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參展科別 **化學**

作品名稱 **Development of new manufacturing method to generate hydrogen energy by using waste silicon ~ Reuse of waste of the semiconductor industry for hydrogen community ~**

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1. Introduction

In Japan the energy self-efficiency is very low: only 6%. Hydrogen (H_2) has been expected as a new and alternative energy source to imported one, such as petroleum resources. Now hydrogen energy comes into the practical use in the field of the fuel cell. Hydrogen must be extracted from other sources, for example, water, fossil fuel, and so on. Hydrogen is obtained from water by using electronic or thermal or photo energy in most cases, whereas it is well-known that hydrogen is given by the oxidation reaction of silicon in alkaline aqueous solution:

$$Si + 2OH^- + H_2O \rightarrow SiO_3^{2-} + 2H_2$$

Free silicon (Si) is not only used in the steel refining, aluminum-casting in the field of fine chemical industries but also is used as a material in semiconductor electronics. However, a lot of used silicon is thrown away as a waste, being not reused and recycled.

In this study we try to apply a waste silicon to obtain hydrogen based on the above reaction. The purpose of the study is to develop a safe and convenient manufacturing method to generate hydrogen for an energy source of the fuel cell.

2. Experiments for hydrogen genaration

2-1. Reactivity of three kinds of alkaline solution with silicon

To examine hydrogen genearation, we made the device which has a valve and a gas collecting bag as shown in Fig. 1. Firstly silicon powder was put into the vessel and then three kinds of alkaline solution (three different concentrations of NaOH solutions, ammonia water or $NaHCO_3$ solution) were added into it, respectively. The results of reaction of silicon powder with alkaline solutions are shown in Table 1. In the table, "Reactiviy" is defined as the production rate of hydrogen gas and "Hydrogen generation" means whether hydrogen was generated or not when alkaine solution is added.

Table 1 Reaction of silicon powder with alkaline solutions

	1 mol/L NaOH	0.1 mol/L NaOH	0.01 mol/L NaOH	1 mol/L NH_3 water	1 mol/L $NaHCO_3$
Reactivity	◎	○	○	△	×
Hydrogen generation	○	○	○	○	×

After NaOH solution was added, small bubbles appeared from the surface of silicon powder in about five minutes. The lower the NaOH concentration, the longer the delay time to generate bubbles and also the slower to generate bubbles. In comparison, when ammonia water was added, we found bubbles after about twenty minutes and its amount was very little. On the other hand, when $NaHCO_3$ solution was added, we could hardly find any bubbles. By using a commercial gas detecting tube, the gas generated was checked to be hydrogen.

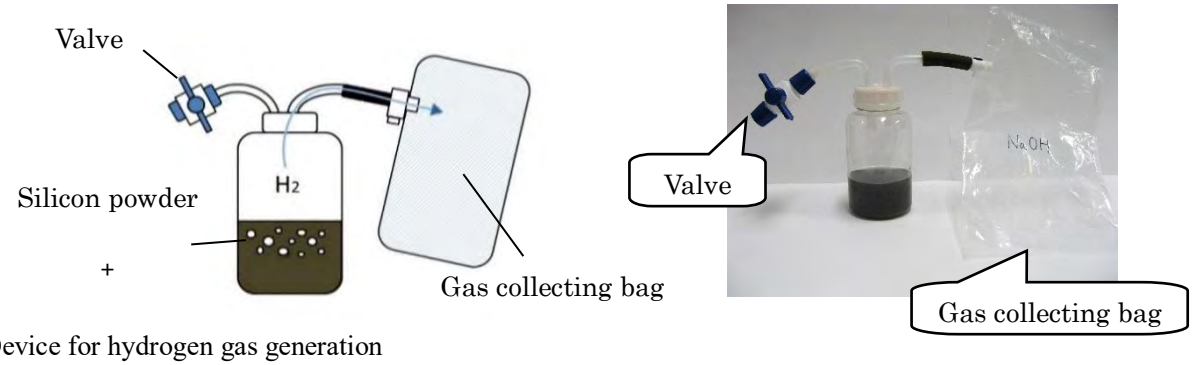


Fig.1 Device for hydrogen gas generation

We confirmed that all the gas generated in these experiments was hydrogen. Considering the reactivity, we found that 1 mol/L NaOH solution was the most effective for hydrogen generation.

