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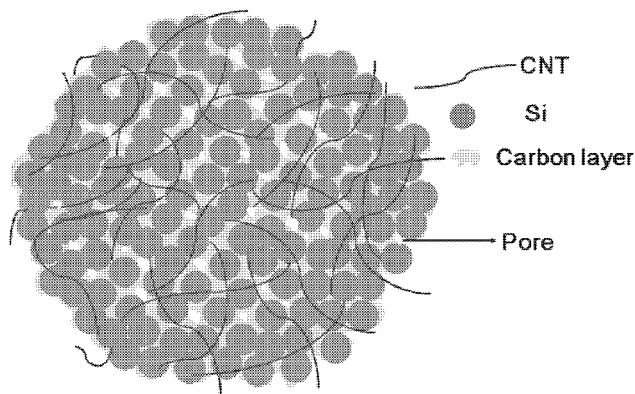


Fig. 1

(57) Abstract: The present invention relates to a silicon-carbon composite, which is present in a form of porous secondary particle and contains silicon nanoparticles, one or more conductive carbon additives, and a conductive carbon coating layer. The present invention further relates to a method for preparing said composite, and an electrode material and a battery comprising said composite.

**SILICON-CARBON COMPOSITE, A METHOD FOR PREPARING SAID
COMPOSITE, AND AN ELECTRODE MATERIAL AND A BATTERY
COMPRISING SAID COMPOSITE**

Technical Field

The present invention relates to a silicon-carbon composite, which is present in a form of porous secondary particle and contains silicon nanoparticles, one or more conductive carbon additives, and a conductive carbon coating layer. The present invention further relates to a method for preparing said composite, and an electrode material and a battery comprising said composite.

Background Art

There are growing demands for the next-generation lithium ion batteries (LIBs) with high energy density as well as long cycle life for large-scale applications like electric vehicles (EV) and stationary utility grids. Silicon is an attractive material for anodes in LIBs because it has ten times the theoretical capacity of its state-of-the-art carbonaceous counterpart. The main challenges associated with silicon anodes are structural degradation and instability of the solid-electrolyte interphase (SEI) caused by the large volume change (~300%) during cycling, leading to fast capacity decay and short cycle life of Si.

Extensive efforts have been made to address these issues, typically by designing well-defined Si nanostructures including nanowires, nanotubes, nanoparticles, porous structure, as well as their composites with carbon materials. Of all the approaches, the design of silicon/carbon composite attracts considerable interest because of the good electronic conductivity and stress-buffer nature of carbon to improve the stability of silicon-based anodes. In recent years, various methods have been employed for preparing silicon/carbon composites, e.g., hydrothermal method, CVD, high-energy mechanical milling (HEMM), spray drying (SD), pyrolysis and sol-gel method. Among these methods, the sol-gel method is not suitable for massive production, while mechanical milling seems unable to bring a high-quality carbon layer. Pyrolysis method can form a fairly complete carbon layer with high conductivity on the Si surface, which is easy to scale up in a commercial view. CVD is the most ideal carbon coating method due to its uniform, adjustable and high quality carbon layer, but it's required to operate under inert atmosphere and high temperature that is quite costly. SD has been widely used for nanoparticle encapsulation in the chemical and food industries owing to its low cost, simple apparatus and easy to scale up. Many research groups focus on Si-based anode material by SD technique.

See How Ng et al reported a spheroidal carbon-coated silicon nanocomposite by spray-pyrolyzing the Si/citric acid/ethanol suspensions at 400°C. This composite showed a reversible capacity of 1489 mAh g⁻¹ over 20 cycles. However, the composite structure was simple assemblies of carbon-coated Si nanostructures in the absence of well-defined pore structures at the level of secondary particles. During repeated charge/discharge processes,

the amorphous carbon layer cannot buffer the volume changes of Si and, as a result, the cycling stability of the composite was poor over long cycles.

Yu-Shi He et al reported a lily-like graphene sheet-wrapped nano-Si composite via a simple SD process. It exhibited a reversible capacity of 1525 mAh g^{-1} over 30 cycles. However, since wrapping of nano-Si by graphene sheet couldn't ensure fully coverage of Si by carbon, the prevention of nano-Si from contacting with electrolyte was limited, therefore, the improvement of cycling stability was limited.

Miao Zhang et al reported silicon@carbon/carbon nanotubes & carbon nanofibres (Si@C/CNTs&CNFs) composites were synthesized by a series of high-energy wet ball milling, closed SD and subsequently chemical vapor deposition methods, in which carbon nanotubes and carbon nanofibers were interweaved with carbon coated silicon (Si@C) spherical composites. The Si@C/CNTs&CNFs composites demonstrated a reversible capacity of 1195 mAh g^{-1} over 50 cycles. However, the composite was prepared by a series of procedures, leading to a low productivity.

For the composites of these three prior art reference documents listed above, their common problem is limited capacity retentions in short cycle numbers, while their long-term cycling performance is not good.

Summary of Invention

It is therefore an object of the present invention to provide a novel silicon-carbon composite, which shows a good long-term cycling performance.

Said object can be achieved by a silicon-carbon composite, which is present in a form of porous secondary particle and contains silicon nanoparticles (Si NPs), one or more conductive carbon additives, and a conductive carbon coating layer.

Said object can also be achieved by a method for producing a silicon-carbon composite, the method including the following steps:

- 1) providing a dispersion containing silicon nanoparticles, one or more conductive carbon additives and a carbon precursor in a solvent;
- 2) spray-drying the dispersion, so that the silicon nanoparticles and the one or more conductive carbon additives are mixed in a form of porous secondary particle and coated with the carbon precursor;
- 3) heating the product obtained from 2), so that the carbon precursor is pyrolyzed to form a conductive carbon coating layer.

According to another aspect of the invention, an electrode material is provided, which comprises the silicon-carbon composite according to the present invention or the silicon-carbon composite produced by the method according to the present invention.

According to another aspect of the invention, a battery is provided, which comprises the silicon-carbon composite according to the present invention or the silicon-carbon composite produced by the method according to the present invention.

The present invention, according to another aspect, relates to the use of the silicon-carbon composite according to the present invention as an electrode active material.

Brief Description of Drawings

Each aspect of the present invention will be illustrated in more detail in conjunction with the accompanying drawings, wherein:

Figure 1 shows a diagrammatic sketch of the Si/CNT@C of Example 1;

Figure 2 shows the XRD profiles of (a) the Si/CNT@C of Example 1, (b) Si, and (c) CNT;

Figure 3 shows the SEM images of (a, b) the Si/CNT@PF and

(c, d) the Si/CNT@C of Example 1;

Figure 4 shows the TEM images of the Si/CNT@C of Example 1, in which the carbon layer is indicated by an arrow;

Figure 5 shows the cycling performance of (a) the pristine Si NPs and

(b) the Si/CNT@C of Example 1;

Figure 6 shows the charge-discharge profiles of (a) the pristine Si NPs and (b) the Si/CNT@C of Example 1 at the 1st, 3rd, 30th, 50th and 100th cycles;

Figure 7 shows the rate performance of (a) the pristine Si NPs and

(b) the Si/CNT@C of Example 1;

Figure 8 shows the cycling performance of the Si/CNT@C of Example 1 at a higher current density;

Figure 9 shows the cycling performance of (a) the Si/CNT@C of Example 1,

(b) the Si/CNT@C of Example 2, and

(c) the Si/CNT/Cu@C of Example 3;

Figure 10 shows the SEM images of (a) the Si/CNT/Cu salt@PF and

(b) the Si/CNT/Cu@C of Example 3;

Figure 11 shows the XRD profiles of (a) the Si/CNT/Cu@C of Example 3, and

(b) the Si/CNT/Cu@C of Example 4;

Figure 12 shows the elemental mapping of Si/CNT/Cu@C of Example 4;

Figure 13 shows the cycling performance of (a) the Si/CNT@C of Example 1, and

(b) the Si/CNT/Cu@C of Example 4;

Figure 14 shows the XRD profiles of (a) the Si/CNT/SnO₂@PF and

(b) the Si/CNT/Sn@C of Example 5;

Figure 15 shows the cycling performance of the Si/CNT/Sn@C of Example 5.

Detailed Description of Preferred Embodiments

All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated, are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range.

The present invention, according to one aspect, relates to a silicon-carbon composite, which is present in a form of porous secondary particle and contains silicon nanoparticles, one or more conductive carbon additives, and a conductive carbon coating layer.

In accordance with an embodiment of the silicon-carbon composite according to the present invention, the porous secondary particle has a pore volume of $0.1 - 1.5 \text{ cm}^3/\text{g}$, preferably $0.3 - 1.2 \text{ cm}^3/\text{g}$, more preferably $0.5 - 1.0 \text{ cm}^3/\text{g}$; a pore diameter of $1 - 200 \text{ nm}$, preferably $10 - 180 \text{ nm}$, more preferably $20 - 150 \text{ nm}$; and a BET specific surface area of $30 - 300 \text{ m}^2/\text{g}$, preferably $40 - 250 \text{ m}^2/\text{g}$, more preferably $50 - 200 \text{ m}^2/\text{g}$.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the particle size of the porous secondary particle is $1 - 10 \text{ }\mu\text{m}$, preferably $2 - 8 \text{ }\mu\text{m}$, more preferably $3 - 7 \text{ }\mu\text{m}$.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the particle size of the silicon nanoparticles is less than 200 nm , preferably $50 - 200 \text{ nm}$, more preferably $80 - 150 \text{ nm}$.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the weight ratio of the silicon nanoparticles to the conductive carbon additives is between $1 : 2$ and $90 : 1$, preferably between $4 : 3$ and $16 : 1$, more preferably between $2 : 1$ and $10 : 1$, most preferably between $5 : 1$ and $8 : 1$.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the thickness of the conductive carbon coating layer is $1 - 10 \text{ nm}$, preferably $2 - 8 \text{ nm}$, more preferably $3 - 6 \text{ nm}$, most preferably about 5 nm .

