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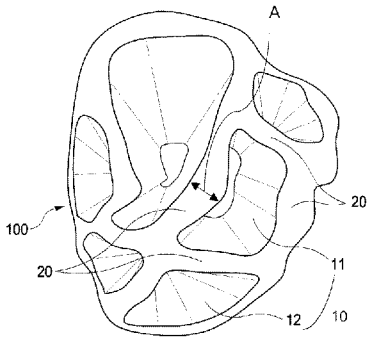
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(54) Title: NEGATIVE ELECTRODE ACTIVE MATERIAL AND NEGATIVE ELECTRODE INCLUDING THE SAME



(57) **Abstract:** Disclosed are a negative electrode active material including a first silicone-based particle; and a negative electrode including the negative electrode active material, wherein the first silicone-based particle includes concave parts; and a skeleton part disposed around the concave parts and configured to partition each of the concave parts. The present invention includes silicone-based particles with concave parts as a negative electrode active material, so that the influence of the volume expansion of the silicon-based particles due to insertion of lithium ions can be reduced. Accordingly, the destruction behavior of silicone-based particles is reduced, and the phenomenon of silicon-based particles being pulverized as the cycle increases is minimized, so that the life characteristics of a secondary battery including the negative electrode active material can be improved.

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Description

Title of Invention: NEGATIVE ELECTRODE ACTIVE MATERIAL AND NEGATIVE ELECTRODE INCLUDING THE SAME

Technical Field

[1] The present invention relates to a negative electrode active material and a negative electrode including the same.

[2]

Background Art

[3] As the electronics, communications, and space industries develop, the demand for secondary batteries as an energy power source is rapidly increasing. In particular, as the importance of global eco-friendly policies is emphasized, the electric vehicle market is growing rapidly, and research and development on secondary batteries are being actively conducted at home and abroad.

[4] Secondary batteries generally consist of a positive electrode containing a positive active material, a negative electrode containing a negative electrode active material, a separator, and an electrolyte. In particular, lithium secondary batteries have high energy density and high capacity, thereby being applied in various fields.

[5] A negative electrode active material constituting a negative electrode is made of a carbon-based material or a silicon oxide. However, in the case of a carbon-based material, the theoretical capacity is only about 400 mAh/g, thereby having the disadvantage of a small capacity.

[6] Accordingly, research has been conducted to replace a carbon-based material using silicon having a high theoretical capacity, as a negative electrode active material. However, the volume of a silicon material expands by about 300% due to lithium insertion, which causes a negative electrode to be destroyed and cycle characteristics to deteriorate. In addition, as the cycle continues, volume expansion continues to occur due to the lithium insertion, causing problems such as loss of contact with a conductive material and a current collector or formation of an unstable Solid Electrolyte Interphase (SEI).

[7]

Disclosure of Invention

Technical Problem

[8] Therefore, the present invention has been made in view of the above problems, and it is one object of the present invention to provide a negative electrode active material

capable of suppressing the volume expansion of a silicon-based active material and exhibiting improved lifespan characteristics, and a negative electrode including the negative electrode active material.

[9]

Solution to Problem

[10] In accordance with an aspect of the present invention, the above and other objects can be accomplished by the provision of a negative electrode active material, including a first silicone-based particle, wherein the first silicone-based particle includes: concave parts; and a skeleton part disposed around the concave parts and configured to partition each of the concave parts.

[11] In an embodiment of the present invention, the first silicone-based particle may have a diameter of 3 ㎛ to 15 ㎛.

[12] In an embodiment of the present invention, a depth of the concave part in a center direction of the first silicone-based particle:a diameter of the first silicone-based particle may be 0.01:1 to 0.80:1.

[13] In an embodiment of the present invention, a ratio of an opening area of the concave part to an area of the first silicone-based particle may be 20 % to 95 %.

[14] In an embodiment of the present invention, a ratio of a volume of the concave part to a volume of the first silicone-based particle may be 5 % to 80 %.

[15] In an embodiment of the present invention, the skeleton part may include a branched structure.

[16] In an embodiment of the present invention, the first silicone-based particle may satisfy Equation 1 below:

[17] [Equation 1]

[18] $1 \leq X/Y \leq 80$

[19] where X represents a depth (nm) of the concave part in a center direction of the first silicone-based particle, and Y represents a length (nm) of the skeleton part in a width direction of the skeleton part.

[20] In an embodiment of the present invention, the negative electrode active material may further include a second silicone-based particle including the concave parts and the skeleton part and having a diameter of 0.1 ㎛ or more and less than 3 ㎛.

[21] In an embodiment of the present invention, the second silicone-based particle may be disposed in at least a portion of the concave parts of the first silicone-based particle.

[22] In an embodiment of the present invention, the first silicone-based particle may include a silicon particle; and a silicon oxide in which a surface of the silicon particle is oxidized.

[23] In an embodiment of the present invention, the silicon particle may have a diameter

of 1 nm to 500 nm.

[24] In an embodiment of the present invention, the silicon oxide may be represented by Formula 1 below:

[25] [Formula 1]

[26] SiO_x ($0<x\leq 9$)

[27] In an embodiment of the present invention, a carbon layer may be formed on at least a portion of the surface of the silicon oxide of the first silicone-based particle.

[28] In accordance with another aspect of the present invention, there is provided a negative electrode, including: a negative electrode current collector; and a negative electrode active material layer formed on at least one surface of the negative electrode current collector, wherein the negative electrode active material layer includes a negative electrode active material, wherein the negative electrode active material includes a first silicone-based particle including concave parts; and a skeleton part disposed around the concave parts and configured to partition each of the concave parts.

[29]

Advantageous Effects of Invention

[30] The present invention includes silicone-based particles with concave parts as a negative electrode active material, so that the influence of the volume expansion of the silicon-based particles due to insertion of lithium ions can be reduced. Accordingly, the destruction behavior of silicone-based particles is reduced, and the phenomenon of silicon-based particles being pulverized as the cycle increases is minimized, so that the life characteristics of a secondary battery including the negative electrode active material can be improved.

[31] In addition, since the silicone-based particles of the present invention have a plurality of concave structures, the surface area of the silicone-based particles increases so that the charging and discharging performance of a secondary battery can be improved, and the volume expansion of the silicone-based particles occurring in various directions can be more efficiently reduced.

[32] In addition, since the silicone-based particles of the present invention have a branched skeletal structure, the mechanical properties can be improved so that the breakage of silicon-based particles due to the manufacturing process of a secondary battery or external shock can be minimized.

[33] Further, the silicone-based particles of the present invention have a composite form including nano-sized silicon particles, a silicon oxide, and a carbon-based coating layer, thereby having superior electrical conductivity, compared to existing silicon oxides, and exhibiting a high silicon ratio, which can increase the capacity of a

secondary battery.

[34]

Brief Description of Drawings

[35] FIG. 1 schematically illustrates a first silicone-based particle according to an embodiment of the present invention.

[36] FIG. 2 schematically illustrates a first silicone-based particle and second silicone-based particle according to another embodiment of the present invention.

[37] FIG. 3 illustrates an SEM photograph of negative electrode active material particles of Manufacturing Example 1.

[38] FIG. 4 illustrates an SEM photograph of negative electrode active material particles of Comparative Example 1.