2-2. Examination of the amount of hydrogen generated

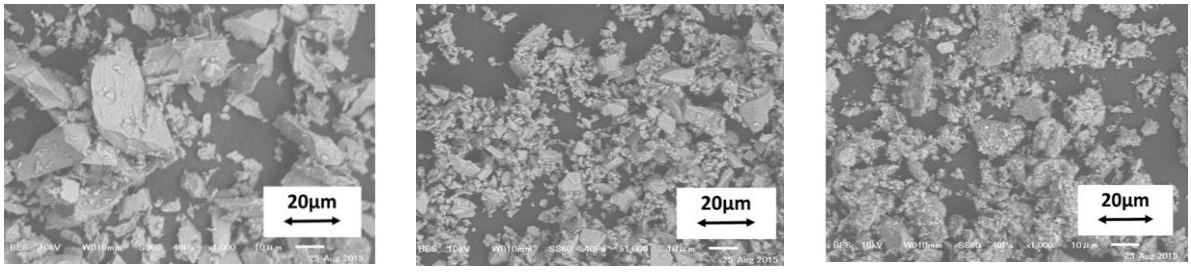
When NaOH solution is added to silicon powder, the following reaction is occurred.

$$Si + 2NaOH + H_2O \rightarrow Na_2SiO_3 + 2H_2 \quad (1)$$

0.31 g of silicon was reacted with NaOH solution under the room temperature (28 ℃). the amount of the hydrogen gas collected in a measuring cylinder by water displacement method was 540 ml hydrogen. From equation (1), theoretical amount of hydrogen gas is calculated to be 545 ml in this condition. This indicated that almost 100% hydrogen was obtained from the silicon powder.

2-3. Effect of silicon size on hydrogen generation

We examined the reactivity of NaOH solution with three kinds of silicon powders. Fig. 2 showed the electron microscope images of silicon powders. The gas generation speed was faster for small particles of silicon and waste silicon powder. On the other hand, that for coarse particles of silicon was slower. Otherwise, we found that the same amount of hydrogen was generated for all kinds of silicon powders. The reaction speed became faster when the surface area is larger. In addition, the amount of hydrogen gas was not affected by particle size within 30 μm of silicon powder. Based on these results, we used small particles of silicon powder in Fig. 2(b) in the following experiments.



(a)Coarse particles of silicon (b)Small particles of silicon (c)Waste silicon powder

Fig.2 Electron microscope images of silicon powders

3. Experiments aiming for practical use

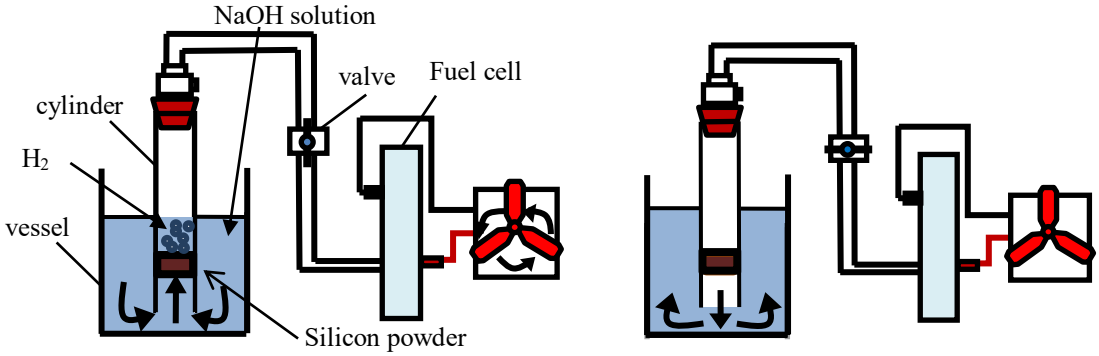
3-1. Production of hydrogen generating device

In general, a large amount of hydrogen gas is dangerous to store because it explodes easily. Thus it is favorable to generate hydrogen only when we need. Then, we made the hydrogen generation device in which uses a principle of the Kipp's gas generator. The schematic view of the device was showed in Fig. 3. The picture of the device we made was shown in Fig. 4.

The Kipp's gas generator (the left apparatus of Figs. 3(a) and (b)) consists of a tall cylinder and a vessel. Silicon powder tip was attached to the lower part of the cylinder and NaOH solution was poured into the vessel. The hydrogen gas generated by silicon and NaOH solution can be supplied to the fuel cell through the valve.

When the valve is open (Fig. 3 (a)), NaOH solution comes into the cylinder by getting lowered pressure inside the cylinder. And hydrogen gas is generated by reacting silicon powder with NaOH solution and comes into the fuel cell. As a result, the fuel cell operates and the propeller begins to turn around.

When the valve is closed (Fig. 3 (b)), NaOH solution is pushed out by higher pressure inside the cylinder because of hydrogen gas pressure. As a result that NaOH solution does not come into contact with silicon powder, the generation of hydrogen stops and the electricity is not generated.



(a) The condition of valve opening (b)The condition of valve closing

Fig.3 Hydrogen generation device by using the Kipp's gas generator.

