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(54) BATTERIES WITH ANODES OF CARBON-COATED MACRO-POROUS SILICON

BATTERIEN MIT ANODEN AUS KOHLENSTOFFBESCHICHTETEM MAKROPORÖSEM SILIZIUM

BATTERIES AVEC ANODES DE SILICIUM MACRO-POREUX REVÊTU DE CARBONE

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Description

BACKGROUND

[0001] Lithium-ion batteries are a type of batteries in which lithium ions move from a negative electrode to a positive electrode during discharge and back when charging. Li-ion batteries can include an electrolyte in contact with an intercalated lithium compound as a cathode, and a carbon-based anode to form a battery cell. Lithium-ion batteries have high energy-to-weight ratios, low or no memory effects, and long charge-holding abilities when not in use. In addition to applications in consumer electronics, lithium-ion batteries are growing in popularity for defense, automotive, and aerospace applications. Such new applications impose a continued need to improve the energy density of lithium-ion batteries.

[0002] CN 105826527 A discloses porous silicon carbon composite and its use as anode material in batteries. WO 2017/052281 A1 identifies negative electrode active material for lithium secondary battery and method of preparing the same. US 2013/189575 A1 identifies porous silicon based anode material formed using metal reduction. In Xiao C., et al., Journal of Materials Chemistry A. 2014, 2, 20494-20499, Large-scale synthesis of Si@C three-dimensional porous structures as high-performance anode materials for lithium-ion batteries is described.

SUMMARY

[0003] This Summary is provided to introduce a selection of concepts in a simplified form that are further described below in the Detailed Description. This Summary is not intended to identify key features or essential features of the claimed subject matter, nor is it intended to be used to limit the scope of the claimed subject matter.

[0004] Certain lithium-ion batteries use carbon-based materials, such as graphite, as anodes. However, such carbon-based materials tend to limit charging capacities of lithium-ion batteries. For example, lithiation of a carbon-based anode can produce a charging capacity of about 372 mA h/g, while lithiation of silicon (Si) can produce a charging capacity of about 4,200 mAh/g. However, lithiation in silicon can involve about 300% volume change. Thus, after a few charge-discharge cycles, a bulk silicon-based anode would be pulverized. Silicon anodes can also form unstable solid-electrolyte interphase layers with electrolytes in lithium batteries. As such, the poor mechanical stability and chemical passivation properties of silicon can render silicon electrodes unsuitable for practical battery systems.

[0005] Several embodiments of the disclosed technology are directed to a battery system having an anode containing a carbon-coated macro-porous silicon material. The carbon-coated macro-porous silicon material can include particles individually containing crystalline silicon having pores of greater than about 100 nm. Both internal and external surfaces of the crystalline silicon can be coated, at least partially, with carbon of an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof. Experiments have shown that batteries having anodes constructed from examples of the carbon-coated silicon material exhibit high electrical capacity and cyclability. Thus, the silicon material disclosed herein is suitable for battery applications.

[0006] In accordance with embodiments of the disclosed technology, the carbon-coated silicon material can be prepared using a CO_2-thermic oxidation process (COOP). Further, the CO_2-thermic oxidation process includes an initial solid state reaction between silicon and a metal or metal mixture to form a metal silicide. Examples of a suitable metal can include magnesium (Mg), calcium (Ca), and barium (Ba). A solid state reaction using magnesium as an example can be as follows:

$$2Mg + Si \rightarrow Mg_2Si$$

In other examples, the solid state reaction can also use a mixture of at least two of the foregoing metals (e.g., both magnesium and calcium). Thus, the formed metal silicide can be a binary, ternary, quaternary, or other suitable orders of metallic system.

[0007] Upon completion of the solid state reaction, the CO_2-thermic oxidation process can include a thermal reaction in which the prepared metal silicide is oxidized using carbon dioxide (CO_2) to form particles of crystalline silicon coated with carbon and having multiple (e.g., hundreds) of nanometer-sized metal oxide structures in a single reaction. One example technique for performing the thermal reaction can include annealing or otherwise processing the metal silicide in a CO_2 environment at a suitable temperature (e.g., 700°C). Under such conditions, the metal silicide (e.g., Mg_2Si) can react with CO_2 to form a metal oxide, silicon, and carbon in a single reaction, for example, as follows:

$$Mg_2Si + CO_2 \rightarrow Si + C + 2MgO$$

[0008] The CO_2-thermic oxidation process can then include an acid leaching operation to remove the metal oxide from the resultant composite of the thermal reaction to form a silicon matrix. The removed metal oxide can thus leave behind macro pores (e.g., several hundred nanometers in size) in the silicon matrix that are distributed randomly or in other suitable manners. As such, the metal oxide (e.g., MgO) can act as a sacrificial template for creating macro porous structures in the crystalline silicon. The resulting particles include carbon-coated macro-porous silicon and can be suitable for use as anodes in batteries. It is believed that the carbon coating can help to form protective solid-electrolyte interphase (SEI) and therefore resulting in good cycling performance. Thus, several embodiments of the CO_2-thermic oxidation process can yield the surface carbon coating and macro-porous structure of the silicon particles simultaneously. As such, separate carbon coating operations, such as time consuming chemical vapor deposition and carbonization of toxic organic precursors may be avoided.

[0009] Without being bound by theory, it is believed that by selecting or adjusting suitable combinations and/or relative compositions of the metal or metal mixture for forming the metal silicide, different macro- and/or micro-scale structures can be formed in the carbon-coated macro-porous silicon particles. For example, morphology of the carbon-coated macro-porous particles of silicon and carbon formed using calcium can be quite different from those formed using magnesium. In particular, experiments showed that using calcium can yield a unique layered two-dimensional silicon morphology in the resulting silicon particles. Thus, combining magnesium with calcium (or other suitable metals) with suitable relative compositions (e.g., molar ratios, percentages, etc.) can yield a unique morphology in the formed silicon particles.

[0010] In addition, the metal or metal mixture can also be in excess of silicon according to stoichiometry during the solid state reaction. It is also believed that by selecting or adjusting a level or percentage of excess of the metal or metal mixture, different macro- and/or micro-scale structures can be formed in the carbon-coated macro-porous silicon material. In the example solid state reaction above, magnesium may be 10%, 20%, 30%, 40%, or more in excess of silicon. The excess magnesium can react with CO_2 during the thermal reaction as follows:

$$2Mg + CO_2 \rightarrow C + 2MgO$$

The formed magnesium oxide (MgO) can then be removed during acid leaching to form macro-scale pores in the final particles. Thus, by adjusting a level of excess of magnesium, different numbers and/or formations of macro-scale pores can be obtained in the resulting silicon particles. Also, the formed carbon on the surface of the silicon can enhance overall electrical conductivity of the resulting silicon particles used for anodes of batteries which may be beneficial to cycling performance. In further implementations, the foregoing selection or adjustments of composition of the metal or metal mixture and corresponding level or percentage of excess may be applied in conjunction to yield a desired morphology in the resulting carbon-coated macro-porous silicon material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

Figures 1A and 1B are schematic diagrams showing an example battery incorporating an anode having a carbon-coated macro-porous silicon material in accordance with embodiments of the disclosed technology.

Figure 2 is a schematic diagram illustrating an example CO_2-thermic oxidation process suitable for forming the carbon-coated macro-porous silicon material in Figures 1A and 1B.

Figures 3A-3D are example scanning electron microscope (SEM) images of corresponding products from each stage of the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 4A shows analysis results of X-ray diffraction (XRD) of example products of a CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 4B shows analysis results of N_2 adsorption-desorption analysis of example products of the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figures 5A and 5B are example transmission electron microscopy (TEM) images of spherical macro pores and carbon layers on a silicon surface and carbon layer (dotted area) on silicon matrix of example products formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figures 5C-5E are example energy-dispersive X-ray spectroscopy (EDS) elemental mapping results showing generally homogeneous distribution of carbon throughout a silicon particle formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 5F shows an example Raman spectroscopy results before and after acid leaching showing that MgO is effectively removed and existence of carbon in a silicon particle formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figures 6A-6C are schematic diagrams showing example reaction kinetics between gaseous CO_2 and Mg_2Si during initial bulk diffusion of gaseous CO_2, surface diffusion causing early formation of MgO/Si/C composite, and subsequent reaction between Mg_2Si and diffused CO_2 in accordance with embodiments of the disclosed technology.

Figure 7A shows an example first cycle voltage profile of a battery incorporating a carbon-coated macro-porous silicon material formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology. In particular, Figure 7A shows lithiation and delithiation capacities of about 2732 mA·h/g and 2273 mA·h/g, respectively, which resulting in >83.2% coulombic efficiency. Figure 7A also includes an inset showing dQ/dV plot for first cycling showing sharp peaks at ~0.05V, indicating phase transition of crystalline Si to amorphous Si.

Figure 7B shows an example rate capability result exhibiting ~1000 mA h/g specific capacity at 1.0 C-rate and recovering back to ~2000 mA h/g at 0.2 C-rate of a battery incorporating a carbon-coated macro-porous silicon material formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 7C shows example representative voltage profiles for C-rate of 0.2, 0.5, 0.8, and 1.0 of a battery incorporating a carbon-coated macro-porous silicon material formed using the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 7D shows a comparison of 0.2 C-rate cycling performance among example bulk silicon material, silicon via air-oxidation of Mg_2Si, and carbon-coated macro-porous silicon from the CO_2-thermic oxidation process in accordance with embodiments of the disclosed technology.

Figure 7E shows example lithiation-delithiation profiles of carbon-coated macro-porous silicon material at different cycles in accordance with embodiments of the disclosed technology.

Figure 8A shows an example SEM image of a layered silicon/carbon composite in accordance with embodiments of the disclosed technology.

Figure 8B shows an example result of an ex-situ XRD analysis showing that major phase is crystalline Si with approximately <10wt% of $FeSi_2$ believed due to the existence of Fe in a starting material in accordance with embodiments of the disclosed technology.

Figure 8C shows an example cycling performance of a layered two-dimensional silicon/carbon composite at 0.5C-rate in accordance with embodiments of the disclosed technology.

Figure 9A shows an example in-situ high temperature XRD (HT-XRD) analysis of Mg_2Si during the CO_2-thermic oxidation process. In particular, Figure 9A shows phase evolution of MgO and Si as well as the decrease of Mg_2Si peak intensity starting at around 500°C.

Figure 9B shows an example peak Intensity change during in-situ HT-XRD showing clear phase evolution of Si and MgO in accordance with embodiments of the disclosed technology.

Figures 9C-9E show example magnified in-situ HT-XRD peaks at around 2θ = 28~29°, 42 ~ 44°, and 39 ~ 40° where evident change in Si, MgO, and Mg_2Si peak intensities, respectively, can be seen with respect to temperature changes.

Figure 10 shows example Gibbs free energies at various temperatures for Mg_2Si formation and subsequent CO_2-thermic oxidation process of Mg_2Si compared with Air (or O_2) oxidation in accordance with embodiments of the disclosed technology.

Figures 11A and 11B show example ex-situ XRD analysis to investigate the influence of temperature (600~800°C) and holding time (50~600 minutes) on complete conversion of Mg_2Si, respectively.

Figures 12A-12J show example SEM images of MgO + Si + C composite at 700°C for various holding times of 50 min, 100 min, 200 min, 400 min, and 600 min. These figures show that overall particle size does not change much but the morphology is significantly altered by the holding time from 50 min to 400 min.

Figure 13 shows example XRD patterns for CaO + Si + C composite after CO_2-thermic oxidation process with $CaSi_2$ (bottom) and Si+C after CaO removal (middle and top) in accordance with embodiments of the disclosed technology.

DETAILED DESCRIPTION

[0012] In a first embodiment of the present invention, a method of forming a silicon material for use in anodes of batteries is provided, the method comprising:

reacting a metal or a mixture of multiple metals with silicon (Si) in a solid state reaction to form a metal silicide;

performing a CO_2-thermic oxidation process on the formed metal silicide with carbon dioxide to form a composite of one or more metal oxides, silicon, and carbon; and

contacting the formed composite of one or more metal oxides, silicon, and carbon with an acid to remove the one or more metal oxides from the composite to produce particles of the silicon material individually having: a crystalline silicon formed in the CO_2-thermic oxidation process; and pores in the crystalline silicon, the pores corresponding to the removed metal oxide by the acid and having surfaces coated with the carbon from the performed CO_2-thermic oxidation process,

wherein reacting the metal or the mixture of multiple metals with silicon includes reacting one of magnesium (Mg), calcium (Ca), or barium (Ba) with silicon (Si); and performing the CO2-thermic oxidation process includes performing the CO_2-termic oxidation process with one of magnesium silicide (Mg_2Si), calcium ($CaSi_2$), and barium silicide ($BaSi_2$) and wherein in case Mg is present, Mg is at least 10 wt% more in excess of silicon.

In a further aspect, a battery is provided, comprising:

a first electrode;
an electrolyte in electrical communication with the first electrode, the electrolyte containing a plurality of metal ions; and
a second electrode spaced apart from the first electrode and in electrical communication with the first electrode via the electrolyte, wherein the second electrode contains particles of a silicon material individually having: the crystalline silicon in a matrix; and pores distributed in the
matrix of the crystalline silicon, the pores having a size greater than 100 nanometers, wherein surfaces of the crystalline silicon in the pores are coated with carbon,
wherein the silicon material is obtainable by a method according to the present invention.

Further, the present invention relates to a silicon material as described and obtained above, namely, comprising

the crystalline silicon in a matrix; and
pores distributed in the matrix of the crystalline silicon, the pores having a size greater than 100 nanometers, wherein surfaces of the crystalline silicon in the pores are coated with carbon.

