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(54) **Titre :** METHODE DE PREPARATION DE PARTICULES DE MATERIAU A BASE DE SI OU SIO_X ET MATERIAU AINSI OBTENU

(54) **Title:** METHOD FOR PREPARING A PARTICULATE OF SI OR SIO_X-BASED ANODE MATERIAL, AND MATERIAL THUS OBTAINED

(57) **Abrégé/Abstract:**

A method for preparing complex Si- or SiO_x-based (or germanium-based) particles which can be alloyed with other elements, wherein the Si- or SiO_x-based particles have a non powdery conductive carbon deposit on at least part of their surface. The method comprises nano-grinding complex silicon based-particle dispersed in a carrier liquid in a bead mill, wherein Si or SiO_x is alloyed and casted in ingot or directly atomized to form a powder, an organic carbon precursor is added to the Si- or SiO_x-based particles, the mixture thus obtained is pyrolyzed, and the size of the particles that are subjected to the nano-grinding, the size of the beads for nano-grinding, and the size of the resulting particles are selected such that: $0,004 \leq MS(SP)/MS(B) \leq 0,12$; $0,0025 \leq MS(FP)/MS(SP) \leq 0,25$, where MS(SP) represents the mean size diameter of the particles before grinding, MS(FP) represents the mean size diameter of the particles after grinding, and MS(B) is the mean size diameter of the grinding beads.

Abstract

A method for preparing complex Si- or SiO_x-based (or germanium-based) particles which can be alloyed with other elements, wherein the Si- or SiO_x-based particles have a non powdery conductive carbon deposit on at least part of their surface. The method comprises nano-grinding complex silicon based-particle dispersed in a carrier liquid in a bead mill, wherein Si or SiO_x is alloyed and casted in ingot or directly atomized to form a powder, an organic carbon precursor is added to the Si- or SiO_x-based particles, the mixture thus obtained is pyrolyzed, and the size of the particles that are subjected to the nano-grinding, the size of the beads for nano-grinding, and the size of the resulting particles are selected such that: $0{,}004 \leq MS(SP)/MS(B) \leq 0{,}12$; $0{,}0025 \leq MS(FP)/MS(SP) \leq 0{,}25$, where MS(SP) represents the mean size diameter of the particles before grinding, MS(FP) represents the mean size diameter of the particles after grinding, and MS(B) is the mean size diameter of the grinding beads.

Method for preparing a particulate of Si or SiOx -based anode material, and material thus obtained

Field of the Invention

The invention relates generally to a method for preparing particles of Si and its alloys or SiO_x , where Si may be also replaced by group IVa elements (such as Ge), as well as the particles compositions obtained by the method, and uses thereof as electrode material.

Background

Lithium-ion batteries have shown phenomenal technical success and commercial growth since the initial work by Sony in the early 90's based on lithium insertion electrodes; essentially consisting of high voltage cobalt oxide cathode invented by J. B. Goodenough and carbon anode using coke or graphitized carbonaceous materials.

Since then, lithium-ion batteries have progressively replaced existing Ni-Cd and Ni-MH batteries, because of their superior performances in most portable electronic applications. However, because of their cost and intrinsic instability under abusive conditions, especially in their fully charged state, only small cell sizes and formats have been commercialized with success.

Existing lithium-ion batteries rely on anodes made from graphite. However, the anode based on the carbonaceous material has a maximum theoretical capacity of only 372 mAh/g (844 mAh/cc), thus suffering from limited increase of capacity thereof. Lithium metals, studied for use as the anode material, have a high energy density and thus may realize high capacity, but have problems associated with safety due to growth of dendrites and a shortened charge/discharge cycle life as the battery is repeatedly charged/discharged. Because of these disadvantages and problems, a number of studies and suggestions have been proposed to utilize silicon, tin or their alloys as a possible candidate material exhibiting high capacity and being capable of substituting for lithium metal. For example, silicon (Si) reversibly absorbs (intercalates) and desorbs (deintercalates) lithium ions through the reaction between silicon and lithium, and has a maximum theoretical capacity of about 4200 mAh/g (9366 mAh/cc, a specific gravity of 2.23) that is substantially greater than the carbonaceous materials and thereby is promising as a high-capacity anode material.

