

SILICON MATERIAL A FOR HYDROGEN GAS PRODUCTION,
SILICON MATERIAL B FOR HYDROGEN GAS PRODUCTION, METHOD FOR
PRODUCING SILICON MATERIAL A FOR HYDROGEN GAS PRODUCTION,
METHOD FOR PRODUCING SILICON MATERIAL B FOR HYDROGEN GAS
5 PRODUCTION, METHOD FOR PRODUCING HYDROGEN GAS, AND DEVICE
FOR PRODUCING HYDROGEN GAS

TECHNICAL FIELD OF THE INVENTION

[0001] The present invention relates to a silicon material
10 A for hydrogen gas production, a silicon material B for
hydrogen gas production, a method for producing a silicon
material A for hydrogen gas production, a method for
producing a silicon material B for hydrogen gas production,
a method for producing hydrogen gas, and a device for
15 producing hydrogen gas.

BACKGROUND OF THE INVENTION

[0002] At present, silicon wafers are being used in large
quantity as substrates of semi-conductor apparatuses. A
20 silicon wafer is produced as follows: first, a cylindrical
silicon ingot is produced by crystal growth of a molten
silicon. Next, an orientation flat or a notch to indicate
a direction of a crystal axis is formed on the silicon
ingot. Next, the silicon ingot is sliced into a
25 predetermined thickness to prepare a silicon wafer.
Slicing is conducted by a dicer or a multi-wire saw. Next,
the silicon wafer is treated by processes such as a lapping

process to cut to a predetermined thickness, an etching process to remove processing distortion, a beveling process to prevent chipping of the periphery, and a mirror polishing process to make a surface a mirror. In such production processes of a silicon wafer, a great amount of silicon waste is generated. Although silicon waste has conventionally been abandoned, it is impossible to ignore a cost load and an environmental load caused by abandonment of the silicon waste.

[0003] On the other hand, it is known that hydrogen gas is generated when silicon is put into an alkaline aqueous solution (for instance, a NaOH aqueous solution) to be heated. The generation of hydrogen gas is caused by a reaction; $\text{Si} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_3^{2-} + 2\text{H}_2\uparrow$. Accordingly, in the case where hydrogen gas can be efficiently obtained from silicon waste, it is extremely advantageous from a point of a cost load and an environmental load.

[0004] Trials to obtain hydrogen gas from silicon waste have previously been carried out. For instance, in Japanese Unexamined Patent Application Publication No. JP 2000-191303 A, silicon waste and an alkaline aqueous solution are put in a tightly sealable reaction chamber and the silicon waste and the alkaline aqueous solution are allowed to react by heating the reaction chamber to collect hydrogen gas generated. While a reaction is rapidly promoted immediately after the start of the reaction as a feature of a reaction between silicon and an alkaline

aqueous solution, subsequently, the reaction stops. This makes it difficult to control the generation of hydrogen gas.

[0005] Further, as is clear from the reaction formula,

5 silicate ions (SiO_3^{2-}) are generated in a reaction of silicon and an alkaline aqueous solution. When the alkaline aqueous solution and silicon are excessive, silicate ions become gelatinized and cover unreacted silicon, resulting in blocking of reaction such as
10 generation of hydrogen gas.

[0006] To solve these problems, in Japanese Unexamined Patent Application Publication No. JP 2001-213609 A, silicon powders are mixed with water to supply sludge (mud).

Supplying silicon powders in a state of sludge makes it
15 possible to inhibit a severe reaction immediately after contacting silicon with the alkaline aqueous solution and inhibit the generation of silicate ions in a gel state. In addition, it is possible to continuously obtain hydrogen gas by additionally supplying silicon sludge and an
20 alkaline aqueous solution so as to retain pressure in the reaction chamber in a predetermined range while taking hydrogen gas out of the reaction chamber.

PRIOR ART DOCUMENTS

25 PATENT DOCUMENTS

[0007] Patent document 1: JP 2000-191303 A

Patent document 2: JP 2001-213609 A

SUMMARY

[0007a] In a first aspect of the present disclosure, there is provided a method for producing hydrogen gas, comprising the steps of:

preparing a silicon material A for hydrogen gas production, the silicon material A for hydrogen gas production comprising: silicon particles; oil content derived from a coolant, the oil content being 0.1 weight % to 10 weight % of the silicon particles; and water;

preparing an alkaline aqueous solution;

supplying the silicon material A for hydrogen gas production and the alkaline aqueous solution in a reaction chamber;

injecting the silicon material A for hydrogen gas production into the reaction chamber while feed-back controlling an injection rate thereof based on a temperature of a mixed liquid of the silicon material A for hydrogen gas production and the alkaline aqueous solution in the reaction chamber and a time change rate of the temperature;

injecting the alkaline aqueous solution into the reaction chamber while feed-back controlling an injection rate thereof by measuring alkali concentration of the mixed liquid and calculating a time change rate of the alkali concentration;

maintaining the mixed liquid in the reaction chamber at a predetermine temperature;

treating gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles by a scrubber, which has been taken out of the reaction chamber, to remove the alkaline aqueous solution mist, the metasilicate hydrate mist, and the silicon particles from the gas P; and
treating gas Q including the hydrogen gas and the steam which is obtained by treating the gas P by the scrubber to remove the steam from the gas Q by treating with a condenser.

[0007b] In a second aspect of the present disclosure, there is provided a method for producing hydrogen gas, comprising the steps of:

preparing a silicon material B for hydrogen gas production comprising: silicon particles; any one of formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl alcohol, polyacrylamide and polyethylene glycol in a range of 0.1 weight % to 10 weight % or a mixture of at least two selected therefrom, and water;

preparing an alkaline aqueous solution;

supplying the reaction chamber with the silicon material B and the alkaline aqueous solution;

injecting the silicon material B for hydrogen gas production into the reaction chamber while feed-back controlling an injection rate thereof based on a temperature of a mixed liquid of the silicon material B for hydrogen gas production and the alkaline aqueous solution in the reaction chamber and a time change rate of the temperature;

injecting the alkaline aqueous solution into the reaction chamber while feed-back controlling an injection rate thereof by calculating a time change rate of the alkali concentration together with measuring the alkali concentration;

maintaining a mixed liquid in the reaction chamber at a predetermine temperature;

treating gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles by a scrubber, which has been taken out of the reaction chamber, to remove the alkaline aqueous solution mist, the metasilicate hydrate mist, and the silicon particles from the gas P; and
treating gas Q including the hydrogen gas and the steam which is obtained by treating the gas P by the scrubber to remove the steam from the gas Q by treating with a condenser.

[0007c] In a third aspect of the present disclosure, there is provided a hydrogen gas producing device, comprising in descending order:

- a hermetically sealed reaction chamber;

- means for supplying the reaction chamber with a silicon material A for hydrogen gas production, the silicon material A for hydrogen gas production comprising: silicon particles; oil content derived from a coolant, the oil content being 0.1 weight % to 10 weight % of the silicon particles; and water;

- means for supplying the reaction chamber with an alkaline aqueous solution;

- means for feed-back controlling an injection rate of the silicon material A for hydrogen gas production by measuring a temperature of a mixed liquid of the silicon material A for hydrogen gas production and the alkaline aqueous solution and calculating a time change rate of the temperature so that the temperature of the mixed liquid in the reaction chamber may be a predetermined temperature;

- means for feed-back controlling an injection rate of the alkaline aqueous solution by calculating a time change rate of alkali concentration together with measuring the alkali concentration of the mixed liquid so that the alkali concentration of the mixed liquid may be a predetermined value;

means for uniformly mixing the alkaline aqueous solution with the silicon material A for hydrogen gas production provided in the reaction chamber;

a thermometer attached to the reaction chamber;

a heater attached to the reaction chamber;

a cooler attached to the reaction chamber;

a scrubber provided at an outlet of hydrogen gas in the reaction chamber;

a condenser provided at an outlet of hydrogen gas in the reaction chamber; and

a regulator provided at an outlet of hydrogen gas in the reaction chamber.

[0007d] In a fourth aspect of the present disclosure, there is provided a hydrogen gas producing device, comprising in descending order:

a hermetically sealed reaction chamber;

means for supplying the reaction chamber with a silicon material B for hydrogen gas production, the silicon material B for hydrogen gas production comprising: silicon particles; any one of formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide,

polyvinyl alcohol, polyacrylamide and polyethylene glycol in a range of 0.1 weight % to 10 weight % or a mixture of at least two selected therefrom, and water;

means for supplying the reaction chamber with an alkaline aqueous solution;

means for feed-back controlling an injection rate of the silicon material B for hydrogen gas production by measuring a temperature of a mixed liquid of the silicon material B for hydrogen gas production and the alkaline aqueous solution and calculating a time change rate of the temperature so that the temperature of the mixed liquid in the reaction chamber may be a predetermined temperature;

means for feed-back controlling an injection rate of the alkaline aqueous solution by measuring alkali concentration of the mixed liquid and calculating a time change rate of the alkali concentration so that the alkali concentration of the mixed liquid may be a predetermined value;

means for uniformly mixing the alkaline aqueous solution with the silicon material B for hydrogen gas production provided in the reaction chamber;

a thermometer attached to the reaction chamber;

a heater attached to the reaction chamber;

a cooler attached to the reaction chamber;

a scrubber provided at an outlet of hydrogen gas in the reaction chamber;

a condenser provided at an outlet of hydrogen gas in the reaction chamber; and
a regulator provided at an outlet of hydrogen gas in the reaction chamber.

