3) The negative electrode for a secondary battery according to (2), characterized in that the current collector substrate has at least a non-smooth or non-glossy surface on which the active material film is formed, the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the active material film forming surface of the current collector substrate is 2 μm or more and 20 μm or less, the S (average spacing of JIS B0601-1994 local calculations) of the active material film formation surface of the current collector substrate is 0.004 mm or more and 0.015 mm or less, and the Sm (JIS B0601-1994 average spacing of irregularities) of the active material film-forming surface of the surface of the current collector substrate is 0.015 mm or more and 0.035 mm or less.
- [0025] (4) A negative electrode for a non-aqueous electrolyte secondary battery characterized in that it is a negative electrode for a non-aqueous electrolyte secondary battery in which a silicone-based active material film is formed on one or both sides of a current collector substrate using copper foil, a silicone-based active material film of 1 to 14 g/m² is formed on the current collector substrate, and the reciprocal of the electric double layer capacity of the negative electrode surface on which the silicone-based active material film is formed is 0.1 to 3 cm²/μF.
- [0026] (5) The negative electrode for a secondary battery according to (4), characterized in that the surface on which the active material film is formed of the current collector substrate is a non-flat surface or a non-glossy surface, the active material film-forming surface of the current collector substrate has a surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of 1.5 μm or more, and the reciprocal of the electric double layer capacity of the active material film formation surface of the current collector substrate is 0.03 to 0.1 cm²/μF.
- [0027] (6) The negative electrode for a secondary battery according to any one of (1), (2), and (4), characterized in that one or more silicone layers containing phosphorus or boron are formed between the current collector substrate and the silicone-based active material film, or at least one upper layer of the silicone-based active material film.
- [0028] (7) The negative electrode for a secondary battery according to any one of (1), (2), and (4), characterized in that the silicone-based active material film contains phosphorus, and the phosphorus content of the entire active material film is 0.1 atomic% or more and 30 atomic% or less.
- [0029] (8) The negative electrode for a secondary battery according to (7), characterized in that the silicone-based active material film further contains oxygen, and the oxygen content of the entire active material film is 1 atomic % or more and 50 atomic % or less.
- [0030] (9) The negative electrode for a secondary battery according to any one of (1), (2), and (4), characterized in that it has a heat-resistant layer or a heat-resistant barrier film in which at least one of a layer containing 0.01 to 0.5 g/m² of nickel or a layer containing 0.001 to 0.1 g/m² of zinc is formed on the surface of the current collector substrate on which the active material film is formed.
- [0031] (10) The negative electrode for a secondary battery according to (9), characterized in that a rust-prevention layer and/or a silane coupling treatment layer are further formed on the heat-resistant layer or the upper layer of the heat-resistant barrier film.
- [0032] (11) The negative electrode for a secondary battery according to (9), characterized in that the zinc in the heat-resistant layer or the heat-resistant barrier film exists as single-layer zinc.
- [0033] (12) The negative electrode for a secondary battery according to (9), characterized in that the zinc in the heat-resistant layer or the heat-resistant barrier film is diffused into a current collector substrate or a nickel layer.
- [0034] (13) A copper foil for electrodes characterized in that it is used in the negative electrode for a secondary battery according to any one of (1), (2), and (4), and has a rough surface with a surface roughness (Rz) of 1 μm or more and 20 μm or less as specified in the Japanese Industrial Standards (JIS B0601-1994 10-point average roughness).
- [0035] (14) A secondary battery using a non-aqueous electrolyte solution, characterized by using the negative electrode according to any one of (1), (2), and (4).
- [0036] (15) A secondary battery, characterized in that the non-aqueous electrolyte solution contains a non-aqueous solvent containing fluorine according to (14)
- [0037] (16) A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized in that copper foil having a rough surface roughness (Rz) (JIS B0601-1994 10-point average roughness) specified in Japanese Industrial Standards of 1 μm or more is used, a process of continuously introducing a current collector substrate with an elongation of 5% or more at a temperature of 180°C into a film production room where silane gas and hydrogen gas are supplied at a supply concentration ratio [H₂]/[SiH₄] within the range of 0 to 100, and by the CVD method maintaining the temperature of the current collector substrate within the range of 100 °C to 350 °C, a process of continuously forming a silicone-based active material layer containing 0.1 atomic % or more and 30 atomic % or less hydrogen on one or both sides of the continuously introduced current collector substrate.

- [0038] (17) A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized by a process of forming a silicone-based active material film by CVD (chemical vapor growth) or EB (electron beam) deposition on one or both sides of a current collector substrate using copper foil having a rough surface, the thickness of the silicone-based active material film being $0.5\ \mu\text{m}$ or more and $6\ \mu\text{m}$ or less, the surface roughness (Rz) (JIS B0601-1994 10-point average roughness) of the surface of the silicone-based active material film being set to $2\ \mu\text{m}$ or more and $20\ \mu\text{m}$ or less, the 3-point average value of S (JIS B0601-1994 average spacing of local calculation peaks) on the surface of the silicone-based active material film being set to $0.005\ \text{mm}$ or more and $0.014\ \text{mm}$ or less, and in addition, the 3-point average value of Sm (JIS B0601-1994 average spacing of irregularities) of the surface of the silicone-based active material film being set to $0.015\ \text{mm}$ or more and $0.040\ \text{mm}$ or less.
- [0039] (18) A method of manufacturing a negative electrode for a non-aqueous electrolyte secondary battery characterized by a process of forming a silicone-based active material film of 1 to $14\ \text{g/m}^2$ by CVD (chemical vapor growth) or EB (electron beam) deposition on one or both sides of a current collector substrate using copper foil having a rough surface, and the reciprocal of the electric double layer capacity of the negative electrode surface on which the silicone-based active material film is formed is 0.1 to $3\ \text{cm}^2/\mu\text{F}$.
- [0040] (19) The method for manufacturing a negative electrode for a secondary battery according to any one of (16) to (18), characterized in that in the CVD method, phosphine gas is further continuously supplied, and in the above process of forming a silicone-based active material film, a silicone-based active material film containing phosphorus is formed.
- [0041] (20) The method of manufacturing a negative electrode for a secondary battery according to any one of (16) to (18), characterized in that after the process of forming the silicone-based active material film, further comprising a step of introducing oxygen into the silicone-based active material film
- [0042] by atmospheric oxidation or heat treatment.

Effectiveness of Invention

- [0043] The negative electrode for a secondary battery of the present invention contains hydrogenated silicone in the silicone-based active material formed on the surface of the current collector substrate using copper foil, so it has flexibility due to the hydrogen group bonding structure to silicone, and as the film is not too dense and has few defects, it is resistant to cracking and the like even against volume changes due to expansion and contraction during charging and discharging, leading to maintenance of cycle life. In addition, as the presence of hydrogenated silicone inhibits the bonding between silicone and oxygen, it suppresses the bonding of lithium and oxygen during the intrusion and detachment of lithium ions during charging and discharging, and is able to reduce irreversible capacity. Therefore, the initial capacity of charging and discharging can be increased, and the decrease in capacity due to repeated cycles can be suppressed.
- [0044] In addition, as the negative electrode for secondary batteries of the present invention specifies the thickness of the silicone-based active material film formed on the surface of the current collector substrate using copper foil, and the roughness characteristic value of the surface of the current collector substrate on which the film is formed, as it has a fine surface shape that ensures reaction sites between Li ions and the active material during charging and discharging, insertion and extraction of Li ions is performed without obstacles. As a result, the effect of reducing the rate of decline in capacity compared to the prior art is obtained even after a long cycle of repeated charging and discharging. Furthermore, as the active material film contains silicone, it has high capacity.
- [0045] The negative electrode for secondary batteries of the present invention defines the thickness of the silicone-based active material film formed on the surface of the current collector substrate using copper foil, and as the size index and range of the actual surface area are defined by (the reciprocal of) the electric double layer capacity per unit area, which can be considered as an index of the size of the total area including the micro actual surface area of the electrode on which the film is formed, the reaction site between Li ions and the active material during charging and discharging is secured, and insertion and extraction of Li ions is performed without a problem. As a result, the effect of reducing the rate of decline in charge/discharge capacity compared to the prior art is obtained even after repeated long cycles. Furthermore, as the active material film contains silicone, it has high capacity.
- [0046] In addition, as silicone-based films are mainly used by CVD or EB deposition, a uniform and homogeneous active material film can be formed industrially and economically. Furthermore, forming a layer containing phosphorus or boron on the upper or lower layer of the silicone-based active material film improves the conductivity of the active material, promotes the movement of Li ions during charging and discharging, and is especially effective when charging and discharging at high rates. In addition, including phosphorus in the silicone active material film improves conductivity and facilitates insertion and deintercalation of Li ions, and further containing oxygen alleviates volume changes due to insertion and deintercalation of Li ions, thereby improving charge and discharge cycle life.

[0047] When a heat-resistant layer or a heat-resistant barrier film, a layer with rust prevention ability, and a silane coupling treatment layer is formed on the current collector copper foil, it has thermal resistance to deterioration over time until the formation of the active material and high temperatures during film formation, and the adhesion between the formed active material film and the surface of the current collector is improved. In addition, as it suppresses the diffusion of copper from the current collector component into the silicone-based active material film, it is possible to prevent a decrease in charge/discharge capacity due to diffusion alloying of the active material and copper, and to obtain the high specific capacity of silicone originally possessed. In particular, diffusion alloying can be prevented by forming a heat-resistant barrier film having a nickel layer on the upper layer of the zinc layer. Secondary batteries using these negative electrodes can achieve high capacity and long lifespan, and additionally, if an electrolyte containing fluorine is used as the non-aqueous solvent of the electrolyte used, a secondary battery can be obtained with less decrease in capacity even with repeated charging and discharging.

Brief Description of the Figures

[0048] FIG. 1 is an enlarged schematic cross-sectional view showing a first example of manufacturing a negative electrode for a secondary battery of the present invention.
FIG. 2 is an enlarged schematic cross-sectional view showing a second example of manufacturing a negative electrode for a secondary battery of the present invention.
FIG. 3 is an enlarged schematic cross-sectional view showing a third example of manufacturing a negative electrode for a secondary battery of the present invention.
FIG. 4 is an enlarged schematic cross-sectional view showing a fourth example of manufacturing a negative electrode for a secondary battery of the present invention.

Specific Details for Implementing the Invention

[0049] (First Embodiment)

[0050] The negative electrode for a secondary battery according to the first embodiment is provided in a form that forms a silicone-based active material film containing hydrogenated silicone with a hydrogen content of at least 0.1 atomic % on a current collector substrate using copper foil. In addition, the secondary battery according to the first embodiment is provided by using the secondary battery negative electrode according to the first embodiment and assembling other constituent materials such as the negative electrode, separator, and electrolyte together as a secondary battery.

[0051] First, copper foil is used as the base material of the current collector (current collector base material) used in the negative electrode for the secondary battery of the first embodiment. During charging and discharging, the volume of the active material expands and contracts due to the insertion and detachment of Li ions, so it is desirable to use copper foil with an elongation of 3% or more until failure in a tensile test at a high temperature of 180°C, meaning that it can follow expansion and contraction due to charging and discharging, so it is more desirable to use copper foil with an elongation rate of 5% or more before breaking.

[0052] Additionally, it is preferable that the tensile strength of the copper foil used for the current collector substrate is in the range of 300 MPa to 1000 MPa (1 GPa). High-capacity active materials such as silicone generate 2 to 4 times volume expansion by alloying with lithium ions. That is why, in alloying during charging, stress or distortion that stretches the copper foil occurs due to volumetric expansion of the active material at the interface between the current collector substrate and the active material film. On the other hand, dealloying during discharge generates stress or distortion that shrinks the copper foil. If the strength of the copper foil is low, this repeated charging and discharging cycle causes wrinkles in the copper foil, and in severe cases, the copper foil breaks. This means that the cycle life is reduced. On the other hand, when the strength of the copper foil exceeds 1 GPa, the copper foil is excessively hardened, and the elongation that can follow expansion and contraction becomes small.

[0053] In addition, only copper foil used for the current collector base material is used because the surface is not smooth and does not have gloss, and at least the surface forming the active material exhibits a rough surface. When copper foil with a smooth surface or glossy copper foil is used as a current collector substrate, the adhesion of the silicone-based active material film formed on the surface is poor, and the active material film may peel off. Therefore, it is preferable to use copper foil having a rough surface on the active material surface having a ten-point average roughness (Rz) of 1 μm or more as specified in JIS B0601-1994 as the current collector substrate. These rough surfaces may be either one side or both sides of the copper foil. There are two types of copper foil: electrolytic copper foil and rolled copper foil. In the case of rolled copper foil, as it itself corresponds to a smooth foil with gloss on both sides, roughening treatment, such as etching or plating, is required at least on the side where the active material is formed. The same applies to the double-sided glossy foil of electrolytic copper foil.

[0054] Rolled copper foil can be manufactured to a predetermined foil thickness by, for example, an ingot obtained by melting and casting pure copper material by sequentially hot rolling, cold rolling, homogenizing treatment, and degreasing by a conventional method. Electrolytic copper foil can use raw copper foil for printed circuits as a base material for the copper foil, and it is manufactured by continuously peeling and winding electrodeposited copper foil by immersing a portion of a rotating drum made of stainless steel or titanium in an acidic electrolyte containing sulfuric acid and copper ions for reduction electrolysis. The desired foil thickness is obtained by setting the electrolysis current and drum rotation speed. In the case of electrolytic copper foil, the electrodeposited surface side (rotating drum surface side) is always a glossy smooth surface, but the electrolyte surface side includes both rough surfaces and glossy smooth surfaces. In the case of a rough surface, it can be used as is in the first embodiment, and can be relatively preferably used as an active material forming surface. When forming an active material on both sides of any copper foil, roughening treatment on at least one side is required. Among the above roughening treatments, the roughening treatment that generates fine particles by electrolytic etching using an electrolyte solution containing chlorine ions for etching and electrolytic copper plating using a current density before or after the limit current density of a copper sulfate-based electrolyte solution conventionally used in copper foils for printed circuits are particularly effective.

- [0055] The negative electrode of the first embodiment is obtained by using a current collector substrate using copper foil as described above and forming a silicone-based active material of the above thickness on the surface. The thickness of the formed film is determined taking into account the actual capacity specifications of the secondary battery. If the film is too thin, the capacity becomes too small and is not realistic, and if the film is too thick, the surface of the current collector and the active material film become smooth and the actual surface area decreases, and therefore the charge/discharge reaction site or surface area becomes small, and the charge/discharge capacity and cycle life may decrease. The lower limit of the film thickness can be about 0.5 μm (1 g/m² as mass per unit area), and the upper limit can be about 8 μm (18 g/m² as mass per unit area). In order to meet the practical capacity specifications, which are sufficient for high-capacity type applications that require high energy, the film thickness is required to be 6 μm or more, and the negative electrode of the first embodiment satisfies this. Therefore, it can be applied to secondary batteries for high-output applications such as uninterruptible power sources, engine starting auxiliary power sources, and hybrid vehicles. In the negative electrode of the first embodiment, the active material formed on the current collector substrate is a silicone-based active material film composed of a material mainly composed of silicone and containing hydrogenated silicone with a hydrogen content of at least 0.1 atomic %. A uniform and homogeneous film can be formed on the surface of the current collector by various CVD (chemical vapor deposition) methods that allow for economical large-area film formation or EB (electron beam) deposition in a hydrogen-containing atmosphere. In this way, an active material film with a thickness of 0.5 μm to 8 μm (1 to 18 g/m² in mass per unit area) is formed on the rough surface of the current collector substrate.
- [0056] Thereby, the effect of the first embodiment is basically obtained.
- [0057] In the first embodiment, the negative electrode active material film mainly composed of silicone, which is formed directly on the current collector copper foil, is formed as follows. One of the film forming methods for this purpose is the CVD (chemical vapor deposition) method. For example, plasma CVD (PECVD, especially using VHF) or catalytic CVD (Cat-CVD, hot wire CVD) is preferably used. The negative electrode active material film obtained by these film forming methods contains hydrogenated silicone, mainly contains SiH or SiH₂, in which hydrogen is bonded to 1 or 2 of the bond number of the silicone group, and the bonding concentration is approximately 0.1 to 12 atomic %, and contains more than 0.1 atomic % as hydrogen concentration. The content ratio varies depending on the film forming method and the film forming conditions, such as film forming temperature and silicone raw material, and can be mainly controlled by the holding temperature of the current collector substrate and the silicone raw material. In particular, in the PE-CVD or Cat-CVD method, the hydrogen concentration can be controlled by the supply amount of monosilane gas (or disilane or hexamethyldisilane HMDS: Si(CH₃)₆NH, etc.), which is the main raw material, or the supply ratio of hydrogen gas that can be added. In addition, it is possible to use only silane gas as a raw material without adding hydrogen gas, which is especially effective in the Cat-CVD method, which has high gas decomposition efficiency and can achieve a high concentration of atomic hydrogen, thereby reducing costs.
- [0058] By introducing hydrogen groups into hydrogenated silicone or silicone, a structure with superior flexibility is obtained compared to the case of silicone monolith, and as for the volume expansion when silicone, which is a negative electrode active material, accepts Li ions and alloys during charging, it is possible to prevent cracks or defects in the silicone-based active material film (negative electrode active material film) itself from breaking the ion movement or conductive path, or preventing a part of the silicone-based active material film from being separated from the current collector. In particular, when dihydrogenated silicone has SiH₂, silicone becomes two-coordinated, thereby increasing structural flexibility and increasing its effectiveness. In addition, as hydrogenated silicone hydrogen terminates defects in unbonded water (dangling bonds) that inevitably exist in silicone-based films, this leads to a reduction in unstable silicone defects and suppresses the occurrence of defects in the conductive path. On the other hand, it is recognized that a silicone-based film with a small or no hydrogenated silicone ratio becomes a dense and hard film, so it is not suitable for this application, and the silicone-based film tends to be easily destroyed and easily separated from the current collector due to volume changes due to repeated charging and discharging.
- [0059] It is composed mainly of silicone-based active materials and inevitably contains materials other than the above hydrogen, and in particular, as a rule, it is preferable not to include other elements such as alloying elements, except in cases where some property improvement effect occurs. In addition, as the presence of hydrogenated silicone inhibits the bonding between silicone and oxygen, as a result, the bonding of lithium and oxygen during charge and discharge of lithium ions can be suppressed and the irreversible capacity can be reduced, and as the first charge/discharge capacity is increased, the decrease in capacity that occurs as the charge/discharge cycle is repeated can be suppressed to a small extent. A silicone-based active material film of 1 g/m² to 18 g/m² is formed on the surface of the current collector substrate. Additionally, the crystallinity of the formed silicone-based active material film is not a problem. It does not matter whether it is amorphous, crystalline such as polycrystalline or microcrystalline, or a mixture of these. The effects of the first embodiment are basically obtained in the same way in any silicone-based active material film.
- [0060] Among the above negative electrode manufacturing methods, the following method is particularly recommended. This is a method of forming a silicone-based active material layer with, as a current collector substrate, a copper foil having a rough surface having an elongation at 180°C of 5% or more, the active material formation surface is not smooth or glossy, and a surface roughness (JIS B0601 ten-point average roughness) (R_z) of 1 μm or more is used, and hydrogen gas and silane gas are continuously supplied within the production room within the supply concentration ratio [H₂]/[SiH₄] within the range of 0 to 100, and by the CVD film forming method that maintains the copper foil temperature within the range of 100°C to 350°C, the continuously introduced active material forming surface on one or both sides of the coiled copper foil contains hydrogen in an amount of 0.1 atomic % or more and 30 atomic % or less (preferably 20 atomic % or less). The condition in which the raw material gas supply concentration ratio is 0 (i.e., no hydrogen gas is supplied) is particularly effective in the Cat-CVD method. When using one sheet at a time as a current collector, batch film forming is performed, but when mass producing coiled large-area copper foil, etc., film forming through continuous processing in roll-to-roll form is economically superior.

- [0061] In the first embodiment, if a layer containing phosphorus or boron is further formed on at least one of the lower layer or upper layer of the silicone-based active material film, the insufficient conductivity of silicone itself is improved, and it facilitates alloying of Li ions with silicone during charging and movement into and out of the layer when Li ions are released during discharge. In particular, if phosphorus is formed in the lower layer of the silicone-based film and boron is formed in the upper layer, Li ions are sufficiently alloyed to penetrate into the silicone-based film during charging. In addition, boron is formed in the lower layer of the silicone film, and also, the structure in which phosphorus is formed in the upper layer facilitates the release of Li ions present by alloying with the silicone-based film after charging by dealloying from the silicone-based film during discharge. As a result, it suppresses the loss of electric quantity that cannot be discharged while charging or the generation of irreversible capacity due to Li ions remaining in the silicone-based film without being released.
- [0062] Here, although it does not specify the conductivity of the silicone-based film itself, considering high rate conditions such as applications requiring instantaneous high-output discharge or high-speed charging, it is desirable to have a conductivity of 10-2 S/cm or more. It is also possible to increase conductivity by doping the silicone-based film itself with phosphorus or boron. As the silicone-based film doped with phosphorus or boron and a silicone-based film with phosphorus or boron formed on the upper layer suppress the formation of an oxide film on silicone, in addition to the effects of hydrogenated silicone, it is possible to reduce the increase in irreversible capacity and the decrease in charge/discharge capacity due to the combination of oxygen and Li ions.
- [0063] On the other hand, when oxygen is added to the phosphorus-doped silicone-based film, the initial charge and discharge efficiency decreases, but the cycle life of repeated charge and discharge improves. This is presumed to be the effect of suppressing the volume change due to alloying and dealloying of lithium during charging and discharging by the introduction of oxygen or oxidation of silicone, in addition to the effect of phosphorus. The phosphorus content of the entire silicone-based film is preferably 0.1 atomic % or more and 30 atomic % or less, and more preferably 0.5 atomic % or more and 10 atomic % or less. If phosphorus is less than 0.1 atomic %, the improvement in conductivity and the effect on the intrusion and detachment of Li ions into silicone are small, and if the amount exceeds 30 atomic %, the amount introduced becomes excessive with respect to silicone and may even cause insertion and detachment of phosphorus itself from Li ions, so it actually causes problems with insertion and removal.
- [0064] The oxygen content of the entire silicone-based film is preferably 1 atomic % or more and 50 atomic % or less, and is selected based on the relationship between charge/discharge efficiency, cycle performance, and phosphorus concentration. At less than 1 atomic %, the effect of suppressing volume change due to insertion and extraction of Li ions is not recognized, and at an introduced concentration exceeding 50 atomic %, it becomes excessive relative to the amount of silicone, so as the thickness or volume of the active material increases, the charge/discharge capacity decreases, or the initial irreversible capacity increases due to an increase in the amount of bonding between oxygen and Li ions, the balance with the positive electrode is lost, so it cannot be done with a secondary battery.
- [0065] When doping silicone with phosphorus, for example, in case of doping with phosphine gas, etc., with boron, a film can be formed by continuously supplying raw material gas such as diborane in the same concentration based on the supply amount of silicone raw material gas such as monosilane gas or hydrogen.
- [0066] In addition, oxygen can be introduced into the silicone-based film by heat-treating the silicone-based film or the silicone-based film containing phosphorus or boron in an atmosphere where the oxygen amount is controlled or oxidized by air. The amount of oxygen, heat treatment temperature, and treatment time depend on the oxygen concentration desired to be contained.
- [0067] In addition, by adjusting and controlling the atmosphere of the film forming area by the gas concentration of argon (Ar) and oxygen (O₂) using a sputtering device or deposition device targeting Si, a reactive sputtering Si film or vapor deposition film containing a desired amount of oxygen can be formed. It is also possible to form a Si film with a controlled oxygen content ratio by sputtering or vapor deposition directly targeting SiO. In this case, along with SiO, Si monolith or SiO₂ targets can also be used to control oxygen concentration. In addition, by simultaneously controlling the oxygen gas concentration of the atmosphere in the film forming area, it becomes possible to further control Si film forming containing a trace amount of oxygen concentration.
- [0068] In the negative electrode according to the first embodiment, when forming each treatment layer of a heat resistance or heat resistance barrier layer, a rust prevention layer, and a silane coupling treatment layer on the lower layer (if a phosphorus or boron layer is formed on the lower layer of the silicone-based active material film, the lower layer) of the silicone-based active material film, it has heat resistance to high temperatures during film formation and deterioration over time until the active material is formed, and the adhesion between the formed negative electrode active material film and the current collector film is improved. In addition, as the copper of the current collector base component and the active material are not diffusion alloyed, this can prevent a decrease in charge/discharge capacity, and obtain the high specific capacity of silicone that is inherent in silicone. In particular, diffusion alloying is prevented by forming a heat-resistant barrier film having a nickel layer on the upper layer of the zinc layer.

