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(54) Title: PRODUCING METHOD OF SILICON NANOMATERIAL AND SILICON NANOMATERIAL THEREOF

(57) Abstract: The present disclosure relates to producing method of a silicon nanomaterial, a silicon nanomaterial produced thereby, an electrode including the silicon nanomaterial, and a battery including the electrode.



WO 2015/091968 A1

PRODUCING METHOD OF SILICON NANOMATERIAL AND
SILICON NANOMATERIAL THEREOF

This application claims priority to Korean Patent application No. 10-2013-0160718 filed on December 20th, 2013, the whole content of this application being incorporated herein by reference for all purposes.

FIELD OF THE INVENTION

5 The present disclosure relates to producing method of a silicon nanomaterial, a silicon nanomaterial produced thereby, an electrode including the silicon nanomaterial, and a battery including the electrode.

BACKGROUND OF THE INVENTION

10 As technology of mobile devices has been developed and the demand for mobile devices has increased, the demand for secondary batteries has also rapidly increased as an energy source for the mobile devices. Among them, a lithium-ion battery having high energy density and high action potential, extended cycle-life, and low self-discharge rate, which has been commercialized and widely used.

15 Further, in recent years, as attention to environmental issues has increased, there has been conducted a lot research on electric vehicles (EV) and hybrid electric vehicles (HEV) that can be substituted for vehicles using fossil fuels, such as gasoline vehicles and diesel vehicles, which are one of the major causes of air pollution. As a power source for such electric vehicles and hybrid electric
20 vehicles, nickel-metal hydride (Ni-MH) secondary batteries are mainly used. However, there has been actively conducted research on using lithium-ion batteries having high energy density, high discharge voltage, and output stability, and some lithium-ion batteries have been commercially available.

25 In lithium-ion secondary batteries, graphite-containing materials have been widely used as an anode active material. When a graphite-containing material releases lithium, an average potential is about 0.2 V (based on Li/Li⁺) and its potential changes in a relatively uniform manner during discharge. Therefore, the voltage of a battery is constantly high. However, a graphite material has a low electrical capacity per unit mass of about 372 mAh/g, but a capacity of a
30 graphite material is currently increased to be close to such a theoretical capacity. Therefore, it is difficult to further increase its capacity.

- 2 -

In order to further increase a capacity of a lithium-ion battery, various anode active materials have been studied. A material forming an intermetallic compound with lithium, such as silicon and tin, has been expected to be promising as an anode active material having a high capacity. In particular, silicon is an alloy-type anode material having a theoretical capacity (about 4,200 mAh/g) about ten times higher than that of graphite and has been drawing attention as an anode active material of a lithium-ion battery at present. Further, silicon is the second most abundant element in the Earth's crust (about 28% by mass), and thus, its mass production can be achieved at a relatively low cost. By way of example, Korean Patent Laid-open Publication No. 2012-0061941 describes a silicon oxide and an anode material for lithium-ion secondary battery.

However, silicon undergoes a great change in volume (~about 400%) during charge and discharge of a battery, and thus, a physical contact between elements is cut off and an ion conductivity, an electrical conductivity, and the like of silicon are sharply decreased. Therefore, an actual capacity tends to be sharply decreased. Accordingly, when silicon having a high theoretical capacity is applied to a lithium-ion battery, development of a technology for minimizing a volume change during charge and discharge is demanded.

BRIEF SUMMARY OF THE INVENTION

In view of the foregoing, the present disclosure provides a producing method of a silicon nanomaterial comprising: powderizing a colloid including a silica-containing material to obtain a powder including the silica-containing material; adding an alkaline earth metal to the powder including the silica-containing material to form a mixture; and heating the mixture to reduce a silica contained in the silica-containing material to a silicon, a silicon nanomaterial produced by the producing method, an electrode comprising the silicon nanomaterial, and a battery including the electrode.

However, the problems to be solved by the present disclosure are not limited to the above description and other problems can be clearly understood by those skilled in the art from the following description.

In accordance with a first aspect of the present disclosure, there is provided a producing method of a silicon nanomaterial including: powderizing a colloid including a silica-containing material to obtain a powder including the silica-containing material; adding an alkaline earth metal to the powder including the silica-containing material to form a mixture; and heating the mixture to reduce a silica contained in the silica-containing material to a silicon.

In accordance with a second aspect of the present disclosure, there is provided a silicon nanomaterial produced by the method of the first aspect of the present disclosure.

5 In accordance with a third aspect of the present disclosure, there is provided an electrode comprising the silicon nanomaterial of the second aspect of the present disclosure.

In accordance with a fourth aspect of the present disclosure, there is provided a battery comprising the electrode of the third aspect of the present disclosure as an anode, a cathode, and an electrolyte.

10 In a producing method in accordance with the present disclosure, it is possible to obtain a silicon nanomaterial in the form of a pure nanoscale silicon crystals from a colloid including a silica-containing material. Since silica is abundant in nature, it is easy to obtain a raw material, and thus, a silicon nanomaterial can be produced economically. Further, the silicon nanomaterial of
15 the present disclosure has high morphological anisotropy and can be easily hybridized with other materials than silica.

In particular, it is possible to obtain a silicon nanomaterial by powderizing a silica in a colloidal state, and it is possible to easily produce the silicon nanomaterial by reducing the silica to a silicon through a magnesiothermic
20 reaction. Further, by adding another material such as graphene oxide to the colloid and then reducing the silica together with the other material, it is possible to produce a silicon material hybridized with the other material.

When a silicon nanomaterial produced by the producing method of a silicon nanomaterial of the present disclosure is used as an electrode-forming
25 material for a battery, for example, a lithium-ion battery, the silicon nanomaterial has a high electrical conductivity and a high electrical capacity.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting and non-exhaustive embodiments will be described in conjunction with the accompanying drawings. Understanding that these
30 drawings depict only several embodiments in accordance with the disclosure and are, therefore, not to be intended to limit its scope, the disclosure will be described with specificity and detail through use of the accompanying drawings, in which :

Figs. 1a to 1c provide results of an X-ray diffraction analysis of a silicon
35 nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 2a to 2c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

5 Figs. 3a to 3c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 4a to 4c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

10 Figs. 5a to 5b provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Fig. 6a provides a result of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure, and Fig. 6b provides a capacity retention analysis graph of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

15 Fig. 7 provides a photo of silica-containing colloid and a powderized silica-containing material prepared in accordance with an example of the present disclosure;

20 Figs. 8a to 8c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 9a to 9c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

25 Figs. 10a to 10c provide an image of transmission electron microscopy (Fig. 10a), an image of high resolution transmission electron microscopy (Fig. 10b), and a selected area electron diffraction pattern (Fig. 10c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

30 Figs. 11a to 11c provide an image of transmission electron microscopy (Fig. 11a), an image of high resolution transmission electron microscopy (Fig. 11b), and a selected area electron diffraction pattern (Fig. 11c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 12a to 12c provide an image of transmission electron microscopy (Fig. 12a), an image of high resolution transmission electron microscopy (Fig. 12b), and a selected area electron diffraction pattern (Fig. 12c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 13a to 13c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

5 Figs. 14a to 14c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 15a to 15c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

10 Figs. 16a to 16c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 17a to 17c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

15 Figs. 18a to 18c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 19a to 19c provide an image of transmission electron microscopy (Fig. 19a), an image of high resolution transmission electron microscopy (Fig. 19b), and a selected area electron diffraction pattern (Fig. 19c) of a silicon
20 nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 20a to 20c provide an image of transmission electron microscopy (Fig. 20a), an image of high resolution transmission electron microscopy (Fig. 20b), and a selected area electron diffraction pattern (Fig. 20c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

25 Figs. 21a to 21c provide an image of transmission electron microscopy (Fig. 21a), an image of high resolution transmission electron microscopy (Fig. 21b), and a selected area electron diffraction pattern (Fig. 21c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

30 Figs. 22a to 22c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 23a to 23c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 24a to 24c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

5 Figs. 25a to 25c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 26a to 26c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

10 Figs. 27a to 27c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 28a to 28c provide an image of transmission electron microscopy (Fig. 28a), an image of high resolution transmission electron microscopy (Fig. 28b), and a selected area electron diffraction pattern (Fig. 28c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

15 Figs. 29a to 29c provide an image of transmission electron microscopy (Fig. 29a), an image of high resolution transmission electron microscopy (Fig. 29b), and a selected area electron diffraction pattern (Fig. 29c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

20 Figs. 30a to 30c provide an image of transmission electron microscopy (Fig. 30a), an image of high resolution transmission electron microscopy (Fig. 30b), and a selected area electron diffraction pattern (Fig. 30c) of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

25 Figs. 31a to 31c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 32a to 32b provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

30 Figs. 33a to 33c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 34a to 34c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure;

35 Figs. 35a to 35c provide results of an X-ray diffraction analysis of a silicon nanomaterial prepared in accordance with an example of the present disclosure;

Figs. 36a to 36c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure; and

5 Figs. 37a to 37c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial prepared in accordance with an example of the present disclosure.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, examples of the present disclosure will be described in detail with reference to the accompanying drawings so that the present disclosure may
10 be readily implemented by those skilled in the art. However, it is to be noted that the present disclosure is not limited to the examples but can be embodied in various other ways. In drawings, parts irrelevant to the description are omitted for simplicity of explanation, and like reference numerals denote like parts through the whole document.

15 Through the whole document, the term “comprises or includes” and/or “comprising or including” used in the document means that one or more other components, steps, operation and/or existence or addition of elements are not excluded in addition to the described components, steps, operation and/or elements unless context dictates otherwise.

20 The term “about or approximately” or “substantially” are intended to have meanings close to numerical values or ranges specified with an allowable error and intended to prevent accurate or absolute numerical values disclosed for understanding of the present disclosure from being illegally or unfairly used by any unconscionable third party. Through the whole document, the term “step of”
25 does not mean “step for”.

Through the whole document, the term “on” that is used to designate a position of one element with respect to another element includes both a case that the one element is adjacent to the another element and a case that any other element exists between these two elements.

30 Through the whole document, the term “combination of” included in Markush type description means mixture or combination of one or more components, steps, operations and/or elements selected from a group consisting of components, steps, operation and/or elements described in Markush type and thereby means that the disclosure includes one or more components, steps,
35 operations and/or elements selected from the Markush group.

Through the whole document, the term “A and/or B” means “A or B, or A and B”.

Hereinafter, illustrative embodiments and examples of the present disclosure will be explained in detail with reference to the accompanying drawings. However, the present disclosure may not be limited to the following illustrative embodiments and examples.

In accordance with a first aspect of the present disclosure, there may be provided a producing method of a silicon nanomaterial including: powderizing a colloid including a silica-containing material to obtain a powder including the silica-containing material; adding an alkaline earth metal to the powder including the silica-containing material to form a mixture; and heating the mixture to reduce a silica contained in the silica-containing material to a silicon.

By way of example, the heating the mixture to reduce a silica contained in the silica-containing material to a silicon may be carried out by means of, but may not be limited to, a magnesiothermic reaction. The magnesiothermic reaction includes a reaction for reducing a material to be reduced by heating a mixture of an alkaline earth metal, for example, magnesium, and the material to be reduced in a reducing atmosphere.

By heating the mixture to reduce a silica contained in the silica-containing material to a silicon, the silica may be reduced while the alkaline earth metal may be oxidized. An alkaline earth metal oxide may be formed from the oxidation of the alkaline earth metal, and the alkaline earth metal oxide may be dissolved in an acidic solution and washed away when etching by using the acidic solution is additionally carried out after the heating the mixture to reduce a silica, but it may not be limited thereto. By way of example, during etching the heated mixture by using the acidic solution, the alkaline earth metal oxide and other impurities are washed away and only the reduced silicon nanomaterial mainly remains, but the present illustrative embodiment may not be limited thereto.

By way of example, the silica-containing material may be a particle, a sheet, a layered sheet, a porous structure, or an amorphous structure, but the present illustrative embodiment may not be limited thereto.

By way of example, the silicon nanomaterial may be a particle, a sheet, a layered sheet, a sheet including mesopores, a layered sheet including mesopores, a porous structure, or an amorphous structure, but the present illustrative embodiment may not be limited thereto.

By way of example, since the silicon nanomaterial has a high specific surface area, a short moving route of a lithium ion, structural characteristics, and stability, the silicon nanomaterial can be used as an excellent electrode-forming material and can also be used as being hybridized with other materials, but the present illustrative embodiment may not be limited thereto. By way of example, the silicon nanomaterial can be hybridized with other materials such as a silicon sheet, and a conductive carbon compound. By way of example, the conductive carbon compound may be selected from the group consisting of carbon black, acetylene black, active carbon, carbon nanotube (CNT), graphite, graphene, and any combinations thereof. In a particular embodiment of the present invention, the silicon nanomaterial can be hybridized with graphene. By way of example, the hybridization may include a covalent bond, an ionic bond, an electrostatic interaction, or a van der Waals bond, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the powderizing a colloid including a silica-containing material may include restacking by adding an alkaline earth metal cation to the colloid including the silica-containing material, or freeze-drying the colloid including the silica-containing material, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the alkaline earth metal cation which is intended for this purpose may include at least one metal cation selected from the group consisting of Be, Mg, Ca, Sr, Ba, and their combinations. In a preferred embodiment of the present invention, the alkaline earth metal cation may include a magnesium cation, but the present illustrative embodiment may not be limited thereto.

By way of example, through the restacking or the freeze-drying, it is possible to obtain the silica-containing material by powderizing the silica-containing material in a colloidal state which cannot be easily obtained in the form of powder, but the present illustrative embodiment may not be limited thereto.

By way of example, the specific surface area of the silicon nanomaterial may be increased by, but may not be limited to, the restacking or freeze-drying. If the specific surface area of the silicon nanomaterial is increased, there is an increase in area where an interaction with an electrolyte occurs. Therefore, performance of a battery, in particular lithium-ion battery, comprising the silicon

- 10 -

nanomaterial can be improved, but the illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the colloid including the silica-containing material may be formed by using a colloidal silica or formed by exfoliating a layered silica-containing material, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the colloid including the silica-containing material may further include a graphene oxide, preferably in a form of nanosheet, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the producing method of a silicon nanomaterial may further include: powderizing the colloid including a silica-containing material further including the graphene oxide to obtain a powder including the silica-containing material and the graphene oxide; adding an alkaline earth metal to the powder to form a mixture; and heating the mixture to reduce a silica contained in the silica-containing material and the graphene oxide to form a composite including a silicon and a graphene, but the present illustrative embodiment may not be limited thereto.

By way of example, if the graphene oxide is further included in the colloid including a silica-containing material, during the reduction process, the silica and the graphene oxide may respectively reduced to silicon and graphene at the same time, and the silicon and the graphene may be hybridized with each other, but the present illustrative embodiment may not be limited thereto. In this case, the silicon nanomaterial may include, but may not be limited to, a silicon-graphene hybrid. By way of example, hybridizing the silicon with the graphene may include, but may not be limited to, forming a covalent bond between the silicon and the graphene.

By way of example, the composite including the silicon and the graphene may be a hybrid of a nanosheet of the silicon and a nanosheet of the graphene, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, at least one of the silicon and the graphene contained in the composite may be in a form of a sheet, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the alkaline earth metal may include magnesium, but the present illustrative embodiment may not be limited thereto.

By way of example, an average particle size of the silicon nanomaterial
5 may be, but may not be limited to, from 10 nm to about 400 nm, from about 30 nm to about 400 nm, from about 50 nm to about 400 nm, from about 80 nm to about 400 nm, from about 100 nm to about 400 nm, from about 150 nm to about 400 nm, from about 200 nm to about 400 nm, from about 250 nm to about 400 nm, from about 300 nm to about 400 nm, from about 350 nm to about 400 nm,
10 from about 10 nm to about 350 nm, from about 10 nm to about 300 nm, from about 10 nm to about 250 nm, from about 10 nm to about 200 nm, from about 10 nm to about 150 nm, from about 10 nm to about 100 nm, from about 10 nm to about 80 nm, from about 10 nm to about 50 nm, from about 10 nm to about 30 nm, from about 100 nm to about 300 nm, from about 100 nm to about 200 nm, or
15 from about 100 nm to about 150 nm.

In accordance with an illustrative embodiment of the present disclosure, the alkaline earth metal may be in the form of powder, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure,
20 the heating may be performed at a temperature of, but may not be limited to, from about 300°C to about 1000°C, from about 400°C to about 800°C, or from about 550°C to about 750°C. By way of example, the heating may be performed at a temperature of, but may not be limited to, from about 300°C to about 1000°C, from about 400°C to about 1000°C, from about 500°C to about 1000°C,
25 from about 600°C to about 1000°C, from about 700°C to about 1000°C, from about 800°C to about 1000°C, from about 900°C to about 1000°C, from about 300°C to about 900°C, from about 300°C to about 800°C, from about 300°C to about 700°C, from about 300°C to about 600°C, from about 300°C to about 500°C, from about 300°C to about 400°C, or from about 400°C to about 800°C.

30 In accordance with an illustrative embodiment of the present disclosure, the producing method of a silicon nanomaterial may further include: after reducing the silica to the silicon, etching the silicon by using an acidic solution to obtain the silicon nanomaterial, but the present disclosure may not be limited thereto.

35 By way of example, the silica-containing material may further include, but may not be limited to, a metallic or nonmetallic element, a metallic or

- 12 -

nonmetallic oxide, a metallic or nonmetallic compound, or a metallic or nonmetallic ion in addition to silica. By way of example, the etching the silicon is carried out to remove impurities containing metals or nonmetals contained in the silicon nanomaterial produced from the silica-containing material, and by the etching the silicon, it is possible to separate and obtain a pure silicon nanomaterial only, but the present illustrative embodiment may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the acidic solution may have, but may not be limited to, a pH of 6 or less, or a pH of 3 or less. By way of example, the acidic solution may have a pH of, but may not be limited to, about 6 or less, about 5 or less, about 4 or less, about 3 or less, about 2 or less or about 1 or less.

In accordance with an illustrative embodiment of the present disclosure, the acidic solution may include, but may not be limited to, an inorganic acid.

In accordance with an illustrative embodiment of the present disclosure, the inorganic acid may include, but may not be limited to, an acid selected from the group consisting of hydrochloric acid, nitric acid, sulfuric acid, phosphoric acid, hydrofluoric acid, perchloric acid, chloric acid, chlorous acid, hypochlorous acid, iodic acid, and combinations thereof.

In accordance with an illustrative embodiment of the present disclosure, the heating the mixture may be performed in an atmosphere including an inert gas, but the present illustrative embodiment may not be limited thereto. By way of example, the inert gas may include, but may not be limited to, a gas selected from the group, but may not be limited to, consisting of a nitrogen gas, an argon gas, a neon gas, a helium gas, and their combinations.

In accordance with an illustrative embodiment of the present disclosure, the heating the mixture may be performed in a reducing atmosphere, but the present illustrative embodiment may not be limited thereto. By way of example, the reducing atmosphere may include, but may not be limited to, a hydrogen gas and an inert gas.

In accordance with an illustrative embodiment of the present disclosure, the colloid including the silica-containing material may be formed by exfoliating a clay, but the present illustrative embodiment may not be limited thereto. By way of example, the exfoliating a clay may be carried out by stirring and/or ultrasonication in an aqueous solution, but the present illustrative embodiment

- 13 -

may not be limited thereto. A method for the exfoliating a clay may be, but may not be limited to, a simple process.

In accordance with an illustrative embodiment of the present disclosure, the clay may include, but may not be limited to, a layered clay.

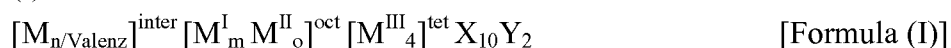
5 By way of example, if the clay includes a silicate mineral, silicon tetrahedrons are bonded in their own ways and form an intrinsic crystalline form. The silicon nanomaterial obtained from the clay may have, but may not be limited to, the intrinsic crystalline form of the used clay. For example, if the layered clay contains a layered silicate mineral, a silicon nanomaterial produced
10 from the layered silicate mineral having an intrinsic bonding in a layered manner may include a layered structure originated from the crystalline form of the layered silicate mineral. However, the present disclosure may not be limited thereto. By way of example, the silica-containing material may be formed by exfoliating the clay and may be in the form of a sheet exfoliated from the clay,
15 but the present disclosure may not be limited thereto.

By way of example, the clay may be, but may not be limited to, an oxide having a layered structure including metal and silicon. By way of example, the metal is not limited in kind, and may include, for example, but not limited to, magnesium, sodium, lithium, or aluminum. The clay is cheap and easily
20 available and includes layered silica (SiO_2), and thus, it is possible to easily and economically prepare a silicon nanomaterial by reducing the silica. By way of example, the metal contained in the clay may be removed during the step of etching by using the acidic solution, but the present illustrative embodiment may not be limited thereto.

25 In accordance with an illustrative embodiment of the present disclosure, the layered clay may include, but may not be limited to, a layered silicate mineral.

In accordance with an illustrative embodiment of the present disclosure, the layered silicate mineral may include, but may not be limited to, a
30 phyllosilicate.

In accordance with an illustrative embodiment of the present disclosure, the phyllosilicate may be represented by, but may not be limited to, a formula (I):



35 wherein

M is a metal cation having oxidation state of from 1 to 3,

- 14 -

MI is a metal cation having oxidation state of 2 or 3,

MII is a metal cation having oxidation state of 1 or 2,

MIII is an atom having oxidation state of 3 or 4,

X is a dianion,

5 Y is a monoanion,

$M \leq 2.0$ for a metal atom MI having the oxidation state 3, and $m \leq 3.0$ for a metal atom MI having the oxidation state of 2,

$O \leq 1.0$, and

a layer charge n is from 0.2 to 0.8.

10 In accordance with an illustrative embodiment of the present disclosure, the phyllosilicate may include, but may not be limited to, a material selected from the group consisting of talc, mica, smectite clays, magadiite, kenyaite, stevensite, halloysite, aluminate oxide, hydrotalcite, and combinations thereof.

The talc is represented by a chemical formula of $\text{Mg}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$. In a
15 crystalline form of the talc, a sheet ($\text{Mg}_{12}\text{O}_{12}\text{H}_4$) containing magnesium is interposed between two silica (SiO_2) sheets. These three sheets are bonded to form a single layer. The single layer is electrically neutral. Respective layers are bonded to each other by a weak van der Waals force.

The laponite also has a structure very similar to the talc. In the laponite, a
20 sheet containing magnesium is interposed between two silica sheets. However, unlike the talc, a part of magnesium in the magnesium sheet of the laponite is substituted with lithium, and thus, respective layers are negatively charged. Therefore, in order to maintain an electrically neutral state overall, sodium (Na) cations are included between the respective layers and the respective layers are
25 bonded to each other by an electrical interaction.

In accordance with an illustrative embodiment of the present disclosure, the smectite clays may include, but may not be limited to, a material selected from the group consisting of montmorillonite, nontronite, beidellite, bentonite, hectorite, laponite, saponite, sauconite, vermiculite, and their combinations.

30 In accordance with an illustrative embodiment of the present disclosure, a mole ratio of the silicon included in the silica-containing material to the alkaline earth metal may be, but may not be limited to, from 1 : 0.1 to 1 : 10 or from 1 : 0.5 to 1 : 5. By way of example, a mole ratio of a silicon included in the silica-containing material to the alkaline earth metal may be, but may not be limited to,
35 from about 1 : 0.1 to about 1 : 10, from about 1 : 0.1 to about 1 : 9, from about 1 : 0.1 to about 1 : 8, from about 1 : 0.1 to about 1 : 7, from about 1 : 0.1 to about

1 : 6, from about 1 : 0.1 to about 1 : 5, from about 1 : 0.1 to about 1 : 4, from about 1 : 0.1 to about 1 : 3, from about 1 : 0.1 to about 1 : 2, from about 1 : 0.1 to about 1 : 1, from about 1 : 0.1 to about 1 : 0.5, from about 1 : 0.5 to about 1 : 10, from about 1 : 1 to about 1 : 10, from about 1 : 2 to about 1 : 10, from about 1 : 3 to about 1 : 10, from about 1 : 4 to about 1 : 10, from about 1 : 5 to about 1 : 10, from about 1 : 6 to about 1 : 10, from about 1 : 7 to about 1 : 10, from about 1 : 8 to about 1 : 10, or from about 1 : 9 to about 1 : 10.