PROBLEMS TO BE SOLVED BY THE INVENTION

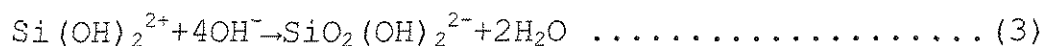
[0008] The inventors of the present invention conducted an experiment for mixing silicon powders with water to supply sludge as disclosed in JP 2001-213609 A. The details of the experiment will be described later as an explanation of a comparative example of FIG. 3 of the present invention. As a result, it was impossible to inhibit a severe reaction caused immediately after contacting silicon with an alkaline aqueous solution, even when sludge is supplied in a mixture of silicon powders and water.

[0009] In a hydrogen gas producing apparatus disclosed in JP 2001-213609 A, silicon powders are mixed with water. In an actual multi-wire saw, however, silicon ingots and wires are cut while being cooled by a coolant. The coolant is not simple water but a fluid obtained by mixing propylene glycol (PG) with water, for instance. Propylene glycol makes a surface tension of water smaller to improve wettability of the wires and penetrability of the silicon ingots into slice grooves. Propylene glycol or a material having similar functions is referred to as oil content in a coolant.

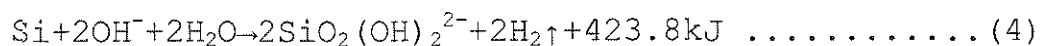
[0010] Therefore, silicon waste generated from a multi-wire saw includes silicon particles and a coolant (water and oil content). In this point, "sludge obtained by mixing silicon powders with water" disclosed in JP 2001-213609 A does not contain oil content and is different from silicon

waste actually generated from a multi-wire saw. The silicon waste generated from the multi-wire saw includes a coolant, so that the oil content in the coolant covers a surface of each of silicon particles. This prevents the silicon particles and the alkaline aqueous solution from being in contact with each other, resulting in inhibition of a reaction of the silicon particles and the alkaline aqueous solution. As a result, an amount of hydrogen gas generation is less than a theoretical value. It is a first object of the present invention to prevent oil content in a coolant from inhibiting the generation of hydrogen gas.

[0011] According to an experiment of the inventors of the present invention, however, a reaction is explosively promoted immediately after the start of the reaction when oil content is completely removed and subsequently, no reaction occurs. The reason is as mentioned below. In a reaction between silicon particles and an alkaline aqueous solution, the following three reactions sequentially occur on a surface of each of the silicon particles:



These three formulas are collectively represented by the following formula:

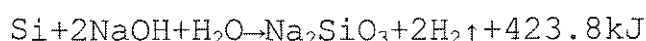


As mentioned above, 1 mole of silicon particles reacts with 2 moles of alkali and then 2 moles of water and 2 moles of

$\text{SiO}_2(\text{OH})_2^{2-}$ (which is a hydrate of metasilicate ions and is water-soluble) and 2 moles of hydrogen gas are generated.

[0012] The number of the mole is consumed twice as great as the silicon particles in the alkaline aqueous solution in the reaction chamber and the alkaline aqueous solution is taken out of the reaction chamber as alkali mist along with hydrogen gas and steam which are further generated. The alkaline aqueous solution deficient in the reaction chamber is immediately supplied by a pump from an alkaline aqueous solution tank. Since water is not only consumed by the aforementioned reaction but also moisture that corresponds to saturation vapor pressure of the temperature of the reaction chamber is evaporated along with hydrogen gas, the deficit is supplied from moisture of a sludge tank and moisture of the alkaline aqueous solution tank.

[0013] In the case where a NaOH aqueous solution is used as an alkaline aqueous solution, a heat-generation reaction of the following occurs:



This reaction has an extremely great calorific value, which is about ten times as great as vaporization heat of water, about twice as great as heat of combustion of hydrogen. That is, when silicon particles are mixed with the NaOH aqueous solution, reaction heat, which is twice as great as reaction heat generated when hydrogen gas is burnt, is generated in addition to generation of hydrogen gas having a mole twice as great as the mole of the mixed silicon

particles. When the reaction-based temperature rises by the reaction heat, the reaction speed is more accelerated to increase the reaction heat. Such a positive feedback makes the reaction between the silicon particles and the alkaline aqueous solution explosively severe, which is extremely difficult to control. Such a state of reaction is thermal runaway.

[0014] When silicon is composed of some μm of fine particles, a surface area thereof is large and thermal runaway of the reaction becomes further severe, resulting in further difficulty in controlling the reaction. It is impossible to suppress a temperature rise of a mixed liquid of silicon particles and an alkaline aqueous solution that is caused by reaction heat even when the reaction chamber is cooled. Accordingly, it has conventionally been difficult to control the generation of hydrogen gas caused by a reaction of silicon particles and an alkaline aqueous solution. It is a second object of the present invention to properly suppress a reaction of silicon particles and an alkaline aqueous solution to constantly obtain hydrogen gas.

[0015] In the hydrogen gas producing apparatus disclosed in JP 2001-213609 A, silicon sludge and an alkaline aqueous solution are additionally supplied so as to keep pressure in the reaction chamber in a predetermined range while taking hydrogen gas out of the reaction chamber. This makes it possible to continuously obtain hydrogen gas. According to FIG. 6 in JP 2001-213609 A, however, pressure

of the reaction chamber fluctuates in a range of 0.1 MPa to 0.2 MPa, which is not always stable. In addition, since FIG. 6 shows simulation results without consideration for reaction heat, FIG. 6 is different from the situation of actual reaction in which a great amount of reaction heat is generated. Further, sludge is discontinuously injected about every 13 minutes and is not a system for continuously and stably controlling the generation of hydrogen gas.

[0016] It is, therefore, a third object of the present invention to materialize a method for producing hydrogen gas and a hydrogen gas producing device having less pressure fluctuations of a reaction chamber. The third object (a method and a device for producing hydrogen gas having less pressure fluctuations) and the second object (to properly suppress a reaction of silicon particles and an alkaline aqueous solution) are closely related.

Consequently, it is impossible to achieve the third object (a hydrogen gas production device having less pressure fluctuations), when the second object (to properly suppress a reaction of silicon particles and an alkaline aqueous solution) is not achieved.

[0017] In Example in JP 2000-191303 A, a reaction chamber has a capacity of 0.2 liter. While there is no description about the capacity of a reaction chamber in Examples of JP 2001-213609 A, the capacity of the reaction chamber is some liters because the alkaline aqueous solution (NaOH aqueous solution) is 1 liter. According to the study of the

inventors of the present invention, while a hydrogen gas producing device for a laboratory in this scale has no problems, a hydrogen producing device for mass production having a scale of 10 times to 100 times as great as the
5 hydrogen gas producing device has problems mentioned below.

[0018] In view of a reaction formula of silicon particles and an alkaline aqueous solution; $\text{Si} + 2\text{OH}^- + \text{H}_2\text{O} \rightarrow \text{SiO}_3^{2-} + 2\text{H}_2\uparrow$, this indicates that what is generated from the reaction chamber is hydrogen gas and steam only. Accordingly, in JP
10 2000-191303 A and JP 2001-213609 A, a condenser is configured to connect to a reaction chamber. The condenser cools a mixture of hydrogen gas and steam to lower a dew point of the mixture and allows steam to condense to water to remove steam from the mixture.

15 [0019] According to the study of the inventors of the present invention, however, in a hydrogen gas producing device in mass production scale, alkaline aqueous mist (an alkaline aqueous solution in a mist state), metasilicate hydrate mist, and silicon particles also scatter from the
20 reaction chamber except for hydrogen gas and steam. In the case of a hydrogen gas producing device in mass production scale, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles enter a condenser when the condenser is connected to the reaction chamber.

25 [0020] The alkaline aqueous solution mist becomes solidified when the alkaline aqueous solution is cooled to lower temperatures by a condenser. In addition, the

alkaline aqueous solution mist corrodes the condenser depending on the material of the condenser. Silicon particles deposit on the condenser. When the deposition of the silicon particles proceeds, a tube inside the condenser is clogged. Therefore, it is a fourth object of the present invention to prevent corrosion and clogging caused by alkaline aqueous mist, metasilicate hydrate mist, and silicon particles.

10 MEANS FOR SOLVING THE PROBLEMS

[0021] [Silicon material A for hydrogen gas production]

In the case where a coolant contains oil content in a silicon material A for hydrogen gas production, oil content of the coolant is not completely removed but an appropriate amount of oil content is left when refining silicon particles. Since oil content inhibits a reaction between silicon particles and an alkaline aqueous solution, hydrogen gas is not generated when the oil content is too great. Conversely, hydrogen gas is explosively generated when the oil content is too small, which is impossible to control. Accordingly, an appropriate amount of oil content of the coolant is left. It is difficult to continuously supply the silicon material A for hydrogen gas production by a pump because the silicon material A for hydrogen gas production is a solid when the silicon material A for hydrogen gas production consists of silicon particles and oil content. Accordingly, water is added to make sludge.

(1) According to the present invention, there is provided a silicon material A for hydrogen gas production which includes: silicon particles; oil content of 0.1 weight % to 10 weight % of the silicon particles; and water.

(2) In the silicon material A for hydrogen gas production of the present invention, the oil content is any one of isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-ethyl-1-hexanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-propanediol, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol or a mixture thereof. These materials may be included in the coolant as oil content.