[0013] Various embodiments of battery systems, devices, and associated methods of making are described herein. Even though the technology is described below using a lithium-ion battery as an example, in other embodiments, the technology may be applicable in other types of batteries (e.g., containing sodium, potassium, calcium, magnesium, cadmium, or copper ions), a chemical sensor, an organic thin film transistor, an electromechanical actuator, a gas separation membrane, a fuel cell, and/or other suitable electronic components. In the following description, specific details of components are included to provide a thorough understanding of certain embodiments of the disclosed technology. A person skilled in the relevant art will also understand that the disclosed technology may have additional embodiments or may be practiced without several of the details of the embodiments described below with reference to Figures 1A-13.

[0014] Certain lithium-ion batteries use carbon-based materials, such as graphite, as anodes. However, such carbon-based materials tend to limit charging capacities of lithium-ion batteries. For example, lithiation of a carbon-based anode can produce a charging capacity of about 372 mA h/g, while lithiation of silicon (Si) can produce a charging capacity of about 4,200 mAh/g. However, lithiation in silicon can involve about 300% volume change. Thus, after a few charge-discharge cycles, a bulk silicon-based anode would be pulverized. Silicon anodes can also form unstable solid-electrolyte interphase layers with electrolytes in lithium batteries. As such, the poor mechanical stability and chemical passivation properties of silicon can render silicon electrodes unsuitable for practical battery systems.

[0015] Several embodiments of the disclosed technology are directed to a battery system having an anode containing a carbon-coated macro-porous silicon material. The carbon-coated macro-porous silicon material can include particles individually containing crystalline silicon having macro-scale pores of greater than about 100 nm. Both internal and external surfaces of the crystalline silicon can be coated, at least partially, with carbon of an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof. Experiments have shown that batteries having anodes constructed from examples of such a carbon-coated macro-porous silicon material exhibit high electrical capacity and cyclability. In addition, examples of the silicon material can be produced using a CO_2-thermic oxidation process to form crystalline silicon and the coated carbon in a single reaction, as discussed in more detail below.

[0016] Figure 1A is a schematic diagram of an example lithium-ion battery 100 during discharging, and Figure 1B is a schematic diagram of the lithium-ion battery 100 during charging in accordance with embodiments of the technology. As shown in Figures 1A and 1B, the lithium-ion battery 100 can include a container 102 holding an anode 104, a cathode 106, an electrolyte 108, and an optional membrane 110 in the electrolyte 108. Even though only certain components are illustrated in Figures 1A and 1B, in other embodiments, the lithium-ion battery 100 can also include insulators, gaskets, vent holes, and/or other suitable components (not shown). In further embodiments, the membrane 110 may be omitted.

[0017] The cathode 106 can be constructed from a layered oxide (e.g., lithium cobalt oxide ($LiCoO_2$)), a polyanion (e.g., lithium iron phosphate ($LiFePO_4$)), or a spinel (e.g., lithium manganese oxide ($LiMn_2O_4$)). Other suitable materials for the cathode 106 can include lithium nickel oxide ($LiNiO_2$), lithium iron phosphate fluoride (Li_2FePO_4F), lithium cobalt nickel manganese oxide ($LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$), $Li(Li_aNi_xMn_yCo_z)O_2$, and/or other suitable cathode materials.. Additional examples of metal compositions suitable for the cathode 106 can also include:

- $LiNiCoAlO_2$ having 80% Nickel, 15% Cobalt, and 5% Aluminum
- $LiCoO_2$ having 100% Cobalt
- $LiMn_2O_4$ having 100% Manganese
- $LiNiMnCoO_2$ having 33.3% Nickel, 33.3% Manganese, and 33.3% Cobalt
- $LiFePO_4$ having 100% Iron

[0018] In certain embodiments, the electrolyte 108 can include a non-aqueous solution of organic carbonates such as ethylene carbonate or diethyl carbonate containing complexes of lithium ions. The electrolyte 108 can contain non-coordinating anion salts such as $LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiBF_4$, and lithium triflate. In other embodiments, the electrolyte 108 may also include an aqueous and/or a partially aqueous solution of lithium salts and/or other suitable compositions.

[0019] The anode 104 can be constructed, at least partially from a carbon-coated macro-porous silicon material. The carbon-coated macro-porous silicon material can include particles individually containing crystalline silicon having macro-scale pores of greater than about 100 nm distributed therein randomly or in other suitable manners. Both internal and external surfaces of the crystalline silicon can be coated, at least partially, with carbon of an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof. Such a silicon material can be formed using a CO_2-thermic oxidation process described herein. The number and/or distribution of the macro-scale pores as well as morphology of the crystalline silicon can be controlled by adjusting one or more of a selection of metal silicide or a level of excess of metal for forming the metal silicide, as discussed in more detail below with reference to Figures 2-13.

[0020] As shown in Figure 1A, during discharging, lithium ions 112 are extracted from the anode 104 and migrate toward the cathode 106 via the electrolyte 108. The lithium ions 112 pass through the optional membrane 110 and are inserted into the cathode 106. As a result, a current 114 flows from the cathode 106 past a load 116 to the anode 104. As shown in Figure 1B, during charging, a charger 118 provides a charging current 120 to the cathode 106. The charging current 120 causes lithium ions 112 to be extracted from the cathode 106 and move toward the anode 104. The lithium ions 112 pass through the optional membrane 110 and are inserted into the anode 104 via, e.g., alloying and/or otherwise combining with the material of the anode 104.

[0021] Several embodiments of the lithium-ion battery 100 can have a higher charging capacity than conventional batteries using a carbon-based material for anode. For example, as discussed above, a conventional lithium-ion battery with a carbon-based anode can have a charging capacity of about 372 mA·h/g while several embodiments of the lithium-ion battery 100 can have a charging capacity of about 2,000 mA h/g. As a result, the charging capacity of the lithium-ion battery 100 may be improved when compared to conventional lithium-ion batteries.

[0022] Several embodiments of the anode 104 of the lithium-ion battery 100 can have improved charging/discharging cyclability. Without being bound by theory, it is believed that several embodiments of the anode 104 can accommodate the large volume changes associated with lithium insertion because the macro pores in the crystalline silicon can contract and expand. For example, the macro pores may contract during lithium insertion and expand during lithium extraction without causing pulverization and/or other structural damage to the anode 104 as a whole. It is also believed that the carbon coating on the silicon material can also protect silicon from forming unstable solid-electrolyte interphase layers with electrolytes in a lithium battery. As such, chemical passivation properties of the silicon material can be improved to render the anode 104 stable for practical battery systems.

[0023] Figure 2 is a schematic diagram illustrating an example CO_2-thermic oxidation process suitable for forming the carbon-coated macro-porous silicon material in Figures 1A and 1B. In Figure 2, magnesium silicide (Mg_2Si) was used to illustrate aspects of the disclosed technology. In other implementations, calcium (Ca), barium (Ba), or other suitable metals may also be used in addition to or in lieu of magnesium in the CO_2-thermic oxidation process.

[0024] An initial stage of the CO_2-thermic oxidation process can include a solid state reaction 200 between a metal and silicon. For example, as illustrated in Figure 2, elemental magnesium (Mg) and silicon (Si) powders can be mixed to form a silicon/magnesium mixture 210. In certain embodiments, the magnesium and silicon can be in stoichiometric proportion of Mg_2Si. In other embodiments, the magnesium can be in excess of stoichiometric proportion of Mg_2Si to ensure full conversion of Si to Mg_2Si. The solid state reaction 200 can then include heating the silicon/magnesium mixture at a reaction temperature (e.g., about 500°C) for a period of time (e.g., about 10 hours) in an inert (e.g., argon) environment to obtain an intermetallic phase of Mg_2Si 212, as follows:

$$2Mg + Si \rightarrow Mg_2Si$$

In other examples, the solid state reaction 200 also can include reacting other suitable materials to form intermetallic compounds, such as magnesium stannide (Mg_2Sn) and Mg_2Cu.

[0025] Subsequent to the solid state reaction 200, the CO_2-thermic oxidation process can also include a thermal reaction 202 at which the formed intermetallic compound is oxidized by carbon dioxide. For example, as shown in Figure 2, the magnesium silicide can be oxidized by carbon dioxide as follows:

$$Mg_2Si + CO_2 \rightarrow 2MgO + Si + C$$

As shown above, products of the thermal reaction 202 can include a matrix of crystalline silicon 214 coated with carbon 216 and magnesium oxide (MgO) 218 dispersed in the crystalline silicon 214 randomly or in other suitable manners. The carbon 216 can be in an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof. In embodiments in which the magnesium is excess of stoichiometric proportion of Mg_2Si, the excess magnesium can react with the carbon dioxide as follows to form additional magnesium oxide 218 and carbon:

$$2Mg + CO_2 \rightarrow 2MgO + C$$

[0026] Upon completion of the thermal reaction 202, the CO_2-thermic oxidation process can further include an acid leaching reaction 204 in which the metal oxide (e.g., MgO) is removed from the crystalline silicon 214 using hydrofluoric acid (HF), hydrochloric acid (HCl), or other suitable types of acid. Thus, as shown in Figure 2, after the acid leaching reaction 206, the magnesium oxide is removed to form macro-scale pore 220 in the crystalline silicon 214. Both the interior and exterior surfaces of the crystalline silicon 214 can be covered with the carbon 216. As such, particles of crystalline silicon 214 can be efficiently formed with macro-scale pores and surface carbon 216 using the CO_2-thermic oxidation process. Changes in morphology of various products during stages of the CO_2-thermic oxidation process are discussed in more detail below with reference to Figures 3A-3D.

[0027] Figures 3A-3D are example scanning electron microscope (SEM) images of example products from each stage of the CO_2-thermic oxidation process of Figure 2 to illustrate change in morphology in accordance with embodiments of the disclosed technology. As shown in Figure 3A, starting silicon powder exhibits smooth facets and average particle size of about 15 μm, which then drastically transforms into lumpy chunk (shown in Figure 3B) after the thermal reaction 202 with magnesium powder. The transition from Si to Mg_2Si may lead to an increase in particle size (e.g., about 20 μm). Based on the solid state reaction 200, approximately 160% of volume increase may occur during a phase transition from Si diamond cubic crystal structure with a lattice parameter of a=0.543 nm to Mg_2Si antifluorite structure with a lattice parameter of a=0.634 nm.

[0028] It is believed that magnesium is a main diffusive species during the solid-state reaction 200 with silicon. In general, the substance with a lower melting point has a relatively weaker atomic bonding and higher molar volume, which allows faster diffusion than the one with a higher melting point. In the illustrated example, the melting points of

Mg and Si are 650°C and 1414°C, respectively. Thus, Mg may easily diffuse into the innermost Si matrix, and hence enables the complete transformation to the intermetallic phase of Mg_2Si. Subsequently, during the thermal reaction 202, thermal oxidation of Mg_2Si occurs and lead to a composite of magnesium oxide 218, crystalline silicon 214, and carbon 216.

[0029] As shown in Figure 3C, the morphology of the composite after the thermal reaction 202 was an irregular-shaped lump with numerous speckles on the surface. During the acid leaching reaction 204, acid leaching was performed to furnish the porous structure by removing magnesium oxide 218, shown in Figure 3D. The removed oxides, such as MgO and possibly SiOx, acted as sacrificial template for creating the macro-porous structure in the crystalline silicon 214. The macro-scale pores are believed to be desirable for Si-based anode materials and can contribute to a higher tap density. Tap density is typically measured by mechanically tapping a container until little further volume change is observed. Tap density is believed to be closely related to size and porosity of a tested material. In certain experiments, the carbon-coated macro-porous silicon material exhibited almost 3 times higher tap density than commercially available nanosized silicon powder.

[0030] Figure 4A shows analysis results of X-ray diffraction (XRD) of example products of a CO_2-thermic reaction in accordance with embodiments of the disclosed technology. The XRD analysis showed various stages of transition from silicon, to magnesium silicide, to a composite of magnesium oxide, silicon, and carbon, and finally to a silicon/carbon composite. N_2 adsorption-desorption analysis performed on the example silicon material showed that the BET surface areas of samples before and after acid leaching were 15.1, and 67.6 m^2/g indicating the role of magnesium oxide 218 as a sacrificial template for creating the macro-porous structure and relatively low surface area compared to typical Nano-engineered Si-based anode materials. Furthermore, the SEM and TEM high magnification images in Figures 5A and 5B show that the Si/C composite after acid leaching exhibits porous structures with size greater than 100 nm and a generally uniform layer of carbon on the porous crystalline silicon.

[0031] To illustrate the formation of carbon 216 via the CO_2-thermic oxidation process with intermetallic compounds, EDS elemental mapping (shown in Figures 5C- 5E) and Raman spectroscopy (shown in Figure 5F) were performed. In the EDS result, generally uniform distribution of carbon throughout the particle were confirmed. Two peaks at around 1350 /cm (D band) and 1580 /cm (G band) in Raman analysis show the existence of carbon in the sample. The intensities in D and G bands are almost 1:1, which implies that the carbon synthesized through the CO_2-thermic oxidation process was a mixture of amorphous (or disordered) and graphitic carbon.

[0032] The reaction mechanism between gaseous CO_2 and Mg_2Si may include three diffusion stages based on the behavior of gaseous CO_2 throughout the conversion, as shown in Figures 6A-6C. Initially, as shown in Figure 6A, CO_2 molecules move towards the Mg_2Si surface through the bulk gas layer. Then, as shown in Figure 6B, surface diffusion of CO_2 molecules along the exterior of Mg_2Si particles occurs, and the first oxidation reaction of Mg_2Si occurs, which leads to the formation of the MgO + Si + C composite at the surface. After the formation of the first surficial MgO + Si + C composite layer, the consecutive supply of CO_2 gas molecules into the interior of the Mg_2Si can be achieved through inter-/intra-particular diffusion of CO_2 molecules through the newly formed MgO + Si + C composite layer to continuously promote the oxidation reaction with internal Mg_2Si until generally a full conversion is achieved.

