Research Article

Hydrogen Production Using Reduced-Iron Nanoparticles by Laser Ablation in Liquids

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A recyclable energy cycle using a pulsed laser and base-metal nanoparticles is proposed. In this energy cycle, iron nanoparticles reduced from iron oxides by laser ablation in liquid are used for hydrogen generation. The laser energy can be stored in the base-metal nanoparticles as the difference between the chemical energies of iron oxide and iron. According to the results of an experiment on hydrogen production using the reduced iron nanoparticles, the reaction efficiency of the hydrogen generation at a temperature of 673 K was more than 94% for the ideal amount of generated hydrogen.

1. Introduction

It has been expected that the application of hydrogen, produced by using clean, renewable energy, such as solar power, will solve the problem of global warming and depletion of fossil fuels. Many researches on hydrogen production have been conducted around the world [1–6]. Among them, the researches on generating hydrogen on the basis of the reaction of a metal with water are particularly interesting for the following reason: the method used to produce the hydrogen is very simple and low cost. Magnesium [2, 3], aluminum [4], and iron [5, 6] have already been used to generate hydrogen. Iron has the advantage of high safety in regard to handling because it hardly reacts with water at low temperature when compared to magnesium and aluminum. In some researches, metal nanoparticles were used to generate hydrogen [6]. It is important to increase the surface area of the metal particles by "micronizing" the particles to improve the reaction efficiency of metals with water. Moreover, the generated metal oxides should return to metals by reducing to realize an energy cycle.

The metal oxides can be reduced to the metal and broken into nanoparticles by using pulsed-laser ablation in liquid [7–13]. This process consists of three steps: first, the metal oxide is heated to a high temperature in a short time by irradiating laser pulses onto a metal-oxide powder in the liquid. Second, after the laser pulse is irradiated, metal oxides are evaporated, and metals are atomized; the separated oxygen is rearranged as the outer shell of the metal particles. Third, after the metals are separated from their oxides near the irradiation point of the laser pulse, the metal atoms are aggregated by cooling, and nanoparticles are produced rapidly. As physical mechanisms, namely, the ablation mechanism of the metal oxide in the liquid, coulomb explosions [14, 15] and thermal ablation have been proposed. With this pulsed-laser ablation in liquid, high reduction efficiency is obtained because the liquid also works as a coolant. Recombination between oxygen and metal particles is prevented because liquid cools the generated metal particles rapidly. Furthermore, it has the advantage that it can create nanoparticles with low cost easily because the produced particles can be collected easily.

As shown in Figure 1, an energy cycle produced by using a pulsed laser and base-metal nanoparticles has been proposed [16]. In general, the metal nanoparticles generated by pulsed-laser ablation in liquid have been applied only to thin-film coatings owing to the high cost of the laser oscillator. As shown in Figure 2, many kinds of solar-pumped lasers have
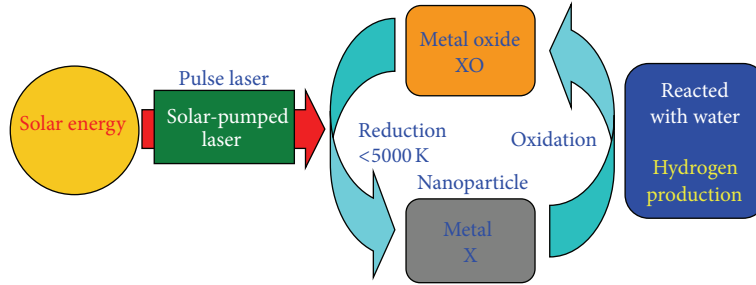
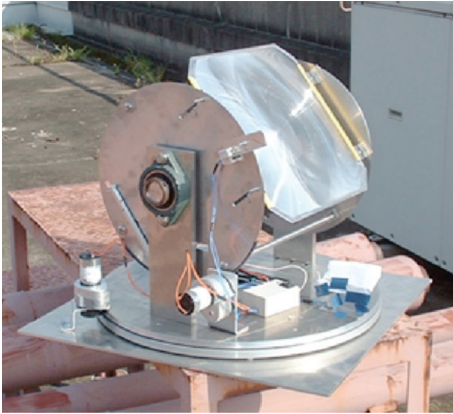Figure 1: Proposed energy cycle using solar energy.