In accordance with an illustrative embodiment of the present disclosure, the producing method of a silicon nanomaterial may further include: after the heating the mixture to reduce a silica contained in the silica-containing material to a silicon, stirring and/or washing the reduced silicon, but the present disclosure may not be limited thereto.

In accordance with an illustrative embodiment of the present disclosure, the stirring and/or washing may be performed by using, but may not be limited to, a polar solvent.

In accordance with an illustrative embodiment of the present disclosure, the polar solvent may include, but may not be limited to, one selected from the group consisting of water, alcohol, an organic polar solvent, and combinations thereof.

In accordance with an illustrative embodiment of the present disclosure, the silicon nanomaterial may be in the form of, but may not be limited to, a particle or sheet.

In accordance with a second aspect of the present disclosure, there may be provided a silicon nanomaterial produced by the method of the first aspect of the present disclosure. The silicon nanomaterial of the present aspect may include all descriptions of the first aspect of the present disclosure.

In accordance with an illustrative embodiment of the present disclosure, the silicon nanomaterial may include, but may not be limited to, a hybridized graphene. By way of example, if the silicon nanomaterial including the hybridized graphene is included in an electrode of a battery, in particular an anode of lithium-ion battery, the anode may have, but may not be limited to, excellent electrical conductivity, electrical capacity, and stability. By way of example, since the silicon nanomaterial including the hybridized graphene may include mesopores and has a large surface area, the silicon nanomaterial may be used as, but may not be limited to, an excellent electrode material for secondary batteries.

In accordance with a third aspect of the present disclosure, there may be provided a composite comprising a silicon nanosheet and a graphene nanosheet. The composite of the present aspect may include all descriptions of the first aspect and the second aspect of the present disclosure.

5 In accordance with a forth aspect of the present disclosure, there may be provided an electrode including the silicon nanomaterial of the second aspect of the present disclosure or the composite of the third aspect of the present disclosure. The electrode of the present aspect may include all descriptions of the first aspect to the third aspect of the present disclosure. By way of example,
10 the electrode can be used for battery, in particular lithium batteries, such as lithium-ion battery, lithium air battery, and lithium sulfur battery, or sodium batteries, such as sodium ion battery, and sodium sulfur battery, but the present invention is not limited thereto. By way of example, the silicon nanomaterial or the composite may be included as, but may not be limited to, an anode active
15 material of a lithium-ion battery.

By way of example, if the silicon nanomaterial of the present disclosure is included in an electrode, since the silicon nanomaterial or the composite has characteristics such as excellent electrical conductivity, electrical capacity, and stability, it can offer, but may not be limited to, an electrode material having an
20 excellent electrical characteristic.

In accordance with a fifth aspect of the present disclosure, there may be provided a battery including the electrode of the forth aspect of the present disclosure as an anode, a cathode, and an electrolyte. The battery of the present aspect may include all descriptions of the first aspect to the forth aspect of the
25 present disclosure.

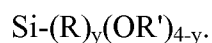
In accordance with an illustrative embodiment of the present disclosure, the battery may be, but may not be limited to, a lithium-ion battery. A lithium-ion battery can be applied in various fields due to its high energy density, high voltage, high discharge speed, fast charge speed, extended service-life, high
30 storage capacity, and high stability. By way of example, the lithium-ion battery may be applied to, but may not be limited to, medical instruments, smartphones, tablet PCs, notebook computers, motor cycles, vehicles, and the like.

In accordance with an illustrative embodiment of the present disclosure, the cathode may include, but may not be limited to, one selected from the group
35 consisting of a lithium-containing oxide, a lithium-containing sulfide, a lithium-containing selenide, a lithium-containing halide, and combinations thereof.

In accordance with an illustrative embodiment of the present disclosure, the lithium-containing oxide may include, but may not be limited to, one selected from the group consisting of Li_xCoO_2 ($0.5 < x < 1.3$), Li_xNiO_2 ($0.5 < x < 1.3$), Li_xMnO_2 ($0.5 < x < 1.3$), $\text{Li}_x\text{Mn}_2\text{O}_4$ ($0.5 < x < 1.3$), $\text{Li}_x(\text{Ni}_a\text{Co}_b\text{Mn}_c)\text{O}_2$ ($0.5 < x < 1.3$, $0 < a < 1$, $0 < b < 1$, $0 < c < 1$, $a+b+c=1$), $\text{Li}_x\text{Ni}_{1-y}\text{Co}_y\text{O}_2$ ($0.5 < x < 1.3$, $0 < y < 1$), $\text{Li}_x\text{Co}_{1-y}\text{Mn}_y\text{O}_2$ ($0.5 < x < 1.3$, $0 \leq y < 1$), $\text{Li}_x\text{Ni}_{1-y}\text{Mn}_y\text{O}_2$ ($0.5 < x < 1.3$, $0 \leq y < 1$), $\text{Li}_x(\text{Ni}_a\text{Co}_b\text{Mn}_c)\text{O}_4$ ($0.5 < x < 1.3$, $0 < a < 2$, $0 < b < 2$, $0 < c < 2$, $a+b+c=2$), $\text{Li}_x\text{Mn}_{2-z}\text{Ni}_z\text{O}_4$ ($0.5 < x < 1.3$, $0 < z < 2$), $\text{Li}_x\text{Mn}_{2-z}\text{Co}_z\text{O}_4$ ($0.5 < x < 1.3$, $0 < z < 2$), Li_xCoPO_4 ($0.5 < x < 1.3$), Li_xFePO_4 ($0.5 < x < 1.3$), and combinations thereof.

In accordance with another illustrative embodiment of the present disclosure, the cathode may include at least one cathode active material which can insert and de-insert sodium, particularly sodium-containing compound, such as sodium-metal mixed oxides. Examples of the cathode active material in the present invention include NaFeO_2 , NaCoO_2 , NaCrO_2 , NaMnO_2 , NaNiO_2 , $\text{NaNi}_{1/2}\text{Ti}_{1/2}\text{O}_2$, $\text{NaNi}_{1/2}\text{Mn}_{1/2}\text{O}_2$, $\text{Na}_{2/3}\text{Fe}_{1/3}\text{Mn}_{2/3}\text{O}_2$, $\text{NaNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, NaMn_2O_4 , $\text{NaNi}_{1/2}\text{Mn}_{3/2}\text{O}_2$, NaFePO_4 , NaMnPO_4 , NaCoPO_4 , $\text{Na}_2\text{FePO}_4\text{F}$, $\text{Na}_2\text{MnPO}_4\text{F}$, $\text{Na}_2\text{CoPO}_4\text{F}$, and any combination thereof, but the present invention is not limited thereto.

By way of example, the electrolyte may include, but may not be limited to, conventional lithium salt and solvent. By way of example, the lithium secondary battery may include, but may not be limited to, an electrolyte containing a silane-based compound represented by the following chemical formula as an additive.



In the above chemical formula, R is an alkyl group or a vinyl group, R' is an alkyl group or an alkyl group substituted for an alkoxy group, and y is an integer selected from 1 to 3.

In the above chemical formula, the alkyl group may be, but may not be limited to, a C_1 - C_{30} alkyl group, and the vinyl group may be, but may not be limited to, C_2 - C_{20} vinyl group. The silane-based compound may be represented by $\text{Si}-(\text{R})_1(\text{OR}')_3$ and may include, but may not be limited to, trimethoxy(methyl)silane ($\text{SiCH}_3(\text{OCH}_3)_3$) or tris(2-methoxyethoxy)vinylsilane ($\text{CH}_2=\text{CHSi}(\text{OCH}_2\text{CH}_2\text{OCH}_2)_3$).

The electrolyte containing the above-described silane-based compound may include a silane-based compound of, but may not be limited to, from about 2 wt% to about 10 wt%. In this case, an inherent function of the electrolyte can be maintained and formation of a protection layer on a surface of a silicon oxide

may be induced efficiently, which may be more advantageous. However, the present disclosure may not be limited thereto.

By way of example, the electrolyte may include, but may not be limited to, an electrolyte including a lithium salt selected from the group consisting of
5 LiTFSi, LiPF₆, LiFSi, and their combinations and a non-aqueous carbonate-based solvent, or a lithium salt selected from the group consisting of LiTFSi, LiPF₆, LiFSi, and their combinations and a room temperature ionic liquid solvent selected from the group consisting of an imidazolium-based solvent, a pyrrolidinium-based solvent, and a piperidinium-based solvent. In a particular
10 embodiment of the present disclosure, the electrolyte may comprise LiPO₂F₂ optionally in combination with one or more above-described lithium salts.

In accordance with an illustrative embodiment of the present disclosure, the electrolyte may comprise at least one solvent additives, in particular fluorinated organic compounds, for example, fluorinated carbonic esters which
15 are selected from the group of fluorosubstituted ethylene carbonates, polyfluorosubstituted dimethyl carbonates, fluorosubstituted ethyl methyl carbonates, and fluorosubstituted diethyl carbonates. Preferred fluorosubstituted carbonates are monofluoroethylene carbonate (F1EC), 4,4-difluoro ethylene carbonate, 4,5-difluoro ethylene carbonate, 4-fluoro-4-methyl ethylene carbonate,
20 4,5-difluoro-4-methyl ethylene carbonate, 4-fluoro-5-methyl ethylene carbonate, 4,4-difluoro-5-methyl ethylene carbonate, 4-(fluoromethyl)-ethylene carbonate, 4-(difluoromethyl)-ethylene carbonate, 4-(trifluoromethyl)-ethylene carbonate, 4-(fluoromethyl)-4-fluoro ethylene carbonate, 4-(fluoromethyl)-5-fluoro ethylene carbonate, 4-fluoro-4,5-dimethyl ethylene carbonate, 4,5-difluoro-4,5-dimethyl
25 ethylene carbonate, and 4,4-difluoro-5,5-dimethyl ethylene carbonate ; dimethyl carbonate derivatives including fluoromethyl methyl carbonate, difluoromethyl methyl carbonate, trifluoromethyl methyl carbonate, bis(difluoro)methyl carbonate, and bis(trifluoro)methyl carbonate ; ethyl methyl carbonate derivatives including 2-fluoroethyl methyl carbonate, ethyl fluoromethyl
30 carbonate, 2,2-difluoroethyl methyl carbonate, 2-fluoroethyl fluoromethyl carbonate, ethyl difluoromethyl carbonate, 2,2,2-trifluoroethyl methyl carbonate, 2,2-difluoroethyl fluoromethyl carbonate, 2-fluoroethyl difluoromethyl carbonate, and ethyl trifluoromethyl carbonate ; and diethyl carbonate derivatives including ethyl (2-fluoroethyl) carbonate, ethyl (2,2-difluoroethyl) carbonate, bis(2-
35 fluoroethyl) carbonate, ethyl (2,2,2-trifluoroethyl) carbonate, 2,2-difluoroethyl 2'-fluoroethyl carbonate, bis(2,2-difluoroethyl) carbonate, 2,2,2-trifluoroethyl 2'-

fluoroethyl carbonate, 2,2,2-trifluoroethyl 2',2'-difluoroethyl carbonate, and bis(2,2,2-trifluoroethyl) carbonate, 4-fluoro-4-vinylethylene carbonate, 4-fluoro-5-vinylethylene carbonate, 4,4-difluoro-4-vinylethylene carbonate, 4,5-difluoro-4-vinylethylene carbonate, 4-fluoro-4,5-divinylethylene carbonate, 4,5-difluoro-4,5-divinylethylene carbonate, 4-fluoro-4-phenylethylene carbonate, 4-fluoro-5-phenylethylene carbonate, 4,4-difluoro-5-phenylethylene carbonate, 4,5-difluoro-4-phenylethylene carbonate and 4,5-difluoro-4,5-diphenylethylene carbonate, fluoromethyl phenyl carbonate, 2-fluoroethyl phenyl carbonate, 2,2-difluoroethyl phenyl carbonate and 2,2,2-trifluoroethyl phenyl carbonate, fluoromethyl vinyl carbonate, 2-fluoroethyl vinyl carbonate, 2,2-difluoroethyl vinyl carbonate and 2,2,2-trifluoroethyl vinyl carbonate, fluoromethyl allyl carbonate, 2-fluoroethyl allyl carbonate, 2,2-difluoroethyl allyl carbonate and 2,2,2-trifluoroethyl allyl carbonate.

The electrolyte may be, but may not be limited to, a room temperature ionic liquid solvent that does not include a lithium salt of LiPF_6 . If a room temperature ionic liquid solvent does not include a lithium salt of LiPF_6 , there is no interfacial reaction between a silicon oxide included in an anode and a LiPF_6 derivative. Further, the room temperature ionic liquid solvent forms a stable SEI (solid electrolyte interphase) layer on a surface of a thin film of a silicon oxide during an initial charge/discharge process and suppresses a future interfacial reaction with the electrolyte. Thus, a charge/discharge cycling performance can be stable.

The solvent is not particularly limited in kind as long as it is typically used in the art, and may include a non-aqueous carbonate-based solvent in addition to the room temperature ionic liquid solvent. If the electrolyte includes the non-aqueous carbonate-based solvent, the electrolyte may include, but may not be limited to, about 5 to 70 parts by weight of the non-aqueous carbonate-based solvent on the basis of 100 parts by weight of the room temperature ionic liquid solvent. In this case, flame retardancy of the ionic liquid solvent can be maintained or ignition can be suppressed, which may be advantageous. However, the present disclosure may not be limited thereto.

The non-aqueous carbonate-based solvent may include, but may not be limited to, dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethylmethyl carbonate (EMC).

The lithium secondary battery includes a silicon nanomaterial produced by the silicon nanomaterial producing method of the present disclosure as an anode

- 20 -

material. The silicon nanomaterial may undergo little change in volume during charge and discharge and may have a high ion conductivity, a high electrical conductivity, and a high capacity.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

Hereinafter, examples of the present disclosure will be explained in detail, but the present disclosure may not be limited thereto.

10 [Examples]

<Example 1: Preparation of silicon nanomaterial from laponite (Restacking)>

500 mL of a laponite suspension including laponite dispersed in distilled water at a concentration of 2 g/L was stirred for 12 hours to exfoliate the laponite. Then, Mg^{2+} was added to colloid containing the exfoliated laponite to restack the exfoliated laponite. To be specific, since the laponite contained Na^+ ions between layers, a Mg^{2+} amount having a sufficient electric charge to substitute the total Na^+ ion was calculated, and then MgCl_2 about twice that amount, i.e. excessive MgCl_2 , was added to the colloid. In the present example, 20 mL of 3.5 M MgCl_2 aqueous solution was added to 100 mL of the colloid containing 0.2 g of the laponite and restacking was carried out with stirring for 12 hours, thereby powderizing the colloid.

The restacked powder was obtained, a ratio of SiO_2 : Mg was determined, and the restacked powder was mixed with the restacked powder with Mg powder. To be specific, a molar amount of the silicon was calculated and the Mg powder was mixed at a ratio of 1 : 2 (SiO_2 : Mg) with respect to the molar amount of the silicon and then ground and mixed in a mortar. Thereafter, the mixture was put into a self-produced tube furnace and heated at a heating rate of $3.3^\circ\text{C}/\text{min}$ to reduce the silica contained in the mixture by a magnesiothermic reaction under an atmosphere of 5% H_2 /95% Ar. A heating temperature for reduction varied in the range of from about 500°C to about 650°C . After the reduction was completed, the mixture was taken out and etched with a 0.5 M hydrochloric acid solution in an amount of 500 mL per 1 g of the mixture with stirring for 24 hours. Then, the etching solution used was removed by centrifugation, and the mixture was stirred again with 500 mL of a new 0.5 M hydrochloric acid solution for 24 hours. Thereafter, the etching solution used was removed by centrifugation, and

then, the mixture was washed with distilled water. Subsequently, the mixture was dried in a vacuum at 200°C for 12 hours.

<Example 2: Preparation of silicon nanomaterial from laponite (Freeze-drying)>

5 A process for stirring 100 mL of a laponite suspension including laponite at a concentration of 5 g/L for 24 hours and dispersing the laponite suspension by using an ultrasonic homogenizer (5510, Branson) for 1 hour was repeated twice to exfoliate the laponite. Then, colloid containing the exfoliated laponite was freeze-dried for 5 days to be powderized. To be specific, the colloid was
10 quickly cooled with a liquid nitrogen and then freeze-dried at -75°C and 5 mTorr within a freeze dryer (Ilsin Boibase Freeze Dryer FD8508).

 The freeze-dried powder was obtained, a molar ratio of SiO_2 : Mg was determined as 1 : 2, and the freeze-dried powder was mixed with Mg powder according to the predetermined ratio. Thereafter, the mixture was put into a self-
15 produced tube furnace and heated at a heating rate of 3.3°C/min to reduce the silica contained in the mixture by a magnesiothermic reaction. A heating temperature for reduction varied in the range of from about 550°C to about 650°C. After the reduction was completed, the mixture was taken out and etched with a 0.5 M hydrochloric acid solution in an amount of 500 mL per 1 g of the
20 mixture with stirring for 24 hours. Then, the etching solution used was removed by centrifugation, and the mixture was stirred again with 500 mL of a new 0.5 M hydrochloric acid solution for 24 hours. Thereafter, the etching solution used was removed by centrifugation, and then, the mixture was washed with distilled water. Subsequently, the mixture was dried in a vacuum at 200°C for 12 hours.

25 **<Example 3: Characteristic analysis of silicon nanomaterial prepared from laponite>**

 In the present example, characteristics of a silicon nanomaterial prepared were analyzed by an X-ray diffraction analysis method (a powder X-ray diffraction analyzer D/max 2000vk, Rigaku). Although silicon nanomaterials
30 were obtained by the methods of Examples 1 and 2, the silicon nanomaterials might contain impurities or crystallinity might be changed depending on a heat treatment condition and a molar ratio of Si : Mg. Therefore, such characteristics were analyzed by the X-ray diffraction analysis method.

 Figs. 1a to 1c provide graphs showing results of an X-ray diffraction
35 analysis of a silicon nanomaterial obtained by powderizing colloid including a silica-containing material from laponite by a restacking method, reducing the

powderized colloid by a magnesiothermic reaction, and etching the resultant product. Figs. 1a to 1c show diffraction patterns of silicon nanomaterials obtained by performing a heat treatment at 550°C for 6 hours as shown in Fig. 1a, at 600°C for 1 hour as shown in Fig. 1b, and at 650°C for 3 hours as shown in Fig. 1c, at a molar ratio of SiO₂ : Mg of 1 : 2. In Figs. 1a and 1b, a wide and gentle peak regarded as an amorphous silicon oxide was observed between 20° and 30° together with apparent peaks of silicon. In Fig. 1c, small peaks presumed to be impurities were observed together with apparent silicon peaks.

Figs. 2a to 2c provide graphs showing results of an X-ray diffraction analysis of a silicon material obtained by powderizing colloid including a silica-containing material from laponite by a restacking method and reducing the powderized colloid by a magnesiothermic reaction without etching. Figs. 2a to 2c show diffraction patterns of silicon materials obtained by performing a heat treatment at 550°C for 6 hours as shown in Fig. 2a, at 600°C for 1 hour as shown in Fig. 2b, and at 650°C for 3 hours as shown in Fig. 2c, at a molar ratio of Si : Mg of 1 : 2. It was observed from Figs. 2a to 2c that the laponite-restacked material was changed to a material containing a silicon nanomaterial, MgO, MgSi₂, and some impurities through a magnesiothermic reaction.

From the above experiment results, it was confirmed that most of the impurities in the reduced silicon material were removed by performing the etching process and only the silicon nanomaterials usually remained.

An electrochemical characteristic was analyzed by conducting an experiment with a Maccor 2000 series charger/discharger in a potential range of from 0.01 V to 1 V at 210 mA/g (0.05°C). Herein, 3 vol% of F1EC as an additive for increasing stability of an anode was added to 1 M LiPF₆ (in EC/DEC 1:1 volume ratio) as an electrolyte.

Figs. 3a to 3c provide graphs showing results of measuring electrochemical characteristics of a silicon nanomaterial obtained by powderizing colloid including a silica-containing material from laponite by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6 hours, and etching the resultant product. Fig. 3a is a graph showing a measurement result of capacity retention, Fig. 3b is a graph showing a measurement result of rate capability, and Fig. 3c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 6% was observed after 18 cycles.

Figs. 4a to 4c provide graphs showing results of measuring electrochemical characteristics of a silicon nanomaterial obtained by powderizing colloid including a silica-containing material from laponite by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. Fig. 4a is a graph showing a measurement result of capacity retention, Fig. 4b is a graph showing a measurement result of rate capability, and Fig. 4c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 4% was observed after 17 cycles.

Figs. 5a and 5b provide graphs showing results of measuring electrochemical characteristics of a silicon nanomaterial obtained by powderizing colloid including a silica-containing material from laponite by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. Fig. 5a is a graph showing a measurement result of capacity retention and Fig. 5b is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 70% was observed after 50 cycles.

Fig. 6a provides a result of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including a silica-containing material from laponite by a freeze-drying method, reducing the powderized colloid by a magnesiothermic reaction with different temperatures and times, and etching the resultant product. The upper graph shows a diffraction pattern of a silicon material obtained by performing a heat treatment at 550°C for 3 hours, and reducing and etching the resultant product, the intermediate graph shows a diffraction pattern of a silicon material obtained by performing a heat treatment at 525°C for 6 hours, and reducing and etching the resultant product, and the lower graph shows a diffraction pattern of a silicon material obtained by performing a heat treatment at 525°C for 3 hours, and reducing and etching the resultant product. From the diffraction patterns of the silicon materials reacted at 525°C for 3 hours, and at 525°C for 6 hours, a wide and gentle peak regarded as an amorphous silicon oxide was observed between 20° and 30° together with apparent silicon peaks. From the diffraction pattern of the silicon material reacted at 550°C for 3 hours, apparent silicon peaks were observed.

Fig. 6b provides a capacity retention analysis graph of a silicon nanomaterial obtained by powderizing colloid including silica-containing

- 24 -

material from laponite by a freeze-drying method, reducing the powderized colloid by a magnesiothermic reaction at 525°C for 6 hours, and etching the resultant product. A ratio of Si : Mg was 1 : 2, and F1EC was not used. The silicon nanomaterial obtained by the freeze-drying method had a low capacity
5 but exhibited a high stability as compared with the silicon nanomaterial obtained by the restacking method.

<Example 4: Preparation of silicon nanomaterial from laponite and graphene oxide (Restacking)>

500 mL of a laponite suspension including laponite at a concentration of 2
10 g/L was stirred for 18 hours to exfoliate the laponite. Then, a suspension containing graphene oxide of 0.05 wt% and prepared by a modified Hummer's method was added to colloid containing the exfoliated laponite. An amount of the graphene oxide added to the colloid containing the exfoliated laponite was determined by comparing a weight of silicon contained in the laponite. The
15 laponite contained SiO₂ of 59.5 wt%, and the SiO₂ contained silicon of 46.7 wt%. Therefore, the laponite contained silicon of 27.8 wt%. In consideration of this, the graphene oxide was added after calculation of a weight to be 10%, 7.5%, and 5% with respect to the silicon contained in a final product (a composite of the graphene oxide and the silicon). In the present example, each of 62 mL, 45 mL,
20 and 29 mL of a suspension containing graphene oxide of 0.05 wt% was added to 500 mL of a suspension containing 1 g of laponite, and 500 mL of a 3.6 mM MgCl₂ solution was added thereto. Then, the laponite and the graphene oxide were restacked together with stirring for 12 hours and washed with distilled water by using a centrifuge, and then dried in an oven at 50°C to be powderized.