[0033] The electrochemical properties (e.g., cycling performance and rate capability) of example carbon-coated macro-porous silicon material produced during experiments were evaluated. As shown in Figure 7A, initial lithiation and delithiation capacities of about 2732 mA·h/g and 2273 mA·h/g, respectively were observed. Such capacities correspond to about 83.2% initial coulombic efficiency. Furthermore, the carbon-coated macro-porous silicon material also showed a good rate capability (shown in Figure 7B) of approximately 1000 mA·h/g at a 1.0 C rate, which recovered back to 2000 mA·h/g at 0.2 C rate. Representative lithiation/delithiation profiles at each C rate were shown in Figure 7C, indicating phase transition of amorphous silicon during cycling. In Figures 7D and 7E, cycling performances at 0.2 C rate of the Si/C composite were compared with bulk Si and air-oxidized Si samples. Results showed good cycling stability of the example silicon material over 400 cycles exhibiting ~87% capacity retention and typical lithiation/delithiation phase transition during cycling.

[0034] Test with $CaSi_2$ via CO_2-thermic oxidation process were also conducted, as shown in Figures 8A-8C and 13. These results showed that $CaSi_2$ is also suitable for having a strong thermodynamic tendency to be oxidized with CO_2. The final morphology of the reaction product from $CaSi_2$ is different than the from Mg_2Si possibly due to the unique crystal structure of $CaSi_2$ resulting in buckled layered two-dimensional silicon morphology. The Si/C composite with layered morphology via CO_2-thermic oxidation process with $CaSi_2$ exhibits stable cycling performance with about 1000 mA·h/g at 90th cycle (shown in Figure 8C).

[0035] Figure 9A shows an example in-situ high temperature XRD (HT-XRD) analysis of Mg_2Si during the CO_2-thermic oxidation process. As shown in Figure 9A, phase evolution of MgO and Si as well as decrease of Mg_2Si peak intensity can be clearly seen starting at around 500°C. Figure 9B shows an example peak intensity change during in-situ HT-XRD showing clear phase evolution of Si and MgO. Figures 9C-9E show example magnified in-situ HT-XRD peaks at around $2\theta = 28{\sim}29°$, $42 \sim 44°$, and $39 \sim 40°$ where evident change in Si, MgO, and Mg_2Si peak intensities, respectively, can be seen with respect to temperature changes. As shown in Figures 9A-9E, phase evolution of MgO and Si as well as the decrease of Mg_2Si peak intensity starting at around 500°C.

[0036] Figure 10 shows example Gibbs free energies at various temperatures for Mg_2Si formation and subsequent CO_2-thermic oxidation process of Mg_2Si compared with Air(or O_2) oxidation in accordance with embodiments of the disclosed technology. As seen in Figure 10, a thermodynamic driving force for this oxidation reaction is sufficient (ΔG=-519 kJ/mol at 700°C), a surficial conversion of magnesium to Mg_2Si may proceed readily. In a CO_2 environment, the reaction is much milder exothermic than the one in air.

[0037] Figures 11A and 11B show example ex-situ XRD analysis to investigate the influence of temperature (600~800°C) and holding time (50~600 minutes) on complete conversion of Mg_2Si, respectively. As shown in Figures 11A and 11B, temperatures from about 650°C to about 800°C and holding times of about 100 minutes to about 600 minutes may be sufficient to convert Mg_2Si into magnesium oxide, silicon, and carbon by reacting with carbon dioxide.

[0038] Figures 12A-12J show example SEM images of MgO + Si + C composite at 700°C for various holding times of 50 min, 100 min, 200 min, 400 min, and 600 min. These figures show that overall particle size does not change much but the morphology is significantly altered by the holding time from 50 min to 400 min. As shown in Figures 12A-12J, overall particle size did not appear to change much but morphology is significantly altered by a holding time from 50 min to 400 min. This morphology change is believed to be closely related to kinetics of the oxidation reaction, such as diffusion of CO_2 into bulk Mg_2Si and reaction rate of $Mg_2Si + CO_2 \rightarrow 2MgO + Si + C$.

[0039] Figure 13 shows example XRD patterns for CaO + Si + C composite after CO_2-thermic oxidation process with $CaSi_2$ (bottom) and Si+C after CaO removal (middle and top) in accordance with embodiments of the disclosed technology. As shown in Figure 13, decrease in impurity phase ($FeSi_2$) can be clearly seen after HF leaching.

EXPERIMENTS

[0040] Certain experiments of the CO_2-thermic oxidation process using intermetallic compounds (Mg_2Si and $CaSi_2$) as model systems were performed, including a thermodynamics feasibility study, an in-situ phase evolution analysis, and intensive microstructural characterization of the CO_2-thermic oxidation reaction.

[0041] The CO_2-thermic oxidation process was found to be an effective way to fabricate suitable anode materials for advanced energy storage systems, such as lithium batteries. The reaction product showed excellent long-term cycling stability and moderate rate capability. These results showed that the proposed CO_2-thermic oxidation process with oxidative intermetallic compounds is a pathway for recycling and utilizing CO_2 gas as for the formation of functional energy materials.

Synthesis of Magnesium Silicide

[0042] Commercially available silicon metal powder was purchased. After manually mixing 1 gram of silicon powder and 2 grams of magnesium powder, the mixture was put into stainless steel autoclave reactor and then tightly sealed in inert environment. Excess magnesium than the stoichiometric ratio of Mg_2Si was used to ensure full conversion of silicon to silicide. To reduce exposure to air, at least three times of inert gas purging was performed prior to sealing the reactor. After the sealing, the reactor was place in a tube furnace with heating condition set to 500 °C for 10 hours at 1 °C/min thermal ramping rate, and then naturally cooled to room temperature.

CO_2-thermic Oxidation Process of Mg_2Si

[0043] 2 grams of prepared magnesium silicide was grinded and spread in an alumina crucible. The crucible was then place in the tube furnace set to 700 °C for 10 hours at 1°C/min thermal ramping rate in carbon dioxide gas flow. After the heat treatment, the resultant powder was immersed in 1 mol/L hydrochloric acid for at least 2 hours to remove magnesium oxide and followed by vacuum filtering and drying at 60°C overnight.

Materials Characterization

[0044] X-ray diffractometers, or XRD were used to investigate the crystalline structure and material composition. Powder morphology was characterized using field emission scanning electron microscope (FEI Quanta 200F) and transmission electron microscope (FEI Technai G2 20 Twin with 200 kV LaB6 electron source). Also, energy dispersive spectroscopy (Tescan Vega3) was used to perform elemental analysis. Raman spectroscopy (Horiba LabRAM HR system equipped with 532nm laser) was used to investigate the structure of the carbon after in-situ synthesized silicon/carbon composite. In-situ XRD data were collected using Rigaku Smartlab equipped with Anton Paar XRK900S high temperature chamber. The XRD data were continuously recorded during heating and cooling. Each scan took approximately 30 minutes and the scan range (2θ) was from 20° to 50° where all the main peaks of silicon, magnesium silicide, magnesium oxide, and carbon can be detected.

Electrochemical Properties Measurements

[0045] To evaluate the electrochemical properties of the silicon/carbon composite, 2032 coin cells, having as-synthesized carbon-coated macro-porous silicon as working electrode and lithium metal chip (MTI) as counter electrode. The electrodes were prepared by slurry casting in which the slurry, composed of the carbon-coated macro-porous silicon material (60 wt%), Super P45 carbon black conducting agent (20wt%), and poly(acrylic acid) (PAA, average molecular weight of 100 g/mol, Sigma Aldrich) / sodium carboxymethyl cellulose (CMC, 5wt% in high purity water, Sigma Aldrich) binder (20wt%, PAA : CMC = 1 : 1 by weight) in purified distilled water, was evenly spread onto copper foil (current collector) and vacuum dried.

[0046] The electrolyte used was 1.3 mol/L lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC) / Diethylene carbonate (DEC) (3:7 by volume) with 10 wt% fluoroethylene carbonate (FEC) additive. Current condition for the battery cycling test was as follows; for the first activation cycle, 0.05 C-rate (very slow current) was applied to measure apparent capacity of each coin cell assembled. Based on the capacity from the first cycle (1 C-rate), subsequent cycling test was performed at 0.2 C-rate between voltage range of 0.01 V and 1.2 V. Based on the apparent capacity of each coin cell, current conditions for subsequent cycling test were recalculated (or adjusted) accordingly. The subsequent cycling test was performed at 0.2 C-rate between voltage range of 0.01 V and 1.2 V.

Claims

1. A method of forming a silicon material for use in anodes of batteries, the method comprising:

reacting a metal or a mixture of multiple metals with silicon (Si) in a solid state reaction to form a metal silicide;
performing a CO_2-thermic oxidation process on the formed metal silicide with carbon dioxide to form a composite of one or more metal oxides, silicon, and carbon; and
contacting the formed composite of one or more metal oxides, silicon, and carbon with an acid to remove the one or more metal oxides from the composite to produce particles of the silicon material individually having: a crystalline silicon formed in the CO_2-thermic oxidation process; and pores in the crystalline silicon, the pores corresponding to the removed metal oxide by the acid and having surfaces coated with the carbon from the performed CO_2-thermic oxidation process,

wherein reacting the metal or the mixture of multiple metals with silicon includes reacting one of magnesium (Mg), calcium (Ca), or barium (Ba) with silicon (Si); and performing the CO_2-thermic oxidation process includes performing the CO_2-termic oxidation process with one of magnesium silicide (Mg_2Si), calcium ($CaSi_2$), and barium silicide ($BaSi_2$) and wherein in case Mg is present, Mg is at least 10 wt% more in excess of silicon.

2. The method of claim 1 wherein reacting the metal or the mixture of multiple metals with silicon includes reacting the metal or the mixture of multiple metals with silicon (Si) in a solid state reaction in an inert reaction environment.

3. The method of claim 1 wherein:

reacting the metal or the mixture of multiple metals with silicon includes performing a solid state reaction between the metal or the mixture of multiple metals and silicon with the metal or the mixture of multiple metals being in excess of stoichiometric proportion, thereby forming the metal silicide along with excess metal or mixture of metal; and
performing the CO_2-thermic oxidation process includes reacting the excess metal or mixture of metal to form additional one or more metal oxides and additional carbon.

4. The method of claim 1 wherein performing the CO_2-thermic oxidation process includes i) performing the CO_2-thermic oxidation process at a reaction temperature of 600°C to 800°C for a reaction period of 50 minutes to 600 minutes or ii) flowing a gas of the carbon dioxide across the formed metal silicide at a reaction temperature of 600°C to 800°C for a reaction period of 50 minutes to 600 minutes, or iii) flowing a gas of the carbon dioxide across the formed metal silicide at a reaction temperature of 600°C to 800°C for a reaction period of 50 minutes to 600 minutes to form the composite of the one or more metal oxides, silicon, and carbon, wherein the one or more metal oxides being distributed in the silicon in the formed composite, and wherein a surface of the silicon is coated generally uniformly with the formed carbon.

5. The method of claim 1 wherein:

reacting the metal or the mixture of multiple metals with silicon includes reacting at least two from the group consisting of magnesium (Mg), calcium (Ca), and barium (Ba) with silicon (Si); and
performing the CO_2-thermic oxidation process includes performing the CO_2-thermic oxidation process with two from the group consisting of magnesium silicide (Mg_2Si), calcium silicide ($CaSi_2$), and barium silicide ($BaSi_2$).

6. The method of claim 1 wherein:

reacting the metal or the mixture of multiple metals with silicon includes i) re-acting magnesium (Mg) with silicon (Si) to form magnesium silicide (Mg_2Si) as follows:

$$2Mg + Si \rightarrow Mg_2Si;$$

performing the CO_2-thermic oxidation process includes performing the CO_2-thermic oxidation process with the magnesium silicide (Mg_2Si) to form a composite of magnesium oxide (MgO), silicon, and carbon, as follows:

$$Mg_2Si + CO_2 \rightarrow Si + C + 2MgO; \text{ and}$$

contacting the formed composite with the acid includes contacting the formed composite with the acid to remove the magnesium oxide (MgO) from the formed composite or ii) reacting calcium (Ca) with silicon (Si) to form calcium silicide ($CaSi_2$) as follows:

$$Ca + 2Si \rightarrow CaSi_2;$$

performing the CO_2-thermic oxidation process includes performing the CO_2-thermic oxidation process with the calcium silicide ($CaSi_2$) to form a composite of calcium oxide (CaO), silicon, and carbon, as follows:

$$2CaSi_2 + CO_2 \rightarrow 4Si + C + 2CaO; \text{ and}$$

contacting the formed composite with the acid includes contacting the formed composite with the acid to remove the calcium oxide (CaO) from the formed composite to produce particles with a layered two-dimensional silicon morphology.

7. A battery, comprising:

a first electrode;
an electrolyte in electrical communication with the first electrode, the electrolyte containing a plurality of metal ions; and
a second electrode spaced apart from the first electrode and in electrical communication with the first electrode via the electrolyte, wherein the second electrode contains particles of a silicon material individually having: the crystalline silicon in a matrix; and pores distributed in the
matrix of the crystalline silicon, the pores having a size greater than 100 nanometers, wherein surfaces of the crystalline silicon in the pores are coated with carbon,

wherein the silicon material is obtainable by a method according to any one of claim 1 to 6.

8. The battery of claim 7 wherein the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly.

9. The battery of claim 7 wherein:

the pores are randomly distributed in the matrix of the crystalline silicon; and
the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly, in particular,
the pores are randomly distributed in the matrix of the crystalline silicon; and
the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly, the carbon being in an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof.