(3) In the silicon material A for hydrogen gas production of the present invention, the silicon particles each have an average particle size of 0.1 μm to 30 μm . When the average particle size of each of the silicon particles is less than 0.1 μm , there is a possibility of reaction control effects of the oil content being insufficient. When the average particle size of each of the silicon particles is over 30 μm , a surface area of each of the silicon particles may be short and the reaction may be insufficient. Further, the silicon particles easily precipitate. As a result, there is a possibility that the silicon particles do not uniformly disperse in the alkaline aqueous solution.

(4) In the silicon material A for hydrogen gas production of the present invention, the water is one time to ten times as heavy as the silicon particles. When the water is less than one time as heavy as the silicon particles, sludge has a too high viscosity. This may make it difficult to supply the silicon material A by a sludge pump. When the water is over ten times as heavy as the silicon particles, a balance between the silicon particles and the alkaline aqueous solution collapses (the concentration of the alkaline aqueous solution becomes too low), alternatively, the liquid temperature of a mixed liquid in the reaction chamber becomes lower. As a result, there is a possibility that and the generation speed of hydrogen gas may be lower.

[0022] [Silicon material B for hydrogen gas production]

In a silicon material B for hydrogen gas production of the present invention, oil content which inhibits a reaction of hydrogen gas generation in a coolant is practically removed when refining silicon particles and then a reaction inhibitor is newly added. Like the oil content, the reaction inhibitor has a function to suppress a reaction between silicon particles and an alkaline aqueous solution. However, there are some reaction inhibitors to be used in the silicon material B for hydrogen gas production of the present invention that are generally not included in the coolant. After the oil

content contained in the coolant that inhibits the reaction of hydrogen gas generation is removed, a reaction inhibitor is added. When oil content remains in the coolant, both the oil content and the reaction inhibitor cause a reaction inhibition action, resulting in difficulty in delicately controlling the reaction inhibition action. Accordingly, the oil content contained in the coolant is once removed and then a reaction inhibitor is added.

(5) According to the present invention, there is also provided a silicon material B for hydrogen gas production which includes: silicon particles; a reaction inhibitor which is 0.1 weight % to 10 weight % of the silicon particles; and water.

(6) In the silicon material B for hydrogen gas production of the present invention, the reaction inhibitor is any one of formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl alcohol, polyacrylamide, polyethylene glycol or a mixture thereof.

(7) In the silicon material B for hydrogen gas production of the present invention, the silicon particles each have an average particle size of 0.1 μm to 30 μm .

(8) In the silicon material B for hydrogen gas production of the present invention, the water is one time to ten times as heavy as the silicon particles.

[0023] [Production method for silicon material A for hydrogen gas production]

A method for producing a silicon material A for hydrogen gas production of the present invention is characterized in leaving an appropriate amount of oil content (0.1 weight % to 10 weight % of silicon particles) in a coolant when refining silicon particles.

(9) According to the present invention, there is also

provided a method for producing a silicon material A for hydrogen gas production which includes the steps of: preparing silicon waste including silicon particles, oil content and water derived from a coolant; centrifuging or filtering the silicon waste

to produce a solid A composed of the silicon particles, the oil content that is 0.1 weight % to 10 weight % of the silicon particles, and a small amount of water; drying the solid A to produce a solid B composed of the silicon particles and the oil content that is 0.1 weight % to 10 weight % of the silicon particles; and adding water to the solid B to produce sludge A.

(10) In the method for producing a silicon material A for hydrogen gas production of the present invention, the oil content is any one of isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-ethyl-1-hexanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-propanediol, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol or a mixture thereof.

(11) In the method for producing a silicon material A for hydrogen gas production of the present invention, the solid A has a drying temperature of 100°C to 120°C. The drying temperature is a temperature at which water is evaporated, however, the oil content is not evaporated.

[0024] [Production method for silicon material B for hydrogen gas production]

In a method for producing a silicon material B for hydrogen gas production of the present invention, oil content which inhibits a reaction of hydrogen gas generation in a coolant is practically removed in a step of high-temperature drying when refining silicon particles and then a reaction inhibitor is newly added.

(12) According to the present invention, there is also provided a method for producing a silicon material B for hydrogen gas production which includes the steps of: preparing silicon waste including silicon particles, oil content and water derived from a

coolant; centrifuging or filtering the silicon waste to produce a solid A composed of the silicon particles, the oil content, and a small amount of the water; drying the solid A to produce a solid B composed of the silicon particles and the oil content; evaporating the oil content by drying the solid B at a high temperature to produce a solid C composed of silicon particles; and adding a reaction inhibitor which is 0.1 weight % to 10 weight% of the silicon particles and water to the solid C to produce sludge B.

(13) In the method for producing a silicon material B for hydrogen gas production of the present invention, the reaction inhibitor is any one of isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-ethyl-1-hexanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-propanediol, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol, formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl

alcohol, polyacrylamide, polyethylene glycol or a mixture thereof.

(14) In the method for producing a silicon material B for hydrogen gas production of the present invention, the solid A has a drying temperature of 100°C to 120°C. The drying temperature is a temperature at which the water is evaporated, however, the oil content is not evaporated.

(15) In the method for producing the silicon material B for hydrogen gas production of the present invention, the solid B has a high-temperature drying temperature of 500°C to 700°C. The high-temperature drying temperature is a temperature at which the oil content contained in the solid B is nearly evaporated.

[0025] [Production method for hydrogen gas]

A method for producing hydrogen gas of the present invention includes the steps of: using a silicon material A for hydrogen gas production or a silicon material B for hydrogen gas production of the present invention; feed-back controlling an injection rate of the silicon material A for hydrogen gas production or the silicon material B for hydrogen gas production based on a temperature of a mixed liquid in a reaction chamber; feed-back controlling an injection rate of an alkaline aqueous solution based on an alkali concentration in the reaction chamber; and scrubbing gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon

particles to remove the alkaline aqueous solution mist, the metasilicate hydrate mist, and the silicon particles from the gas P.

(16) According to the present invention, there is also

5 provided a method for producing hydrogen gas which includes the steps of: preparing a silicon material A for hydrogen gas production or a silicon material B for hydrogen gas production; preparing an alkaline aqueous solution; injecting one of the silicon
10 material A for hydrogen gas production and the silicon material B for hydrogen gas production into a reaction chamber while feed-back controlling an injection rate thereof based on a temperature of a mixed liquid in the reaction chamber; injecting the alkaline aqueous
15 solution into the reaction chamber while feed-back controlling an injection rate thereof based on an alkali concentration in the reaction chamber; maintaining a mixed liquid of the silicon material A for hydrogen gas production or the silicon material B
20 for hydrogen gas production and the alkaline aqueous solution in the reaction chamber at a predetermine temperature; treating gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles by a scrubber,
25 which has been taken out of the reaction chamber, to remove the alkaline aqueous solution mist, the metasilicate hydrate mist, and the silicon particles

from the gas P; and treating gas Q including the hydrogen gas and the steam which is obtained by treating the gas P by the scrubber to remove the steam from the gas Q by treating with a condenser.

5 (17) In the method for producing hydrogen gas of the present invention, the alkaline aqueous solution is one of a NaOH aqueous solution and a KOH aqueous solution.

10 (18) In the method for producing hydrogen gas of the present invention, one of a NaOH aqueous solution and a KOH aqueous solution has a concentration of 1 mol/L to 8 mol/L.

(19) In the method for producing hydrogen gas of the present invention, the predetermined temperature is
15 50°C to 90°C.

[0026] [Hydrogen gas producing device]

(20) According to the present invention, there is also provided a hydrogen gas producing device which includes in descending order: a hermetically sealed reaction chamber;
20 means for supplying the reaction chamber with one of a silicon material A for hydrogen gas production and a silicon material B for hydrogen gas production; means for supplying the reaction chamber with an alkaline aqueous solution; a thermometer fitted to the reaction chamber; a
25 heater fitted to the reaction chamber; and a cooler fitted to the reaction chamber; a scrubber provided at an outlet of hydrogen gas in the reaction chamber; a condenser

provided at the outlet of hydrogen gas in the reaction chamber; and a regulator provided at the outlet of hydrogen gas in the reaction chamber.

(21) In the hydrogen gas producing device of the present invention, the scrubber removes alkaline aqueous mist, metasilicate hydrate mist, and silicon particles from the reaction chamber.

(22) In the hydrogen gas producing device of the present invention, the means for supplying one of the silicon material A for hydrogen gas production and the silicon material B for hydrogen gas production is preferably one of a mono pump and a gear pump. The mono pump and the gear pump can stably deliver a sludge-like material.

(23) In the hydrogen gas producing device of the present invention, the reaction chamber includes means for mixing one of the silicon material A for hydrogen gas production and the silicon material B for hydrogen gas production with the alkaline aqueous solution.

20 ADVANTAGES OF THE INVENTION

[0027] The silicon material A for hydrogen gas production of the present invention includes an appropriate oil content to properly suppress a reaction between the silicon particles and the alkaline aqueous solution. The oil content is derived from a coolant. Oil content which is over 10% of the weight of the silicon particles is contained in silicon waste obtained by separating a

recycled coolant from a waste coolant of a multi-wire saw. As mentioned above, when oil content contained in the silicon waste is too great, this inhibits the reaction between the silicon particles and the alkaline aqueous solution. As a result, even when the alkaline aqueous solution is added to the silicon waste, hydrogen gas that is obtainable is less than a theoretical value. It is impossible to use such silicon waste as a silicon material for hydrogen gas production as it stands now.