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the conductive carbon additives can be selected from the group consisting of carbon nanotube, graphene, and carbon black. Preferably the carbon nanotube has an outer diameter of $10 - 50 \text{ nm}$, preferably $15 - 40 \text{ nm}$, more preferably $20 - 30 \text{ nm}$; and a length of $1 - 30 \text{ }\mu\text{m}$, preferably $5 - 25 \text{ }\mu\text{m}$, more preferably $10 - 20 \text{ }\mu\text{m}$.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the silicon-carbon composite can further contain one or more metal materials not participating in the lithiation/delithiation, preferably one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, and Ti, more preferably Cu, in the form of an intermetallic compound of silicon and the one or more metal materials. The intermetallic compound has properties intermediate between an ionic compound and an alloy. Said one or more metal materials, specifically the intermetallic compound of silicon and the one or more metal materials, can be uniformly distributed on

the surface of the Si nanoparticles. Particularly preferably, the metal material can be copper in the form of an intermetallic compound of copper and silicon, such as Cu_3Si and Cu_5Si .

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the silicon-carbon composite can further contain one or more metal materials participating in the lithiation/delithiation, preferably one or more metal materials selected from the group consisting of Ge, Sn, Al, Mg, Ag, Zn, and In, more preferably Sn. Said one or more metal materials can be uniformly distributed on the surface of the Si nanoparticles.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the silicon-carbon composite can further contain one or more metal materials not participating in the lithiation/delithiation in combination with one or more metal materials participating in the lithiation/delithiation.

In accordance with another embodiment of the silicon-carbon composite according to the present invention, the silicon-carbon composite can further contain one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, Ti, Ge, Sn, Al, Mg, Ag, Zn, and In. Said one or more metal materials can be uniformly distributed on the surface of the Si nanoparticles.

Preferably, when said silicon-carbon composite contains one or more metal materials, the weight ratio of silicon element to metal element in said silicon-carbon composite is between 4 : 1 and 20 : 1, preferably between 5 : 1 and 15 : 1, more preferably between 6 : 1 and 13 : 1.

According to the present invention, the Si nanoparticles (Si NPs) and the conductive carbon additives are uniformly mixed and fully encapsulated by an amorphous carbon layer, so as to form 3D porous spherical secondary particles. Since the Si nanoparticles are fully covered by a conductive carbon coating layer, any direct contact of Si nanoparticles with electrolyte can be avoided. The conductive carbon coating layer can be formed by spray drying and pyrolysis. The conductive carbon coating layer and the conductive carbon additives not only constitute a 3D continuous and highly conductive network, but also provide elastic void spaces to accommodate the strain and stress of the volume changes of Si and avoid the aggregation and pulverization of Si NPs during cycling. Due to the design of porous nano/micro secondary structure, the resulting composite (Si/CNT@C) shows a superior cycle stability with a retention of 78.3% after 110 cycles and a high reversible capacity.

The present invention, according to another aspect, relates to a method for producing a silicon-carbon composite, the method including the following steps:

- 1) providing a dispersion containing silicon nanoparticles, one or more conductive carbon additives and a carbon precursor in a solvent;
- 2) spray-drying the dispersion, so that the silicon nanoparticles and the one or more conductive carbon additives are mixed in a form of porous secondary particle and coated with the carbon precursor;
- 3) heating the product obtained from 2), so that the carbon precursor is pyrolyzed to form a conductive carbon coating layer.

In accordance with an embodiment of the method according to the present invention, the particle size of the silicon nanoparticles is less than 200 nm, preferably 50 – 200 nm, more preferably 80 – 150 nm.

In accordance with another embodiment of the method according to the present invention, the weight ratio of the silicon nanoparticles to the conductive carbon additives is between 1 : 2 and 90 : 1, preferably between 4 : 3 and 16 : 1, more preferably between 2 : 1 and 10 : 1, most preferably between 5 : 1 and 8 : 1.

In accordance with another embodiment of the method according to the present invention, the carbon precursor can be selected from the group consisting of phenol formaldehyde resin, citric acid, sucrose, epoxy resin, and poly(vinylidene fluoride).

In accordance with another embodiment of the method according to the present invention, the amount of the carbon precursor can be selected, so that the thickness of the conductive carbon coating layer is 1 – 10 nm, preferably 2 – 8 nm, more preferably 3 – 6 nm, most preferably about 5 nm.

In accordance with another embodiment of the method according to the present invention, the conductive carbon additives can be selected from the group consisting of carbon nanotube, graphene, and carbon black. Preferably the carbon nanotube has an outer diameter of 10 – 50 nm, preferably 15 – 40 nm, more preferably 20 – 30 nm; and a length of 1 – 30 μm , preferably 5 – 25 μm , more preferably 10 – 20 μm .

In accordance with another embodiment of the method according to the present invention, in step 1) the dispersion can further contain one or more metal material precursors for one or more metal materials not participating in the lithiation/delithiation, preferably for one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, and Ti, more preferably Cu. In particular, the one or more metal material precursors can be reacted with the silicon nanoparticles by heating to obtain an intermetallic compound of silicon and the one or more metal materials. The intermetallic compound has properties intermediate between an ionic compound and an alloy. Said one or more metal materials, specifically the intermetallic compound of silicon and the one or more metal materials, can be uniformly distributed on the surface of the Si nanoparticles. Particularly preferably, the metal material precursor can be one or more copper precursors selected from the group consisting of copper nanoparticles and an organic copper salt, such as copper ethylacetoacetate.

In accordance with another embodiment of the method according to the present invention, in step 1) the dispersion can further contain one or more metal material precursors for one or more metal materials participating in the lithiation/delithiation, preferably for one or more metal materials selected from the group consisting of Ge, Sn, Al, Mg, Ag, Zn, and In, more preferably Sn. Said one or more metal materials can be uniformly distributed on the surface of the Si nanoparticles. Particularly preferably, the metal material precursor can be a tin precursor, such as SnO_2 , which can be reduced to Sn during step 3) by the equation $\text{SnO}_2 + 2\text{C} = \text{Sn} + 2\text{CO}$.

In accordance with another embodiment of the method according to the present invention, in step 1) the dispersion can further contain one or more metal material precursors for one or more metal materials not participating in the lithiation/delithiation in combination with one

or more metal material precursors for one or more metal materials participating in the lithiation/delithiation.

In accordance with another embodiment of the method according to the present invention, in step 1) the dispersion can further contain one or more metal material precursors for one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, Ti, Ge, Sn, Al, Mg, Ag, Zn, and In. Said one or more metal materials can be uniformly distributed on the surface of the Si nanoparticles.

Preferably, when the dispersion contains one or more metal material precursors for one or more metal materials, the weight ratio of silicon element to metal element in the resulting silicon-carbon composite is between 4 : 1 and 20 : 1, preferably between 5 : 1 and 15 : 1, more preferably between 6 : 1 and 13 : 1.

In accordance with another embodiment of the method according to the present invention, in step 2), the inlet temperature is 100 – 220°C, preferably 120 – 200°C, more preferably 150 – 180°C, and the outlet temperature is 80 – 140°C, preferably 90 – 130°C, more preferably 100 – 120°C.

In accordance with another embodiment of the method according to the present invention, step 3) can be carried out at a temperature of 800 – 1200°C, preferably 850 – 1100°C, more preferably 900 – 1000°C, for 1 – 48 hours, preferably 5 – 24 hours, more preferably 10 – 12 hours.

The method according to the present invention is facile and feasible, which provides an avenue for large-scale production of Si-based composites.

The present invention, according to another aspect, relates to an electrode material, which comprises the silicon-carbon composite according to the present invention or the silicon-carbon composite produced by the method according to the present invention.

The present invention, according to another aspect, relates to a battery, which comprises the silicon-carbon composite according to the present invention or the silicon-carbon composite produced by the method according to the present invention.

The present invention, according to another aspect, relates to the use of the silicon-carbon composite according to the present invention as an electrode active material.

Example 1:

Firstly, 0.73 g Si NPs (size of 50-200nm, Alfa-Aesar), 0.11 g CNT (OD of 10-20 nm, length of 10-30 μ m, Chengdu Organic Chemicals Co., Ltd) and 0.37 g PF (Shandong Shenquan Group) were dispersed in 150 mL absolute ethyl alcohol, stirred and ultrasonicated for 1h. Secondly, the mixture was spray-dried (inlet temperature: 170°C; outlet temperature: 100°C) to form PF-wrapped Si NPs and CNT (Si/CNT@PF) composite microparticles. Finally, the obtained Si/CNT@PF composite was heated to 900°C for 2 h at 5°C/min under an argon atmosphere and the PF was pyrolyzed to amorphous carbon. The resulting composite was Si/CNT@C. Since the residual carbon ratio of PF is 58%, the the calculated weight ratio of Si NPs : CNTs : C coating in the Si/CNT@C composite was 69 : 10 : 21.