[39] FIG. 5 illustrates an SEM photograph of negative electrode active material particles of Comparative Example 2.

[40]

Best Mode for Carrying out the Invention

[41] Structural or functional descriptions of embodiments disclosed in the present specification or application are merely illustrated for the purpose of explaining embodiments according to the technical idea of the present invention, embodiments according to the technical idea of the present invention may be implemented in various forms other than the embodiments disclosed in the present specification or application, and it is not to be construed that the technical idea of the present invention is limited to the embodiments described in the present specification or application.

[42] In the present specification or application, when a certain component is "included", this indicates that only the component is included or the component may further include another component unless there is no different disclosure. In addition, it should be understood that all numerical ranges representing physical property values, dimensions, etc. of components described in the present specification or application are modified by the term 'about' in all cases unless otherwise specified.

[43] In this specification or application, "silicone-based" means containing about 50% by weight or more of silicon.

[44]

[45] Hereinafter, a negative electrode active material according to the present invention and a negative electrode including the same are described.

[46]

[47] <Negative active material>

[48] The negative electrode active material according to the present invention includes a first silicone-based particle. FIG. 1 schematically illustrates the first silicone-based

particle according to an embodiment of the present invention. Referring to FIG. 1, a first silicone-based particle 100 includes concave parts 10; and a skeleton part 20 disposed around the concave parts 10 and partitioning each of the concave parts 10.

[49] The concave part 10 may have a depth of 100 nm to 5 ㎛, 100 nm to 4 ㎛, 100 nm to 3 ㎛, 100 nm to 2 ㎛, 100 nm to 1 ㎛, or 100 nm to 900 nm in the center direction of the first silicone-based particle 100. Since the first silicone-based particle 100 includes the concave part 10 having the depth, the volume expansion of a silicon particle due to the insertion of lithium ions may be absorbed as much as the space of the concave portion 10. Accordingly, the volume expansion of a silicone-based particle itself may be significantly suppressed, so that the phenomenon of micronization of the silicon-based particle as a cycle increases may be minimized.

[50] The first silicone-based particle 100 may have a diameter of 3 ㎛ to 15 ㎛, 3 ㎛ to 12 ㎛, 3 ㎛ to 10 ㎛, 3 ㎛ to 9 ㎛, 3 ㎛ to 8 ㎛, or 3 ㎛ to 7.5 ㎛. In a diameter distribution curve of the diameter, the diameter may be determined as a diameter corresponding to 50% of a volume accumulation. For example, the diameter may be measured using a laser diffraction method. When the range is satisfied, the content of the first silicone-based particles may be increased, and the pulverization of the first silicone-based particles during electrode rolling may be minimized.

[51] The depth of the concave part 10:the diameter of the first silicone-based particle 100 in the center direction of the first silicone-based particle may be 0.01:1 to 0.80:1. Preferably, the depth of the concave part 10:the diameter of the first silicone-based particle 100 may be 0.10:1 to 0.80:1, 0.10:1 to 0.75:1, 0.20:1 to 0.75:1, 0.20:1 to 0.60:1, or 0.20:1 to 0.50:1. When the range is satisfied, the volume expansion of the silicone-based particle itself may be significantly suppressed without reducing mechanical strength.

[52] The concave part 10 may include a first concave part 11 and a second concave part 12 adjacent to the first concave part 11. A plurality of concave parts such as the first concave part 11 and the second concave part 12 are formed in the first silicone-based particle 100, so that the volume expansion of the silicone-based particle which can occur in various directions may be more efficiently suppressed.

[53] A ratio of an opening area of the concave part 10 to the area of the first silicone-based particle 100 may be 20 % to 95 %, 25 % to 95 %, 30 % to 95 %, 35 % to 95 %, 35 % to 90 %, or 40 % to 90 %. The ratio of the opening area of the concave part 10 refers to a ratio of the opening area of the concave part 10 to the area of the first silicone-based particle 100 on a plane. The ratio of the opening area of the concave part 10 may be obtained by observing a portion of the surface of the first silicone-based particle 100 using a scanning electron microscope (SEM), and then calculating a ratio of the opening area of the concave part 10 in the surface area.

[54] A ratio of a volume of the concave part 10 to a volume of the first silicone-based particle 100 may be 5 % to 80 %, 7 % to 80 %, 10 % to 80 %, 15 % to 80 %, 18 % to 80 %, 20 % to 80 %, or 25 % to 80 %. The volume ratio of the concave part 10 refers to a ratio of the volume of the concave part 10 to the volume of a virtual external shape of the first silicone-based particle 100. The virtual external shape of the first silicone-based particle 100 refers to a volume in the case where the concave part 10 does not exist, i.e., refers to the case where the space of the concave part 10 is assumed to be filled. The volume of the concave part 10 may be obtained by calculating an increased weight of the first silicone-based particle 100 when immersed in a solvent, and the density of the solvent.

[55] When the range is satisfied, the volume expansion of the silicon-based particle due to insertion of lithium ions may be significantly suppressed, and the lifespan characteristics and charge/discharge performance of a secondary battery may be improved due to an increased surface area of the silicone-based particle.

[56] The skeleton part 20 may include a branched structure. The skeleton part 20 may include a structure branched in a first direction, a second direction, a third direction, or a fourth direction. The skeleton part 20 may include a structure extending in any one of the first to fourth directions with the branched point as the center. Since the skeleton part 20 has a branched structure, mechanical properties may be improved and, accordingly, the phenomenon of silicon-based material being broken due to the manufacturing process of a secondary battery or external shock may be minimized.

[57] The first silicone-based particle 100 may satisfy Equation 1 below:

[58] [Equation 1]

[59] $1 \leq X/Y \leq 80$

[60] where X represents the depth (nm) of the concave part 10 in the center direction of the first silicone-based particle 100, and Y represents the length (A, nm) of the skeleton part in the width direction of the skeleton part 20. The depth of the concave part 10 refers to a maximum depth among a plurality of concave portions 10, and the length (A) of the skeleton part 20 refers to a minimum length between adjacent concave parts 10 in a width direction.

[61] X/Y in Equation 1 may satisfy $2 \leq X/Y \leq 80$, $2 \leq X/Y \leq 75$, $2 \leq X/Y \leq 70$, $5 \leq X/Y \leq 70$, or $10 \leq X/Y \leq 70$. When the range is satisfied, mechanical properties may be improved, and the volume expansion of the silicon-based particle due to insertion of lithium ions may be significantly suppressed.

[62]

[63] FIG. 2 schematically illustrates a first silicone-based particle 100 and second silicone-based particle 200 according to another embodiment of the present invention. Referring to FIG. 2, the negative electrode active material according to the present

invention includes the concave part and the skeleton part and may further include a second silicone-based particle 200 having a diameter of 0.1 ㎛ or more and less than 3 ㎛. Preferably, the second silicone-based particle 200 may have a diameter of 0.2 ㎛ or more and less than 3 ㎛, 0.2 ㎛ to 2 ㎛, 0.2 ㎛ to 1 ㎛, or 0.3 ㎛ to 1 ㎛. The diameter may be measured in the same method as the diameter measurement method of the first silicone-based particle.