[0028] Since the silicon material for hydrogen gas production of the present invention includes less oil content than the silicon waste, hydrogen gas which is exactly the same as the theoretical value is obtainable by adding the alkaline aqueous solution. In addition, an appropriate amount of oil content (0.1 weight % to 10 weight % of the silicon particles) to suppress the reaction between the silicon particles and the alkaline aqueous solution is contained in the silicon material for hydrogen gas production of the present invention, so that the reaction is not explosive. This makes it possible to properly suppress the reaction between the silicon particles and the alkaline aqueous solution and constantly generate hydrogen gas over a long period of time. As a result, the first object (oil content inhibits the generation of hydrogen gas) and the second object (to properly suppress a reaction between silicon particles and an alkaline aqueous solution) are achieved at the same time.

[0029] The silicon material B for hydrogen gas production of the present invention is obtainable by mixing a desired kind of reaction inhibitor only as much as desired with silicon particles after removing oil content derived from a coolant by evaporating the oil content employing high-temperature drying. As well as the oil content, the reaction inhibitor has functions to properly suppress a reaction between silicon particles and an alkaline aqueous solution. Mechanisms that the reaction inhibitor properly suppresses the reaction between the silicon particles and the alkaline aqueous solution are the same as mechanisms caused by the oil content derived from the coolant. While a substance that is different from the oil content of the coolant is usually used as a reaction inhibitor contained in the silicon material B for hydrogen gas production, the same substance as the oil content of the coolant may be used. Even when the silicon material B for hydrogen gas production is used, it is possible to properly suppress the reaction between the silicon particles and the alkaline aqueous solution and constantly generate hydrogen gas over a long period of time.

[0030] The silicon material for hydrogen gas production of the present invention is in the state of sludge by the addition of water one time to ten times as heavy as the silicon particles, more preferably one time to five times as heavy as the silicon particles, further more preferably twice to four times as heavy as the silicon particles.

This makes it possible to precisely inject the silicon material in the reaction chamber with a sludge pump.

[0031] According to the method for producing a silicon material A for hydrogen gas production of the present

5 invention, oil content contained in the coolant is utilized, so that the production process needs a short period of time. On the other hand, according to the method for producing a silicon material B for hydrogen gas production of the present invention, it is possible to precisely mix any
10 reaction inhibitor.

[0032] According to the method for producing hydrogen gas of the present invention, a silicon material for hydrogen gas production and an alkaline aqueous solution are continuously injected while feed-back controlling an

15 injection rate of the silicon material for hydrogen gas production and the alkaline aqueous solution based on the temperature and the alkali concentration of a mixed liquid in the reaction chamber. This makes it possible to continuously obtain a certain amount of hydrogen gas. The
20 reason why it is possible to continuously inject the alkaline aqueous solution and the silicon material is that the second object (to properly suppress a reaction between silicon particles and an alkaline aqueous solution) has been achieved. This makes it possible to achieve the third
25 object (pressure fluctuations of the reaction chamber).

[0033] According to the hydrogen gas producing device of the present invention, a scrubber is provided between a

reaction chamber and a condenser. Hydrogen gas generated in the reaction chamber is guided by the scrubber. Alkaline aqueous solution mist, metasilicate hydrate, and silicon particles scattering from the reaction chamber are removed by the scrubber before entering the condenser. This makes it possible to achieve the fourth object (corrosion and clogging caused by alkaline aqueous solution mist, metasilicate hydrate, and silicon particles).

10 BRIEF DESCRIPTION OF THE DRAWINGS

[0034]

FIG. 1 is a production flow chart of silicon materials for hydrogen gas production of the present invention;

FIG. 2 is a block diagram of a hydrogen gas producing device;

FIG. 3 shows graphs of a hydrogen gas production experiment (effects of a reaction inhibitor);

FIG. 4. is a graph of a hydrogen gas production experiment (Example 1); and

FIG. 5 is a graph of a hydrogen gas production experiment (Example 2).

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0035] To achieve the first object (oil content in a coolant inhibits the generation of hydrogen gas) and the second object (to properly suppress a reaction between silicon particles and an alkaline aqueous solution), a

silicon material A for hydrogen gas production and a silicon material B for hydrogen gas production of the present invention are produced in accordance with a flow chart of FIG. 1.

5 [0036] As shown in the flow chart of FIG. 1, a silicon ingot 102 is placed on a multi-wire saw 101 and is cut while cooling the silicon ingot 102 with a coolant 103 (a mixed liquid of water and oil content) to produce a silicon wafer 104. A portion (notch, kerf loss) cut by a wire is
10 an amorphous silicon particle having a size of 0.1 μm to 30 μm . In the silicon material A for hydrogen gas production and the silicon material B for hydrogen gas production, silicon particles each preferably have an average particle size of about 1 μm . A waste coolant 105 includes silicon
15 particles and a coolant 103. Oil content contained in the coolant 103 is typically propylene glycol.

[0037] As shown in the flow chart of FIG. 1, the waste coolant 105 is first put in a centrifugal separator A106 to separate into a top clear layer in a fluid and a
20 precipitate. The top clear layer in a fluid contains water and oil content and is used again in the multi-wire saw 101 as a recycled coolant 107. The precipitate is referred to as silicon waste 108 and includes water, oil content, and silicon particles. Since the silicon waste 108 contains
25 oil content of over 10% of the weight of the silicon particles, the reaction with the alkaline aqueous solution is easily inhibited.

[0038] As shown in the flow chart of FIG. 1, to decrease oil content in the silicon waste 108, the silicon waste 108 is placed in the centrifugal separator B109 again, alternatively, the silicon waste 108 is filtered through a filter 110. When the silicon waste 108 is centrifuged again, water and oil content are contained in the top clear layer 111 in a fluid. The top clear layer 111 in a fluid is abandoned. In the precipitate of the centrifugal separation, a solid A112 essentially consists of silicon particles includes oil content (0.1 weight % to 10 weight % of the silicon particles) and a small amount of water.

[0039] When the silicon waste 108 is filtered through the filter 110, filtrate 113 includes water and oil content. The filtrate 113 is abandoned. The solid A112 includes oil content (0.1 weight % to 10 weight % of the silicon particles) and a small amount of water. As shown in the flow chart of FIG. 1, since it is possible to move on the solid A112 obtained by centrifugal separation and the solid A112 obtained by filtering to the next step (drying), no distinction is particularly made hereinafter.

[0040] As shown in the flow chart of FIG. 1, the solid A112 is dried by a drying furnace 114. The object of drying is to remove a small amount of moisture contained in the solid A112. Accordingly, the drying furnace 114 preferably has a temperature of 100°C to 120°C. While water is evaporated, oil content is not evaporated. A solid B115 after being dried is composed of silicon particles and oil content (0.1

weight % to 10 weight % of the silicon particles).

[0041] According to an experiment of the inventors of the present invention, it is possible to make the solid B115 contain oil content of 0.1 weight % to 10 weight %

5 (typically, 3 weight %) of the weight of silicon particles by adjusting the number of rotations and rotation time of the centrifugal separator 106. Alternatively, it is possible to make the solid B115 contain 0.1 weight % to 10 weight % (typically, 3 weight %) of oil content by
10 adjusting the size of narrow holes of molecular size and filtering pressure of the filter 110.

[0042] A portion where silicon is exposed and a portion where silicon is covered with oil content mixedly exist in a surface of each silicon particle in the solid B115. The
15 portion where silicon is exposed reacts with an alkaline aqueous solution and the portion where silicon is covered with oil content does not react with the alkaline aqueous solution. When the entire surface of each of the silicon particles is covered with oil content, no reaction between
20 the silicon particles and the alkaline aqueous solution occurs. When a portion where silicon is exposed and a portion covered with oil content are mixed at an appropriate ratio on a surface of each of the silicon particles, the silicon particles gradually react with the
25 alkaline aqueous solution and the reaction between the silicon particles and the alkaline aqueous solution continues over a long period of time, which makes it

possible to constantly generate hydrogen gas.

[0043] Water 116 is added to the solid B115 obtained by drying by use of the drying furnace 114 to produce sludge A117. Further, to distinguish sludge obtained by adding
5 water 116 to the solid B115 from sludge obtained by adding a reaction inhibitor 121 and water 123 to a solid C in a further later process, the sludge obtained by adding the water 116 to the solid B115 is referred to as sludge A117 and the sludge obtained by adding the reactor inhibitor 121
10 and the water 123 to the solid C is referred to as sludge B124. The sludge A117 is a silicon material A for hydrogen gas production of the present invention. The reasons why the water 116 is added to the solid B115 to produce the sludge A117 are firstly, to make the solid B a state
15 suitable for being fed under pressure with a sludge pump; secondly, to cool reaction heat of the silicon particles and the alkaline aqueous solution with water; thirdly, to add water to be consumed by the reaction. An additive amount of water 116 is preferably one time to ten times as
20 heavy as the silicon particles contained in the solid B115, more preferably one time to five times, further preferably, twice to four times. When the water 116 which is one time to ten times as heavy as the silicon particles is added, the silicon particles are uniformly dispersed into the
25 water 116, which prevents piping or a pump from clogging.

[0044] According to the study of the inventors of the present invention, when oil content that is 0.1 weight % to

10 weight % of the silicon particles, preferably 0.5 weight % to 5 weight % of the silicon particles, more preferably 2 weight % to 4 weight % of the silicon particles, typically 3 weight % of the silicon particles, is mixed with the silicon material A for hydrogen gas production (sludge A117), the silicon particles continue reacting with the alkaline aqueous solution over a long period of time, which makes it possible to constantly generate hydrogen gas.

10 [0045] Even in the case where the dispersion state of the silicon particles in the silicon material A for hydrogen gas production (sludge A117) is good, there is a possibility that the silicon particles may precipitate after allowing to stand for a long period of time.