Structural evaluation:

Figure 1 shows a diagrammatic sketch of the Si/CNT@C. The Structure of Si/CNT@C can be described as follows: Micron scale spheres were composed of nano-sized silicon particles with CNT distributed inside. Carbon layer with several nanometers thickness was uniformly coated on the surface of Si/CNT spheres.

Figure 2 shows the X-ray diffraction (XRD) profiles of (a) the Si/CNT@C, (b) Si, and (c) CNT. The Si/CNT@C exhibited highly crystalline structure, which matched well with the standard Si peaks (JCPDS 27-1402). The peaks at 28°, 47°, 56°, 69° and 76° can be indexed as the (111), (220), (311), (400) and (331) planes of Si crystals, respectively. The main peaks of CNT were also appeared in Si/CNT@C. The broad diffraction peak from 20 to 25° corresponded to amorphous PF-pyrolyzed carbon.

Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed to characterize the size and structure of the products (see Figures 3 and 4).

Detailed structure of the composite was porous nano/micro secondary particle, as shown from the SEM and TEM photos. Si NPs and CNTs were embedded in an amorphous carbon layer, forming a 3D porous spherical secondary structure.

As shown in Figure 3, the samples before and after pyrolysis kept the same spherical structure, indicating that the pyrolysis process didn't change the morphology of the sample after spray. The secondary particles ranged from 1 to 7 μm .

It can be determined from Figure 4b, the PF-pyrolyzed carbon on Si NPs was ca. 5 nm thick.

Cells assembling and electrochemical evaluation:

The electrochemical performance of the as-prepared composites was evaluated using two electrode coin-type cells. The working electrodes were prepared by pasting a mixture of active material, Super P conductive carbon black (40nm, Timical), and styrene butadiene rubber/sodium carboxymethyl cellulose (SBR/SCMC, 3:5 by weight, dissolved in distilled water) as binder at a weight ratio of 60: 20: 20. After coating the mixture onto Cu foil, the electrodes were dried, cut to $\Phi 12\text{mm}$ disks, pressed at 3MPa, and finally dried at 50°C in vacuum for 4h. The CR2016 coin cells were assembled in an argon-filled glove box (MB-10 compact, MBraun) using 1M LiPF_6 in dimethyl carbonate (DMC) and ethylene carbonate (EC) mixed solvent of 1:1 by volume, including 2 wt.% vinylene carbonate (VC) as electrolyte, PE membrane (TEKLON UH2045.5) as separator, and lithium metal as counter electrode. The cycling performance was evaluated on a LAND battery test system (CT2007A, Wuhan Jinnuo Electronics, Ltd.) at 25°C with constant current densities. The cut-off voltage was 0.01 V versus Li^+/Li for discharge (Li insertion) and 1.2 V versus Li^+/Li for charge (Li extraction). The specific capacity was calculated on the basis of the weight of Si/CNT@C composites. The mass loading of active materials (Si and C) in every electrode was ca. 0.5 mg/cm^2 .

Figure 5 shows the cycling performance of (a) the pristine Si NPs and (b) the Si/CNT@C. The coin cell was discharged at 0.1 A g^{-1} for the first two cycles and 0.3 A g^{-1} in the following cycles between 0.01 and 1.2V vs Li/Li^+ .

As shown in Figure 5, comparing with pristine Si NPs, the cycling performance of the Si/CNT@C composite was greatly improved, with a stable reversible capacity of ca. 1800 mAh g⁻¹ after 110 cycles. The superior cycling performance could be attributed to the porous nano/micro secondary structure and the carbon coating on Si NPs, which can suppress the particle volume change caused by alloying of Li and Si and the corrosion of Si by fluoride salt electrolyte, leading to a more stable conducting network in the electrode and the interfacial property.

Figure 6 shows the charge-discharge profiles of (a) the pristine Si NPs and (b) the Si/CNT@C at the 1st, 3rd, 30th, 50th and 100th cycles. The coin cell was discharged at 0.1 A g⁻¹ for the first two cycles and 0.3 A g⁻¹ in the following cycles between 0.01 and 1.2V vs Li/Li⁺.

Though pure Si exhibited a higher initial charge capacity, its capacity dropped quickly and the voltage polarization got very serious during cycling. In contrast, the capacity retention and voltage polarization of the Si/CNT@C composite of Example 1 were much improved. During 100 cycles, its specific capacity was basically stabilized at ca. 1800 mAh g⁻¹. The initial Coulombic efficiency (CE) of Si/CNT@C was 82.0%, slightly lower than that of Si (85.2%). The reasons may be: (1) the porous secondary structure had a larger surface area, which would form more irreversible SEI; (2) the carbon from PF via pyrolysis had a very low CE due to its amorphous structure with a large number of defects, which would trap and consume the intercalated lithium.

Figure 7 shows the rate performance of (a) the pristine Si NPs and (b) the Si/CNT@C. The coin cell was charged/discharged at different current densities. It can be seen from Figure 7 that although Si showed a higher capacity than the Si/CNT@C at a low current density of 0.1 A g⁻¹, it decreased fast at high current densities. In comparison, the Si/CNT@C still showed a high capacity of 1248 mAh/g even at 5 A g⁻¹. The good rate performance of the Si/CNT@C could be attributed to the good conductive network formed by CNT and the carbon coating layer.

Figure 8 shows the cycling performance of the Si/CNT@C at 2 A g⁻¹ (=1C). The coin cell was discharged at 0.1 A g⁻¹ for the first two cycles and 2 A g⁻¹ in the following cycles between 0.01 and 1.2V vs Li/Li⁺. It can be seen from Figure 8 that even at a high current rate of 2 A g⁻¹ (=1C), the capacity of the Si/CNT@C can be maintained at ca. 1000 mAh g⁻¹ over 300 cycles.

In this Example, the agglomeration structure of the Si/CNT@C composite was designed and synthesized. The carbon conductivity network was formed within the agglomeration by the CNT and carbon coating layer. The volume change during the charge-discharge process could be buffered by the porosity of agglomeration and the carbon layer.

The cycling performance was better than the above three prior art reference documents. This Example achieved a reversible capacity of 1826 mAh g⁻¹ over 110 cycles, comparing to 1489 mAh g⁻¹ over 20 cycles, 1525 mAh g⁻¹ over 30 cycles and 1195 mAh g⁻¹ over 50 cycles in the above three prior art reference documents, respectively. After 110 cycles, the capacity retention was 78.3%. This Example also used a high current rate of 2 A g⁻¹ and achieved a stable reversible capacity of ca. 1000 mAh g⁻¹ after 300 cycles. In See How Ng et al and

Miao Zhang et al, cycling performance at high current rate was not given while in Yu-Shi He et al, the highest current rate was 0.6 A g^{-1} .

The weight content of Si was higher than See How Ng et al and Miao Zhang et al. The weight content of Si was 44% in See How Ng et al, while the weight content of Si was 69% in this Example. Since the carbon content in the composite would decrease the energy density and lower the capacity, it should be controlled to maximize the volume buffer effect at a controllable energy density and capacity cost. The reversible capacity was ca. 1800 mAh g^{-1} , higher than those in the above three prior art reference documents.

Example 2:

Example 2 was carried out similar to Example 1, except that the calculated weight ratio of Si NPs : CNTs : C coating in the resulting Si/CNT@C composite was 54 : 10 : 36.

Figure 9 shows the cycling performance of (b) the Si/CNT@C of Example 2.

Example 3:

Example 3 was carried out similar to Example 1, except that copper ethylacetoacetate (Cu salt) as the copper source was additionally dispersed in the absolute ethyl alcohol, the intermediate product of step 2) was PF-wrapped Si NPs + CNT + Cu salt (Si/CNT/Cu salt@PF), and the calculated weight ratio of Si NPs : CNTs : Cu : C coating in the resulting composite (Si/CNT/Cu@C) was 60 : 10 : 10 : 20.

Figure 9 shows the cycling performance of (c) the Si/CNT/Cu@C of Example 3; Figure 10 shows the SEM images of (a) the Si/CNT/Cu salt@PF and (b) the Si/CNT/Cu@C of Example 3; and Figure 11 shows the XRD profiles of (a) the Si/CNT/Cu@C of Example 3.

It can be seen from Figure 9 that the cycling performance of the Si/CNT/Cu@C composite of Example 3 was further enhanced by the addition of copper.

Example 4:

Example 4 was carried out similar to Example 1, except that copper nanoparticles (Cu NPs) as the copper source were additionally dispersed in the absolute ethyl alcohol, the intermediate product of step 2) was PF-wrapped Si NPs + CNT + Cu NPs (Si/CNT/Cu@PF), and the calculated weight ratio of Si NPs : CNTs : Cu : C coating in the resulting composite (Si/CNT/Cu@C) was 65 : 10 : 5 : 20.