[64] The second silicone-based particle 200 may be disposed in at least a portion of the concave part 10 of the first silicone-based particle 100. Since the second silicone-based particle 200 having a smaller diameter than the diameter of the first silicone-based particle 100 is included in the concave part 10 of the first silicone-based particle 100, the volume expansion of the second silicone-based particle 200 in the space of the concave part 10 of the first silicone-based particle 100 may be suppressed even if the volume of the second silicone-based particle 200 expands during lithium charging and discharging, the structural collapse of the second silicone-based particle may be prevented. In addition, when the second silicone-based particle 200 is included in the concave part 10 of the first silicone-based particle 100, the content of silicon is high compared to the same volume, which may increase the capacity of a secondary battery.

[65] The first silicone-based particle 100 may include a silicon particle; and a silicon oxide in which the surface of the silicon particle is oxidized. The first silicone-based particle 100 may have a form of the silicon particle and a primary particle in which the surface of the silicon particle is oxidized or a secondary particle in which the primary particle is aggregated.

[66] Conventionally, as silicon-based active materials were manufactured by mixing silicon particles and silicon oxide physically or chemically, cracks occurred at the boundary between the silicon particles and the silicon oxide during the charging and discharging of a secondary battery. Since the first silicone-based particle according to the present invention includes the silicon oxide oxidized from the silicon particle, the concentration of the silicon oxide may decrease from the surface of the silicon oxide toward the center rather than forming a boundary between the silicon particle and the silicon oxide, so that the occurrence of cracks at the boundary between the silicon particle and the silicon oxide during charging and discharging may be reduced.

[67] The silicon particle may be a spherical silicon nanoparticle. The silicon particle may have a diameter of 1 nm to 500 nm, 1 nm to 400 nm, 10 nm to 400 nm, 10 nm to 350 nm, 10 nm to 300 nm, 10 nm to 250 nm, 10 nm to 200 nm, or 10 nm to 150 nm. The diameter may be measured in the same method as the diameter measurement method of the first silicone-based particle. When the range is satisfied, manufacturing costs may not be significantly increased, and battery capacity and lifespan characteristics may be improved.

[68] The silicon oxide may be represented by Formula 1 below:

[69] [Formula 1]

[70] SiO_x ($0<x\leq 9$)

[71] In Formula 1, when x satisfies the range, the generation of irreversible products such as Li_2O and Li-silicate ($Li_xSi_yO_z$) due to reaction between lithium ions and oxygen may be minimized and, accordingly, the problem that lithium ions, which have reacted with a negative electrode active material, are trapped inside a negative electrode rather than returning to an electrolyte or a positive electrode to cause capacity reduction may be minimized. The second silicone-based particle 200 may also include the above-described silicon particle; and a silicon oxide in which the surface of the silicon particle is oxidized.

[72]

[73] In the first silicone-based particle 100, a carbon layer may be formed on at least a portion of the surface of the silicon oxide. The carbon layer may improve the electrical conductivity of the first silicone-based particle 100. The carbon layer may also be formed in the second silicone-based particle 200, and may improve the electrical conductivity of the second silicone-based particle 200.

[74] To form the carbon layer, a carbonaceous conductive material may be used. The carbonaceous conductive material may be one or more selected from among natural graphite, artificial graphite, acetylene black, Ketjen black, channel black, furnace black, lamp black, thermal black, graphene, carbon nanotubes, and a conductive polymer.

[75] The carbonaceous conductive material may be amorphous carbon. The amorphous carbon may refer to an amorphous structure in which carbon corresponding to a diamond structure and carbon corresponding to a graphite structure are irregularly mixed. A ratio of carbon atoms corresponding to a diamond structure among the amorphous carbon may be 5 % to 70 %, 10 % to 70 %, 15 % to 70 %, 18 % to 70 %, 20 % to 70 %, or 30 % to 70 %. When the range is satisfied, electrical conductivity may be improved while partially suppressing the volume expansion of the silicone-based particle, thereby improving the capacity and lifespan characteristics of a secondary battery. The ratio of carbon atoms corresponding to the diamond structure and carbon atoms corresponding to the graphite structure may be calculated by electron energy-loss spectroscopy using a transmission electron microscope (TEM).

[76] The carbon layer may be formed by the carbonization of a carbon precursor such as a saccharide. The saccharide may be a compound including a C_nH_{2n} cycloalkane ring having 3 to 6 carbon atoms. For example, the saccharide may be any one or more selected from the group consisting of glucose, fructose, galactose, sucrose, maltose, and lactose.

[77] The carbon layer may have a thickness of 1 nm to 10 nm, 1 nm to 9 nm, 1 nm to 8 nm, 2 nm to 8 nm, 2 nm to 7 nm, or 2 nm to 6 nm. In addition, the carbon layer coating layer may be formed to cover 70% or more, 75% or more, 80% or more, 85% or more, 90% or more, or 95% or more of the surface area of the silicone-based particle. When the range is satisfied, the movement of lithium ions is not hindered and the electrical conductivity may be increased.

[78]

[79] The negative electrode active material according to the present invention may further include natural graphite particles. The natural graphite particles may include a carbon layer formed on the natural graphite particles. the carbon layer may reduce micropores of the natural graphite particles, may reduce a side reaction with an electrolyte solution, and may improve structural stability.

[80] The carbon layer may include the natural graphite particles in an amount of 1 % by weight to 10 % by weight, 1 % by weight to 9 % by weight, 2 % by weight to 9 % by weight, 2 % by weight to 8 % by weight, or 3 % by weight to 8 % by weight. When the range is satisfied, excessive lithium insertion and desorption may be prevented while improving the structural stability of the natural graphite particles.

[81] The carbon layer may include amorphous carbon. For example, the carbon layer may be formed by providing at least one carbon layer precursor selected from the group consisting of pitch, rayon, and polyacrylonitrile-based resin to the natural graphite particles, followed by heat treatment.

[82] The natural graphite particles may have a BET specific surface area of 1.0 m^2/g to 5.0 m^2/g, 1.2 m^2/g to 5.0 m^2/g, 1.2 m^2/g to 4.8 m^2/g, 1.5 m^2/g to 4.8 m^2/g, or 1.5 m^2/g to 4.5 m^2/g. When the range is satisfied, the lifespan characteristics of a secondary battery may be improved by preventing a side reaction with an electrolyte solution, and high output characteristics may be realized.

[83] The natural graphite particles may have a sphericity degree of 0.6 to 1, 0.7 to 1, 0.8 to 1, 0.9 to 1, or 0.95 to 1. The sphericity degree may be measured using a known sphericity measurement method. When the range is satisfied, packing between particles may be smoothened, and stress applied to particles when manufacturing a negative electrode may be alleviated, reducing the swelling phenomenon.

[84]

[85] The negative electrode active material according to the present invention may further include artificial graphite particles. The artificial graphite particles may be a primary particle, a secondary particle, or a mixture of a primary particle and a secondary particle. The primary particle may refer to a single particle that is not aggregated. The secondary particle may refer to an aggregate of the primary particles.

[86] The carbon layer may be included in an amount of 1 % by weight to 10 % by weight,

1 % by weight to 9 % by weight, 2 % by weight to 9 % by weight, 2 % by weight to 8 % by weight, or 3 % by weight to 8 % by weight based on the artificial graphite particles. When the range is satisfied, excessive lithium insertion and desorption may be prevented while improving the structural stability of the artificial graphite particles.

