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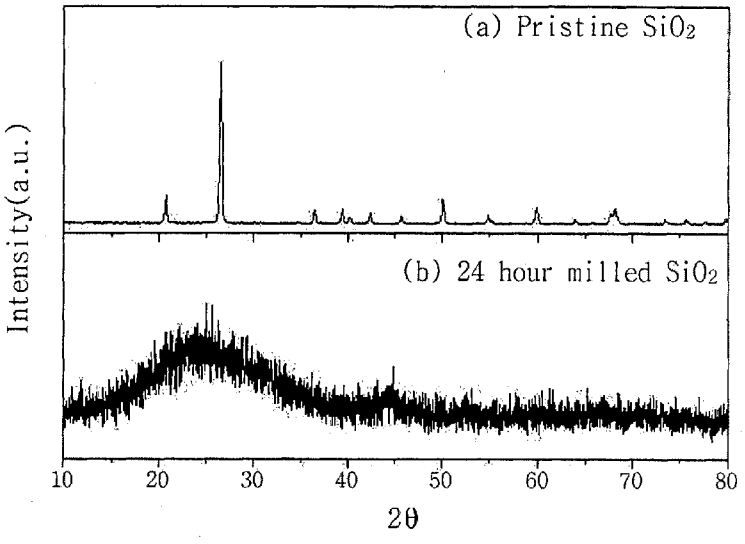

(57) Abstract: Provided is an anode active material for a lithium secondary battery, including silicon dioxide. Provided also is a method for preparing an anode active material for a lithium secondary battery, including carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles. The method simplifies the process and reduces the processing time. In addition, the method provides a cost-efficient anode active material for a lithium secondary battery capable of realizing high capacity.

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【DESCRIPTION】

【Invention Title】

ANODE ACTIVE MATERIALS USING SILICON DIOXIDE AND SILICON DIOXIDE-CONTAINING MINERAL FOR LITHIUM SECONDARY BATTERY AND METHOD FOR PREPARING THE SAME

【Technical Field】

<1> This disclosure relates to an anode active material for a lithium secondary battery using silicon dioxide and a silicon dioxide-containing mineral, and a method for preparing the same. More particularly, this disclosure relates to a method for preparing an anode active material for a lithium secondary battery, including carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles, as well as to an anode active material including silicon dioxide.

【Background Art】

<2> As portable electronic/communication instruments have been developed rapidly and energy/environment problems have been on the rise, importance of secondary batteries as portable electric power sources and as next-generation vehicle driving sources have been spotlighted. Particularly, since lithium has an energy density as high as 3860 mAh/g, secondary batteries using lithium metal as an anode material have an advantage of very high capacity. However, when using lithium metal as an anode material, there are problems in that a short circuit may occur in a battery due to dendrite growth during charge and charge/discharge efficiency is low.

<3> To solve the above-mentioned problems related with lithium metal, many studies have been conducted about materials capable of forming an alloy with lithium. Lithium alloy materials have advantages in that they realize higher charge/discharge efficiency per unit weight/volume as compared to limited capacity of a carbonaceous anode active material and are applicable to high charge/discharge current. However, lithium alloy materials undergo a phase change during charge/discharge, resulting in a change in volume, and the stress generated thereby destroys the electrode material. As a result, there are problems in that the capacity decreases after repeating cycles.

<4> Therefore, studies have been actively conducted recently to apply various materials including silicon or tin as anode materials for secondary batteries. For example, there is suggested a method including mixing a metal precursor of silicon or tin with carbon homogeneously in a liquid phase, followed by evaporation of the resultant mixture at room temperature, so that silicon or tin and metal are precipitated totally in carbon to provide an electrode active material.

<5> However, the method provides increased electrode capacity during several cycles at the initial time, but shows poor initial efficiency and leaves much room for improvement in terms of high-rate charge/discharge characteristics and cycle characteristics.

<6> Silicon has a capacity of 4400 mAh/g, which is higher charge/discharge capacity as compared to a commercially available carbonaceous anode material (372 mAh/g). However, an electrode using silicon has a problem in that it may be destroyed by a volumetric expansion (400%) during charge/discharge.

<7> To minimize a drop in capacity caused by such a volumetric change, use of nano-sized powder has been suggested. However, nano-sized powder is obtained by a complicated chemical process, such as reduction or coprecipitation. Moreover, irreversible side reactions caused by salts formed during such chemical processes result in poor initial efficiency.

<8> Further, the obtained nanopowder is expensive and causes agglomeration during charge/discharge cycles. Due to such agglomeration, crude particles are formed and a change in volume occurs, resulting in a rapid drop in capacity caused by the destruction of an electrode.

【Disclosure】

【Technical Problem】

<9> This disclosure is directed to providing a method for preparing an anode active material for a lithium secondary battery, containing silicon dioxide having high charge/discharge capacity, by a simple process including mechanical pulverization and alloying of low-cost silicon dioxide or silicon dioxide-containing mineral particles.

【Technical Solution】

<10> In one general aspect, there is provided a method for preparing an anode active material for a lithium secondary battery, comprising carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles.

<11> According to an embodiment, the anode active material may comprise 0.01-20 wt% of silicon based on the total weight of the anode active material, and Fourier transformation infrared spectroscopy (FT-IR) analysis of the anode active material shows a Si-O stretching peak positioned at 1150-950 cm^{-1} after red-shift.