Figure 11 shows the XRD profiles of (b) the Si/CNT/Cu@C of Example 4; Figure 12 shows the elemental mapping of Si/CNT/Cu@C of Example 4; and Figure 13 shows the cycling performance of (b) the Si/CNT/Cu@C of Example 4.

It can be seen from Figure 12 that copper was distributed on the Si NPs very uniformly. Moreover, the cycling performance of the Si/CNT/Cu@C composite of Example 4 was further enhanced by the addition of copper (see Figure 13).

Example 5:

Example 5 was carried out similar to Example 1, except that SnO_2 nanoparticles as the tin source were additionally dispersed in the absolute ethyl alcohol, the intermediate product of step 2) was PF-wrapped Si NPs + CNT + SnO_2 (Si/CNT/ SnO_2 @PF), and the calculated weight ratio of Si NPs : CNTs : Sn : C coating in the resulting composite (Si/CNT/Sn@C) was 65 : 10 : 5 : 20.

Figure 14 shows the XRD profiles of (a) the Si/CNT/ SnO_2 @PF and (b) the Si/CNT/Sn@C of Example 5; and Figure 15 shows the cycling performance of the Si/CNT/Sn@C of Example 5.

It can be seen from Figure 15 that the cycling performance of the Si/CNT/Sn@C composite of Example 5 was further enhanced by the addition of tin.

While certain embodiments have been described, these embodiments have been presented by way of example only, and are not intended to limit the scope of the inventions. The attached claims and their equivalents are intended to cover all the modifications, substitutions and changes as would fall within the scope and spirit of the invention.

CLAIMS

1. A silicon-carbon composite, characterized in that the silicon-carbon composite is present in a form of porous secondary particle and contains silicon nanoparticles, one or more conductive carbon additives, and a conductive carbon coating layer.
2. The silicon-carbon composite of claim 1, characterized in that the porous secondary particle has a pore volume of $0.1 - 1.5 \text{ cm}^3/\text{g}$, a pore diameter of $1 - 200 \text{ nm}$, and a BET specific surface area of $30 - 300 \text{ m}^2/\text{g}$.
3. The silicon-carbon composite of claim 1 or 2, characterized in that the particle size of the porous secondary particle is $1 - 10 \text{ }\mu\text{m}$.
4. The silicon-carbon composite of any one of claims 1 to 3, characterized in that the particle size of the silicon nanoparticles is less than 200 nm .
5. The silicon-carbon composite of any one of claims 1 to 4, characterized in that the weight ratio of the silicon nanoparticles to the conductive carbon additives is between $1 : 2$ and $90 : 1$, preferably between $4 : 3$ and $16 : 1$.
6. The silicon-carbon composite of any one of claims 1 to 5, characterized in that the thickness of the conductive carbon coating layer is $1 - 10 \text{ nm}$.
7. The silicon-carbon composite of any one of claims 1 to 6, characterized in that said conductive carbon additives are selected from the group consisting of carbon nanotube, graphene, and carbon black.
8. The silicon-carbon composite of claim 7, characterized in that the carbon nanotube has an outer diameter of $10 - 50 \text{ nm}$ and a length of $1 - 30 \text{ }\mu\text{m}$.
9. The silicon-carbon composite of any one of claims 1 to 8, characterized in that said silicon-carbon composite further contains one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, Ti, Ge, Sn, Al, Mg, Ag, Zn, and In.
10. The silicon-carbon composite of claim 9, characterized in that the weight ratio of silicon element to metal element in said silicon-carbon composite is between $4 : 1$ and $20 : 1$, preferably between $5 : 1$ and $15 : 1$.
11. The silicon-carbon composite of any one of claims 1 to 10, characterized in that the silicon nanoparticles are fully covered by the conductive carbon coating layer.

12. The silicon-carbon composite of any one of claims 1 to 11, characterized in that the conductive carbon coating layer is formed by spray drying and pyrolysis.
13. A method for producing a silicon-carbon composite, said method including the following steps:
 - 1) providing a dispersion containing silicon nanoparticles, one or more conductive carbon additives and a carbon precursor in a solvent;
 - 2) spray-drying the dispersion, so that the silicon nanoparticles and the one or more conductive carbon additives are mixed in a form of porous secondary particle and coated with the carbon precursor;
 - 3) heating the product obtained from 2), so that the carbon precursor is pyrolyzed to form a conductive carbon coating layer.
14. The method of claim 13, characterized in that the particle size of the silicon nanoparticles is less than 200 nm.
15. The method of claim 13 or 14, characterized in that the weight ratio of the silicon nanoparticles to the conductive carbon additives is between 1 : 2 and 90 : 1, preferably between 4 : 3 and 16 : 1.
16. The method of any one of claims 13 to 15, characterized in that the carbon precursor is selected from the group consisting of phenol formaldehyde resin, citric acid, sucrose, epoxy resin, and poly(vinylidene fluoride).
17. The method of any one of claims 13 to 16, characterized in that the amount of the carbon precursor is selected, so that the thickness of the conductive carbon coating layer is 1 – 10 nm.
18. The method of any one of claims 13 to 17, characterized in that said conductive carbon additives are selected from the group consisting of carbon nanotube, graphene, and carbon black.
19. The method of claim 18, characterized in that the carbon nanotube has an outer diameter of 10 – 50 nm and a length of 1 – 30 μm .
20. The method of any one of claims 13 to 19, characterized in that in step 2), the inlet temperature is 100 – 220°C, and the outlet temperature is 80 – 140°C.
21. The method of any one of claims 13 to 20, characterized in that step 3) is carried out at a temperature of 800 – 1200°C for 1 – 24 hours.

22. The method of any one of claims 13 to 21, characterized in that in step 1) the dispersion further contains one or more metal material precursors for one or more metal materials selected from the group consisting of Cu, Ni, stainless steel, Fe, Ti, Ge, Sn, Al, Mg, Ag, Zn, and In.
23. The method of claim 22, characterized in that the weight ratio of silicon element to metal element in said silicon-carbon composite is between 4 : 1 and 20 : 1, preferably between 5 : 1 and 15 : 1.
24. An electrode material, characterized in that it comprises the silicon-carbon composite of any one of claims 1 to 12 or the silicon-carbon composite prepared by the method of any one of claims 13 to 23.
25. A battery, characterized in that it comprises the silicon-carbon composite of any one of claims 1 to 12 or the silicon-carbon composite prepared by the method of any one of claims 13 to 23.
26. The use of the silicon-carbon composite of any one of claims 1 to 12 or the silicon-carbon composite prepared by the method of any one of claims 13 to 23 as an electrode active material.