- [0069] This heat-resistant layer or heat-resistant barrier film covers the copper foil surface, and there is at least one layer of film formed between the copper of the current collector copper foil and silicone, the negative electrode active material, to prevent them from easily mixing with each other. Furthermore, regarding the high temperature at the time of forming the silicone film formed on the current collector copper foil, the environmental temperature and long-term aging while used as a secondary battery, it can also be defined as a film that suppresses or prevents diffusion alloying of the current collector component into the copper-silicone active material. Heat-resistant elements that suppress the diffusion of copper and are somewhat general-purpose include zinc, nickel, cobalt, and tin. When using elements that alloy with lithium, such as tin, care must be taken because they themselves function as active materials, and they easily form diffusion compounds with copper. This heat-resistant layer or heat-resistant barrier film is a layer composed of at least a nickel-based layer or a zinc-based layer, and in the case of a heat-resistant layer that does not need to have barrier properties, the order of the nickel layer and zinc layer in the upper copper foil layer does not matter. As a heat-resistant barrier film, in the case of the functional purpose of preventing diffusion into the copper active material film, which is a current collector base component, it is preferable to form zinc on copper foil and then form a nickel layer. This can also suppress the diffusion of the formed zinc itself into the active material film. Cobalt has the same purpose-oriented functional characteristics as nickel in the first embodiment, but it is more expensive than nickel and may be less economical.
- [0070] As a heat-resistant layer that does not require the complete barrier properties, for example, a heat-resistant film containing at least nickel is preferably formed on the copper foil surface and is present in the upper layer of the copper foil surface. The heat-resistant layer preferably has a nickel content of 0.01 to 0.2 g/m². If the nickel content is low, the heat resistance decreases, and if the nickel content is too high, the rough surface of the copper foil surface of the current collector substrate becomes smooth, which actually reduces the adhesion to the active material. In addition, zinc needs to exist as a single layer on the upper layer of nickel, or spread on the surface of the nickel or copper foil to form a heat-resistant layer.
- [0071] Zinc can be very easily diffusion-alloyed into copper and can provide heat resistance that prevents copper oxidation, especially high-temperature oxidation. If the total amount is too small, the above-mentioned effect will be small, and if it is too large, the contactability of the copper may be reduced, or it may thicken between the upper layer film and actually reduce the adhesion, so it should preferably be in the range of 0.003 to 0.05 g/m². Zinc imparts heat resistance by diffusion into copper as described above, so by forming a layer containing nickel, which is insufficient in terms of preventing the diffusion of copper into the upper active material layer and functions as a physical shielding layer without diffusion itself, heat resistance is achieved without diffusion of copper, etc. of the current collector component into the active material. In addition, various methods such as wet methods or dry methods can be used to form nickel and zinc films, and as it is economical and a uniform and homogeneous film can be easily obtained under electrolytic conditions, an electroplating method using a known sulfuric acid bath, etc. can be recommended.
- [0072] Further, as a preferred example of the heat-resistant barrier film, at least zinc is formed on the surface of the copper foil and is diffused into the upper layer of the copper foil surface, or is present on the copper foil surface in a single layer of zinc. Zinc is diffusion-alloyed into copper and can provide heat resistance that prevents copper oxidation, especially high-temperature oxidation. If the total amount is too small, the above effect will be small, and if there is too much, it may reduce the current collecting ability of the copper, or it may thicken between the upper layer film and actually reduce adhesion, so it is preferable to form it in the range of 0.001 to 0.1 g/m², and it is more preferable to form it in the range of 0.003 to 0.07 g/m².
- [0073] In addition, the structure in which a heat-resistant film containing nickel is formed on the upper layer of zinc is good. Zinc imparts heat resistance by diffusion into copper as described above, but if the formation amount is small, it is insufficient in terms of preventing diffusion of copper and zinc themselves into the upper active material layer, but if the amount formed is large, diffusion into the active material layer may occur, resulting in a decrease in charge/discharge capacity. Furthermore, by forming a layer containing nickel or cobalt, which itself functions as a physical barrier film that is difficult to diffuse, the heat-resistant barrier property that prevents copper, etc. of the current collector component from diffusing into the active material is improved. For example, the heat-resistant barrier film preferably has a nickel content of 0.01 to 0.5 g/m², and if there is not enough, the barrier property decreases, and if it is too thick, the rough shape of the surface of the current collector copper foil is smoothed, which reduces adhesion to the active material and may also cause film cracking, and in this case, conductivity and current collecting properties are deteriorated and cycle life is shortened. Additionally, a combination of zinc and nickel in appropriate amounts can be used. In addition, as a method of forming the zinc and nickel film, an electroplating method using a known sulfuric acid bath, etc., similar to the heat-resistant layer described above, may be recommended.
- [0074] Rust prevention treatment may be performed on the heat resistance or heat resistance barrier treatment layer. This is because it is not limited to forming the active material film immediately after manufacturing the current collector. A rust prevention layer is obtained by forming a thin layer with a passivation function using an organic film or an inorganic film dielectric. As an organic film, in addition to benzotriazoles and trityltriangles of the triazole class used for new products and rolled copper foil, the forming organic thin layer obtained by immersion in an aqueous solution of thiazoles, imidazoles, mercaptans, triethanolamines, etc. or an alcohol-containing solvent is preferred. As an inorganic film, a thin chromate layer, which is a chromium hydrated oxide obtained by immersion in an aqueous solution of chromium hydrochloric acid or dichromate or electrolytic treatment, is preferably used, and unlike the organic thin layer, it has good heat resistance. In addition, it prevents environmental deterioration of the copper foil during the period from manufacturing the copper foil of the current collector substrate to forming the active material film, and also helps with heat resistance during active material film formation. Additionally, a silane coupling treatment layer may be formed on the rust prevention treatment layer or the heat resistance treatment layer to improve adhesion between the heat resistance treatment layer or the current collector and the silicone-based active material film. Silane coupling treatment is generally performed by immersing the copper foil for a current collector on which the heat resistance treatment layer or the rust prevention treatment layer is formed in an aqueous solution in which a silane coupling agent is dissolved. The silane coupling agent is selected from its chemical structure and substituents according to the heat resistance treatment layer or the rust prevention treatment layer. In particular, silane coupling agents such as kryloxy-based or epoxy-based may be recommended.

- [0075] The secondary battery using the negative electrode of the above first embodiment has high capacity and has the characteristic that the charging and discharging capacity does not decrease even with repeated charging and discharging cycles. Additionally, if a non-aqueous solvent containing fluorine is used or added to an electrolyte solution using a non-aqueous solvent that constitutes a secondary battery, the period during which the capacity does not deteriorate even after repeated charging and discharging is extended, resulting in a longer lifespan. The fluorine-containing solvent alleviates the volume expansion of the silicone-based film due to alloying with Li ions during charging, especially during the first charging process, so capacity decline due to charging and discharging can be suppressed. Fluorinated ethylene carbonate, fluorinated chain carbonate, etc. can be used as the fluorine-containing non-aqueous solvent. Fluorinated ethylene carbonates include mono-tetra-fluoroethylenecarbonate (4-fluoro-1,3-dioxolane-2-one, FEC), fluorinated chain carbonates include methyl 2,2,2-trifluoroethyl carbonate, ethyl 2,2,2-trifluoroethyl carbonate, etc., and these can be used singly or in combination by adding them to the electrolyte solution. As fluorine groups are easy to combine with silicone and are also strong, it appears that charge alloying with Li ions can stabilize the film and contribute to suppressing expansion even during expansion. As such, the negative electrode, negative electrode current collector, and non-aqueous solvent electrolyte secondary battery according to the first embodiment can be used as a driving power source for mobile electronic devices or power tools over a long period of time, as well as for industrial purposes or electric vehicles that require high energy.
- [0076] (Second Embodiment)
- [0077] Copper foil is used as the base material of the current collector (current collector base material) used in the negative electrode for the secondary battery of the second embodiment. During charging and discharging, the volume of the active material expands and contracts due to the insertion and detachment of Li ions, so it is desirable to use copper foil with an elongation of 3% or more until failure in a tensile test at a high temperature of 180°C, meaning that it can follow expansion and contraction due to charging and discharging, so it is more desirable to use copper foil with an elongation rate of 5% or more before breaking. Additionally, it is preferable that the tensile strength of the copper foil used for the current collector substrate is in the range of 300 MPa to 1000 MPa (1 GPa).
- [0078] In addition, only copper foil used for the current collector base material is used because the surface is not smooth and does not have gloss, and at least the surface forming the active material exhibits a rough surface. These rough surfaces may be formed on one side of the copper foil, or may be formed on both sides. There are two types of copper foil: electrolytic copper foil and rolled copper foil. In the case of rolled copper foil, as it itself corresponds to a smooth foil with gloss on both sides, roughening treatment, such as etching or plating, is required at least on the side where the active material is formed. The same applies to the double-sided glossy foil of electrolytic copper foil.
- [0079] Rolled copper foil can be manufactured to a predetermined foil thickness by, for example, an ingot obtained by melting and casting pure copper material by sequentially hot rolling, cold rolling, homogenizing treatment, and degreasing by a conventional method. Electrolytic copper foil can use raw copper foil for printed circuits as a base material for the copper foil, and it is manufactured by continuously peeling and winding electrodeposited copper foil by immersing a portion of a rotating drum made of stainless steel or titanium in an acidic electrolyte containing sulfuric acid and copper ions for reduction electrolysis. The desired foil thickness is obtained by setting the electrolysis current and drum rotation speed. In the case of electrolytic copper foil, the electrodeposited surface side (rotating drum surface side) is always a glossy smooth surface, but the electrolyte surface side includes both rough surfaces and glossy smooth surfaces. In the case of a rough surface, it can be used as is in the second embodiment, and can be relatively preferably used as an active material forming surface. When forming an active material on both sides of any copper foil, roughening treatment on at least one side is required. Among the above roughening treatments, the roughening treatment that generates fine particles by electrolytic etching using an electrolyte solution containing chlorine ions for etching and electrolytic copper plating using a current density before or after the limit current density of a copper sulfate-based electrolyte solution conventionally used in copper foils for printed circuits can be used. The latter method is particularly effective for obtaining a copper foil surface with a fine surface shape used in the current collector of the negative electrode for a secondary battery of the second embodiment. By immersing an aqueous solution containing sulfuric acid and copper as main components in an electrolyte solution with a lower copper concentration than a typical copper plating solution, and performing cathode electrolysis at a high current density in the room temperature range, microscopic copper particles are reduced and grown on the copper foil surface depending on the processing time (so-called burning plating). Then, immediately, general copper plating, electrolytic plating is performed at a general low or medium current density by heating a copper sulfate-based electrolyte solution with a high copper concentration, and the just-produced copper particles are fixed and electrodeposited on the copper foil surface. By adjusting the copper concentration, components, liquid temperature, current density, electrolysis time, etc. in the above two-stage electrolytic treatment, copper foil for a current collector having a fine surface shape can be manufactured.

[0080] In the negative electrode of the second embodiment, the active material formed on the current collector copper foil is composed of a material mainly composed of silicone, and is a silicone-based active material film containing at least silicone. A uniform and homogeneous film can be formed on the surface of the current collector by various CVD (chemical vapor deposition) deposition methods that allow for economical large-area film formation. On the rough surface of the current collector, 0.5 μm to 6 μm (surface roughness (Rz) (10-point average roughness shown in JIS B0601-1994) after film formation with a thickness of 1 to 14 g/m² as mass per unit area) represents 2 to 20 μm , and the 3-point average value of the spacing (S) (JIS B0601-1994 above) between local calculations on the rough surface is 0.005 to 0.014 mm, and in addition, a rough surface shape in which the 3-point average value of the average spacing (Sm) of rough surface irregularities (JIS B0601-1994 above) is 0.015 to 0.040 mm is required. When a silicone-based active material film having such a surface shape is formed to a thickness of 0.5 to 6 μm , the effect of the second embodiment is basically obtained. As it maintains the active material film surface with a fine uniform uneven rough surface shape, it can react with a large actual surface area during alloying and dealloying reactions of charging and discharging with Li ions, and as there is little decline in the large specific capacity even with repeated charging and discharging, the secondary battery using the negative electrode or negative electrode current collector of the second embodiment can be used for a long period of time. Here, the upper limit of Rz is set at 20 μm because, although the active material itself has a high capacity with a small film thickness, if the negative electrode has too large an irregularity height, the effect as a thin film electrode is lost. Large irregularities do not deteriorate the performance of the negative electrode itself, but in the case of cylindrical, square, or module products, which are the final forms of secondary batteries, the total capacity may be reduced, so in order to ensure the effectiveness of the thin film negative electrode, it is necessary to limit the upper thickness.

[0081] In order to obtain surface roughness after forming the silicone-based active material film, or to obtain a negative electrode for a secondary battery suitable for the second embodiment, the surface roughness (Rz) of the surface forming the active material at least on the current collector surface is 2 to 20 μm , and a current collector copper foil having a surface shape in which the spacing (S) between the local ridges of the rough surface is 0.004 to 0.015 mm and the average spacing (Sm) of the irregularities of the rough surface is 0.015 to 0.035 mm can be used. The surface is rough, not smooth, and has no gloss. The negative electrode of the second embodiment is obtained by forming a silicone-based active material of the above thickness on the surface using such copper foil, and it is necessary to consider the relationship between the surface roughness of the current collector and the thickness of the silicone-based active material film formed. In other words, if a too thick active material film is formed on the surface of the current collector copper foil with low surface roughness, care must be taken as smoothing the rough surface of the copper foil may result in the surface roughness after formation being reduced. For applications that require a thick film, it is necessary to use copper foil with high surface roughness as the current collector. However, for the upper limit of Rz, as it is necessary to provide a film thickness limit for the same purpose as a thin film electrode as above, it needs to be 20 μm or less, the same as after forming the active material film. Meanwhile, the thickness of the formed film may be determined by considering the actual capacity specifications of the secondary battery. If it is too thin, the capacity is too small and unrealistic, and if it is too thick, the current collector surface becomes smooth and the charge/discharge cycle life decreases. The lower limit applicable to high-output secondary batteries such as uninterruptible power sources, engine starting auxiliary power sources, and hybrid vehicles can be about 0.5 μm , and in addition to this, the upper limit thickness can be set to about 6 μm , which satisfies practical capacity specifications that are sufficient for high-capacity type applications that require high energy. Thus, it is designed by considering the surface roughness of the current collector copper foil used and the thickness of the forming active material film so that the range of surface roughness of the surface of the forming active material can be obtained.

[0082] In the second embodiment, the negative electrode active material film mainly composed of silicone, which is formed directly on the current collector copper foil, is formed as follows. One film forming method is the CVD (chemical vapor deposition) method. For example, plasma CVD (PECVD, especially using VHF) and catalytic CVD (Cat-CVD, hot wire CVD) are preferably used, and it is also thought to be possible in the future to use LPCVD and atmospheric pressure plasma CVD, which are expected to be used in the future. In addition, deposition methods may be used, and the electron beam (EB) deposition method, which allows large-area film formation, is particularly preferable as it is economical. The silicone film layer formed mainly by the CVD-based film forming method contains hydrogenated silicone, mainly contains SiH or SiH₂, in which hydrogen is bonded to 1 or 2 of the bond number of the silicone group, and the bonding concentration is approximately 0.1 to 12 atomic %, and contains more than 0.1 atomic % as hydrogen concentration. The content ratio varies depending on the film forming method and the film forming conditions, such as film forming temperature and silicone raw material, and can be mainly controlled by the holding temperature of the current collector copper foil and the silicone raw material. In particular, in each CVD method, PE- or Cat-, it can be controlled by the supply amount of monosilane gas, which is the main raw material, or the supply ratio of hydrogen gas that can be added. By introducing hydrogen groups into hydrogenated silicone or silicone, a structure with superior flexibility is obtained compared to the case of silicone monolith, and as for the volume expansion when silicone, which is a negative electrode active material, accepts Li ions and alloys during charging, it is possible to prevent cracks or defects in the silicone-based film itself from breaking the ion movement or conductive path, or preventing a part of it from being separated from the current collector. In addition, as hydrogenated silicone hydrogen terminates defects in unbonded water (dangling bonds) that inevitably exist in silicone-based films, this leads to a reduction in unstable silicone defects and suppresses the occurrence of defects in the conductive path. Silicone-based active materials are composed mainly of silicone and inevitably contains materials other than the above hydrogen, and in particular, as a rule, it is preferable not to include other elements such as alloying elements, except in cases where some property improvement effect occurs.

- [0083] In the second embodiment, if a layer containing phosphorus or boron is further formed on at least one of the lower layer or upper layer of the silicone-based active material film, the insufficient conductivity of silicone itself is improved, and it facilitates alloying of Li ions with silicone during charging and movement into and out of the layer when Li ions are released during discharge. In particular, if phosphorus is formed in the lower layer of the silicone-based film and boron is formed in the upper layer, Li ions are sufficiently alloyed to penetrate into the silicone-based film during charging. In addition, the configuration of forming boron in the lower layer of the silicone-based film and phosphorus in the upper layer facilitates the release by dealloying from the silicone-based film at the time of discharge of Li ions that are alloyed with the silicone-based film after charging, so that they are not released but remain in the silicone-based film, suppressing the loss of electricity that cannot be discharged while charging and the occurrence of irreversible capacity. Although it does not specify the conductivity of the silicone-based film itself, considering high rate conditions such as applications requiring instantaneous high-output discharge or high-speed charging, it is desirable to have a conductivity of 10-2 S/cm or more. It is also possible to heighten conductivity by doping the silicone-based film itself with phosphorus or boron. As the silicone-based film doped with phosphorus or boron and a silicone-based film with phosphorus or boron formed on the upper layer suppress the formation of an oxide film on silicone, it is possible to prevent increases in irreversible capacity due to the combination of oxygen and Li ions, that is, the decrease in charge/discharge capacity.
- [0084] On the other hand, when oxygen is added to the phosphorus-doped silicone-based film, the initial charge and discharge efficiency decreases, but the cycle life of repeated charge and discharge improves. This is presumed to be the effect of suppressing the volume change due to alloying and dealloying of lithium during charging and discharging by the introduction of oxygen or oxidation of silicone, in addition to the effect of phosphorus. The phosphorus content of the entire silicone-based film is preferably 0.1 atomic % or more and 30 atomic % or less, and more preferably 0.5 atomic % or more and 10 atomic % or less. If phosphorus is less than 0.1 atomic %, the improvement in conductivity and the effect on the intrusion and detachment of Li ions into silicone are small, and if the phosphorus amount exceeds 30 atomic %, the amount introduced becomes excessive with respect to silicone and may even cause insertion and detachment of phosphorus itself from Li ions, so it actually causes problems with insertion and removal.
- [0085] The oxygen content of the entire silicone-based film is preferably 1 atomic % or more and 50 atomic % or less, and is selected based on the relationship between charge/discharge efficiency, cycle performance, and phosphorus concentration. At less than 1 atomic %, the effect of suppressing volume change due to insertion and extraction of Li ions is not recognized, and at an introduced concentration exceeding 50 atomic %, it becomes excessive relative to the amount of silicone, so as the thickness or volume of the active material increases, the charge/discharge capacity decreases, or the initial irreversible capacity increases due to an increase in the amount of bonding between oxygen and Li ions, the balance with the positive electrode is lost, so it cannot be done with a secondary battery.
- [0086] When doping silicone with phosphorus, for example, in case of doping with phosphine gas, etc., with boron, a film can be formed by continuously supplying raw material gas such as diborane in the same concentration based on the supply amount of silicone raw material gas such as monosilane gas or hydrogen.
- [0087] In addition, oxygen can be introduced into the silicone-based film by heat-treating the silicone-based film or the silicone-based film containing phosphorus or boron in an atmosphere where the oxygen amount is controlled or oxidized by air. The amount of oxygen, heat treatment temperature, and treatment time depend on the oxygen concentration desired to be contained. Other methods of forming a silicone-based film into which oxygen is introduced may include sputtering or vacuum evaporation into which oxygen is introduced.
- [0088] In a negative electrode according to the second embodiment, when heat resistance is formed on the lower layer of the silicone-based active material film or the rough surface of the current collector copper foil, and each treatment layer for rust prevention and silane coupling is formed, it has heat resistance to high temperatures during film formation and deterioration over time until the active material is formed, and the adhesion between the active material film and the current collector film is improved. In addition, diffusion alloying of the copper of the current collector component and the active material is suppressed, thereby preventing a decrease in charge and discharge capacity.
- [0089] This heat-resistant layer is at least one layer of film formed between copper, a component of the current collector base material, and silicone, a negative electrode active material, to prevent mixing with each other, and covers the surface of the copper foil. Preferably, a heat-resistant film containing at least nickel is formed on the surface of the copper foil. By forming a layer containing nickel that does not diffuse itself and acts as a physical shielding layer, heat resistance that suppresses diffusion into the active material of copper, which is a component of the current collector base material, is achieved when exposed to high temperatures when forming a silicone-based film or over a long period of time. It is preferable that the heat-resistant layer contains nickel in an amount of 0.01 to 0.2 g/m². This is because if the amount is small, heat resistance decreases, and if the amount is too large, the rough surface shape of the copper foil surface of the current collector is smoothed, which actually reduces adhesion to the active material.