25 The restacked powder was obtained, a molar ratio of SiO₂ : Mg was determined as 1 : 2, and the restacked powder was mixed with Mg powder. Thereafter, the mixture was put into a self-produced tube furnace and heated at a heating rate of 3.3°C/min to reduce the silica contained in the mixture by a magnesiothermic reaction. A heating temperature for reduction varied in the
30 range of from about 500°C to about 650°C. After the reduction was completed, the mixture was taken out and etched with a 0.5 M hydrochloric acid solution in an amount of 500 mL per 1 g of the mixture with stirring for 24 hours. Then, the etching solution used was removed by centrifugation, and the mixture was stirred again with 500 mL of a new 0.5 M hydrochloric acid solution for 24 hours.
35 Thereafter, the etching solution used was removed by centrifugation, and then,

the mixture was washed with distilled water. Subsequently, the mixture was dried in a vacuum at 200°C for 24 hours.

In Fig. 7, the photo on the left shows a colloid including a silica-containing material and the photo on the right shows a powderized silica-containing material prepared in accordance with the present example.

<Example 5: Characteristic analysis of silicon nanomaterial prepared from laponite and graphene oxide (Restacking)>

In the present example, characteristics of a silicon nanomaterial prepared were analyzed by an X-ray diffraction analysis method.

(1) In the case where a graphene was contained in as amount of 5 wt% in a silicon nanomaterial

In the present example, an analysis was conducted on characteristics of a silicon nanomaterial prepared by using laponite and a graphene oxide solution such that a mass ratio of graphene in a final product became 5% by mass.

Figs. 8a to 8c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 8a to 8c show analysis results of silicon nanomaterials obtained by performing an etching process after a heat treatment at 550°C for 6 hours as shown in Fig. 8a, at 600°C for 1 hour as shown in Fig. 8b, and at 650°C for 3 hours as shown in Fig. 8c. In Figs. 8a and 8c, a wide and gentle peak regarded as an amorphous silicon oxide were observed between 20° and 30° together with a diffraction pattern of silicon.

Figs. 9a to 9c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method and reducing the powderized colloid by a magnesiothermic reaction without etching. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 9a to 9c show diffraction patterns of silicon materials obtained by performing a heat treatment at 550°C for 6 hours as shown in Fig. 9a, at 600°C for 1 hour as shown in Fig. 9b, and at 650°C for 3 hours as shown in Fig. 9c. According to Figs. 9a and 9b, it was confirmed that a material containing a silicon nanomaterial, MgO, MgSi₂, and some impurities was produced, and according to Fig. 9c, it was confirmed that a material containing a silicon nanomaterial and MgO was produced.

From the above experiment results, it was confirmed that most of the impurities in the reduced silicon material were removed by performing the etching process and only the silicon nanomaterials usually remained.

5 Figs. 10a to 10c provide an image of transmission electron microscopy (Fig. 10a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 10b), and a selected area electron diffraction (SAED) pattern (Fig. 10c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6
10 hours, and etching the resultant product. From Fig. 10a, it was observed that particles of 50 nm or less were concentrated on particles of about 300 nm. From Fig. 10b, a grid on a (111) silicon plane with an inter-planar distance of 0.30 nm was observed. From Fig. 10c, a pattern formed by crystals of silicon was observed.

15 Figs. 11a to 11c provide an image of transmission electron microscopy (Fig. 11a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 11b), and a selected area electron diffraction (SAED) pattern (Fig. 11c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1
20 hour, and etching the resultant product. From Fig. 11a, it was observed that particles of about 100 nm or 50 nm or less were concentrated on large particles of about 500 nm. From Fig. 11b, a grid on a (111) silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 11c, a pattern formed by
25 crystals of silicon was observed.

Figs. 12a to 12c provide an image of transmission electron microscopy (Fig. 12a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 12b), and a selected area electron diffraction (SAED) pattern (Fig. 12c) of a silicon nanomaterial obtained by powderizing colloid including silica-
30 containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. From Fig. 12a, particles without containing small particles of about 400 nm were observed. From Fig. 12b, a grid on a (111) silicon plane with an inter-planar distance of 0.30 nm was observed.
35 From Fig. 12c, a pattern formed by crystals of silicon was observed.

Figs. 13a to 13c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. Figs. 13a to 13c provide analysis results of silicon nanomaterials obtained by reduction at 550°C for 6 hours as shown in Fig. 13a, at 600°C for 1 hour as shown in Fig. 13b, and at 650°C for 3 hours as shown in Fig. 13c. According to the analysis results, pore sizes of the silicon nanomaterials were about 10.8 nm or less as shown in Fig. 13a, about 10.1 nm or less as shown in Fig. 13b, and about 10.7 nm or less as shown in Fig. 13c.

Figs. 14a to 14c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6 hours, and etching the resultant product. Fig. 14a is a graph showing a measurement result of capacity retention, Fig. 14b is a graph showing a measurement result of rate capability, and Fig. 14c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 23% was observed after 50 cycles.

Figs. 15a to 15c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. Fig. 15a is a graph showing a measurement result of capacity retention, Fig. 15b is a graph showing a measurement result of rate capability, and Fig. 15c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 17% was observed after 48 cycles.

Figs. 16a to 16c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. Fig. 16a is a graph showing a measurement result of capacity retention, Fig. 16b is a graph showing a measurement result of rate capability, and Fig. 16c is a graph showing a

measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 35% was observed after 40 cycles.

(2) In the case where a graphene was contained in as amount of 7.5 wt% in a silicon nanomaterial

5 In the present example, an analysis was conducted on characteristics of a silicon nanomaterial prepared by using laponite and a graphene oxide solution such that a mass ratio of graphene in a final product became 7.5% by mass.

10 Figs. 17a to 17c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 17a to 17c show analysis results of silicon nanomaterials obtained by performing an etching process after a heat treatment at 550°C for 6 hours as shown in Fig. 17a, at 15 600°C for 1 hour as shown in Fig. 17b, and at 650°C for 3 hours as shown in Fig. 17c. In Figs. 17a and 17c, a wide and gentle peak regarded as an amorphous silicon oxide were observed between 20° and 30° together with a diffraction pattern of silicon.

20 Figs. 18a and 18c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method and reducing the powderized colloid by a magnesiothermic reaction without etching. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 18a to 18b show analysis results of materials obtained by performing a heat treatment at 550°C for 6 hours as shown in Fig. 18a and at 600°C for 1 hour as shown in Fig. 18b. According to 25 Figs. 18a and 18b, it was confirmed that a material containing a silicon nanomaterial, MgO, MgSi₂, and some impurities was produced through a magnesiothermic reaction. Fig. 18c shows an analysis result of a material obtained by performing a heat treatment at 650°C for 3 hours. According to Fig. 30 18c, it was confirmed that a material containing a silicon nanomaterial and MgO was produced through a magnesiothermic reaction.

From the above experiment results, it was confirmed that most of the impurities in the reduced silicon material were removed by performing the etching process and only the silicon nanomaterials usually remained.

35 Figs. 19a to 19c provide an image of transmission electron microscopy (Fig. 19a), an image of high resolution transmission electron microscopy (HR-

TEM) (Fig. 19b), and a selected area electron diffraction (SAED) pattern (Fig. 19c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6 hours, and etching the resultant product. From Fig. 19a, particles of about 400 nm without containing small particles were observed. From Fig. 19b, a grid on a (111) silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 19c, a pattern formed by crystals of silicon was observed.

Figs. 20a to 20c provide an image of transmission electron microscopy (Fig. 20a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 20b), and a selected area electron diffraction (SAED) pattern (Fig. 20c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. From Fig. 20a, particles of about 400 nm rarely containing small particles were observed. From Fig. 20b, a grid on a (111) silicon plane with an inter-planar distance of 0.30 nm was observed. From Fig. 20c, a pattern formed by crystals of silicon was observed.

Figs. 21a to 21c provide an image of transmission electron microscopy (Fig. 21a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 21b), and a selected area electron diffraction (SAED) pattern (Fig. 21c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. From Fig. 21a, it was observed that the synthesized material contained small particles having various sizes from about 10 nm or less to about 100 nm or less. From Fig. 21b, a grid on a (111) silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 21c, a pattern formed by crystals of silicon was observed.

Figs. 22a to 22c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. Figs. 22a to 22c provide analysis results of silicon nanomaterials obtained by reduction at 550°C for 6 hours as shown in Fig. 22a, at 600°C for 1 hour as shown in Fig. 22b, and at 650°C for 3 hours as shown in

Fig. 22c. According to the analysis results, pore sizes of the silicon nanomaterials were about 8.3 nm or less as shown in Fig. 22a, about 8.7 nm or less as shown in Fig. 22b, and about 12.0 nm or less as shown in Fig. 22c.

5 Figs. 23a to 23c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6 hours, and etching the resultant product. Fig. 23a is a graph showing a measurement result of capacity retention, Fig. 23b is a graph showing
10 a measurement result of rate capability, and Fig. 23c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 23% was observed after 50 cycles.

Figs. 24a to 24c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including
15 silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. Fig. 24a is a graph showing a measurement result of capacity retention, Fig. 24b is a graph showing a measurement result of rate capability, and Fig. 24c is a graph showing a
20 measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 18% was observed after 50 cycles.

Figs. 25a to 25c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking
25 method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. Fig. 25a is a graph showing a measurement result of capacity retention, Fig. 25b is a graph showing a measurement result of rate capability, and Fig. 25c is a graph showing a measurement result of charge-discharge profile. According to an analysis result
30 from the graphs, a capacity loss of about 39% was observed after 30 cycles.

(3) In the case where a graphene was contained in as amount of 10 wt% in a silicon nanomaterial

In the present example, an analysis was conducted on characteristics of a silicon nanomaterial prepared by using laponite and a graphene oxide solution
35 such that a mass ratio of graphene in a final product became 10% by mass.

Figs. 26a to 26c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 26a to 26c show analysis results of silicon nanomaterials obtained by performing an etching process after a heat treatment at 550°C for 6 hours as shown in Fig. 26a, at 600°C for 1 hour as shown in Fig. 26b, and at 650°C for 3 hours as shown in Fig. 26c. In Figs. 26a and 26c, a wide and gentle peak regarded as an amorphous silicon oxide were observed between 20° and 30° together with a diffraction pattern of silicon.

Figs. 27a to 27c provide results of an X-ray diffraction analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method and reducing the powderized colloid by a magnesiothermic reaction without etching. A molar ratio of Si : Mg was determined as 1 : 2. Figs. 27a and 27b show analysis results of materials obtained by performing a heat treatment at 550°C for 6 hours as shown in Fig. 27a and at 600°C for 1 hour as shown in Fig. 27b. According to Figs. 27a and 27b, it was confirmed that a material containing a silicon nanomaterial, MgO, MgSi₂, and some impurities was produced through a magnesiothermic reaction. Fig. 27c shows an analysis result of a material obtained by performing a heat treatment at 650°C for 3 hours. According to Fig. 27c, it was confirmed that a material containing a silicon nanomaterial and MgO was produced.

From the above experiment results, it was confirmed that most of the impurities in the reduced silicon material were removed by performing the etching process and only the silicon nanomaterials usually remained.

Figs. 28a to 28c provide an image of transmission electron microscopy (Fig. 28a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 28b), and a selected area electron diffraction (SAED) pattern (Fig. 28c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 6 hours, and etching the resultant product. From Fig. 28a, graphene and small particles of about 20 nm or less were observed. From Fig. 28b, a grid on a (111)

silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 28c, a pattern formed by crystals of silicon was observed.

Figs. 29a to 29c provide an image of transmission electron microscopy (Fig. 29a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 29b), and a selected area electron diffraction (SAED) pattern (Fig. 29c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. From Fig. 29a, small particles of about 20 nm or less were observed. From Fig. 29b, a grid on a (111) silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 29c, a pattern formed by crystals of silicon was observed.

Figs. 30a to 30c provide an image of transmission electron microscopy (Fig. 30a), an image of high resolution transmission electron microscopy (HR-TEM) (Fig. 30b), and a selected area electron diffraction (SAED) pattern (Fig. 30c) of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. From Fig. 30a, particles of about 400 nm and small particles of about 20 nm were observed. From Fig. 30b, a grid on a (111) silicon plane with an inter-planar distance of 0.31 nm was observed. From Fig. 30c, a pattern formed by crystals of silicon was observed.

Figs. 31a to 31c provide results of an N₂ adsorption/desorption isotherm analysis of a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction, and etching the resultant product. Figs. 31a to 31c provide analysis results of silicon nanomaterials obtained by reduction at 550°C for 6 hours as shown in Fig. 31a, at 600°C for 1 hour as shown in Fig. 31b, and at 650°C for 3 hours as shown in Fig. 31c. According to the analysis results, pore sizes of the silicon nanomaterials were about 10.2 nm or less as shown in Fig. 31a, about 11.2 nm or less as shown in Fig. 31b, and about 9.7 nm or less as shown in Fig. 31c.

Figs. 32a to 32b provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at

550°C for 6 hours, and etching the resultant product. Fig. 32a is a graph showing a measurement result of rate capability, and Fig. 32b is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, this silicon nanomaterial was not much different in speed characteristic but had a relatively low capacity as compared with a nanomaterial heat-treated at a different temperature.

Figs. 33a to 33c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 600°C for 1 hour, and etching the resultant product. Fig. 33a is a graph showing a measurement result of capacity retention, Fig. 33b is a graph showing a measurement result of rate capability, and Fig. 33c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 32% was observed after 40 cycles.

Figs. 34a to 34c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a restacking method, reducing the powderized colloid by a magnesiothermic reaction at 650°C for 3 hours, and etching the resultant product. Fig. 34a is a graph showing a measurement result of capacity retention, Fig. 34b is a graph showing a measurement result of rate capability, and Fig. 34c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a capacity loss of about 11% was observed after 50 cycles.

<Example 6: Preparation of silicon nanomaterial using laponite and graphene oxide (Freeze-drying)>

In the present example, a silicon nanomaterial was prepared by powderizing colloid including silica-containing material from laponite and graphene oxide by a freeze-drying method and reducing the powderized colloid.

500 mL of a laponite suspension including laponite at a concentration of 5 g/L was stirred for 48 hours to exfoliate the laponite. Then, a suspension containing graphene oxide of 0.05 wt% and prepared by a modified Hummer's method was added to colloid containing the exfoliated laponite. An amount of the graphene oxide was determined by comparing a weight of silicon contained in the laponite. The laponite contained SiO₂ of 59.5 wt%, and the SiO₂ contained silicon of 46.7 wt%. Therefore, the laponite contained silicon of 27.8

- 34 -

wt%. In consideration of this, the graphene oxide was added after calculation of a weight to be 6.5%, 10%, and 12.5% with respect to the silicon contained in a final product (a composite of the graphene oxide and the silicon). In the present example, 170 mL of dispersed laponite was added to 30 mL of colloid containing graphene oxide of 0.05 wt%, 155 mL of dispersed laponite was added to 45 mL of colloid containing graphene oxide of 0.05 wt%, or 146 mL of dispersed laponite was added to 54 mL of colloid containing graphene oxide of 0.05 wt%, and then stirred for 1 hour. Thereafter, the mixed colloid was freeze-dried for 5 days to be powderized. To be specific, the colloid was quickly cooled with a liquid nitrogen and then freeze-dried at -75°C and 5 mTorr within a freeze dryer (Ilsin Boibase Freeze Dryer FD8508).

Then, with various molar ratios of SiO_2 : Mg, the powder was mixed with Mg powder. To be specific, molar ratios of SiO_2 : Mg was 1 : 2, 1 : 2.5, 1 : 3, and 1 : 4. Thereafter, the mixture was put into a self-produced tube furnace and heated at a heating rate of 3.3°C/min to reduce the silica contained in the mixture by a magnesiothermic reaction. A heating temperature for reduction varied in the range of from about 520°C to about 550°C. The reduction was carried out under a gas atmosphere of 5% H_2 /95% Ar, the temperature was maintained for 3 hours after the temperature was increased. After the reduction was completed, the mixture was taken out and etched with a 0.5 M hydrochloric acid solution in an amount of 500 mL per 1 g of the mixture with stirring for 24 hours. Then, the etching solution used was removed by centrifugation, and the mixture was stirred again with 500 mL of a new 0.5 M hydrochloric acid solution for 24 hours. Thereafter, the etching solution used was removed by centrifugation, and then, the mixture was washed with distilled water. Subsequently, the mixture was dried in a vacuum at 180°C for 24 hours.

<Example 7: Characteristic analysis of silicon nanomaterial prepared from laponite and graphene oxide>

In the present example, an analysis was conducted on characteristics of silicon nanomaterials prepared with various concentrations of a graphene oxide solution used for preparing silicon nanomaterials and various reduction conditions.

Figs. 35a to 35c provide results of an X-ray diffraction analysis of silicon nanomaterials obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a freeze-drying method, and reducing the powderized colloid. Figs. 35a to 35c show analysis results of

silicon nanomaterials containing a 6.5 wt% graphene as shown in Fig. 35a, containing a 10% graphene as shown in Fig. 35b, and containing a 12.5% graphene as shown in Fig. 35c.

5 The upper graph of Fig. 35a shows a result of an X-ray diffraction analysis of a silicon material obtained by reduction at 520°C for 3 hours, and in this case, a molar ratio of Si : Mg was 1 : 2.5. The lower graph of Fig. 35a shows a result of an X-ray diffraction analysis of a silicon material obtained by reduction at 520°C for 1.5 hours, and in this case, a molar ratio of Si : Mg was 1 : 2.

10 The upper graph of Fig. 35b shows a result of an X-ray diffraction analysis of a silicon material obtained by reduction at 550°C for 3 hours, and in this case, a molar ratio of Si : Mg was 1 : 4. The lower graph of Fig. 35b shows a result of an X-ray diffraction analysis of a silicon material obtained by reduction at 550°C for 3 hours, and in this case, a molar ratio of Si : Mg was 1 : 3.

15 Fig. 35c shows a result of an X-ray diffraction analysis of a silicon material obtained by reduction at 550°C for 3 hours, and in this case, a molar ratio of Si : Mg was 1 : 2.

20 Figs. 36a to 36c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a freeze-drying method, reducing the powderized colloid by a magnesiothermic reaction at 550°C for 3 hours. A silicon nanomaterial containing 10 wt% graphene was used, and a molar ratio of Si : Mg was 1 : 4. Fig. 36a is a graph showing a measurement result of capacity retention, Fig. 36b is a graph showing a measurement result of rate capability, and Fig. 36c is a graph showing a measurement result of charge-discharge profile. According to an analysis result from the graphs, a change in capacity of a silicon nanomaterial containing 10 wt% graphene depending on a content of F1EC could be checked. However, this result was not considered to be changed entirely depending on a content of F1EC. When an electrolyte contained 10% F1EC, a capacity loss of about 12% was observed after 50 cycles. Figs. 36b and 36c provide graphs showing stable capacity even at a high current density, and stable potential vs. capacity.

35 Figs. 37a to 37c provide graphs showing electrochemical characteristics measured on a silicon nanomaterial obtained by powderizing colloid including silica-containing material from laponite and graphene oxide by a freeze-drying method, reducing the powderized colloid by a magnesiothermic reaction. Fig. 37a shows capacity retention of a silicon nanomaterial containing a 10%

- 36 -

graphene at a molar ratio of Si : Mg of 1 : 3. Fig. 37b shows rate capability of a silicon nanomaterial containing a 12.5% graphene at a molar ratio of Si : Mg of 1 : 2 without containing F1EC. Fig. 37c shows charge-discharge profile of a silicon nanomaterial containing a 12.5% graphene at a molar ratio of Si : Mg of 1 : 2 without containing F1EC. According to an analysis result from the graphs, in the case of charge/discharge at a current density of 0.05 C, capacity was stable but as low as about 600 mAh/g.

The above description of the present disclosure is provided for the purpose of illustration, and it would be understood by those skilled in the art that various changes and modifications may be made without changing technical conception and essential features of the present disclosure. Thus, it is clear that the above-described embodiments are illustrative in all aspects and do not limit the present disclosure. For example, each component described to be of a single type can be implemented in a distributed manner. Likewise, components described to be distributed can be implemented in a combined manner.

The scope of the present disclosure is defined by the following claims rather than by the detailed description of the embodiment. It shall be understood that all modifications and embodiments conceived from the meaning and scope of the claims and their equivalents are included in the scope of the present disclosure.

CLAIMS

1. A producing method of a silicon nanomaterial, comprising:

powderizing a colloid including a silica-containing material to obtain a powder including the silica-containing material;

5 adding an alkaline earth metal to the powder including the silica-containing material to form a mixture; and

heating the mixture to reduce a silica contained in the silica-containing material to a silicon.
2. The producing method of the silicon nanomaterial of claim 1,
10 wherein powderizing the colloid including the silica-containing material includes restacking by adding an alkaline earth metal cation to the colloid including the silica-containing material, or freeze-drying the colloid including the silica-containing material.
3. The producing method of the silicon nanomaterial of claim 2,
15 wherein the alkaline earth metal cation includes a magnesium cation.
4. The producing method of the silicon nanomaterial of any one of claims 1 to 3, wherein the colloid including the silica-containing material is formed by using a colloidal silica or formed by exfoliating a layered silica-containing material.
- 20 5. The producing method of the silicon nanomaterial of any one of claims 1 to 4, wherein the colloid including the silica-containing material further includes a graphene oxide.
6. The producing method of the silicon nanomaterial of claim 5,
including powderizing the colloid including a silica-containing material further
25 including the graphene oxide to obtain a powder including the silica-containing material and the graphene oxide;

adding an alkaline earth metal to the powder to form a mixture; and

- 38 -

heating the mixture to reduce a silica contained in the silica-containing material and the graphene oxide to form a composite including a silicon and a graphene.

7. The producing method of the silicon nanomaterial of claim 6,
5 wherein at least one of the silicon and the graphene contained in the composite is in a form of a sheet.

8. The producing method of the silicon nanomaterial of any one of claims 1 to 7, further comprising:

10 after reducing the silica to the silicon, etching the heated mixture by using an acidic solution to obtain the silicon nanomaterial.

9. The producing method of the silicon nanomaterial of any one of claims 1 to 8, wherein the colloid including the silica-containing material is formed by exfoliating a clay.

10. The producing method of the silicon nanomaterial of claim 9,
15 wherein the clay includes a material selected from the group consisting of montmorillonite, nontronite, beidellite, bentonite, hectorite, laponite, saponite, sauconite, vermiculite, and their combinations.

11. A silicon nanomaterial produced by a method of any one of claims 1 to 10.

20 12. The silicon nanomaterial of claim 11, wherein the silicon nanomaterial includes a hybridized graphene.

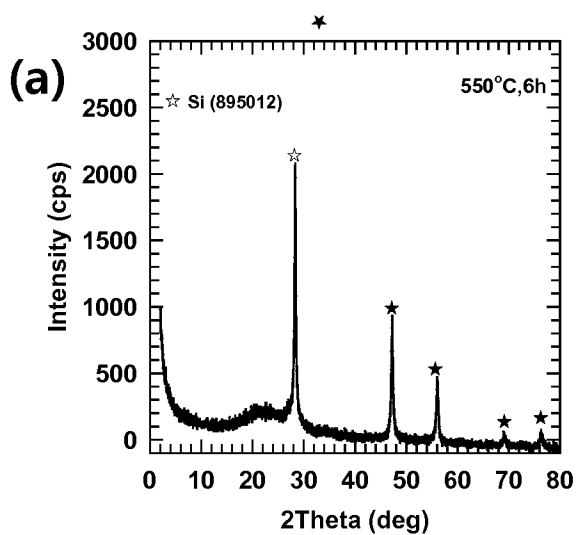
13. A composite comprising a silicon nanosheet and a graphene nanosheet.