10. The battery of claim 7 wherein:

the first electrode is constructed from one of lithium cobalt oxide ($LiCoO_2$), lithium iron phosphate ($LiFePO_4$), lithium manganese oxide ($LiMn_2O_4$), lithium nickel oxide ($LiNiO_2$), lithium iron phosphate fluoride (Li_2FePO_4F), $LiNiCoAlO_2$ having 80% Nickel, 15% Cobalt, and 5% Aluminum, $LiCoO_2$ having 100% Cobalt, $LiMn_2O_4$ having 100% Manganese, $LiNiMnCoO_2$ having 33.3% Nickel, 33.3% Manganese, and 33.3% Cobalt, $LiFePO_4$ having 100% Iron, or lithium cobalt nickel manganese oxide ($LiCo_{1/3}Ni_{1/3}Mn_{1/3}O2$); and
the electrolyte contains $LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiBF_4$, or lithium triflate.

11. The battery according to any one of claims 7 to 10 wherein the silicon material is obtained according to a method of claim 6.

12. A silicon material according to claim 1, comprising:

the crystalline silicon in a matrix; and
pores distributed in the matrix of the crystalline silicon, the pores having a size greater than 100 nanometers, wherein surfaces of the crystalline silicon in the pores are coated with carbon.

13. The silicon material of claim 12 wherein the surfaces of the_crystalline silicon in the pores are coated with carbon generally uniformly.

14. The silicon material of claim 12 wherein:

the pores are randomly distributed in the matrix of the crystalline silicon; and
the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly, in particular, wherein:
the pores are randomly distributed in the matrix of the crystalline silicon; and
the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly, the carbon being in an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof.

15. The silicon material of claim 12 wherein:

the pores are randomly distributed in the matrix of the crystalline silicon;
the surfaces of the crystalline silicon in the pores are coated with carbon generally uniformly, the carbon being in an amorphous form, a semi-crystalline or crystalline form, or a mixture thereof; and
the matrix of the crystalline silicon has a layered two-dimensional silicon morphology.

Patentansprüche

1. Verfahren zur Herstellung eines Siliziummaterials zur Verwendung in Anoden von Batterien, wobei das Verfahren umfasst:

Umsetzen eines Metalls oder einer Mischung mehrerer Metalle mit Silizium (Si) in einer Festkörperreaktion, um ein Metallsilicid zu bilden;
Durchführen eines CO_2-thermischen Oxidationsprozesses an dem gebildeten Metallsilicid mit Kohlendioxid, um einen Komposit aus einem oder mehreren Metalloxiden, Silizium und Kohlenstoff zu bilden; und
Inkontaktbringen des gebildeten Komposits aus einem oder mehreren Metalloxiden, Silizium und Kohlenstoff mit einer Säure, um das eine oder die mehreren Metalloxide aus dem Komposit zu entfernen, um Partikel des Siliziummaterials zu erzeugen, die einzeln aufweisen: ein kristallines Silizium, das in dem CO_2-thermischen Oxidationsprozess gebildet wurde; und Poren in dem kristallinen Silizium, wobei die Poren dem durch die Säure entfernten Metalloxid entsprechen und Oberflächen aufweisen, die mit dem Kohlenstoff aus dem durchgeführten CO_2-thermischen Oxidationsprozess beschichtet sind,
wobei das Umsetzen des Metalls oder der Mischung mehrerer Metalle mit Silizium das Umsetzen von einem aus Magnesium (Mg), Calcium (Ca) oder Barium (Ba) mit Silizium (Si) einschließt; und das Durchführen des CO_2-thermischen Oxidationsverfahrens das Durchführen des CO_2-thermischen Oxidationsverfahrens mit einem von Magnesiumsilicid (Mg_2Si), Calcium ($CaSi_2$) und Bariumsilicid ($BaSi_2$) einschließt, und wobei, falls Mg vorhanden ist, Mg mindestens 10 Gew.-% mehr im Überschuss zu Silizium ist.

2. Verfahren nach Anspruch 1, wobei das Umsetzen des Metalls oder der Mischung mehrerer Metalle mit Silizium das

Umsetzen des Metalls oder der Mischung mehrerer Metalle mit Silizium (Si) in einer Festkörperreaktion in einer inerten Reaktionsumgebung umfasst.

3. Verfahren nach Anspruch 1, wobei:

das Umsetzen des Metalls oder des Gemischs mehrerer Metalle mit Silizium die Durchführung einer Festkörperreaktion zwischen dem Metall oder dem Gemisch mehrerer Metalle und Silizium umfasst, wobei das Metall oder das Gemisch mehrerer Metalle über das stöchiometrische Verhältnis hinausgehend vorliegt, wodurch das Metallsilicid zusammen mit dem überschüssigen Metall oder Metallgemisch gebildet wird; und
die Durchführung des CO_2-thermischen Oxidationsverfahrens die Umsetzung des überschüssigen Metalls oder Metallgemischs unter Bildung eines oder mehrerer zusätzlicher Metalloxide und zusätzlichen Kohlenstoffs einschließt.

4. Verfahren nach Anspruch 1, wobei die Durchführung des CO_2-thermischen Oxidationsverfahrens folgendes umfasst: i) Durchführung des CO_2-thermischen Oxidationsverfahrens bei einer Reaktionstemperatur von 600°C bis 800°C für eine Reaktionsdauer von 50 Minuten bis 600 Minuten oder ii) Strömen eines Gases des Kohlendioxids über das gebildete Metallsilicid bei einer Reaktionstemperatur von 600°C bis 800°C für eine Reaktionsdauer von 50 Minuten bis 600 Minuten, oder iii) Strömen Kohlendioxidgas über das gebildete Metallsilicid bei einer Reaktionstemperatur von 600°C bis 800°C für eine Reaktionszeit von 50 Minuten bis 600 Minuten, um den Komposit aus dem einen oder den mehreren Metalloxiden, Silizium und Kohlenstoff zu bilden, wobei das eine oder die mehreren Metalloxide in dem Silizium in dem gebildeten Komposit verteilt sind, und wobei eine Oberfläche des Siliziums im Allgemeinen gleichmäßig mit dem gebildeten Kohlenstoff beschichtet ist.

5. Verfahren nach Anspruch 1, wobei:

das Metall oder das Gemisch mehrerer Metalle mit Silizium umgesetzt wird, was die Reaktion von mindestens zwei Metallen aus der Gruppe Magnesium (Mg), Calcium (Ca) und Barium (Ba) mit Silizium (Si) einschließt; und
das Durchführen des CO_2-thermischen Oxidationsverfahrens das Durchführen des CO_2-thermischen Oxidationsverfahrens mit zwei aus der Gruppe, bestehend aus Magnesiumsilicid (Mg2Si), Calciumsilicid (CaSi2) und Bariumsilicid (BaSi2), umfasst.

6. Das Verfahren nach Anspruch 1, wobei:

die Umsetzung des Metalls oder der Mischung mehrerer Metalle mit Silizium i) die Reaktion von Magnesium (Mg) mit Silizium (Si) zur Bildung von Magnesiumsilicid (Mg_2Si) wie folgt umfasst:

$$2Mg + Si \rightarrow Mg_2Si;$$

Durchführen des CO_2-thermischen Oxidationsverfahrens beinhaltet das Durchführen des CO_2-thermischen Oxidationsverfahrens mit dem Magnesiumsilicid (Mg_2Si), um einen Komposit aus Magnesiumoxid (MgO), Silizium und Kohlenstoff zu bilden, wie folgt:

$$Mg_2Si + CO2 \rightarrow Si + C + 2MgO;$$

und
Inkontaktbringen des gebildeten Komposits mit der Säure umfasst das Inkontaktbringen des gebildeten Komposits mit der Säure, um das Magnesiumoxid (MgO) aus dem gebildeten Komposit zu entfernen, oder ii) Reagieren von Calcium (Ca) mit Silizium (Si), um Calciumsilicid ($CaSi_2$) wie folgt zu bilden:

$$Ca + 2Si \rightarrow CaSi_2;$$

die Durchführung des CO_2-thermischen Oxidationsverfahrens umfasst die Durchführung des CO_2-thermischen Oxidationsverfahrens mit dem Calciumsilicid ($CaSi_2$), um einen Komposit aus Calciumoxid (CaO), Silizium und Kohlenstoff zu bilden, wie folgt:

$$2CaSi_2 + CO2 \rightarrow 4Si + C + 2CaO; \text{ und}$$

das In-Kontakt-Bringen des gebildeten Komposits mit der Säure beinhaltet das In-Kontakt-Bringen des gebildeten Komposits mit der Säure, um das Calciumoxid (CaO) aus dem gebildeten Komposit zu entfernen, um Teilchen mit einer geschichteten zweidimensionalen Siliziummorphologie herzustellen.

7. Batterie, umfassend:

eine erste Elektrode;
einen Elektrolyten in elektrischer Verbindung mit der ersten Elektrode, wobei der Elektrolyt eine Vielzahl von Metallionen enthält; und
eine zweite Elektrode, die von der ersten Elektrode beabstandet ist und über den Elektrolyten mit der ersten Elektrode in elektrischer Verbindung steht, wobei die zweite Elektrode Partikel eines Siliziummaterials enthält, die einzeln folgendes aufweisen: das kristalline Silizium in einer Matrix; und Poren, die in der Matrix des kristallinen Siliziums verteilt sind, Wobei die Poren eine Größe von mehr als 100 Nanometern aufweisen, wobei die Oberflächen des kristallinen Siliziums in den Poren mit Kohlenstoff beschichtet sind,
wobei das Siliziummaterial durch ein Verfahren nach einem der Ansprüche 1 bis 6 erhältlich ist.

8. Batterie nach Anspruch 7, wobei die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind.

9. Batterie nach Anspruch 7, wobei:

die Poren statistisch in der Matrix des kristallinen Siliziums verteilt sind; und
die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind, insbesondere,
die Poren statistisch in der Matrix des kristallinen Siliziums verteilt sind; und
die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind, wobei der Kohlenstoff in einer amorphen Form, einer halbkristallinen oder kristallinen Form, oder einer Mischung davon vorliegt.

10. Batterie nach Anspruch 7, wobei:

die erste Elektrode aus einem der folgenden Materialien aufgebaut ist: Lithiumkobaltoxid ($LiCoO_2$), Lithiumeisenphosphat ($LiFePO_4$), Lithiummanganoxid ($LiMn_2O_4$), Lithiumnickeloxid ($LiNiO_2$), Lithiumeisenphosphatfluorid (Li_2FePO_4F), $LiNiCoAlO_2$ mit 80% Nickel, 15% Kobalt und 5% Aluminium, $LiCoO_2$ mit 100% Kobalt, $LiMn_2O_4$ mit 100% Mangan, $LiNiMnCoO_2$ mit 33. 3% Nickel, 33,3% Mangan und 33,3% Kobalt, $LiFePO_4$ mit 100% Eisen oder Lithium-Kobalt-Nickel-Mangan-Oxid ($LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$); und
der Elektrolyt enthält $LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiBF_4$ oder Lithiumtriflat.

11. Batterie nach einem der Ansprüche 7 bis 10, wobei das Siliziummaterial gemäß einem Verfahren nach Anspruch 6 erhalten wird.

12. Siliziummaterial nach Anspruch 1, umfassend:

das kristalline Silizium in einer Matrix; und
Poren, die in der Matrix des kristallinen Siliziums verteilt sind, wobei die Poren eine Größe von mehr als 100 Nanometern haben, wobei die Oberflächen des kristallinen Siliziums in den Poren mit Kohlenstoff beschichtet sind.

13. Siliziummaterial nach Anspruch 12, wobei die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind.

14. Siliziummaterial nach Anspruch 12, wobei:

die Poren statisch in der Matrix des kristallinen Siliziums verteilt sind; und
die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind, insbesondere wobei:

> die Poren statistisch in der Matrix des kristallinen Siliziums verteilt sind; und
> die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff be-

schichtet sind, wobei der Kohlenstoff in einer amorphen Form, einer halbkristallinen oder kristallinen Form, oder einer Mischung davon vorliegt.

15. Siliziummaterial nach Anspruch 12, wobei:

die Poren statistisch in der Matrix des kristallinen Siliziums verteilt sind;
die Oberflächen des kristallinen Siliziums in den Poren im Allgemeinen gleichmäßig mit Kohlenstoff beschichtet sind, wobei der Kohlenstoff in einer amorphen Form, einer halbkristallinen oder kristallinen Form, oder einer Mischung davon vorliegt; und
die Matrix des kristallinen Siliziums eine geschichtete zweidimensionale Siliziummorphologie aufweist.

Revendications

1. Procédé de formation d'un matériau de silicium pour une utilisation dans des anodes de batteries, le procédé comprenant :

la mise en réaction d'un métal ou d'un mélange de plusieurs métaux avec du silicium (Si) dans une réaction à l'état solide pour former un siliciure métallique ;
la réalisation d'un processus d'oxydation thermique de CO_2 sur le siliciure métallique formé avec du dioxyde de carbone pour former un composite d'un ou plusieurs oxydes métalliques, de silicium et de carbone ; et
la mise en contact du composite formé d'un ou plusieurs oxydes métalliques, de silicium et de carbone avec un acide pour éliminer l'oxyde ou les oxydes métalliques du composite pour produire des particules du matériau de silicium ayant individuellement : un silicium cristallin formé dans le processus d'oxydation thermique de CO_2 ; et des pores dans le silicium cristallin, les pores correspondants à l'oxyde métallique éliminé par l'acide et ayant des surfaces revêtues par le carbone provenant du processus d'oxydation thermique de CO_2 réalisé,

la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium comprenant la mise en réaction d'un parmi le magnésium (Mg), le calcium (Ca) ou le baryum (Ba) avec du silicium (Si) ; et la réalisation du processus d'oxydation thermique de CO_2 comprenant la réalisation du processus d'oxydation thermique de CO_2 avec l'un parmi le siliciure de magnésium (Mg_2Si), de calcium ($CaSi_2$) et le siliciure de baryum ($BaSi_2$) et, dans le cas où Mg est présent, Mg est présent à raison de 10 % en poids de plus que le silicium.

