Development of Hydrogen energy creation type fuel cell system and Ubiquitous hydrogen energy supply system

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Abstract

Reduction of greenhouse gas is one of the most important subjects for prevention of global warming. It is necessary to adopt renewable energies as much as possible to realize low-carbon societies. At the same time, supply-demand optimization and effective utilization of energies, backed by modern information technologies, are also important subjects to be examined. In order to let the present situation be advanced, it is considered that the utilization of controllable powers by means of fuel cells is effective as a more positive answer. This is because fuel cells are able to compensate the instability of renewable energies and to make them stabilized.

Hydrogen energy, which is the driving force of fuel cells, is said to be one of the most useful energies as it can be converted to electrical energy with high efficiency. However, in order to use hydrogen energy as an alternative of fossil energies, it is essential to ensure a new technology, which makes it possible to store hydrogen as pressurized by 2,000 to 3,000 times higher than normal pressure. Also it is essential to ensure safe and easy handling scheme and to satisfy the supply of low-cost hydrogen.

It is highly required to realize a more advanced hydrogen supply system which meets above-mentioned requirements. The authors have been working for the research and development on a more advanced hydrogen supply system, which utilizes sodium borohydride, and have succeeded in developing the elemental technology of the system. The fundamental idea is to handle hydrogen as a solid substance by containing it in a chemical composition, and not to handle it as a gaseous substance.

Key words: Global warming, Renewable energy, Low-carbon society, Controllable power, Fuel cell, Fossil energy, Hydrogen supply system, Sodium borohydride

1. Introduction

Today, the worldwide energy mainly depends on the fossil fuels. Electrical energy, among others, is the most useful and convenient energy as it is available anywhere via cables or wires, it is easy to control and it can be obtained by conversion of the most of the primary energies.

On the other hand, the reduction of greenhouse gas is one of the most important matters of concern as it is essential for the prevention of global warming. Studies aiming to accomplish this have been worked on. Such study as supply-demand optimization of energy [1] and efficient utilization of the available energies are effective for realizing low-carbon societies [2]. This will be carried out by introducing the renewable energies backed by modern information technologies. As to realize this, the authors propose 'the utilization of controllable electric power generated by fuel cells'. This is considered to be a more effective and positive solution which can solve unstableness of renewable energies.

Hydrogen energy, the driving force of fuel cells, is superior energy as it is efficiently convertible into electrical energy and just suitable for the present high energy-consuming societies. In order to make the hydrogen energy more practical as a substitute of fossil fuels, however, there should be such important technologies to be accomplished as how to store hydrogen pressurized 2,000 to 3,000 times as high as atmospheric pressure, how to handle it safely and how to make its production cost cheaper.

A highly efficient hydrogen supply system is definitely needed for the realization of the above-mentioned requirements. The authors have successfully developed elementary components of the system. 'To treat the hydrogen which exists inside of compounds as a solid body' is authors' fundamental idea and this is completely different from the well-known existing idea, 'to treat it as a gaseous body'.

2. Study of hydrogen storage

What is required for hydrogen storage is to be able to store a large amount of hydrogen gas and, upon request, to take a required amount out of the storage and to supply it to the customers. The authors have developed the hydrogen storing system that meets these requirements.

It is understood that the form of hydrogen stored inside the fossil fuels is a form of hydrogen chemical compound and this tells the reason why they have high hydrogen density. According to the axiom of chemistry, one mole of any substance contains 6.02×10^{23} molecules of the substance [3]. Therefore, higher hydrogen density storage can be attained by storing quite a number of hydrogen atomics in one molecule of a chemical compound than by storing two hydrogen atomics in one hydrogen molecule. In addition, the mass density of a substance increases by more than several hundreds to thousand times higher when it changes its state from gas to liquid or solid. It means that the hydrogen energy density can also be increased stably to such extent as stated above if a compound is used for hydrogen storing. It is understandable that the fossil fuels are typical examples of this fact.

If we use a solid chemical compound, which is stable in the atmospheric environment, as a hydrogen storing material, it enables to make its handling, storing and preservation easy and safe. Moreover, the volume of a solid compound is much smaller than gaseous or liquid compounds. This makes a hydrogen storing facility smaller, simpler and safer. Thus, the authors decided to use a solid chemical compound as the hydrogen storing material. To be more concrete, the authors have chosen sodium borohydride, one of inorganic hydrides, for the storage material.