Figure 2: Small-scale solar-pumped laser.

been developed [16–18]. They can directly convert from incoherent solar light to laser light. And they have an advantage in terms of consuming almost only solar power when generating a laser beam. Now, optical-optical conversion efficiency of solar-pumped lasers has been improved to almost 60% (i.e., from solar light to laser light) by improvements in optical technology [18]. Moreover, these lasers can generate laser pulses with high energy and high peak intensity. Accordingly, they can be used for reducing metal oxide and fabricating metal nanoparticles in our proposed energy cycle. The production of hydrogen by using reduced metal powder with nanometer-order diameters by continuous wave (CW) or pulsed laser has not been reported until now except for our report. In this study, iron nanoparticles were synthesized by reduction by pulsed laser in liquids, and the reaction efficiency of producing hydrogen by reacting the fabricated metal nanoparticles with vaporized water was experimentally investigated.

2. Experimental Setup

2.1. Laser Ablation in Liquids. The required energy for reducing iron metal oxides is determined as follows. Fe_2O_3, Fe_3O_4, and FeO are generally known as "iron oxides." According to crystal structure, there are many types. The chemical formula for the reduction of Fe_2O_3 is given as

$$\frac{1}{2}Fe_2O_3\,(s) \longrightarrow Fe\,(s) + \frac{3}{4}O_2\,(g), \quad \Delta H = 412\,\text{kJ/mol.} \quad (1)$$
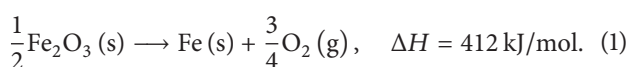
The chemical formula for the reduction of Fe_3O_4 is given as

$$\frac{1}{3}Fe_3O_4\,(s) \longrightarrow Fe\,(s) + \frac{2}{3}O_2\,(g), \quad \Delta H = 373\,\text{kJ/mol.} \quad (2)$$
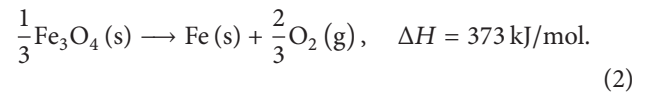
Here, ΔH is the enthalpy energy required for reducing unit mol Fe. The basic enthalpy energy required for reducing Fe_2O_3 to Fe_3O_4 is 39/2 kJ per unit mol of Fe_3O_4. These chemical reactions are all endothermic reactions. It is clear from (1) and (2) that the required chemical energy to separate the iron and oxygen atoms is large. As for the temperature required to change the Fe_2O_3 to Fe_3O_4, 2100 K is required, once the temperature is reduced to 1700 K. After Fe_2O_3 is changed to Fe_3O_4, the Fe_3O_4 must be heated to 1900 K to reduce it to FeO. Iron can then be obtained after heating the FeO to a higher temperature still. It is generally considered that FeO did not exist to change Fe_3O_4 and iron by disproportionate ambient temperature. After FeO particles are generated, they will change to iron and Fe_3O_4 particles due to the disproportionate reaction below 850 K.

The following metal-oxide powders were used to reduce and produce metal nanoparticles: Fe_2O_3 powder, 98% purity, mean size: $45\,\mu$m (325 mesh); Fe_3O_4 powder (Kojyundo Chemical Laboratory, Japan), mean size: $1\,\mu$m; and iron powder (Kojyundo Chemical Laboratory, Japan), mean size: below $5\,\mu$m. Since the metal oxides are small, it is supposed that the size of the powder n in the case of laser ablation in liquids is submicron.