Silicon-based anodes theoretically offer as much as a ten-fold capacity improvement over graphite, but silicon-based anodes have not been stable enough to cycling for practical use. One way of improving the cycle performance of silicon is to reduce the size of the particles that are used in the anode and coat them with carbon. The smaller size helps to control the volume change and stresses in the Si particles. The carbon coating on the silicon acts like a electrical path way so that even when there is a volume change, contact is not lost with the current collector.

Silicon is produced industrially by carbothermal reduction of silicon dioxide (quartzite) with carbon (coal, charcoal, petroleum coke, wood) in arc furnaces by a reaction that in an idealized form can be written as:

$$SiO_2 + 2C \rightarrow Si + 2CO$$

In industry, the available raw materials are not pure and the product will contain other elements (principally Fe, Al, Ca and Ti). With pure operation and pure raw materials and electrodes, it is possible to obtain silicon with less than 1-2% percent of other elements. This product is traditionally called metallurgical grade silicon metal even though solid silicon is not a metal.

If higher purity is required, metallurgical treatments like gas blowing (dry air, O_2, Cl_2) may reduce alkaline species (K, Na, Mg, Ca, Al, Sr) at temperatures higher than 1410°C. Those species will either be volatized from the liquid metal surface or be physically separated in a slag phase. If transition elements (Fe, Ti, Cu, Cr, Mn, V, Ni, Zn, Zr, etc) need to be reduced, directional solidification may be used. Another efficient method consists of finely grinding solid silicon and expose the intermetallic phases to acid (HF, HCl, H_2SO_4 or a mixture). With those metallurgical treatments, the silicon metal purity can reach 99.999% (5N level).

For higher purity, chemical vapour deposition of Si from precursor species like $SiHCl_3$ or SiH_4 is needed. The so-called Siemens process is a perfect example. This process can easily reach a 9N purity level.

Silicon-based anode material can be prepared at low cost from solid crystalline ingots or micron size powders by conventional grinding process (jaw crusher, cone crusher, roll crusher, jet mill, etc). A mechanical attrition process is one of the most used processes to produce fine particles. More recently, industrial wet nano-grinding bead mill equipment has become available commercially, which can be used to reduce particle size down to 10 to 20 nm (See for example WO 2007/100918 for lithium metal phosphate ultrafine grinding). Those techniques are especially useful for high purity Si or Ge.

Si (or Ge) can be co-alloyed in liquid phase with other elements to improve the anode material performance to cycling. They exhibit a coarse metallic phase structure when solidified as ingots at a slow cooling rate (10-10^2 K/sec). For this reason, ingot casting is not the preferred way for Si-alloy or Ge-alloy anode material production. There are a number of methods which can be used to produce rapid solidification, including melt spinning, splat quenching, laser surface melting and several types of atomization. Of these, atomization is probably the most industrially important.

Gas atomization, whether by air, water or inert gas, accounts for the largest volumetric tonnage of powder. It is commercially adaptable, and hence the most commercially available technique that is utilized on the largest scale. The reason for using this method is the ability to generate favourable microstructures which cannot be produced by conventional bulk ingot processing methods; the typical cooling rate between 10^3-10^6 K/sec (see Figure 1). A typical process for atomized powder production using Vacuum Induction Gas Atomization [VIGA] is shown schematically in Figure 2.

In the gas atomization process, silicon is melted, alloyed, and sprayed through a nozzle to form a stream of very fine particles that are rapidly cooled, most often by an expanding gas.

The gas atomization process has a large number of operating variables, including melt temperature and viscosity as the melt enters the nozzle, liquid alloy composition, metal feed rate, gas type, gas pressure, gas feed rate and velocity, nozzle geometry, gas temperature and residual atmosphere. All of these parameters are important to the final properties of the powder, and can, to some extend, be adjusted to tailor the powder characteristics. A typical particle size distribution of selected alloys is shown in Figure 3.

Because silicon crystals are insoluble in hydrochloric acid (HCl) or hydrofluoric acid (HF), it is advantageous to “chemically grind” the Si-alloys when dissolving intermetallic compounds.