<12> According to an embodiment, the method may further comprise pretreating the mineral particles by heat treatment.

<13> According to an embodiment, the mineral may be at least one selected from the group consisting of feldspar, kaolin, fayalite and pyroxene.

<14> According to an embodiment, the mechanical pulverization and alloying may comprise adding at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W) to the silicon dioxide or silicon dioxide-containing mineral particles, and carrying out mechanical pulverization and alloying thereof.

<15> According to an embodiment, the additional element may be present in an amount of 0.001-60 wt% based on the total weight of the anode active material.

<16> According to an embodiment, the mechanical pulverization and alloying may be carried out by ball milling.

<17> According to an embodiment, the silicon particles in the anode active material may have an average particle size of 100 nm or less.

<18> In another general aspect, there is provided an anode active material for a lithium secondary battery, including silicon dioxide.

<19> According to an embodiment, the silicon dioxide may be a silicon

dioxide-containing mixed phase.

<20> According to an embodiment, the anode active material may further comprise at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W).

<21> According to an embodiment, the silicon particles in the anode active material may have an average particle size of 100 nm or less.

<22> According to an embodiment, the method may further comprise carrying out carbon coating by using an organic material containing at least one selected from the group consisting of polyvinyl alcohol (PVA), sucrose, polyvinyl chloride (PVC) and polyacrylonitrile (PAN).

<23> According to an embodiment, the mechanical pulverization is carried out by using a system capable of amorphization of the silicon dioxide or silicon dioxide-containing mineral particles, wherein the system may be at least one selected from the group consisting of a vibratory mill, z-mill, planetary mill and an attrition mill.

<24> According to an embodiment, the additional element and silicon dioxide may be present in a weight ratio of 0.001:100 - 60:100.

<25> In still another general aspect, there is provided a lithium secondary battery including the anode active material.

【Advantageous Effects】

<27> According to the anode active material for a lithium secondary battery, using silicon dioxide and a silicon dioxide-containing mineral, and the method for preparing the same disclosed herein, it is possible to obtain a silicon dioxide-based anode active material in a simple and efficient manner with no need for a complicated and inefficient chemical process. It has been known that silicon dioxide is not reactive to lithium. However, the method disclosed herein is not complicated because it does not use many types of materials, has a benefit of high capacity provided by silicon, includes a

simplified process to reduce the processing time, and realizes higher capacity as compared to a carbonaceous anode.

【Description of Drawings】

<28> The above and other aspects, features and advantages of the disclosed exemplary embodiments will be more apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

<29> Fig. 1 is a graph showing the X-ray diffraction (XRD) results of the anode active material for a lithium secondary battery according to an embodiment, before and after mechanical pulverization and alloying;

<30> Fig. 2 is a photograph of the anode active material for a lithium secondary battery according to an embodiment, taken by transmission electron microscopy (TEM);

<31> Fig. 3a-Fig. 3c are graphs showing charge/discharge behavior of the anode active material for a lithium secondary battery according to an embodiment during repetition of charge/discharge cycles, wherein Fig. 3a shows charge/discharge behavior of a lithium secondary battery using silicon (Si) as an anode active material, Fig. 3b shows that of a lithium secondary battery using non-treated silicon dioxide (SiO_2) as an anode active material, and Fig. 3c shows that of a lithium secondary battery using an anode active material subjected to mechanical pulverization and alloying; and

<32> Fig. 4 is a graph showing improvement in initial efficiency and cycle characteristics, caused by the anode active material for a lithium secondary battery having an additional element according to an embodiment, as compared to the same material having no additional element.

<33>

【Best Mode】

<34> In one aspect, there is provided a method for preparing an anode active material for a lithium secondary battery, including carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles.

<35> Silicon dioxide (SiO_2) is a constitutional ingredient of the most abundant mineral on Earth and is cheap, but is known to have no reactivity

toward lithium. Thus, SiO_2 has not been applied to lithium secondary batteries until now. However, it has now been found by the method disclosed herein that an anode active material for a lithium secondary battery may be obtained from such cost-efficient silicon dioxide or minerals containing the same, thereby reducing the cost significantly. In addition, the method disclosed herein merely uses a simple mechanical pulverization and alloying process to obtain a silicon dioxide-based anode active material, thereby simplifying the processing operations and reducing the processing time. As a result, it is possible to obtain an inexpensive anode active material for a lithium secondary battery in a simple and efficient manner.

<36> The anode active material disclosed herein may include 0.01-20 wt% of silicon based on the total weight of the anode active material, the balance being crystalline or amorphous silica. To improve the initial capacity of an anode material, it is ideal that silicon is present in an amount of 0.01 wt% or more. However, when silicon is present in an amount greater than 20 wt%, cycle stability may be degraded due to a change in volume of silicon.

<37> In addition, Fourier transformation infrared spectroscopy (FT-IR) analysis of the anode active material disclosed herein shows a Si-O stretching peak positioned at 1150-950 cm^{-1} after red-shift. Red-shift is a measure of amorphization of silicon dioxide substance per se. Only a peak within the above-defined range may be defined as a Si-O stretching peak of amorphous silicon dioxide.