25 14. An electrode, comprising a silicon nanomaterial of claim 11 or 12, or the composite of claim 13.

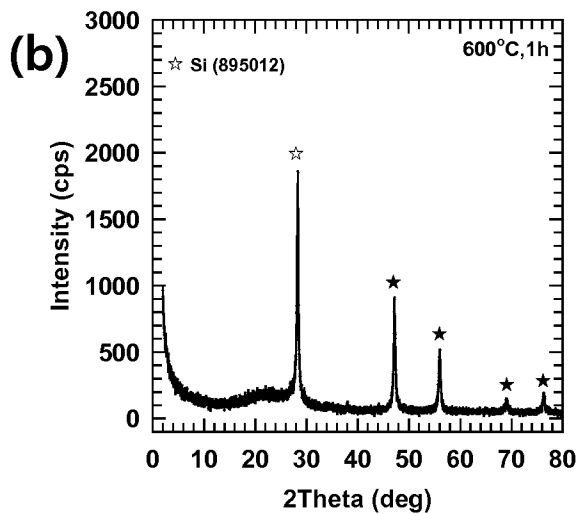
15. A battery comprising the electrode of claim 14 as an anode, a cathode, and an electrolyte.

[FIGURES]

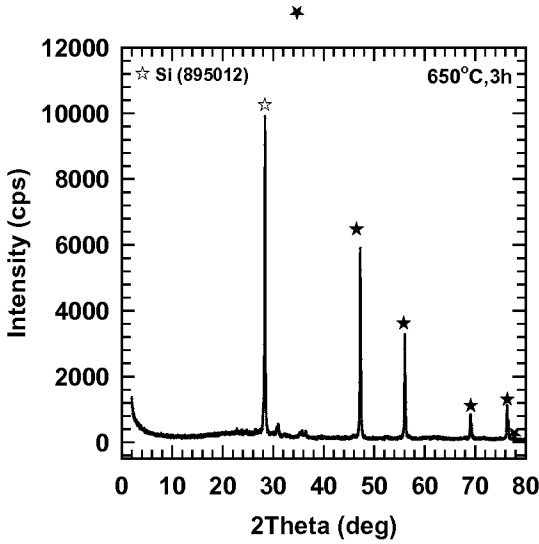
[Fig 1a]



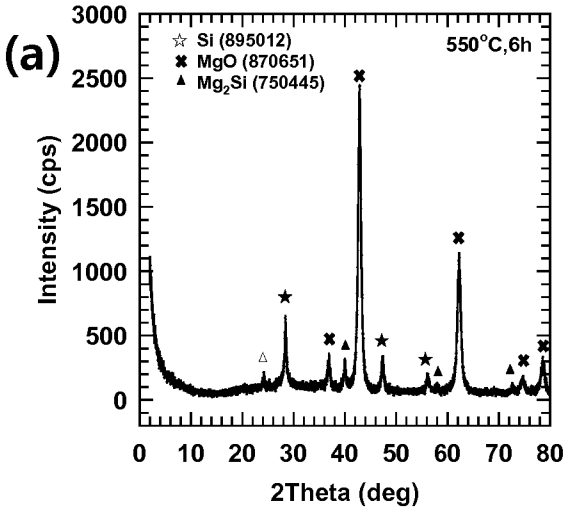
[Fig 1b]



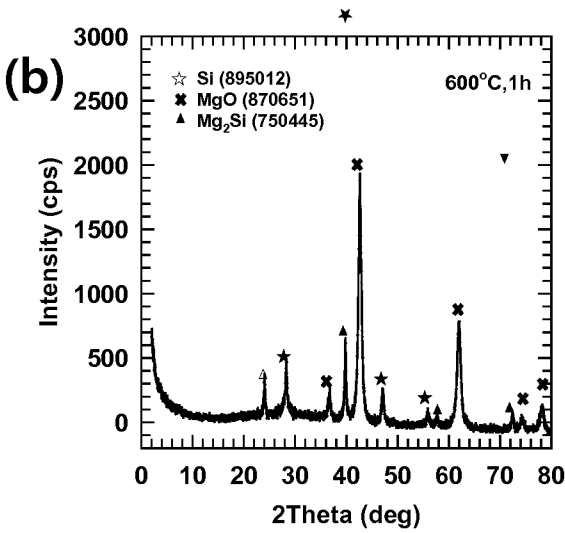
[Fig 1c]



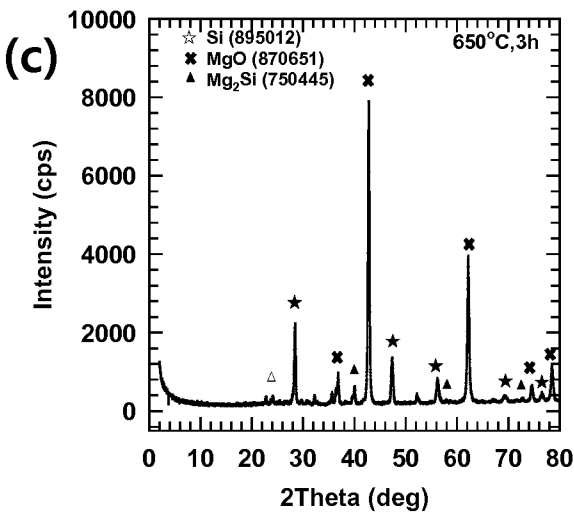
[Fig 2a]



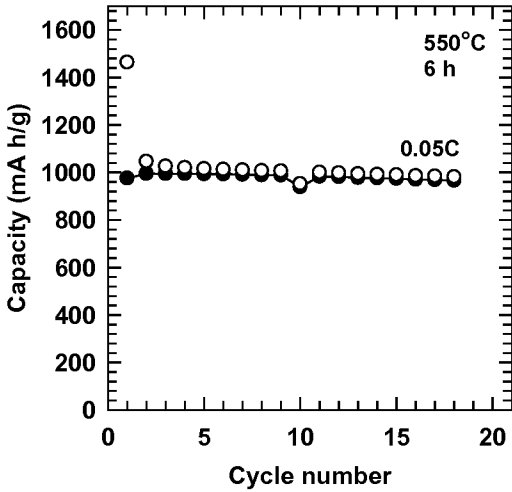
[Fig 2b]



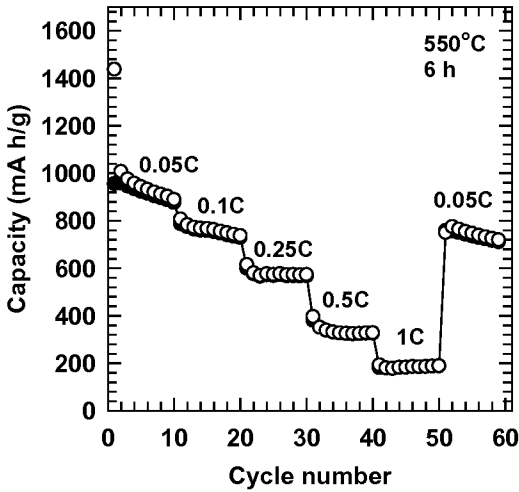
[Fig 2c]



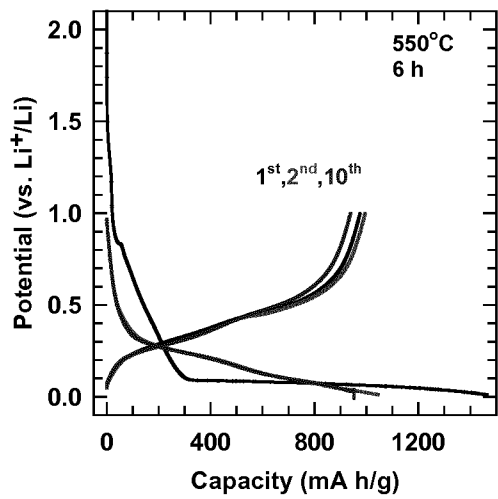
[Fig 3a]



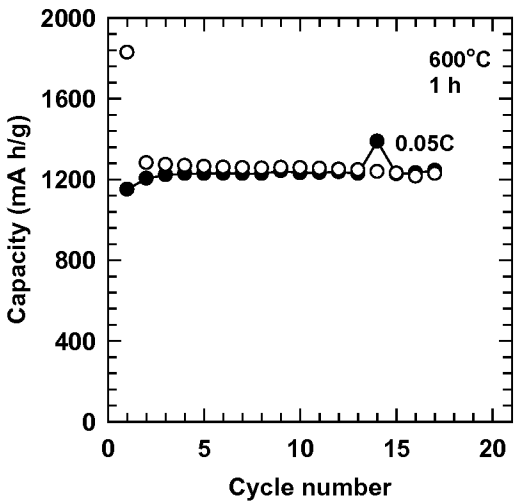
[Fig 3b]



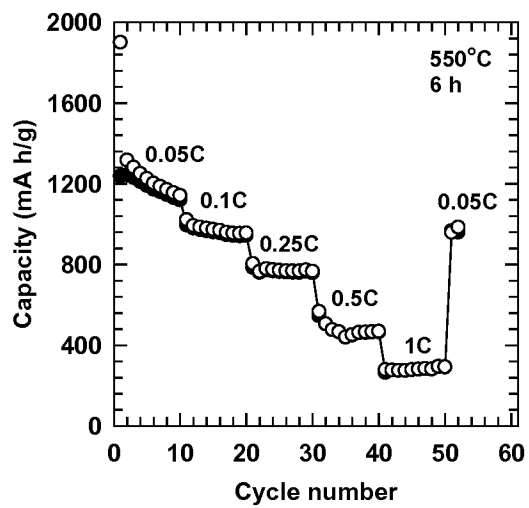
[Fig 3c]



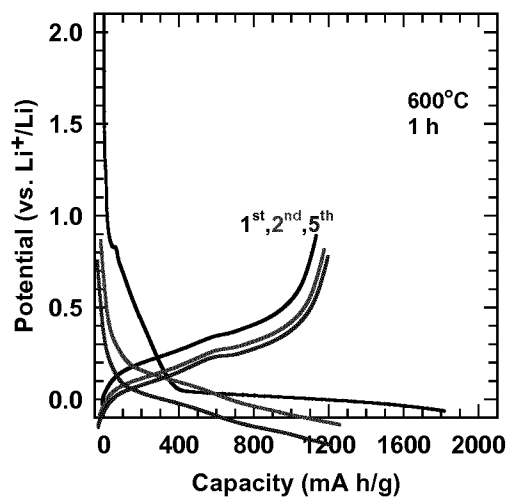
[Fig 4a]



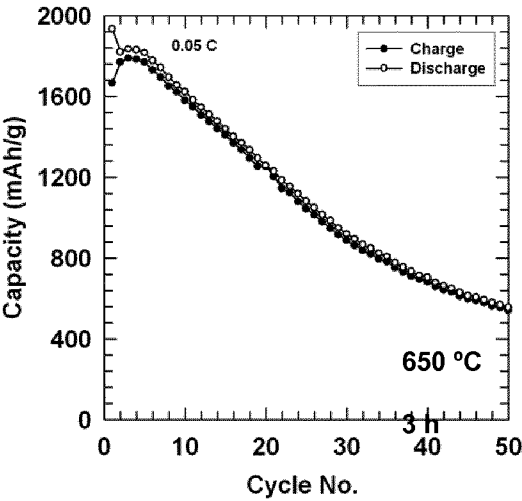
[Fig 4b]



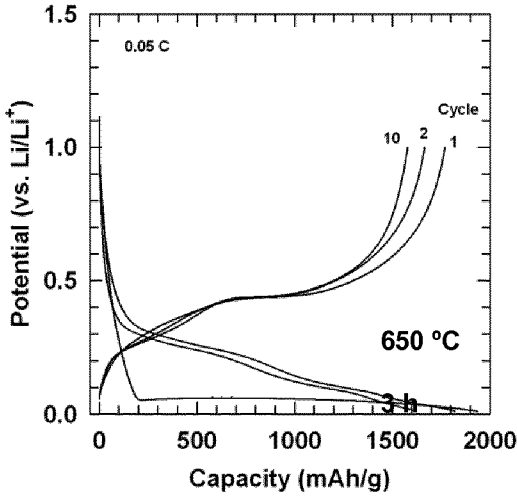
[Fig 4c]



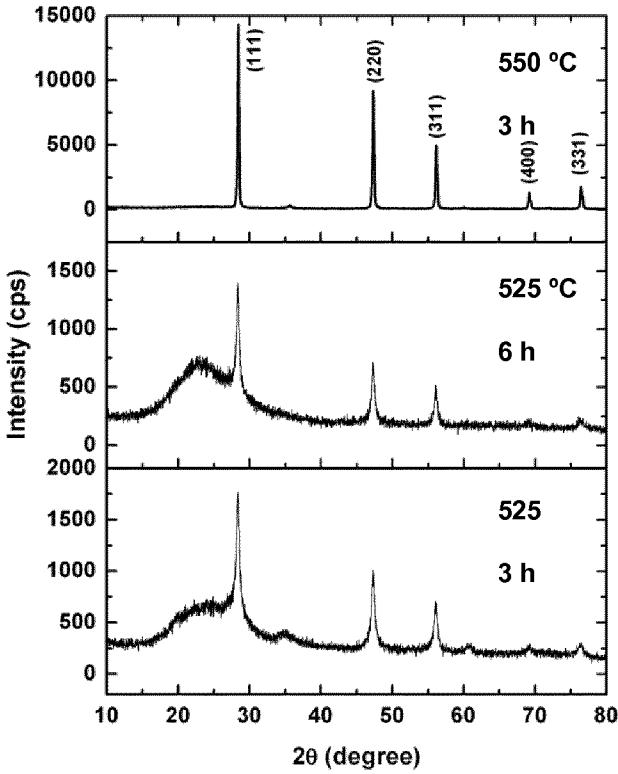
[Fig 5a]



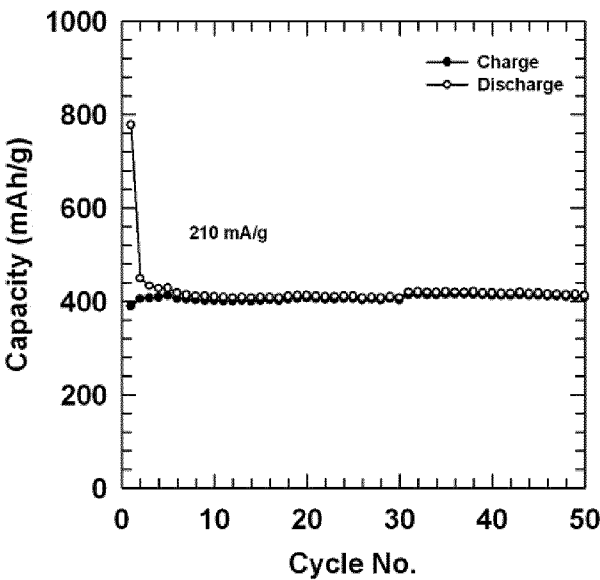
[Fig 5b]



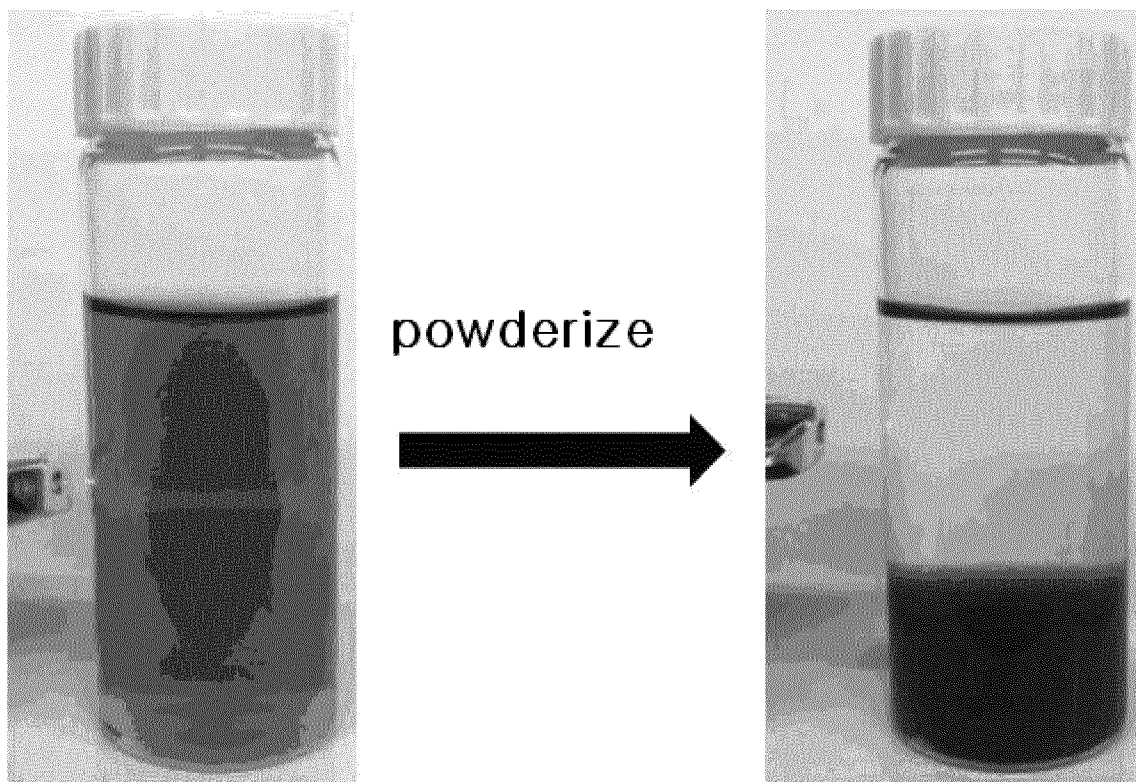
[Fig 6a]



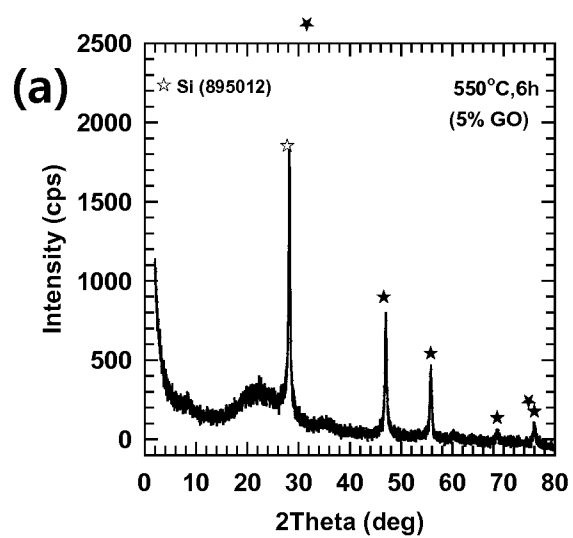
[Fig 6b]



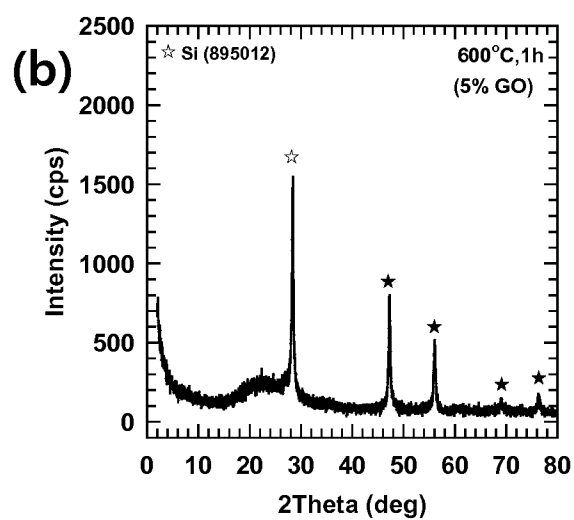
[Fig 7]



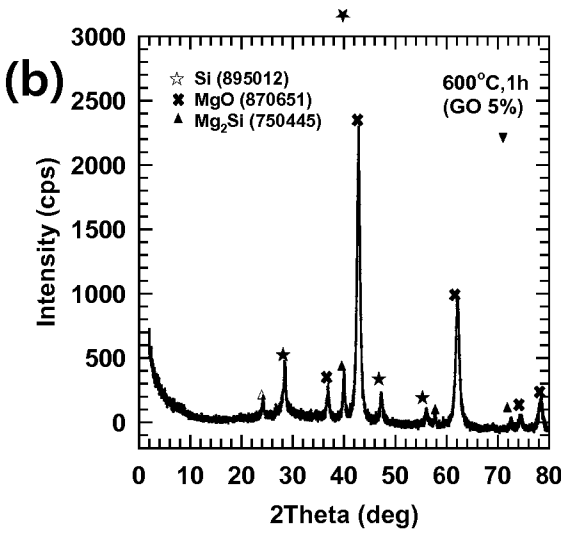
[Fig 8a]



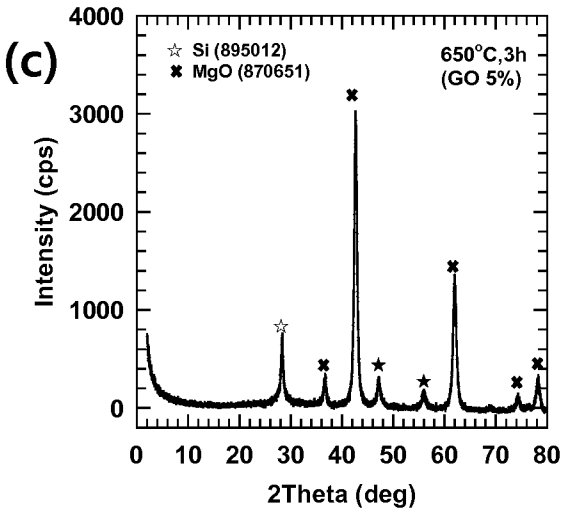
[Fig 8b]



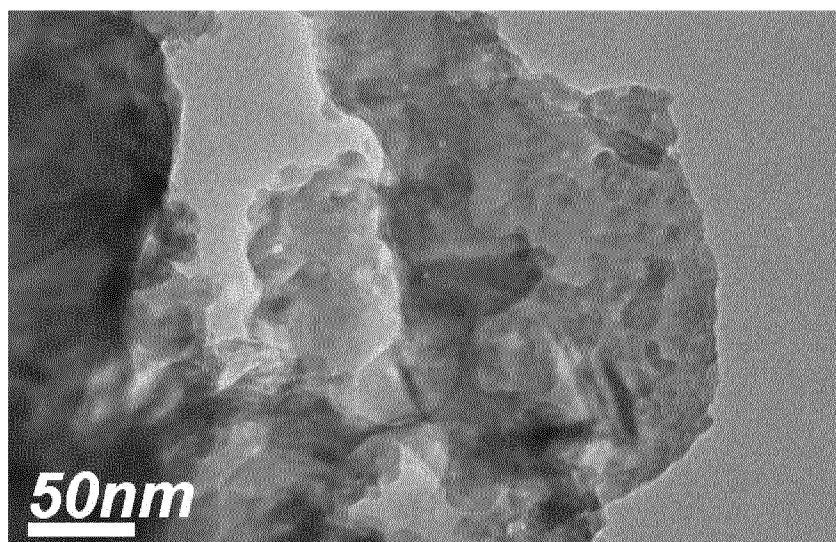
[Fig 9b]