2. Procédé selon la revendication 1, la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium comprenant la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium (Si) dans une réaction à l'état solide dans un environnement de réaction inerte.

3. Procédé selon la revendication 1,

la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium comprenant la réalisation d'une réaction à l'état solide entre le métal ou le mélange de plusieurs métaux et le silicium, le métal ou le mélange de plusieurs métaux étant en excès de proportion stœchiométrique, formant ainsi le siliciure métallique ainsi qu'un métal ou mélange de métaux en excès ; et
la réalisation du processus d'oxydation thermique de CO_2 comprenant la mise en réaction du métal ou mélange de métaux en excès pour former un ou plusieurs oxydes métalliques supplémentaires et du carbone supplémentaire.

4. Procédé selon la revendication 1, la réalisation du processus d'oxydation thermique de CO_2 comprenant i) la réalisation du processus d'oxydation thermique de CO_2 à une température de réaction de 600 °C à 800 °C pendant une période de réaction de 50 minutes à 600 minutes ou ii) l'écoulement d'un gaz du dioxyde de carbone à travers le siliciure métallique formé à une température de réaction de 600 °C à 800 °C pendant une période de réaction de 50 minutes à 600 minutes, ou iii) l'écoulement d'un gaz du dioxyde de carbone à travers le siliciure métallique formé à une température de réaction de 600 °C à 800 °C pendant une période de réaction de 50 minutes à 600 minutes pour former le composite de l'oxyde ou des oxydes métalliques, de silicium et de carbone, l'oxyde ou les oxydes métalliques étant distribués dans le silicium dans le composite formé, et une surface du silicium étant revêtue de manière généralement uniforme par le carbone formé.

5. Procédé selon la revendication 1,

la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium comprenant la mise en réaction d'au moins deux du groupe constitué par le magnésium (Mg), le calcium (Ca) et le baryum (Ba) avec du silicium (Si) ; et
la réalisation du processus d'oxydation thermique de CO_2 comprenant la réalisation du processus d'oxydation thermique de CO_2 avec deux du groupe constitué par le siliciure de magnésium (Mg_2Si), le siliciure de calcium ($CaSi_2$) et le siliciure de baryum ($BaSi_2$) .

6. Procédé selon la revendication 1,

la mise en réaction du métal ou du mélange de plusieurs métaux avec du silicium comprenant i) la mise en réaction de magnésium (Mg) avec du silicium (Si) pour former du siliciure de magnésium (Mg_2Si) comme suit :

$$\mathbf{2Mg + Si \rightarrow Mg_2Si;}$$

la réalisation du processus d'oxydation thermique de CO_2 comprenant la réalisation du processus d'oxydation thermique de CO_2 avec le siliciure de magnésium (Mg_2Si) pour former un composite d'oxyde de magnésium (MgO), de silicium et de carbone, comme suit :

$$\mathbf{Mg_2Si + CO_2 \rightarrow Si + C + 2MgO;} \text{ et}$$

la mise en contact du composite formé avec l'acide comprenant la mise en contact du composé formé avec l'acide pour éliminer l'oxyde de magnésium (MgO) du composite formé ou ii) la mise en réaction de calcium (Ca) avec du silicium (Si) pour former du siliciure de calcium ($CaSi_2$) comme suit :

$$\mathbf{Ca + 2Si \rightarrow CaSi_2;}$$

la réalisation du processus d'oxydation thermique de CO_2 comprenant la réalisation du processus d'oxydation thermique de CO_2 avec le siliciure de calcium ($CaSi_2$) pour former un composite d'oxyde de calcium (CaO), de silicium et de carbone, comme suit :

$$\mathbf{2CaSi_2 + CO_2 \rightarrow 4Si + C + 2CaO;} \text{ et}$$

la mise en contact du composite formé avec l'acide comprenant la mise en contact du composite formé avec l'acide pour éliminer l'oxyde de calcium (CaO) du composite formé pour produire des particules dotées d'une morphologie de silicium bidimensionnel stratifié.

7. Batterie, comprenant :

une première électrode ;
un électrolyte en communication électrique avec la première électrode, l'électrolyte contenant une pluralité d'ions métalliques ; et
une deuxième électrode à distance de la première électrode et en communication électrique avec la première électrode via l'électrolyte, la deuxième électrode contenant des particules d'un matériau de silicium ayant individuellement :
le silicium cristallin dans une matrice ; et des pores distribués dans la matrice du silicium cristallin, les pores ayant une taille plus grande que 100 nanomètres, des surfaces de silicium cristallin dans les pores étant revêtues par du carbone, le matériau de silicium pouvant être obtenu par un procédé selon l'une quelconque des revendications 1 à 6.

8. Batterie selon la revendication 7, les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme.

9. Batterie selon la revendication 7,

les pores étant distribués de manière aléatoire dans la matrice du silicium cristallin ; et
les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme, en particulier,
les pores étant distribués de manière aléatoire dans la matrice du silicium cristallin ; et

les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme, le carbone étant sous une forme amorphe, une forme semi-cristalline ou cristalline, ou un mélange correspondant.

10. Batterie selon la revendication 7,

la première électrode étant construite à partir d'un parmi l'oxyde de lithium et de cobalt ($LiCoO_2$), le phosphate de lithium et de fer ($LiFePO_4$), l'oxyde de lithium et de manganèse ($LiMn_2O_4$), l'oxyde de lithium et de nickel ($LiNiO_2$), le fluorure de phosphate de lithium et de fer (Li_2FePO_4F), $LiNiCoAlO_2$ ayant 80 % de nickel, 15 % de cobalt et 5 % d'aluminium, $LiCoO_2$ ayant 100 % de cobalt, $LiMn_2O_4$ ayant 100 % de manganèse, $LiNiMnCoO_2$ ayant 33,3 % de nickel, 33,3 % de manganèse et 33,3 % de cobalt, $LiFePO_4$ ayant 100 % de fer, ou l'oxyde de lithium de cobalt de nickel et de manganèse ($LiCo_{1/3}Ni_{1/3}Mn_{1/3}O2$) ; et
l'électrolyte contenant $LiPF_6$, $LiAsF_6$, $LiClO_4$, $LiBF_4$, ou du triflate de lithium.

11. Batterie selon l'une quelconque des revendications 7 à 10, le matériau de silicium étant obtenu selon un procédé selon la revendication 6.

12. Matériau de silicium selon la revendication 1, comprenant :

le silicium cristallin dans une matrice ; et
des pores distribués dans la matrice du silicium cristallin, les pores ayant une taille plus grande que 100 nanomètres, des surfaces du silicium cristallin dans les pores étant revêtues par du carbone.

13. Matériau de silicium selon la revendication 12, les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme.

14. Matériau de silicium selon la revendication 12, les pores étant distribués de manière aléatoire dans la matrice du silicium cristallin ; et
les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme, en particulier :

les pores étant distribués de manière aléatoire dans la matrice du silicium cristallin ; et
les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme, le carbone étant sous une forme amorphe, une forme semi-cristalline ou cristalline, ou un mélange correspondant.

15. Matériau de silicium selon la revendication 12,

les pores étant distribués de manière aléatoire dans la matrice du silicium cristallin ;
les surfaces du silicium cristallin dans les pores étant revêtues par du carbone généralement de manière uniforme, le carbone étant sous une forme amorphe, une forme semi-cristalline ou cristalline, ou un mélange correspondant ; et
la matrice du silicium cristallin ayant une morphologie de silicium bidimensionnel stratifié.

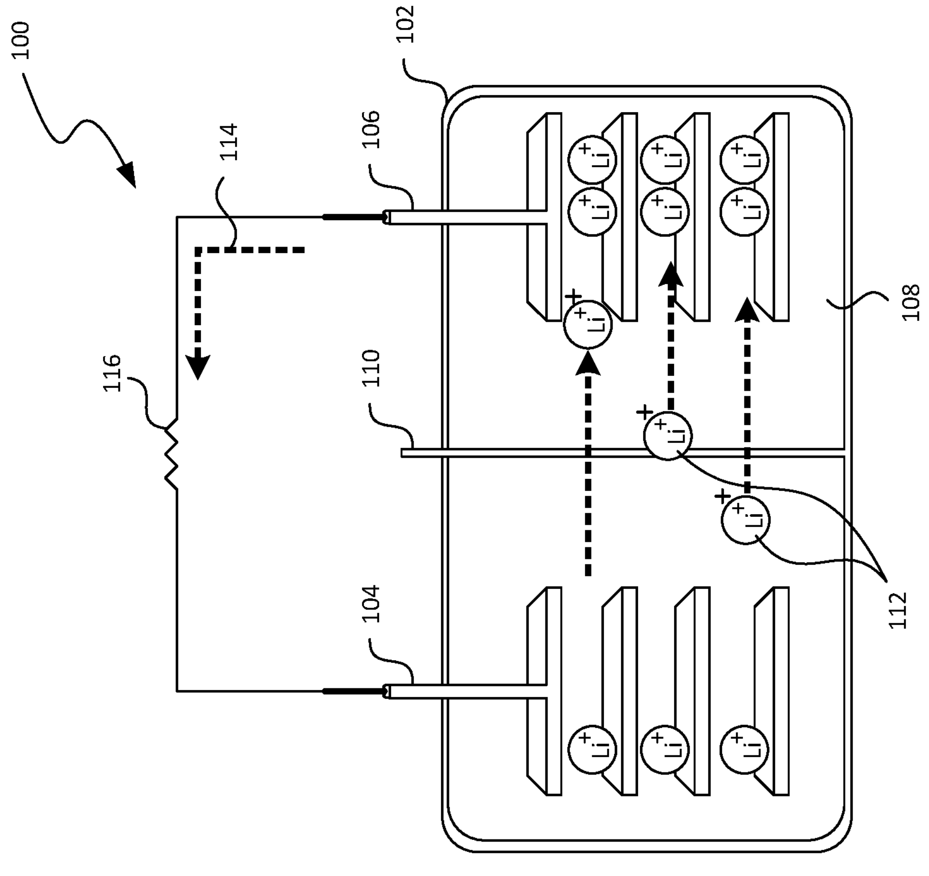
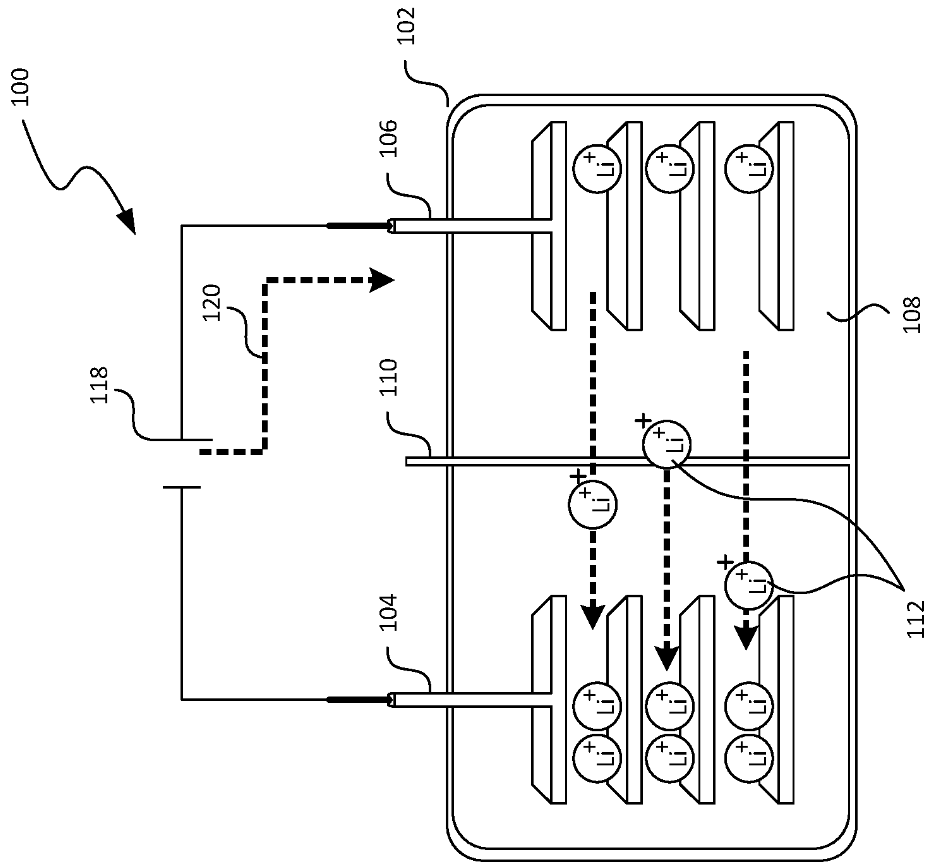

100
102
106
114
116
110
108
104
112
Li+

FIG. 1A


100
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106
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108
104
112
Li+