<38> According to an embodiment, silicon dioxide per se or silicon dioxide-containing mineral particles may be used as a starting material. The mineral may be at least one selected from the group consisting of feldspar, kaolin, fayalite and pyroxene, but is not limited thereto. Any mineral may be used as long as it contains silicon dioxide. Particular examples of the silicon dioxide-containing mineral particles include sand, silica or clay.

<39> The method may further include pretreating the mineral particles by heat treatment. In the case of a mineral containing water, such as kaolin, the method may be carried out by subjecting the mineral to heat treatment as pretreatment and then to mechanical pulverization and alloying. Naturally

occurring minerals other than the above-mentioned case may be used as starting materials with no additional treatment, thereby simplifying the process and reducing the cost.

<40> The method includes carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles. The mechanical pulverization and alloying may be carried out in a manner generally known to those skilled in the art.

<41> Through the mechanical pulverization and alloying, silicon dioxide having a size of several micrometers and introduced as a starting material is pulverized mechanically, thereby forming Si nano-particles and various types of amorphous SiOx materials. The mechanical pulverization and alloying is carried out at room temperature, but the actual temperature in a reactor may be increased to 200℃ or higher and the pressure may be increased up to 6 GPa. After silicon dioxide is subjected to mechanical pulverization and alloying under such a high temperature and high pressure, it is provided as silicon particles dispersed in a matrix of amorphized silicon oxide (SiOx;$1 \leq x \leq 2$). The formed silicon particles in the anode active material has an average particle size of 100 nm or less, particularly 10 nm or less, and more particularly 5 nm or less, are reactive to lithium, and shows stable performance even at 200 cycles or higher.

<42> The mechanical pulverization and alloying may be carried out by using a system capable of amorphization of the silicon dioxide or silicon dioxide-containing mineral particles. Particularly, the mechanical pulverization and alloying may be carried out by ball milling. Particular examples of systems for carrying out ball milling may include at least one selected from the group consisting of a vibratory mill, z-mill, planetary mill and an attrition mill. Any ball milling systems capable of high-energy mechanical milling may be used.

<43> Hereinafter, an exemplary embodiment of the method for preparing an anode active material by ball milling will be explained. First, silicon dioxide as a starting material is introduced into a cylindrical vial together with balls and the vial is mounted to a high-energy ball milling system.

Next, the ball milling system is operated at 800 rpm to perform mechanical pulverization and alloying. In this manner, it is possible to obtain a silicon dioxide electrode and an anode active material containing silicon dioxide added with an additional element, respectively. The weight ratio of the balls to the starting material is maintained, for example, within a range of 10:1 - 30:1. In addition, all of the operations for assembling the system before the ball milling may be performed in a glove box under argon gas atmosphere to prevent introduction of oxygen and moisture.

<44> According to an embodiment, the mechanical pulverization and alloying may be carried out for a time of 1 hour to 50 hours. An excessively long time may cause formation of crude silicon particles and particle agglomeration, resulting in degradation of cycle characteristics.

<45> The anode active material obtained by the above-described method allows Si and SiOx ($1 \leq x \leq 2$) to react with lithium, and thus realizes a capacity (about 750-800) at least two times higher than the capacity (about 370) of a commercially available graphite electrode. In addition, unlike the methods according to the related art, the method does not use chemical treatment but merely uses mechanical alloying, thereby simplifying the process and reducing the processing time. Further, during repetition of charge/discharge cycles, no silicon particle agglomeration occurs, thereby preventing rapid degradation of performance.

<46> According to an embodiment, the method may further comprise, before or during the mechanical pulverization and alloying, adding at least one additional element, and carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles together with the additional element. Particularly, the method may include adding at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W) to the silicon dioxide or silicon dioxide-containing mineral

particles, and carrying out mechanical pulverization and alloying them together. Through the additional element, it is possible to minimize irreversible capacity occurring when an electrode material is subjected to charge/discharge cycles in the presence of an excessively large amount of oxygen and silicon, which is a main cause of irreversible capacity created during charge (lithium insertion). In addition, it is possible to minimize degradation of performance caused by a change in volume and crude particle formation and to enhance the conductivity of an electrode material, thereby improving cycle life characteristics.

<47> The additional element may be added before the mechanical pulverization and alloying. In a variant, an additional element may be added during the alloying to obtain optimized results.

<48> The additional element may be added in an amount of 0.001-60 wt% based on the total weight of the anode active material. When the additional element is added in an amount less than 0.001 wt%, it is not possible to obtain a sufficient effect. On the other hand, when the additional element is added in an amount greater than 60 wt%, degradation of capacity occurs.

<49> According to an embodiment, the method may further comprise carrying out carbon coating by using an organic material containing at least one selected from the group consisting of polyvinyl alcohol (PVA), sucrose, polyvinyl chloride (PVC) and polyacrylonitrile (PAN). The carbon coating is carried out after the amorphization caused by mechanical pulverization. Particularly, the carbon coating material is dissolved in a solvent capable of dissolving the material, the anode active material is added thereto, and then the resultant mixture of the anode active material with the carbon coating material is subjected to heat treatment to perform carbon coating.