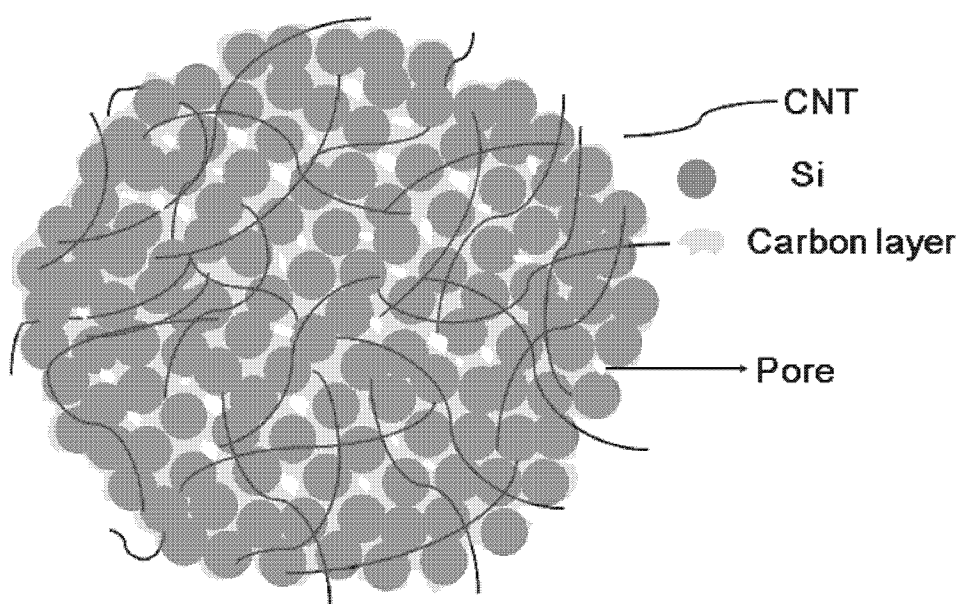
Fig. 1

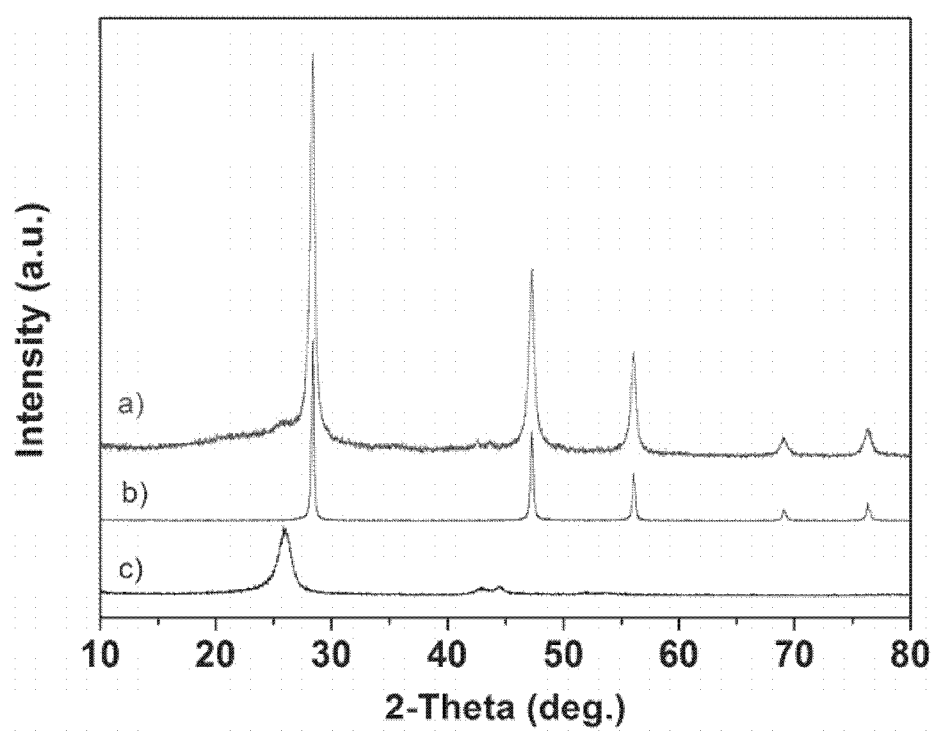
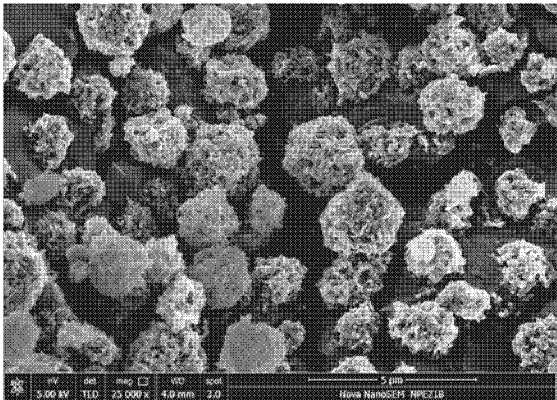
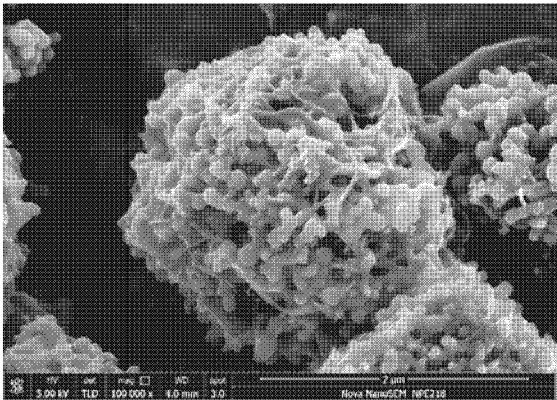
Fig. 2

Fig. 3

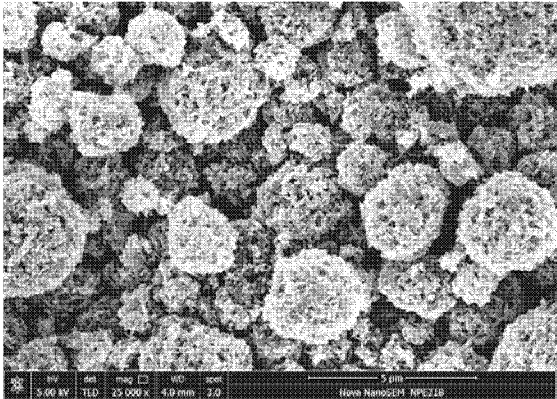
a)



b)



c)



d)