FIG. 1B

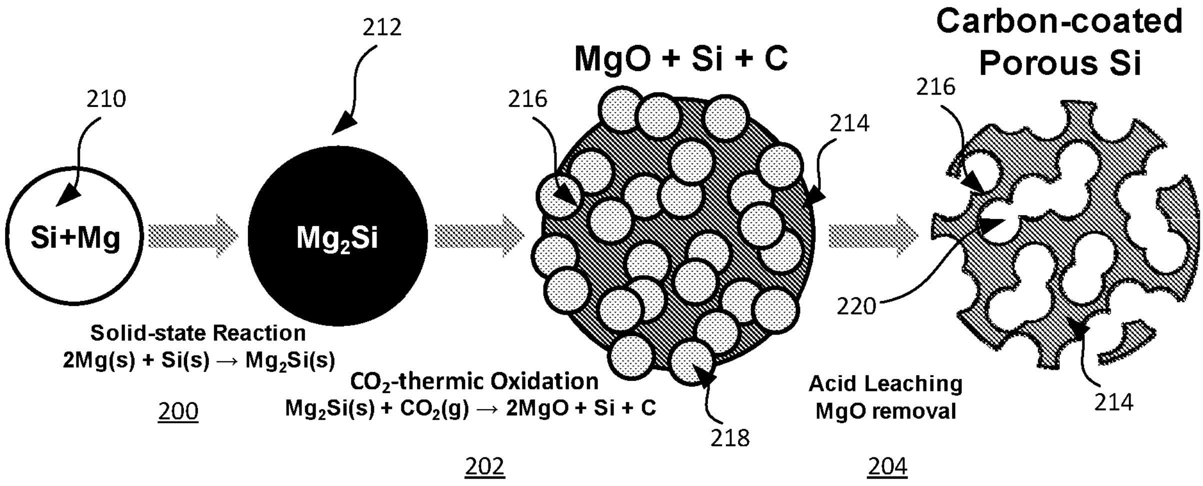
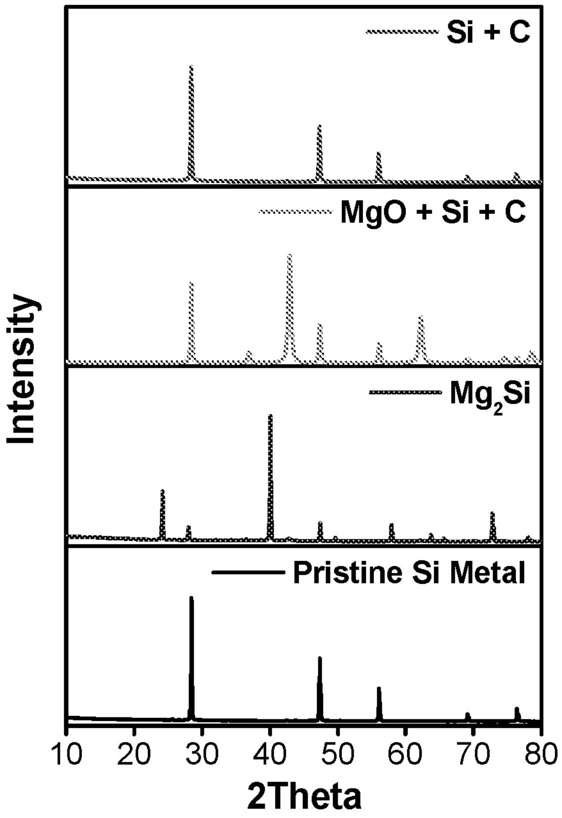


FIG. 2



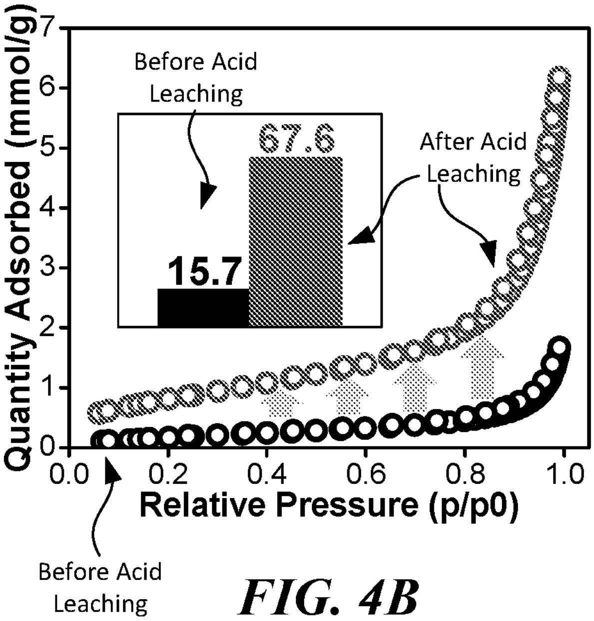


FIG. 4B

FIG. 4A

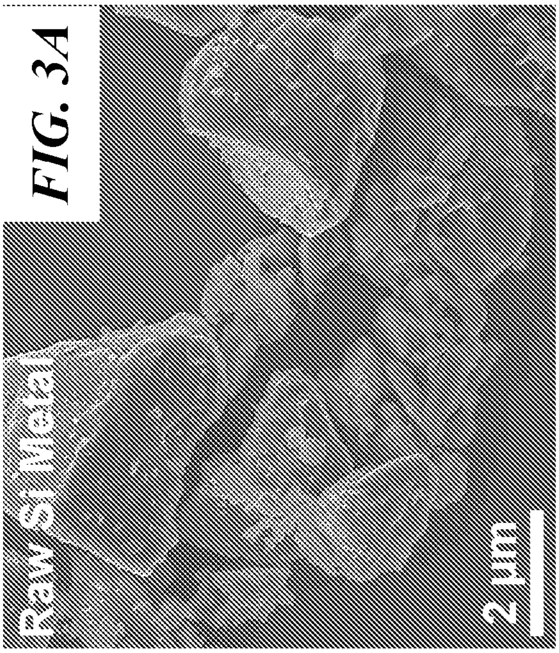


FIG. 3A

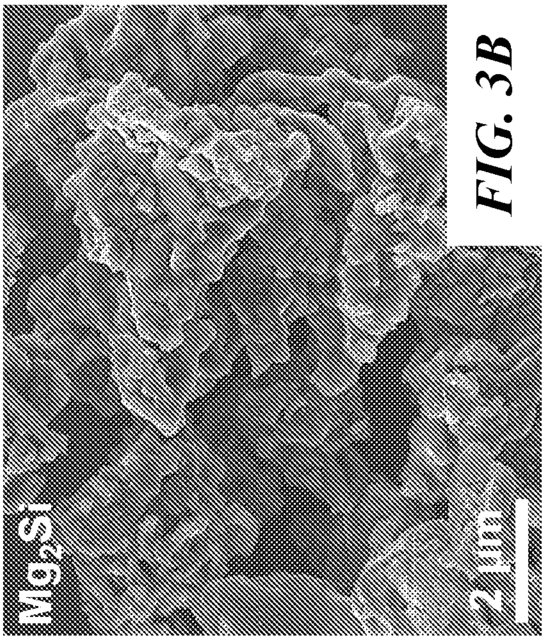


FIG. 3B

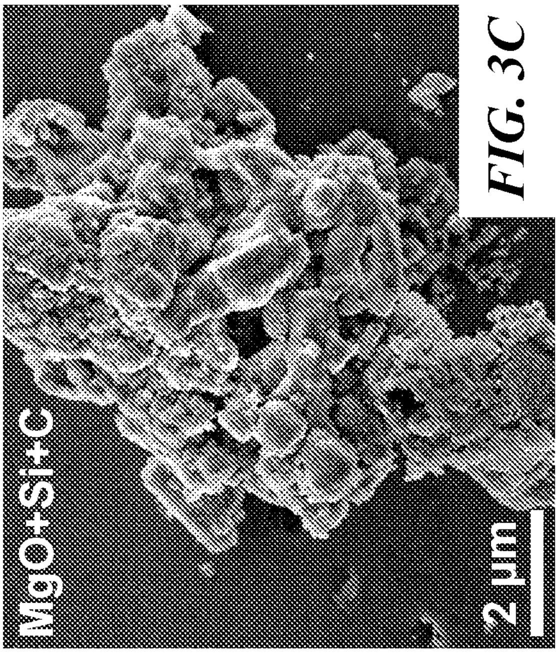


FIG. 3C

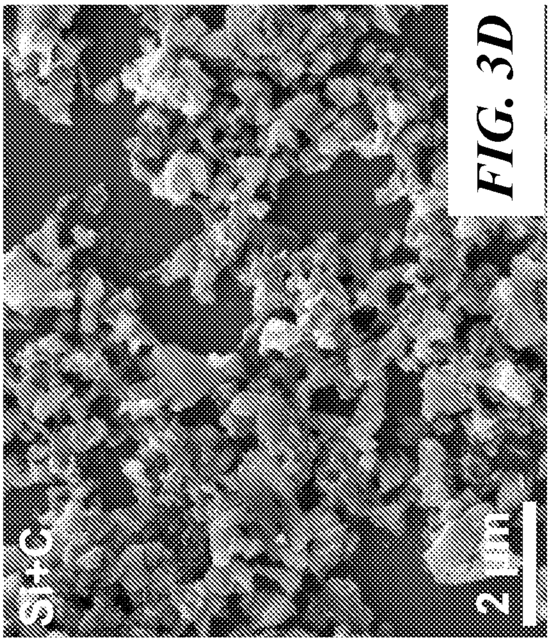


FIG. 3D

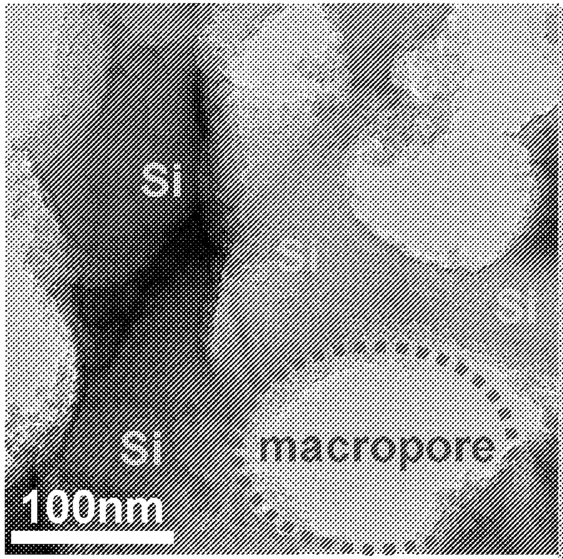


FIG. 5A

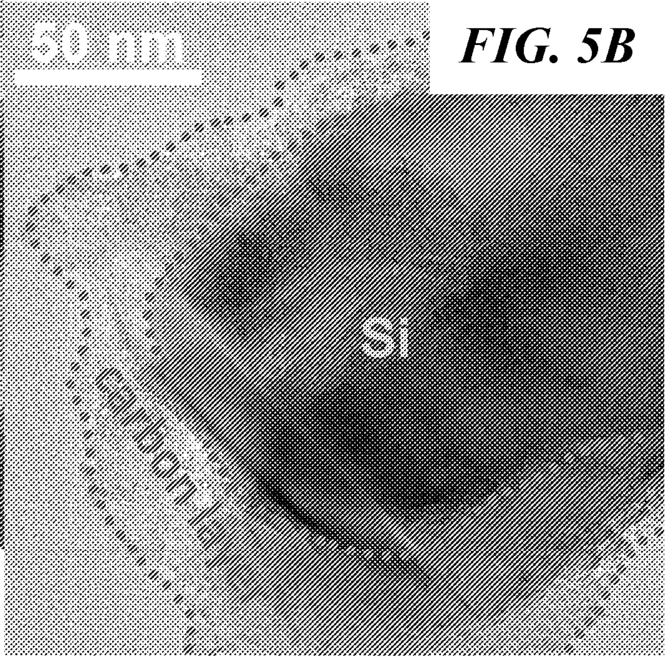


FIG. 5B

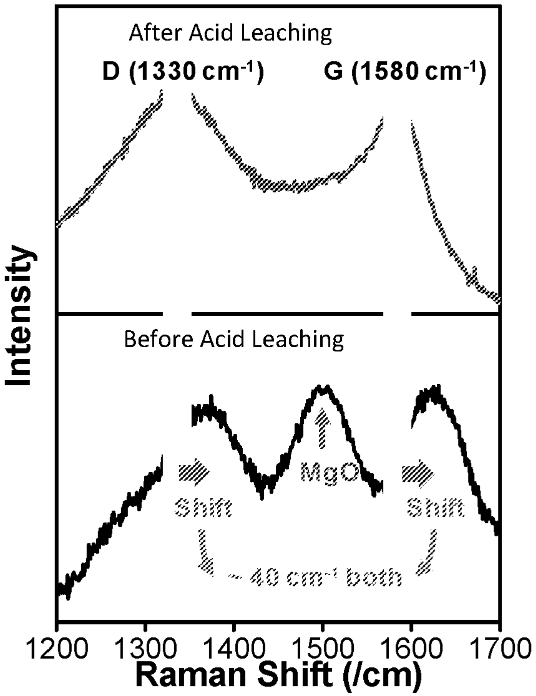


FIG. 5F

FIG. 5C

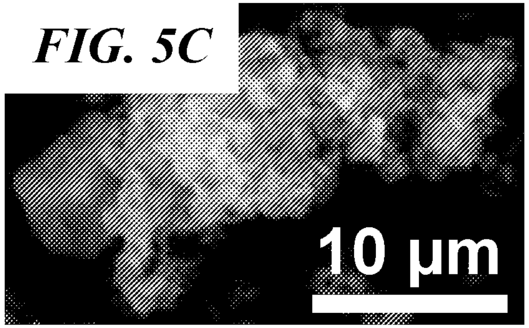


FIG. 5D

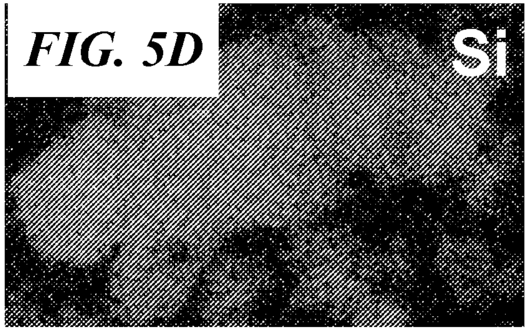
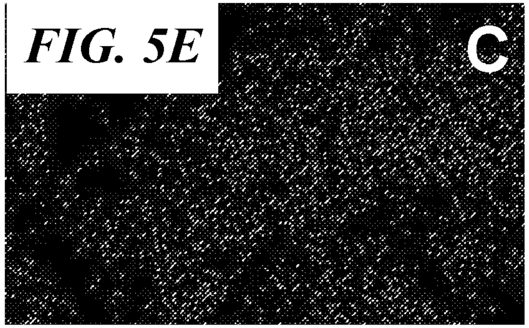
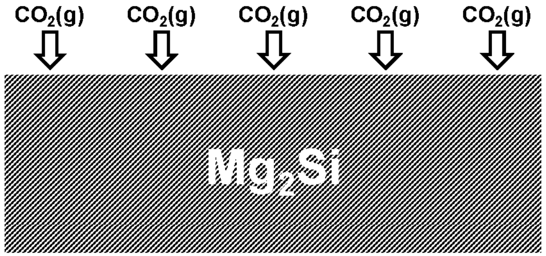