<50> In another aspect, there is provided an anode active material for a lithium secondary battery, including silicon dioxide. Silicon particles in the anode active material disclosed herein has an average particle size of 100 nm or less, particularly 10 nm or less, and more particularly 5 nm or less. That is, silicon in the anode active material disclosed herein has a nano-scaled size. According to the related art, silicon dioxide having no

reactivity to lithium has not been used as an anode active material for a battery. However, the anode active material using silicon dioxide disclosed herein realizes excellent capacity of such nano-sized silicon, thereby functioning as a high-quality anode active material.

<51> The silicon dioxide contained in the anode active material disclosed herein may be a silicon dioxide-containing mixed phase. In other words, the silicon dioxide is a Si-SiOx mixed phase having Si and amorphized silicon oxides (SiOx).

<52> According to an embodiment, the anode active material may further comprise at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W). When the anode active material further comprises such additional elements, it is possible to minimize a change in volume occurring during charge/discharge cycles and to use high capacity provided by silicon. It is also possible to reduce initial irreversible capacity. Therefore, it is possible to improve mechanical properties and electrochemical properties at the same time. This is one of the most important factors required for an anode material for a lithium secondary battery. The weight ratio of the additional element to silicon dioxide may be 0.001:100 to 60:100. When the additional element is added in an amount greater than the above-defined range, degradation of capacity occurs. On the other hand, when the additional element is added in an amount less than the above-defined range, it is not possible to improve initial efficiency sufficiently.

<53> In still another aspect, there is provided a lithium secondary battery comprising the anode active material. The secondary battery including the anode active material may be obtained through a method generally known to those skilled in the art. In other words, the battery may have a structure in which a porous separator is disposed between a cathode and an anode and

the three constitutional elements are supported in an electrolyte. The lithium secondary battery has high energy density, charge voltage and output stability.

<54> The anode active material for a lithium secondary battery ensures stable life characteristics by preventing degradation of performance caused by a change in volume, while maximizing the advantageous high capacity of silicon. Thus, the anode active material disclosed herein is useful as a substitute for a commercially available graphite anode material. In addition, the method for preparing an anode active material for a lithium secondary battery disclosed herein does not include a specific chemical or physical process but merely includes mechanical pulverization and alloying, thereby reducing the processing time.

【Mode for Invention】

<56> The examples and experiments will now be described. The following examples and experiments are for illustrative purposes only and not intended to limit the scope of this disclosure.

<57>

<58> [Example 1] Preparation of Anode Active Material Using Silicon Dioxide (SiO_2)

<59> 1-1. Preparation of Silicon Dioxide (SiO_2) Anode Active Material

<60> Commercially available silicon dioxide (SiO_2) powder was introduced to a cylindrical vial made of SKD11 and having a diameter of 5.5 cm and a height of 9 cm together with balls, in a weight ratio of ball : powder of 20:1, and then the vial was mounted to a ball milling system to perform mechanical pulverization and alloying.

<61> At that time, the system was assembled in a glove box under argon gas atmosphere to minimize an effect of oxygen and moisture introduction.

<62> The mechanical pulverization and alloying was carried out at 800 rpm for 24 hours to obtain a silicon dioxide anode active material.

<63>

<64> 1-2. Preparation of Anode Active Material Containing Silicon Dioxide

(SiO_2) and Aluminum Element

<65> The mechanical pulverization and alloying was carried out under the same condition as described in Example 1-1, except that aluminum having a size of 20 ㎛ or less is added in an amount of 10-30 wt%. The mixture added with aluminum was introduced to a cylindrical vial made of SKD11 and having a diameter of 5.5 cm and a height of 9 cm together with balls, in a weight ratio of ball : mixture of 20:1, and then the vial was mounted to a ball milling system to perform mechanical pulverization and alloying.

<66> Introduction of each starting material to the vial was carried out in a glove box under argon gas atmosphere to minimize an effect of oxygen and moisture introduction.

<67> Fig. 1 is a graph showing the X-ray diffraction (XRD) results of silicon dioxide (SiO_2) before and after mechanical alloying. As can be seen from Fig. 1, amorphized silicon oxide powder is formed through the alloying process.

<68> In addition, Fig. 2 is a photograph of the silicon dioxide anode active material, taken by transmission electron microscopy (TEM), after the completion of the mechanical alloying. As can be seen from Fig. 2, silicon particles having a size of about 5 nm or less is distributed uniformly through a silicon oxide (SiOx, $(1 \leq x \leq 2)$) matrix.

<70> [Example 2] Manufacture of Lithium Secondary Battery Using Silicon Dioxide Anode Active Material

<71> First, 70 wt% of the powder type silicon dioxide obtained from Example 1-1, 15 wt% of Ketchen black (conductive agent) and 15 wt% of polyimide (binder) were added to NMP (solvent) to provide a mixed slurry. The resultant slurry was coated on an acid-cleaned thin copper film and dried in a vacuum oven at 200℃ for 4 hours. Thin lithium plates were used as a counter electrode and a reference electrode.

<72> As a separator, a Celgard membrane (Celgard 2400™) having insulating property and high ion conductivity was used.

<73> As an electrolyte, a mixture of ethylene carbonate (EC) and diethyl

carbonate (DEC) (EC:DEC= 3:7, v/v), to which 1M $LiPF_6$ salt and 10% fluoroethylene carbonate (FEC) were added, is used.