[87] The carbon layer may include amorphous carbon. For example, the carbon layer may be formed by providing at least one carbon layer precursor selected from the group consisting of pitch, rayon, and polyacrylonitrile-based resin to the natural graphite particles, followed by heat treatment.

[88] The natural graphite particles may have a BET specific surface area of 0.5 m^2/g to 3.0 m^2/g, 0.5 m^2/g to 2.5 m^2/g, 0.5 m^2/g to 2.0 m^2/g, 0.5 m^2/g to 1.8 m^2/g, or 0.5 m^2/g to 1.5 m^2/g. When the range is satisfied, the lifespan characteristics of a secondary battery may be improved by preventing a side reaction with an electrolyte solution, and high output characteristics may be realized.

[89] The natural graphite particles may have a sphericity degree of 0.65 to 1, 0.68 to 1, 0.7 to 1, 0.8 to 1, or 0.9 to 1. The sphericity degree may be measured using a known sphericity measurement method. When the range is satisfied, packing between particles may be smoothened, and stress applied to particles when manufacturing a negative electrode may be alleviated, reducing the swelling phenomenon.

[90]

[91] <Method of manufacturing negative electrode active material>

[92] A method of manufacturing a negative electrode active material according to the present invention may include a step (a) of adding silicon particles and beads to a solvent and then milling it to prepare a first silicon slurry, a step (b) of adding the first silicon slurry to a carbon-based polymer solution and then stirring it to prepare a second silicon slurry, and a step (c) of heat-treating the second silicon slurry in a temperature range of 1,000 ℃ to 1,500 ℃ in an inert atmosphere.

[93] In the step (a), the silicon particles may be spherical silicon nanoparticles. Each of the silicon particles may have a diameter of 0.5 nm to 500 nm, 1 nm to 400 nm, 10 nm to 400 nm, 10 nm to 350 nm, 10 nm to 300 nm, 10 nm to 250 nm, 10 nm to 200 nm, or 10 nm to 150 nm. In a diameter distribution curve of the diameter, the diameter may be determined as a diameter corresponding to 50% of a volume accumulation. For example, the diameter may be measured using a laser diffraction method. When the range is satisfied, battery capacity and life characteristics may be improved.

[94] The beads may be zirconium oxide balls (YTZ). Each of the zirconium oxide balls may have a diameter of 0.01 mm to 1 mm, 0.05 mm to 1 mm, 0.05 mm to 0.5 mm, or 0.05 mm to 0.3 mm. The solvent is not particularly limited, but may be isopropyl alcohol. The silicon particles and beads are included in an amount of 10 % by weight to 50 % by weight, 10 % by weight to 40 % by weight, 10 % by weight to 35 % by

weight, or 15 % by weight to 35 % by weight based on a total weight of the solvent and may be subjected to a milling process.

[95] In the step (a), a milling process may be performed under a temperature condition of 45 ℃. As the temperature condition is a silicon-based active material with suppressed oxidation reaction may be manufactured. If necessary, the solvent may be additionally added in the milling process.

[96]

[97] In the step (b), a carbon layer may be formed on the surface of the silicon-based active material by the carbon-based polymer solution.

[98] After the step (b), a step (b-1) of homogenizing the second silicon slurry under a pressure condition of 800 bar to 1,200 bar may be included. By the homogenizing step, the mixing property between the second silicon slurry and the carbon-based polymer solution may be improved.

[99] After the step (b-1), a step (b-2) of spray-drying the second silicon slurry may be included. By the spray-drying step, a silicone-based carbon polymer precursor may be manufactured. As the precursor is manufactured, the density of the negative electrode active material may be improved.

[100]

[101] By the heat-treating of the step (c), a carbon coating layer may be formed on the surface of the silicon oxide. In addition, a solvent may be evaporated by the step (c), and a concave part may be formed in the space, from which the solvent has been evaporated, in the silicone-based particle.

[102]

[103] <Negative electrode>

[104] A negative electrode according to the present invention includes a negative electrode current collector; and a negative electrode active material layer formed on at least one surface of the negative electrode current collector, the negative electrode active material layer includes a negative electrode active material, and the negative electrode active material includes a first silicone-based particle including concave parts; and a skeleton part which is disposed around the concave parts and respectively partitions the concave parts.

[105] The negative electrode active material and the first silicone-based particle may be the same as the above-described negative electrode active material and first silicone-based particle.

[106] The negative electrode current collector is not particularly limited as long as it is conductive without causing chemical changes in a secondary batter and may be made of, for example, copper; stainless steel; aluminum; nickel; titanium; fired carbon; copper or stainless steel surface-treated with carbon, nickel, titanium, silver, etc.;

aluminum-cadmium alloy; or the like. In addition, fine irregularities may be formed on the surface to strengthen the bonding power of a negative electrode active material, and various forms such as a film, a sheet, a foil, a net, a porous material, a foam, and a non-woven material may be used.

[107]

[108] The negative electrode active material layer may further include a binder. The binder may be used to maintain a molded body by binding particles contained in the negative electrode active material. The binder may be a non-aqueous binder or an aqueous binder. For example, the non-aqueous binder may be, polyvinyl alcohol, carboxymethyl cellulose, hydroxypropylene cellulose, diacetylene cellulose, polyvinyl chloride, polyvinylpyrrolidone, polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVdF), polyethylene, polypropylene, or the like, and the aqueous binder may be one selected from the group consisting of acrylonitrile-butadiene rubber, styrene-butadiene rubber, and acrylic rubber, or a mixture of two or more thereof. The aqueous binder is more economical and environmentally friendly than the non-aqueous binder, is harmless to workers' health, and has a superior binding effect compared to the non-aqueous binder, so the ratio of an active material per same volume may be increased, enabling high capacity. Particularly, a styrene-butadiene rubber may be used as the aqueous binder.

[109] The binder may be included in an amount of 0.1 % by weight to 10 % by weight, 0.1 % by weight to 8 % by weight, 0.1 % by weight to 7 % by weight, 0.1 % by weight to 6 % by weight, or 0.1 % by weight to 5 % by weight based on a total weight of a slurry for producing a negative electrode active material layer. When the range is satisfied, the effect as a binder may be excellent without a decrease in capacity per volume due to a decrease in a relative content of a negative electrode active material.

[110] The negative electrode active material layer may further include a conductive material. The conductive material is not particularly limited as long as it is conductive without causing chemical changes in a secondary batter. The conductive material may be, for example, graphite such as natural graphite or artificial graphite; carbon black such as acetylene black, Ketjen black, channel black, furnace black, lamp black, or summer black; conductive fiber such as carbon fiber or metal fiber; metal powder such as carbon fluoride, aluminum, or nickel powder; conductive whiskers such as zinc oxide or potassium titanate; a conductive metal oxide such as titanium oxide; a conductive material such as a polyphenylene derivative; or the like. The conductive material may be included in an amount of 0.1 % by weight to 10 % by weight, 0.1 % by weight to 8 % by weight, 0.1 % by weight to 7 % by weight, 0.1 % by weight to 6 % by weight, or 0.1 % by weight to 5 % by weight based on a total weight of a slurry for producing a negative electrode active material layer. When the range is satisfied,

electrical conductivity may be improved without a decrease in capacity per volume due to a decrease in a relative content of an active material.