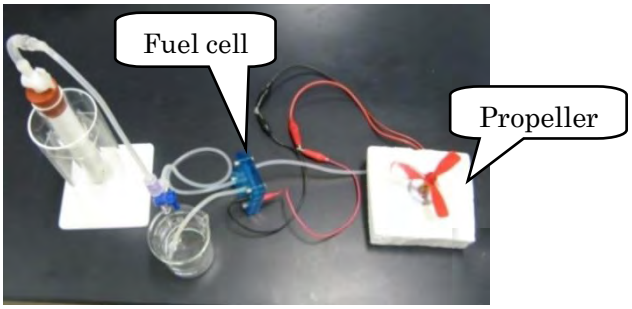


Fig. 4 The picture of the device manufactured.

By sealing the fuel cell, the valve can be unnecessary for controlling the pressure inside the cylinder. When the switch of electrical load (ex. propeller) is off, hydrogen does not consume by fuel cell, which enables the pressure inside the cylinder keep high. In contrast when the switch is on, hydrogen consumes and the pressure inside the cylinder becomes low, then the level of NaOH solution in the cylinder goes up to the part of silicon. In other words, this generator can be controlled automatically. It is possible to generate hydrogen only when we need it by combining a fuel cell and this kind of generator.

Solar power generation is increasing attention as one of sustainable energy sources nowadays. However, this strongly depends on the weather and hours of daylight. Here, by combinig solar power generation and this hydrogen generation system, it can keep the amount of power generation constant all day automatically. We can put into practical use such as introducing the small-scale power generation system as an auxiliary power source and the reserve fuel of vehicles.

3-2. Improvement of the safety handling of alkaline solution

NaOH is a deleterious substance. We proposed a new method creating NaOH by reaction of calcium hydroxide and sodium carbonate according to equation (2).

$$Ca(OH)_2 + Na_2CO_3 \rightarrow \quad 2NaOH \quad + \quad CaCO_3 \qquad (2)$$

Both chemicals can be stored safely because they are not deleterious substances. From the reaction of calcium hydroxide (1.64 g) and sodium carbonate (2.34 g), water (50 ml) with silicon powder (0.31 g), 536 ml of hydrogen was generated, yeilding almost 100% hydrogen.

Fig.5 showed the continuous supplying system of hydrogen attaching the multiple connection. Using this system hydrogen gas was generated continuously by periodically changing the container including Silicon, $Ca(OH)_2$ and Na_2CO_3.

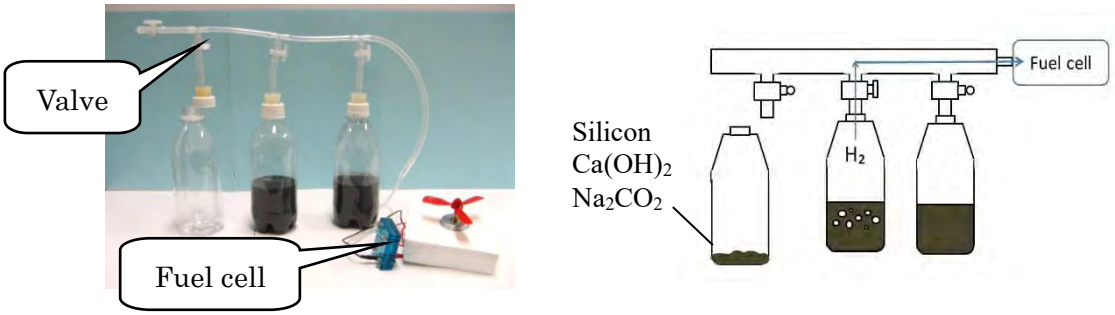


Fig. 5 the continuous supplying system of hydrogen

Also, we obtained the precipitate consisting of Na2SiO3 as a by-product. The precipitate was heat-treated at 1350 ℃ for 1 hour and cooled down rapidly, resulting in raw material of glass. This raw material can be used for making glass. The picture of the obtained raw material of glass was shown in Fig. 6.

Fig. 6 The picture of the obtained raw material of glass.

Finally, we proposed the view of application in the future for the practical use. The set of the system is composed of (1) hydrogen generation device described in 3-2, (2) some containers of calcium hydroxide, sodium carbonate, and silicon powder, and (3) the fuel cell. When you need the electric power, you combine the above components and set the system. Since amount of generated hydrogen is determined by the number of (2), you can get the necessary amount of electric energy continuously with controlling the number of (2). This system will be applied to the in-house power generation (depicted in Fig. 7, right). When the disaster occurs and the electric supply is stopped in the stricken area, you dispatch a rescue truck equipped with the system of above (1)-(3). (depicted in Fig. 7, left)

Fig. 7 The setting place of this system for application

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The study is focusing on the penetration of hydrogen using waste silicon. Hydrogen was successfully produced when Si was mixed with NaOH solution. Of is interesting to see that the reaction of calcium hydroxide and hydroxide. This reaction improved the safety of handling NaOH Solution.