- [0090] Additionally, a method of forming zinc at least on the rough surface of copper foil or on the upper layer of the nickel is also preferable. Zinc is diffused on the upper layer of the copper foil surface, or exists on the copper foil surface or the nickel film in a single layer. Zinc can be very easily diffusion-alloyed into copper or present in the nickel phase to provide heat resistance that prevents oxidation of copper or nickel, especially high-temperature oxidation. If the total amount is too small, the above-mentioned effect will be small, and if it is too large, the current collecting ability of the copper or nickel may be reduced, or it may thicken between the upper layer film and actually reduce the adhesion, so it should preferably be in the range of 0.003 to 0.05 g/m². As mentioned above, zinc imparts heat resistance by diffusion into copper or nickel or by its presence in the surface layer, but if there is too much zinc, the zinc itself may diffuse into the upper active material layer, so this needs to be taken into consideration. Also preferred is a combination of forming a layer containing nickel after forming zinc. In addition, various methods such as wet methods or dry methods can be used to form nickel and zinc, and as it is economical and a uniform and homogeneous film can be easily obtained under electrolytic conditions, an electroplating method using a known sulfuric acid bath, etc. can be recommended.
- [0091] In addition, in the second embodiment, the heat-resistant barrier film used in the first embodiment may be used instead of the heat-resistant layer. The heat-resistant barrier film has at least one of a layer containing 0.01 to 0.5 g/m² of nickel or a layer containing 0.001 to 0.1 g/m² of zinc.
- [0092] As the rust prevention treatment layer formed on the heat-resistant layer or on the rough surface of the current collector copper foil, a thin layer having a passivation function by an organic film or an inorganic film dielectric is used. The rust prevention layer prevents environmental deterioration of the copper foil during the period from manufacturing the copper foil of the current collector substrate to forming the active material film, and also helps with heat resistance during active material film formation. As an organic film, in addition to benzotriazoles and trityltriazoles of the triazole class used for new products and rolled copper foil, the forming organic thin layer obtained by immersion in an aqueous solution of thiazoles, imidazoles, mercaptans, triethanolamines, etc. or an alcohol-containing solvent is preferred. As an inorganic film, a thin chromate layer obtained by immersion in an aqueous solution of chromate or dichromate or electrolytic treatment is preferably used, and unlike the organic thin layer, it has good heat resistance.
- [0093] In addition, when a silane coupling treatment layer is formed on the rust prevention treatment layer, the heat resistance layer, or the current collector rough surface, adhesion and corrosion between the heat-resistant treatment layer or current collector and the silicone-based active material film are improved. Silane coupling treatment is generally performed by immersing the copper foil for a current collector on which the heat resistance and rust prevention treatment layer is formed in an aqueous solution in which a silane coupling agent is dissolved. The silane coupling agent is selected from its chemical structure and substituents according to its heat resistance and rust prevention layer. In particular, silane coupling agents such as kryloxy-based or epoxy-based may be recommended.
- [0094] The secondary battery using the negative electrode of the above second embodiment, or the negative electrode using a current collector, has high capacity and has the characteristic that the charging and discharging capacity does not decrease even with repeated charging and discharging cycles. Additionally, if a non-aqueous solvent containing fluorine is used or added to an electrolyte solution using a non-aqueous solvent that constitutes a secondary battery, the period during which the capacity does not deteriorate even after repeated charging and discharging is extended, resulting in a longer lifespan. The fluorine-containing solvent alleviates the volume expansion of the silicone-based film due to alloying with Li ions during charging, so capacity decline due to charging and discharging can be suppressed. Fluorinated ethylene carbonate, fluorinated chain carbonate, etc. can be used as the fluorine-containing non-aqueous solvent. Fluorinated ethylene carbonates include mono-tetra-fluoroethylenecarbonate (4-fluoro-1,3-dioxolane-2-one, FEC), fluorinated chain carbonates include methyl 2,2,2-trifluoroethyl carbonate, ethyl 2,2,2-trifluoroethyl carbonate, etc., and these can be used singly or in combination by adding them to the electrolyte solution. As fluorine groups are easy to combine with silicone and are also hard, it appears that charge alloying with Li ions can stabilize the film and contribute to suppressing expansion even during expansion. As such, the negative electrode, negative electrode current collector, and non-aqueous solvent electrolyte secondary battery according to the second embodiment can be used as a driving power source for mobile electronic devices or power tools over a long period of time, as well as for industrial purposes or electric vehicles that require high energy.
- [0095] (Third Embodiment)
- [0096] Copper foil is used as the base material of the current collector (current collector base material) used in the negative electrode for the secondary battery of the third embodiment. During charging and discharging, the volume of the active material expands and contracts due to the insertion and detachment of Li ions, so it is desirable to use copper foil with an elongation of 3% or more until failure in a tensile test at a high temperature of 180°C, meaning that it can follow expansion and contraction due to charging and discharging, so it is more desirable to use copper foil with an elongation rate of 5% or more before breaking. Additionally, it is preferable that the tensile strength of the copper foil used for the current collector substrate is in the range of 300 MPa to 1000 MPa (1 GPa).

- [0097] In addition, only copper foil used for the current collector base material is used because the surface is not smooth and does not have gloss, and at least the surface forming the active material exhibits a rough surface. These rough surfaces may be formed on one side of the copper foil, or may be formed on both sides. There are two types of copper foil: electrolytic copper foil and rolled copper foil. In the case of rolled copper foil, as it itself corresponds to a smooth foil with gloss on both sides, roughening treatment, such as etching or plating, is required at least on the side where the active material is formed. The same applies to the double-sided glossy foil of electrolytic copper foil.
- [0098] Rolled copper foil can be manufactured to a predetermined foil thickness by, for example, an ingot obtained by melting and casting pure copper material by sequentially hot rolling, cold rolling, homogenizing treatment, and degreasing by a conventional method. Electrolytic copper foil can use raw copper foil for printed circuits as a base material for the copper foil, and it is manufactured by continuously peeling and winding electrodeposited copper foil by immersing a portion of a rotating drum made of stainless steel or titanium in an acidic electrolyte containing sulfuric acid and copper ions for reduction electrolysis. The desired foil thickness is obtained by setting the electrolysis current and drum rotation speed. In the case of electrolytic copper foil, the electrodeposited surface side of the rotating drum surface (rotating drum surface side) is always a glossy smooth surface, but the electrolyte surface side includes both rough surfaces and glossy smooth surfaces. In the case of a rough surface, it can be used as is in the third embodiment, and can be relatively preferably used as an active material forming surface. When forming an active material on both sides of any copper foil, roughening treatment on at least one side is required. Among the above roughening treatments, the roughening treatment that generates fine particles by electrolytic etching using an electrolyte solution containing chlorine ions for etching and electrolytic copper plating using a current density before or after the limit current density of a conventional copper sulfate-based electrolyte solution method used in copper foils for printed circuits can be used. The latter method is particularly effective for obtaining a copper foil surface with a fine surface shape used in the current collector of the negative electrode for a secondary battery of the third embodiment. By immersing an aqueous solution containing sulfuric acid and copper as main components in an electrolyte solution with a lower copper concentration than a typical copper plating solution, and performing cathode electrolysis at a high current density in the room temperature range, microscopic copper particles are reduced and grown on the copper foil surface depending on the processing time (so-called burning plating). Then, immediately, general copper plating, electrolytic plating is performed at a general low or medium current density by heating a copper sulfate-based electrolyte solution with a high copper concentration, and the just-produced copper particles are fixed and electrodeposited on the copper foil surface. By adjusting the copper concentration, components, liquid temperature, current density, electrolysis time, etc. in the above two-stage electrolytic treatment, copper foil for a current collector having a fine surface shape can be manufactured.
- [0099] In the negative electrode of the third embodiment, the active material formed on the current collector copper foil is composed of a material mainly composed of silicone, and is a silicone-based film containing at least silicone. A uniform and homogeneous film can be formed on the surface of the current collector by various CVD (chemical vapor deposition) deposition methods that allow for economical large-area film formation. A silicone-based film with a thickness of 0.5 μm to 6 μm (1 to 14 g/m² in mass per unit area) is formed on the fine roughened surface of the current collector copper foil, and it is necessary that the reciprocal of the electric double layer capacity of the surface after film formation is 0.1 to 3 cm²/μF. Thereby, the effect of the third embodiment is basically obtained.
- [0100] In order to obtain the reciprocal of the electric double layer capacity of the negative electrode surface after forming the silicone-based active material film, this characteristic can be easily obtained by using copper foil whose current collector surface is at least the reciprocal of the electric double layer capacity of the surface forming the active material of 0.03 to 0.1 cm²/μF. Additionally, this copper foil is a copper foil with a rough surface with at least an active material formation surface that is not smooth or has no gloss and a surface roughness (JIS B0601-1994, ten-point average roughness) (Rz) of 1.5 μm or more. If copper foil with a smooth or glossy surface rather than a rough surface is used, as the formed active material silicone may peel off in some cases, it is preferable to use the above-mentioned rough copper foil as the current collector substrate. The negative electrode of the third embodiment is obtained by forming a silicone-based active material of the above thickness on the surface using the current collector copper foil of the third embodiment, and it is necessary to consider the relationship between the roughness of the surface of the current collector and the reciprocal of the electric double layer capacity of the surface, which is an indicator of the surface area, and the thickness of the silicone-based active material film to be formed. That is, forming a thick active material film on the fine rough surface shape having a large actual surface area of the aggregate copper foil of the third embodiment leads to smoothing the rough surface, and so care must be taken as the electric double layer capacity of the surface after forming the active material may decrease (or its reciprocal increase). For applications requiring a thick film, it is preferable to use copper foil with a small electric double layer capacity and a high surface roughness. Meanwhile, the thickness of the formed film may be determined by considering the actual capacity specifications of the secondary battery. If the active material film is too thin, the capacity becomes too small to be realistic, and if it is too thick, the current collector surface is smoothed and the actual surface area becomes small, and so the reaction site or surface area for charging and discharging becomes smaller, which ultimately leads to a decrease in cycle life. The lower limit thickness applicable to high-output secondary batteries such as uninterruptible power sources, engine starting auxiliary power sources, and hybrid vehicles can be about 0.5 μm , and in such cases, the upper limit specification of the reciprocal electric double layer capacity of the copper foil surface can be set to about 0.1 cm²/μF. The upper limit of thickness can be up to about 6 μm , which satisfies the practical capacity for high-energy, high-capacity applications, and in such cases, copper foil with a lower limit specification of about 0.03 cm²/μF as the reciprocal of the electric double layer capacity can be used. In addition, the relationship between the reciprocal electric double layer capacity of the surface of the current collector copper foil and the reciprocal electric double layer capacity of the surface where the active material film is formed is roughly recognized considering the thickness of the formed film among the same silicone-based active material film group. Thus, it is designed by considering the reciprocal of the electric double layer capacity of the surface of the current collector copper foil used and the thickness of the formed active material film so that a range of 0.1 to 3 cm²/μF of the reciprocal of the electric double layer capacity of the surface of the formed active material can be obtained.

- [0101] In the third embodiment, the negative electrode active material film mainly composed of silicone, which is formed directly on the current collector copper foil, is formed as follows. One film forming method is the CVD (chemical vapor deposition) method. For example, plasma CVD (PECVD, especially using VHF) and catalytic CVD (Cat-CVD, hot wire CVD) are preferably used, and it is also thought to be possible in the future to use LPCVD and atmospheric pressure plasma CVD, which are expected to be used in the future. In addition, deposition methods may be used, and the EB (electron beam) deposition method, which allows large-area film formation, is particularly preferable as it is economical. The silicone film layer formed by the CVD-based film forming method contains hydrogenated silicone, mainly contains SiH or SiH₂, in which hydrogen is bonded to 1 or 2 of the bond number of the silicone group, and the bonding concentration is approximately 0.1 to 12 atomic %, and contains more than 0.1 atomic % as hydrogen concentration. The content ratio varies depending on the film forming method and the film forming conditions, such as film forming temperature and silicone raw material, and can be mainly controlled by the holding temperature of the base current collector copper foil and the silicone raw material. In particular, in CVD methods, PE-CVD or Cat-, it can be controlled by the supply amount of silane gas, which is the main raw material, or the supply ratio of hydrogen gas that can be added. By introducing hydrogen groups into hydrogenated silicone or silicone, a structure with superior flexibility is obtained compared to the case of silicone monolith, and as for the volume expansion when silicone, which is a negative electrode active material, accepts Li ions and alloys during charging, it is possible to prevent cracks or defects in the silicone-based film itself from breaking the ion movement or conductive path, or suppressing a part of it from being separated from the current collector. In addition, as hydrogenated silicone hydrogen terminates defects in unbonded water (dangling bonds) that inevitably exist in silicone-based films, this leads to a reduction in unstable silicone defects and suppresses the occurrence of defects in the conductive path. Silicone-based active materials are composed mainly of silicone and inevitably contains materials other than the above hydrogen, and in particular, as a rule, it is preferable not to include other elements such as alloying elements, except in cases where some property improvement effect occurs. Such a silicone-based active material film is formed to a thickness of 0.5 to 6 μm on the surface of the current collector copper foil.
- [0102] In the third embodiment, if a layer containing phosphorus or boron is further formed on at least one of the lower layer or upper layer of the silicone-based active material film, the insufficient conductivity of silicone itself is improved, and it facilitates alloying of Li ions with silicone during charging and movement into and out of the layer when Li ions are released during discharge. In particular, if phosphorus is formed in the lower layer of the silicone-based film and boron is formed in the upper layer, Li ions are sufficiently alloyed to penetrate into the silicone-based film during charging. In addition, the configuration of forming boron in the lower layer of the silicone-based film and phosphorus in the upper layer facilitates the release by dealloying from the silicone-based film at the time of discharge of Li ions that are alloyed with the silicone-based film after charging, so that they are not released but remain in the silicone-based film, suppressing the loss of electricity that cannot be discharged while charging and the occurrence of irreversible capacity. Although it does not specify the conductivity of the silicone-based film itself, considering high rate conditions such as applications requiring instantaneous high-output discharge or high-speed charging, it is desirable to have a conductivity of 10-2 S/cm or more. It is also possible to heighten conductivity by doping the silicone-based film itself with phosphorus or boron. As the silicone-based film doped with phosphorus or boron and a silicone-based film with phosphorus or boron formed on the upper layer suppress the formation of an oxide film on silicone, it is possible to prevent increases in irreversible capacity due to the combination of oxygen and Li ions, that is, the decrease in charge/discharge capacity.
- [0103] On the other hand, when oxygen is added to the phosphorus-doped silicone-based film, the initial charge and discharge efficiency decreases, but the cycle life of repeated charge and discharge improves. This is presumed to be the effect of suppressing the volume change due to alloying and dealloying of lithium during charging and discharging by the introduction of oxygen or oxidation of silicone, in addition to the effect of phosphorus. The phosphorus content of the entire silicone-based film is preferably 0.1 atomic % or more and 30 atomic % or less, and more preferably 0.5 atomic % or more and 10 atomic % or less. If phosphorus is less than 0.1 atomic %, the improvement in conductivity and the effect on the intrusion and detachment of Li ions into silicone are small, and if the amount exceeds 30 atomic %, the amount introduced becomes excessive with respect to silicone and may even cause insertion and detachment of phosphorus itself from Li ions, so it actually causes problems with insertion and removal.
- [0104] The oxygen content of the entire silicone-based film is preferably 1 atomic % or more and 50 atomic % or less, and is selected based on the relationship between charge/discharge efficiency, cycle performance, and phosphorus concentration. At less than 1 atomic %, the effect of suppressing volume change due to insertion and extraction of Li ions is not recognized, and at an introduced concentration exceeding 50 atomic %, it becomes excessive relative to the amount of silicone, so as the thickness or volume of the active material increases, the charge/discharge capacity decreases, or the initial irreversible capacity increases due to an increase in the amount of bonding between oxygen and Li ions, the balance with the positive electrode is lost, so it cannot be done with a secondary battery.
- [0105] When doping silicone with phosphorus, for example, in case of doping with phosphine gas, etc., with boron, a film can be formed by continuously supplying raw material gas such as diborane in the same concentration based on the supply amount of silicone raw material gas such as monosilane gas or hydrogen.
- [0106] In addition, oxygen can be introduced into the silicone-based film by heat-treating the silicone-based film or the silicone-based film containing phosphorus or boron in an atmosphere where the oxygen amount is controlled or oxidized by air. The amount of oxygen, heat treatment temperature, and treatment time depend on the oxygen concentration desired to be contained. Other methods of forming a silicone-based film into which oxygen is introduced may include sputtering or vacuum evaporation into which oxygen is introduced.

- [0107] In the negative electrode according to the third embodiment, it is heat resistant to the lower layer of the silicone-based active material film or to any of the phosphorus or boron lower layers that may be formed there, and in addition, when each treatment layer for rust prevention and silane coupling is formed, it maintains heat resistance to high temperatures during film formation and deterioration over time until the active material is formed, and the adhesion between the formed active material film and the current collector film is improved. In addition, as the copper of the film current collector component and the active material are not diffusion alloyed, this can prevent a decrease in charge/discharge capacity.
- [0108] This heat-resistant layer is at least one layer of film formed between the copper of the current collector copper foil and silicone, a negative electrode active material, to prevent mixing with each other, and covers the surface of the copper foil. Preferably, a heat-resistant film containing at least nickel is formed on the surface of the copper foil. By forming a layer containing nickel that does not diffuse itself and acts as a physical shielding layer, heat resistance that suppresses diffusion into the active material of copper, which is a component of the current collector, is achieved when exposed to high temperatures when forming a silicone-based film or over a long period of time. It is preferable that the heat-resistant layer includes nickel in an amount of 0.01 to 0.2 g/m². This is because if the amount is small, heat resistance decreases, and if the amount is too large, the rough surface shape of the copper foil surface of the current collector is smoothed, which actually reduces adhesion to the active material.
- [0109] Additionally, a method of forming zinc at least on the rough surface of copper foil or on the upper layer of the nickel is also preferable. Zinc is diffused on the upper layer of the copper foil surface, or exists on the copper foil surface or the nickel film in a single layer. Zinc can be very easily diffusion-alloyed into copper or present in the nickel phase to provide heat resistance that prevents oxidation of copper or nickel, especially high-temperature oxidation. If the total amount is too small, the above-mentioned effect will be small, and if it is too large, the current collecting ability of the copper or nickel may be reduced, or it may thicken between the upper layer film and actually reduce the adhesion, so it should preferably be in the range of 0.003 to 0.05 g/m². As mentioned above, zinc imparts heat resistance by diffusion into copper or nickel or by its presence in the surface layer, but if there is too much zinc, the zinc itself may diffuse into the upper active material layer, so this needs to be taken into consideration. Also preferred is a combination of forming a layer containing nickel after forming zinc. In addition, various methods such as wet methods or dry methods can be used to form nickel and zinc, and as it is economical and a uniform and homogeneous film can be easily obtained under electrolytic conditions, an electroplating method using a known sulfuric acid bath, etc. can be recommended.
- [0110] In addition, in the third embodiment, the heat-resistant barrier film used in the first embodiment may be used instead of the heat-resistant layer. The heat-resistant barrier film has at least one of a layer containing 0.01 to 0.5 g/m² of nickel or a layer containing 0.001 to 0.1 g/m² of zinc.
- [0111] As the rust prevention treatment layer formed on the heat resistance treatment layer, a thin layer having a passivation function by an organic film or an inorganic film dielectric is used. The rust prevention layer prevents environmental deterioration of the copper foil during the period from manufacturing the copper foil of the current collector substrate to forming the active material film, and also helps with heat resistance during active material film formation. As an organic film, in addition to benzotriazoles and trityltriazoles of the triazole class used for new products and rolled copper foil, the forming organic thin layer obtained by immersion in an aqueous solution of thiazoles, imidazoles, mercaptans, triethanolamines, etc. or an alcohol-containing solvent is preferred. As an inorganic film, a thin chromate layer, which is a hydrated chromium oxide obtained by immersion in an aqueous solution of chromate or dichromate or electrolytic treatment, is preferably used, and unlike the organic thin layer, it has good heat resistance.
- [0112] In addition, when a silane coupling treatment layer is formed on the rust prevention treatment layer, the adhesion between the heat resistance treatment layer or the current collector and the silicone-based active material film is improved. Silane coupling treatment is generally performed by immersing the copper foil for a current collector on which the heat resistance and rust prevention treatment layer is formed in an aqueous solution in which a silane coupling agent is dissolved. The silane coupling agent is selected from its chemical structure and substituents according to its heat resistance and rust prevention layer. In particular, silane coupling agents such as kryloxy-based or epoxy-based may be recommended.
- [0113] The secondary battery using the negative electrode of the above third embodiment, or the negative electrode using a current collector, has high capacity and has the characteristic that the charging and discharging capacity does not decrease even with repeated charging and discharging cycles. If a non-aqueous solvent containing fluorine is used or added to an electrolyte solution using a non-aqueous solvent that constitutes a secondary battery, the period during which the capacity does not deteriorate even after repeated charging and discharging is extended, resulting in a longer lifespan. The fluorine-containing solvent alleviates the volume expansion of the silicone-based film due to alloying with Li ions during charging, so capacity decline due to charging and discharging can be suppressed. Fluorinated ethylene carbonate, fluorinated chain carbonate, etc. can be used as the fluorine-containing non-aqueous solvent. Fluorinated ethylene carbonates include mono-tetra-fluoroethylenecarbonate (4-fluoro-1,3-dioxolane-2-one, FEC), fluorinated chain carbonates include methyl 2,2,2-trifluoroethyl carbonate, ethyl 2,2,2-trifluoroethyl carbonate, etc., and these can be used singly or in combination by adding them to the electrolyte solution. As fluorine groups are easy to combine with silicone and are also hard, it is expected to stabilize the film against expansion due to alloying when charging with Li ions and contribute to suppressing expansion. As such, the negative electrode, negative electrode current collector, and non-aqueous solvent electrolyte secondary battery according to the third embodiment can be used as a driving power source for mobile electronic devices or power tools over a long period of time, as well as for industrial purposes or electric vehicles that require high energy.

- [0114] (Preferred manufacturing example of negative electrode for secondary battery of the present invention)
- [0115] Below, a preferred manufacturing example of the negative electrode for a secondary battery of the present invention will be described with reference to the figures. Additionally, the present invention is not limited to these manufacturing examples.
- [0116] FIG. 1 is an enlarged schematic cross-sectional view showing the first example of manufacturing the negative electrode of the present invention.
- [0117] The mountain-shaped rough surface of the current collector copper foil raw material (1) is used as a current collector base material without any new roughening treatment. Examples of the mountain-shaped rough surface of the current collector copper foil raw material (1) include the rough surface formed on the electrolyte liquid surface side of the electrolytic copper foil. After forming a heat-resistant layer or a heat-resistant barrier layer and a rust-prevention treatment layer or a silane coupling treatment layer (2) on this surface, a silicone-based active material film (3) is prepared.
- [0118] FIG. 2 is an enlarged schematic cross-sectional view showing the second example of manufacturing the negative electrode of the present invention.
- [0119] The mountain-shaped rough surface of the current collector copper foil raw material (1), further subjected to roughening treatment with fine copper particles (4), is used as a base material. After forming a heat-resistant layer or a heat-resistant barrier layer and a rust-prevention treatment layer or a silane coupling treatment layer (2) on this surface, a silicone-based active material film (3) is prepared.
- [0120] FIG. 3 is an enlarged schematic cross-sectional view showing the third example of manufacturing the negative electrode of the present invention.
- [0121] A current collector copper foil (5) further subjected to a roughening treatment with fine copper particles (4) on both sides of the copper foil to be smooth or glossy on one side is used as a base material. Examples of one side of the current collector copper foil raw material (5) that are smooth or glossy include the side of rolled copper foil and the side of the rotating drum surface of electrolytic copper foil. After forming a heat-resistant layer or a heat-resistant barrier layer and a rust-prevention treatment layer or a silane coupling treatment layer (2) on this surface, a silicone-based active material film (3) is prepared.
- [0122] FIG. 4 is an enlarged schematic cross-sectional view showing the fourth example of manufacturing the negative electrode of the present invention.
- [0123] A current collector copper foil (5) further subjected to a roughening treatment with fine copper particles (4) on both sides of the copper foil to be smooth or glossy on both sides is used as a base material. A heat-resistant layer or heat-resistant barrier layer and a rust-prevention treatment layer or silane coupling treatment layer (2) are formed on both roughened surfaces, respectively, and then a silicone-based active material film (3) is provided on each surface, and is a type in which the film structure on one side of FIG. 3 is configured on both sides. In addition, in FIG 3 and FIG. 4, only one layer of fine copper particles 4 is stacked, but when actually performing roughening treatment, the fine copper particles (4) are often stacked in multiple layers.
- [0124] As the negative electrode for secondary battery of the present invention shown in FIGS. 1, 2, 3, and 4 is formed by forming a silicone-based active material film after providing a heat-resistant layer or a heat-resistant barrier layer, a rust-prevention treatment layer, or a silane coupling treatment layer on a copper foil having a predetermined rough surface constituting the current collector substrate, as the copper component of the current collector substrate is not diffusion alloyed with the active material and has good adhesion, the high capacity originally possessed by silicone can be obtained during charging and discharging.
- [0125] Example
- [0126] (Example for First Embodiment)
- [0127] Examples 1-1 ~ 1-52, and Comparative Examples 1-1 ~ 1-14
- [0128] Below, the first embodiment will be described in detail through examples. This embodiment shows an example of the present invention with a single-side coating configuration described in FIGS. 1 to 3, but is not limited to this. For example, the same process can be performed in the double-sided film forming form shown in FIG. 4 in which the film forming treatment on one side is performed on both sides.
- [0129] (1) Sample Preparation of Examples and Comparative Examples
- [0130] First, a silicone-based negative electrode sample according to the present invention for test and evaluation, a negative electrode current collector used therefor, and a silicone-based negative electrode sample used for comparison were produced as follows.