[111]

[112] <Secondary battery>

[113] A secondary battery according to the present invention may include a negative electrode, a positive electrode, and a separator interposed between the negative electrode and the positive electrode.

[114] The negative electrode may be the same as the above-described negative electrode.

[115] The positive electrode may be manufactured by a general method known in the art. For example, a positive electrode may be manufactured by mixing and stirring a positive active material with a solvent, a binder, a conductive material, and a dispersant to produce a slurry, and then applying the slurry to a positive electrode current collector, followed by compressing and drying it.

[116]

[117] The positive electrode current collector is a highly conductive metal to which a slurry of the positive active material can easily adhere, and is not particularly limited as long as it has high conductivity without causing chemical changes in a secondary battery. The positive electrode current collector may be, for example, stainless steel; aluminum; nickel; titanium; calcined carbon; the surface of aluminum or stainless steel treated with carbon, nickel, titanium, silver, etc.; or the like. In addition, the adhesive force of a positive active material may be increased by forming fine irregularities on the surface of the positive electrode current collector. The positive electrode current collector may be used in various forms such as a film, a sheet, a foil, a net, a porous material, a foam, and a non-woven material, and may have a thickness of 3 ㎛ to 500 ㎛.

[118]

[119] The positive active material is a compound capable of reversible intercalation and deintercalation of lithium, and may include, specifically, a lithium composite metal oxide containing lithium and one or more metals such as cobalt, manganese, nickel, or aluminum.

[120] Particularly, the lithium composite metal oxide may be a lithium-manganese-based oxide (e.g., $LiMnO_2$, $LiMn_2O_4$, etc.), a lithium-cobalt-based oxide (e.g., $LiCoO_2$, etc.), a lithium-nickel-based oxide (e.g., $LiNiO_2$, etc.), a lithium-nickel-manganese oxide (e.g., $LiNi_{1-Y}Mn_YO_2$ (where $0<Y<1$), $LiMn_{2-z}Ni_zO_4$ (where $0<Z<2$), etc.), a lithium-nickel-cobalt-based oxide (e.g., $LiNi_{1-Y1}Co_{Y1}O_2$ (where $0<Y1<1$), etc.), a lithium-manganese-cobalt-based oxide (e.g., $LiCo_{1-Y2}Mn_{Y2}O_2$ (where $0<Y2<1$), $LiMn_{2-Z1}Co_{Z1}O_4$ (where $0<Z1<2$), etc.), a lithium-nickel-manganese-cobalt-based oxide (e.g., $Li(Ni_pCo_qMn_{r1})O_2$ (where $0<p<1$, $0<q<1$, $0<r1<1$, $p+q+r1=1$) or $Li(Ni_{p1}Co_{q1}Mn_{r2})O_4$

(where $0<p1<2$, $0<q1<2$, $0<r2<2$, p1+q1+r2=2), etc.), or a lithium-nickel-cobalt-transition metal (M) oxide (e.g., $Li(Ni_{p2}Co_{q2}Mn_{r3}M_{S2})O_2$ (where M is selected from the group consisting of Al, Fe, V, Cr, Ti, Ta, Mg and Mo, p2, q2, r3 and s2 are each independent atomic fraction of elements, $0<p2<1$, $0<q2<1$, $0<r3<1$, $0<s2<1$, and p2+q2+r3+s2=1), etc.), or the like, and may include a compound of one or more thereof. In terms of improving the capacity characteristics and stability of the battery, the lithium composite metal oxide may be $LiCoO_2$, $LiMnO_2$, $LiNiO_2$, a lithium nickel manganese cobalt oxide (e.g., $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$, $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$, or $Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O_2$, etc.), a lithium nickel cobalt aluminum oxide (e.g., $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$, etc.), or the like among the oxides, and when considering the remarkable improvement effect due to control of the type and content ratio of the constituent elements forming the lithium composite metal oxide, the lithium composite metal oxide may be $Li(Ni_{0.6}Mn_{0.2}Co_{0.2})O_2$, $Li(Ni_{0.5}Mn_{0.3}Co_{0.2})O_2$, $Li(Ni_{0.7}Mn_{0.15}Co_{0.15})O_2$, $Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O_2$ or the like or a mixture of one or more thereof.

[121]

[122] The solvent may be an organic solvent such as N-methyl pyrrolidone (NMP), dimethyl formamide (DMF), acetone or dimethyl acetamide, or water, and these solvents may be used alone or in a mixture of two or more thereof. The use amount of the solvent is sufficient so long as it is an amount capable of dissolving and dispersing the positive active material, the binder, and the conductive material, considering the application thickness of a slurry and a manufacturing yield.

[123]

[124] The binder may be a variety of binders such as a polyvinylidenefluoride-hexafluoropropylene copolymer (PVDF-co-HFP), polyvinylidenefluoride, polyacrylonitrile, polymethylmethacrylate, polyvinyl alcohol, carboxymethylcellulose (CMC), starch, hydroxypropylcellulose, regenerated cellulose, polyvinylpyrrolidone, tetrafluoroethylene, polyethylene, polypropylene, polyacrylic acid, an ethylene-propylene-diene monomer (EPDM), sulfonated EPDM, styrene butadiene rubber (SBR), fluorine rubber, poly acrylic acid and its polymers whose hydrogen is substituted with Li, Na, or Ca, and various copolymers.

[125]

[126] The conductive material is not particularly limited as long as it is conductive without causing chemical changes in a secondary batter. The conductive material may be, for example, graphite such as natural graphite or artificial graphite; carbon black such as acetylene black, Ketjen black, channel black, furnace black, lamp black, or summer black; conductive fiber such as carbon fiber or metal fiber; conductive tubes such as carbon nanotubes; metal powder such as fluorocarbon, aluminum, or nickel powder; conductive whiskers such as zinc oxide or potassium titanate; a conductive metal oxide

such as titanium oxide; a conductive material such as a polyphenylene derivative; or the like. The conductive material may be used in an amount of 1 % by weight to 20 % by weight based on a total weight of the positive electrode slurry.

[127] The dispersant may be an aqueous dispersant or an organic dispersant such as N-methyl-2-pyrrolidone.

[128]

[129] The separator may be interposed between the negative electrode and the positive electrode. The separator is configured to prevent electrical short circuit between a negative electrode and a positive electrode and to generate a flow of ions. The separator may include a porous polymer film or a porous non-woven fabric. Here, the porous polymer film may be composed of a single layer or multiple layers containing a polyolefin-based polymer such as an ethylene polymer, a propylene polymer, an ethylene/butene copolymer, an ethylene/hexene copolymer, or an ethylene/ methacrylate copolymer. The porous non-woven fabric may include glass fiber with a high melting point or polyethylene terephthalate fiber. However, it is not limited thereto, and the separator may be a highly heat-resistant separator (Ceramic Coated Separator; CCS) containing ceramic depending on an embodiment.

[130] The positive electrode, the negative electrode and the separator may be manufactured into an electrode assembly by a winding, lamination, folding, or zigzag stacking process. In addition, the electrode assembly may be provided with an electrolyte solution so that it may be manufactured into the secondary battery according to the present invention. The secondary battery may be one of cylindrical, square, pouch, and coin types using a can, without being limited thereto.