15 Accordingly, it is preferable to re-disperse the silicon particles by use of a dispersing apparatus immediately before injecting the silicon material A for hydrogen gas production into the reaction chamber.

[0046] The next process of the flow chart in FIG. 1 is further performed when including a reaction inhibitor which is different from oil content, alternatively, when controlling the amount of the reaction inhibitor more precisely. As shown in the flow chart of FIG. 1, the solid B115 including oil content is burnt by a high-temperature furnace 118 and oil content 119 derived from the coolant is evaporated to obtain a solid C120 consisting of silicon particles. The high-temperature furnace 118 preferably has

a temperature of 500°C to 700°C, more preferably 600°C. The oil content 119 is evaporated at this temperature. Nitrogen gas is flown into the high-temperature furnace 118 to prevent surface oxidation of the silicon particles, oxidation and burning of the oil content 119.

[0047] The solid C120 burnt by the high-temperature furnace 118 contains practically no oil content. As a result, the reaction inhibitor 121 and water 123 are mixed with the solid C120 to produce sludge B122. The amount of the reaction inhibitor 121 is 0.1 weight % to 10 weight %, preferably 0.5 weight % to 5 weight %, more preferably 2 weight % to 4 weight %, typically 3 weight % of the silicon particles. The reaction inhibitor 121 may be the same substance as the oil content 119 and may also be a different substance.

[0048] While examples of the reaction inhibitor to be mixed will be described later, reaction inhibitors such as carboxylic acid, water-soluble polymer, and monomer are not practically contained in the coolant. Accordingly, when a reaction inhibitor such as particularly carboxylic acid or water-soluble polymer or monomer is used, a process after burning by the high-temperature furnace 118 is needed.

[0049] Sludge B124 is the silicon material B for hydrogen gas production of the present invention. The first reason why the water 123 is added is to uniformly mix the silicon particles and a reaction inhibitor to make a state suitable for feeding the sludge B124 under pressure with a sludge

pump. The second reason is to cool the reaction heat of the silicon particles and the alkaline aqueous solution. The third reason is to add water to be consumed by the reaction. The additive amount (weight) of the water 123 is preferably one time to ten times, more preferably one time to five times, further preferably twice to four times as heavy as the solid C120 (silicon particles).

[0050] According to experiments of the inventors of the present invention, the state of hydrogen gas generation was similar in the case where the sludge A117 containing 3 weight % of oil content (propylene glycol) derived from the coolant, and sludge B124 in which 3 weight % of a reaction inhibitor (propylene glycol) which is the same kind of the oil content is mixed after burning by a high-temperature furnace are used as a silicon material for hydrogen gas production. Accordingly, when oil content contained in the coolant 103 is used, it is advantageous to use the sludge A117 having a short-time production process. However, when a reaction inhibitor, which is not contained in the coolant 103 as oil content, is used, it is needed to use the sludge B124 produced in the process after the high-temperature furnace 118 in the flow chart of FIG. 1.

[0051] The following water-soluble organic substances or mixtures thereof are preferable as reaction inhibitors:

- (1) and (2) may be contained in a coolant as oil content.
- (3) and (4) are usually not contained in a coolant and even so in a very small amount.

(1) monovalent alcohol: isopropanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2-methyl-2-propanol, 2-ethyl-1-hexanol

(2) polyvalent alcohol: ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-

5 propanediol, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol, 1,5-pentanediol (the aforementioned monovalent alcohol and polyvalent alcohol are combined to represent as $X-(OH)_n$. X is here a saturated or an unsaturated hydrocarbon group having carbon number C_m of 3 to 7. n is an integer not
10 less than 1, $n < C_m$).

(3) Carboxylic acid

· Saturated fatty acid: formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid,

15 decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid

· Unsaturated aliphatic carboxylic acid: acrylic acid, oleic acid

· Hydroxy acid: malic acid, citric acid

20 · Dicarboxylic acid: oxalic acid, maleic acid, fumaric acid

(4) Water-soluble polymer, monomer

Vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl alcohol, polyacrylamide, polyethylene glycol.

25 [0052] FIG. 2 is a block diagram of a hydrogen gas producing device 200 of the present invention. A silicon material 202 for hydrogen gas production is injected in a

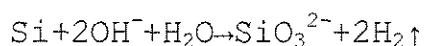
hermetically sealed reaction chamber 201 with a sludge pump 203. The silicon material 202 for hydrogen gas production is sludge A117 (silicon material A for hydrogen gas production) or sludge B122 (silicon material B for hydrogen gas production) in the flow chart of FIG. 1. Accordingly, a mono pump or a gear pump that can feed sludge under pressure is suitable as sludge pump 203.

[0053] An alkaline aqueous solution 204 (typically, a NaOH aqueous solution) is injected into the reaction chamber 201 with an alkaline aqueous solution pump 205. A fluorine resin pump or a polyethylene alkali-resistant pump is typically suitable for the alkaline aqueous solution pump 205. Hydrogen gas is generated in the reaction chamber 201 and the reaction chamber 201 is under pressure, which makes pressure resistance necessary. In addition, the reaction chamber 201 needs to be alkali-resistant. As a result, the reaction chamber 201 is preferably a stainless pressure-resistant container.

[0054] The alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production are mixed in the reaction chamber 201 to produce a mixed liquid 208. Since the silicon material 202 for hydrogen gas production is sludge (sludge state), it is not easy to uniformly mix the silicon material 202 for hydrogen gas production with the alkaline aqueous solution 204 and disperse the silicon material 202 for hydrogen gas production in the alkaline aqueous solution 204. Accordingly, ultrasonic vibration is

provided by an ultrasonic vibrator 206, alternatively, agitation is carried out by an agitator not shown so as to uniformly mix the silicon material 202 for hydrogen gas production and the alkaline aqueous solution 204.

- 5 [0055] When the silicon material 202 for hydrogen gas production is mixed with the alkaline aqueous solution 204, the following chemical reaction occurs and hydrogen gas is generated:



- 10 The generated hydrogen gas remains in an internal space of the reaction chamber 201.

- [0056] The reaction that causes hydrogen gas for the aforementioned formula is slow in reaction speed at an ordinary temperature, so that the temperature of the mixed liquid 208 in the reaction chamber 201 is risen by a heater 207 before pouring the silicon material 202 for hydrogen gas production into the reaction chamber 201. The heater 207 is controlled while measuring the temperature of the mixed liquid 208 by use of a thermometer 209. The
- 20 temperature of the mixed liquid 208 is controlled so as to be 50°C to 90°C (preferably 60°C to 80°C) by the heater 207. When the temperature of the mixed liquid 208 is lower than 50°C, the reaction speed thereof becomes slower (generation of hydrogen gas becomes smaller). When the temperature of
- 25 the mixed liquid 208 is higher than 90°C, while the reaction speed thereof is faster (generation of hydrogen gas becomes greater), there is a high possibility of the

reaction being thermal runaway. In addition, there is little time to deal with the thermal runaway. Accordingly, the temperature of the mixed liquid 208 is suitable between 50°C and 90°C.

- 5 [0057] Once reaction heat between the silicon material 202 for hydrogen gas production and the alkaline aqueous solution 204 is generated, heating of the heater 207 is weakened or stopped. In the case where the reaction heat is generated more and the temperature of the mixed liquid
10 208 becomes higher than the maximum temperature even when the heater is switched off, the mixed liquid 208 is cooled down by a cooler 210. At the same time, the injection of the silicon material 202 for hydrogen gas production becomes lesser or stops.
- 15 [0058] When a NaOH aqueous solution is used as an alkaline aqueous solution 204, the NaOH aqueous solution preferably has a concentration of 1 mol/L to 8 mol/L, more preferably 3 mol/L to 4 mol/L. When the NaOH aqueous solution has a concentration of over 8 mol/L, the NaOH aqueous solution
20 has a too high viscosity and is difficult to be uniformly mixed with the silicon material 202 for hydrogen gas production. When the silicon material 202 for hydrogen gas production is injected, sodium metasilicate is formed. Accordingly, the mixed liquid 208 has a further high
25 viscosity, which makes the NaOH aqueous solution difficult to be uniformly mixed with the silicon material 202 for hydrogen gas production. In the case where the NaOH

aqueous solution and the silicon material 202 for hydrogen gas production are not uniformly mixed, there are fears that the reaction may be non-uniform. When the NaOH aqueous solution has a concentration of less than 1 mol/L, there are fears that the hydrogen gas generation reaction may not sufficiently develop. Accordingly, the NaOH aqueous solution preferably has a concentration of 1 mol/L to 8 mol/L.

[0059] In a hydrogen gas producing device 200 of the present invention, to achieve the second object (to properly suppress a reaction between silicon particles and an alkaline aqueous solution), a silicon material A for hydrogen gas production or a silicon material B for hydrogen gas production produced according to the flow chart of FIG. 1 is used. The silicon material A for hydrogen gas production or the silicon material B for hydrogen gas production contains a certain oil content or a reaction inhibitor. This enables to suppress silicon particles and an alkaline aqueous solution to abruptly react. However, the oil content and the reaction inhibitor are not as great in amount as the amount that inhibits the reaction, resulting in generation of hydrogen gas exactly the same as a theoretical value. In the hydrogen gas producing device 200 of the present invention, since the silicon particles and the alkaline aqueous solution 204 gradually react, the reaction between the silicon particles and the alkaline aqueous solution 204 continues over a long

period of time. This makes it possible to constantly produce hydrogen gas.