Experimental setups based on laser ablation in liquid to reduce metal-oxide powders are shown in Figure 3. The experimental setup based on the laser ablation in liquid to reduce Fe_2O_3 powders using a low-repetition Nd:YAG pulsed laser (Surelite II SLI-10 Continuum; wavelength: 1064 nm; pulse duration: 8 ns; repetition frequency: 10 Hz) is shown in Figure 3(a). The diameter of the output laser beam was 6 mm (e^{-2}). A pear-shaped silicon-glass bottle was used to reduce the Fe_2O_3 powders. Laser pulses are entered to a mirror in the horizontal direction, and they change direction to the vertical direction under the glass bottle. The laser pulses were irradiated on the bottom of the glass bottle. About 4% of the irradiated laser energy was reflected on the surface of the bottle by the Fresnel reflection. The laser pulses were focused in the acetone liquid at a distance of 15 mm from the bottom of the glass bottle. The quantity of acetone in the bottle was 30 mL. Oxygen in the acetone was removed by
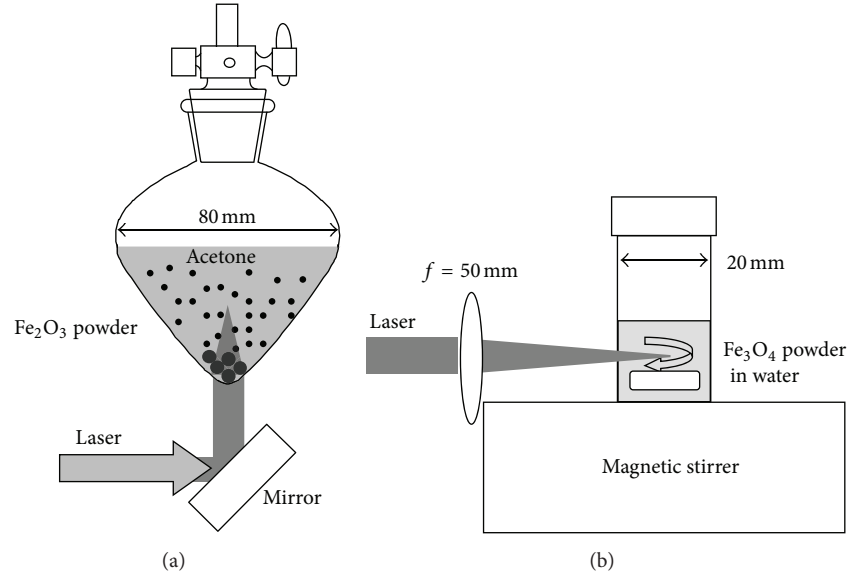
FIGURE 3: Experimental setup for laser ablation in liquid. (a) Reducing Fe_2O_3 powder with 10-Hz Nd:YAG pulsed laser, and (b) reducing Fe_3O_4 powder with high-repetition-rate Nd:YAG pulsed laser.

using argon for eight minutes. Here, the irradiation fluence was evaluated to be more than $20\,J/cm^2$. Free convection was thus generated in the glass bottle. The effect is the same as that caused by the mixing. The irradiation time was 20 minutes. To obtain reduced 50 mg of iron nanoparticles, the reduction experiment was repeated 14 times. The total weight of the Fe_2O_3 powder used was 70 mg.

The experimental setup based on laser ablation in liquid to reduce Fe_3O_4 powders by using a high-repetition Nd:YAG pulsed laser is shown in Figure 3(b). In this study, we used high-repetition microchip Nd:YAG pulsed laser. Maximum output-averaged laser power was 250 mW, laser wavelength was 1064 nm, repetition rate of the laser pulses was 18 kHz, and pulse duration was 8 ns. A beam with a diameter of 6 mm ($1/e^2$) was focused by using a lens with a focal length of 50 mm. The diameter of the focused beam was thus $20\,\mu m$ at the front of each glass bottle. Glass bottles with a diameter of 20 mmΦ and length of 38 mmL were used in the experiment. 100 mg of Fe_3O_4 was confined in the glass bottles with 5 mL of pure water and stirred. The water was mixed by magnetic stirrer (rotation velocity: 1200 rpm) during laser pulses irradiation. Laser pulses were irradiated to the water with the metal oxides in glass bottle for 10 minutes. Here, the fluence of the irradiated laser pulse was estimated to be $4.5\,J/cm^2$. After laser irradiation, the water was removed from the glass bottle, and the powder was dried. This process was repeated five times. The reduced powder was collected, and a part of all the reduced iron nanoparticles with the weight of 100 mg was picked up and measured. The reduced iron nanoparticles were used for the hydrogen production.

Fluence (J/cm^2) and the intensity (W/cm^2) of the irradiating laser pulses are important for reducing metal oxides by laser ablation in liquids. The fluence must be adequately more than $0.1\,J/cm^2$ to heat the metal-oxide particles to a high temperature over their melting point, and the intensity

must be over sub $0.1\,GW/cm^2$ due to induction of avalanche ionization and extraction of electrons from the metal oxides.