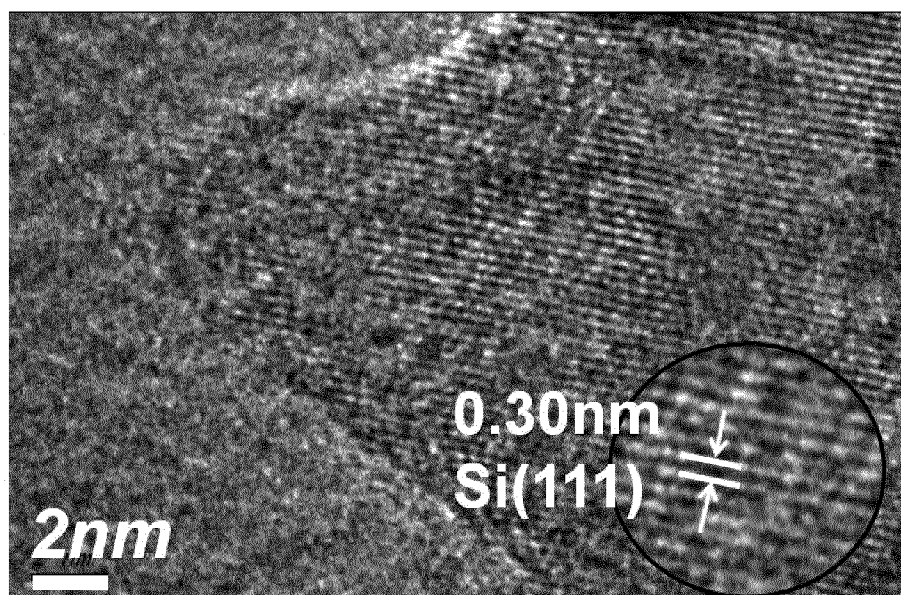
[Fig 9c]



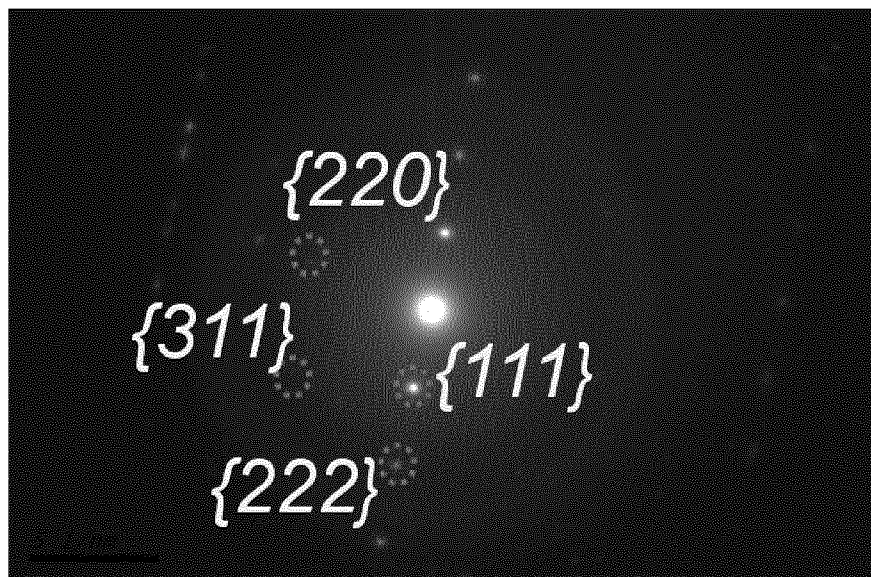
[Fig 10a]



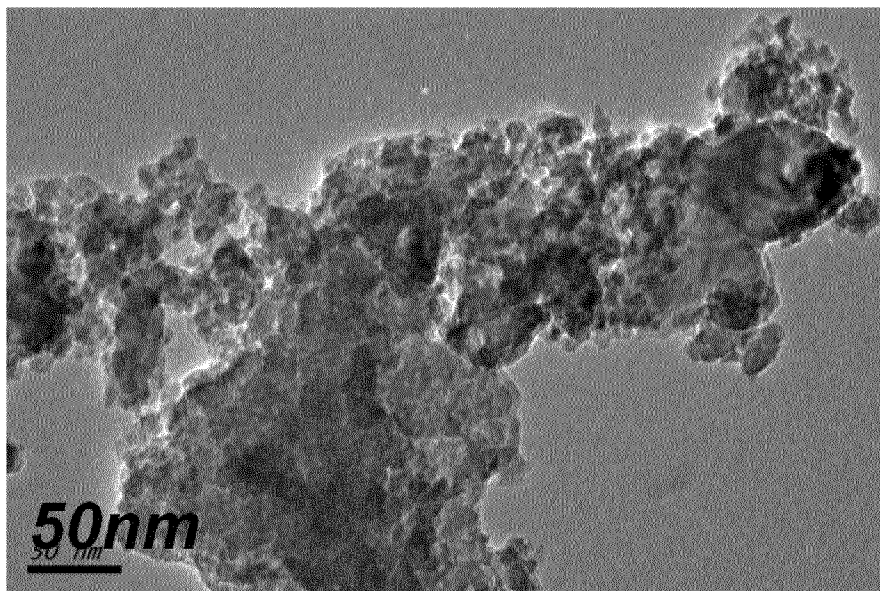
[Fig 10b]



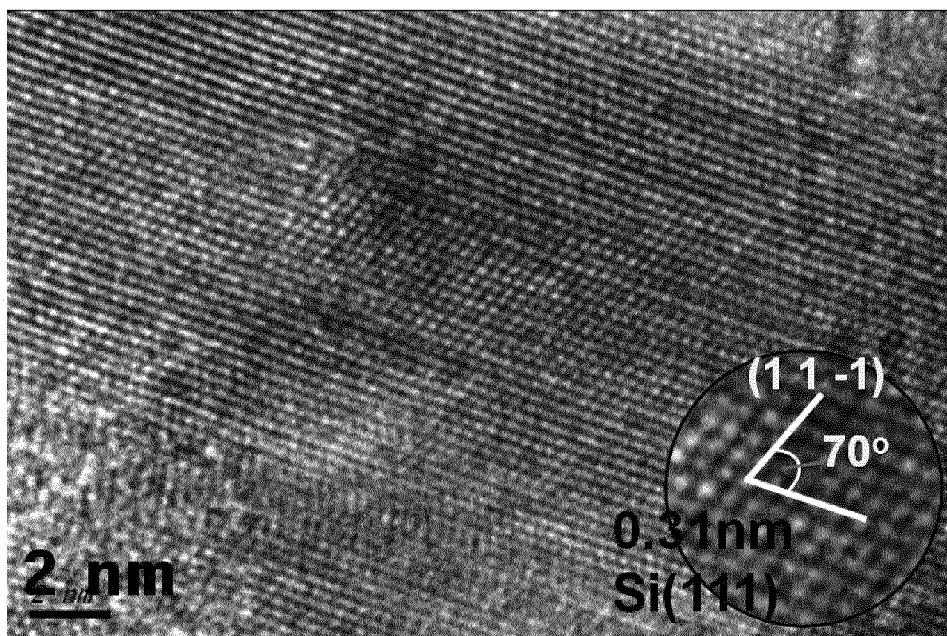
[Fig 10c]



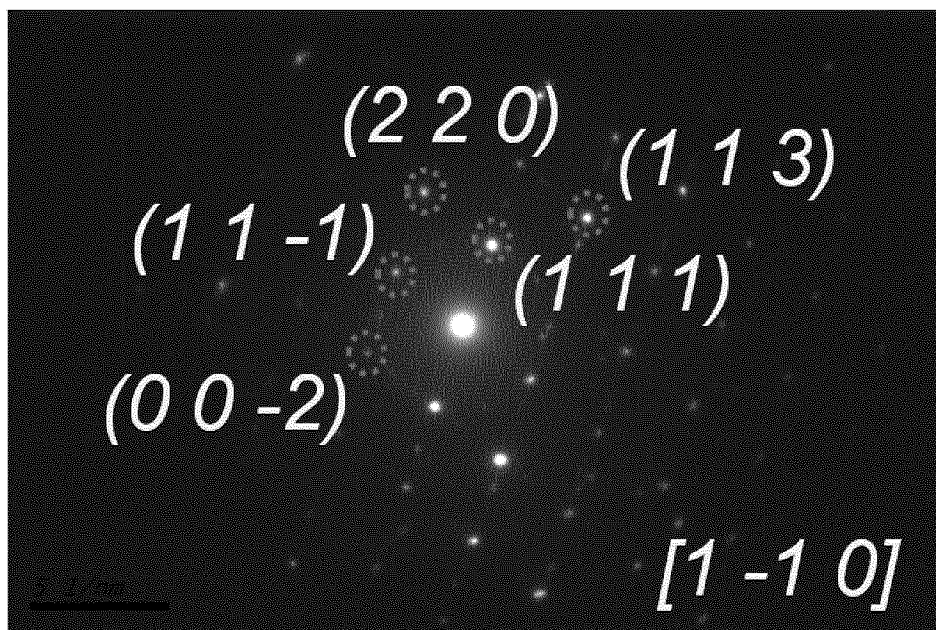
[Fig 11a]



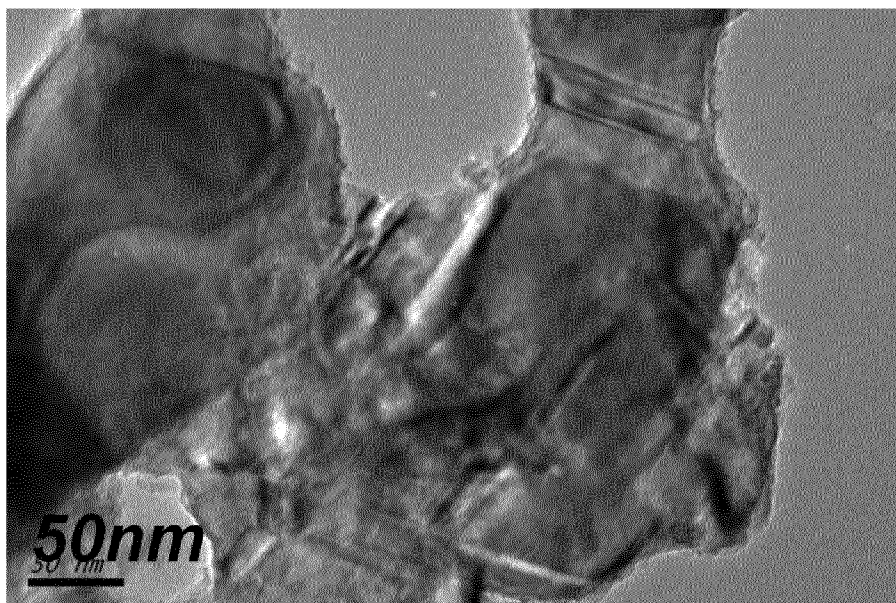
[Fig 11b]



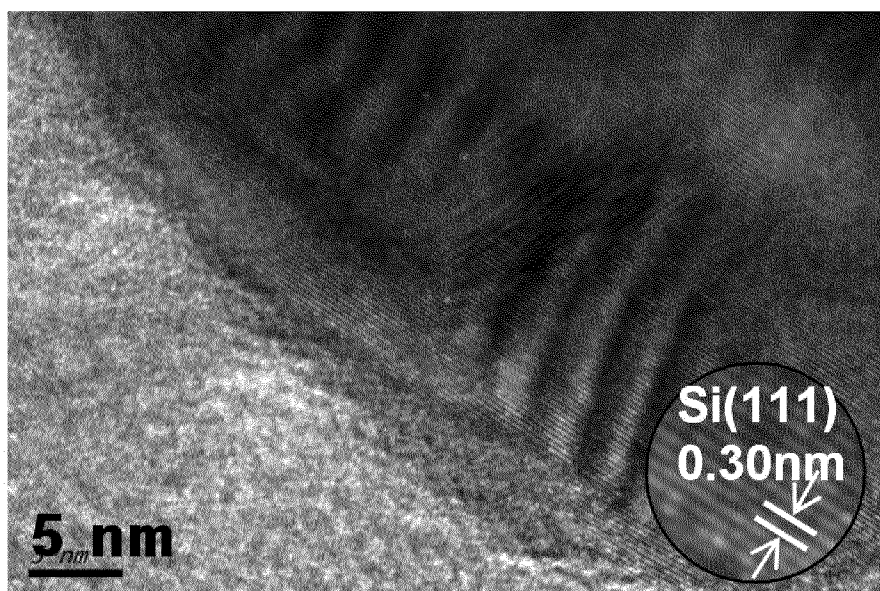
[Fig 11c]



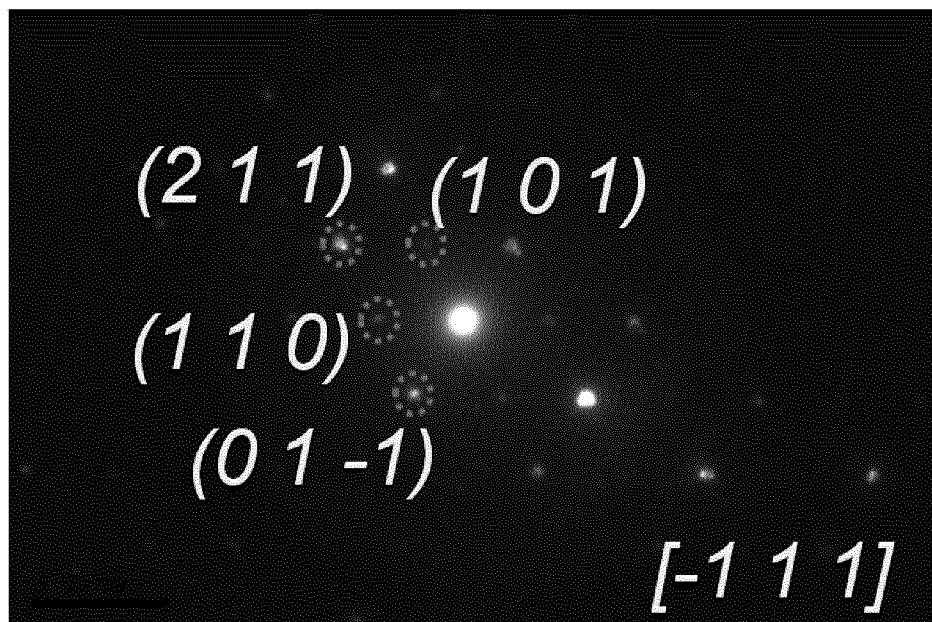
[Fig 12a]



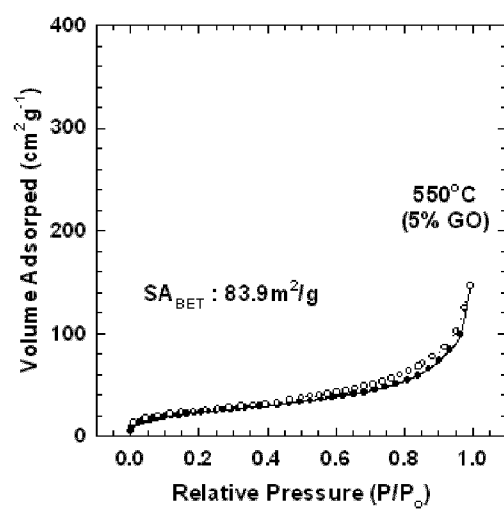
[Fig 12b]



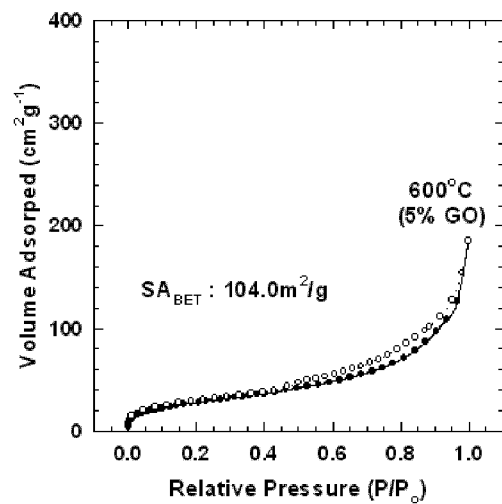
[Fig 12c]



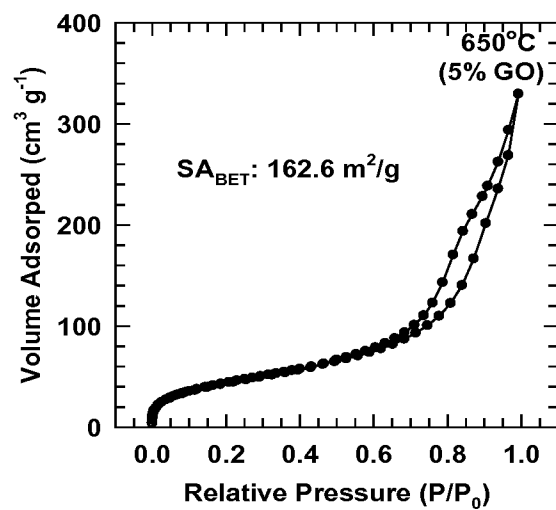
[Fig 13a]



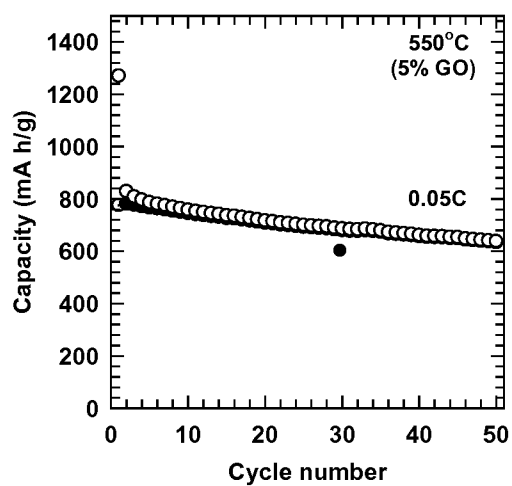
[Fig 13b]



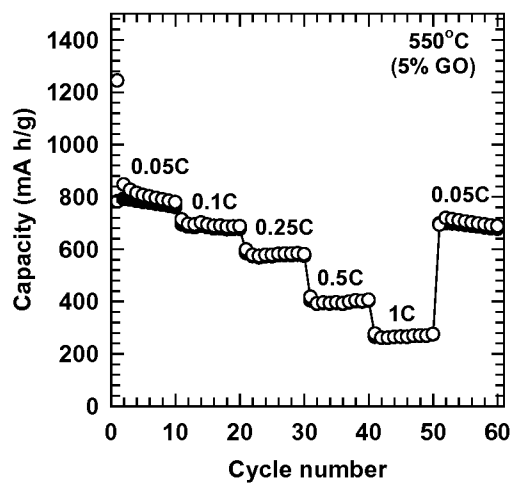
[Fig 13c]



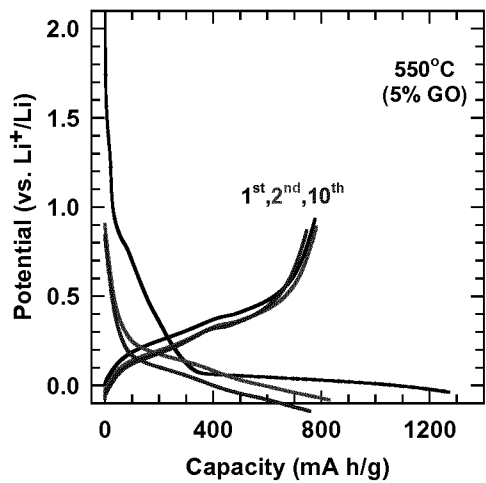
[Fig 14a]



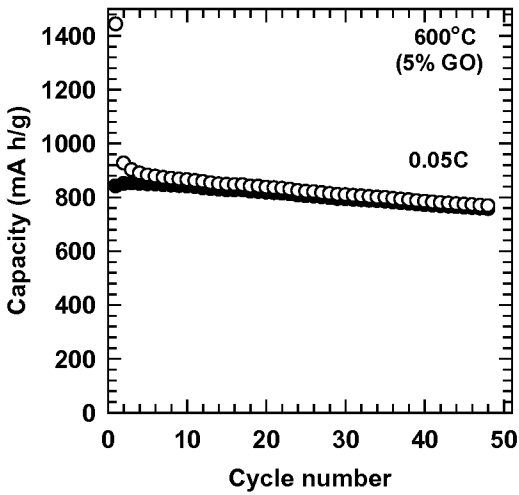
[Fig 14b]



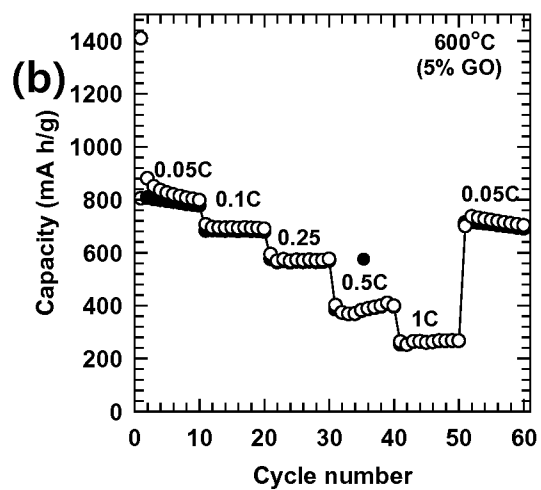
[Fig 14c]



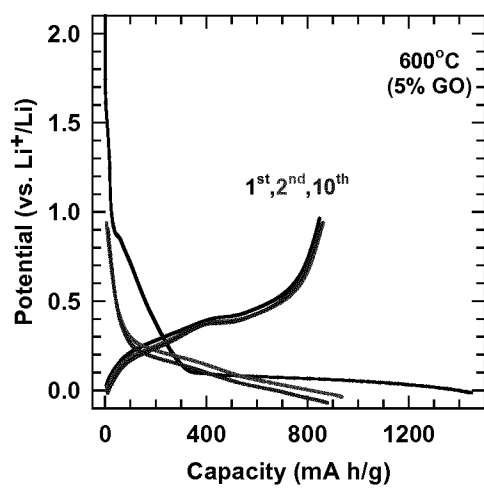
[Fig 15a]



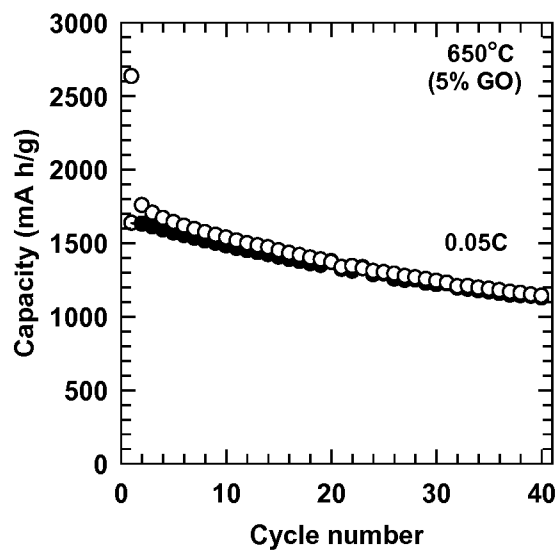
[Fig 15b]



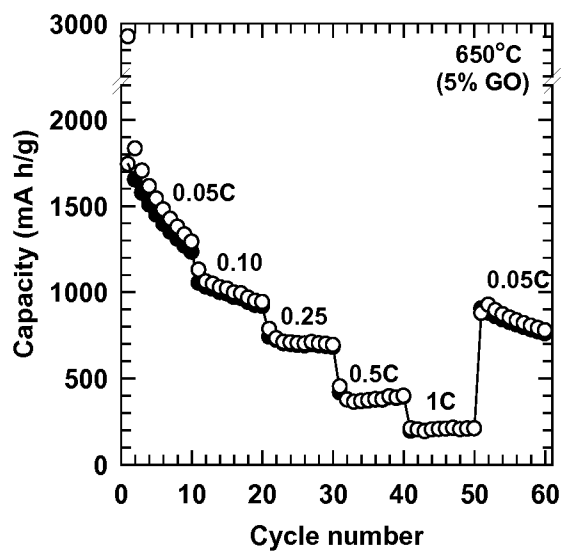
[Fig 15c]