- [0131] For the raw copper foil (copper foil base without surface treatment) used for current collector copper foil, rolled copper foil (manufactured by Nihon Seihaku Co., Ltd.) and electrolytic copper foil (manufactured by Furukawa Denki Kogyo Co., Ltd.) of various thicknesses were used. The rolled foil used was a double-sided glossy type of 12 μ m, and the electrolytic foil used a double-sided glossy type of 12 μ m, and a single-side glossy type of 12 μ m and 18 μ m were used. When roughening the surface of these raw materials, copper foil for printed circuit use was subjected to roughening treatment by (a) copper fine grain growth plating (so-called burning plating performed at a high current density that is above or close to the critical current density) and (b) conventional copper smooth plating (general copper plating performed below the limit current density to prevent applied particles from falling off), which were copper plating using a known copper sulfate-based aqueous solution. Also, as an example of processing to provide a heat-resistant layer, (c) nickel plating using a known nickel sulfate-based plating solution, or (d) zinc plating using a known zinc sulfate-based plating solution, and in the case of multiple layers, zinc plating was performed after nickel plating. On the other hand, in the case of forming a multi-layer as an example of forming a heat-resistant barrier film, nickel plating was performed after zinc plating. In addition, for the rust prevention treatment, (e) immersion in an aqueous benzotriazole solution or (f) electrolysis in an aqueous chromium trioxide solution was used, and for the adhesion improvement treatment, (g) immersion in an aqueous silane coupling agent solution was performed. In order to use these copper foils as current collectors, they were stored indoors for 3 months before forming a silicone-based active material into a film. In addition, the elongation of these copper foils for current collectors after being held at 180°C for 5 minutes was measured by a tensile test using a Tensiron tester, and surface roughness (Rz) was measured with a stylus-type roughness tester (manufactured by Kosaka Kenkyusho) according to JIS B0601 (1994 edition). The amount of nickel and zinc in the heat-resistant layer was measured by ICP (inductively coupled plasma) emission spectroscopy of an aqueous solution in which the surface film of the sample was dissolved per unit area.
- [0132] The silicone-based active material film was formed by the methods (h) to (l) below, and Examples 1-1 to 1-52 and Comparative Examples 1-1 to 1-14 were done. Silicon film formation was performed for each sample for a predetermined time based on the relationship between film forming thickness and film forming time based on the film forming speed determined in advance, and after film formation, confirmation was made from observation of the cross section of the sample using a SEM (scanning electron microscope). In addition, the amount of silicone film, which is a negative electrode active material, was determined from the mass measurement per unit area before and after silicone film formation. First, the bonding state of hydrogen was analyzed from the infrared absorption spectrum analysis of the formed silicone film using FT-IR (Fourier transform infrared spectrophotometer), and then, the hydrogen concentration was measured by SIMS (secondary ion mass spectrometry). Regarding the series including the above (a) example in which zinc plating was formed after nickel plating as the heat-resistant layer, the specifications of the current collector copper foil used for each sample are shown in Table 1, and the appearance abnormalities after indoor storage before film formation and film formation specifications are shown in Table 2. Next, for the series mentioned in (b) examples of heat-resistant barrier film formation, each specification is similarly shown in Table 4, and the appearance abnormalities after indoor storage and film formation specifications are shown in Table 5. After producing Examples 1-53 to 1-55 in which the film forming thickness was changed according to the film forming conditions of Example 1-12, oxygen was introduced by the method (m) below. This is shown in Table 7 along with the test evaluation results shown below. Phosphorus and oxygen contained in the silicone-based active material are subject to the above ICP analysis.
- [0133] (a) Burning plating of roughening treatment: Without heating in an electrolyte containing 30 g/dm³ of copper and 150g/dm³ of sulfuric acid as main components, the current density was appropriately selected in the range of 10 to 20A/dm² along with the electrolysis time, and cathodic electrolysis was performed under conditions to obtain a predetermined surface shape.
- [0134] (b) Smooth copper plating with roughening treatment: In an electrolyte containing 70 g/dm³ of copper and 100g/dm³ of sulfuric acid as main components and maintained at a temperature of 40°C, the cathodic electrolysis was performed under appropriately selected conditions with a current density in the range of 5 to 10 A/d m² and an electrolysis time to obtain a predetermined surface shape determined in advance along with the conditions (a).
- [0135] (c) Nickel plating solution: Cathodic electrolysis was performed by selecting a time according to the formation amount under the conditions of 160 g/dm³ of nickel sulfate (hexahydrate), 30 g/dm³ of boric acid, and 1A/dm².
- [0136] (d) Zinc plating: Cathodic electrolysis was performed by appropriately selecting a plating time according to the plating amount under the conditions of zinc 10 g/dm³, pH 12, and 0.1A/dm².
- [0137] (e) Rust prevention treatment 1: Immersion in 1% by weight benzotriazole aqueous solution
- [0138] (f) Rust prevention treatment 2: 70g/dm³ chromium trioxide aqueous solution, pH2, 1C/dm², cathode electrolysis
- [0139] (g) Silane coupling treatment: Immersion in 4 gd m³ aqueous solution of kryloxy-based silane coupling agent (manufactured by Shinetsu Chemical Co., Ltd.)
- [0140] (h) Silicon film forming method 1, and phosphorus or boron doping method for silicone: Using the Cat-CVD device (Anerva Co., Ltd. product, total discharge frequency 13.56~40MHz), a monosilane gas of 20 sccm (Standard cc/min.: Standard condition volume flow rate), a current collector temperature of 250°C, and a tungsten precatalyst temperature of 1800°C were used as basic conditions, and an appropriate film forming time was selected according to the film forming thickness. In the case of film formation while doping phosphorus, 10sccm of phosphine gas was supplied, and in the case of doping boron, diborane gas was supplied simultaneously with monosilane gas. Additionally, when forming a layer containing phosphorus or boron on the upper or lower layer of the silicone-based film, it was formed according to the film forming method of doping phosphorus or boron. Depending on the sample, hydrogen gas was simultaneously supplied to the raw material gas such as silane gas to form a film. By changing the supply concentration ratio [H₂]/[SiH₄] of hydrogen gas and monosilane gas, that is, the hydrogen dilution ratio, silicone-based active material films with different hydrogenated silicone content ratios were formed.
- [0141] (i) Silicone film formation method 2: By a parallel plate type CVD (PECVD) device (discharge frequency 60 MHz) equipped

with a plasma electrode of a shower head structure, using a current collector temperature of 200°C and a single supply concentration of 100 sccm of silane gas with a hydrogen dilution ratio of 0 as standard conditions, the film was formed by changing the hydrogen dilution ratio as described above.

- [0142] (j) Silicone film formation method 3: High-purity silicone raw material was sublimated by heating at 200 W using EB (electron beam) gun and a silicone evaporation source using an evaporation device (manufactured by Ulvac Co., Ltd.) and deposited on the current collector. Here, a hydrogen atmosphere was not used, such as by supplying hydrogen gas.
- [0143] (k) Silicone film formation method 4: Film was attached and formed on the current collector using a sputtering device (manufactured by Ulvac Co., Ltd.) equipped with a high-purity silicone raw material and a sputter cathode at 80 sccm of argon gas (sputter gas) and 1 kW of high-frequency output.
- [0144] (l) Silicone film formation method 5: The raw materials were melted and volatilized by resistance heating using a vacuum evaporation device (manufactured by Ulvac Co., Ltd.) equipped with high-purity silicone raw materials and a resistance heating source to form a film.
- [0145] (m) Oxidation treatment: Heat treatment was performed at 100°C in the air for a predetermined period of time depending on the introduced oxygen concentration.
- [0146] (2) Test evaluation of samples

[0147] Next, it was produced as above. Test evaluation of the silicone-based negative electrode sample according to the present invention and the silicone-based negative electrode sample used for comparison was conducted as follows.

[0148] A hole with a diameter of 20 mm was made in the negative electrode sample and this was used as a test electrode, and a three-electrode cell using lithium foil as a dipole and reference electrode used an electrolyte in which 1M lithium hexafluorophosphate (LiPF₆) is dissolved in a non-aqueous electrolyte with a volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) of 3: 7, and was assembled as a closed cell at 25°C in a dry atmosphere with a humidity of 7% or less. However, in some embodiments, a solvent having a volume ratio of fluoroethylene carbonate (FEC) and methyltrifluoroethyl carbonate (MFEC), which are non-aqueous solvents containing fluorine in their chemical structure, of 1: 3 was used. The first charging process was carried out at a constant current rate of 0.1C up to a potential of +0.02V based on the redox potential of lithium as described above, and the first charging capacity obtained at this time was tested and measured for each sample and converted to per unit mass of the active material silicone. In the first discharge treatment that followed, discharge was performed at a 0.1C rate constant current to 1.5V for the same lithium potential standard as above, and likewise, the first discharge capacity was measured for each and converted to per unit mass of silicone. In addition, the first actual discharge capacity value was obtained from the previously measured film forming mass and discharge current of the silicone active material. After completion of the first charge/discharge process, the charge/discharge rate was set to 0.2C, and charge/discharge cycles were performed 50 times until each end potential of the first charge/discharge process was completed. The discharge capacity at the end of 50 cycles was determined for each sample and converted to per unit mass. The above first charge/discharge capacity, actual discharge capacity, and discharge capacity after 50 cycles are shown in Table 3 for a series of samples including (a) a heat-resistant layer, and (b) the heat-resistant barrier film is shown in Table 6. For the samples of Examples 1-5, 1-12, and 1-53 to 1-55, the charging capacity was regulated to 1000 mAh/g, and a charge/discharge cycle test based on capacity regulation in which discharge was performed as above was performed for 1000 cycles, as shown in Table 7.

TABLE 1

[0149]

No	Current collector copper foil									
	Manufacturing method and foil thickness (μm)	Type of raw copper foil	Whether or not roughening has been carried out	Appearance of active material formation surface	180°C elongation	Surface roughness (Rz) (μm)	Heat-resistant layer (g/㎡)		Rust treatment layer	Adhesion improvement treatment layer
Example 1-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	3.0	0.015	0.01	Benzotriazole	Silane coupling
Comparative Example 1-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	0.8	0.015	0.01	Benzotriazole	Silane coupling
Example 1-2	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	1.3	0.016	0.007	Chromate	Silane coupling
Example 1-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	1.5	0.016	0.007	Chromate	Silane coupling
Example 1-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	3.9	0.01	0.008	Chromate	Silane coupling
Comparative Example 1-2	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	3.9	0.01	0.008	Chromate	Silane coupling
Example 1-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.2	0.01	0.008	Chromate	Silane coupling
Comparative Example 1-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.2	0.01	0.008	Chromate	Silane coupling

Example 1-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.1	2.2	0.015	0.011	Chromate	Silane coupling
Example 1-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	3.3	0.05	0.01	Chromate	Silane coupling
Example 1-8	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	3.3	0.05	0.01	Chromate	Silane coupling
Comparative Example 1-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	3.3	0.05	0.01	Chromate	Silane coupling
Example 1-9	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Comparative Example 1-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Comparative Example 1-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Example 1-10	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Comparative Example 1-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Example 1-11	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	4.0	0.01	0.006	Chromate	Silane coupling
Example 1-12	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Comparative Example 1-8	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.1	2.0	0.013	0.01	Chromate	Silane coupling
Example 1-13	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Comparative Example 1-9	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.4	0.009	0.008	Chromate	Silane coupling
Example 1-14	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Comparative Example 1-10	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Example 1-15	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Example 1-16	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling
Example 1-17	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	3.5	0.01	0.008	Chromate	Silane coupling
Example 1-18	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	2.5	0.008	0.05	Chromate	Silane coupling
Example 1-19	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.011	0.05	Chromate	Silane coupling
Example 1-20	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	3.7	—	0.04	Chromate	Silane coupling
Example 1-21	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	—	0.06	Chromate	Silane coupling
Example 1-22	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.008	0.004	Chromate	Silane coupling
Example 1-23	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.008	0.002	Chromate	Silane coupling
Example 1-24	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	—	Chromate	Silane coupling
Example 1-25	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.012	—	Chromate	Silane coupling
Example 1-26	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.18	—	Chromate	Silane coupling

Example 1-27	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.22	—	Chromate	Silane coupling
Example 1-28	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	—	—	Chromate	Silane coupling
Example 1-29	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	N/A	N/A
Example 1-30	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	Chromate	N/A
Example 1-31	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	N/A	Silane coupling
Example 1-32	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling
Example 1-33	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling
Comparative Example 1-11	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling
Comparative Example 1-12	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling
Comparative Example 1-13	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling
Example 1-34	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	3.1	4.0	0.011	0.01	Chromate	Silane coupling
Example 1-35	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	5.3	3.8	0.012	0.01	Chromate	Silane coupling
Example 1-36	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	2.5	4.2	0.01	0.01	Chromate	Silane coupling
Example 1-37	Electrolysis 12	Glossy on one side (FIG. 2)	Has one side	Non-glossy	7.7	6.8	0.015	0.006	Chromate	Silane coupling
Example 1-38	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.013	0.008	Chromate	Silane coupling
Example 1-39	Electrolysis 18	Glossy on one side (FIG. 2)	Has one side	Non-glossy	8.7	8.2	0.018	0.012	Chromate	Silane coupling
Example 1-40	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.011	0.01	Chromate	Silane coupling
Comparative Example 1-14	Electrolysis 12	Double-sided gloss (FIG. 3)	N/A	Gloss	7.2	1.0	0.02	0.005	Chromate	Silane coupling

Table 2

[0150]

No	Appearance before formation (after 3 months of indoor storage)	Lower layer film	Active material film											Upper layer film	Remarks
		Si layer containing p P, B	Thickness (μm)	Mass (g/m ²)	Si	SiHx (FT-IR)	H concentration (%)	Doping element	Hydrogen dilution ratio [H ₂]/[SiH ₄]	Current collector heating temperature (°C)	Formation method	Formation time (minutes)	Si layer containing p P, B		
Example 1-1		—	1.0	2.30	○	SiH, SiH ₂	15	—	10	200	PECVD	—	—	—	
Comparative Example 1-1		—	1.0	2.30	○	SiH, SiH ₂	14	—	10	200	PECVD	—	—	—	
Example 1-2		—	1.0	2.30	○	SiH, SiH ₂	14	—	10	200	PECVD	6	—	—	
Example 1-3		—	1.0	2.30	○	SiH, SiH ₂	12	—	8	250	PECVD	6	—	—	

Exempl e 1-4		-	0.6	1.40	○	SiH,Si H2	4	-	1	250	PECVD	-	-	-
Compar ative Exempl e 1-2		-	0.3	0.70	○	SiH,Si H2	4	-	1	250	PECVD	-	-	-
Exempl e 1-5		-	5.0	11.50	○	SiH,Si H2	3	-	0.5	350	PECVD	-	-	-
Compar ative Exempl e 1-3		-	8.5	19.50	○	SiH,Si H2	2	-	0.5	350	PECVD	-	-	-
Exempl e 1-6		-	7.5	17.30	○	SiH,Si H2	2	-	0.5	350	PECVD	-	-	-
Exempl e 1-7		-	2.0	4.70	○	SiH,Si H2	20	-	50	250	PECVD	-	-	-
Exempl e 1-8		-	2.0	4.70	○	SiH,Si H2	30	-	50	125	PECVD	-	-	-
Compar ative Exempl e 1-4		-	2.0	4.70	○	SiH,Si H2	50	-	120	85	PECVD	-	-	Occurrence of particles
Exempl e 1-9		-	2.0	4.70	○	SiH,Si H2	0.15	-	0	350	PECVD	-	-	-
Compar ative Exempl e 1-5		-	2.0	4.70	○	SiH	0.05	-	0	450	PECVD	-	-	-
Compar ative Exempl e 1-6		-	2.0	4.70	○	(H)	0.03	-	0	550	PECVD	-	-	-
Exempl e 1-10		-	2.0	4.70	○	SiH,Si H2	5	-	0	250	Cat-C VD	11	-	-
Compar ative Exempl e 1-7		-	2.0	4.70	○	SiH	0.05	-	110	450	Cat-C VD	11	-	-
Exempl e 1-11		-	2.0	4.70	○	SiH,Si H2	0.15	-	90	400	Cat-C VD	11	-	-
Exempl e 1-12		-	1.0	2.30	○	SiH,Si H2	7	P	0.5	250	Cat-C VD	-	-	-
Compar ative Exempl e 1-8		-	1.0	2.30	○	SiH	0.08	P	20	400	Cat-C VD	-	-	-
Exempl e 1-13		-	1.0	2.30	○	SiH,Si H2	5	B	1	250	Cat-C VD	-	-	-
Compar ative Exempl e 1-9		-	1.0	2.30	○	SiH	0.07	B	30	450	Cat-C VD	-	-	-
Exempl e 1-14		P0.1 μm	1.0	2.30	○	SiH,Si H2	9	-	2	250	Cat-C VD	-	-	-
Compar ative Exempl e 1-10		P0.1 μm	1.0	2.30	○	SiH	0.06	-	0	450	Cat-C VD	-	-	-
Exempl e 1-15		-	1.0	2.30	○	SiH,Si H2	5	-	0	300	Cat-C VD	-	B0.1 μm	-
Exempl e 1-16		P0.1 μm	1.0	2.30	○	SiH,Si H2	6	-	0	250	Cat-C VD	-	B0.1 μm	-
Exempl e 1-17		-	2.0	4.70	○	SiH,Si H2	7	-	0.5	250	Cat-C VD	-	-	-
Exempl e 1-18		-	1.0	2.30	○	SiH,Si H2	7	-	0.5	250	Cat-C VD	6	-	(Zn trace diffusion)

Examp e 1-1 9		-	1.0	2.30	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 0		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 1		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	(Zn trace diffusio n)
Examp e 1-2 2		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 3		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	Cu small amount diffusio n
Examp e 1-2 4		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	Cu small amount diffusio n
Examp e 1-2 5		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 6		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 7		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-2 8		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	Cu diffusio n alloyin g
Examp e 1-2 9	Brown rust discolor ation	-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 0		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 1	Spot discolor ation	-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 2		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	12	-	-
Examp e 1-3 3		-	2.0	4.70	○	SiH ₄ Si H ₂	8	-	5	250	PECVD	33	-	-
Compar ative Examp e 1-1 1		-	2.0	4.70	○	(H)	-	-	-	-	EB depositi on	50	-	-
Compar ative Examp e 1-1 2		-	2.0	4.70	○	-	-	-	-	-	Sputter	333	-	-
Compar ative Examp e 1-1 3		-	2.0	4.70	○	(H)	-	-	-	-	Resista nce heat depositi on	167	-	-
Examp e 1-3 4		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 5		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 6		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-
Examp e 1-3 7		-	2.0	4.70	○	SiH ₄ Si H ₂	7	-	0.5	250	Cat-C VD	-	-	-

Example 1-3 8		—	2.0	4.70	○	SiH ₂ SiH ₂	7	—	0.5	250	Cat-C VD	—	—	—
Example 1-3 9		—	2.5	5.80	○	SiH ₂ SiH ₂	7	—	0.5	250	Cat-C VD	—	—	—
Example 1-4 0		—	2.0	4.70	○	SiH ₂ SiH ₂	7	—	0.5	250	Cat-C VD	—	—	—
Comparative Example 1-1 4		—	Partial peeling	—	○	—	—	—	0.5	250	Cat-C VD	—	—	—

Table 3

[0151]

No	Test evaluation results				
	Non-aqueous solvent of electrolyte	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	Actual discharge capacity (mAh)	Discharge capacity after 50 charges/discharges (mAh/g)
Example 1-1	Does not contain F	3,415	3,210	2.6	1,368
Comparative Example 1-1	Does not contain F	2,654	2,442	2.0	354
Example 1-2	Does not contain F	3,078	2,770	2.2	621
Example 1-3	Does not contain F	3,537	3,360	2.7	1,025
Example 1-4	Does not contain F	3,370	3,134	1.5	1,008
Comparative Example 1-2	Does not contain F	2,314	2,025	0.5	426
Example 1-5	Does not contain F	3,380	3,177	12.7	876
Comparative Example 1-3	Does not contain F	2,865	2,664	18.1	208
Example 1-6	Does not contain F	3,055	2,933	17.6	603
Example 1-7	Does not contain F	3,076	2,922	4.7	1,022
Example 1-8	Does not contain F	2,881	2,737	4.4	964
Comparative Example 1-4	Does not contain F	2,069	1,966	3.1	652
Example 1-9	Does not contain F	3,462	3,289	5.3	916
Comparative Example 1-5	Does not contain F	3,046	2,894	4.6	388
Comparative Example 1-6	Does not contain F	2,765	2,627	4.2	152
Example 1-10	Does not contain F	3,507	3,332	5.3	1,327
Comparative Example 1-7	Does not contain F	3,211	3,050	4.9	447
Example 1-11	Does not contain F	3,464	3,291	5.3	1,045
Example 1-12	Does not contain F	3,706	3,521	2.8	1,697
Comparative Example 1-8	Does not contain F	3,288	3,124	2.5	605
Example 1-13	Does not contain F	3,744	3,557	2.8	1,733
Comparative Example 1-9	Does not contain F	3,355	3,187	2.5	633
Example 1-14	Does not contain F	3,742	3,555	2.8	1,733
Comparative Example 1-10	Does not contain F	3,156	2,998	2.4	677
Example 1-15	Does not contain F	3,752	3,564	2.9	1,742
Example 1-16	Does not contain F	3,760	3,572	2.9	1,799
Example 1-17	Does not contain F	3,674	3,490	5.6	1,206
Example 1-18	Does not contain F	3,311	3,152	2.5	1,285
Example 1-19	Does not contain F	3,452	3,269	2.6	1,397
Example 1-20	Does not contain F	2,941	2,800	4.5	1,266
Example 1-21	Does not contain F	2,779	2,646	4.2	1,130
Example 1-22	Does not contain F	3,016	2,871	4.6	1,169
Example 1-23	Does not contain F	2,813	2,644	4.2	964
Example 1-24	Does not contain F	2,725	2,578	4.1	918
Example 1-25	Does not contain F	2,133	2,983	4.8	1,084
Example 1-26	Does not contain F	3,374	3,212	5.1	1,226
Example 1-27	Does not contain F	3,246	3,090	4.9	1,023
Example 1-28	Does not contain F	2,025	1,928	3.1	623
Example 1-29	Does not contain F	1,807	1,446	2.3	545
Example 1-30	Does not contain F	3,198	3,029	4.8	1,234
Example 1-31	Does not contain F	2,506	2,373	3.8	718
Example 1-32	Does not contain F	3,657	3,474	5.6	1,438
Example 1-33	Does not contain F	3,315	3,149	5.0	1,165
Comparative Example 1-11	Does not contain F	3,207	3,047	4.9	946
Comparative Example	Does not contain F	2,819	2,678	4.3	374