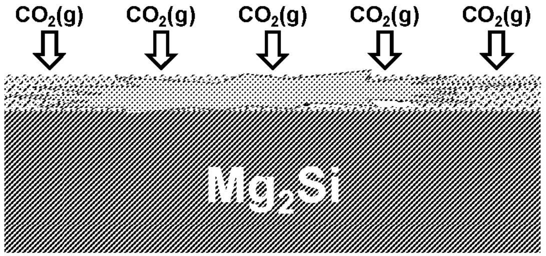
FIG. 5E





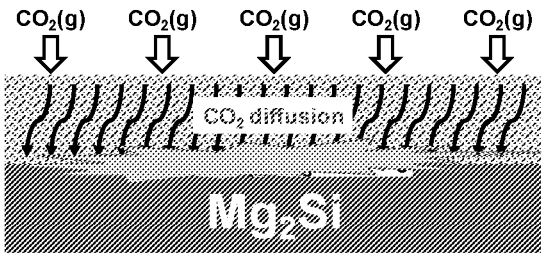
CO_2(g) Bulk Diffusion

FIG. 6A



Surface Diffusion

FIG. 6B



Inter-/Intra- Particular Diffusion

FIG. 6C

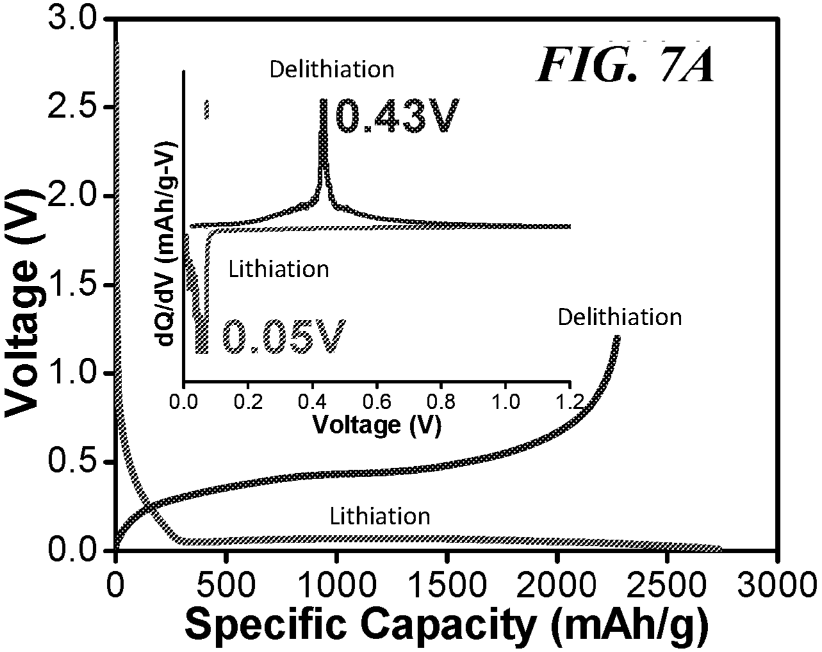


FIG. 7A

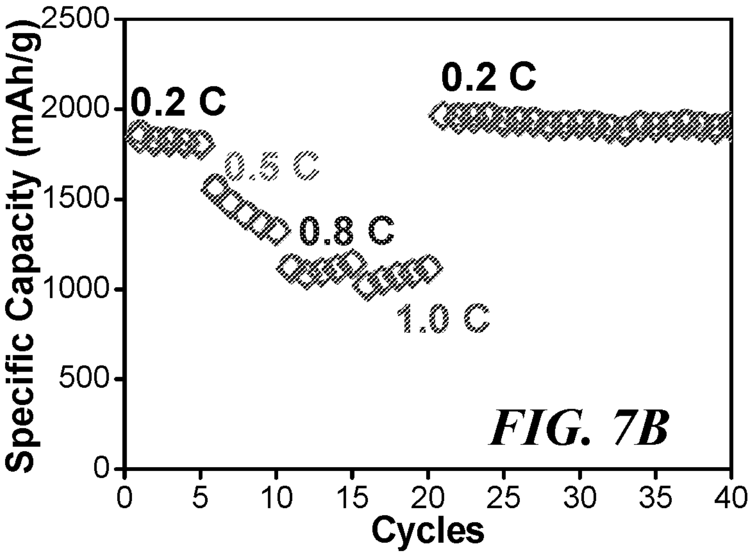


FIG. 7B

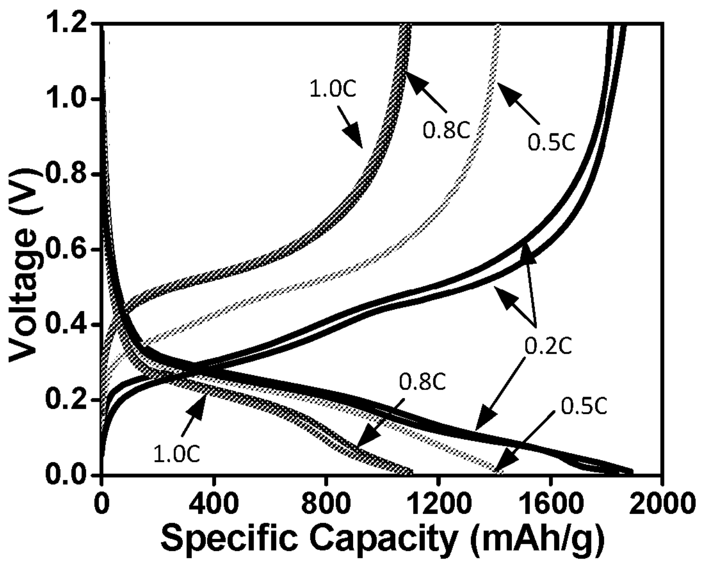


FIG. 7C

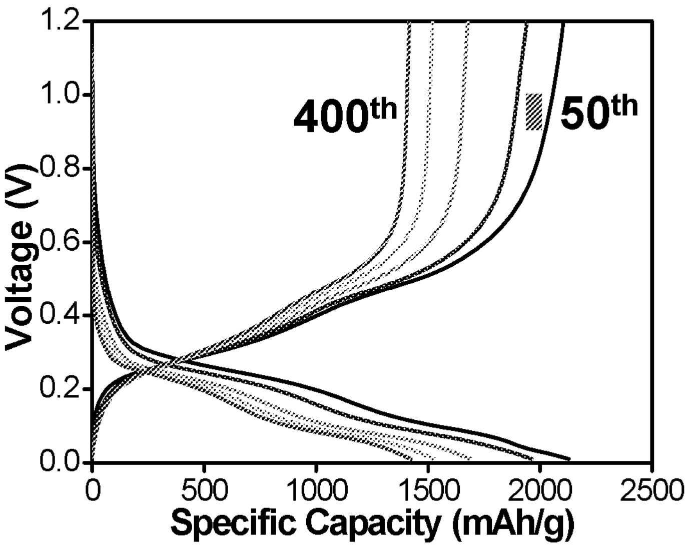


FIG. 7E

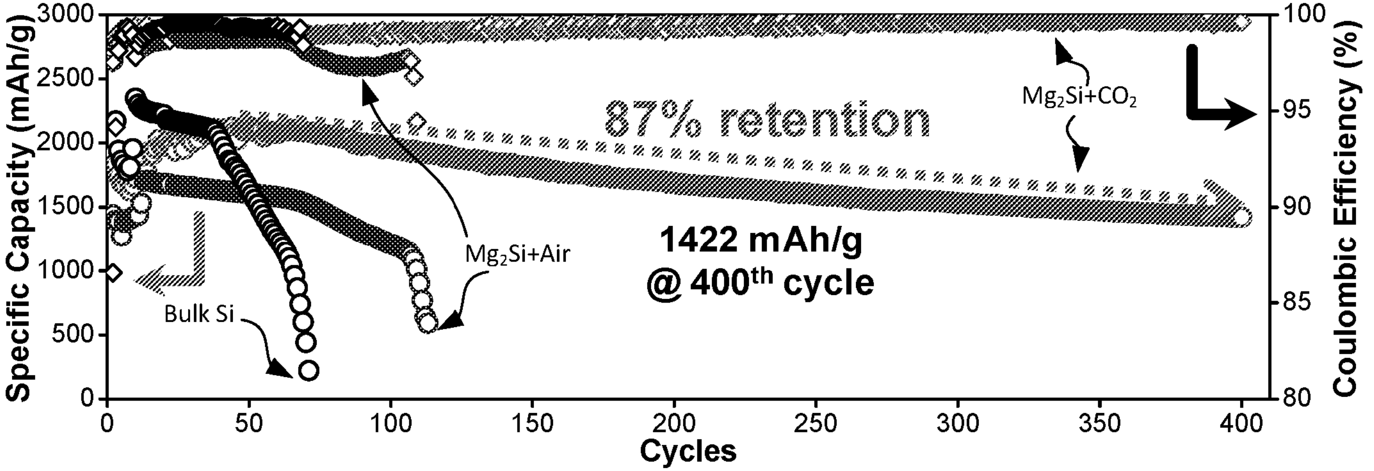


FIG. 7D

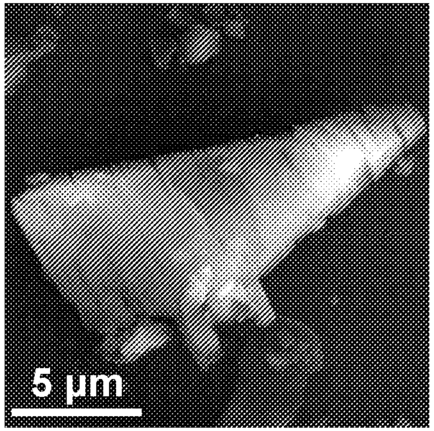


FIG. 8A

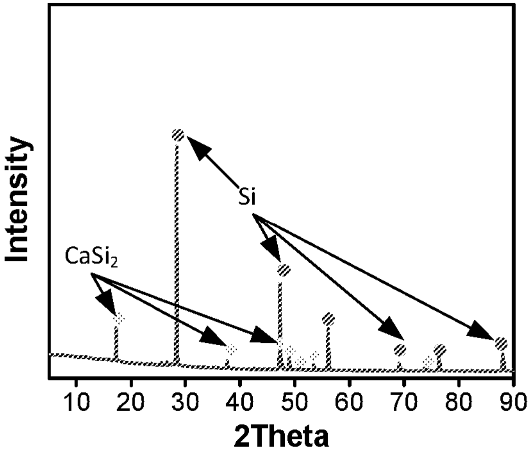


FIG. 8B

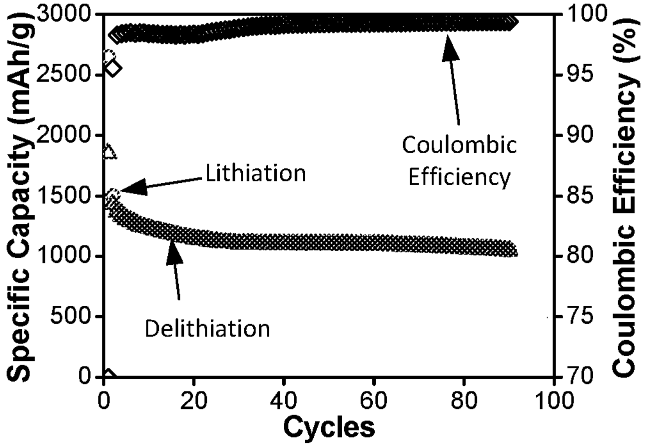


FIG. 8C

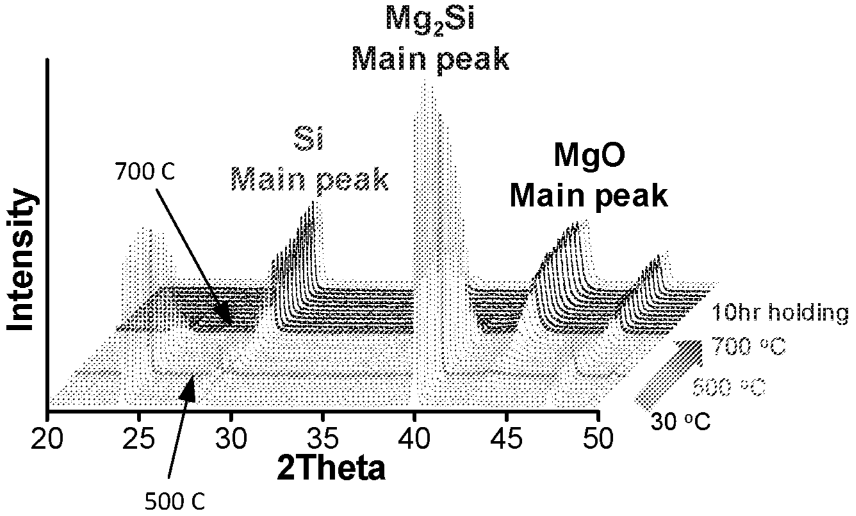


FIG. 9A

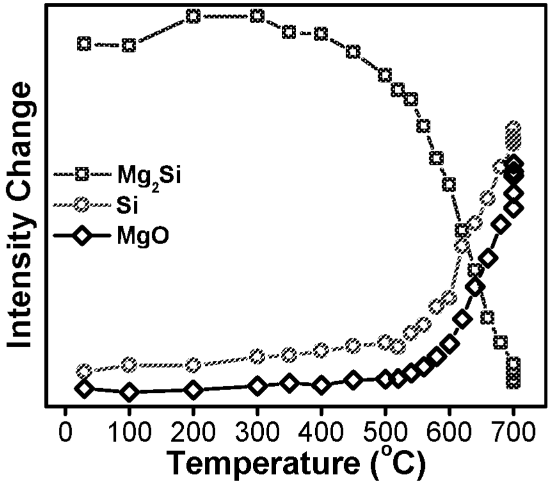


FIG. 9B

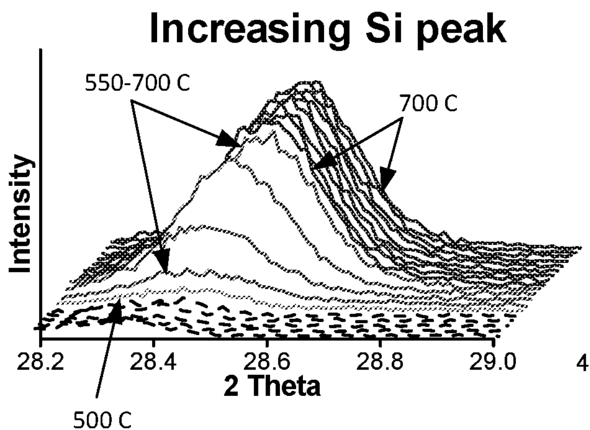


FIG. 9C

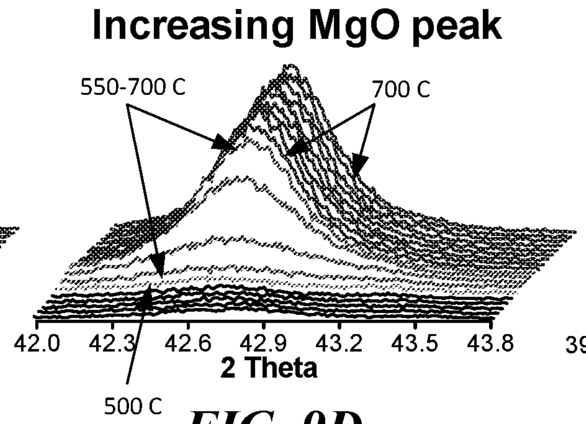


FIG. 9D

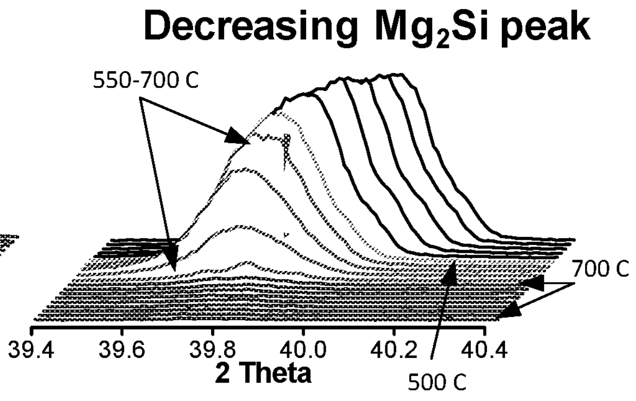


FIG. 9E

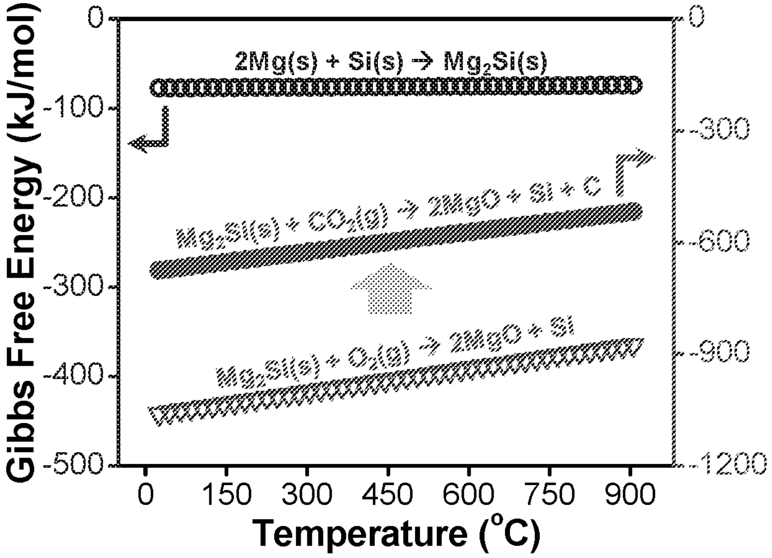


FIG. 10

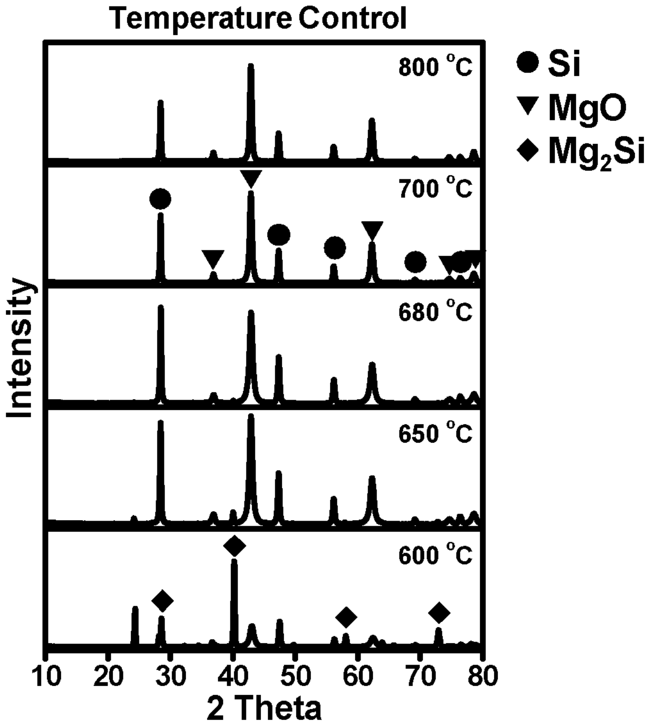


FIG. 11A