[0060] The reason why pressure fluctuations in the reaction chamber in a hydrogen gas producing apparatus (FIG. 6) in

5 JP 2001-213609 A is that silicon sludge and an alkaline aqueous solution is intermittently injected. In the hydrogen gas producing apparatus disclosed in JP 2001-213609 A, the silicon sludge rapidly reacts with the alkaline aqueous solution. This makes it impossible to
10 continuously inject the silicon sludge and the alkaline aqueous solution, so that the silicon sludge and the alkaline aqueous solution are intermittently injected.

[0061] In the hydrogen gas producing device 200 of the present invention, to achieve the third object (pressure

15 fluctuations of the reaction chamber), the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production are continuously injected as a general rule (Since the silicon material 202 for hydrogen gas production to be used in the hydrogen gas producing device 200 of the
20 present invention does not rapidly react, it is possible to continuously inject the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production).

Continuous injection of the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production

25 makes it possible to stably and continuously obtain hydrogen gas. The injection rate of the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas

production is, however, not limited to be constant. The reason is that there is a possibility of the generation speed of hydrogen gas being not constant even when the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production are injected at a constant rate. [0062] In the hydrogen gas producing device 200 of the present invention, the injection rate of the alkaline aqueous solution 204 is controlled so that the mixed liquid 208 in the reaction chamber 201 may have a predetermined value of concentration (In the case of using a NaOH aqueous solution, 1 mol/L to 8 mol/L, preferably 3 mol/L to 4 mol/L). The injection rate of the alkaline aqueous solution 204 is feed-back controlled by calculating a change rate (time differential) of the alkali concentration together with measuring the alkali concentration so that the alkali concentration of the mixed liquid 208 may be a predetermined value. The alkali concentration of the mixed liquid 208 is measured by titrating a liquid sampled from a sampling terminal 211 for neutralization titration by a neutralization apparatus (not shown). The injection of the alkaline aqueous solution 204 may be stopped depending on controlling results.

[0063] $\text{SiO}_2(\text{OH})_2^{2-}$ in the reaction formula (4) is stored in the reaction chamber 201. This hydrate ($\text{SiO}_2(\text{OH})_2^{2-}$) is so-called water glass and has buffer action of pH. As a result, it is impossible to exactly know the alkali concentration of the mixed liquid 208 even when the pH of

the mixed liquid 208 is measured. Accordingly, the alkali concentration is measured by titrating the sample of the mixed liquid 208.

[0064] Further, the injection rate of the silicon material
5 202 for hydrogen gas production is controlled so that the temperature of the mixed liquid 208 in the reaction chamber 201 may be a predetermined value (50°C to 90°C, preferably 60°C to 80°C). The injection rate of the silicon material 202 for hydrogen gas production is feed-back controlled by
10 calculating a change rate (time differential) of the temperature together with measuring the temperature with a thermometer 209 so that the temperature of the mixed liquid 208 may be a predetermined value. There is a possibility that the injection of the alkaline aqueous solution 204 and
15 the silicon material 202 for hydrogen gas production may be stopped depending on controlling results. Further, there is a possibility of the mixed liquid 208 being cooled down by a cooler 210.

[0065] Reaction heat raises the temperature of the mixed
20 liquid 208. On the other hand, injection of the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production lowers the temperature of the mixed liquid 208 (That is because the temperature of the alkaline aqueous solution 204 and the temperature of the silicon
25 material 202 for hydrogen gas production are lower than the temperature of the mixed liquid 208). To suppress the temperature rise of the mixed liquid 208 caused by the

reaction heat by the injection of the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production, it is preferable to keep the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production before injection at about 20°C.

[0066] As mentioned above, it is possible to make the generation speed of hydrogen gas constant by controlling the injection rate of the alkaline aqueous solution 204 and the silicon material 202 for hydrogen gas production on the basis of the alkali concentration and the temperature of the mixed liquid 208. There is a possibility that injection of the silicon material 202 for hydrogen gas production may be stopped depending on controlling results.

[0067] In a conventional hydrogen gas producing apparatus, hydrogen gas generated in the reaction chamber was filled in a condenser. In the hydrogen gas producing device 200 of the present invention, a scrubber 214 is being provided between the reaction chamber 201 and a condenser 213 to achieve the fourth object (clogging caused by the alkaline aqueous solution mist and silicon particles). Hydrogen gas generated in the reaction chamber 201 is filled in the scrubber 214. It is possible to remove alkaline aqueous solution mist, metasilicate hydrate, and silicon particles that disperse from the reaction chamber 201 by the scrubber 214 before entering the condenser 213.

[0068] While the scrubber 214 is not shown, a number of chemical resistance fillers each having a high clearance

ratio (typically a basket made from polyethylene) are filled in a chemical resistance (typically made from chloroethylene) treatment container. A treatment liquid (water or acid solution, preferably dilute sulfuric acid in the case of the present invention) is sprinkled over the entire fillers from an upper part of the treatment container to flow gas to be treated from a lower part of the treatment container. In the hydrogen gas producing device 200 of the present invention, gas to be treated (gas P) includes hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles. Gas P reacts with the treatment liquid while passing through a clearance of each of the fillers. The alkaline aqueous solution mist is neutralized or dissolved by the treatment liquid. The treatment liquid washes away the metasilicate hydrate mist and the silicon particles. As a result, gas Q that has passed through the scrubber 214 includes hydrogen gas and steam. On the other hand, the gas Q does not contain alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles. Since this makes it possible to obtain gas Q (hydrogen gas and steam), it is possible to remove clogging of the condenser 213.

[0069] Since hydrogen gas is mixed with steam in the gas Q that has passed through the scrubber 214, steam is removed via the condenser 213. In the condenser 213, moisture is typically removed by cooling the gas Q and condensing steam

by use of cooling water. Hydrogen gas that has been treated by the condenser 213 practically contains no moisture. The temperature of the dew point in the condenser 213 is determined in accordance with

5 specifications of a supplier of hydrogen gas.

[0070] A back pressure regulator 215 is installed at an outlet of the condenser to regulate pressure from the reaction chamber 201 to the condenser 213. Pressure in the reaction chamber 201 is measured by a pressure gauge 212.

10 The regulated pressure is preferably 0.05 MPa to 0.5 MPa, more preferably 0.05 MPa to 0.15 MPa. When hydrogen gas is generated more than the regulated pressure, the hydrogen gas is delivered to a compressor 216 and is compressed under pressure to be stored in a cylinder 217. While

15 pressurizing in the compressor 216 is based on the standards of the cylinder 217, in the case of a hydrogen station for fuel cell vehicles (FCV), the pressure is 35 MPa or 70 MPa.

[0071] In the hydrogen gas producing device 200 of the

20 present invention, hydrogen gas treated by the condenser 213 has high purity (typically 99.9%), so that it is possible to use as it is depending on the intended use. In the case where hydrogen gas is used as such intended use, hydrogen gas treated by the condenser 213 is filled in the

25 cylinder 217 through the compressor 216, resulting in hydrogen gas as a product.

[0072] When hydrogen gas with higher purity is needed,

hydrogen gas is treated by passing through a hydrogen gas refiner 218. The hydrogen gas refiner 218 is typically a palladium alloy layer. Since the palladium alloy layer does not allow gas except for hydrogen gas to pass through
 5 (for instance, nitrogen gas, oxygen gas, noble gas), hydrogen gas that has passed through the palladium alloy layer becomes high-purity hydrogen gas. The high-purity hydrogen gas is pressurized by the compressor 216 to be high-pressure high-purity hydrogen gas and is filled in the
 10 cylinder 217. As a result, high-purity hydrogen gas is produced as a product.

[0073] $\text{SiO}_2 (\text{OH})_2^{2-}$ in the reaction formula (4) is stored in the reaction chamber 201. H_2O is deducted from this to become SiO_3^{2-} , which is metasilicate ions. This hydrate
 15 $(\text{SiO}_2 (\text{OH})_2^{2-})$ is so-called water glass. Water glass indicates strong alkaline by hydrolysis and has buffer action of pH. It is needed to remove the hydrate $(\text{SiO}_2 (\text{OH})_2^{2-})$ when a certain amount of the hydrate $(\text{SiO}_2 (\text{OH})_2^{2-})$ is stored in the reaction chamber 201. It is possible to
 20 simultaneously measure the concentration of the hydrate $(\text{SiO}_2 (\text{OH})_2^{2-})$ at the time of the aforementioned neutralization titration. It should be determined to what extent of the concentration of the hydrate $(\text{SiO}_2 (\text{OH})_2^{2-})$ hydrogen gas production should be continued in view of
 25 overall hydrogen gas production costs.

[0074] When the generation of hydrogen gas is judged to be lesser by the storing of the hydrate $(\text{SiO}_2 (\text{OH})_2^{2-})$ in view

of a cumulative injection amount of the silicon material 202 for hydrogen gas production and a cumulative generation amount of hydrogen gas, the injection of the silicon material 202 for hydrogen gas generation is stopped. After
5 confirming that all of the silicon material 202 for hydrogen gas production in the reaction chamber 201 reacts, the mixed liquid 208 including the hydrate ($\text{SiO}_2 (\text{OH})_2^{2-}$) is taken out of the reaction chamber 201 to clean the reaction chamber 201.