Sodium borohydride ($NaBH_4$) (abbreviated **SBH**) is made from borax which is easily acquired from rich deposits scattered worldwide. The authors' objective is to put the hydrogen energy into practical use and to complete it as a ubiquitous energy that has such advantages as being comparable to the fossil fuels in terms of high density energy, easy to handle in atmospheric environment and low price.

3. Hydrogen storing material: Sodium borohydride (SBH)

Physical properties of SBH are shown in Table 1.

Table 1 Properties

IUPAC name	**sodium borohydride (sodium tetrahydridoborate)**
Molecular formula	**$NaBH_4$**
Molar mass	**37.83 g / mol**
Appearance	**white crystals**
Density	**1.074 g / cm^3**
Solubility in water	**℃ / g / H_2O・100g** **0 / 25** **25 / 55** **60 / 88.5**
Melting point	**400℃**
Boiling point	**500℃**
Other features	**・white solid, stable in dry air up to 300℃** **・hydrogen content：10.6 wt%** **・soluble in water, reacts with water easily, generates H_2 two times as much as its hydrogen content**

SBH is one of coordination compounds [4]. It is easy to control its chemical reaction as the reaction proceeds slowly and it is widely used as a reducing agent for industrial use and a reagent. Its solubility in water is high and the chemical reaction in water, it is known as hydrolysis, proceeds easily. Therefore, the reaction can produce hydrogen in a stable manner.

SBH is known as a high density hydrogen storing material because it has high hydrogen mass density of 10.6 weight percent (wt %) that is 1.5 times higher than that of liquid hydrogen. Also SBH has a long track record as a hydrogen rich reducing agent and, after knowing it is a good hydrogen storing material, studies aiming to utilize it have been conducted but so far we cannot find any practically effective results.

SBH is easily dehydrogenated on-site. The dehydrogenating reaction, that is hydrolysis, proceeds slowly at room temperature up to critical state. However, reaction itself is accelerated by the heat of the reaction during the process. This makes it possible to produce hydrogen on industrial basis at room temperature.

It should be noted that the amount of hydrogen produced at that time is just two times more than the amount of hydrogen stored in SBH. The reason is that, in addition to the hydrogen stored in SBH, the one generated from the water of the solution can be counted as well. The sum of these two makes the total amount double. The authors call this ‘hydrogen proliferation’. This is the most important and outstanding point of the idea that differentiates the authors’ concept from those of any other hydrogen storing systems. By utilizing this, the authors are now underway to accomplish ‘Hydrogen energy creation type fuel cell system’.

It should be noted that the hydrogen proliferated in this process does not contain carbon at all as it is generated by the hydrolysis. Therefore, even if we use such SBH that consists of hydrogen produced through a carbon originated process, still we can keep the rate of carbon content originated from the hydrogen to a half. This means that the system just meets an ideal hydrogen storing system and is suitable for realization of low carbon societies.

4. Development of ‘hydrogen energy creation type fuel cell system’

Fig. 1 gives the full picture of the system that composed of two processes. One is a process that generates hydrogen on-site and the other is a hydrogenating process that recycles the used hydrogen fuel.

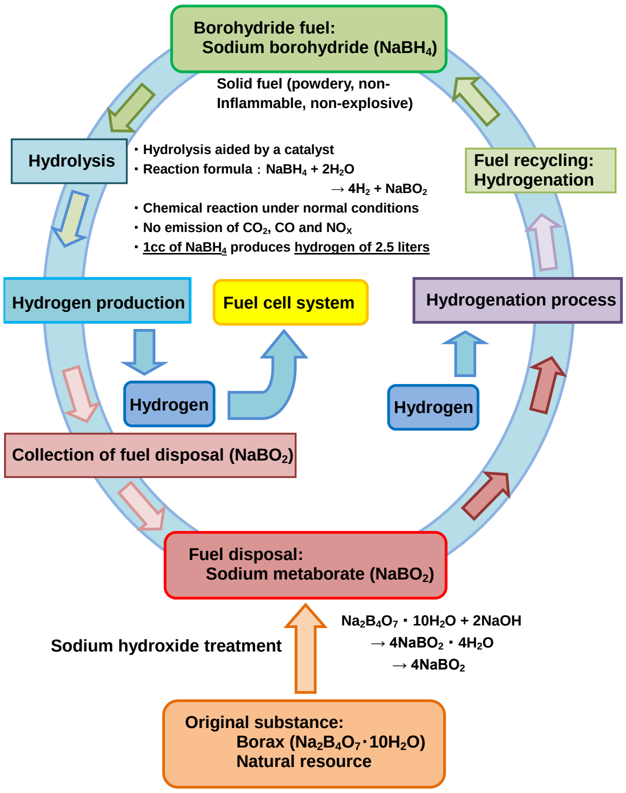

Fig.1 Hydrogen generation from SBH and recycling of used SBH

As shown in Fig. 1, the system does not produce any environmentally hazardous substance as all the products in the processes are to be recycled.