<74>

<75> [Comparative Example 1]

<76> An electrode is obtained and a lithium secondary battery is provided by the same method as described in Example 2, except that silicon (Si) having a size of about 4 ㎛ is used.

<77>

<78> [Comparative Example 2]

<79> An electrode is obtained and a lithium secondary battery is provided by the same method as described in Example 2, except that silicon dioxide that is not subjected to mechanical alloying used.

<80>

<81> [Test Example 1] Test of Charge/Discharge Characteristics of Lithium Secondary Batteries

<82> The lithium secondary batteries according to Example 2 and Comparative Examples 1 and 2 are tested to determine their charge/discharge characteristics. The test was carried out by using a coin cell-like device fabricated in a laboratory while applying a constant current within a range of 0.0V to 2.0V. This was also made in a glove box. Lithium intercalation corresponds to charge and lithium deintercalation corresponds to discharge.

<83> During charge/discharge cycles, behaviors of Comparative Example 1 (Si) and Comparative Example 2 (non-treated silicon dioxide) are taken only at the 1^{st}, 2^{nd} and 10^{th} cycle, and are shown in Fig. 3a and Fig. 3b, respectively. In the case of Example 2 (silicon dioxide subjected to mechanical pulverization and alloying), charge/discharge behaviors at the 1^{st}, 2^{nd}, 10^{th}, 100^{th} and 200^{th} cycles are shown in Fig. 3c. The following Table 1 shows the charge/discharge capacity and initial efficiency (1^{st} cycle), in the lithium secondary batteries using silicon (Comparative Example 1) and silicon dioxide that is not subjected to mechanical alloying (Comparative Example 2) as an electrode material.

<84> 【Table 1】

<85>

Electrode Material Type	Charge Capacity (1^{st} cycle; mAh g^{-1})	Discharge Capacity (1^{st} cycle; mAh g^{-1})	Initial Efficiency (Coulombic efficiency)
Comp. Ex. 1-silicon (Si)	3320	1347	40.5
Comp. Ex. 2-Silicon dioxide (SiO_2), No ball milling	84	35	41.6

Referring to Fig. 3a, the anode active material including pristine silicon alone shows rapid degradation of charge/discharge characteristics before the 10^{th} cycle. Referring to Fig. 3b, it can be seen that there is no lithium insertion/extraction (i.e. no charge/discharge occurs).

<86> On the contrary, referring to Fig. 3c, the initial efficiency is similar to the initial efficiency provided by silicon. However, from the 10^{th} cycle, it can be seen that the efficiency reaches over 99% during repetition of charge/discharge cycles. In addition, referring to cycle characteristics of silicon dioxide subjected to mechanical pulverization, it can be seen that charge/discharge capacity is maintained stably over 700 $mAhg^{-1}$ up to at least the 200^{th} cycle.

<87>

<88> [Test Example 2] Test of Cycle Characteristics of Lithium Secondary Batteries

<89> The cycle characteristics of the lithium secondary batteries including the anode active materials according to Example 1-1 and Example 1-2 were determined. An increase in initial efficiency caused by addition of aluminum (Al) to silicon dioxide is determined as compared to the anode active material including silicon dioxide alone. The results are shown in Fig. 4.

<90> As can be seen from Fig. 4, Example 1-1 maintains excellent cycle

characteristics. Further, Example 1-2 (added with aluminum) shows a drop in charge capacity, but provides a higher initial efficiency as compared to Example 1-1 and maintains excellent cycle characteristics.

<91>

<92> While the exemplary embodiments have been shown and described, it will be understood by those skilled in the art that various changes in form and details may be made thereto without departing from the spirit and scope of this disclosure as defined by the appended claims.

【CLAIMS】

【Claim 1】

<94> A method for preparing an anode active material for a lithium secondary battery, comprising carrying out mechanical pulverization and alloying of silicon dioxide or silicon dioxide-containing mineral particles.

<95>

【Claim 2】

<96> The method according to claim 1, wherein the anode active material comprises 0.01-20 wt% of silicon based on the total weight of the anode active material, and Fourier transformation infrared spectroscopy (FT-IR) analysis of the anode active material shows a Si-O stretching peak positioned at 1150-950 cm^{-1} after red-shift.

<97>

【Claim 3】

<98> The method according to claim 1, which further comprises pretreating the mineral particles by heat treatment.

<99>

【Claim 4】

<100> The method according to claim 1, wherein the mineral is at least one selected from the group consisting of feldspar, kaolin, fayalite and pyroxene.

<101>

【Claim 5】

<102> The method according to claim 1, wherein the mechanical pulverization and alloying comprises adding at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W) to the silicon dioxide or silicon dioxide-containing mineral particles, and carrying out mechanical pulverization and alloying thereof.

<103>

【Claim 6】

<104> The method according to claim 5, wherein the additional element is present in an amount of 0.001-60 wt% based on the total weight of the anode active material.

<105>

【Claim 7】

<106> The method according to claim 1, wherein the mechanical pulverization and alloying is carried out by ball milling.