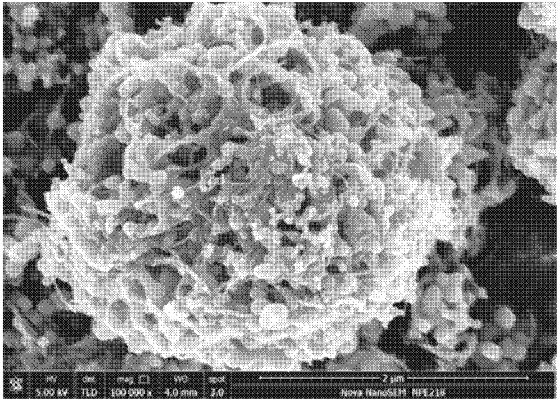


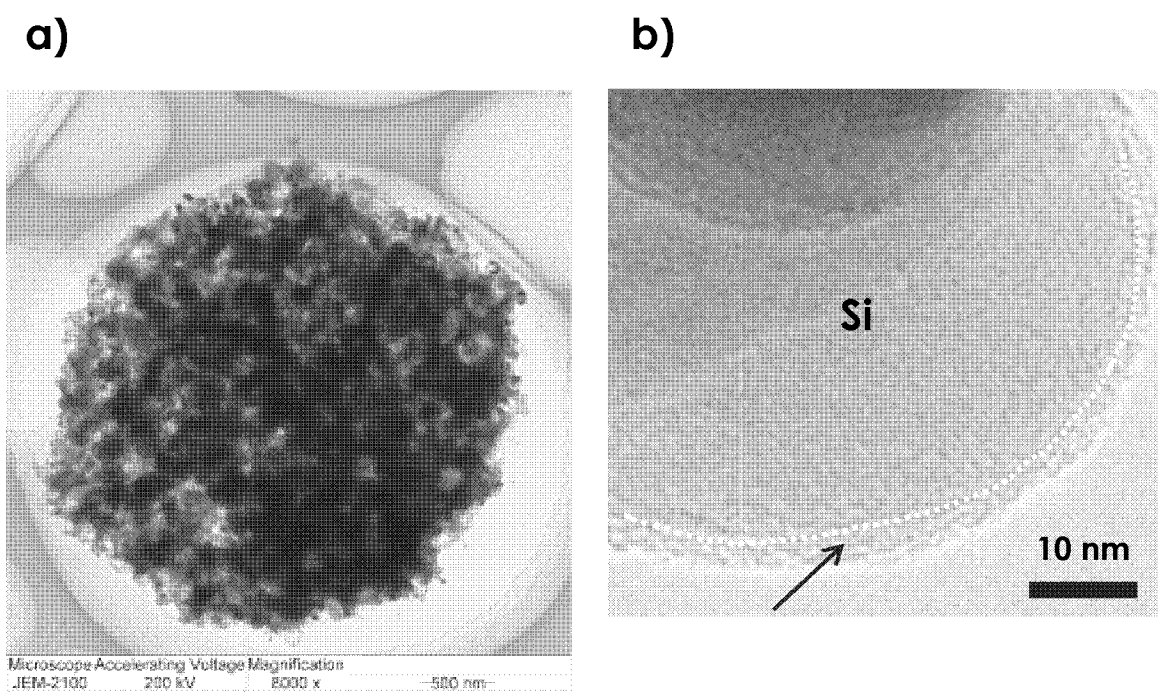
Fig. 4

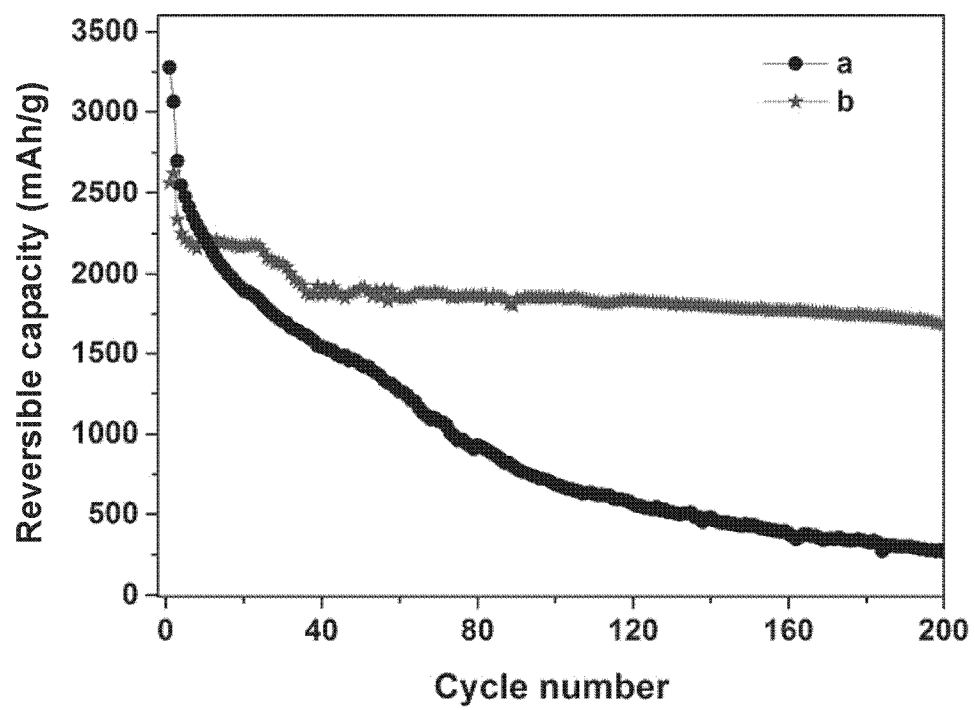
Fig. 5

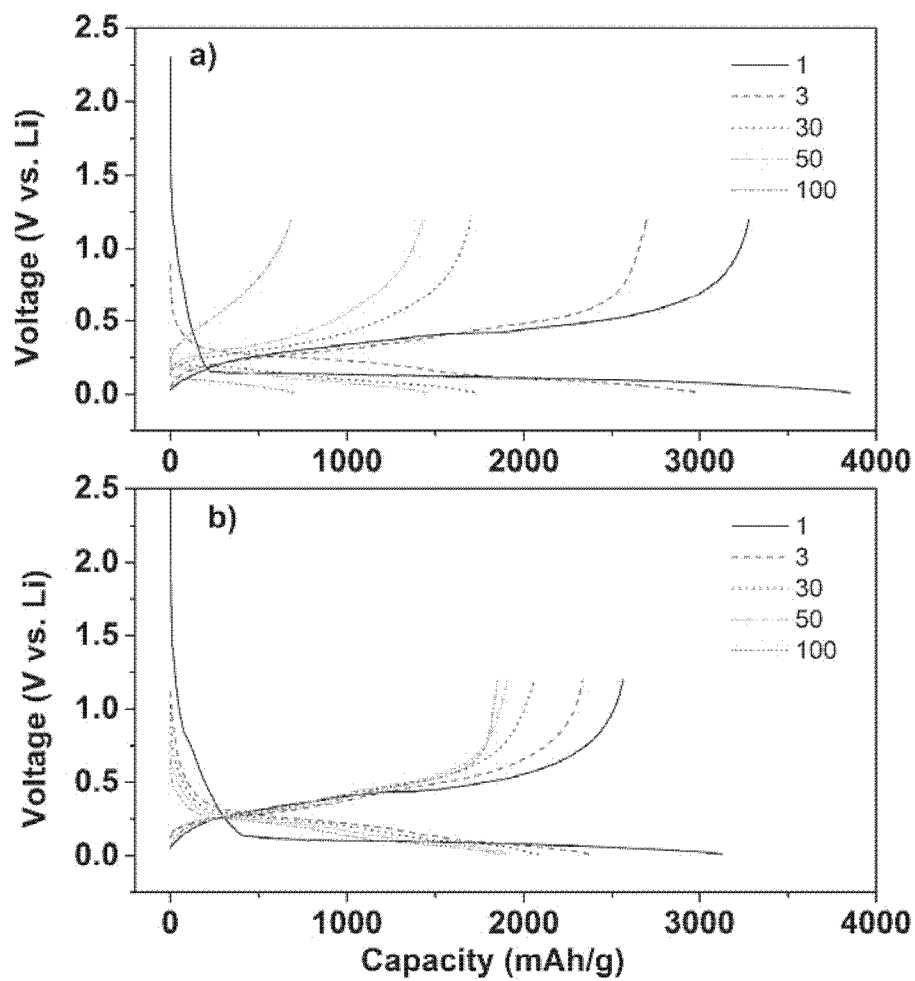
Fig. 6

Fig. 7

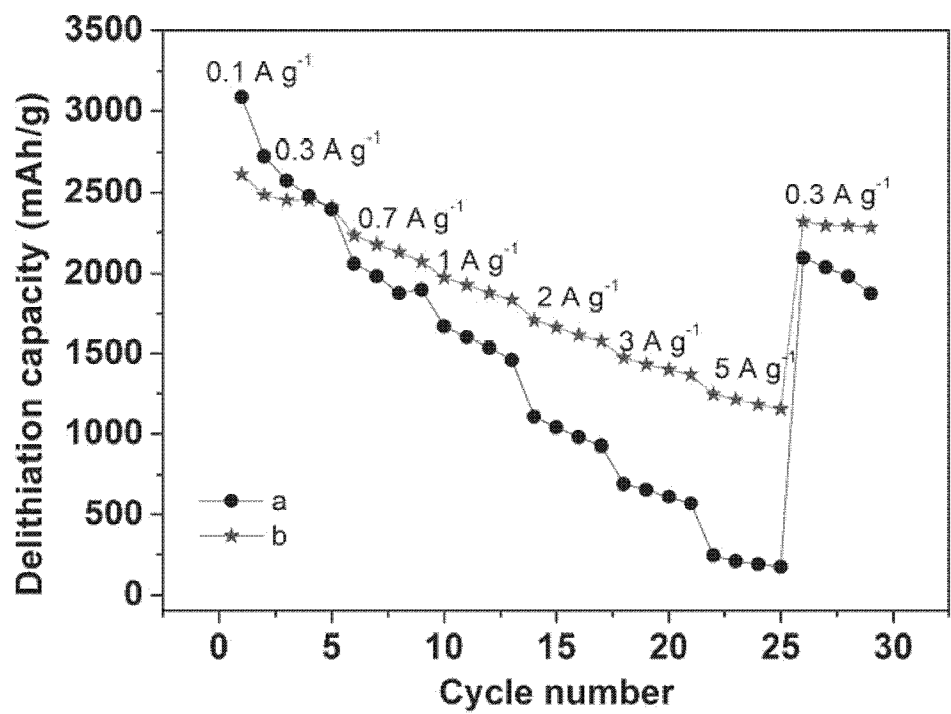


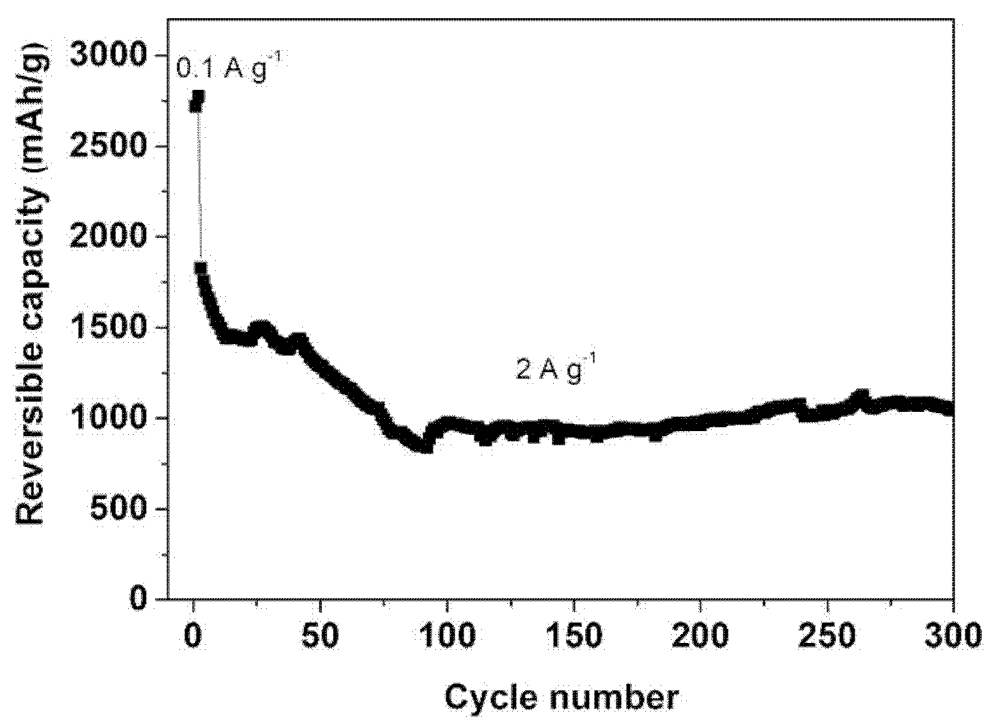
Fig. 8

Fig. 9

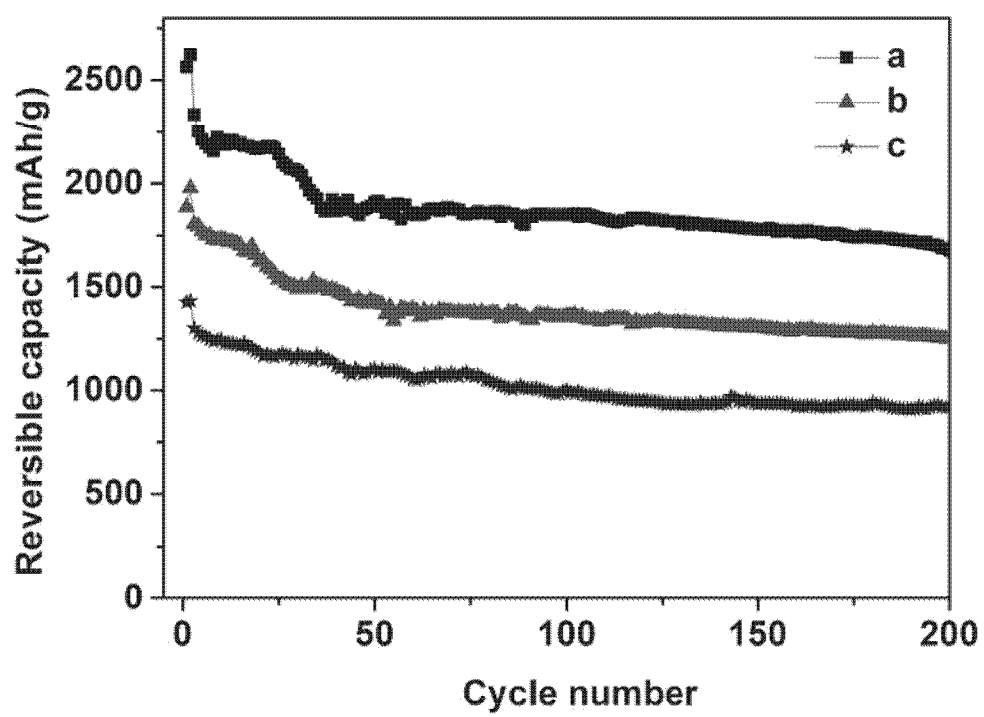


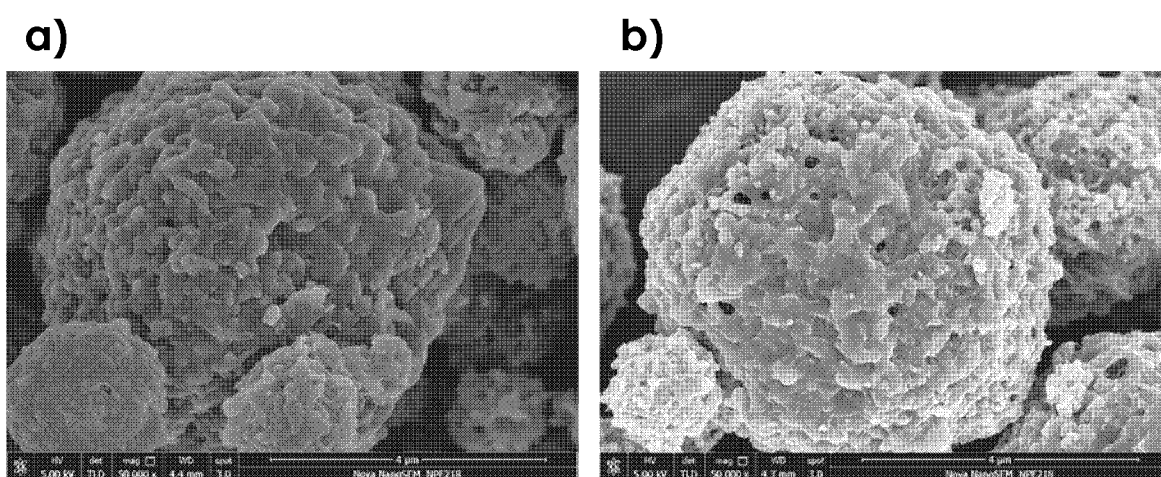
Fig. 10

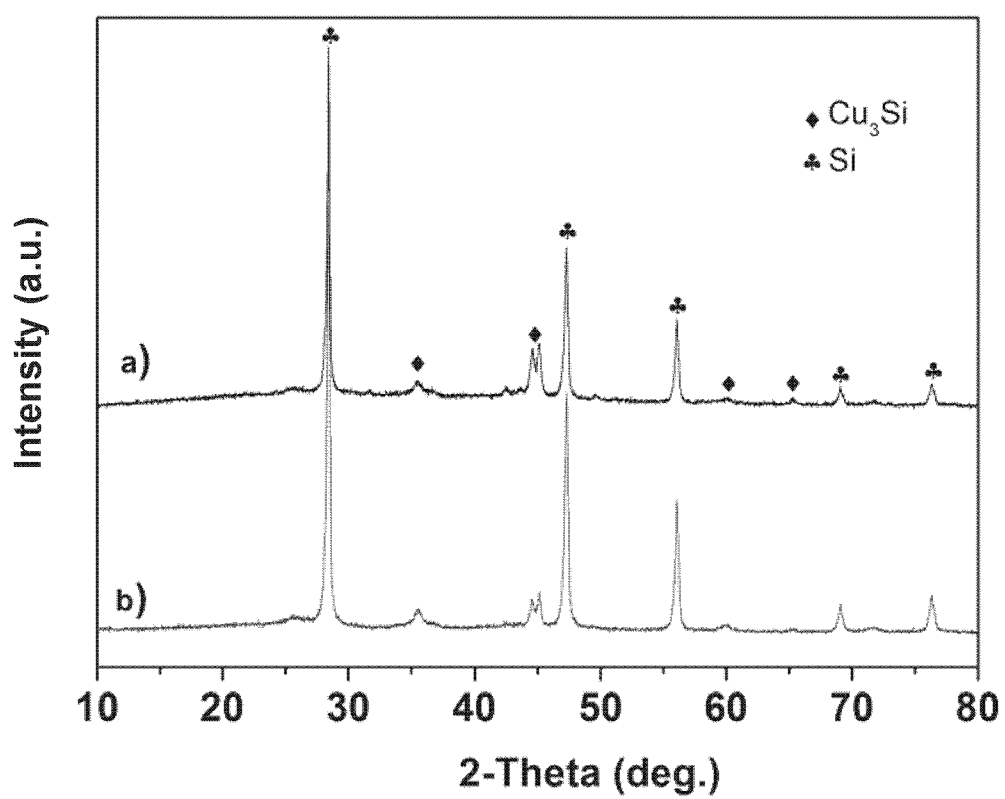
Fig. 11

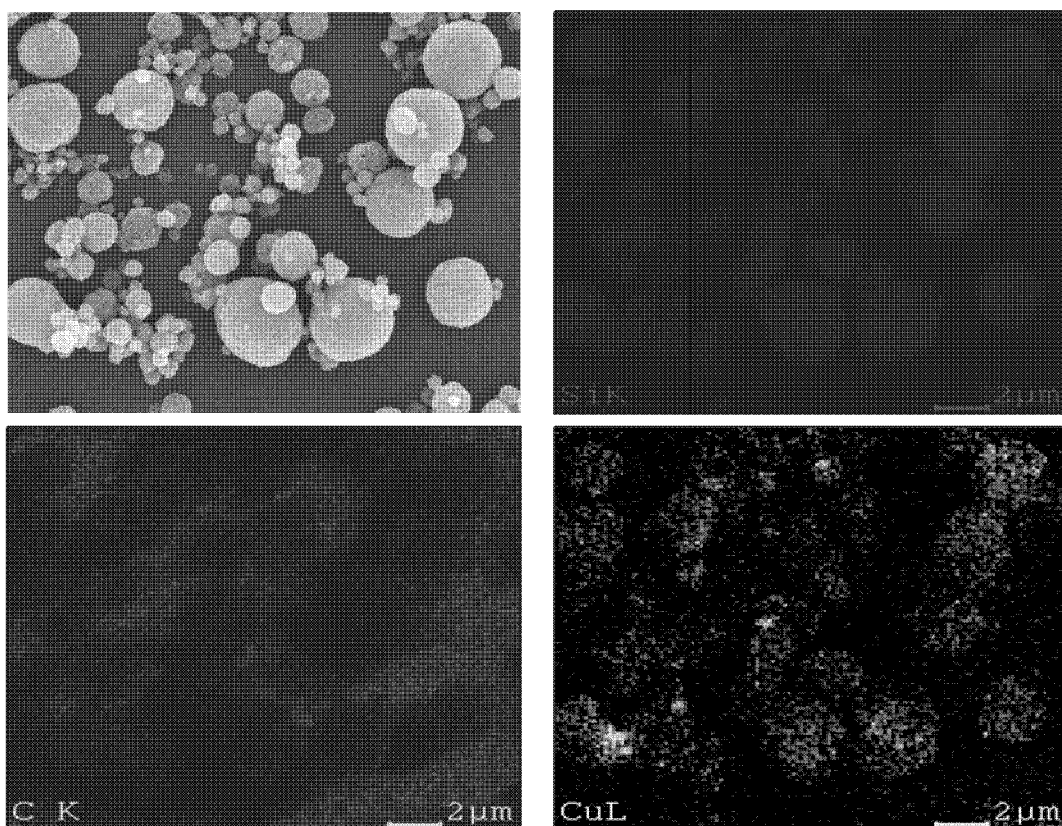
Fig. 12

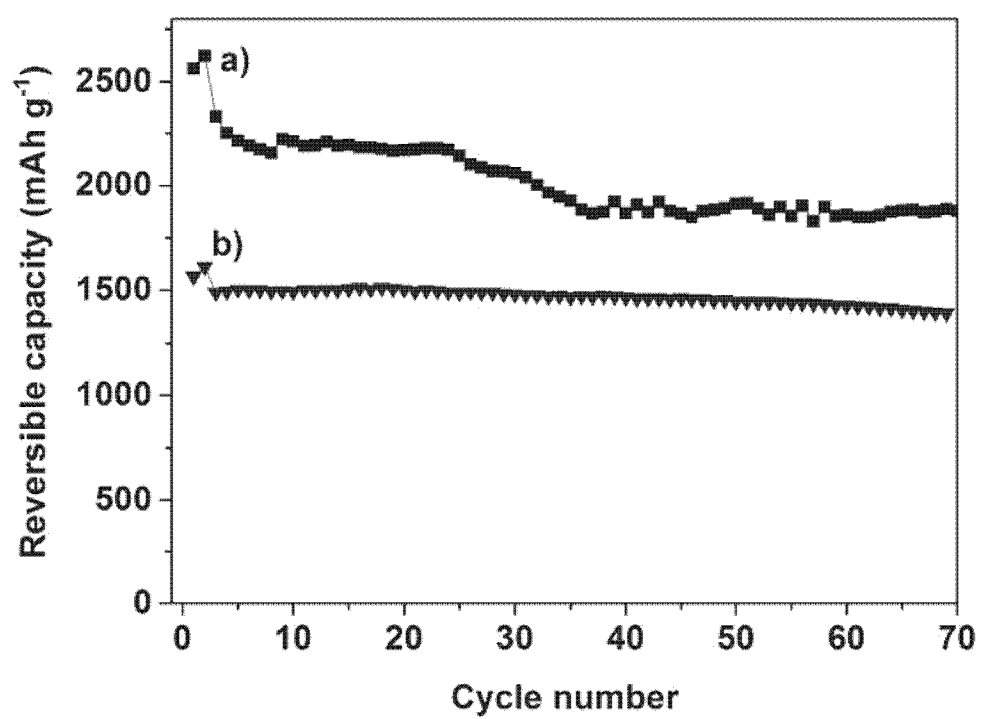
Fig. 13

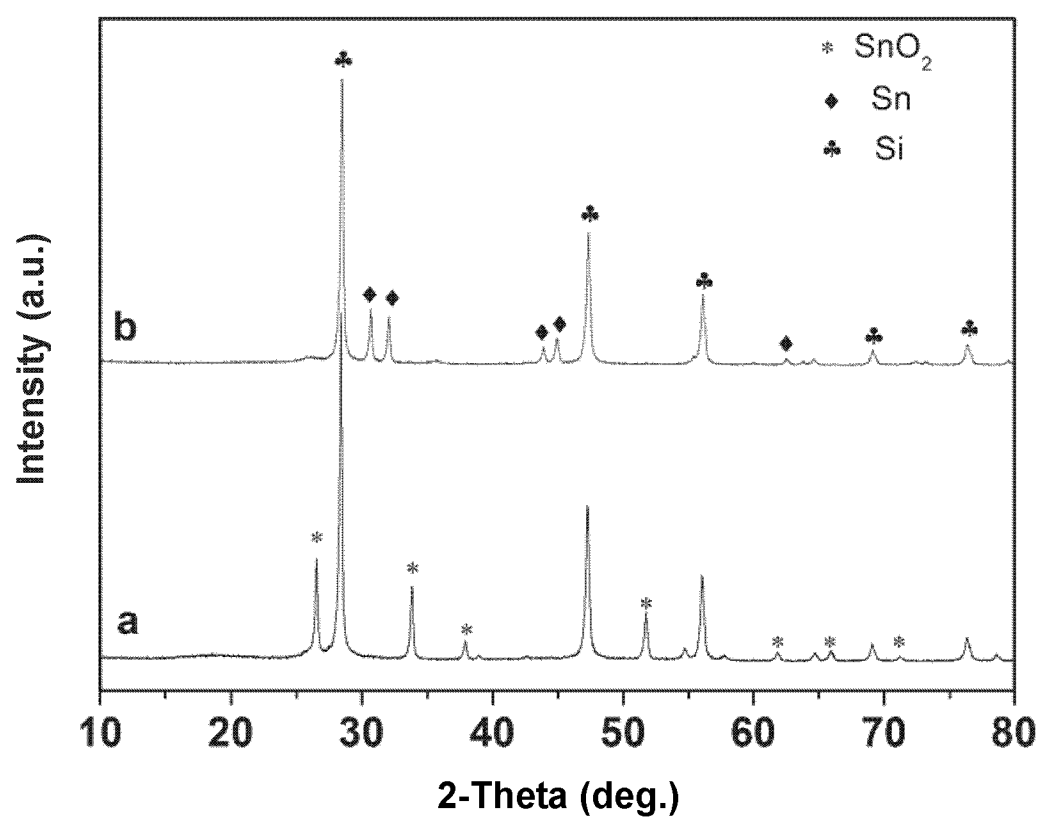
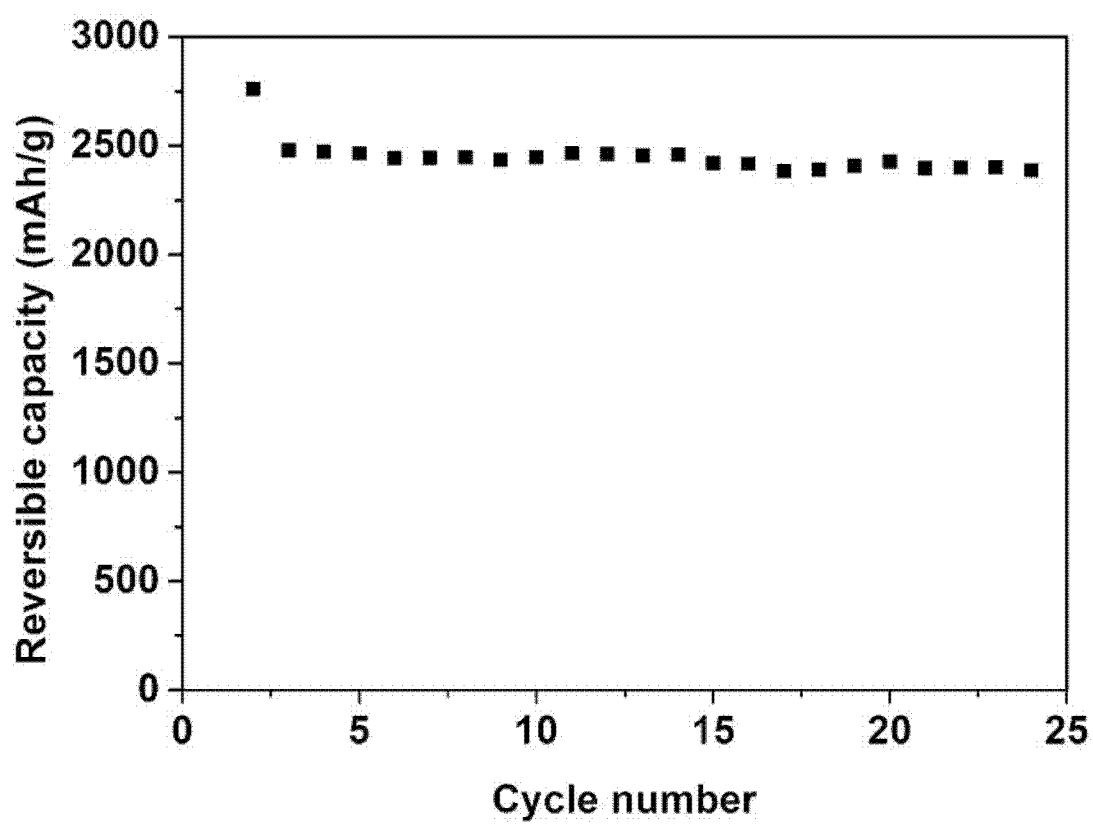
Fig. 14

Fig. 15

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/095288

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/134(2010.01)i; H01M 4/1395(2010.01)i; H01M 10/0525(2010.01)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

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

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