[131]

[132] The electrolyte solution may be a non-aqueous electrolyte. The electrolyte solution may include lithium salt and an organic solvent. The organic solvent may include at least one of propylene carbonate (PC), ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), ethylmethyl carbonate (EMC), methylpropyl carbonate (MPC), dipropyl carbonate (DPC), vinylene carbonate (VC), dimethyl sulfoxide, acetonitrile, dimethoxyethane, diethoxyethane, sulfolane, gamma-butyrolactone, propylene sulfide, and tetrahydrofuran.

[133]

[134] The present invention may provide a battery module including the secondary battery as a unit battery. The battery module may be used as a power source for medium and large devices that require high-temperature stability, long cycle characteristics, high rate characteristics, and the like.

[135] Examples of the medium and large devices include, but are not limited to, electric motor-driven power tools; electric vehicles (EVs), hybrid electric vehicles (HEVs), and

plug-in hybrid electric vehicles (PHEVs); electric two-wheeled vehicles such as e-bikes and e-scooters; electric golf carts; and systems for storing power.

[136]

[137] Hereinafter, the present invention will be described in more detail based on examples and comparative examples. However, the following examples and comparative examples are only examples to explain the present invention in more detail, and the present invention is not limited by the following examples and comparative examples.

[138]

[139] **Manufacturing examples - Manufacturing of negative electrode active material**

[140] **Manufacturing Example 1**

[141] Silicon with a particle size of about 800 nm and zirconia beads (YTZ) with a particle size of about 0.1 mm were added to an isopropyl alcohol solvent. Next, milling was performed for 9 hours while maintaining a temperature of 45°C or lower to produce a first silicon slurry with a particle size of about 100 nm and 30% by weight of metallic silicon solid content.

[142] The first silicon slurry was stirred in a homogenization reactor (2,500 rpm) for 10 minutes, and then polyvinyl pyrrolidone (PVP) was added thereto. This was re-stirred in the homogenization reactor for 10 minutes to produce a second silicon slurry.

[143] The second silicon slurry was subjected to a homogenization process twice under a pressure of 1,000 bar in a high-pressure homogenizer. Next, the second silicon slurry was spray-dried under the conditions of 100°C, 0.5 Mpa pressure, and 3 L/h flow rate. Next, heat treatment was performed at 1,200 ℃ a nitrogen condition, thereby producing a negative electrode active material.

[144] **Manufacturing Example 2**

[145] A negative electrode active material was manufactured by the same process as in Manufacturing Example 1 except that metal silicon with a particle size of about 80 nm was used instead of the metal silicon with a particle size of about 100 nm of Manufacturing Example 1.

[146] **Manufacturing Example 3**

[147] A negative electrode active material was manufactured by the same process as in Manufacturing Example 1 except that spray-drying was performed at a flow rate of 2 L/h instead of the spray-drying at a flow rate of 3 L/h of Manufacturing Example 1.

[148] **Manufacturing Example 4**

[149] A negative electrode active material was manufactured by the same process as in Manufacturing Example 1 except that spray-drying was performed at a flow rate of 4 L/h instead of the spray-drying at a flow rate of 3 L/h of Manufacturing Example 1.

[150]

[151] **Examples**

[152] **Example 1**

[153] <Manufacturing of negative electrode>

[154] A slurry was prepared by mixing the negative electrode active material:conductive material (Super-P):binder (SBR-CMC) of Manufacturing Example 1 in a weight ratio of 8:1:1 in an N-methyl pyrrolidone solvent. Next, the slurry was applied to a copper thin film and then dried in a vacuum oven at 80°C for 8 hours to manufacture a negative electrode.

[155] <Manufacturing of coin-type half-cell>

[156] A metal lithium foil with a thickness of 0.3 mm was used as an opposite electrode (positive electrode) of the manufactured negative electrode, and a polypropylene sheet with a thickness of 0.1 mm was used as a separator. A coin-type half-cell was manufactured using an electrolyte solution prepared by dissolving 1M LiPF6 in ethylene carbonate and ethyl methyl carbonate mixed in a volume ratio of 3:7 in a solvent.

[157] **Example 2**

[158] A coin-type half-cell was manufactured in the same manner as in Example 1 except that the negative electrode active material of Manufacturing Example 2 was used instead of the negative electrode active material of Manufacturing Example 1.

[159] **Example 3**

[160] A coin-type half-cell was manufactured in the same manner as in Example 1 except that the negative electrode active material of Manufacturing Example 3 was used instead of the negative electrode active material of Manufacturing Example 1.

[161] **Example 4**

[162] A coin-type half-cell was manufactured in the same manner as in Example 1 except that the negative electrode active material of Manufacturing Example 4 was used instead of the negative electrode active material of Manufacturing Example 1.

[163] **Comparative Example 1**

[164] A coin-type half-cell was manufactured in the same manner as in Example 1 except that DMSO-H85 silicon oxide composite (shown in FIG. 4) of DAEJOO ELECTRONIC MATERIALS Co., Ltd.), instead of the negative electrode active material of Manufacturing Example 1, was used as a negative electrode active material.

[165] **Comparative Example 2**

[166] A coin-type half-cell was manufactured in the same manner as in Example 1 except that a silicon carbide composite (shown in FIG. 5) of BTR company, instead of the negative electrode active material of Manufacturing Example 1, was used as a negative electrode active material.

[167]

[168] **Experimental examples**

[169] **Experimental Example 1 - SEM analysis**

[170] The scanning electron microscopy (SEM) analysis result of the negative electrode active material of Manufacturing Example 1 is shown in FIG. 3. In addition, the scanning electron microscopy (SEM) analysis results of the negative electrode active materials of Comparative Examples 1 and 2 are shown in FIGS. 4 and 5, respectively.

[171] Referring to FIGS. 3 to 5, it was confirmed that concave parts and a skeleton part respectively partitioning the concave parts were formed in the negative electrode active material of Manufacturing Example 1. In contrast, a concave part was not observed in the negative electrode active materials of Comparative Examples 1 and 2.

[172] **Experimental Example 2 - Discharge capacity maintenance rate**

[173] To perform a battery stabilization process, a process of charging the coin-type half-cell manufactured in each of Examples 1 to 4 and Comparative Examples 1 to 2 with a constant current of 0.1C until the voltage reached 0.01V and discharging it with a constant current of 0.1C until the voltage reached 1.5V was performed three times.

[174] Next, the coin-type half-cell was charged with a constant current of 0.5C until the voltage reached 0.01V, and discharged with a constant current of 0.5C until the voltage reached 1.0V. This process was performed 50 times. After the 50th charge and discharge, a discharge capacity maintenance rate compared to the 1st charge and discharge was measured. Results are shown in Table 1 below.

[175] **Experimental Example 3 - Swelling ratio**

[176] A swelling ratio during the charge/discharge process according to Experimental Example 2 was measured and calculated according to Equation 1 below. Results are shown in Table 1 below.

[177] [Equation 1]

[178] Swelling ratio(%) = [(t2-t1)/t1] X 100

[179] where t1 represents the thickness of a negative electrode before the 1st charge and discharge, and t2 is the thickness of the negative electrode after the 50th charge and discharge.