<107>

【Claim 8】

<108> The method according to claim 1, wherein the mechanical pulverization and alloying is carried out by using a system capable of amorphization of the silicon dioxide or silicon dioxide-containing mineral particles, and the system is at least one selected from the group consisting of a vibratory mill, z-mill, planetary mill and an attrition mill.

<109>

【Claim 9】

<110> The method according to claim 1, wherein the silicon particles in the anode active material have an average particle size of 100 nm or less.

<111>

【Claim 10】

<112> The method according to claim 1, which further comprises carrying out carbon coating by using an organic material comprising at least one selected from the group consisting of polyvinyl alcohol (PVA), sucrose, polyvinyl chloride (PVC) and polyacrylonitrile (PAN).

<113>

【Claim 11】

<114> An anode active material for a lithium secondary battery, comprising silicon dioxide.

<115>

【Claim 12】

<116> The anode active material for a lithium secondary battery according to claim 11, wherein the silicon dioxide is a silicon dioxide-containing mixed phase.

<117>

【Claim 13】

<118> The anode active material for a lithium secondary battery according to claim 11, which further comprises at least one additional element selected from the group consisting of aluminum (Al), titanium (Ti), magnesium (Mg), calcium (Ca), lithium (Li), zirconium (Zr), beryllium (Be), carbon (C), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), zinc (Zn), silicon (Si), tin (Sn), lead (Pb) and tungsten (W).

<119>

【Claim 14】

<120> The anode active material for a lithium secondary battery according to claim 13, wherein the additional element and silicon dioxide are present in a weight ratio of 0.001:100 - 60:100.

<121>

【Claim 15】

<122> The anode active material for a lithium secondary battery according to claim 11, wherein the silicon particles in the anode active material have an average particle size of 100 nm or less.