1-12					
Comparative Example 1-13	Does not contain F	2,944	2,797	4.5	634
Example 1-34	Does not contain F	3,421	3,259	5.2	1,010
Example 1-35	Does not contain F	3,601	3,448	5.5	1,259
Example 1-36	Does not contain F	3,369	3,260	5.2	789
Example 1-37	Does not contain F	3,483	3,309	5.3	975
Example 1-38	Does not contain F	3,657	3,474	5.6	1,452
Example 1-39	Does not contain F	3,434	3,262	6.5	1,238
Example 1-40	Contains F	3,766	3,578	5.7	1,804
Comparative Example 1-14	—	—	—	—	—

Table 4

[0152]

No	Current collector copper foil									
	Manufacturing method and foil thickness (μm)	Type of raw copper foil	Whether or not roughening has been carried out	Appearance of active material formation surface	180°C elongation (%)	Surface roughness (Rz) (μm)	Heat-resistant barrier film (g/m ²)		Rust treatment layer	Adhesion improvement treatment layer
							1st layer Zn	2nd layer Ni		
Example 1-41	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	3.1	0.03	—	Chromate	Silane coupling
Example 1-42	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.3	2.6	0.05	0.008	Chromate	Silane coupling
Example 1-43	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.3	2.6	0.05	0.011	Chromate	Silane coupling
Example 1-44	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	3.1	0.09	—	Chromate	Silane coupling
Example 1-45	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	3.1	0.11	—	Chromate	Silane coupling
Example 1-46	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	3.1	0.004	0.008	Chromate	Silane coupling
Example 1-47	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	3.1	0.002	0.008	Chromate	Silane coupling
Example 1-48	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.1	2.4	—	0.008	Chromate	Silane coupling
Example 1-49	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.1	2.4	—	0.012	Chromate	Silane coupling
Example 1-50	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.1	2.4	—	0.48	Chromate	Silane coupling
Example 1-51	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.1	2.4	—	0.52	Chromate	Silane coupling
Example 1-52	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.1	2.4	—	—	Chromate	Silane coupling

Table 5

[0153]

No	Appearance before formation (after 3 months of indoor storage)	Lower layer film P, B	Active material film									Upper layer film P, B	Diffusion of current collector components
			Thickness (μm)	Mass (g/m2)	Silicone	SiHx (FT-I R)	H concentration (%)	Doping element	Hydrogen dilution ratio [H2]/[SiH4]	Current collector heating temperature (°C)	Formation method		
Example 1-41		—	1.5	3.50	○	SiH ₃ SiH ₂	5	—	0	250	Cat-CVD	—	—

Examp e 1-4 2		-	1.0	2.30	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-(Zn trace diffusio n)
Examp e 1-4 3		-	1.0	2.30	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-
Examp e 1-4 4		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-(Zn trace diffusio n)
Examp e 1-4 5		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-(Zn trace diffusio n)
Examp e 1-4 6		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-
Examp e 1-4 7		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	Cu small amount diffusio n
Examp e 1-4 8		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	Cu small amount diffusio n
Examp e 1-4 9		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-
Examp e 1-5 0		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-
Examp e 1-5 1		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	-
Examp e 1-5 2		-	2.0	4.70	○	SiH ₂ SiH ₂	5	-	0	250	Cat-C VD	-	Cu diffusio n alloying

Table 6

[0154]

No	Test evaluation results				
	Non-aqueous solvent of electrolyte	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	Actual discharge capacity (mAh)	Discharge capacity after 50 charge/discharge cycles (mAh/g)
Example 1-41	Does not contain F	3,286	3,128	3.8	1,315
Example 1-42	Does not contain F	3,305	3,146	2.5	1,338
Example 1-43	Does not contain F	3,410	3,229	2.6	1,462
Example 1-44	Does not contain F	2,946	2,805	4.5	1,271
Example 1-45	Does not contain F	2,832	2,696	4.3	1,115
Example 1-46	Does not contain F	2,887	2,748	4.4	1,066
Example 1-47	Does not contain F	2,802	2,634	4.2	894
Example 1-48	Does not contain F	2,751	2,619	4.2	813
Example 1-49	Does not contain F	3,278	3,121	5.0	1,079
Example 1-50	Does not contain F	3,459	3,293	5.3	1,246
Example 1-51	Does not contain F	3,450	3,284	5.3	1,097
Example 1-52	Does not contain F	1,898	1,807	2.9	644

Table 7

[0155]

No	Active material film	100°C air oxidation treatment	Test evaluation results
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	Thickness (μm)	Mass (g/m ²)	Si	P- doping/at omic %	Oxygen/a tomic %	Non- aqueous solvent of electrolyt e	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	1000th charging capacity (mAh/g)	1000th discharge capacity (mAh/g)
Example 1-5	5.0	11.50	○	—	—	Does not contain F	1,000	1,000	—	—
Example 1-12	1.0	2.30	○	3	—	Does not contain F	1,000	1,000	541	528
Example 1-53	5.0	11.50	○	10	40	Does not contain F	1,000	1,000	1,000	1,000
Example 1-54	3.0	6.90	○	3	25	Does not contain F	1,000	1,000	1,000	1,000
Example 1-55	1.0	2.30	○	1	10	Does not contain F	1,000	1,000	1,000	1,000

[0156] From the above sample production and test evaluation, the following can be seen. First of all, (a) the main examples are mentioned through a series of Examples 1-1 to 1-40 and Comparative Examples 1-1 to 1-14 including the heat-resistant layer shown in Tables 1 to 3. Comparing the first charge capacity, discharge capacity, and discharge capacity after 50 cycles of each sample, it can be seen that the charge and discharge characteristics of the sample according to the example are good. For example, in Examples 1-1 to 1-2 and Comparative Example 1-1, which used rolled copper foil as the current collector, in the Comparative Example where the copper foil surface roughness (R_z) was as small as $0.8\ \mu\text{m}$, the adhesion between the current collector and the active material film was weak due to insufficient real area and unevenness of the current collector surface, and the capacity after 50 repeated charge and discharge cycles decreased significantly, resulting in less than 400 mAh/g. This appears to be due to repeated expansion and contraction during charging and discharging, resulting in a gap occurring at the interface between the active material and the copper foil, resulting in deterioration of current collecting properties, etc. In Examples 1-1 to 1-2, which have R_z of $1\ \mu\text{m}$ or more and a predetermined current collector surface roughness, the discharge capacity after 50 cycles exceeded 500 mAh/g. In addition, Example 1-3 using the same double-sided glossy electrolytic foil with R_z exceeding $1\ \mu\text{m}$ also showed good charge and discharge characteristics, and after 50 cycles, the discharge capacity was over 1000 mAh/g.

[0157] The amount of film formation of the silicone-based active material can be seen from comparison between Examples 1-4 to 1-6 and Comparative Examples 1-2 to 1-3. In cases where it is too thin, such as Comparative Example 1-2, the initial capacity per unit mass is also lower than that of others, and is generally too small for the practical amount of electricity required for devices, remaining at a capacity of one-tenth of the approximately 5 mAh required for electronic devices. Additionally, a large decrease in discharge capacity after the cycle, which is assumed to be due to irreversible capacity, is also seen. Even in the case of high-output applications that can be applied even with a small capacity per unit cell, it is preferable to be $0.5\ \mu\text{m}$ or more in Example 1-4, or $1\ \text{g/m}^2$ or more. In addition, the upper limit of the active material film is set at $8\ \mu\text{m}$ or $18\ \text{g/m}^2$ because, in the case of a collector with a low surface roughness, forming a thicker film flattens the fine surface shape and leads to a decrease in adhesion, which greatly deteriorates the discharge capacity after a charge/discharge cycle in the case of a too thick active material formation example of $8.5\ \mu\text{m}$, shown in Comparative Examples 1-3. Therefore, even when using a current collector with such a low roughness, it is better to limit the thickness to $8\ \mu\text{m}$ or more or the formation amount to $18\ \text{g/m}^2$ or less as shown in Examples 1-5 to 1-6.

[0158] From Examples 1-7 to 1-11 and Comparative Examples 1-4 to 1-7, the hydrogenated silicone and hydrogen concentration contained in the silicone-based active material, the hydrogen dilution ratio of the feedstock gas, and the current collector temperature at the time of film formation are determined. In Example 1-7, a silicone-based film containing 20 atomic% hydrogen was obtained under the conditions of increasing the hydrogen supply concentration of the raw material gas at a standard base current collector copper foil heating temperature of 250°C during film formation, and although the initial capacity decreased, the capacity after the cycle test was maintained at 1000 mAh/g. However, under the conditions in which the current collector temperature was lowered in Example 1-8, a film with a hydrogen concentration of 30 atomic % was obtained, the initial capacity was 3000 mAh/g, and the capacity after the cycle test was less than 1000 mAh/g. In addition, under the film forming conditions of Comparative Example 1-4, in which the heating temperature was set to less than 100°C and the hydrogen supply concentration was increased to a dilution ratio of 120, particles were generated, indicating poor film forming. When the hydrogen supply ratio or hydrogen content ratio is increased, a tendency for particles (granular deposition) at the time of film forming is observed, and a decrease in the initial capacity and a decrease in the capacity after the cycle are also recognized, and so it is preferable that the upper limit of the hydrogen content in the silicone film is about 30 atomic %, the current collector heating temperature under film forming conditions is about 100°C or more, and the hydrogen dilution ratio of the raw material gas is preferably 100 or less. In addition, in the conditions in which the current collector was heated to a high temperature of 450°C and 550°C without hydrogen dilution in the PECVD of Comparative Examples 1-5 to 1-6, and in the Cat-CVD of Comparative Example 1-7, in the conditions where the hydrogen dilution ratio was 110 and the current collector was 450°C , a silicone-based film with a hydrogen content of less than 0.1 atomic percent was obtained, and the discharge capacity after cycling was less than 500 mAh/g. On the other hand, as the silicone-based films containing 0.15 atomic% hydrogen of Examples 1-9 and 1-11 showed the same capacity around 1000 mAh/g, as hydrogenated silicone, it is necessary to include a certain amount of hydrogen in the silicone-based film, and the amount of hydrogen is preferably 0.1 atomic % or more. In addition to this, as only SiH is detected from FT-IR analysis of the silicone-based films of Comparative Examples 1-5 and 1-7, it is presumed that the fact that it does not contain SiH₂, which exhibits an organic structure, is the cause of the small discharge capacity after cycling from comparison with Examples 1-9 or 1-11. In addition, in Comparative Example 1-6, in which the amount of hydrogen was small, SiH was not detected and it was designated as a silicone-based film containing no hydrogenated silicone, showing lower charge and discharge characteristics. In other words, as the silicone-based film that does not contain hydrogen groups is dense and hard, even if the initial capacity is obtained relatively high, it is assumed that film deterioration occurs during the repeated process of alloying and dealloying with Li

ions during charging and discharging. In addition, Example 1-10 shows an example in which a film sufficiently containing hydrogenated silicone can be obtained by Cat-CVD film formation even under the condition of a silane gas-only feedstock without hydrogen dilution.

[0159] Examples 1-12 to 1-13 and Comparative Examples 1-8 to 1-9 show examples of film formation in which silicone of the active material was doped with phosphorus or boron. Doped Examples 1-12 and 1-13 showed the same good charge/discharge characteristics as the non-doped examples. However, in all of the comparative examples in which the hydrogenated silicone did not meet 0.1 atomic % as a hydrogen concentration, the capacity after 50 cycles was greatly reduced compared with the examples. In the Comparative Example, the film formation result was similar to the above example and did not contain SiH₂.

[0160] Examples 1-14 to 1-16 and Comparative Example 1-10 show examples in which a silicone layer containing phosphorus or boron was further formed on the lower or upper layer of the silicone active material film. The silicone-based film with low hydrogen concentration of Comparative Example 1-10 had a significantly lower discharge capacity compared to Example 1-14, as described above. In an example of the present invention according to three embodiments, it showed good charge/discharge characteristics, and in particular, Examples 1-16 showed the best results among tests using a non-fluorine-containing non-aqueous electrolyte solution. It is presumed that this is because the film structure of forming a layer containing phosphorus in the lower layer and boron in the upper layer promotes the movement of Li ions and electrons due to the electric field drift effect, thereby lowering the irreversible capacity associated with the secondary battery.

[0161] The formation amount and evaluation of the nickel layer and zinc layer formed at least partially as the heat-resistant layer are mainly determined from comparison of 1-17 to 1-28. In Example 1-28, in which no film is formed, the copper of the current collector component is diffusion alloyed in the active material film, and the first charge/discharge capacity is around 2000 mAh/g, which is low compared to others, and the capacity after 50 cycles is also below 700 mAh/g. In the case of a nickel single layer, a small amount of copper diffusion remained at 0.008 g/m² in Example 1-24, and this did not occur at 0.012 g/m² in Example 1-25, so it was sufficient to form 0.01 g/m² or more. In Examples 1-26 to 1-27, the capacity decreases when the cycle is repeated, the upper limit in the case of the heat-resistant layer is preferably 0.2 g/m² or less. When combined with a zinc layer of 0.003 g/m² or more, the nickel amount may be 0.01 g/m² or less, as can be seen from the comparison of Examples 1-22 to 1-23. Also, as shown in Examples 1-18 to 1-21, when the amount of zinc is large, it is recognized that the active material capacity tends to decrease due to diffusion of zinc into the silicone-based film, so it can be seen that this needs to be taken into consideration. In addition, while a single-layer film with an increased zinc content of about 0.02 to 0.04 g/m² is also effective, if it is too high, the capacity will decrease, so in the case of a heat-resistant layer, it is better to set the upper limit to about 0.05 g/m². As even in Example 1-17, which did not have a particularly thick heat-resistant layer, standard good cycle characteristics were shown, and the negative effect of lowering the initial capacity due to the thick heat-resistant layer was also recognized, typically, a balanced heat-resistant layer of two layers is preferable.

[0162] Next, the effects of the rust prevention treatment and the adhesion improvement treatment are evident from comparison with Examples 1-29 to 1-31 and examples other than these. In Example 1-29, in which nothing was done, rust occurred during indoor storage until film forming, and charge/discharge characteristics were poor. On the other hand, Example 1-30, in which only rust prevention treatment was performed, showed good charge and discharge characteristics, and Example 1-31, in which only the adhesion improvement treatment was performed, had a low initial charge/discharge capacity and spotted discoloration occurred, but had a capacity of more than 700 mAh/g after the end of the cycle. In case there is a possibility of long-term inventory until film formation, it is advisable to also perform rust prevention treatment or adhesion improvement treatment. In addition, rust prevention treatment with benzotriazole, an organic dielectric film of Example 1-1, showed the same rust prevention effect as the chromate treatment layer and also had good charge and discharge characteristics.

[0163] Next, when comparing Examples 1-32 to 1-33 and Comparative Examples 1-11 to 1-13 with respect to the film forming method of the silicone-based active material film, the time required to form a 2 μm film was relatively short for Cat-CVD and PECVD, followed by EB deposition. The film forming speed was difficult for mass production using sputtering or resistance heating source deposition. Additionally, hydrogenated silicone was not detected in the film formed in the Comparative Example. However, in the case of EB deposition method that can be applied to mass production, hydrogenated silicone could also be introduced through vapor deposition due to a hydrogen gas supply atmosphere, etc., which was not performed in the Comparative Example. By these, the former two film forming methods are preferable for large-area film forming applications of the current collector copper foil of the present invention, but it is recognized that the hydrogen atmosphere EB deposition method has potential. Additionally, according to the latter two film forming methods, the discharge capacity after the end of the cycle decreases, and this is thought to be the effect of deterioration due to radiant heat caused by long-term film forming, despite low film adhesion and no heating of the substrate. In other words, the film forming method using the CVD method is good, and among them, it has been found that a negative electrode having a silicone-based film with a concentration ratio of silane to hydrogen and a hydrogen concentration of 0.1 atomic % to 30 atomic % according to a manufacturing method based on the concentration ratio of silane to hydrogen and the heating temperature of the electrode exhibits excellent charge and discharge characteristics.

- [0164] In Examples 1-34 to 1-36, the mechanical properties of the current collector copper foil, such as the high temperature elongation value and charge/discharge characteristics at 180°C, can be seen, and in Example 1-34 showing an elongation of 3.1%, 1000 mAh/g was maintained after the cycle test was completed, but Example 1-36, which shows an elongation of less than 3%, shows a low capacity, and in this case, as a result of deterioration of the interfacial adhesion between the current collector and the active material film due to volumetric expansion and contraction of the silicone film due to repeated charging and discharging, it is believed that some areas have deteriorated current collection and film conductivity. Example 1-35, which showed an elongation of 5% or more, showed the same cycle characteristics as the other examples. Considering the results of other examples, it can be said that the high temperature elongation at 180°C, which is one of the mechanical properties of the current collector copper foil, is preferably 3% or more, and preferably 5% or more. When the volume expands or the temperature rises, the possibility of problems occurring due to current collector insulation or grain boundary cracking decreases.
- [0165] In addition, for the current collector copper foil of Examples 1-34 to 1-40, a one-sided glossy foil, which is also a general-purpose foil for printed circuits, was used, and among these, in Examples 1-37 and 1-39, a silicone-based film was formed on the foil that had been roughened on the rough side. Although there are examples in which the influence of the mechanical characteristics of the current collector is recognized, any of them showed charge/discharge characteristics without any particular problems.
- [0166] In Example 1-40, an example was given in which a non-aqueous solvent containing fluorine was included in the electrolyte solution in the three-electrode cell test. According to this, the first charge and discharge capacity was also high, and the discharge capacity after the 50 cycle test showed the highest remaining residual result. Compared to conventional types of non-aqueous solvents that do not contain fluorine, this is thought to be a result of a small volume change in volume expansion and contraction during charging and discharging due to the alloying and dealloying of Li ions and silicone, and suppression of the deterioration of adhesion and current collection between the active material and the current collector, and conductivity within the active material film.
- [0167] In Comparative Example 1-14, an attempt was made to form a silicone film directly on the glossy surface of the original double-sided glossy foil without roughening treatment, but as partial film peeling occurred, it could not be helpful in test evaluation as a battery negative electrode sample.
- [0168] Next, (b) the heat-resistant barrier film is mentioned according to Examples 1-41 to 1-52 shown in Tables 4 to 6. The formation amount and evaluation of the zinc layer and nickel layer formed at least partially as a heat-resistant barrier film are mainly determined from comparison of Examples 1-41 to 1-52. In Example 1-52, in which no film is formed, the copper of the current collector component is diffusion alloyed in the active material film, and the first charge/discharge capacity is a low value below 2000 mAh/g, and the capacity after 50 cycles is also below 1,000 mAh/g. In the case of a nickel single layer, which is the main barrier film, of course, a small amount of copper diffusion occurs at 0.008 g/m² in Example 1-48, but this does not occur at 0.012 g/m² in Example 1-49, so it is better to form 0.01 g/m² or more. If it is formed too thick, there is a possibility that the film may crack, and in Examples 1-50 to 1-51, capacity decreases when the cycle is repeated, and therefore the upper limit is preferably 0.5 g/m² or less. When combined with a zinc layer of 0.003 g/m² or more, it can be seen from Examples 1-46 and 1-47 that even a nickel amount of 0.01 g/m² or less is sufficient for a heat-resistant barrier film. Also, as shown in Examples 1-41 to 1-45, when the amount of zinc is great, it is recognized that the active material capacity tends to decrease due to zinc diffusion, so it is preferable that the amount of nickel in the two-layer formation is 0.01 g/m² or more. In addition, the single-layer film of Example 1-41 in which the amount of zinc was increased to about 0.03 g/m² also had sufficient heat resistance, and because, if the increase is increased to the same level as in Examples 1-44 to 1-45, a decrease in discharge capacity is caused, which is believed to be due to diffusion of zinc into the silicone-based film, it is recommended that the upper limit is around 0.1 g/m².
- [0169] Also, as shown in the capacity regulation cycle test results in Table 7, the P-doping of Example 1-5 also cannot achieve capacity under conditions that do not contain oxygen, but in the P-doped Si of Example 1-12, charge/discharge capacity remained even after 1000 cycles, so Examples 1-53 to 1-55, in which P-doping and oxygen atoms were introduced at a predetermined concentration, are all good as they have 1000 mAh/g. In other words, it can be seen that the charge/discharge cycle characteristics of the silicone-based film that is P-doped and contains oxygen are better.
- [0170] (Example for Second Embodiment)
- [0171] Examples 2-1 ~ 2-35 and Comparative Examples 2-1 ~ 2-8
- [0172] Below, the second embodiment will be described in detail through examples. This embodiment shows an example of the present invention with a single-side coating configuration described in FIGS. 1 to 3, but is not limited to this. For example, the same process can be performed in the double-sided film forming form shown in FIG. 4 in which the film forming treatment on one side is performed on both sides.
- [0173] (1) Sample Preparation of Examples and Comparative Examples