If a secondary phase exhibits ductility, grinding may be difficult at room temperature. The use of cryo-grinding is a good way to solve such a problem.

One significant improvement to the problem of low electronic conductivity of complex metal alloy anode powders, and more specifically of Si-based materials, was achieved with the use of an organic carbon precursor that is pyrolysed onto the anode material or its precursor to improve electrical conductivity at the level of the anode particles.

It is also known that the electrical conductivity of a silicon powder is improved by intimately mixing conductive carbon black or graphite powder with the Si powder or the Si-alloys before grinding. Such addition of carbon black or graphite powder involves usually relatively large quantities of C to achieve good connectivity and does not result in a good bonding of the C to the silicon-based material crystal structure. This intimate bonding is a characteristic that is judged to be essential to maintain contact despite volume variations during long term cycling.

Problems remain however to optimize the processability, cost and performance of the electrode material, especially when power, energy and cyclability are required simultaneously.

Summary

The present inventors found that the use of agglomerates of primary and secondary nanoparticles which are produced at a micron-size scale or larger (by spray drying, for example), instead of elementary nanoparticles, facilitates ions and electron diffusion and the electrochemical reaction. This is the result of using nano dimensions at the level of the active material nanoparticles while, benefiting from the ease of manipulating micron-size agglomerates.

As a general rule, electrochemical performance optimization of such agglomerates of nanoparticles or nanocomposite material requires a material having a high proportion of active silicon metal, a low proportion of electrochemically inert conductive carbon and a controlled degree of open porosity of the agglomerates or the nanocomposite material. Furthermore, pore channel dimensions must be designed to allow solvated lithium ion in the electrolyte to penetrate and reach elementary nano-sized particles to support high charge or discharge rate currents.

The present invention provides a method for preparing carbon-coated nano materials, obtained from molten silicon/silicon alloys and ingots in an easy process that results in a high performance anode material.

In one aspect, the present invention provides a method for preparing complex Si- or SiO_x-based (or germanium-based) particles which can be alloyed with other elements (for example, Li, Al, Mg, Fe, Ge, C, Bi, Ag, Sb, Sn, Zn, B, Ti, Sr, P, O, etc), wherein the Si- or SiO_x-based particles have a non powdery conductive carbon deposit on at least part of their surface. The method comprises nano-grinding complex silicon based particles, wherein:

- a fusion step for alloying Si or SiO_x and casted in ingot or directly atomized to form a powder;
- an organic carbon precursor added to the Si- or SiO_x-based particles before, during or after nano-grinding, and pyrolysing the mixture thus obtained;

- a stabilizing agent is optionally added to the oxide particles or oxide precursor particles before, during or after nano-grinding;
- the nanogrinding step is performed in a bead mill on particles dispersed in a carrier liquid; and
- the size of the particles that are subjected to the nano-grind process, the size of the beads used to nano-grind, and the size of the resulting particles are important process characteristics, and are selected such that :

$$0{,}004 \leq MS(SP)/MS(B) \leq 0{,}12;$$

$$0{,}0025 \leq MS(FP)/MS(SP) \leq 0{,}25$$

wherein MS(SP) represents the mean size diameter of the particles before grinding (starting particles), MS(FP) represents mean size diameter of the particles after grinding (final particles), and MS(B) is mean size diameter of the grinding beads.

As a very empirical rule, optimizing can be started with a D_{90} (SP) to (B) ratio of 1/10, and a (B) to D_{90}(FP) ratio of 1000. A preferred mean size of beads ranges from 100-500 μm.

In another aspect, the invention provides a particle composition, which having a complex oxide core and a conductive carbon deposit on at least part of the surface of the core, wherein:

- the particles comprise nanoparticles having a nanoscale size and agglomerates of nanoparticles having a submicron to micron scale particle size;
- said conductive carbon deposit is a non powdery deposit, and is present on at least part of the surface of the elementary particles and the surface of the agglomerates.

In a further aspect, the invention is related to the use of the particle composition as an active electrode material, a nanocomposite electrode material comprising said particle composition as the active electrode material, and an electrochemical cell wherein at least one electrode comprises said nanocomposite electrode material.