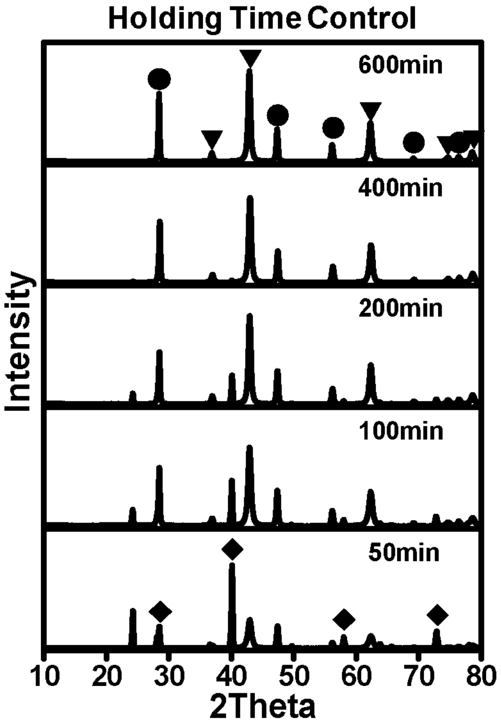


FIG. 11B

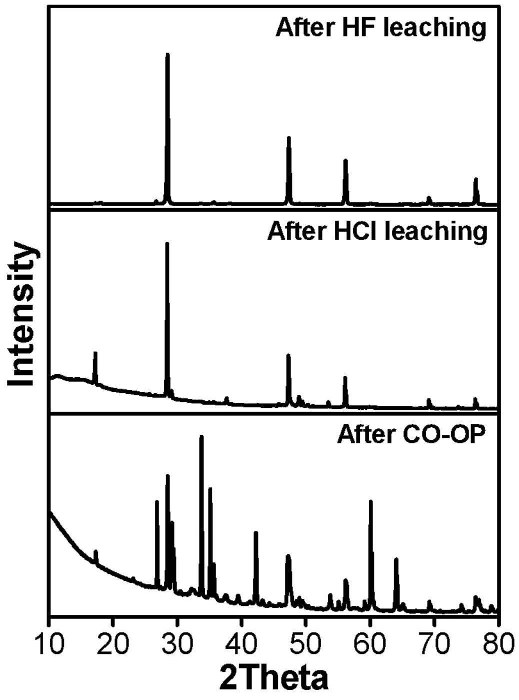
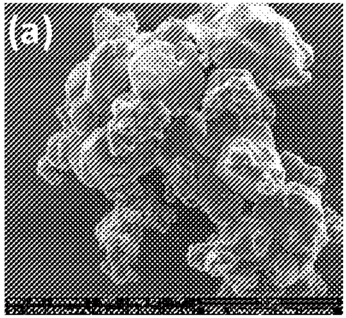


FIG. 13

FIG. 12A

50min



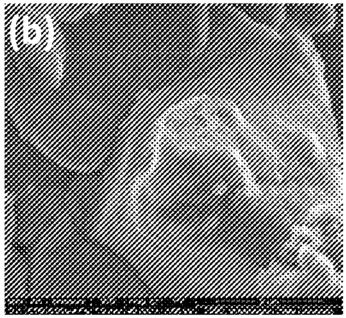
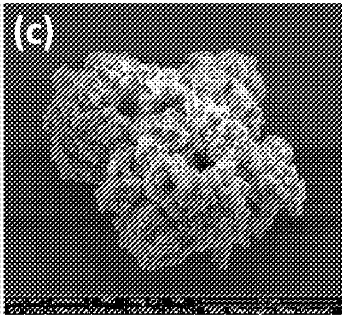


FIG. 12B

FIG. 12C

100min



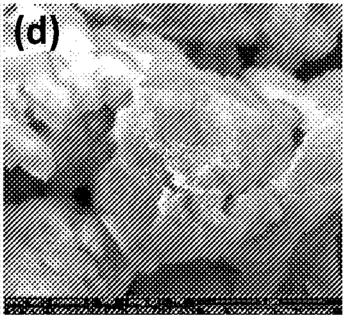
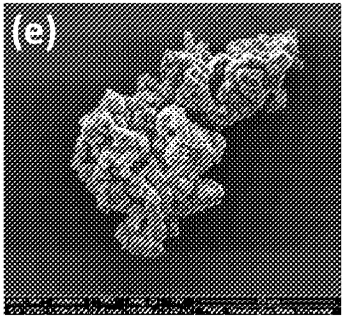


FIG. 12D

FIG. 12E

200min



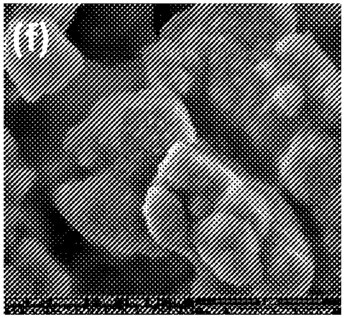
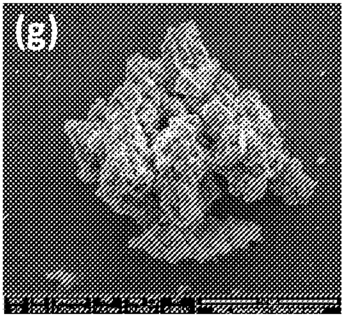


FIG. 12F

FIG. 12G

400min



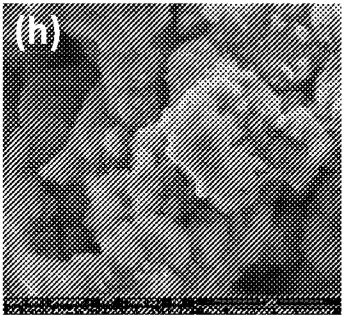
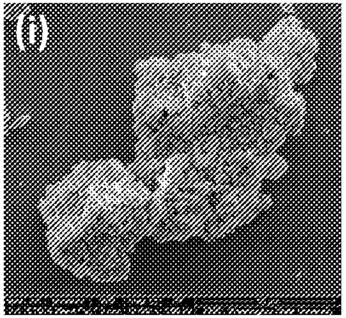


FIG. 12H

FIG. 12I

600min



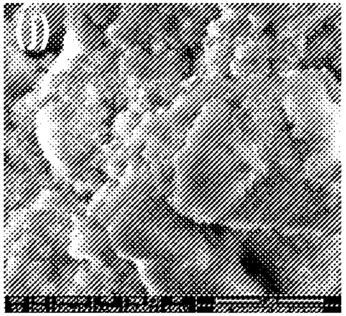


FIG. 12J

REFERENCES CITED IN THE DESCRIPTION

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- CN 105826527 A **[0002]**
- WO 2017052281 A1 **[0002]**
- US 2013189575 A1 **[0002]**

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- **XIAO C. et al.** *Journal of Materials Chemistry A,* 2014, vol. 2, 20494-20499 **[0002]**