The conditions for the irradiation intensity of the laser pulses and the high absorption coefficient are adequate for reducing Fe_3O_4 powders. However, for reducing Fe_2O_3 by using the high-repetition Nd:YAG pulsed laser, the absorption coefficient at 1064 nm wavelength is low, the irradiation intensity and fluence are low, and it has been found that the reduction of Fe_2O_3 using a high-repetition Nd:YAG pulsed laser is hard. Accordingly, in this study, a low-repetition Nd:YAG pulsed laser was used for reducing the Fe_2O_3 powder. Additionally, it has already been found in our experiments that the Fe_3O_4 powders can be reduced by using this low-repetition Nd:YAG pulsed laser.

Analysis of crystal structure by X-ray Diffraction (XRD) (MAXima_X XRD-7000, Shimadzu, Japan) was performed to check the quantities of iron in the Fe_3O_4 powders irradiated by the high-repetition Nd:YAG pulsed laser. K-α X-ray radiation of copper was irradiated onto the samples.

2.2. Hydrogen Production. The method used for hydrogen production is described in the following. The chemical formula for reacting Fe_3O_4 powders with vaporized water is given as

$$Fe_3O_4\,(s) + \frac{1}{2}H_2O\,(g) \longrightarrow \frac{3}{2}Fe_2O_3\,(s) + \frac{1}{2}H_2\,(g),$$

$$\Delta H = 364.8\,kJ/mol. \tag{3}$$
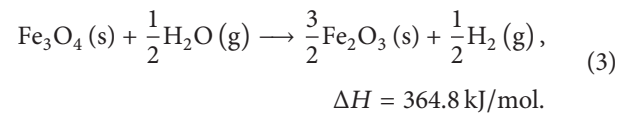
And the chemical formula for reacting iron powders with vaporized water is given as

$$Fe\,(s) + \frac{4}{3}H_2O\,(g) \longrightarrow \frac{1}{3}Fe_3O_4\,(s) + \frac{4}{3}H_2\,(g),$$

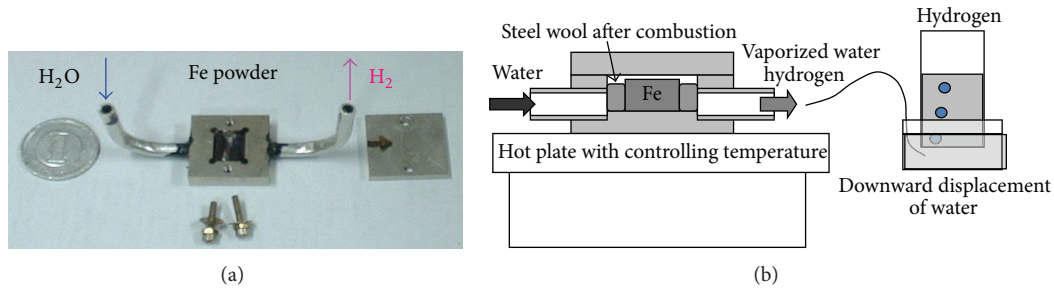$$\Delta H = -50.6\,kJ/mol. \tag{4}$$
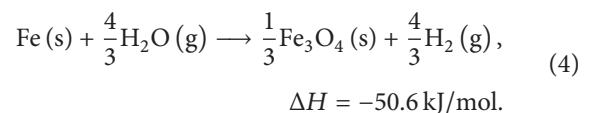
FIGURE 4: Hydrogen production: (a) photo of instrument for hydrogen production and (b) experimental setup.

In (3), the enthalpy energy is for per unit mol Fe to react with vaporized water. In the reaction of Fe_3O_4 with water, the water must be at high temperature and vaporized. The reaction of Fe_3O_4 with water is endothermic, and the reaction of iron with water is exothermic. It is clear that a certain amount of energy, which is required for reducing metal oxide, is needed for reacting Fe_3O_4 with water. Thus, the reaction for hydrogen production using Fe_3O_4 powder is difficult at 673 K. Equation (4) shows that 12% of the stored potential energy when the metal oxide was reduced is wasted as heat. The experimental setup for generating hydrogen is shown in Figure 4. A photo of the reaction container is shown in Figure 4(a), and experimental setup for generating hydrogen is shown in Figure 4(b). The outer size of the aluminum container was $20 \times 20 \text{ mm}^2 \times 9$ mmt, and the container is solid and does not react with pure water at up to 973 K. The inner size of the aluminum container was $5 \times 8 \text{ mm}^2 \times 3$ mmt. The center of the device was placed on the reduced iron nanoparticles placed on an aluminum-foil sheet, and steel wool was set between the container and the right aluminum tube to prevent outflow of the powder. The aluminum container was heated in the range of 523 to 673 K by hot plate (CHP-170AN, Asone, Japan). Pure water at a temperature of 295 K was injected into the container from the left aluminum tube. Once the water was absorbed, the steel wool combusted, and the water was vaporized and reacted with the iron powder. After the reaction, hydrogen was extracted from the right aluminum tube. The generated hydrogen was collected by the water-replacement method. The generated hydrogen was gathered in a silicon glass bottle.