How to proceed is:

1) As the origin of the system, sodium metaborate ($NaBO_2$) is made from borax ($Na_2B_4O_7$) which is well known as one of the resources easily available worldwide.

2) SBH (hydrogen mass density: 10.6 %) is made from sodium metaborate through the hydrogenation process.

The SBH is powdered at processing factories and conveyed to sites. It is stored there and distributed through distribution structures. It is understood that as the molecule of SBH plays the role of a firm hydrogen container, none of strong and large hydrogen tank for the storage is needed.

3) The distribution of the SBH will be done by simple infrastructures such as a transportation via pipe lines or a freight traffic as the form of the SBH is solid (powder). These simple infrastructures will be possible to be attached to existing gas stations if it is so requested.

4) Usually pyrolysis under high temperature is used for the dehydrogenation of coordination compounds. However, SBH is dehydrogenated as shown in reaction formula (1) at room temperature and then, with the aid of a catalyst, we can generate certain amount of hydrogen rapidly without heating equipments.

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \quad \cdots (1)$$

By utilizing this merit, the authors have developed a compact centrifugal reactor for dehydrogenation as shown in Fig. 2 which is suitable for on-site use.

Fig. 2 Outer looking of centrifugal reactor Compact size of 450 heights, 250 widths and 250 depths (in mm)

Fig. 3 shows the aspect of rate of flow of hydrogen and accumulated amount of hydrogen generated for the time period of about one hour when the target rate of flow was set to 18 liters per minute.

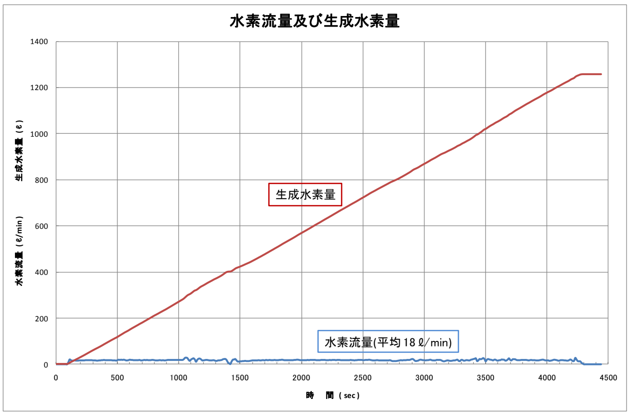

Fig. 3 Flow rate and cumulated volume of H_2 generated by the centrifugal reactor

Sodium metaborate ($NaBO_2$) generated as shown in formula (1) is separated from the hydrogen fuel by the centrifugal reactor and led to the disposal tank. The collected sodium metaborate will be recycled to SBH by off-site hydrogenating processes. This hydrogen storing material, SBH, has an advantage of long term use as it is refreshed by the recycling without any mechanical wear or fatigue that may shorten its life time span.

5) Rough explanation of the term 'hydrogen proliferation' is stated in section 3 above; however, let us explain it more closely here:

The hydrogen is generated on-site as per formula (1). The hydrogen generated ($4H_2$) is the sum of two moles of the hydrogen (H_4) contained in $NaBH_4$ and two moles of the one ($2H_2$) contained in $2H_2O$. As is shown in Fig. 4, this reaction takes place when 4H from $NaBH_4$ is replaced by the oxygen (2O) from $2H_2O$ through substitution reaction; that is, $2H_2$ is generated by the separation of the oxygen (O) from $2H_2O$ while $NaBH_4$ changes to $NaBO_2$, which is chemically much more stable. As this reaction takes place by the internal energy of substances, no energy from outside to promote this reaction is needed. The authors call this 'hydrogen proliferation'; that is the result of chemical decomposition of water. In addition, the water ($2H_2O$) necessary for the reaction can be supplied by utilizing the water ($4H_2O$) generated at the anode of the fuel cell as shown in Fig. 4.