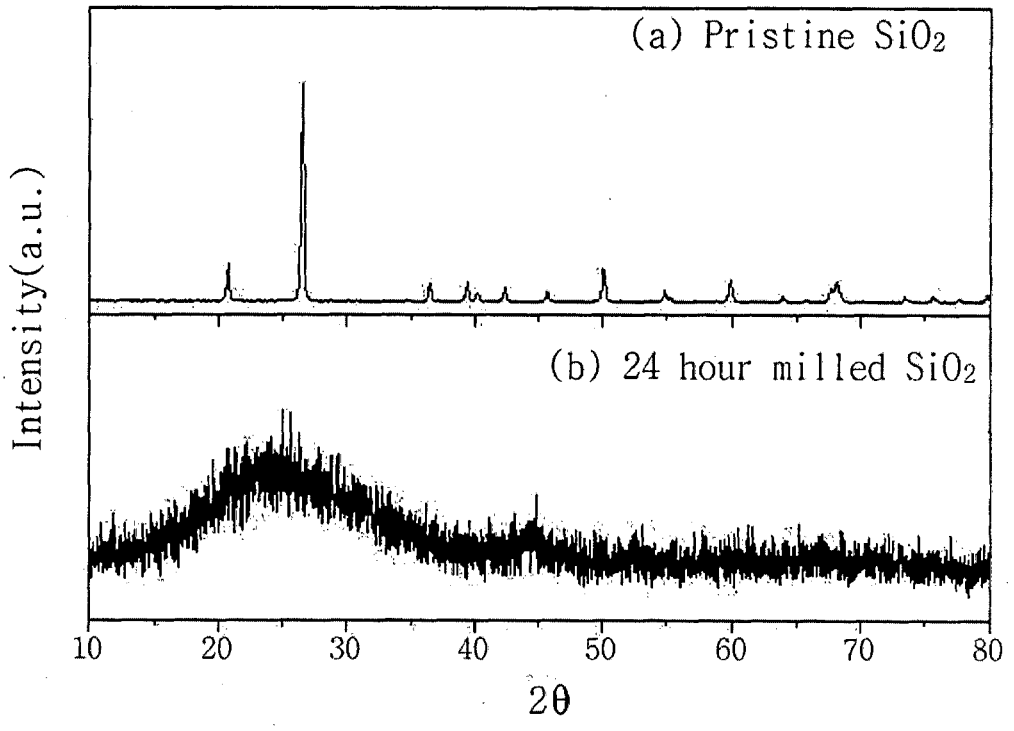
<123>

【Claim 16】

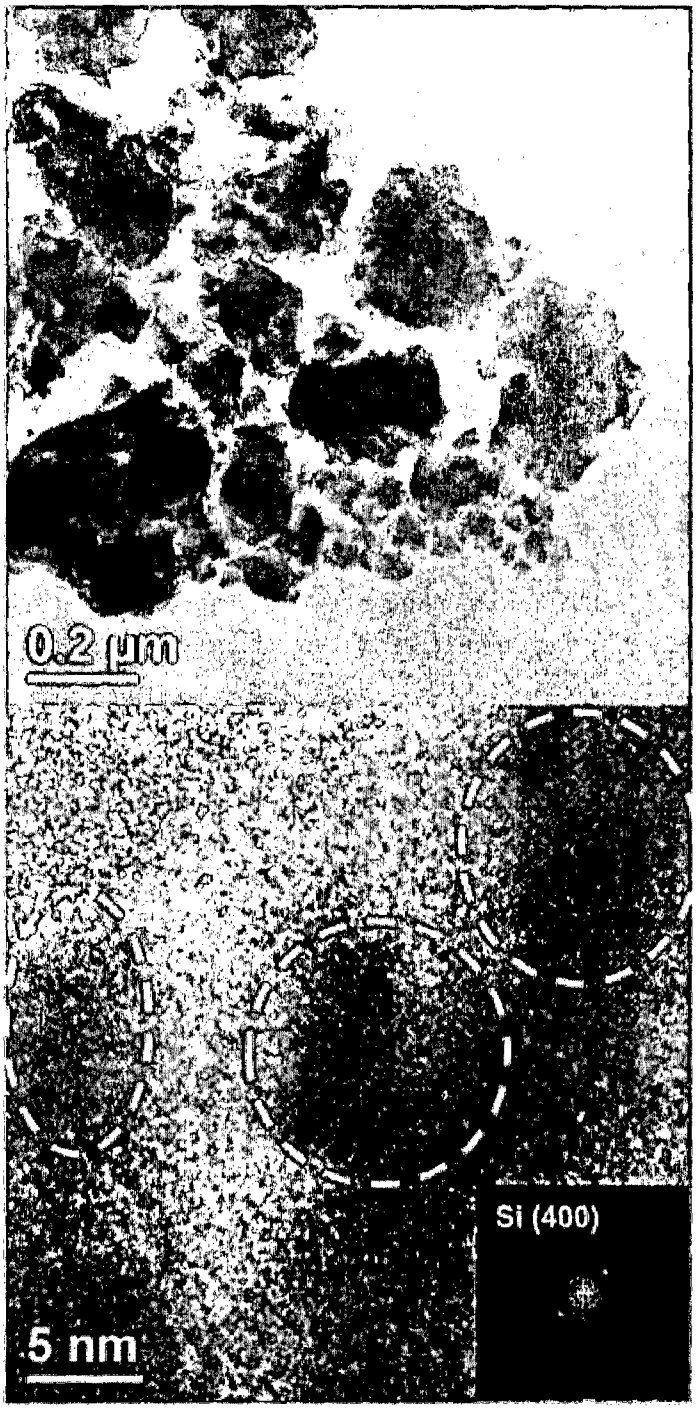
<124> A lithium secondary battery comprising the anode active material as defined in claim 11.