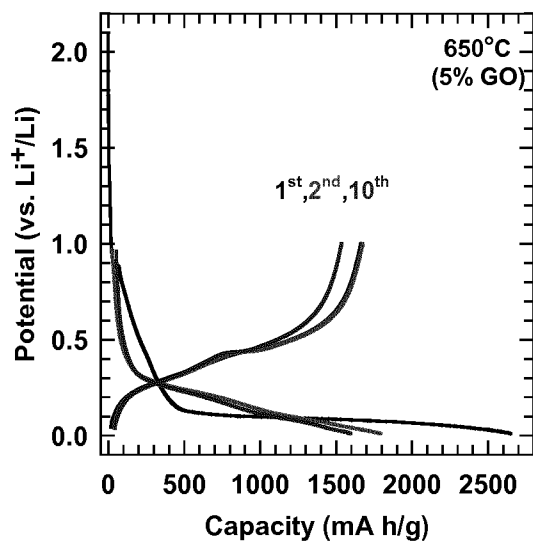
[Fig 16a]



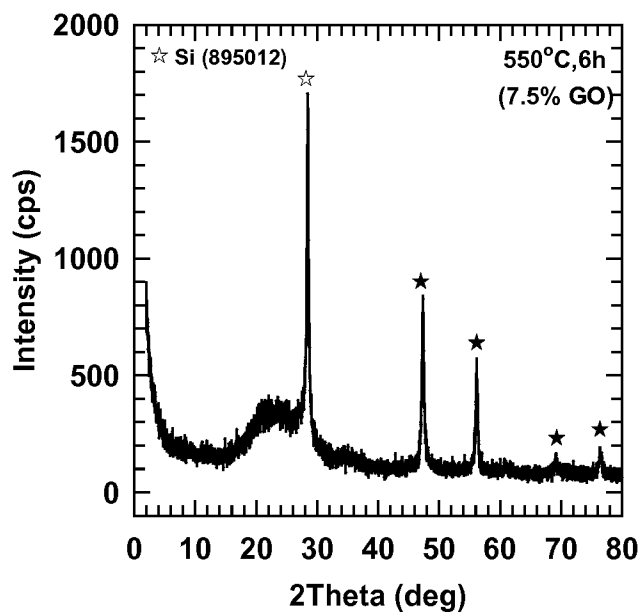
[Fig 16b]



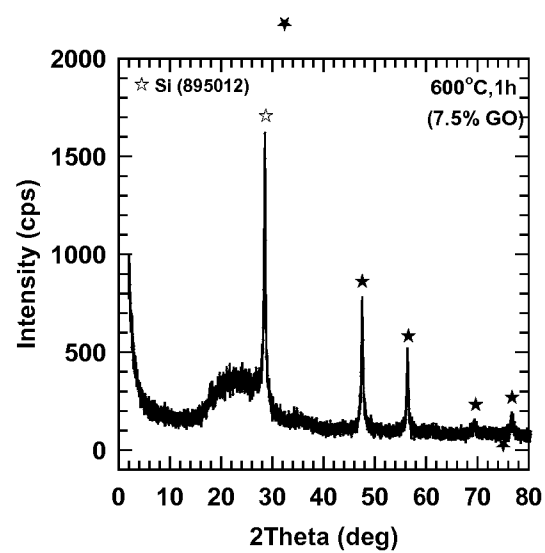
[Fig 16c]



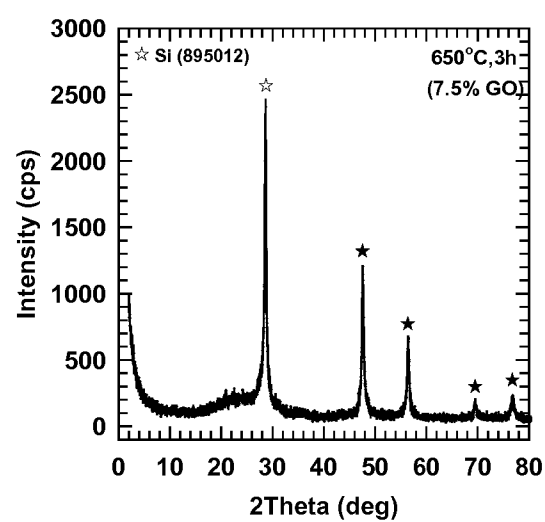
[Fig 17a]



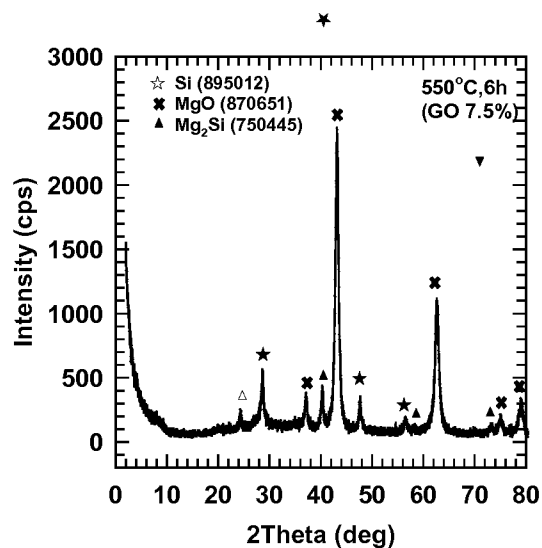
[Fig 17b]



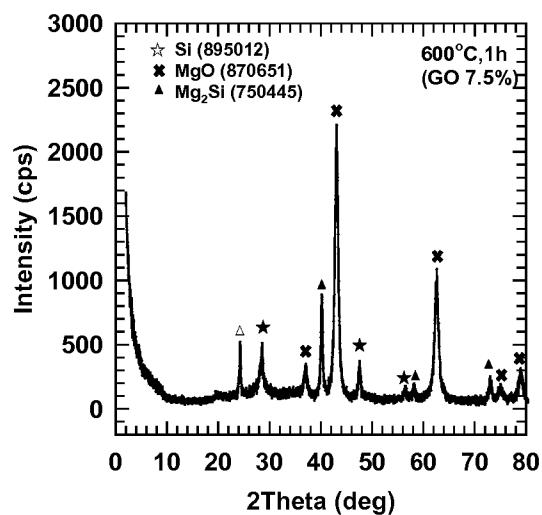
[Fig 17c]



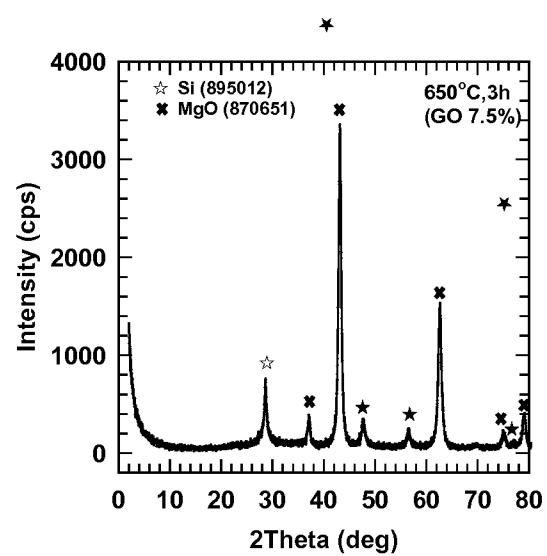
[Fig 18a]



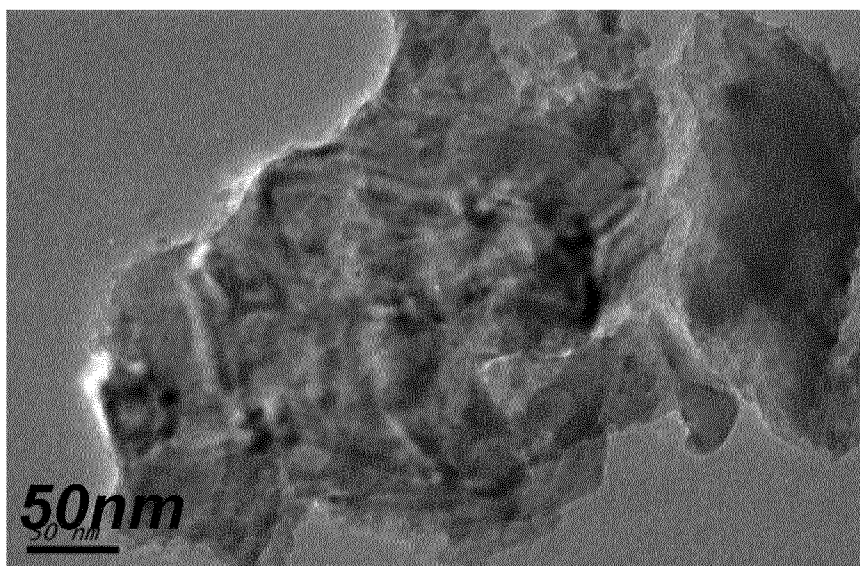
[Fig 18b]



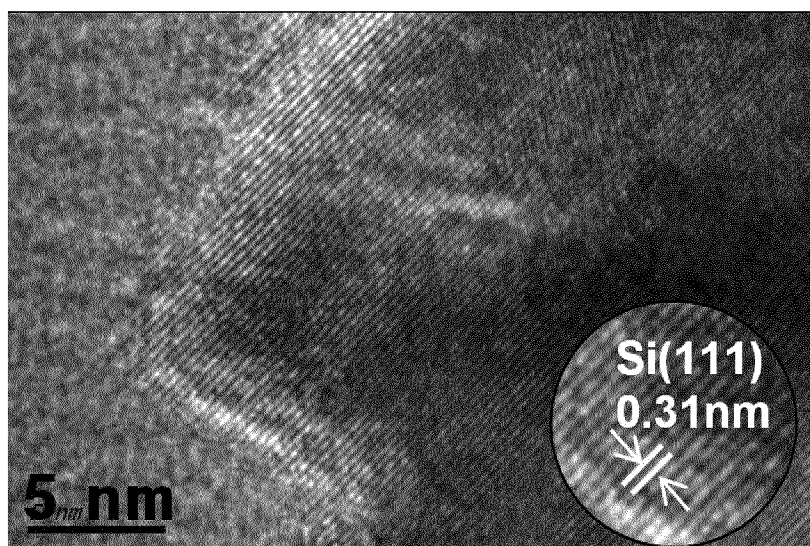
[Fig 18c]



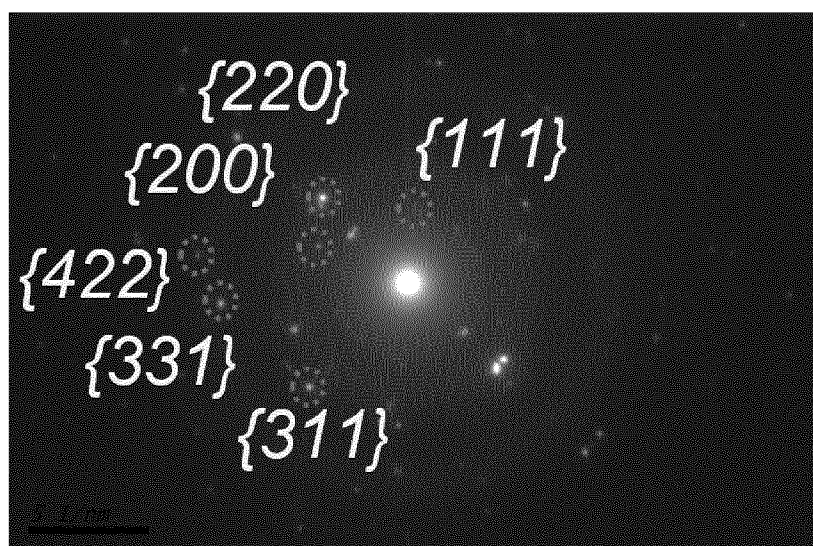
[Fig 19a]



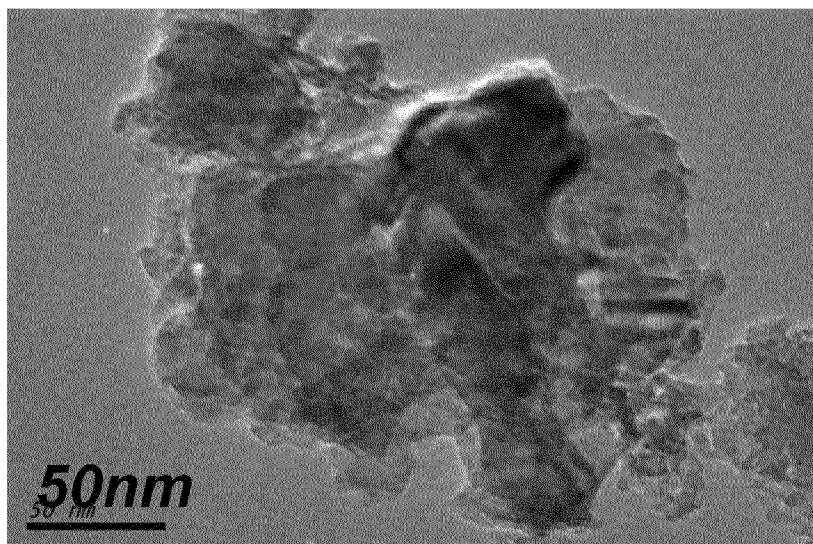
[Fig 19b]



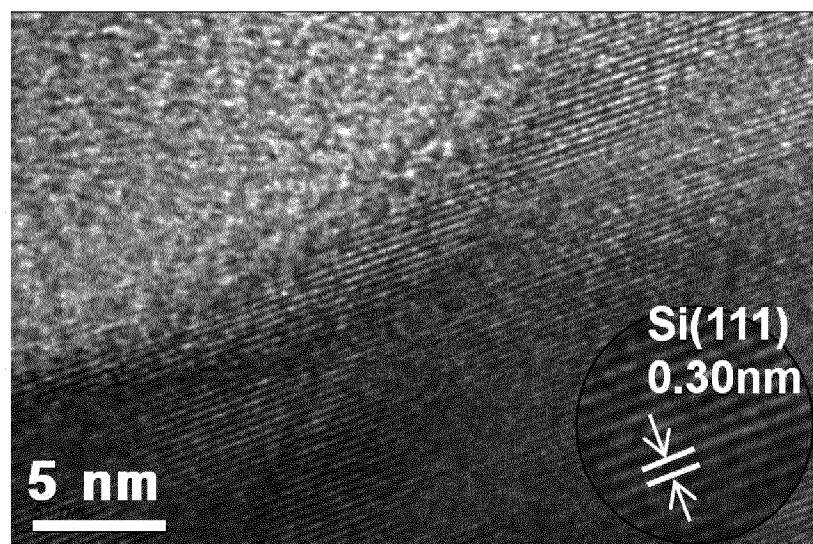
[Fig 19c]



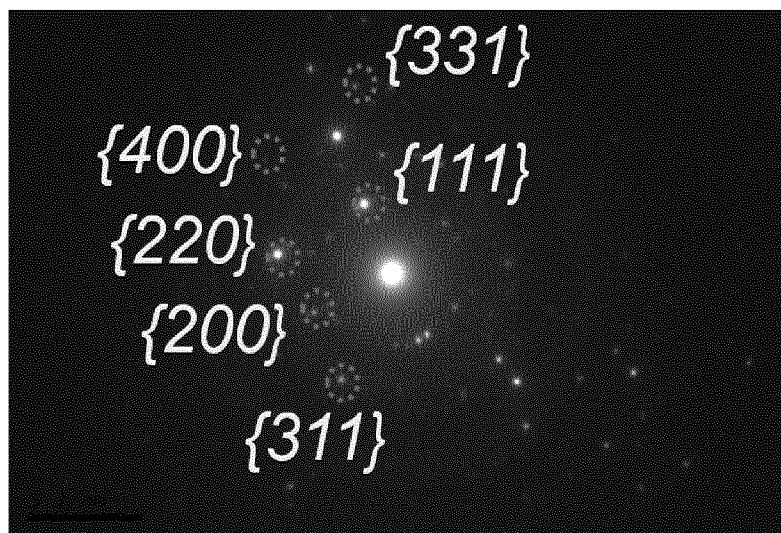
[Fig 20a]



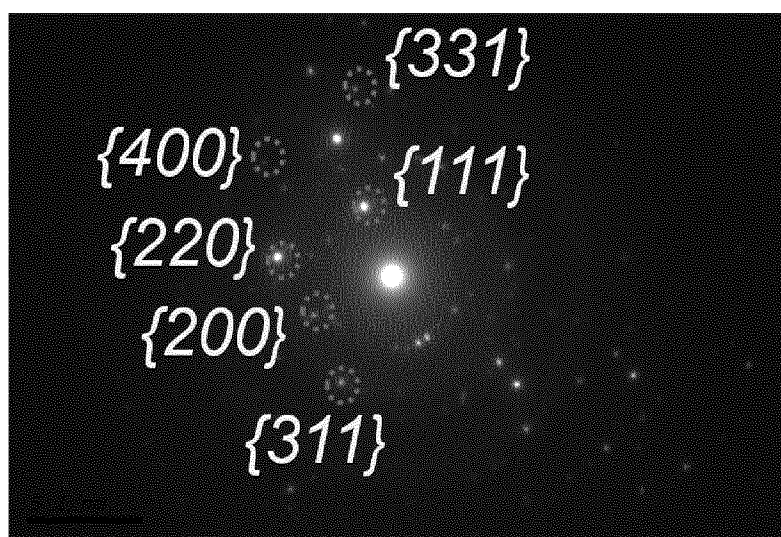
[Fig 20b]



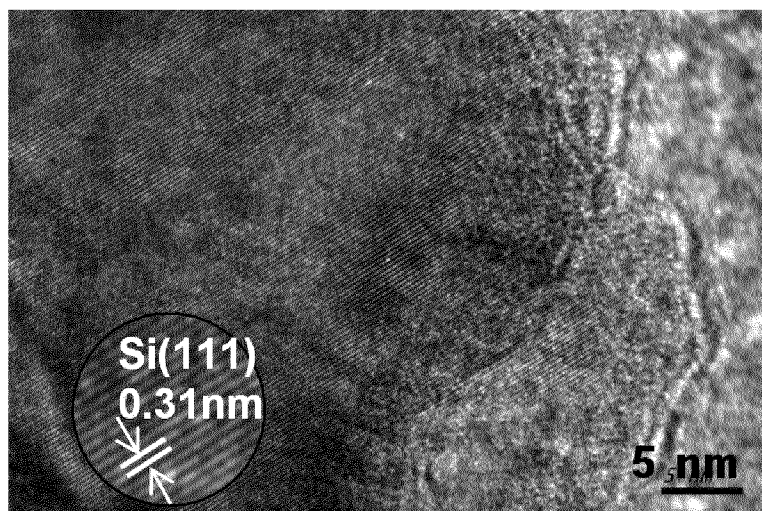
[Fig 20c]



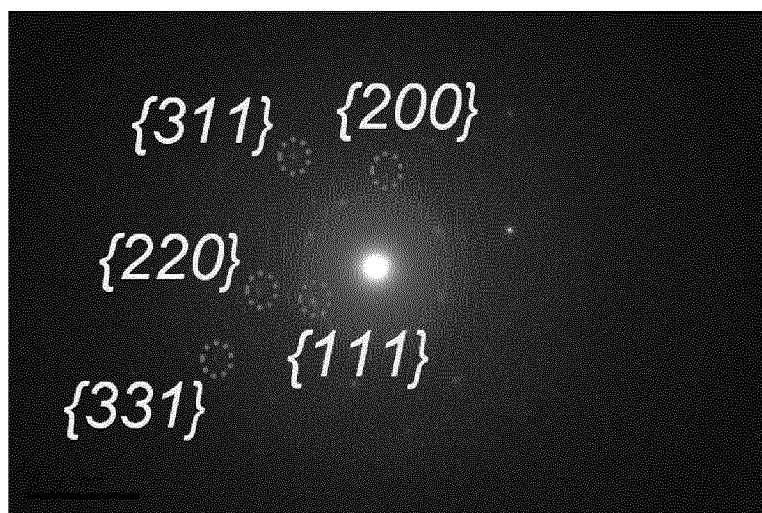
[Fig 21a]



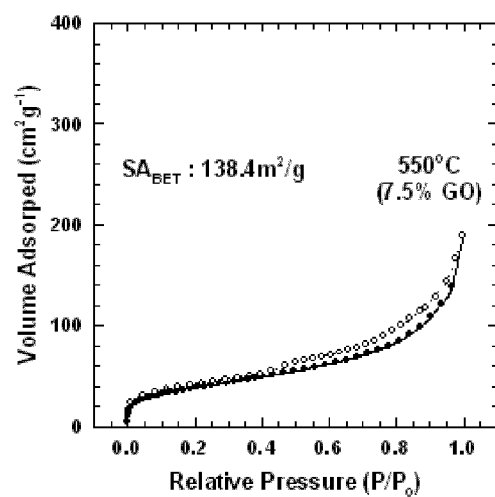
[Fig 21b]



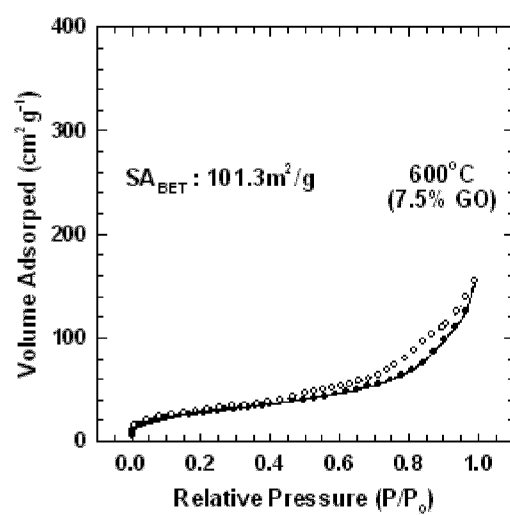
[Fig 21c]



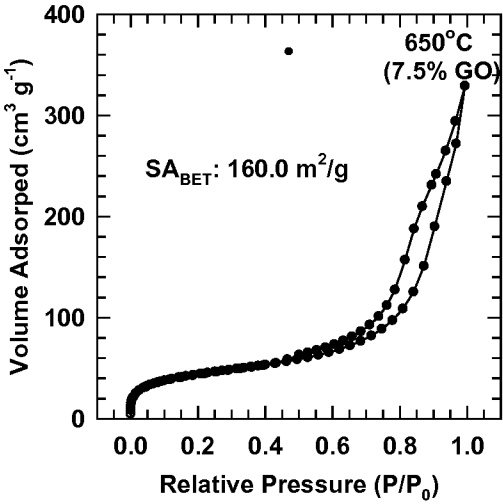
[Fig 22a]



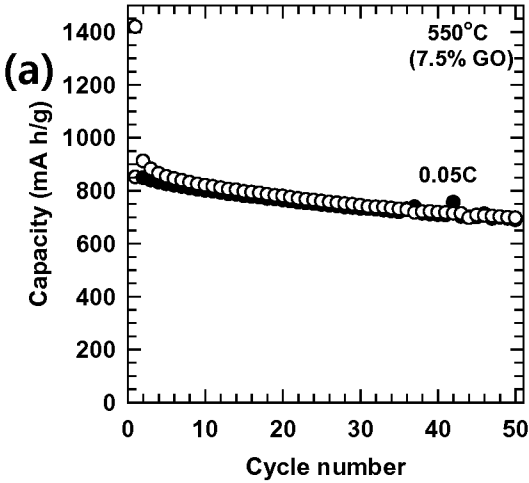
[Fig 22b]