By using alloying elements (for example, Li, Al, Mg, Fe, Ge, C, Bi, Ag, Sb, Sn, Zn, B, Ti, Sr, P, O, etc), the precipitation of a ductile secondary phase improves resistance of the material to crack propagation, and increases the cyclability of the material.

Advantageously, eutectic modifiers (such as P and Sr) can be used during alloy preparation to change the primary silicon crystals shape and/or grain refiners (such as Ti and B)., to reduce grain size to nano-scale.

A vacuum induction gas atomisation furnace may be advantageous to provide the cooling speed necessary for intimate mixing of the Si primary phase to secondary phase intermetallic phase at the nano-scale level and for particle size reduction.

The atmosphere may be composed of an inert gas (such as N_2, Ar, He) and may be mixed with oxidizing gases (air, H_2O, O_2, CO_2, Cl_2) or a reducing gas (CO, volatile hydrocarbons). It was also found that surface carbonisation of atomized particles may be carried out by using a reducing atmosphere with a combination of gaseous hydrocarbons (such as natural gas, methane, acetylene, propane, etc). It was found that the use of gaseous hydrocarbons in the atmosphere is advantageous because it produces carbonization of the particles surface and passivates the particle surface.

Pre-lithiation of the silicon alloy changes the expansion/contraction ratio of the Si-based material vs. binder interface stresses distribution.

Brief Description of the Drawings

Figure 1 shows alloy Al-18Si using VIGA.

Figure 2 shows Vacuum Induction Gas Atomization equipment.

Figure 3 shows particle size distribution of various alloys.

Description of Preferred Embodiments and Examples

Example 1

In this example, in the first step, the commercially available metallurgical Si was melted in an induction furnace using a graphite crucible under argon atmosphere for homogenization. The liquid silicon temperature was raised to 1450°C, then casted in a graphite mold and cooled down to room temperature. The impurity phase accounts for less than 2% of the total materials.

In the second step, the ingot was crushed into millimeter sized particles using a jaw crusher with tungsten carbide liner to lower metal contamination. The millimeter sized particles are further ground by using ball milling to achieve micrometer sized particles. Finally, the micrometer sized powders were dispersed in isopropyl alcohol (IPA) solution at 10-15% of solid concentration and then ground on a bead mill using 0.2 mm zirconia beads to achieve nanometer sized particles.

TEM observations show that wet milling leads to nanometer sized primary particles in the range of 20-30 nm, and these primary nanoparticles are re-agglomerated to submicron sized particles in the range of 100-500 nm depending on the concentration of solid in liquid, the nature of the liquid media and the surfactant used. There is a thin mechanically and chemically distorted surface layer on the particle surface.

In a third step, a solution of poly(maleic anhydride-1-alt-octadecene) dissolved in IPA is mixed with the Si in IPA, in a ratio of 5wt.% poly(maleic anhydride-1-alt-octadecene) over Si. The mixed solution was stirred thoroughly and then dried at room temperature by blowing with dry air while stirring.

In a final fourth step, the dried powder is heated to 727°C at 6°C/min and held for 1 h at 727°C in a rotary kiln under argon flow, and then cooled at a cooling rate of 2°C/min. After this treatment, large aggregates of carbon coated nanoparticles having a diameter of 50-200nm are obtained. The pyrolytic carbon content is 1.4%, as measured by a C, S analyzer (LECO method). The product thus obtained is designated by C-Si.

X-ray analysis shows that the sintered product contains mainly Si as the major phase with a small proportion of $FeSi_2$ minor phase. The diffraction peaks become sharper in comparison to that of the as-milled product due to grain growth and structure restoration through the thermal treatment. The crystallite size is about 190 nm after thermal treatment. The strain is sharply reduced from 2% to 0.38%. SEM and TEM observations show that a thin layer of carbon is deposited on the nanoparticle surface, and that the nanoparticles are bonded together by carbon-bridge forming aggregates showing evidence of open porosity. The crystallite size of the thermal treated materials is roughly the same as the primary particle size. This indicates that the each primary particle is a single crystal after thermal treatment. TEM observation indeed confirms that each primary particle is single crystal.