When iron nanoparticles were used for hydrogen production, it was necessary to heat them. Compared with these results using reduced Fe nanoparticles, micron-diameter iron powder with a weight of 100 mg irradiated laser pulses was used for the hydrogen production. The reduction process was repeated 10 times. The synthesized iron nanoparticles were also used for the hydrogen production.

3. Results

3.1. Reduced Iron Nanoparticles from Iron Oxides.
The XRD analysis shows that the iron nanoparticles have a lot of γFe. The results of analyzing iron powders by XRD are shown in Figure 5. In common cases, determining the quantity of iron was difficult because the peak spectrum of Fe_3O_4 is

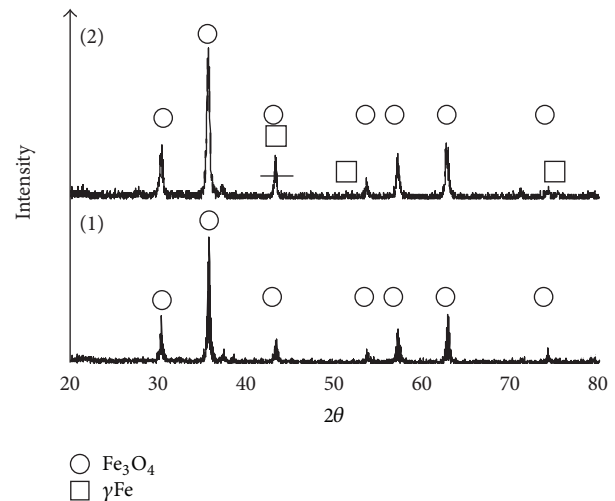FIGURE 5: Results of analyzed Fe_3O_4 powder and reduced iron nanoparticles by XRD. (1) Fe_3O_4 powder and (2) Fe_3O_4 powder after irradiating laser pulses.

larger than that of αFe or γFe at the same quantity. Two components of γFe, at angles of 42.8 and 75 degrees, can be seen in Figure 5. The γFe component was clearly recognized. The spectrum peak of iron at 42.8 degrees was evaluated by extracting the Fe_3O_4 component and is nearly as high as that of Fe_3O_4 at 43.1 degrees. Thus, the reduced iron nanoparticles contain a large quantity of γFe but a negligible quantity of Fe_3O_4. In the common case, the αFe and Fe_3O_4 components are recognized at angles of 44.7 and 43.1 degrees. The αFe component is normally observed. However, it has been already reported that when a CW laser or a pulsed laser was used to heat the surface of a stainless plate, αFe is changed to γFe by a high temperature generated by laser [19].