CNABS, CNTXT, VEN, google: composite, carbon, silicon, coat, spray, pyrolysis, Cu, Ni, Fe, Ti, Ge, Sn, Al, Mg, Ag, Zn, In, steel, precursor

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Jun Lai et al. "Preparation and characterization of flake graphite/silicon/carbon spherical composite as anode materials for lithium-ion batteries" <i>Journal of Alloys and Compounds</i> , Vol. VOLUME 530, 29 March 2012 (2012-03-29), ISSN: ISSN 0925-8388, pages 30-34	1-8, 11-21, 24-26
Y	Jun Lai et al. "Preparation and characterization of flake graphite/silicon/carbon spherical composite as anode materials for lithium-ion batteries" <i>Journal of Alloys and Compounds</i> , Vol. VOLUME 530, 29 March 2012 (2012-03-29), ISSN: ISSN 0925-8388, pages 30-34	9-12, 22-26
X	CN 101944592 A (GENG S) 12 January 2011 (2011-01-12) description, paragraphs [0011]-[0022]	1-10, 24-26
Y	CN 102630355 A (ENVIA SYSTEMS INC) 08 August 2012 (2012-08-08) description, paragraphs [0101]-[0135] and [0175]-[0189]	9-12, 22-26
X	CN 103094533 A (UNIV CENT SOUTH) 08 May 2013 (2013-05-08) description, paragraphs [0004]-[0036], and figures 1 and 2	1-8, 11-21, 24-26



Further documents are listed in the continuation of Box C.



See patent family annex.

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“&” document member of the same patent family

Date of the actual completion of the international search

02 July 2015

Date of mailing of the international search report

29 July 2015

Name and mailing address of the ISA/CN

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Telephone No. (86-10)62089424

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2014/095288**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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A	WO 2014030112 A1 (COMMISSARIAT ENERGIE ATOMIQUE) 27 February 2014 (2014-02-27) the whole document	1-26

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2014/095288

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