10

EXAMPLES

[0075] [Production of silicon material A for hydrogen gas production]

A mixed liquid of 90 weight % of water and 10 weight %
15 of propylene glycol was used as a coolant. Using this coolant, silicon ingots were cut by a multi-wire saw to produce silicon wafers. Cut waste included in a waste coolant was each a silicon particle having an average particle size of 1 μm . The waste coolant was subject to
20 centrifugal separation by a centrifugal separator A (2,500 rpm).

[0076] Next, silicon waste was subject to centrifugal separation by a centrifugal separator B (3,000 rpm) to obtain a solid A. Further, the solid A was heated by a
25 drying furnace at 105°C to obtain a solid B. The composition of the solid B was 97 weight % of silicon particles and 3 weight % of propylene glycol. As mentioned

above, it is possible to adjust an amount of oil content contained in the solid B to a desired value (any value in a range of 0.1 weight % to 10 weight % of the silicon particles) by adjusting an amount of oil content contained in the coolant 103 which is a starting material and the number of rotations of the centrifugal separator B.

[0077] FIG. 3 shows effects of oil content or a reaction inhibitor in a hydrogen gas production experiment. A lateral axis indicates time and a longitudinal axis

indicates the amount of hydrogen gas generated (accumulation) in an upper graph in FIG. 3. A lateral axis indicates time and a longitudinal axis indicates the temperature of a mixed liquid of silicon particles and an alkaline aqueous solution in a lower graph in FIG. 3. In the upper and lower graphs in FIG. 3, a curve A is a graph in the case where sludge with pure (without including oil content or a reaction inhibitor) silicon particles (1.2 g) and 17 g of pure water mixed is injected by an injector for 5 seconds in a reactor chamber (2 liters) in which a 3.4 mol/L of NaOH aqueous solution (1.2 liters). A solid C120 (aggregates of silicon particles), in which oil content is removed through a high-temperature furnace 118 shown in the flow chart of FIG. 1, was smashed to be used as silicon particles which do not include oil content or a reaction inhibitor.

[0078] In the upper and lower graphs in FIG. 3, a curve B is a graph in the case where a silicon material for

hydrogen gas production obtained by mixing silicon particles (1.2 g) containing 3 weight % of oil content and 17 g of pure water is injected into a reaction chamber (2 liters) including 3.4 mol/L of a NaOH aqueous solution (1.2
5 liters) for 5 seconds by an injector. The silicon material for hydrogen gas production containing 3 weight % of oil content falls under the sludge A117 in the flow chart of FIG. 1. The oil content is propylene glycol.

[0079] In the case of sludge (curve A) obtained by mixing

10 pure silicon particles and water, a reaction between the silicon particles and the NaOH aqueous solution explosively occurred immediately after the mixture and ended for 43 seconds. No generation of hydrogen gas can be seen 43 seconds onwards. The maximum generation speed of hydrogen
15 gas (slope of the curve A) was 11 liters/minute. The reaction explosively generating hydrogen gas in such a manner is uncontrollable and it is difficult to constantly obtain hydrogen gas. As a result, it is impossible to use silicon particles in which oil content or a reaction
20 inhibitor is not mixed even when producing sludge by mixing the silicon particles with water.

[0080] In the case of a silicon material for hydrogen gas production (curve B) containing 3 weight % of oil content, a reaction between silicon particles and a NaOH aqueous
25 solution is much more slower than the sludge (curve A) composed of pure silicon particles and water. As can be seen from the upper graph in FIG. 3, the cumulative

hydrogen gas amount of hydrogen gas obtained from the sludge (curve A) composed of pure silicon particles and water is equal to the cumulative hydrogen gas amount obtained from the silicon material for hydrogen gas production (curve B) containing 3 weight % of oil content. That is, while the silicon material for hydrogen gas production (curve B) containing 3 weight % of oil content has slow reaction, hydrogen gas is generated exactly the same as a theoretical value. While reaction time of the sludge (curve A) composed of pure silicon particles and water is about 30 seconds, reaction time of the silicon material for hydrogen gas production (curve B) containing 3 weight % of oil content is about 800 seconds. Accordingly, the reaction speed becomes about $1/27$ by containing 3 weight % of oil content. Such a gradual reaction is controllable.

[0081] With reference to temperature changes of the mixed liquid of silicon particles and an alkaline aqueous solution in the lower graph in FIG. 3, in the case of pure silicon particles (curve A), although the temperature of the mixed liquid dropped by 0.7°C immediately after injecting the silicon particles, the temperature of the mixed liquid rose soon by 2.7°C . The reason why the temperature dropped by 0.7°C at first was that sludge was at room temperature. The reason why the temperature rose by 2.7°C was that the mixed liquid was heated by reaction heat. In the case of silicon particles (curve B) with 3

weight % of oil content mixed, the temperature changes of the mixed liquid are within 1°C. This is because reaction heat per hour has a small amount of generation due to gradual reaction.

5 [0082] FIG. 4 (Example 1) is a graph indicating hydrogen gas generation amount and the temperature of a mixed liquid at the time when continuously injecting a silicon material A for hydrogen gas production obtained by the mixture of silicon particles, 3 weight % of oil content (propylene
10 glycol) contained in the silicon particles, and pure water which is three times as heavy as the silicon particles into a reaction chamber (2 liters) including 3.4 mol/L of a NaOH aqueous solution for 221 seconds with a mono pump. A lateral axis indicates time, a left longitudinal axis
15 indicates hydrogen gas amount (accumulation), and a right longitudinal axis indicates temperatures. The injection amount of silicon particles is 4.8 g/minute.

[0083] A cumulative hydrogen gas amount increased approximately in proportion to time and the maximum
20 hydrogen gas generation rate was 3 liters/minute during the injection of the silicon material A for hydrogen gas production. Although the injection of the silicon material A for hydrogen gas production stopped for 221 seconds, hydrogen gas was continuously generated afterward and the
25 generation of hydrogen gas has not yet finished over 1,500 seconds. The hydrogen gas amount generated after the injection of the silicon material A for hydrogen gas

production became three times as great as the hydrogen gas amount generated during the injection of the silicon material A for hydrogen gas production.

[0084] The temperature of the mixed liquid also rose

5 approximately in proportion to time during the injection of the silicon material A for hydrogen gas production.

Although the injection of the silicon material A for hydrogen gas production stopped after 221 seconds, the temperature subsequently increased at a similar slope and
10 increased by 8.6°C and then slowly decreased. However, the temperature has not yet returned to the state before reaction after 1,500 seconds. This is because the injection amount of the silicon material A for hydrogen gas production is too great compared with the capacity of the
15 reaction chamber. As mentioned above, even when oil content is contained, it is difficult to continuously and stably produce hydrogen gas when the injection amount of the silicon material A for hydrogen gas production is too great compared with the capacity of the reaction chamber.
20 Explosive reaction is, however, inhibited because oil content is contained.

[0085] FIG. 5 (Example 2) is a graph indicating hydrogen gas generation amount and temperature changes of a mixed liquid at the time when continuously injecting a silicon

25 material A for hydrogen gas production obtained by the mixture of silicon particles, 3 weight % of oil content (propylene glycol) contained in the silicon particles, and

pure water which is three times as heavy as the silicon particles into a reaction chamber (2 liters) including 3.4 mol/L of a NaOH aqueous solution for 857 seconds with a mono pump. A lateral axis indicates time, a left

5 longitudinal axis indicates hydrogen gas amount (accumulation), and a right longitudinal axis indicates temperatures. The injection amount of silicon particles is 1.3 g/minute.

[0086] The hydrogen gas generation amount (accumulation)
10 increase approximately in proportion to time during the injection of the silicon material A for hydrogen gas production and the generation speed (slope of the graph) becomes gradual after the injection of the silicon material A for hydrogen gas production stops. The maximum hydrogen
15 gas generation speed during the injection of the silicon material A for hydrogen gas production was 1.2 liter/minute. The hydrogen gas amount generated after the injection of the silicon material A for hydrogen gas production is about one half of the hydrogen gas amount generated during the
20 injection of sludge.

[0087] The temperature of the mixed liquid increased approximately in proportion to time during the injection of the silicon material A for hydrogen gas production. And the temperature of the mixed liquid gradually decreased
25 when the injection of the silicon material A for hydrogen gas production stopped. As a result, the temperature of the mixed liquid returned to the temperature before the

reaction in about 1,400 seconds after the injection of the silicon material A for hydrogen gas production started. The maximum temperature rise was only 2.2°C. Temperature rise of the mixed liquid is caused by reaction heat, not caused by heating by a heater. The graph of temperature changes indicates that the injection amount of the silicon material A for hydrogen gas production is practically suitable for the capacity of the reaction chamber. In such a manner, it is possible to continuously and stably produce hydrogen gas when the injection amount of the silicon material A for hydrogen gas production is suitable for the capacity of the reaction chamber.

[0088] The aforementioned description is with reference to silicon materials for hydrogen gas production produced from silicon waste generated by a multi-wire saw. However, silicon waste generated by dicer cutting or lapping or the like may also be used as silicon materials for hydrogen gas production by appropriately changing the flow chart in FIG. 1. Oil content is not contained in dicer cutting because pure water is used instead of a coolant. Consequently, the silicon waste generated by dicer cutting is centrifuged to be dried and then an appropriate reaction inhibitor is mixed to produce a silicon material for hydrogen gas production. A coolant (including oil content) and abrasive grains are mixed in silicon waste in lapping, so that it is possible to produce a silicon material for hydrogen gas production in such treatment as treatment of the silicon

waste generated by a multi-wire saw after removing the abrasive grains.

[0089] A laser diffraction/scattering-type grain size distribution measuring apparatus (Horiba, Ltd.) employing
5 measuring principles of the Mie scattering theory was used for measuring an average grain size of silicon particles.