As for Fe_2O_3 reduction, it is easy to judge the state of iron oxides by their color when laser irradiation was conducted. The color of the Fe_2O_3 in the glass bottle changed from red to black. And some reduced iron nanoparticles became glossy. The color of the iron was silvery-white. As for Fe_3O_4 reductions, when the reduced iron was observed, the color of a few iron particles was gray, and most of the remaining powder was black. However, inside the reduced iron was pure iron, and only the outside of the reduced iron was oxidized. The mean size of the produced iron nanoparticles
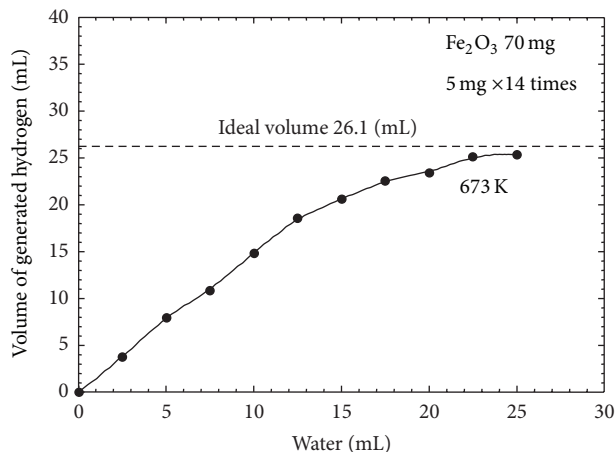
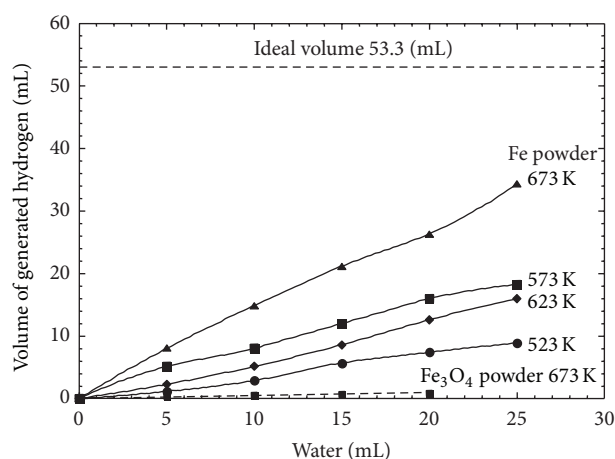FIGURE 6: Hydrogen generated by using Fe_2O_3 after laser-pulse irradiation.

FIGURE 7: Hydrogen production using pure iron powder.

- —— Fe powder after laser irradiation
- ----- Fe_3O_4 powder after laser irradiation
- ·—·— Fe_3O_4 powder

FIGURE 8: Hydrogen production using pure iron and Fe_3O_4 powder after laser-pulse irradiation.

was measured by a particle-size analyzer to be a mean size in the order of 20 nm.

3.2. Hydrogen Production. Density of generated hydrogen was measured by a hydrogen meter (Finch-Mono II, Japan). The obtained hydrogen was diluted once with 500 mL air, and the density was measured. The density of the hydrogen was compared with that of the hydrogen produced by electrolysis. It was thereby confirmed that the hydrogen concentration was near 99% and almost the same as that produced by electrolysis.

Hydrogen production was conducted using reduced iron nanoparticles from Fe_2O_3 powder. The experimental results are shown in Figure 6. The instrument for producing hydrogen was heated by the hot plate at up to 673 K. About 25 mL of hydrogen was obtained, when the instrument was heated at 673 K. The theoretical volume needed for generating hydrogen using 50 mg of iron nanoparticles was 26.1 mL, when all of the Fe_2O_3 particles (with the weight of 70 mg) were reduced. The maximum reaction efficiency using reduced
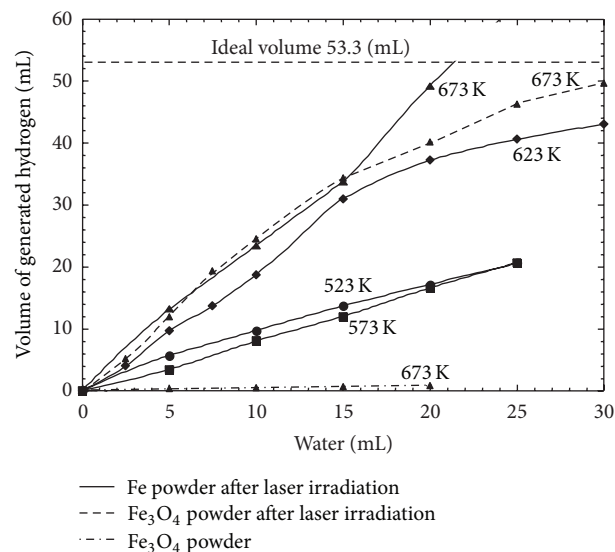
iron nanoparticles from Fe_2O_3 powder was evaluated to be 96% from the experimental result.

Hydrogen production was produced by using 100 mg of pure iron powder in the reactor. The experimental results are shown in Figure 7. The reactor was heated at 523, 573, 623, and 673 K, and 25 mL of water was used. Most of hydrogen (35 mL) was obtained when the temperature of the heated reactor was at 673 K. The theoretical volume to generate hydrogen using iron powder with a weight of 100 mg is 53.3 mL. The maximum volume of hydrogen was generated at 673 K, and the reaction efficiency for hydrogen generation was evaluated to be 66%, while less than 0.3 mL of hydrogen was obtained using Fe_3O_4 particles with the mean size of 1μm, when the instrument was heated at 673 K.