Example 2

A suspension in IPA of nanometer sized particles of Si obtained after step 2 of Example 1 was dried at room temperature by blowing dry air. The obtained Si was the re-dispersed in a water-lactose solution by ultrasonic action. The ratio of lactose to Si was 10 wt.%. After drying, lactose coated Si particles are obtained.

Thermal treatment of Si and carbonization of the lactose were performed in a rotary kiln, as described in example 1. SEM and TEM observation revealed that the nanoparticles obtained after thermal treatment are bigger when lactose is used as the carbon precursor, even starting from the same wet milled particle precursors.

C-Si, as prepared in the present example was used as an anode for a liquid electrode battery. C-Si powder, polyimide polymer (from UBE, Japan) and SNG12 graphite powder (from Hydro-Quebec) were thoroughly mixed in N-methyl pyrolidone (NMP) with zirconia balls (80/10/10 wt% proportion of the components) and ball milled for 1 hour. This slurry was then coated on a copper foil with a doctor blade coater. The coating was dried under vacuum at 120°C for 24 hours prior to storage in a glove box. A button-type battery consisting of the anode thus obtained, a 25 μm microporous separator (from Celgard) impregnated with 1M/l $LiPF_6$ salt in EC: DEC electrolyte and lithium foil as counter electrode was assembled and sealed in a glove box.

The electrochemical evaluation of the electrode prepared in this example has a reversible capacity of 1600 mAh/g obtained at a rate of C/24 between 2.5V and 0.010V.

Example 3

A mixture of C-SiO powder (obtained by the same method of example 1), having a diameter of 50-200nm and graphite powder SNG12 (from Hydro-Quebec) (1:1 by weight) was milled by a planetary ball mill for 18 hours. The milled composites were dispersed in solvent consisting of furfuryl alcohol, ethanol, and water. Then diluted hydrochloric acid was added to the slurry to polymerize the furfuryl alcohol. The solid was dried by heating under argon atmosphere at 1000°C.

The same procedure as example 2 was used to produce an electrode, which had a reversible capacity of 1250 mAh/g.

Claims

1. A method for preparing carbon coated Si-, and SiO_x-based particle composition or their mixture, obtained from molten silicon/silicon alloys and ingots wherein the Si- or SiO_x-based particles have a non powdery conductive carbon deposit on at least part of their surface, said method comprises nano-grinding Si- or SiO_x-based particles, wherein:

- under controlled atmosphere (vacuum, inert or reactive gas);
- an organic carbon precursor is added to the Si- or SiO_x-based particles before, during or after nano-grinding, and pyrolyzing the mixture thus obtained;
- a stabilizing agent is optionally added to the oxide particles or oxide precursor particles before, during or after nano-grinding;
- the nano-grinding step is performed in a bead mill on particles dispersed in a carrier solvent; and
- the size of the particles subjected to the nano-grinding step, the size of the beads used to nano-grind, and the size of the resulting particles are selected such that:

$$0{,}004 \leq MS(SP)/MS(B) \leq 0{,}12$$

$$0{,}0025 \leq MS(FP)/MS(SP) \leq 0{,}25$$

wherein MS(SP) represents the mean size diameter of the particles before nano-grinding (starting particles), MS(FP) represents the mean size diameter of the particles after nano-grinding (final particles), and MS(B) is the mean size diameter of the nangrinding beads.

2. The method of claim 1 characterized in that the carrier solvent is a reactive solvent.

3. The method of claim 2 characterized in that the carrier solvent is water, isopropanol or furfuryl alcohol.

4. The method of claim 1, which further comprises a step that is performed after grinding and before pyrolysis, said further step comprising conditioning the reaction mixture in order to adsorb the carbon precursor on the Si- or SiO_x-based particles, or to polymerize or cross link a carbon precursor which is a monomer.

5. The method of claim 1, which further comprises a step consisting of aggregating the reaction mixture comprising the carbon precursor and the Si and alloy precursor after grinding.

6. The method of claim 5, wherein aggregation is performed by flocculating, by spray drying, or by charge effect.

7. The method of claim 1, wherein an organic carbon precursor selected from fatty acid salts is added to the Si- or SiO_x-based particles.