[180]

[181] [Table 1]

	Discharge capacity maintenance rate	Swelling ratio
Example 1	96.8%	20%
Example 2	96.5%	21%
Example 3	96.3%	20%
Example 4	96.4%	20%
Comparative Example 1	88.4%	28%

Comparative Example 2	87.9%	29%

[182]

[183] As shown in Table 1, it was confirmed that Examples 1 to 4 exhibited a higher discharge capacity maintenance rate than Comparative Examples 1 to 2, and the change in the thickness of the negative electrode after the cycle was significantly reduced. Therefore, the volume expansion of the silicon-based particle due to insertion of lithium ions can be suppressed as the silicon-based particle according to the present invention includes a concave part. In addition, the phenomenon of micronization of silicone-based particles is minimized as the cycle increases, so that the discharge capacity maintenance rate of the secondary battery increases, thereby reducing the swelling ratio of the negative electrode.

[184]

Industrial Applicability

[185] An embodiment of the present invention can be applied to a negative electrode active material and a negative electrode including the same.

Claims

[Claim 1] A negative electrode active material, comprising a first silicone-based particle,
wherein the first silicone-based particle comprises:
concave parts; and
a skeleton part disposed around the concave parts and configured to partition each of the concave parts.

[Claim 2] The negative electrode active material according to claim 1, wherein the first silicone-based particle has a diameter of 3 ㎛ to 15 ㎛.

[Claim 3] The negative electrode active material according to claim 1, wherein a depth of the concave part in a center direction of the first silicone-based particle:a diameter of the first silicone-based particle is 0.01:1 to 0.80:1.

[Claim 4] The negative electrode active material according to claim 1, wherein a ratio of an opening area of the concave part to an area of the first silicone-based particle is 20 % to 95 %.

[Claim 5] The negative electrode active material according to claim 1, wherein a ratio of a volume of the concave part to a volume of the first silicone-based particle is 5 % to 80 %.

[Claim 6] The negative electrode active material according to claim 1, wherein the skeleton part comprises a branched structure.

[Claim 7] The negative electrode active material according to claim 1, wherein the first silicone-based particle satisfies Equation 1 below:
[Equation 1]
$1 \leq X/Y \leq 80$
where X represents a depth (nm) of the concave part in a center direction of the first silicone-based particle, and Y represents a length (nm) of the skeleton part in a width direction of the skeleton part.

[Claim 8] The negative electrode active material according to claim 1, further comprising a second silicone-based particle comprising the concave parts and the skeleton part and having a diameter of 0.1 ㎛ or more and less than 3 ㎛.

[Claim 9] The negative electrode active material according to claim 8, wherein the second silicone-based particle is disposed in at least a portion of the concave parts of the first silicone-based particle.

[Claim 10] The negative electrode active material according to claim 1, wherein the first silicone-based particle comprises a silicon particle; and a

silicon oxide in which a surface of the silicon particle is oxidized.

[Claim 11] The negative electrode active material according to claim 10, wherein the silicon particle has a diameter of 1 nm to 500 nm.

[Claim 12] The negative electrode active material according to claim 10, wherein the silicon oxide is represented by Formula 1 below:

[Formula 1]

SiO_x ($0<x\leq 9$).

[Claim 13] The negative electrode active material according to claim 10, wherein a carbon layer is formed on at least a portion of the surface of the silicon oxide of the first silicone-based particle.

[Claim 14] A negative electrode, comprising:

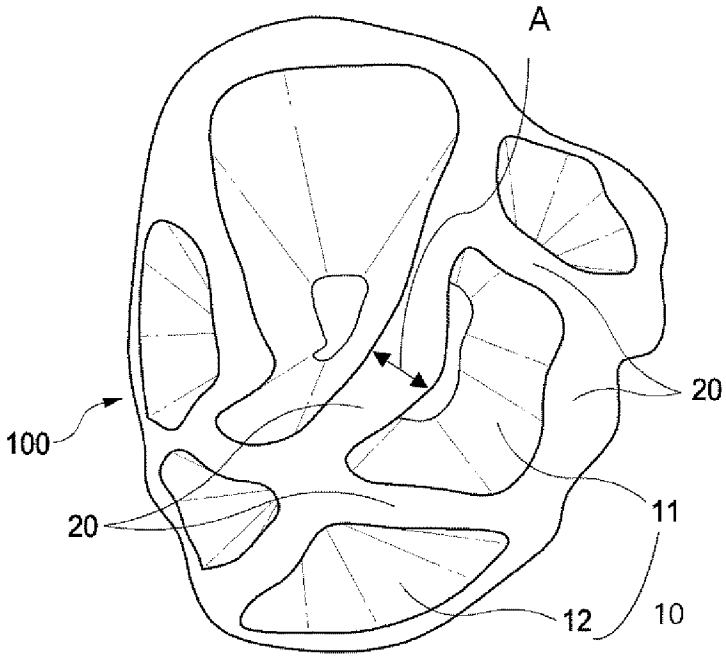
a negative electrode current collector; and

a negative electrode active material layer formed on at least one surface of the negative electrode current collector,

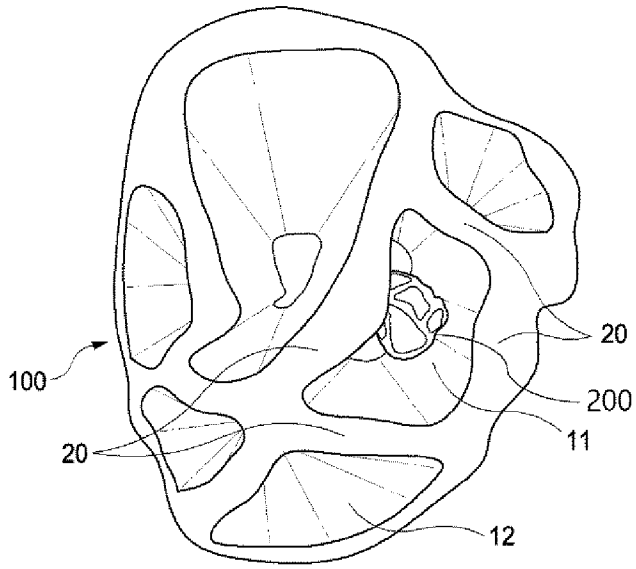
wherein the negative electrode active material layer comprises a negative electrode active material,

wherein the negative electrode active material comprises a first silicone-based particle comprising concave parts; and a skeleton part disposed around the concave parts and configured to partition each of the concave parts.