Hydrogen production was conducted using iron nanoparticles (with a weight of 100 mg) made from pure iron powder irradiated by a high-repetition-rate microchip Nd:YAG pulsed laser in water. The experimental results are shown in Figure 8. The reactor was also heated at 523, 573, and 673 K. The amount of water used was 20 mL. The maximum volume of generated hydrogen was 50 mL at reactor temperature of 673 K. The reaction efficiency for hydrogen generation was evaluated as about 94%. The theoretical volume of hydrogen that can be generated is 53.3 mL. It has been found that the reaction speed and efficiency using iron powder irradiated by laser pulses were improved because the mean size of the iron powder became 10 nm order, and the surface area of reacting iron particles increased. A maximum amount of hydrogen was also observed at 673 K.

Finally, hydrogen production was conducted using reduced iron nanoparticles (with a weight of 100 mg) from Fe_3O_4 powder irradiated by the high-repetition-rate microchip Nd:YAG pulsed laser in liquid. The reactor was heated at 523, 573, 623 and 673 K, and 25 mL of pure water

was used. The experimental results are shown in Figure 8. The maximum amount of hydrogen obtained was 50 mL, when the temperature of the reactor was 673 K. The reaction efficiency of the hydrogen generation was evaluated to be 94% for a theoretical volume of generated hydrogen of 53.3 mL.

4. Discussion

Fe_2O_3, Fe_3O_4, and iron powders were reduced by using laser ablation in liquid. Iron oxide was chosen as a metal oxide for the energy cycle because the Clarke number was the third, and the iron amount in recoverable reserves, which could be mined economically and technically, is about 10 times that of aluminum oxide. Iron is easy to obtain and use.

We discuss the absorption of laser pulses to metal oxides. The absorption process of a laser pulse by metal oxides has two possibilities: normal linear absorption and multiphoton absorption. In this experiment, in laser ablation in liquids, the latter mainly occurs. Smaller particles make electrons in the metal oxides more active, and electron emission will thus occur actively. The absorption coefficients of Fe_2O_3 and Fe_3O_4 are markedly different. Fe_3O_4 powder should be used for the energy recycle because its absorption coefficient at 1064 nm wavelength is high, and after producing hydrogen, Fe_3O_4 powders are mainly produced.

If a CW laser is used for reduction of the metal oxides, the reduction efficiency will be low because the generated temperature of the metal oxides is low. The CW laser has a low peak power, and it cannot heat the metal oxides up to a melting temperature in a short time. Moreover, the low intensity results in no avalanche ionization and less electron ejection.

The coulomb explosion and thermal ablation had been proposed as the ablation mechanism of the metal oxide in the liquid. The coulomb explosion was mainly considered in this study. It has been suggested that metal-oxide particles are broken into pieces in the Coulomb explosion. Firstly, the metal oxide is heated to over its melting temperature, at which it changes to form a gel. Electrons in the atoms of the metal oxide are ejected by the intense electric field of the irradiated laser pulses. After the particles become positively charged, the metal oxides repel each other by the same positive charge. Finally, a plasma is produced and atomized. In the case of using water for laser ablation, a subreaction occurs. In the coulomb explosion, the ejected electrons and oxide atom react with the water, and OH^- ions are generated. As a result, the water becomes alkaline. This phenomenon had already been observed in some experiments.

Two lasers, high- and low-repetition-rate Nd:YAG pulsed lasers, were used to reduce Fe_2O_3 and Fe_3O_4 by laser ablation in liquid. It was found that the high-repetition-rate laser attained higher reduction efficiency than the low-repetition-rate laser. The reduction efficiency of the metal oxides generated by using the high-repetition laser pulses was higher than that for the low-repetition pulsed laser for the same averaged laser power. The reduction efficiency will depend on the interaction time between the metal oxides and laser pulses. The emission time of electrons should be

determined by a single factor, namely, multiplication of pulse duration and repetitive rate. Thus, it will be possible to reduce 100 mg of metal oxides in less than 10 minutes by using a high-repetition-pulse laser. Moreover, metal with more than 200 mg of oxides can be reduced in 10 minutes. Reduction of metal oxide will occur in single laser pulse.