8. The method of claim 7 wherein the fatty acid contains at least 6 carbon atoms.

9. The method of claim 8 wherein fatty acid is selected from stearate, oleate, linoleate, linolenate, ricinolenate.

10. The method of claim 1, wherein the mean size diameter of the grinding beads is from 100 to 500 μm.

11. The method of claim 1, wherein the organic carbon precursor is added to the Si- or SiO_x-based particles.

12. The method of claim 11, wherein an organic stabilizing agent is added before grinding.

13. The method of claim 12, wherein the organic stabilizing agent is a conductive carbon precursor.

14. The method of claim 11, wherein pyrolysis is performed before, or during the synthesis of the Si- or SiO_x-based particles from the precursors thereof.

15. The method of claim 11, wherein the organic carbon precursor also acts as the stabilizing agent.

16. The method of claim 1, wherein the organic carbon precursor is added to Si- or SiO_x-based particles.

17. The method of claim 16, wherein the SiO_x-based particles are prepared by a solid state reaction of Si powder and oxide under controlled atmosphere.

18. The method of claim 16, wherein the Si-alloy particles are prepared by a solid state reaction under controlled atmosphere of Si powder and at least one of the elements; such as Li, Al, Mg, Fe, Ge, C, Bi, Ag, Sb, Sn, Zn, B, Ti, Sr, P, Ge;.

19. The method of claim 16, wherein the intermetallic compound or eutectic alloy are Al--Si, Mn--Si, Fe--Si or Ti--Si.

20. The method of claim 16, wherein the Si- or SiO_x-based particles is prepared by reacting the precursors in molten state in controlled atmosphere, the material being pre-ground after synthesis and solidification.

21. A particle composition comprising particles having a Si- or SiO_x-based core and a conductive carbon deposit on at least part of the surface of the core, wherein :

- the particles comprise elementary nanoparticles having a nanoscale size and agglomerates or aggregates of elementary nanoparticles having a submicron to micron scale particle size;
- said conductive carbon deposit is a non powdery deposit, and is present on at least part of the surface of the elementary particles and on the surface of the aggregates.

22. A particle composition of claim 21, wherein the particles comprise elementary nanoparticles and micron size agglomerates or aggregates of elementary nanoparticles, wherein

- said elementary nanoparticles have dimensions ranging from 5 nm to 1.0 μm and comprise primary nanoparticles and secondary particles,
- said primary particles are made of Si- or SiO_x-based particles with or without C,
- said secondary particle is an agglomerate or an aggregate of primary particles,
- an aggregate of primary nanoparticles is a micron-size assembly of primary nanosize particles held together by physical or chemical interaction, by carbon bridges, or bridges of locally sintered Si- or SiO_x-based containing of internal open porosity and carbon deposit lower than 30%,
- an agglomerate is an assembly of particles loosely held together by low forces.

23. A particle composition of claim 22, which further contains at least one element selected from internal or external C-deposit or carbon bridging or particulate carbon, inert or conductive phases or sintering necks.

24. A particle composition of claim 22, which further has porosity.

25. A particle composition of claim 21, wherein the carbon deposit is in the form of carbon nanotubes.

26. A nanocomposite electrode material comprising a particle composition of claim 20 as the active electrode material.

27. A nanocomposite electrode material of claim 26, wherein at least 50% of the elementary nanoparticles of the particle composition have a size between 5 nm and 900 nm diameters, said nanoparticles being not aggregated or sintered.

28. A nanocomposite electrode material of claim 26, which comprises a particle composition wherein the elementary nanoparticles are aggregated to form agglomerates having a size from 0.2 μm and 10 μm.

29. A nanocomposite electrode material of claim 26, wherein the conductive carbon deposit attached to the Si- or SiO_x-based particles crystal structure on at least part of the surface of the nanoparticle has a nanoscale thickness.

30. An anode comprising a nanocomposite electrode material of claim 25 on a current collector, wherein the material is Si- or SiO_x-based particles.

31. An electrochemical cell comprising an electrolyte, a cathode and an anode, wherein the anode is an anode of claim 30.

Application number / numéro de demande: 2752844

Figures: 1, 2, 3

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