- [0174] First, a silicone-based negative electrode sample according to the present invention for test and evaluation, a negative electrode current collector used therefor, and a silicone-based negative electrode sample used for comparison were produced as follows.
- [0175] For the raw copper foil (copper foil base without surface treatment) used for current collector copper foil, rolled copper foil (manufactured by Nihon Seihaku Co., Ltd.) and electrolytic copper foil (manufactured by Furukawa Denki Kogyo Co., Ltd.) of various thicknesses were used. The rolled foil used was a double-sided glossy type of 12 μ m, and the electrolytic foil used a double-sided glossy type of 12 μ m, and a single-side glossy type of 12 μ m and 18 μ m were used. When roughening the surface of these raw materials, copper foil for printed circuit use was subjected to roughening treatment by (a) copper fine grain growth plating (so-called burning plating performed at a high current density that is above or close to the critical current density) and (b) conventional copper smooth plating (general copper plating performed below the limit current density to prevent applied particles from falling off), which were copper plating using a known copper sulfate-based aqueous solution. In addition, as a treatment for providing a heat-resistant layer, (c) nickel plating using a known nickel sulfate-based plating solution or (d) zinc plating using a known zinc sulfate-based plating solution was performed. In addition, for the rust prevention treatment, (e) immersion in an aqueous benzotriazole solution or (f) electrolysis in an aqueous chromium trioxide solution was used, and for the adhesion improvement treatment, (g) immersion in an aqueous silane coupling agent solution was performed. In order to use these copper foils as current collectors, they were stored indoors for 3 months before forming a silicone-based active material into a film. In addition, the elongation of these copper foils for current collectors after being held at 180°C for 5 minutes was measured by a tensile test using a Tensiron tester, and surface roughness (Rz, S, Sm) was measured with a stylus-type roughness tester (manufactured by Kosaka Kenkyusho) according to JIS B0601 (1994 edition). The amount of nickel and zinc in the heat-resistant layer was measured by ICP (inductively coupled plasma) emission spectroscopy of an aqueous solution in which the surface film of the sample was dissolved per unit area. The silicone-based active material film was formed by the methods (h) to (l) below, and Examples 2-1 to 2-35 and Comparative Examples 2-1 to 2-8 were obtained. Silicon film formation was performed for each sample for a predetermined time based on the relationship between film forming thickness and film forming time based on the film forming speed determined in advance, and after film formation, confirmation was made from observation of the cross section of the sample using a SEM (scanning electron microscope). In addition, the amount of silicone film, which is a negative electrode active material, was determined from the mass measurement per unit area before and after silicone film formation. Then, the bonding state of hydrogen was analyzed from the analysis using FT-IR (Fourier transform infrared spectrophotometer) of the formed silicone-based film. In addition, the surface roughness (Rz, S, Sm) of the surface of the silicone-based active material after film formation was measured using a stylus-type roughness tester in the same manner as above. The specifications of the current collector copper foil used for each sample above are shown in Table 8, and the appearance abnormalities after indoor storage before film formation and film formation specifications are shown in Table 2. After producing Examples 2-36 to 2-39 using the description of Example 2-19 with the film forming thickness changed according to the phosphorus doped silicone film forming conditions in (h) below, oxygen was introduced by the method (m) below. This is shown in Table 11 along with the test evaluation results shown below. Phosphorus and oxygen contained in the silicone-based active material are subject to the above ICP analysis.
- [0176] (a) Burning plating of roughening treatment: Without heating in an electrolyte containing 30 g/dm³ of copper and 150g/dm³ of sulfuric acid as main components, the current density was appropriately selected in the range of 10 to 20A/dm² along with the electrolysis time, and cathodic electrolysis was performed under conditions to obtain a predetermined surface shape.
- [0177] (b) Smooth copper plating with roughening treatment: In an electrolyte containing 70 g/dm³ of copper and 100g/dm³ of sulfuric acid as main components and maintained at a temperature of 40°C, the cathodic electrolysis was performed under appropriately selected conditions with a current density in the range of 5 to 10 A/d m² and an electrolysis time to obtain a predetermined surface shape determined in advance along with the conditions (a).
- [0178] (c) Nickel plating solution: Cathodic electrolysis was performed by selecting a time according to the formation amount under the conditions of 160 g/dm³ of nickel sulfate (hexahydrate), 30 g/dm³ of boric acid, and 1A/dm².
- [0179] (d) Zinc plating: Cathodic electrolysis was performed by appropriately selecting a plating time according to the plating amount under the conditions of zinc 10 g/dm³, pH 12, and 0.1A/dm².
- [0180] (e) Rust treatment 1: Immersion in 1% by weight benzotriazole aqueous solution
- [0181] (f) Rust treatment 2: 70g/dm³ chromium trioxide aqueous solution, pH12, 1C/dm², cathode electrolysis
- [0182] (g) Silane coupling treatment: Immersion in 4 g/dm³ aqueous solution of kryloxy-based silane coupling agent (manufactured by Shinetsu Chemical Co., Ltd.)
- [0183] (h) Silicon film forming method 1, and phosphorus or boron doping method for silicone: Using the Cat-CVD device (Anerva Co., Ltd. product, total discharge frequency 13.56~40MHz), a monosilane gas of 20 sccm (Standard cc/min.: Standard condition volume flow rate), a current collector temperature of 250°C, and a tungsten precatalyst temperature of 1800°C were used as basic conditions, and an appropriate film forming time was selected according to the film forming thickness. In the case of film formation while doping phosphorus, 10sccm of phosphine gas was supplied, and also, in the case of doping boron, diborane gas was supplied simultaneously with monosilane gas. Additionally, when forming a layer containing phosphorus or boron on the upper or lower layer of the silicone-based film, it was formed due to the film forming method of doping phosphorus or boron. In addition, depending on the sample, hydrogen gas was supplied in the same amount as silane gas to form a film.

- [0184] (i) Silicone film formation method 2: The film was formed using a parallel plate CVD (PECVD) device (discharge frequency 60 MHz) equipped with a plasma electrode of a shower head structure at a supply flow rate of 100 sccm of monosilane gas with 10% hydrogen dilution and a current collector temperature of 200°C.
- [0185] (j) Silicone film formation method 3: High-purity silicone raw material was sublimated by heating at 200 W using electron beam (EB) gun and a silicone evaporation source using an evaporation device (manufactured by Ulvac Co., Ltd.) and deposited on the current collector.
- [0186] (k) Silicone film formation method 4: Film was attached and formed on the current collector using a sputtering device (manufactured by Ulvac Co., Ltd.) equipped with a high-purity silicone raw material and a sputter cathode at 80 sccm of argon gas (sputter gas) and 1 kW of high-frequency output.
- [0187] (l) Silicone film formation method 5: The raw materials were melted and volatilized by resistance heating using a vacuum evaporation device (manufactured by Ulvac Co., Ltd.) equipped with high-purity silicone raw materials and a resistance heating source to form a film.
- [0188] (m) Oxidation treatment: Heat treatment was performed at 100°C in the air for a predetermined period of time depending on the introduced oxygen concentration.
- [0189] (2) Test evaluation of samples
- [0190] Next, it was produced as above. Test evaluation of the silicone-based negative electrode sample according to the present invention and the silicone-based negative electrode sample used for comparison was conducted as follows.
- [0191] A hole with a diameter of 20 mm was made in the negative electrode sample and this was used as a test electrode, and a three-electrode cell using lithium foil as a dipole and reference electrode used an electrolyte in which 1M lithium hexafluorophosphate (LiPF₆) is dissolved in a non-aqueous electrolyte with a volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) of 3: 7, and was assembled as a closed cell at 25°C in a dry atmosphere with a humidity of 7% or less. However, in some embodiments, a solvent having a volume ratio of fluoroethylene carbonate (FEC) and methyltrifluoroethyl carbonate (MFEC), which are non-aqueous solvents containing fluorine in their chemical structure, of 1: 3 was used. The first charging process was carried out at a constant current rate of 0.1C up to a potential of +0.02V based on the redox potential of lithium, and the first charging capacity obtained at this time was tested and measured for each sample and converted to per unit mass of the active material silicone. In the first discharge treatment that followed, discharge was performed at a 0.1C rate constant current to 1.5V for the same lithium potential standard as above, and likewise, the first discharge capacity was measured for each and converted to per unit mass of silicone. In addition, the first actual discharge capacity value was obtained from the previously measured film forming mass and discharge current of the silicone active material. After completion of the first charge/discharge process, the charge/discharge rate was set to 0.2C, and charge/discharge cycles were performed 50 times until each end potential of the first charge/discharge process was completed. The discharge capacity at the end of 50 cycles was determined for each sample and converted to per unit mass. The above first charge/discharge capacity, actual discharge capacity, and discharge capacity after 50 cycles are shown in Table 10 for each sample. For the samples of Examples 2-18, 2-19, 2-36 to 2-39, the charging capacity was regulated to 1000 mAh/g, and a charge/discharge cycle test was performed for 1000 cycles by discharging as described above, as shown in Table 11.

Table 8

[0192]

No	Current collector copper foil											
	Manufacturing method and foil thickness (μm)	Type of raw copper foil	Whether or not roughening has been carried out	Appearance of active material formation surface	180°C elongation	Surface roughness (R z) (μm)	Surface roughness (S) (mm)	Surface roughness (S m) (mm)	Heat-resistant layer (g/m ²)		Rust treatment layer	Adhesion improvement treatment layer
									1st layer Ni	2nd layer Zn		
Example 2-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	3.4	0.007	0.028	0.015	0.01	Benzotriazole	Silane coupling
Comparative Example 2-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	1.8	0.003	0.009	0.015	0.01	Benzotriazole	Silane coupling
Example 2-2	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	2.2	0.004	0.016	0.016	0.007	Chromate	Silane coupling
Example 2-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.6	4.1	0.009	0.028	—	0.03	Chromate	Silane coupling
Example 2-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.008	0.025	0.008	0.02	Chromate	Silane coupling
Example 2-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.008	0.025	0.011	0.02	Chromate	Silane coupling

Example 2-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.009	0.028	—	0.04	Chromate	Silane coupling
Example 2-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.009	0.028	—	0.06	Chromate	Silane coupling
Example 2-8	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.009	0.028	0.008	0.004	Chromate	Silane coupling
Example 2-9	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.009	0.028	0.008	0.002	Chromate	Silane coupling
Example 2-10	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	0.026	0.008	—	Chromate	Silane coupling
Example 2-11	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	0.026	0.012	—	Chromate	Silane coupling
Example 2-12	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	0.026	0.18	—	Chromate	Silane coupling
Example 2-13	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	0.026	0.22	—	Chromate	Silane coupling
Example 2-14	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	0.026	—	—	Chromate	Silane coupling
Example 2-15	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.01	0.01	N/A	N/A
Example 2-16	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.01	0.01	Chromate	N/A
Example 2-17	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.01	0.01	N/A	Silane coupling
Comparative Example 2-2	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.008	0.025	0.016	0.007	Chromate	Silane coupling
Example 2-18	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.008	0.025	0.016	0.007	Chromate	Silane coupling
Comparative Example 2-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.008	0.025	0.22	0.01	Chromate	Silane coupling
Comparative Example 2-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.5	5.5	0.014	0.037	0.01	0.01	Chromate	Silane coupling
Example 2-19	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.5	5.0	0.015	0.034	0.01	0.01	Chromate	Silane coupling
Comparative Example 2-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.5	5.9	0.016	0.040	0.01	0.01	Chromate	Silane coupling
Example 2-20	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.5	3.6	0.009	0.021	0.01	0.01	Chromate	Silane coupling
Example 2-21	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-22	Electrolysis 12	Double-sided gloss	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling

		(FIG. 3)										
Example 2-23	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Comparative Example 2-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Comparative Example 2-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-24	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-25	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-26	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-27	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-28	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.010	0.030	0.05	0.01	Chromate	Silane coupling
Example 2-29	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	3.1	4.0	0.013	0.032	0.011	0.016	Chromate	Silane coupling
Example 2-30	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	5.3	3.8	0.012	0.030	0.012	0.015	Chromate	Silane coupling
Example 2-31	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	2.5	4.2	0.014	0.030	0.01	0.014	Chromate	Silane coupling
Example 2-32	Electrolysis 12	Glossy on one side (FIG. 2)	Has one side	Non-glossy	7.7	6.8	0.014	0.030	0.015	0.006	Chromate	Silane coupling
Example 2-33	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.015	0.035	0.013	0.008	Chromate	Silane coupling
Example 2-34	Electrolysis 18	Glossy on one side (FIG. 2)	Has one side	Non-glossy	8.7	8.2	0.018	0.035	0.018	0.012	Chromate	Silane coupling
Example 2-35	Electrolysis 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.015	0.035	0.013	0.008	Chromate	Silane coupling
Comparative Example 2-8	Electrolysis 12	Double-sided gloss (FIG. 3)	N/A	Gloss	7.2	1.7	0.002	0.008	0.02	0.005	Chromate	Silane coupling

Table 9

[0193]

No	Appearance before	Lower layer film	Active material film	Upper layer film
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	formation (after 3 months of indoor storage)	Si layer containing P, B	Thickness (μm)	Mass (g/m ²)	Surface roughness (Rz) (μm)	Surface roughness (S) (mm)	Surface roughness (Sm) (mm)	Si	Other elements	Diffusion of current collector components	Formation method	Formation time (minutes)	Si layer containing P, B
Example 2-1		-	1.5	3.50	3.2	0.009	0.030	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-1		-	1.5	3.50	1.8	0.004	0.014	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-2		-	1.5	3.50	2.2	0.005	0.016	○	H, SH, SH2	-	Cat-CVD	8	-
Example 2-3		-	1.5	3.50	3.8	0.010	0.030	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-4		-	1.0	2.30	3.4	0.008	0.026	○	H, SH, SH2	- (Zn trace diffusion)	Cat-CVD	6	-
Example 2-5		-	1.0	2.30	3.4	0.009	0.029	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-6		-	2.0	4.70	3.5	0.010	0.033	○	H, SH, SH2	- (Zn trace diffusion)	Cat-CVD	-	-
Example 2-7		-	2.0	4.70	3.3	0.011	0.035	○	H, SH, SH2	- (Zn trace diffusion)	Cat-CVD	-	-
Example 2-8		-	2.0	4.70	4.0	0.011	0.031	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-9		-	2.0	4.70	4.0	0.011	0.031	○	H, SH, SH2	- Cu small amount diffusion	Cat-CVD	-	-
Example 2-10		-	2.0	4.70	3.3	0.010	0.033	○	H, SH, SH2	- Cu small amount diffusion	Cat-CVD	-	-
Example 2-11		-	2.0	4.70	3.5	0.011	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-12		-	2.0	4.70	3.0	0.012	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-13		-	2.0	4.70	2.7	0.013	0.039	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-14		-	2.0	4.70	3.8	0.009	0.030	○	H, SH, SH2	- Cu diffusion alloying	Cat-CVD	-	-
Example 2-15	Brown rust discoloration	-	2.0	4.70	4.5	0.012	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-16		-	2.0	4.70	4.5	0.012	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-17	Spot discoloration	-	2.0	4.70	4.5	0.012	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-2		-	0.4	0.90	3.7	0.007	0.026	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-18		-	5.9	13.75	2.5	0.013	0.037	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-3		-	6.5	15.20	1.9	0.015	0.043	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-4		-	2.0	4.70	6.3	0.014	0.060	○	H, SH, SH2	-	Cat-CVD	-	-

Example 2-19		-	2.0	4.70	4.8	0.014	0.038	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-5		-	2.0	4.70	5.7	0.020	0.071	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-20		-	2.0	4.70	4.0	0.014	0.045	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-21		-	2.0	4.70	4.5	0.012	0.035	○	H, SH, SH2	-	Cat-CVD	12	-
Example 2-22		-	2.0	4.70	4.6	0.012	0.037	○	H, SH, SH2	-	PECVD	33	-
Example 2-23		-	2.0	4.70	4.8	0.014	0.040	○	H	-	EB deposition	50	-
Comparative Example 2-6		-	2.0	4.70	4.7	0.013	0.040	○	-	-	Sputter	333	-
Comparative Example 2-7		-	2.0	4.70	5.0	0.013	0.040	○	H	-	Resistance heat deposition	167	-
Example 2-24		P0.1 μm	2.0	4.70	4.5	0.011	0.037	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-25		-	2.0	4.70	4.5	0.012	0.034	○	H, SH, SH2	-	Cat-CVD	-	B0.1 μm
Example 2-26		P0.1 μm	2.0	4.70	4.5	0.012	0.036	○	H, SH, SH2	-	Cat-CVD	-	B0.1 μm
Example 2-27		-	2.0	4.70	4.5	0.012	0.038	○	P.H.S H,SH2	-	Cat-CVD	-	-
Example 2-28		-	2.0	4.70	4.5	0.012	0.038	○	B.H.S H,SH2	-	Cat-CVD	-	-
Example 2-29		-	2.0	4.70	3.7	0.014	0.038	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-30		-	2.0	4.70	3.5	0.013	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-31		-	2.0	4.70	3.1	0.013	0.032	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-32		-	2.0	4.70	7.5	0.015	0.035	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-33		-	2.0	4.70	4.4	0.012	0.032	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-34		-	2.5	5.90	8.5	0.014	0.040	○	H, SH, SH2	-	Cat-CVD	-	-
Example 2-35		-	2.0	4.70	4.4	0.012	0.032	○	H, SH, SH2	-	Cat-CVD	-	-
Comparative Example 2-8		-	Partial peeling	-	-	-	-	○	H, SH, SH2	-	Cat-CVD	-	-

Table 10

[0194]

No	Test evaluation results
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	Non-aqueous solvent of electrolyte	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	Actual discharge capacity (mAh)	Discharge capacity after 50 charges/discharges (mAh/g)
Example 2-1	Does not contain F	3,325	3,209	3.9	1,248
Comparative Example 2-1	Does not contain F	2,765	2,544	3.1	587
Example 2-2	Does not contain F	2,887	2,743	3.3	1,056
Example 2-3	Does not contain F	3,128	2,978	3.6	1,273
Example 2-4	Does not contain F	3,329	3,169	2.5	1,305
Example 2-5	Does not contain F	3,510	3,324	2.7	1,402
Example 2-6	Does not contain F	2,941	2,800	4.5	1,285
Example 2-7	Does not contain F	2,826	2,690	4.3	1,132
Example 2-8	Does not contain F	3,046	2,900	4.6	1,191
Example 2-9	Does not contain F	2,854	2,683	4.3	972
Example 2-10	Does not contain F	2,746	2,598	4.2	923
Example 2-11	Does not contain F	3,185	3,032	4.9	1,104
Example 2-12	Does not contain F	3,395	3,232	5.2	1,238
Example 2-13	Does not contain F	3,276	3,119	5.0	1,032
Example 2-14	Does not contain F	2,033	1,935	3.1	678
Example 2-15	Does not contain F	1,828	1,462	2.3	459
Example 2-16	Does not contain F	3,226	3,055	4.9	1,245
Example 2-17	Does not contain F	2,512	2,379	3.8	725
Comparative Example 2-2	Does not contain F	2,895	2,533	0.8	516
Example 2-18	Does not contain F	3,562	3,420	16.1	664
Comparative Example 2-3	Does not contain F	3,488	3,314	17.2	294
Comparative Example 2-4	Does not contain F	3,562	3,384	5.4	568
Example 2-19	Does not contain F	3,645	3,463	5.5	1,409
Comparative Example 2-5	Does not contain F	3,529	3,353	5.4	468
Example 2-20	Does not contain F	2,851	2,708	4.3	840
Example 2-21	Does not contain F	3,469	3,296	5.3	1,472
Example 2-22	Does not contain F	3,324	3,158	5.1	1,175
Example 2-23	Does not contain F	3,237	3,075	4.9	955
Comparative Example 2-6	Does not contain F	2,803	2,663	4.3	378
Comparative Example 2-7	Does not contain F	2,954	2,806	4.5	641
Example 2-24	Does not contain F	3,637	3,455	5.5	1,645
Example 2-25	Does not contain F	3,734	3,547	5.7	1,678
Example 2-26	Does not contain F	3,762	3,574	5.7	1,745
Example 2-27	Does not contain F	3,496	3,321	5.3	1,515
Example 2-28	Does not contain F	3,536	3,359	5.4	1,552
Example 2-29	Does not contain F	3,430	3,259	5.2	1,016
Example 2-30	Does not contain F	3,629	3,448	5.5	1,277
Example 2-31	Does not contain F	3,432	3,260	5.2	685
Example 2-32	Does not contain F	3,512	3,336	5.3	986
Example 2-33	Does not contain F	3,675	3,491	5.6	1,468
Example 2-34	Does not contain F	3,440	3,268	6.5	1,246
Example 2-35	Contains F	3,775	3,586	5.7	1,853
Comparative Example 2-8	—	—	—	—	—

Table 11

[0195]

No	Active material film	100°C air	Test evaluation results
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	Thickn ess (μm)	Mass (g/m^2)	Surface roughness			Si	P- doping/ atomic %	oxidation treatment	Non- aqueous solvent of electrolyte	First chargin g capacit y (mAh/g)	First dischar ge capacit y (mAh/g)	1000th chargin g capacit y (mAh/g)	Discha rge capacit y after 1,000 times (mAh/g)
			Rz (μm)	S (mm)	Sm (mm)								
Examp le 2-18	5.9	13.75	2.5	0.013	0.037	○	—	—	Does not contain F	1,000	1,000	—	—
Examp le 2-19	2.0	4.70	4.8	0.014	0.038	○	—	—	Does not contain F	1,000	1,000	258	246
Examp le 2-36	5.5	12.80	2.7	0.011	0.036	○	10	—	Does not contain F	1,000	1,000	418	405
Examp le 2-37	3.0	6.90	3.5	0.013	0.039	○	3	—	Does not contain F	1,000	1,000	511	502
Examp le 2-38	5.3	12.35	2.8	0.012	0.036	○	5	50	Does not contain F	1,000	1,000	1,000	1,000
Examp le 2-39	2.5	5.75	4.0	0.014	0.040	○	1.5	10	Does not contain F	1,000	1,000	1,000	1,000

[0196] From the above sample production and test evaluation, the following can be seen.

[0197] Comparing the first charge capacity, discharge capacity, and discharge capacity after 50 cycles of each sample, it can be seen that the charge and discharge characteristics of the sample according to the example are good. For example, in Example 2-1 and Comparative Example 2-1 using rolled copper foil, in the Comparative Example, where the surface roughness (Rz) was as small as 1.8 μm , the adhesion was poor and it seemed that the current collecting properties were deteriorated due to volumetric expansion and contraction of the active material through repeated charging and discharging, with the result being that the capacity after 50 cycles was less than 600 mAh/g . On the other hand, in the case of Example 2-2 with an Rz of 2.2 μm using the same double-sided glossy electrolytic foil, the temperature was 1000 mAh/g or more even after 50 cycles.

[0198] The formation amount and evaluation of the nickel layer and zinc layer formed at least partially as the heat-resistant layer are mainly determined from comparison of Examples 2-3 to 2-14. In Example 2-14, in which no film is formed, the copper of the current collector component is diffusion alloyed in the active material film, and the first charge/discharge capacity is around 2000 mAh/g , which is a low value compared to others, and the capacity after 50 cycles is also below 700 mAh/g . In the case of a nickel single layer, a small amount of copper diffusion remained at 0.008 g/m^2 in Example 2-10, and this did not occur at 0.012 g/m^2 in Example 2-11, so it was sufficient to form 0.01 g/m^2 or more. If it is formed too thick, there is a possibility that the film may crack, and in Examples 2-12 to 2-13, capacity decreases when the cycle is repeated, so the upper limit is preferably 0.2 g/m^2 or less. When combined with a zinc layer of 0.003 g/m^2 or more, the nickel amount may be 0.01 g/m^2 or less, as can be seen from the comparison of Examples 2-8 to 2-9. Also, as shown in Examples 2-4 to 2-7, when the amount of zinc is great, it is recognized that the active material capacity tends to decrease due to zinc diffusion, so it is preferable that the amount of nickel in the two-layer formation is 0.01 g/m^2 or more. In addition, while a single-layer film with an increased zinc content of about 0.03 g/m^2 is also effective, if it is too high, the capacity will decrease, so it is better to set the upper limit to about 0.05 g/m^2 .

[0199] Next, the effects of the rust prevention treatment and the silane coupling improvement treatment are evident from comparison with Examples 2-15 to 2-17 and examples other than these. In Example 2-15, in which nothing was done, rust occurred during indoor storage until film forming, and charge/discharge characteristics were poor. On the other hand, Example 2-16, in which only rust prevention treatment was performed, showed good charge and discharge characteristics, and Example 2-17, in which only the adhesion improvement treatment was performed, had a low initial charge/discharge capacity and spotted discoloration occurred, but had a capacity of more than 700 mAh/g after the end of the cycle. In case there is a possibility of long-term inventory until film formation, it is advisable to also perform rust prevention treatment or adhesion improvement treatment. In addition, rust prevention treatment with benzotriazole, an organic dielectric film of Example 2-1, showed the same rust prevention effect as the chromate treatment layer and also had good charge and discharge characteristics.