【DRAWINGS】

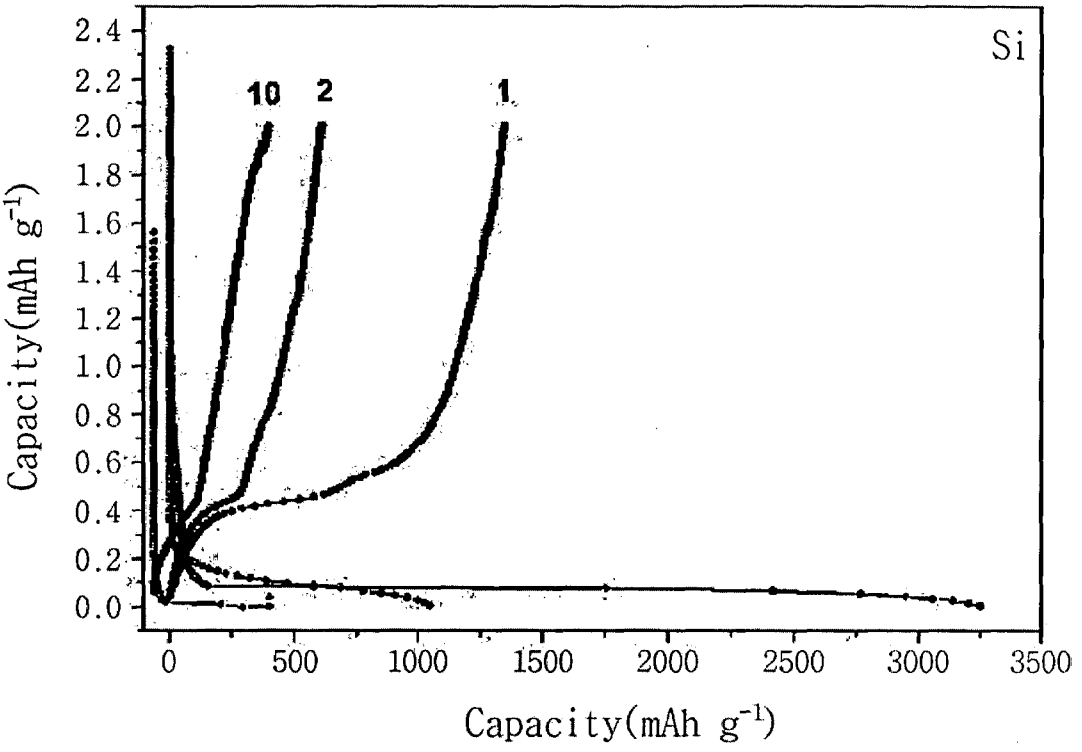
【Figure 1】



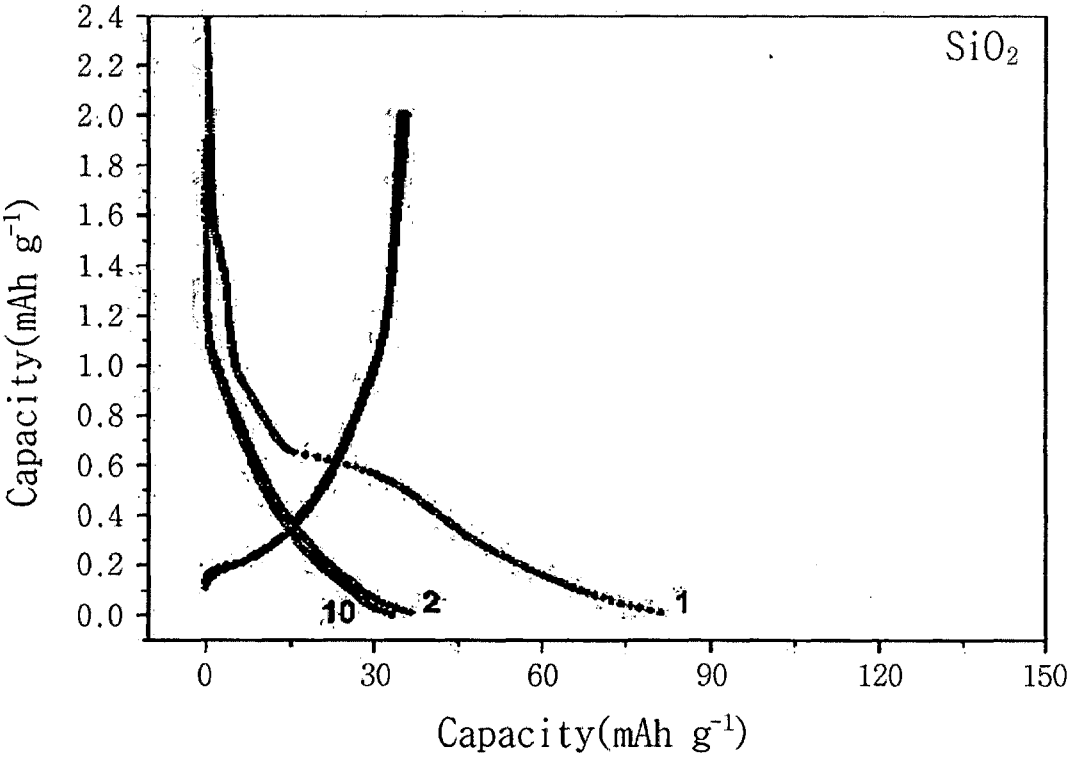
【Figure 2】



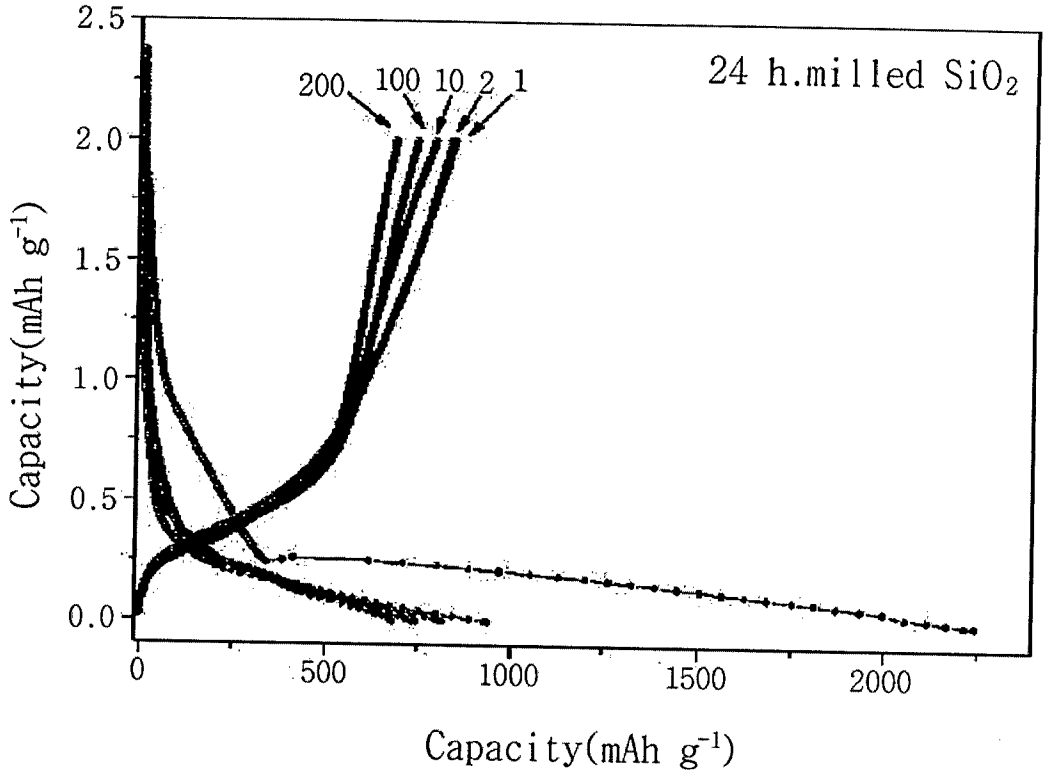
【Figure 3a】



【Figure 3b】



【Figure 3c】



【Figure 4】