INDUSTRIAL APPLICABILITY

[0090] A large amount of silicon waste is generated in a
10 production process of silicon wafers. While silicon waste has conventionally been abandoned, a cost load and an environmental load caused by waste are not negligible. According to the present invention, it becomes possible to constantly obtain hydrogen gas from silicon waste, which
15 makes it possible to utilize silicon waste which has been abandoned.

CLAIMS

1. A method for producing hydrogen gas, comprising the steps of:

- 5 preparing a silicon material A for hydrogen gas production, the silicon material A for hydrogen gas production comprising: silicon particles; oil content derived from a coolant, the oil content being 0.1 weight % to 10 weight % of the silicon particles; and water;
- 10 preparing an alkaline aqueous solution;
- supplying the silicon material A for hydrogen gas production and the alkaline aqueous solution in a reaction chamber;
- injecting the silicon material A for hydrogen gas
- 15 production into the reaction chamber while feed-back controlling an injection rate thereof based on a temperature of a mixed liquid of the silicon material A for hydrogen gas production and the alkaline aqueous solution in the reaction chamber and a time change rate of the
- 20 temperature;
- injecting the alkaline aqueous solution into the reaction chamber while feed-back controlling an injection rate thereof by measuring alkali concentration of the mixed liquid and calculating a time change rate of the alkali
- 25 concentration;
- maintaining the mixed liquid in the reaction chamber at a predetermine temperature;

treating gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles by a scrubber, which has been taken out of the reaction chamber, to remove the alkaline aqueous solution mist, the metasilicate hydrate mist, and the silicon particles from the gas P; and

treating gas Q including the hydrogen gas and the steam which is obtained by treating the gas P by the scrubber to remove the steam from the gas Q by treating with a condenser.

2. The method for producing hydrogen gas according to claim 1, wherein the oil content is any one of 1-butanol, 2-methyl-1-propanol, 2-ethyl-1-hexanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-propanediol, 1,4-butanediol, 1,2-butanediol, 1,3-butanediol and 1,5-pentanediol or a mixture of at least two selected therefrom.

3. The method for producing hydrogen gas according to claim 1 or claim 2, wherein the silicon particles each have an average particle size of 0.1 μm to 30 μm .

4. The method for producing hydrogen gas according to any one of claims 1 to 3, wherein the water is one time to ten times as heavy as the silicon particles.

5. A method for producing hydrogen gas, comprising the steps of:

preparing a silicon material B for hydrogen gas production comprising: silicon particles; any one of formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid, hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl alcohol, polyacrylamide and polyethylene glycol in a range of 0.1 weight % to 10 weight % or a mixture of at least two selected therefrom, and water;

preparing an alkaline aqueous solution;

supplying the reaction chamber with the silicon material B and the alkaline aqueous solution;

injecting the silicon material B for hydrogen gas production into the reaction chamber while feed-back controlling an injection rate thereof based on a temperature of a mixed liquid of the silicon material B for hydrogen gas production and the alkaline aqueous solution in the reaction chamber and a time change rate of the temperature;

injecting the alkaline aqueous solution into the reaction chamber while feed-back controlling an injection

rate thereof by calculating a time change rate of the alkali concentration together with measuring the alkali concentration;

maintaining a mixed liquid in the reaction chamber at a
5 predetermine temperature;

treating gas P including hydrogen gas, steam, alkaline aqueous solution mist, metasilicate hydrate mist, and silicon particles by a scrubber, which has been taken out of the reaction chamber, to remove the alkaline aqueous
10 solution mist, the metasilicate hydrate mist, and the silicon particles from the gas P; and

treating gas Q including the hydrogen gas and the steam which is obtained by treating the gas P by the scrubber to remove the steam from the gas Q by treating with a
15 condenser.

6. The method for producing hydrogen gas according to claim 5, wherein the silicon particles each have an average particle size of 0.1 μm to 30 μm .

20

7. The method for producing hydrogen gas according to claim 5 or claim 6, wherein the water is one time to ten times as heavy as the silicon particles.

8. The method for producing hydrogen gas according to
25 any one of claims 1 to 7, wherein the alkaline aqueous solution is one of a NaOH aqueous solution and a KOH aqueous solution.

9. The method for producing hydrogen gas according to claim 8, wherein the alkaline aqueous solution is one of the NaOH aqueous solution and the KOH aqueous solution
5 which has a concentration of 1 mol/L to 8 mol/L.

10. The method for producing hydrogen gas according to any one of claims 1 to 9, wherein the predetermined temperature is 50°C to 90°C.

10

11. A hydrogen gas producing device, comprising in descending order:

a hermetically sealed reaction chamber;

means for supplying the reaction chamber with a

15 silicon material A for hydrogen gas production, the silicon material A for hydrogen gas production comprising: silicon particles; oil content derived from a coolant, the oil content being 0.1 weight % to 10 weight % of the silicon particles; and water;

20 means for supplying the reaction chamber with an alkaline aqueous solution;

means for feed-back controlling an injection rate of the silicon material A for hydrogen gas production by measuring a temperature of a mixed liquid of the silicon

25 material A for hydrogen gas production and the alkaline aqueous solution and calculating a time change rate of the

temperature so that the temperature of the mixed liquid in the reaction chamber may be a predetermined temperature;

means for feed-back controlling an injection rate of the alkaline aqueous solution by calculating a time change
5 rate of alkali concentration together with measuring the alkali concentration of the mixed liquid so that the alkali concentration of the mixed liquid may be a predetermined value;

means for uniformly mixing the alkaline aqueous
10 solution with the silicon material A for hydrogen gas production provided in the reaction chamber;

a thermometer attached to the reaction chamber;

a heater attached to the reaction chamber;

a cooler attached to the reaction chamber;

15 a scrubber provided at an outlet of hydrogen gas in the reaction chamber;

a condenser provided at an outlet of hydrogen gas in the reaction chamber; and

a regulator provided at an outlet of hydrogen gas in
20 the reaction chamber.

12. The hydrogen gas producing device according to claim 11, wherein the oil content derived from the coolant is any one of 1-butanol, 2-methyl-1-propanol, 2-ethyl-1-
25 hexanol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, glycerin, 1,2-propanediol, 1,4-

butanediol, 1,2-butanediol, 1,3-butanediol and 1,5-pentanediol or a mixture of at least two selected therefrom.

13. The hydrogen gas producing device according to
5 claim 11 or claim 12, wherein the silicon particles each have an average particle size of 0.1 μm to 30 μm .

14. The hydrogen gas producing device according to any
one of claims 11 to 13, wherein the water is one time to
10 ten times as heavy as the silicon particles.

15. The hydrogen gas producing device according to
claims 11 to 14, wherein the scrubber removes the alkaline
aqueous solution mist, the metasilicate hydrate mist, and
15 the silicon particles from the reaction chamber.

16. The hydrogen gas producing device according to
claims 11 to 15, wherein the means for supplying the
silicon material A for hydrogen gas production is one of a
20 mono pump and a gear pump.

17. A hydrogen gas producing device, comprising in
descending order:

a hermetically sealed reaction chamber;
25 means for supplying the reaction chamber with a
silicon material B for hydrogen gas production, the silicon
material B for hydrogen gas production comprising: silicon

particles; any one of formic acid, lactic acid, acetic acid, propane acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tetradecanoic acid,

5 hexadecanoic acid, heptadecanoic acid, acrylic acid, oleic acid, malic acid, citric acid, oxalic acid, maleic acid, fumaric acid, vinyl pyrrolidone, polyvinyl pyrrolidone, sodium polyacrylate, polyethylene oxide, polyethylene imide, polyvinyl alcohol, polyacrylamide and polyethylene glycol
10 in a range of 0.1 weight % to 10 weight % or a mixture of at least two selected therefrom, and water;

means for supplying the reaction chamber with an alkaline aqueous solution;

means for feed-back controlling an injection rate of
15 the silicon material B for hydrogen gas production by measuring a temperature of a mixed liquid of the silicon material B for hydrogen gas production and the alkaline aqueous solution and calculating a time change rate of the temperature so that the temperature of the mixed liquid in
20 the reaction chamber may be a predetermined temperature;

means for feed-back controlling an injection rate of the alkaline aqueous solution by measuring alkali concentration of the mixed liquid and calculating a time change rate of the alkali concentration so that the alkali
25 concentration of the mixed liquid may be a predetermined value;

means for uniformly mixing the alkaline aqueous solution with the silicon material B for hydrogen gas production provided in the reaction chamber;

a thermometer attached to the reaction chamber;

5 a heater attached to the reaction chamber;

a cooler attached to the reaction chamber;

a scrubber provided at an outlet of hydrogen gas in the reaction chamber;

10 a condenser provided at an outlet of hydrogen gas in the reaction chamber; and

a regulator provided at an outlet of hydrogen gas in the reaction chamber.

18. The hydrogen gas producing device according to
15 claim 17, wherein the silicon particles each have an average particle size of 0.1 μm to 30 μm .

19. The hydrogen gas producing device according to claim 17 or claim 18, wherein the water is one time to ten
20 times as heavy as the silicon particles.

20. The hydrogen gas producing device according to any one of claims 17 to 19, wherein the scrubber removes alkaline aqueous mist, metasilicate hydrate mist, and silicon particles from the reaction chamber.

25

21. The hydrogen gas producing device according to any one of claims 17 to 20, wherein the means for supplying the

silicon material B for hydrogen gas production is one of a mono pump and a gear pump.