[0200] If the film formation amount of the silicone-based active material is too thin as in Example 2-2, there is no problem with the charge/discharge characteristic value per unit mass, but in general, this is an example that is too small for practical capacity, which is the absolute value of the amount of electricity required for the device, and for example, the capacity remains at about one-sixth of the approximately 5 mAh required for electronic devices, and furthermore, a decrease in discharge capacity after the

cycle, which is presumed to be due to irreversible capacity, is also seen. In addition, the upper limit of the active material film is set to $6\mu\text{m}$ in the present invention because when using a current collector with a small surface roughness in the extremely thick film forming specification of $6.5\mu\text{m}$ shown in Comparative Example 2-3, the surface roughness is made smaller and the specific fine surface shape is flattened, thereby deteriorating the charge/discharge cycle characteristics. This is because the $5.6\mu\text{m}$ thickness of Example 2-18 is close to 700 mAh/g and is more than twice as good as the above example with a thickness exceeding $6\mu\text{m}$.

[0201] The surface shape and evaluation after forming the silicone film are shown. Regarding the lower limits of surface roughness S and Sm, from Comparative Example 2-1 and Example 2-2, if S is 0.005 or more and Sm is 0.015 or more along with Rz, the capacity after 50 repetitions exceeds 1000 mAh/g , which is good. Additionally, regarding the upper limit, whether it is good or not can be evaluated by comparing Comparative Examples 2-4 to 2-5, Examples 2-19 to 2-20, and Examples 2-32 and 2-34. Among examples other than Example 2-32 in which Rz exceeds 2 and S represents 0.014, only Examples 2-19 and 2-34 with Sm of 0.040 or less had high capacities exceeding 1000 mAh/g after 50 cycles. Even if Sm was 0.040 or less, Example 2-32, in which S slightly exceeded 0.014, showed a capacity slightly below 1000 mAh/g . Examples that have other typical heat-resistant layers, anti-rust layers, etc. and fall within the ranges of S and Sm also show a capacity after repeated charging and discharging exceeding 1000 mAh/g . Thus, The shape of the negative electrode surface after forming a silicone-based film to obtain good charge/discharge capacity is shown to be excellent with Rz being $2\mu\text{m}$ or more, S being in the range of 0.005 to 0.014, and Sm being 0.015 to 0.040.

[0202] The lower limit of the roughness, which represents the shape of the surface of the current collector copper foil before forming the silicone-based film, is determined from the above Comparative Example 2-1 and Example 2-2. If Rz, S, and Sm are too small, they will be below the predetermined roughness after forming the silicone-based film. This is because, if the upper limit is too large from the above Comparative Examples 2-4 to 2-5, Examples 2-19 to 2-20, Examples 2-32, and Example 2-34, the predetermined roughness will often be exceeded after forming the silicone-based film, and it is preferable that S is 0.015 or less and Sm is 0.035 or less. However, depending on the rough surface shape or the conditions for forming the silicone film, even if the roughness parameter of the current collector surface is outside the specifications, if it is within a predetermined range after film formation, good charge/discharge characteristics are exhibited. Example 2-34 is an example, and although the current collector surface (S) showed a high value of 0.018, both surface S and Sm after film formation were within specifications, and the discharge capacity after 50 cycles was also good. This is believed to be due to the fact that the current collector surface, which exhibits a uniform, mountain-shaped rough surface, is suitable for the negative electrode manufacturing method of the present invention.

[0203] Next, when comparing Examples 2-21 to 2-23 and Comparative Examples 2-6 to 2-7 regarding the film forming method of the silicone-based active material film, the time required to form a $2\mu\text{m}$ film was relatively short in the case of Cat-CVD, PECVD, and EB deposition, while the deposition method using sputtering and a resistance heating source took a long time, greatly exceeding 2 hours. For large-area film forming of current collector copper foil, the former three film forming methods are preferable. Additionally, according to the latter two film forming methods, the discharge capacity after completion of the cycle is different. This is thought to be the effect of deterioration due to radiant heat due to long-term film forming, despite low film adhesion or no substrate heating.

[0204] From Examples 2-24 to 2-26, in which a silicone layer containing phosphorus or boron was formed on the lower or upper layer of the silicone active material film, excellent charge/discharge characteristics were obtained even compared to other examples that did not form these. In particular, Example 2-26, which formed a layer containing phosphorus in the lower layer and boron in the upper layer, showed the best results among tests using a non-fluorine-containing non-aqueous electrolyte solution. This is thought to be because the movement of Li ions and electrons is promoted due to the electric field drift effect, and the irreversible capacity associated with the secondary battery decreases.

[0205] Examples 2-27 to 2-28, in which silicone was doped with phosphorus or boron, showed the same good charge/discharge characteristics as the non-doped example, and relatively excellent capacity remained after 50 cycles.

[0206] In Examples 2-29 to 2-31, the mechanical properties of the current collector copper foil, such as the high temperature elongation value and charge/discharge characteristics at 180°C , can be seen, and in Example 2-29 showing an elongation of 3%, 1000 mAh/g was maintained after the cycle test was completed, but Example 2-31, which shows an elongation of less than 3%, shows a low capacity, and in this case, as a result of deterioration of the interfacial adhesion between the current collector and the active material film due to volumetric expansion and contraction of the silicone film due to repeated charging and discharging, it is believed that many areas have deteriorated current collection and film conductivity. Example 2-30, which showed an elongation of 5% or more, showed the same cycle characteristics as the other examples.

[0207] For the current collector copper foil of Examples 2-29 to 2-35, a one-sided glossy foil, which is also a general-purpose foil for printed circuits, was used, and among these, in Examples 2-32 and 2-34, a silicone-based film was formed on the foil that had been roughened on the rough side. All showed charge/discharge characteristics without any particular problems.

- [0208] In Example 2-35, an example was given in which a non-aqueous solvent containing fluorine was included in the electrolyte solution in the three-electrode cell test. According to this, the first charge and discharge capacity was also high, and the discharge capacity after the 50 cycle test showed the highest remaining residual result. Compared to conventional types of non-aqueous solvents that do not contain fluorine, this is thought to be the result of a small volume change in volume expansion and contraction during charging and discharging due to the alloying and dealloying of Li ions and silicone, and suppression of the deterioration of adhesion and current collection between the active material and the current collector, and conductivity within the active material film.
- [0209] In Comparative Example 2-8, an attempt was made to form a silicone film directly on the glossy surface of the original double-sided glossy foil without roughening treatment, but as partial film peeling occurred, it could not be helpful in test evaluation as a battery negative electrode sample.
- [0210] In addition, as shown in the capacity regulation cycle test results in Table 11, the charge/discharge capacity of the P-doped Si of Examples 2-36 and 2-37 after 1000 cycles was higher than that of the P-doped Si of Examples 2-18 and 2-19 without oxygen, and Examples 2-38 to 2-39, in which P-doping and oxygen atoms were introduced at a predetermined concentration, were all good, having 1000 mAh/g. In other words, it can be seen that the charge/discharge cycle characteristics of the silicone-based film that is P-doped and further contains oxygen are good.
- [0211] (Example for Third Embodiment)
- [0212] Examples 3-1 to 3-43 and Comparative Examples 3-1 to 3-15
- [0213] Below, the third embodiment will be described in detail through examples. This embodiment shows an example of the present invention with a single-side coating configuration described in FIGS. 1 to 3, but is not limited to this. For example, the same process can be performed in the double-sided film forming form shown in FIG. 4 in which the film forming treatment on one side is performed on both sides.
- [0214] (1) Sample Preparation of Examples and Comparative Examples
- [0215] First, a silicone-based negative electrode sample according to the present invention for test and evaluation, a negative electrode current collector used therefor, and a silicone-based negative electrode sample used for comparison were produced as follows.
- [0216] For the raw copper foil (copper foil base without surface treatment) used for current collector copper foil, rolled copper foil (manufactured by Nihon Seihaku Co., Ltd.) and electrolytic copper foil (manufactured by Furukawa Denki Kogyo Co., Ltd.) of various thicknesses were used. The rolled foil used was a double-sided glossy type of 12 μ m, and the electrolytic foil used a double-sided glossy type of 12 μ m, and a single-side glossy type of 12 μ m and 18 μ m were used. When roughening the surface of these raw materials, copper foil for printed circuit use was subjected to roughening treatment by (a) copper fine grain growth plating (so-called burning plating performed at a high current density that is above or close to the critical current density) and (b) conventional copper smooth plating (general copper plating performed below the limit current density to prevent applied particles from falling off), which were copper plating using a known copper sulfate-based aqueous solution. In addition, as a treatment for providing a heat-resistant layer, (c) nickel plating using a known nickel sulfate-based plating solution or (d) zinc plating using a known zinc sulfate-based plating solution was performed. In addition, for the rust prevention treatment, (e) immersion in an aqueous benzotriazole solution or (f) electrolysis in an aqueous chromium trioxide solution was used, and the silane coupling treatment was performed by (g) immersion in an aqueous silane coupling agent solution. In order to use these copper foils as current collectors, they were stored indoors for 3 months before forming a silicone-based active material into a film. In addition, the elongation of these copper foils for current collectors after being held at 180°C for 5 minutes was measured by a tensile test using a Tensiron tester, and surface roughness (R_z) was measured with a stylus-type roughness tester (manufactured by Kosaka Kenkyusho) according to JIS B0601 (1994 edition). The amount of zinc and nickel in the heat-resistant layer was measured by ICP (inductively coupled plasma) emission spectroscopy of an aqueous solution in which the surface film of the sample was dissolved per unit area. The silicone-based active material film was formed by the methods (h) to (l) below, and Examples 3-1 to 3-43 and Comparative Examples 3-1 to 3-15 were done. Silicon film formation was performed for each sample for a predetermined time based on the relationship between film forming thickness and film forming time based on the film forming speed determined in advance, and after film formation, confirmation was made from observation of the cross section of the sample using a SEM (scanning electron microscope). In addition, the amount of silicone film, which is a negative electrode active material, was determined from the mass measurement per unit area before and after silicone film formation. Then, the bonding state of hydrogen was analyzed from the analysis using FT-IR (Fourier transform infrared spectrophotometer) of the formed silicone-based film. In addition, the electric double layer capacity of the surface before and after film formation was measured using a direct-reading double layer capacity meter (manufactured by Kita Denshi Co., Ltd.) using a 0.1N aqueous potassium acetate solution in the electrolyte under the condition of a step current of 50 μ A/cm², and the reciprocal (1/C) was calculated and output. The specifications of the current collector copper foil used for each sample above are shown in Table 12, and the appearance abnormalities after indoor storage before film formation and film formation specifications are shown in Table 13. Additionally, Examples 3-44 and 3-45 were produced using Examples 3-9 and 3-11 in which oxygen was introduced into the active material film by the method (m) below. This is shown in Table 15 along with the test evaluation results shown below. Phosphorus and oxygen contained in the silicone-based active material are subject to the above ICP analysis.
- [0217] (a) Burning plating of roughening treatment: Without heating in an electrolyte containing 30 g/dm³ of copper and 150g/dm³ of sulfuric acid as main components, the current density was appropriately selected in the range of 10 to 20A/dm² along with the electrolysis time, and cathodic electrolysis was performed under conditions to obtain a predetermined surface shape.

- [0218] (b) Smooth copper plating with roughening treatment: In an electrolyte containing 70 g/dm³ of copper and 100g/dm³ of sulfuric acid as main components and maintained at a temperature of 40°C, the cathodic electrolysis was performed under appropriately selected conditions with a current density in the range of 5 to 10 A/d m² and an electrolysis time to obtain a predetermined surface shape determined in advance along with the conditions (a).
- [0219] (c) Nickel plating solution: Cathodic electrolysis was performed by selecting a time according to the formation amount under the conditions of 160 g/dm³ of nickel sulfate (hexahydrate), 30 g/dm³ of boric acid, and 1A/dm².
- [0220] (d) Zinc plating: Cathodic electrolysis was performed by appropriately selecting a plating time according to the plating amount under the conditions of zinc 10 g/dm³, pH 12, and 0.1A/dm².
- [0221] (e) Rust treatment 1: Immersion in 1% by weight benzotriazole aqueous solution
- [0222] (f) Rust treatment 2: 70g/dm³ chromium trioxide aqueous solution, pH12, 1C/dm², cathode electrolysis
- [0223] (g) Silane coupling treatment: Immersion in 4 gd m³ aqueous solution of kryloxy-based silane coupling agent (manufactured by Shinetsu Chemical Co., Ltd.)
- [0224] (h) Silicon film forming method 1, and phosphorus or boron doping method for silicone: Using the Cat-CVD device (Anerva Co., Ltd. product, total discharge frequency 13.56–40MHz), a monosilane gas of 20 sccm (Standard cc/min.: Standard condition volume flow rate), a current collector temperature of 250°C, and a tungsten precatalyst temperature of 1800°C were used as basic conditions, and an appropriate film forming time was selected according to the film forming thickness. In the case of film formation while doping phosphorus, 10sccm of phosphine gas was supplied, and also, in the case of doping boron, diborane gas was supplied simultaneously with monosilane gas. Additionally, when forming a layer containing phosphorus or boron on the upper or lower layer of the silicone-based film, it was formed due to the film forming method of doping phosphorus or boron. In addition, depending on the sample, hydrogen gas was supplied in the same amount as silane gas to form a film.
- [0225] (i) Silicone film formation method 2: The film was formed using a parallel plate CVD (PECVD) device (discharge frequency 60 MHz) equipped with a plasma electrode of a shower head structure at a supply flow rate of 100 sccm of silane gas with 10% hydrogen dilution and a current collector temperature of 200°C.
- [0226] (j) Silicone film formation method 3: High-purity silicone raw material was sublimated by heating at 200 W using BE (electron beam) gun and a silicone evaporation source using an evaporation device (manufactured by Ulvac Co., Ltd.) and deposited on the current collector.
- [0227] (k) Silicone film formation method 4: Film was attached and formed on the current collector using a sputtering device (manufactured by Ulvac Co., Ltd.) equipped with a high-purity silicone raw material and a sputter cathode at 80 sccm of argon gas (sputter gas) and 1 kW of high-frequency output.
- [0228] (l) Silicone film formation method 5: The raw materials were melted and volatilized by resistance heating using a vacuum evaporation device (manufactured by Ulvac Co., Ltd.) equipped with high-purity silicone raw materials and a resistance heating source to form a film.
- [0229] (m) Oxidation treatment: Heat treatment was performed at 100°C in the air for a predetermined period of time depending on the introduced oxygen concentration.
- [0230] (2) Test evaluation of samples
- [0231] Next, it was produced as above. Test evaluation of the silicone-based negative electrode sample according to the present invention and the silicone-based negative electrode sample used for comparison was conducted as follows.
- [0232] A hole with a diameter of 20 mm was made in the negative electrode sample and this was used as a test electrode, and a three-electrode cell using lithium foil as a dipole and reference electrode used an electrolyte in which 1M lithium hexafluorophosphate (LiPF₆) is dissolved in a non-aqueous electrolyte with a volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC) of 3: 7, and was assembled as a closed cell at 25°C in a dry atmosphere with a humidity of 7% or less. However, in some embodiments, a solvent having a volume ratio of fluoroethylene carbonate (FEC) and methyltrifluoroethyl carbonate (MFEC), which are non-aqueous solvents containing fluorine in their chemical structure, of 1: 3 was used. The first charging process was carried out at a constant current rate of 0.1C up to a potential of +0.02V based on the redox potential of lithium, and the first charging capacity obtained at this time was tested and measured for each sample and converted to per unit mass of the active material silicone. In the first discharge treatment that followed, discharge was performed at a 0.1C rate constant current to 1.5V for the same lithium potential standard as above, and likewise, the first discharge capacity was measured for each and converted to per unit mass of silicone. In addition, the first actual discharge capacity value was obtained from the previously measured film forming mass and discharge current of the silicone active material. After completion of the first charge/discharge process, the charge/discharge rate was set to 0.2C, and charge/discharge cycles were performed 50 times until each end potential of the first charge/discharge process was completed. The discharge capacity at the end of 50 cycles was determined for each sample and converted to per unit mass. The above first charge/discharge capacity, actual discharge capacity, and discharge capacity after 50 cycles are shown in Table 14 for each sample. For the samples of Examples 3-4, 3-9, 3-11, 3-44 to 3-45, the charging capacity was regulated to 1000 mAh/g, and a charge/discharge cycle test based on the capacity regulation for discharging as described above was performed for 1000 cycles, as shown in Table 15.

Table 12

[0233]	No	Current collector copper foil
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	Manufacturing method and foil thickness (μm)	Type of raw copper foil	Whether or not roughening has been carried out	Appearance of active material formation surface	180°C elongation (%)	Surface roughness (R_z) (μm)	Heat-resistant layer (g/m^2)		Rust treatment layer	Adhesion improvement treatment layer	Reciprocal of electric double layer capacity ($\text{mF}/\mu\text{F}$)
							1st layer Ni	2nd layer Zn			
Example 3-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	2.8	0.015	0.01	Benzotriazole	Silane coupling	0.08
Comparative Example 3-1	Rolled 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.0	1.2	0.015	0.01	Benzotriazole	Silane coupling	0.13
Comparative Example 3-2	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	1.7	0.016	0.007	Chromate	Silane coupling	0.11
Example 3-2	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	1.7	0.016	0.007	Chromate	Silane coupling	0.11
Example 3-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.8	2.0	0.01	0.005	Chromate	Silane coupling	0.09
Comparative Example 3-3	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.2	2.1	0.01	0.005	Chromate	Silane coupling	0.05
Example 3-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-4	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-5	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	3.3	0.05	0.01	Chromate	Silane coupling	0.06
Example 3-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	2.5	0.02	0.009	Chromate	Silane coupling	0.04
Comparative Example 3-6	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.6	2.0	0.03	0.007	Chromate	Silane coupling	0.02
Example 3-8	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-9	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-10	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-11	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-7	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-8	Electrolysis 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.1	2.5	0.015	0.011	Chromate	Silane coupling	0.04

Comparative Example 3-9	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.1	2.0	0.013	0.01	Chromate	Silane coupling	0.02
Example 3-12	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	9.1	1.3	0.025	0.009	Chromate	Silane coupling	0.12
Comparative Example 3-10	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.4	0.009	0.008	Chromate	Silane coupling	0.11
Example 3-13	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-14	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-15	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-16	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-11	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.9	0.01	0.01	Chromate	Silane coupling	0.05
Example 3-17	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Comparative Example 3-12	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	2.9	0.01	0.01	Chromate	Silane coupling	0.05
Example 3-18	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-19	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.2	4.1	0.01	0.008	Chromate	Silane coupling	0.08
Example 3-20	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	2.5	0.008	0.05	Chromate	Silane coupling	0.07
Example 3-21	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	7.4	3.5	0.011	0.05	Chromate	Silane coupling	0.07
Example 3-22	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	3.7	–	0.04	Chromate	Silane coupling	0.07
Example 3-23	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	–	0.06	Chromate	Silane coupling	0.07
Example 3-24	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.008	0.004	Chromate	Silane coupling	0.07
Example 3-25	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	5.7	4.0	0.008	0.002	Chromate	Silane coupling	0.07
Example 3-26	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.008	–	Chromate	Silane coupling	0.07
Example 3-27	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.012	–	Chromate	Silane coupling	0.07

Example 3-28	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.18	—	Chromate	Silane coupling	0.07
Example 3-29	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	0.22	—	Chromate	Silane coupling	0.07
Example 3-30	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	8.2	3.5	—	—	Chromate	Silane coupling	0.07
Example 3-31	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	N/A	N/A	0.07
Example 3-32	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	Chromate	N/A	0.07
Example 3-33	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.01	0.01	N/A	Silane coupling	0.07
Example 3-34	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling	0.07
Example 3-35	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling	0.07
Example 3-36	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling	0.07
Comparative Example 3-13	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling	0.07
Comparative Example 3-14	Electrolysis is 12	Double-sided gloss (FIG. 3)	Has one side	Non-glossy	6.3	4.3	0.05	0.01	Chromate	Silane coupling	0.07
Example 3-37	Electrolysis is 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	3.1	4.0	0.011	0.01	Chromate	Silane coupling	0.07
Example 3-38	Electrolysis is 12	Glossy on one side (FIG. 1)	N/A	Non-glossy	5.3	3.8	0.012	0.01	Chromate	Silane coupling	0.08
Example 3-39	Electrolysis is 12	One side gloss (FIG. 1)	N/A	Non-glossy	2.5	4.2	0.01	0.01	Chromate	Silane coupling	0.06
Example 3-40	Electrolysis is 12	Glossy on one side (FIG. 2)	Has one side	Non-glossy	7.7	6.8	0.015	0.006	Chromate	Silane coupling	0.06
Example 3-41	Electrolysis is 12	One side gloss (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.013	0.008	Chromate	Silane coupling	0.07
Example 3-42	Electrolysis is 18	Glossy on one side (FIG. 2)	Has one side	Non-glossy	8.7	8.2	0.018	0.012	Chromate	Silane coupling	0.04
Example 3-43	Electrolysis is 12	One side gloss (FIG. 1)	N/A	Non-glossy	7.7	4.7	0.011	0.01	Chromate	Silane coupling	0.05
Comparative Example 3-15	Electrolysis is 12	Double-sided gloss (FIG. 3)	N/A	Gloss	7.2	1.0	0.02	0.005	Chromate	Silane coupling	0.20

Table 13

[0234]

No	Appearance before	Lower layer film	Active material film	Upper layer film
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	formation (after 3 months of indoor storage)	Si layer containing P, B	Thickness (μm)	Mass (g/m^2)	Si	Other elements	Diffusion of current collector components	Formation method	Formation time (minutes)	Si layer containing P, B	Reciprocal of electric double layer capacity ($\text{mF}/\mu\text{F}$)
Example 3-1		—	2.0	4.66	○	H, SH, SH ₂	—	Cat-CVD	—	—	1.25
Comparati ve Example 3-1		—	3.0	6.99	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.09
Comparati ve Example 3-2		—	5.0	11.65	○	H, SH, SH ₂	—	Cat-CVD	28	—	0.08
Example 3-2		—	1.5	3.50	○	H, SH, SH ₂	—	Cat-CVD	8	—	0.10
Example 3-3		—	1.5	3.50	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.80
Comparati ve Example 3-3		—	1.0	2.33	○	H, SH, SH ₂	—	Cat-CVD	—	—	3.15
Example 3-4		—	2.5	5.83	○	H, SH, SH ₂	—	Cat-CVD	—	—	1.50
Example 3-5		—	1.5	3.50	○	H, SH, SH ₂	—	Cat-CVD	—	—	2.50
Comparati ve Example 3-4		—	0.5	1.17	○	H, SH, SH ₂	—	Cat-CVD	—	—	3.30
Comparati ve Example 3-5		—	0.3	0.70	○	H, SH, SH ₂	—	Cat-CVD	—	—	4.20
Example 3-6		—	1.0	2.33	○	H, SH, SH ₂	—	Cat-CVD	—	—	1.00
Example 3-7		—	1.0	2.33	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.50
Comparati ve Example 3-6		—	1.0	2.33	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.08
Example 3-8		—	1.0	2.31	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.50
Example 3-9		—	2.5	5.77	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.20
Example 3-10		—	2.5	5.82	○	Trace amounts of P,H,SH,S H ₂	—	Cat-CVD	—	—	0.15
Example 3-11		—	5.0	11.53	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.15
Comparati ve Example 3-7		—	6.5	14.99	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.08
Comparati ve Example 3-8		—	5.5	12.69	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.08
Comparati ve Example 3-9		—	2.5	5.77	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.06
Example 3-12		—	2.5	5.77	○	P,H,SH,S H ₂	—	Cat-CVD	—	—	0.11
Comparati ve Example 3-10		—	1.0	2.32	○	B,H,SH,S H ₂	—	Cat-CVD	—	—	0.09
Example 3-13		—	1.0	2.32	○	B,H,SH,S H ₂	—	Cat-CVD	—	—	0.60
Example 3-14		—	2.0	4.64	○	B,H,SH,S H ₂	—	Cat-CVD	—	—	0.40
Example 3-15		P0.1 μm	2.0	4.66	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.25
Example 3-16		P0.1 μm	1.0	2.33	○	H, SH, SH ₂	—	Cat-CVD	—	—	0.55