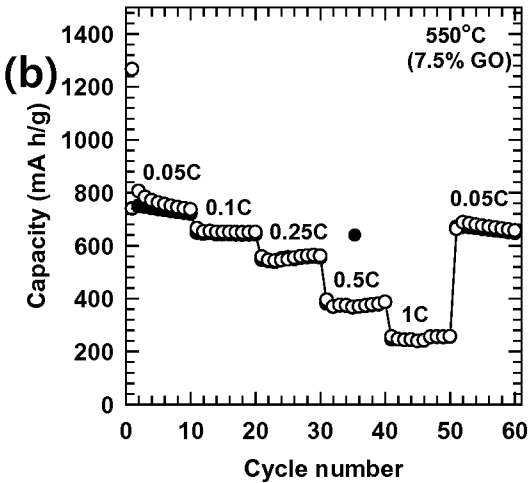
[Fig 22c]



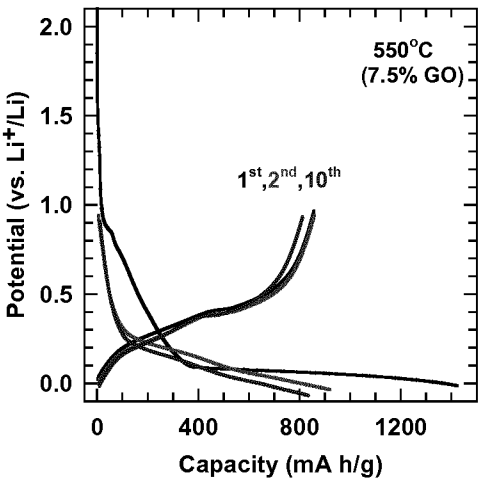
[Fig 23a]



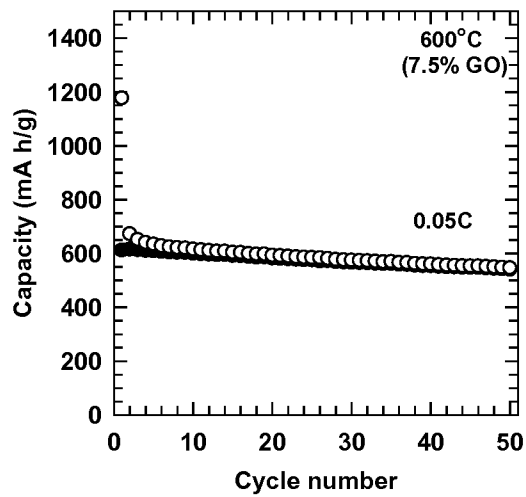
[Fig 23b]



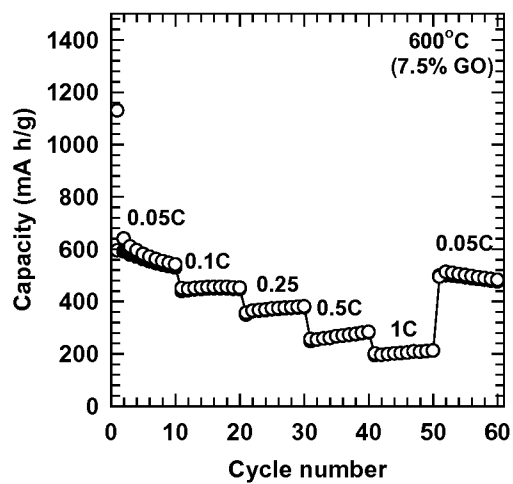
[Fig 23c]



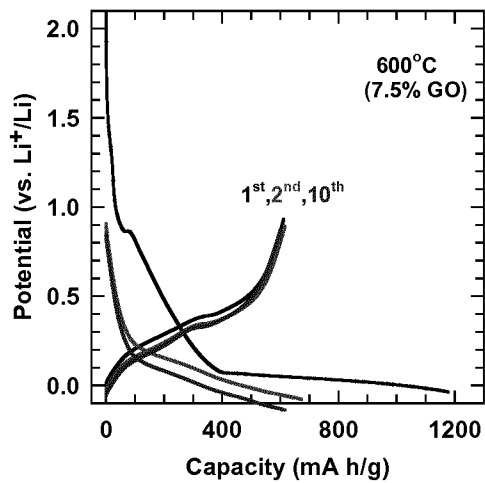
[Fig 24a]



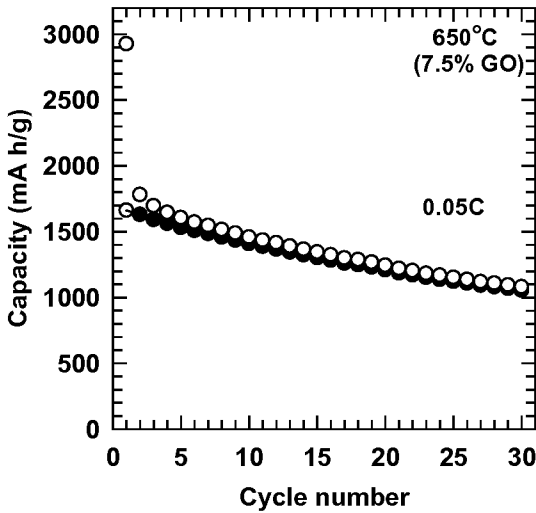
[Fig 24b]



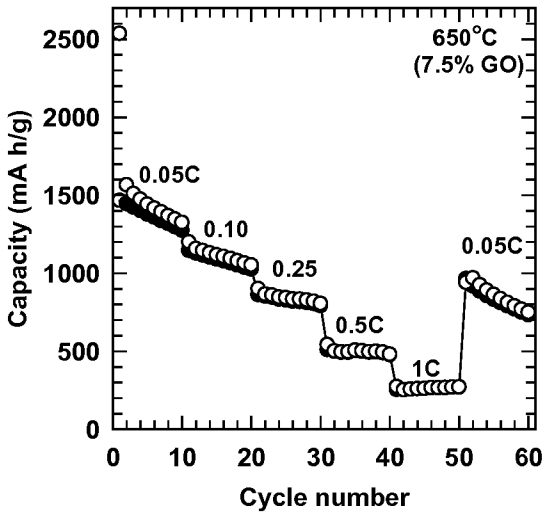
[Fig 24c]



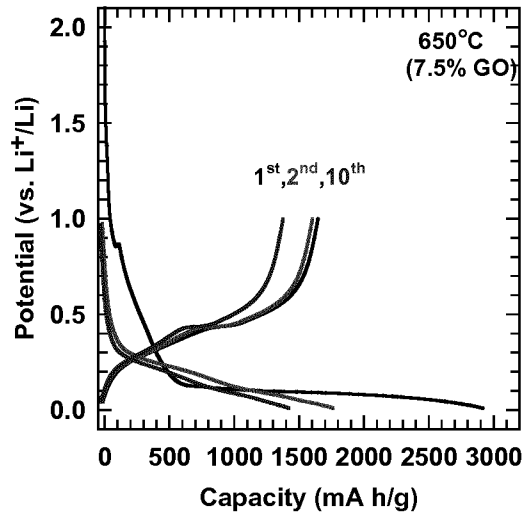
[Fig 25a]



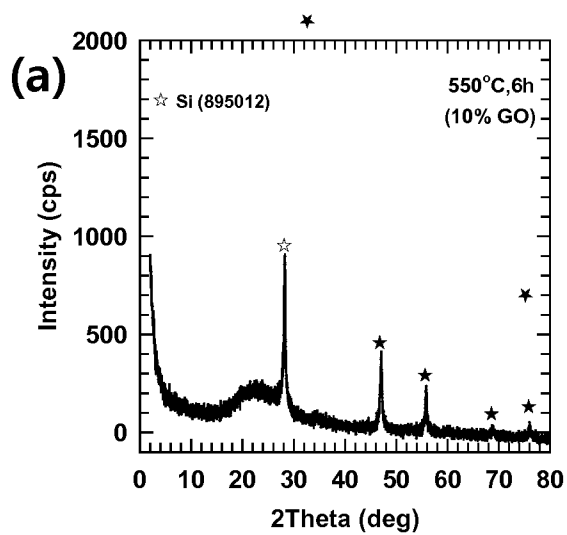
[Fig 25b]



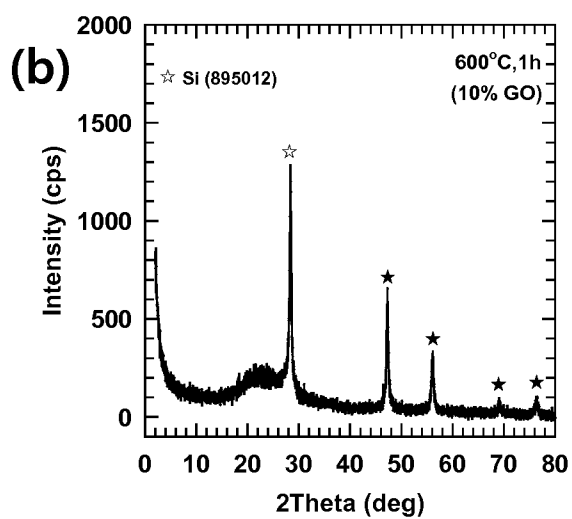
[Fig 25c]



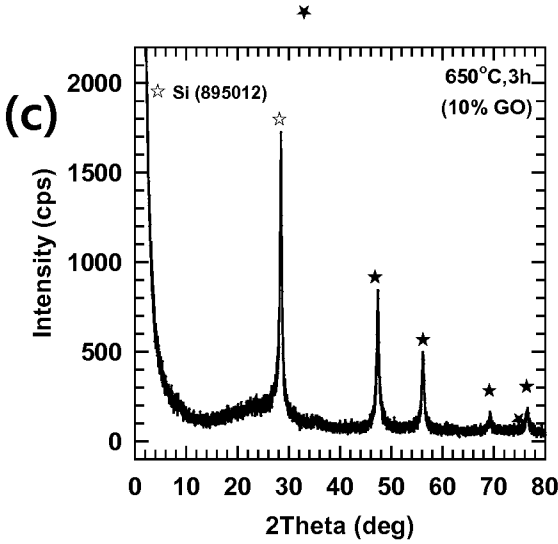
[Fig 26a]



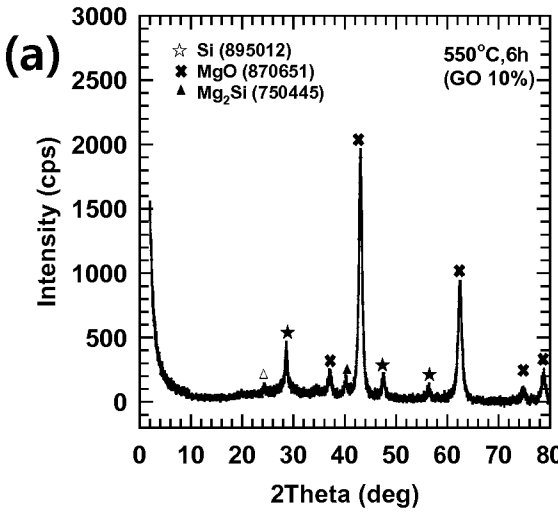
[Fig 26b]



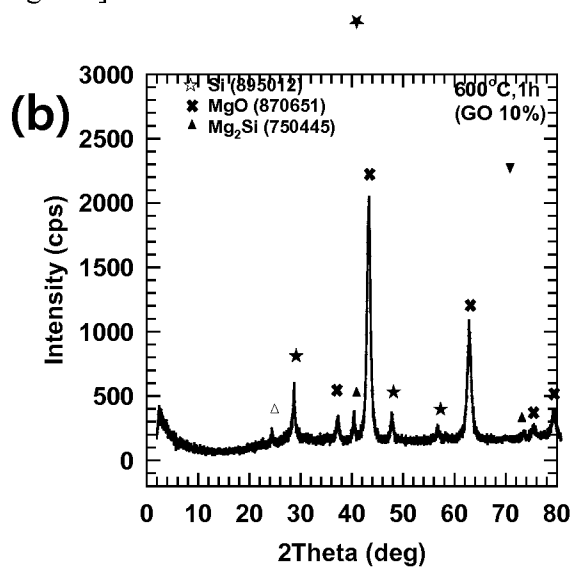
[Fig 26c]



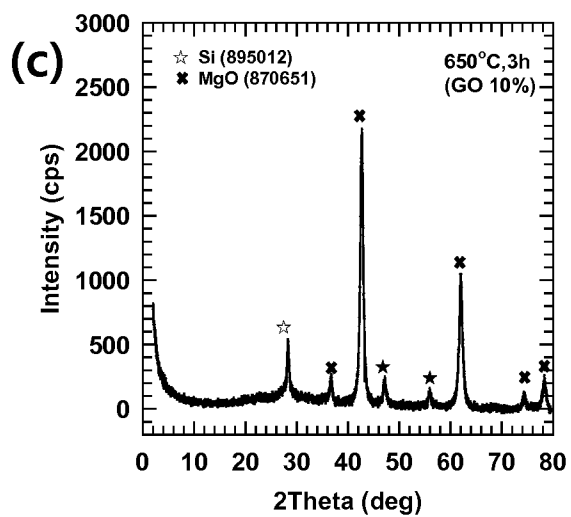
[Fig 27a]



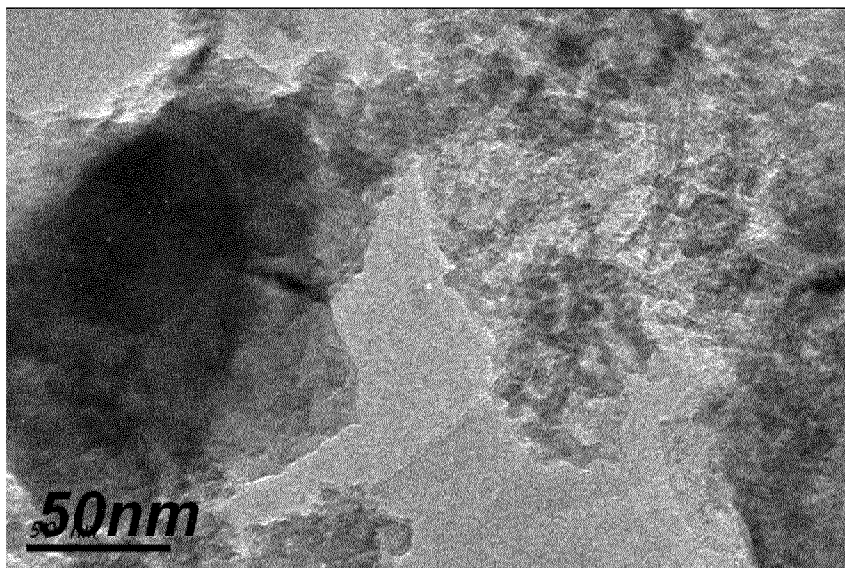
[Fig 27b]



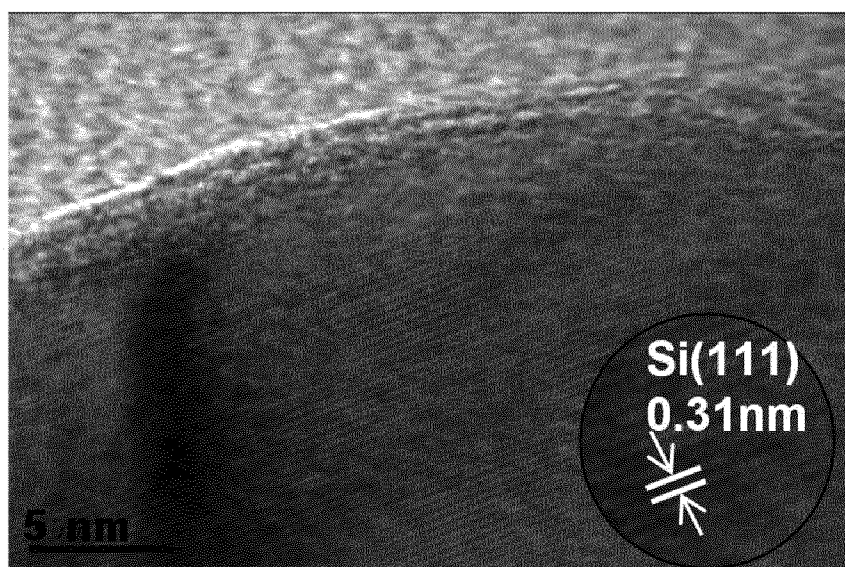
[Fig 27c]



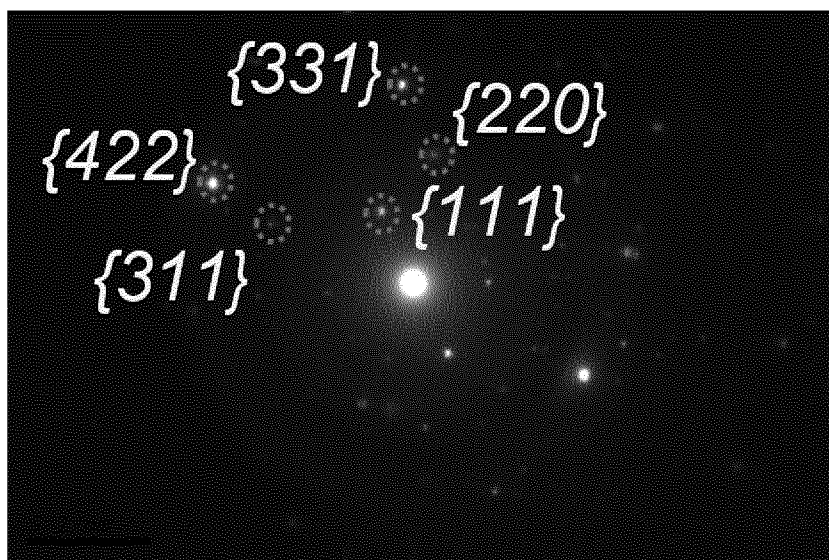
[Fig 28a]



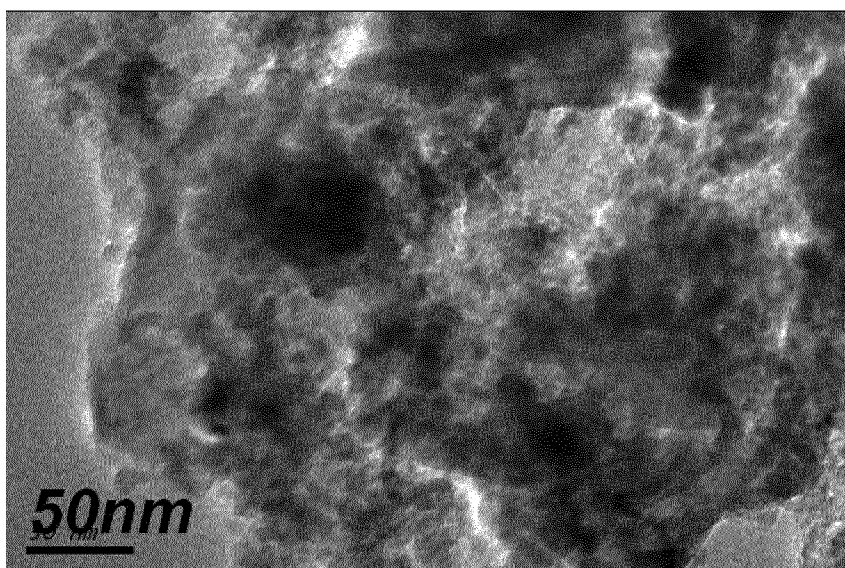
[Fig 28b]



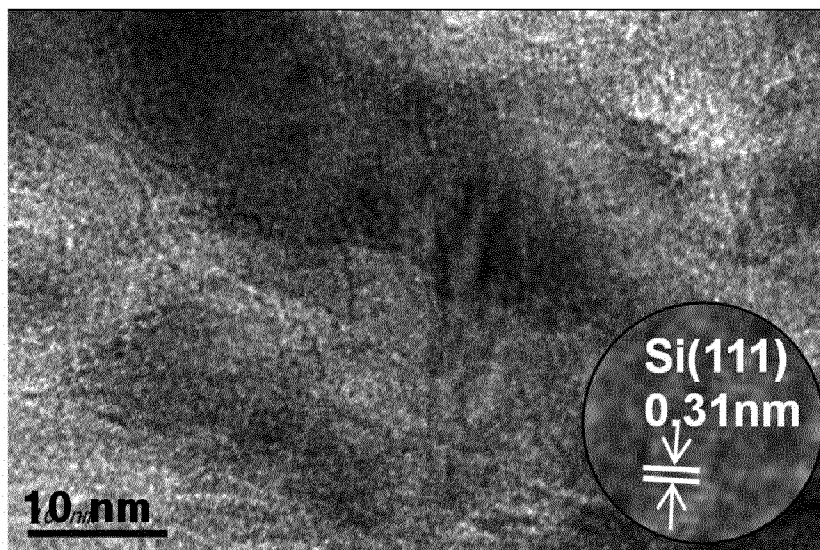
[Fig 28c]



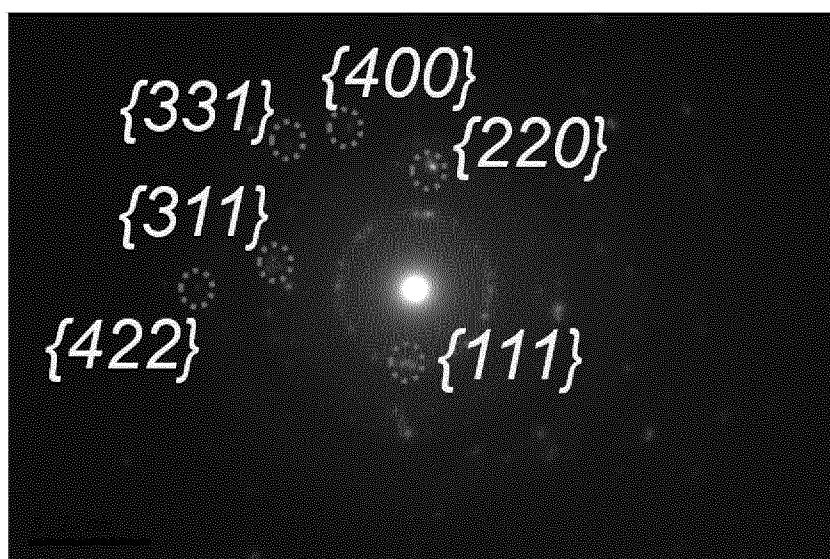
[Fig 29a]



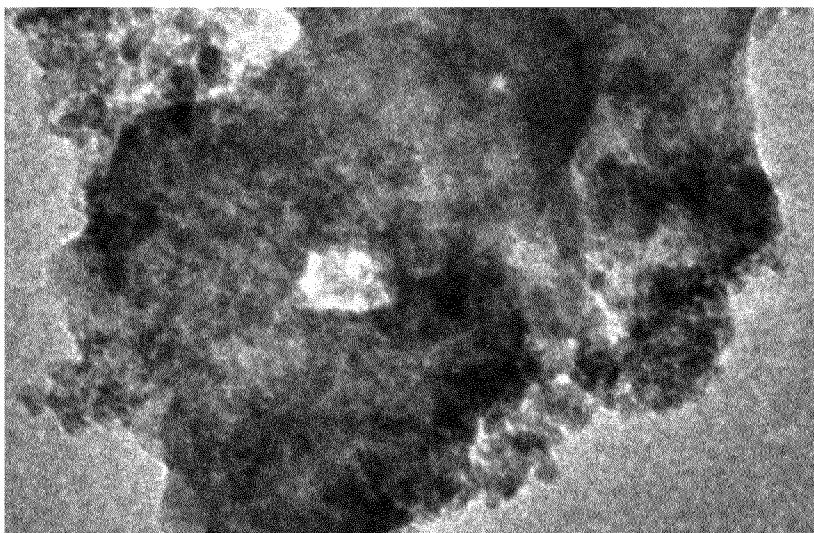
[Fig 29b]