We conducted hydrogen production by using small instrument for hydrogen production and the reduced iron. Hydrogen was produced by using a small instrument and the reduced iron. As a consequence, the obtained reaction efficiency of hydrogen generation using iron nanoparticles reduced by laser pulses was 94%, which is high enough in the case that the particles have oxide shells. It means that the reduction of the metal particles by laser ablation in liquids was almost complete. Moreover, power generation in the hydrogen fuel cell was confirmed.

If the particle sizes of the iron nanoparticles were less than 10 nm, it is predicted that iron nanoparticles will react with water completely by heating the temperature of the instrument for hydrogen production to be close to 373 K.

For producing hydrogen using iron nanoparticles reduced from Fe_3O_4, a dispersing agent for protecting the condensed nanoparticles is commonly used. An agent was not used in the present study because the condensation should not affect the reaction efficiency. In the case of using water for producing hydrogen, the surfaces of the produced iron nanoparticles are oxidized. However, the oxide surface did not affect the reaction efficiency of hydrogen production.

An energy loss occurs in the process of producing hydrogen for the produced iron nanoparticles. The energy loss is one eighth of the stored energy in the iron nanoparticles as the difference of the potential energy between iron oxides and iron in the reducing process. It is small and converts to heat. However, only 43 mg of water is needed to react with 100 mg of pure iron. In this experiment, the weight of the water used was 25 g. Thus, a lot of water was wasted without reacting with the iron nanoparticles. To eliminate this waste, first, the water should be confined in the reactor to improve the reaction efficiency with iron nanoparticles. Second, the reaction efficiency of the iron nanoparticles should be suppressed to 90% because the production rate of hydrogen degrades remarkably. It introduces to save the required water and electricity to heat and to recycle efficiently.

Solar energy or other natural energies are considered as sources of laser power for laser ablation in liquid. However, the most suitable lasers for energy cycles are considered to be solar-pumped lasers because common lasers have low electro-optical conversion efficiency.

In the future, we will establish a clean-energy hydrogen-production cycle that is simple, low-cost, no-carbon, and recyclable by combining a solar-pumped laser and laser ablation.
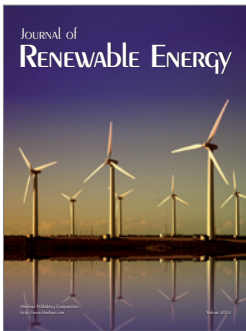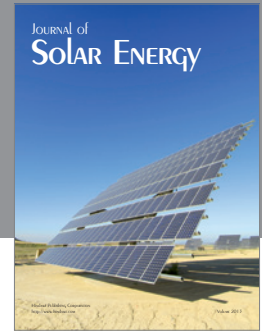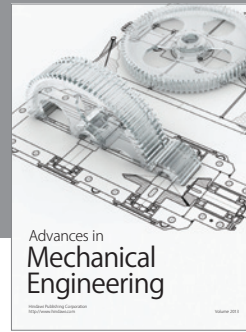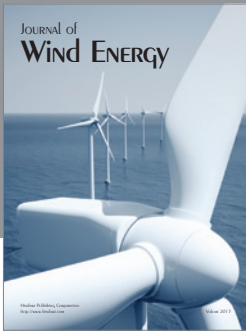
5. Conclusion

Fe_2O_3 and Fe_3O_4 powders were reduced with high efficiency by Nd:YAG pulsed lasers based on laser ablation in liquids. It was experimentally demonstrated that the produced iron

nanoparticles can be used for hydrogen generation in an energy cycle. For hydrogen production using the reduced iron nanoparticles, the reaction efficiency of the hydrogen generation at a temperature of 673 K was more than 94% for the theoretically ideal amount of generated hydrogen. Fe_3O_4 powders remain after the hydrogen is produced, and they should be reduced by pulsed laser. Iron nanoparticles are reproduced and used for producing hydrogen again.

The laser pulses should be generated using a natural energy source, such as solar power or wind power. Furthermore, the laser pulses can be generated directly from solar light by using solar-pumped lasers. It has been expected that our proposed energy cycle by using pulsed laser and the Fe nanoparticles will be realized. The proposed energy cycle using a pulsed laser and iron nanoparticles is expected to provide simple, low-cost, and no-carbon production of recyclable hydrogen.

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