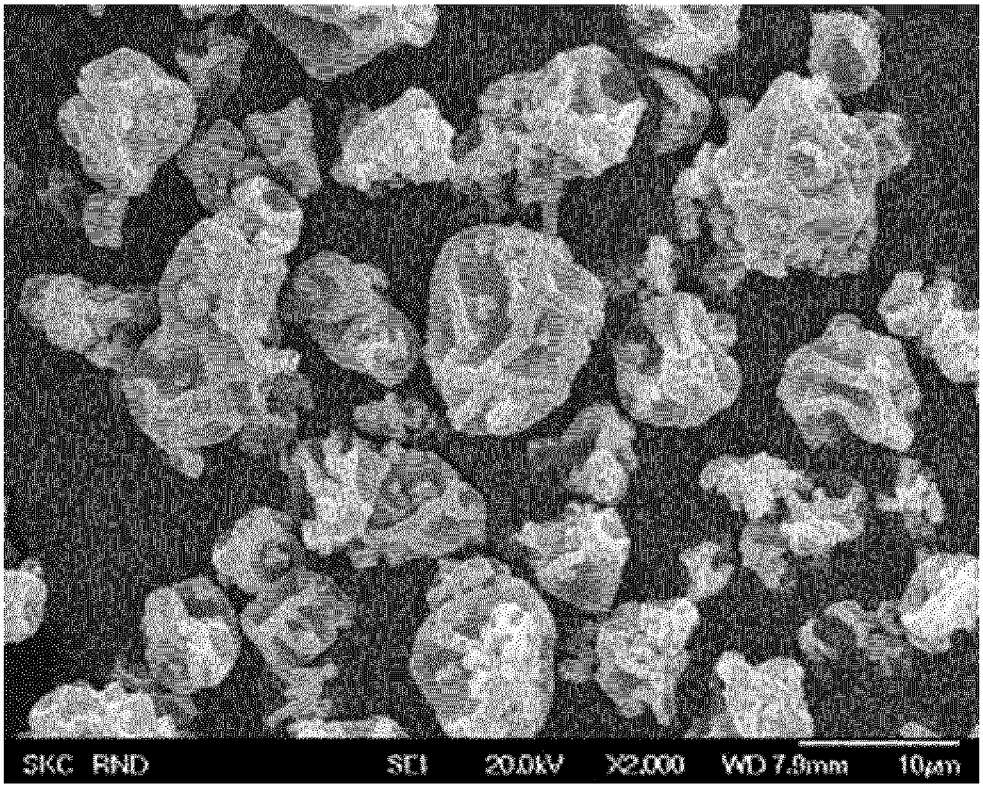
[Fig. 1]



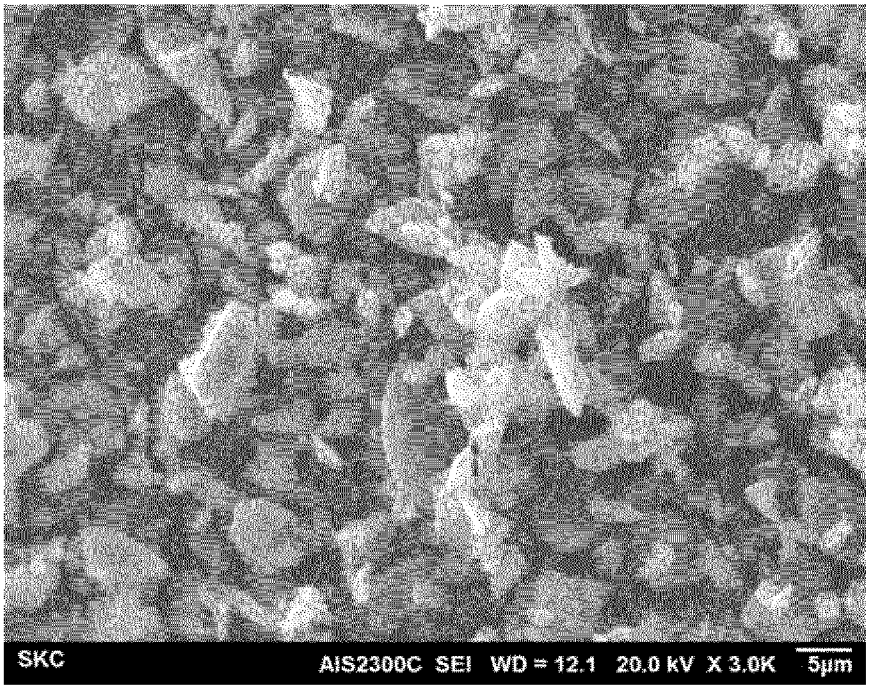
[Fig. 2]



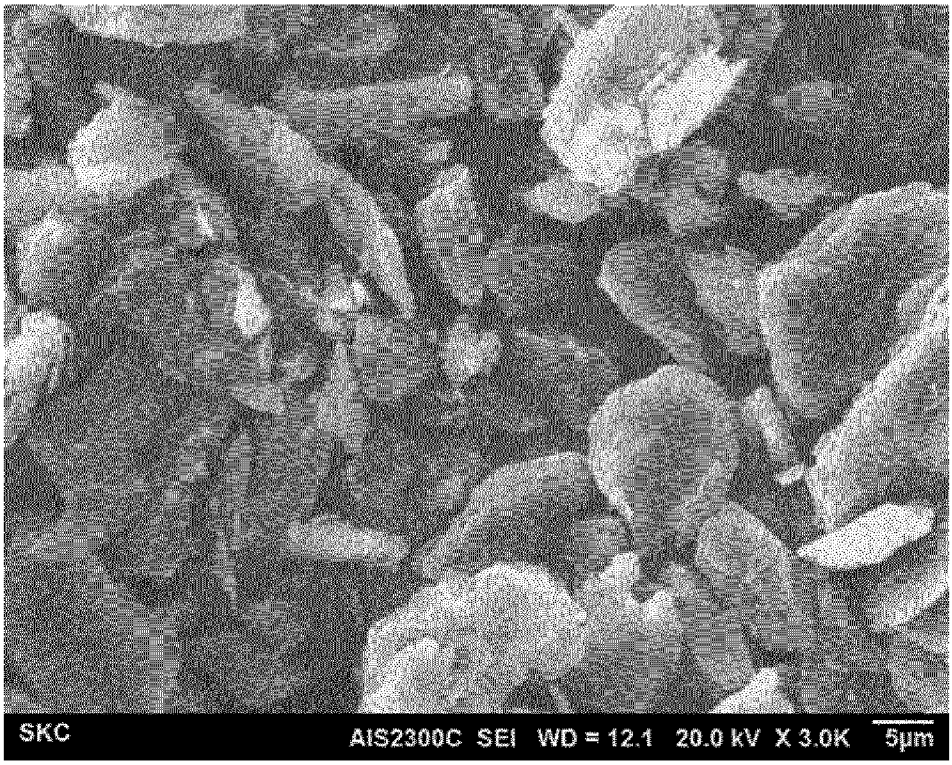
[Fig. 3]


SKC BND SEI 20.0kV X2,000 WD 7.8mm 10μm

[Fig. 4]


SKC AIS2300C SEI WD = 12.1 20.0 kV X 3.0K 5μm

[Fig. 5]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2024/004879

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/38(2006.01)i; **H01M 4/36**(2006.01)i; **H01M 4/48**(2010.01)i; **H01M 4/134**(2010.01)i; **H01M 4/02**(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01M 4/38(2006.01); H01M 10/052(2010.01); H01M 10/0525(2010.01); H01M 4/131(2010.01); H01M 4/48(2010.01); H01M 4/58(2010.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: silicone, anode, active material, carbon, pore

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y		10-13
A		8-9
Y	KR 10-1753946 B1 (LG CHEM, LTD. et al.) 04 July 2017 (2017-07-04) claims 1-2; paragraph [0022]	10-13
A	KR 10-2022-0029488 A (LG ENERGY SOLUTION, LTD.) 08 March 2022 (2022-03-08) the whole document	1-14
A	KR 10-2021-0077487 A (LG ENERGY SOLUTION, LTD.) 25 June 2021 (2021-06-25) the whole document	1-14

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05 August 2024	**05 August 2024**

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2024/004879

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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