Comparative Example 3-11			3.5	8.16	○	H, SH, SH2		Cat-CVD		B0.1 μm	0.09
Example 3-17			2.0	4.66	○	H, SH, SH2		Cat-CVD		B0.1 μm	0.30
Comparative Example 3-12		P0.1 μm	3.0	6.99	○	H, SH, SH2		Cat-CVD		B0.1 μm	0.08
Example 3-18		P0.1 μm	2.0	4.66	○	H, SH, SH2		Cat-CVD		B0.1 μm	0.24
Example 3-19			2.0	4.66	○	H, SH, SH2		Cat-CVD			1.60
Example 3-20			1.0	2.30	○	H, SH, SH2	- (Zn trace diffusion)	Cat-CVD	6		2.60
Example 3-21			1.0	2.30	○	H, SH, SH2		Cat-CVD			2.50
Example 3-22			2.0	4.70	○	H, SH, SH2		Cat-CVD			2.05
Example 3-23			2.0	4.70	○	H, SH, SH2	- (Zn trace diffusion)	Cat-CVD			2.00
Example 3-24			2.0	4.70	○	H, SH, SH2		Cat-CVD			1.80
Example 3-25			2.0	4.70	○	H, SH, SH2	Cu small amount diffusion	Cat-CVD			1.70
Example 3-26			2.0	4.70	○	H, SH, SH2	Cu small amount diffusion	Cat-CVD			1.75
Example 3-27			2.0	4.70	○	H, SH, SH2		Cat-CVD			1.65
Example 3-28			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.90
Example 3-29			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.60
Example 3-30			2.0	4.70	○	H, SH, SH2	Cu diffusion alloying	Cat-CVD			2.20
Example 3-31	Brown rust discoloration		2.0	4.70	○	H, SH, SH2		Cat-CVD			1.80
Example 3-32			2.0	4.70	○	H, SH, SH2		Cat-CVD			1.85
Example 3-33	Spot discoloration		2.0	4.70	○	H, SH, SH2		Cat-CVD			1.75
Example 3-34			2.0	4.70	○	H, SH, SH2		Cat-CVD	12		1.85
Example 3-35			2.0	4.70	○	H, SH, SH2		PECVD	33		2.00
Example 3-36			2.0	4.70	○	H		EB deposition	50		1.40
Comparative Example 3-13			2.0	4.70	○			Sputter	333		1.20
Comparative Example 3-14			2.0	4.70	○	H		Resistance heating deposition	167		1.00
Example 3-37			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.60
Example 3-38			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.70
Example 3-39			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.50
Example 3-40			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.20
Example 3-41			2.0	4.70	○	H, SH, SH2		Cat-CVD			0.40
Example 3-42			2.5	5.90	○	H, SH, SH2		Cat-CVD			0.12

Example 3-43		—	2.0	4.70	○	H, SH, SH2	—	Cat-CVD	—	—	0.25
Comparative Example 3-15		—	Partial peeling	—	○	H, SH, SH2	—	Cat-CVD	—	—	—

Table 14

[0235]

No	Test evaluation results				
	Non-aqueous solvent of electrolyte	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	Actual discharge capacity (mAh)	Discharge capacity after 50 charges/discharges (mAh/g)
Example 3-1	Does not contain F	3,286	3,089	4.9	1,220
Comparative Example 3-1	Does not contain F	2,654	2,442	5.9	276
Comparative Example 3-2	Does not contain F	3,078	2,770	11.1	251
Example 3-2	Does not contain F	3,294	3,129	3.8	854
Example 3-3	Does not contain F	3,428	3,257	3.9	1,067
Comparative Example 3-3	Does not contain F	2,815	2,618	2.1	588
Example 3-4	Does not contain F	3,543	3,295	6.6	1,077
Example 3-5	Does not contain F	3,418	3,179	3.8	1,482
Comparative Example 3-4	Does not contain F	3,004	2,794	1.1	467
Comparative Example 3-5	Does not contain F	2,661	2,328	0.6	244
Example 3-6	Does not contain F	3,717	3,531	2.8	1,656
Example 3-7	Does not contain F	3,630	3,449	2.8	1,465
Comparative Example 3-6	Does not contain F	3,016	2,865	2.3	483
Example 3-8	Does not contain F	3,725	3,539	2.8	1,688
Example 3-9	Does not contain F	3,580	3,401	6.8	1,533
Example 3-10	Does not contain F	3,682	3,498	7.0	1,078
Example 3-11	Does not contain F	3,615	3,398	13.6	883
Comparative Example 3-7	Does not contain F	3,367	3,131	16.3	294
Comparative Example 3-8	Does not contain F	3,551	3,409	15.0	753
Comparative Example 3-9	Does not contain F	3,484	3,310	6.6	377
Example 3-12	Does not contain F	3,525	3,349	6.7	881
Comparative Example 3-10	Does not contain F	3,678	3,494	2.8	655
Example 3-13	Does not contain F	3,744	3,557	2.8	1,660
Example 3-14	Does not contain F	3,667	3,484	5.6	1,503
Example 3-15	Does not contain F	3,691	3,506	5.6	1,654
Example 3-16	Does not contain F	3,765	3,577	2.9	1,716
Comparative Example 3-11	Does not contain F	3,540	3,363	9.4	706
Example 3-17	Does not contain F	3,771	3,582	5.7	1,724
Comparative Example 3-12	Does not contain F	3,603	3,387	8.1	722
Example 3-18	Does not contain F	3,790	3,601	5.8	1,756
Example 3-19	Does not contain F	3,674	3,490	5.6	1,206
Example 3-20	Does not contain F	3,311	3,152	2.5	1,285
Example 3-21	Does not contain F	3,452	3,269	2.6	1,397
Example 3-22	Does not contain F	2,941	2,800	4.5	1,266
Example 3-23	Does not contain F	2,779	2,646	4.2	1,130
Example 3-24	Does not contain F	3,016	2,871	4.6	1,169
Example 3-25	Does not contain F	2,813	2,644	4.2	964
Example 3-26	Does not contain F	2,725	2,578	4.1	918
Example 3-27	Does not contain F	3,133	2,983	4.8	1,084
Example 3-28	Does not contain F	3,374	3,212	5.1	1,226
Example 3-29	Does not contain F	3,246	3,090	4.9	1,023
Example 3-30	Does not contain F	2,025	1,928	3.1	623
Example 3-31	Does not contain F	1,807	1,446	2.3	545
Example 3-32	Does not contain F	3,198	3,029	4.8	1,234
Example 3-33	Does not contain F	2,506	2,373	3.8	718
Example 3-34	Does not contain F	3,657	3,474	5.6	1,438
Example 3-35	Does not contain F	3,315	3,149	5.0	1,165
Example 3-36	Does not contain F	3,207	3,047	4.9	946

Comparative Example 3-13	Does not contain F	2,819	2,678	4.3	374
Comparative Example 3-14	Does not contain F	2,944	2,797	4.5	634
Example 3-37	Does not contain F	3,421	3,259	5.2	1,010
Example 3-38	Does not contain F	3,601	3,448	5.5	1,259
Example 3-39	Does not contain F	3,369	3,260	5.2	789
Example 3-40	Does not contain F	3,483	3,309	5.3	975
Example 3-41	Does not contain F	3,657	3,474	5.6	1,452
Example 3-42	Does not contain F	3,434	3,262	6.5	1,238
Example 3-43	Contains F	3,766	3,578	5.7	1,804
Comparative Example 3-15	—	—	—	—	—

Table 15

No	Active material film					100°C air oxidation treatment	Test evaluation results				
	Thickness (μm)	Mass (g/m ²)	Reciprocal of electric double layer capacity (cm ² /μF)	Si	P-doping/at omic %	Oxygen/at omic %	Non-aqueous solvent of electrolyte	First charging capacity (mAh/g)	First discharge capacity (mAh/g)	1000th charging capacity (mAh/g)	1000th discharge capacity (mAh/g)
Example 3-4	2.5	5.83	1.50	○	—	—	Does not contain F	1,000	1,000	—	—
Example 3-9	2.5	5.77	0.20	○	3	—	Does not contain F	1,000	1,000	455	439
Example 3-11	5.0	11.53	0.15	○	10	—	Does not contain F	1,000	1,000	220	211
Example 3-44	2.5	5.80	0.15	○	2	10	Does not contain F	1,000	1,000	1,000	1,000
Example 3-45	5.0	11.60	0.10	○	5	45	Does not contain F	1,000	1,000	1,000	1,000

From the above sample production and test evaluation, the following can be seen.

Comparing the first charge capacity, discharge capacity, and discharge capacity after 50 cycles of each sample, it can be seen that the charge and discharge characteristics of the sample according to the example are good. For example, in Example 3-1 and Comparative Example 3-1 using rolled copper foil, in the comparative example where the surface roughness (Rz) is small at 1.2 μm, the reciprocal electric double layer capacity of the current collector surface is large due to insufficient real area and irregularities of the current collector surface, and furthermore, as the thickness per unit area of the dielectric layer on the surface of the film is thick, the reciprocal value of the surface electric double layer capacitance (hereinafter referred to as 1/C) after film formation also becomes small, and the result is that the capacity after 50 cycles is less than 300 mAh/g. It appears that deterioration of current collecting properties, etc. occurred due to volumetric contraction and expansion of the active material through repeated charging and discharging. In Example 3-1, which has the roughness and 1/C of the current collector surface and 1/C of the film surface within a predetermined range, the discharge capacity after 50 cycles of 1000 mAh/g or more is shown. On the other hand, while Comparative Example 3-2 and Example 3-2 with an Rz of 1.7 μm use the same double-sided glossy electrolytic foil deviate from the current collector surface 1/C, in Comparative Example 3-2 other than the 1/C regulation after film formation, it is below 300 mAh/g after the cycle test, but Example 3-2, which falls within the regulations, maintains a capacity below 1000 mAh/g but exceeding 800 mAh/g. In Example 3-3, the Rz of the surface of the current collector is 2 μm, and the 1/C of both the current collector and the film surface falls within the specifications, and the discharge capacity after 50 cycles is 1000 mAh/g or more. On the other hand, the current collector (Rz) was the same at 2.1 μm, but in Comparative Example 3-3, where 1/C is small and 1/C after forming a 1 μm Si film is more than the specified 3 cm²/μF, the initial capacity was small, and the capacity after cycling was also less than 600 mAh/g. It appears that the thin surface dielectric layer became thicker per unit area, and the irreversible capacity also increased. Similarly, in Comparative Examples 3-4 to 3-5, where 1/C after film formation exceeds the specified value of 3, the initial capacity was low, and only a low discharge capacity with a post-cycle value of less than 500 mAh/g could be obtained. However, in Examples 3-4 to 3-5, where 1/C was within the specifications, the capacity was maintained at 1000 mAh/g. In addition, in comparison between Examples 3-6 to 3-7 and Comparative Example 3-6, which showed the lower limit of the current collector 1/C, in Comparative Example 3-6, where the current collector 1/C was 0.02, the 1/C after film formation was 0.08, which is below the standard, and the capacity after cycling was also low, and Examples 3-6 to 3-7, which showed 1/C above the lower limit within the specifications, also showed 1/C on the surface of the film within the specifications, and the discharge capacity after the cycle was also 1000 mAh/g or more.

Examples 3-8 to 3-14 and Comparative Examples 3-7 to 3-10 showed examples of film formation in which silicone of the active material was doped with phosphorus or boron. The doped example shows the same good charge/discharge characteristics as the non-doped example. However, in Comparative Examples 3-7 to 3-8, where the film thickness was thick, the capacity after 50

cycles was low, and the surface shape of the film was flattened, showing that cycle characteristics were deteriorated. Comparative Example 3-9 using a current collector below the 1/C lower limit showed a result where the 1/C after film formation was also below the 1/C and the discharge capacity after the cycle was also low. Additionally, in Example 3-12, the current collector Rz and 1/C are not specified, but the 1/C after forming the phosphorus-doped silicone-based film exceeded the specified lower limit, so it did not meet 1000 mAh/g, but showed a discharge capacity close to 900, leaving a relatively excellent capacity. Even in the case of the boron doped film, the cycle capacity was low in Comparative Example 3-10 where 1/C was outside the specified range, and good results were shown in Examples 3-13 to 3-14 of the present invention.

[0240] Examples 3-15 to 3-18 and Comparative Examples 3-11 to 3-12 show examples in which a silicone layer containing phosphorus or boron was further formed on the lower or upper layer of the silicone active material film. In the Comparative Example, which was below the 1/C standard after film formation, the result was obtained that the discharge capacity after the cycle was lower compared to the example within the standard. The examples that fall within the specifications generally showed good results in both the first charge/discharge capacity and the discharge capacity after the cycle, even when compared with other examples. In particular, Example 3-18, which formed a layer containing phosphorus in the lower layer and boron in the upper layer, showed the best results among tests using a non-fluorine-containing non-aqueous electrolyte solution. This is thought to be because the movement of Li ions and electrons is promoted due to the electric field drift effect, and the irreversible capacity associated with the secondary battery decreases.

[0241] The formation amount and evaluation of the nickel layer and zinc layer formed at least partially as the heat-resistant layer are mainly determined from comparison of Examples 3-19 to 3-30. In Example 3-30, in which no film is formed, the copper of the current collector component is diffusion alloyed in the active material film, and the first charge/discharge capacity is around 2000 mAh/g, which is low compared to others, and the capacity after 50 cycles is also below 700 mAh/g. In the case of a nickel single layer, a small amount of copper diffusion remained at 0.008 g/m² in Example 3-26, and this did not occur at 0.012 g/m² in Example 3-27, so it was sufficient to form 0.01 g/m² or more. If it is formed too thick, there is a possibility that the film may break, and in Examples 3-28 to 3-29, a decrease in capacity was observed when the cycle was repeated, so the upper limit is preferably 0.2 g/m² or less. When combined with a zinc layer of 0.003 g/m² or more, the nickel amount may be 0.01 g/m² or less, as can be seen from the comparison of Examples 3-24 to 3-25. Also, as shown in Examples 3-20 to 3-23, when the amount of zinc is great, it is recognized that the active material capacity tends to decrease due to zinc diffusion, so it is preferable that the amount of nickel in the two-layer formation is 0.01 g/m² or more. In addition, while a single-layer film with an increased zinc content of about 0.02 to 0.04 g/m² is also effective, if it is too high, the capacity will decrease, so it is better to set the upper limit to about 0.05 g/m². As even in Example 3-19, which did not have a particularly thick heat-resistant layer, standard good cycle characteristics were shown, and the negative effect of lowering the initial capacity due to the thick heat-resistant layer was also recognized, typically, a balanced heat-resistant layer of two layers is preferable.

[0242] Next, the effects of the rust prevention treatment and the adhesion improvement treatment are evident from comparison with Examples 3-31 to 3-33 and examples other than these. In Example 3-31, in which nothing was done, rust occurred during indoor storage until film forming, and charge/discharge characteristics were poor. On the other hand, Example 3-32, in which only rust prevention treatment was performed, showed good charge and discharge characteristics, and Example 3-33, in which only the adhesion improvement treatment was performed, had a low initial charge/discharge capacity and spotted discoloration occurred, but had a capacity of more than 700 mAh/g after the end of the cycle. In case there is a possibility of long-term inventory until film formation, it is advisable to also perform rust prevention treatment or adhesion improvement treatment. In addition, rust prevention treatment with benzotriazole, an organic dielectric film of Example 3-1, showed the same rust prevention effect as the chromate treatment layer and also had good charge and discharge characteristics.

[0243] If the film formation amount of the silicone-based active material is too thin as in Comparative Example 3-5, there is no problem even if the charge/discharge characteristic value per unit mass is lower than that of other examples, but in general, this is an example that is too small for practical capacity, which is the absolute value of the amount of electricity required for the device, and for example, the capacity remains at about one-eighth of the approximately 5 mAh required for electronic devices, and furthermore, a decrease in discharge capacity after the cycle, which is presumed to be due to irreversible capacity, is also seen. Even in the case of high-output applications that can be applied even with a small capacity per unit cell, it is preferable to have a thickness of 0.5 μm or more in Comparative Example 3-4. In addition, the reason for setting the upper limit of the active material film to 6 μm in the present invention is that when forming a thick film using the excessively thick film forming specification of 6.5 μm shown in Comparative Example 3-7 and the low-roughness current collector of Comparative Example 3-8, as a result of flattening the specific fine surface shape, the actual surface area decreases, and 1/C also falls below the lower limit of 0.1, which reduces the discharge capacity after the charge and discharge cycle. Although it depends on the surface shape of the current collector used, even in the case of an appropriate current collector, it is desirable to limit the thickness to about 6 μm .

[0244] Next, comparing Examples 3-34 to 3-36 and Comparative Examples 3-13 to 3-14 with respect to the film forming method of the silicone-based active material film, the time required to form a 2 μm film was relatively short in the case of Cat-CVD, PECVD, and EB deposition, while the deposition method using sputtering and a resistance heating source took a long time, significantly exceeding 2 hours. For large-area film forming of current collector copper foil, the former three film forming methods are preferable. Additionally, according to the latter two film forming methods, the discharge capacity after completion of the cycle is different. This is thought to be the effect of deterioration due to radiant heat due to long-term film forming, despite low film adhesion or no substrate heating.

- [0245] In Examples 3-37 to 3-39, the mechanical properties of the current collector copper foil, such as the high temperature elongation value and charge/discharge characteristics at 180°C, can be seen, and in Example 3-37 showing an elongation of 3.1%, 1000 mAh/g was maintained after the cycle test was completed, but Example 3-39, which shows an elongation of less than 3%, shows a low capacity, and in this case, as a result of deterioration of the interfacial adhesion between the current collector and the active material film due to volumetric expansion and contraction of the silicone film due to repeated charging and discharging, it is believed that some areas have deteriorated current collection and film conductivity. Example 3-38, which showed an elongation of 5% or more, showed the same cycle characteristics as the other examples. Considering the results of other examples, it can be said that the high temperature elongation at 180°C, which is one of the mechanical properties of the current collector copper foil, is preferably 3% or more, and preferably 5% or more. When the temperature rises during volume expansion, the possibility of problems due to current collector insulation or grain boundary cracking decreases.
- [0246] In addition, for the current collector copper foil of Examples 3-37 to 3-43, a one-sided glossy foil, which is also a general-purpose foil for printed circuits, was used, and among these, in Examples 3-40 and 3-42, a silicone-based film was formed on the foil that had been roughened on the rough side. Although there are examples in which the influence of the mechanical characteristics of the current collector is recognized, all of them showed charge/discharge characteristics without any particular problems.
- [0247] In Example 3-43, an example was given in which a non-aqueous solvent containing fluorine was included in the electrolyte solution in the three-electrode cell test. According to this, the first charge and discharge capacity was also high, and the discharge capacity after the 50 cycle test showed the highest remaining residual result. Compared to conventional types of non-aqueous solvents that do not contain fluorine, this is thought to be the result of a small volume change in volume expansion and contraction during charging and discharging due to the alloying and dealloying of Li ions and silicone, and suppression of the deterioration of adhesion and current collection between the active material and the current collector, and conductivity within the active material film.
- [0248] In Comparative Example 3-15, an attempt was made to form a silicone film directly on the glossy surface of the original double-sided glossy foil without roughening treatment, but as partial film peeling occurred, it could not be helpful in test evaluation as a battery negative electrode sample.
- [0249] Also, as shown in the capacity regulation cycle test results in Table 15, the P-doping of Example 3-4 also cannot achieve capacity after 1000 cycles under oxygen-free conditions, but a certain amount of charge and discharge capacity remains in the P-doped Si of Examples 3-9 and 3-11 after 1000 cycles, and furthermore, in Examples 3-44 to 3-45 in which P-doping and oxygen atoms were introduced at predetermined concentrations, the temperature was maintained at 1000 mAh/g, which was good. In other words, it can be seen that the charge/discharge cycle characteristics of the silicone-based film that is P-doped and further contains oxygen are good.
- [0250] As described above, a negative electrode formed by forming a given silicone-based film shown in the present invention on a given current collector copper foil can be used as a negative electrode that exhibits excellent charge and discharge characteristics in chargeable and dischargeable secondary batteries, including lithium ion secondary batteries that use a non-aqueous solvent as an electrolyte. It is possible to impart characteristics of high energy and high output that have not been achieved before to secondary batteries for industrial and automotive applications, including those used in conventional electrical appliances, which are soon to be commercialized in the future. Moreover, copper foil that has already been mass-produced can be used as a current collector, and the active material can be formed directly in a way that allows large-area film formation, making it possible to use it industrially under economically advantageous conditions.

Description of Symbols

- [0251] 1 : Current collector copper foil base material (raw foil with mountain-shaped rough surface)
- 2 : Heat-resistant layer or heat-resistant barrier layer and anti-rust treatment layer or silane coupling treatment layer
- 3 : Silicone-based active material film
- 4 : Copper-type fine particles attached by roughening treatment
- 5 : Current collector copper foil base material (flat smooth foil or glossy foil)

Figures

FIG. 1

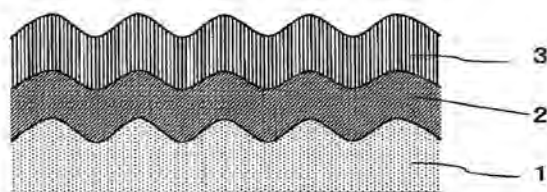


FIG. 2

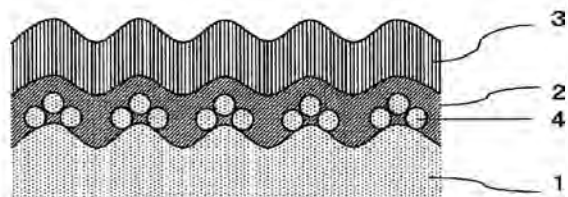


FIG. 3

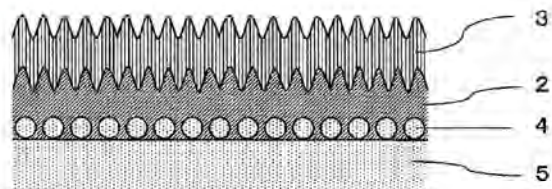


FIG. 4