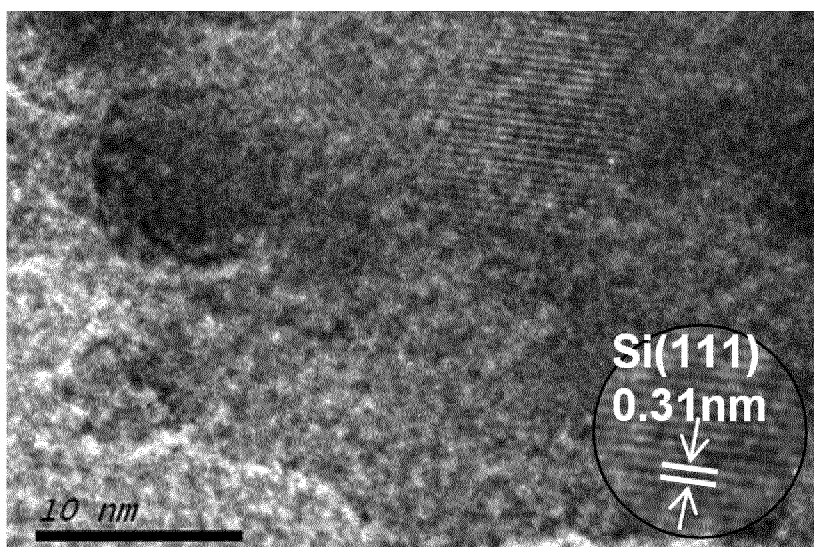
[Fig 29c]



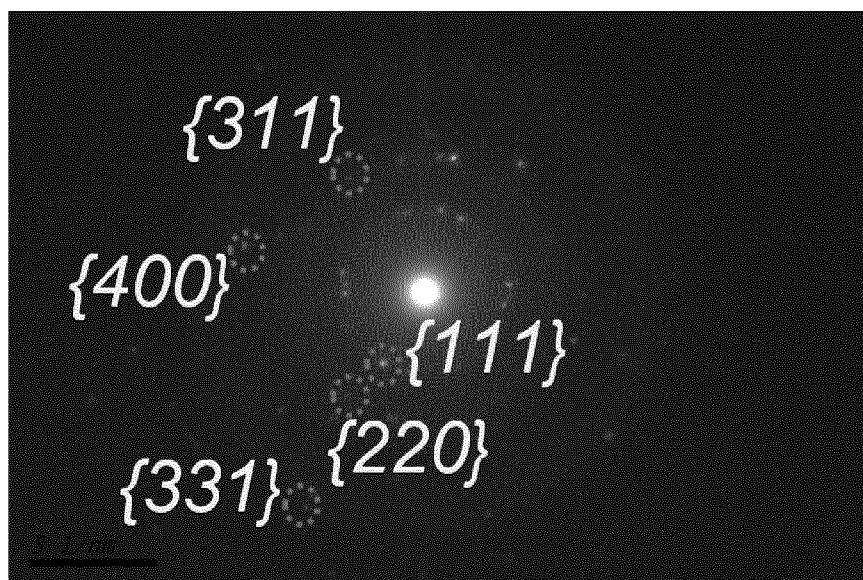
[Fig 30a]



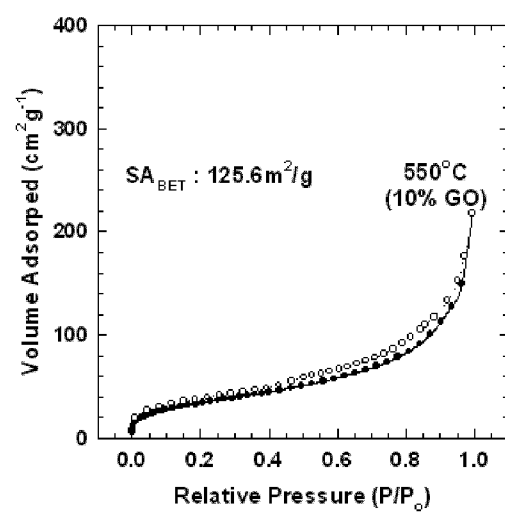
[Fig 30b]



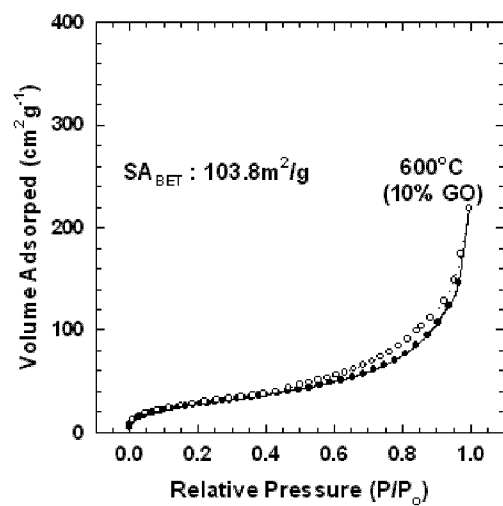
[Fig 30c]



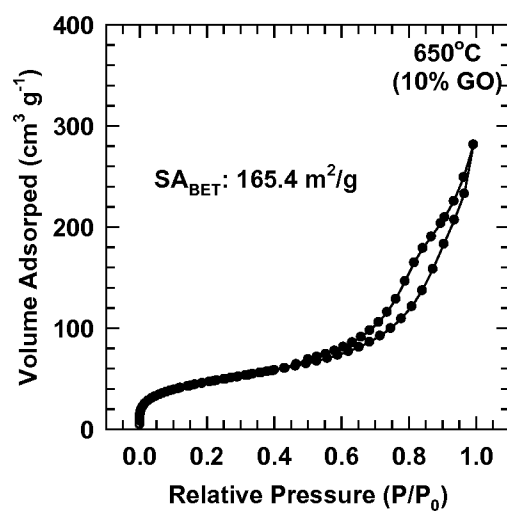
[Fig 31a]



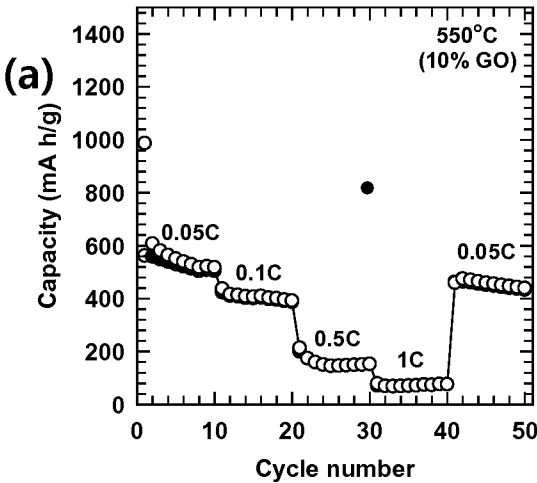
[Fig 31b]



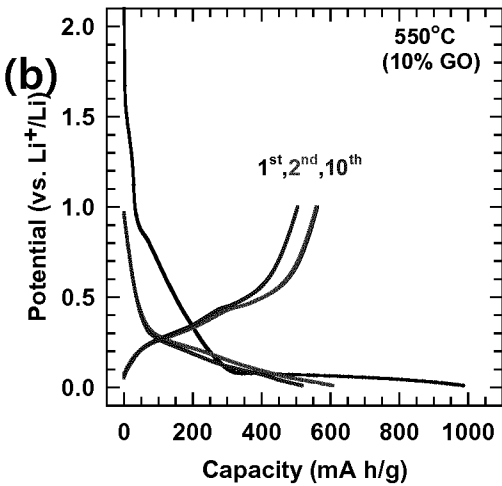
[Fig 31c]



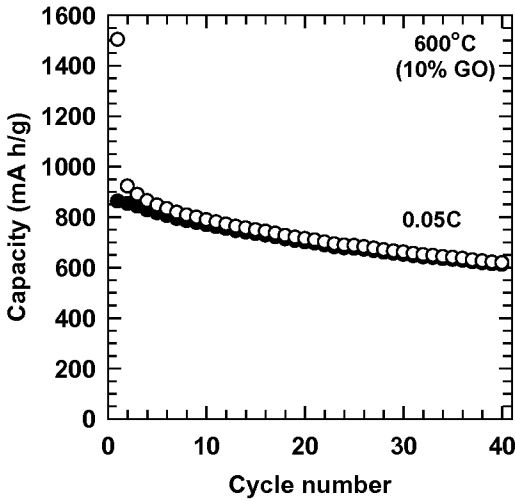
[Fig 32a]



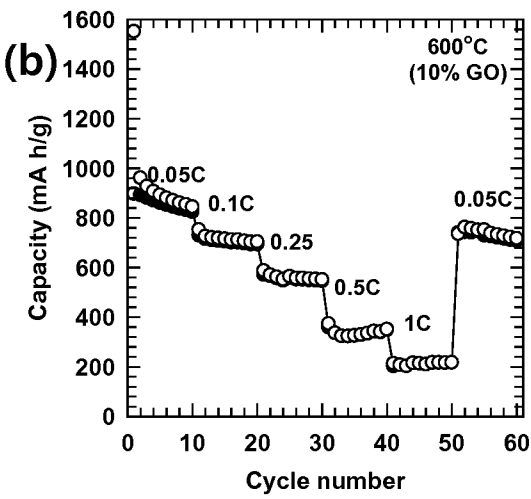
[Fig 32b]



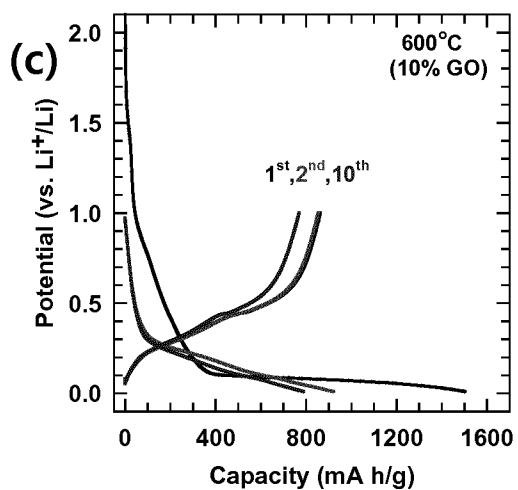
[Fig 33a]



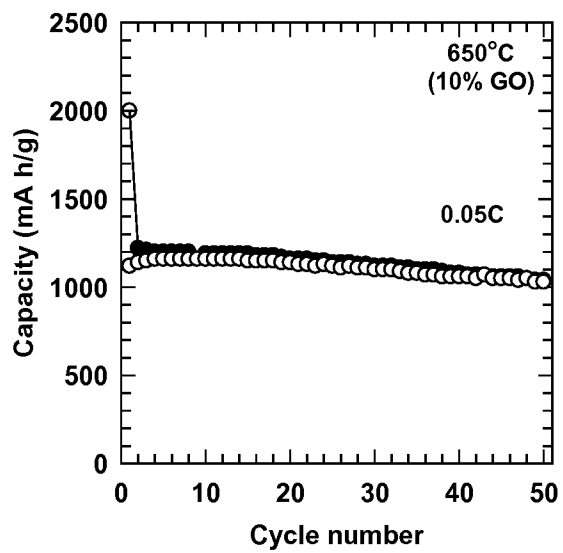
[Fig 33b]



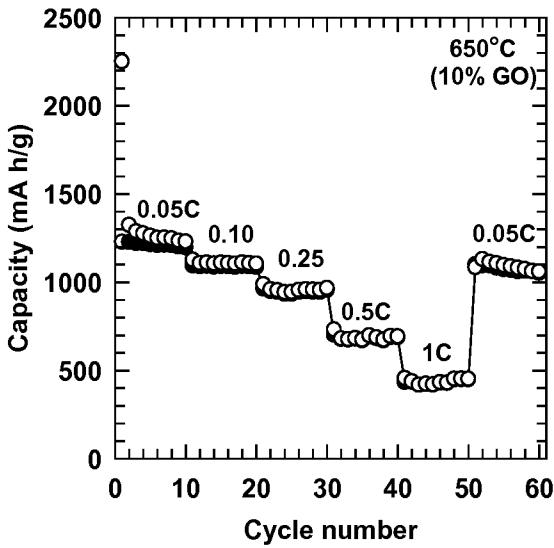
[Fig 33c]



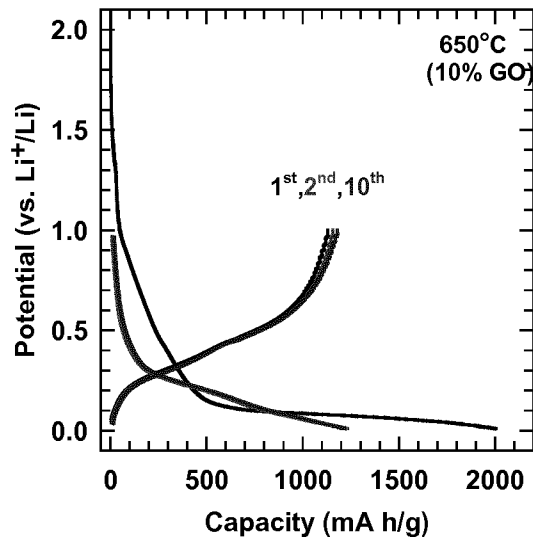
[Fig 34a]



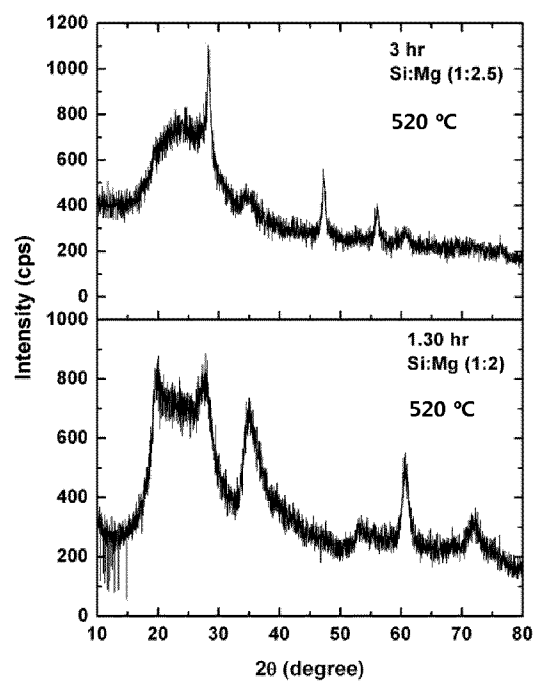
[Fig 34b]



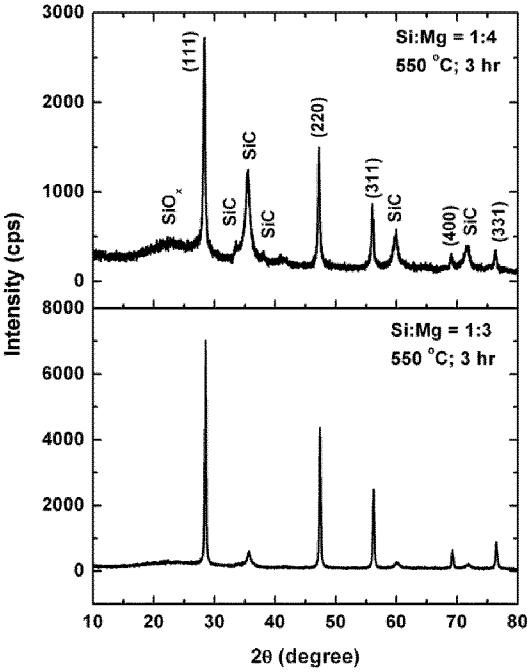
[Fig 34c]



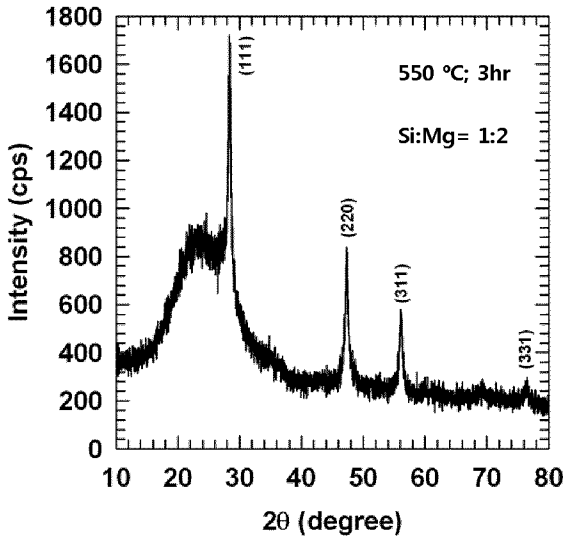
[Fig 35a]



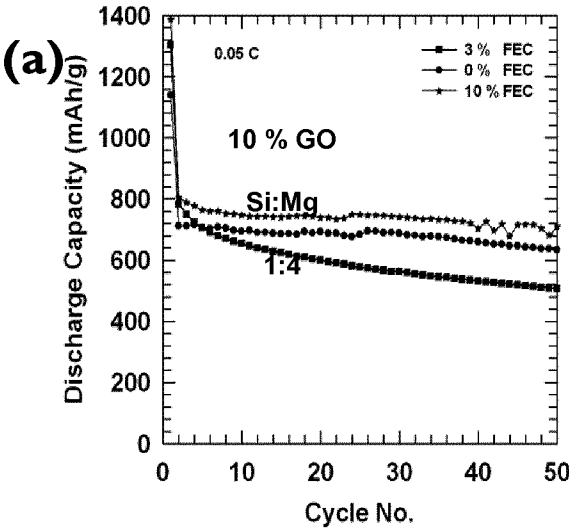
[Fig 35b]



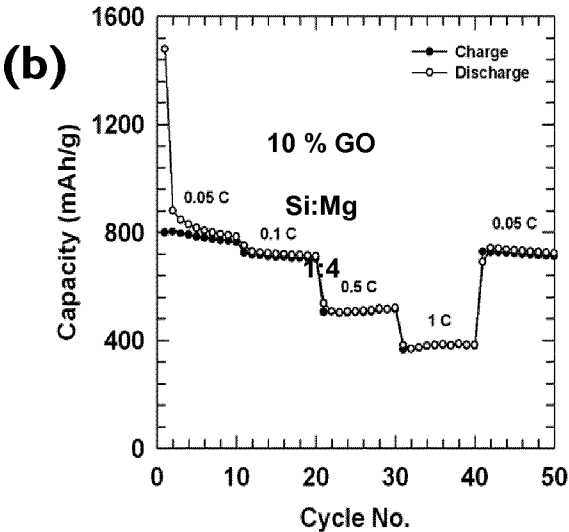
[Fig 35c]



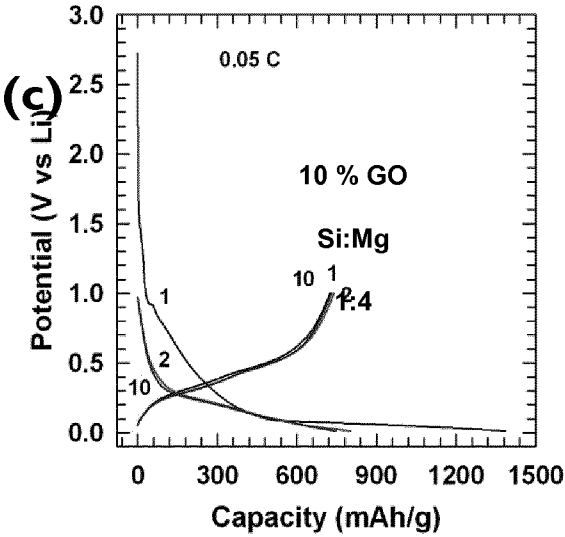
[Fig 36a]



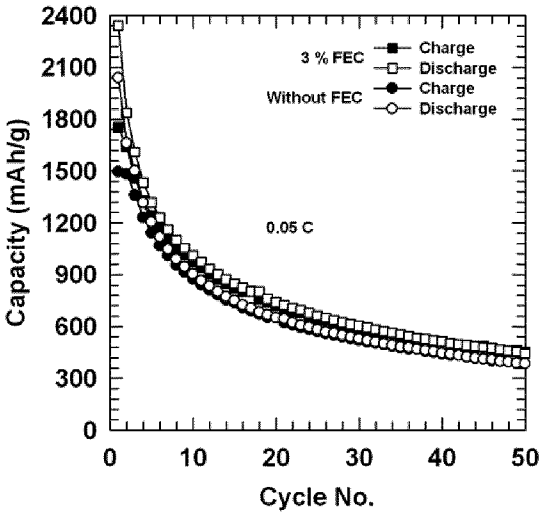
[Fig 36b]



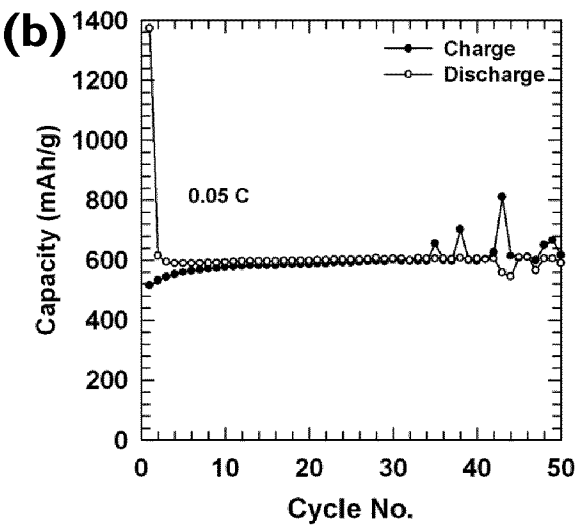
[Fig 36c]



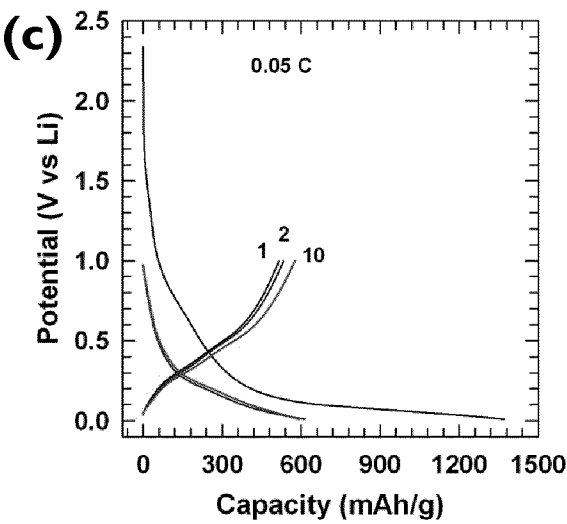
[Fig 37a]



[Fig 37b]



[Fig 37c]



INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2014/078775

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01M4/134 H01M4/36 H01M4/38 C01B33/023
ADD.

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 C01B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	XING XIN ET AL: "A 3D porous architecture of Si/graphene nanocomposite as high-performance anode materials for Li-ion batteries", JOURNAL OF MATERIALS CHEMISTRY, ROYAL SOCIETY OF CHEMISTRY, GB, vol. 22, 9 March 2012 (2012-03-09), pages 7724-7730, XP002721158, ISSN: 0959-9428, DOI: 10.1039/C2JM00120A [retrieved on 2012-03-09] Experimental, Conclusions; column 10, lines 18-21 -----	1-15
X	US 2013/149549 A1 (BORRELLI NICHOLAS FRANCIS [US] ET AL) 13 June 2013 (2013-06-13) example 1 -----	1,3,4,8, 10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

16 April 2015

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Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/078775

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013149549 A1	13-06-2013	CN 104271505 A	07-01-2015
		EP 2791058 A1	22-10-2014
		JP 2015500787 A	08-01-2015
		US 2013149549 A1	13-06-2013
		WO 2013090153 A1	20-06-2013