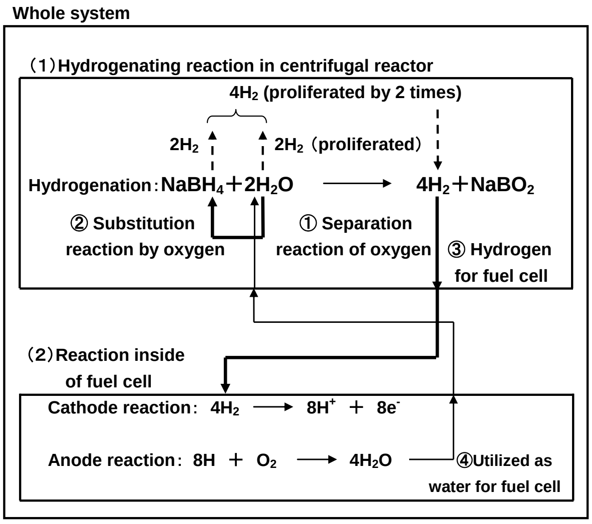

Fig. 4 Flow of proliferated hydrogen and water

By circulating the water within the system, the decomposition reaction is kept maintained automatically. Consequently, $2H_2O$ shown in the left hand side of formula (1) is not necessarily supplied as a part of the fuel. Thus, four moles of hydrogen is produced from one mole of SBH and the weight percent of the produced hydrogen is equivalent to 21.2 wt %. This was confirmed by the experiments conducted by the authors. The reaction proceeds rapidly owing to the exothermic reaction. This is one of the outstanding characteristics of the system and this makes it possible to keep the dehydrogenating reaction stably continuous.

The 'hydrogen proliferation' stated above also makes it possible to realize the high energy efficiency of the system as stated hereinafter. Namely, thanks to the realization of highly efficient hydrogen storing faculty and the hydrogen of which energy density enriched to double, 'hydrogen energy creation type fuel cell system' is possible to be realized.

5. Realization of high total efficiency of energy in various systems

Fig. 5 shows the total efficiency of energies obtained by trial calculations made on a hydrogen fuel cell vehicle [5] [6] as an example.

Method	Efficiency 'Well to Tank': η_1	Efficiency 'Tank to Wheel': η_2	Total efficiency
Gasoline	84 %	23 %	19 %(1)
EV	39 %	85 %	33 %(2)
Pressure-lized hydrogen (70MPa)	H_2 from methane reforming Mining / Refining / Conveying 88 % → Hydrogen producing 85 % → Compressing 90 %	→ Fuel cell 65 % → Motor inverter 90 %	40 %(3)
	Total efficiency : 88×85×90＝67 %	Total efficiency : 65×90＝59 %	
Sodium boro-hydride (SBH)	H_2 from methane reforming Mining / Refining / Conveying 88 % → Hydrogen producing 85 % → Hydrogenating 65 %	H_2 generation (⊿H＝0) 49＋100＝149 % → Fuel cell 65 % → Motor inverter 90 % +100 % (proliferated H_2)	88 % (＝149 ×59)
	Total efficiency : 88×85×65＝49 %	Total efficiency : 65×90＝59 %	
	H_2 from electrolysis of water Power 40 % → Electrolysis of water 80 % → Hydrogenation 65 %	H_2 generation (⊿H＝0) 21＋100＝121 % → Fuel cell 65 % → Motor inverter 90 % +100 % (proliferated H_2)	71 % (＝121 ×59)
	Total efficiency : 40×80×65＝21 %	Total efficiency : 65×90＝59 %	

Notes: (1),(2),(3) per Toyota's trial calculation (Materials of 2011 Hydrogen Storage Forum)

Fig. 5 Trial calculation of total efficiency of energy in various fuel systems

As for SBH method, the hydrogen reformed from methane gas and the one produced by electrolysis of water were used as the source hydrogen. The total efficiency is calculated by formula (2). The efficiency of the hydrogen produced by 'hydrogen proliferation' which equals to ＋100 % (efficiency ＝＋1.0) is added to the energy efficiency of 'well to tank' (＝η_1) and the sum is used for obtaining the total energy efficiency.

$$\text{Total energy efficiency} = (\eta_1 + 1.0) \times \eta_2 = (\eta_1 \times \eta_2) + (\eta_2) \quad \cdots \quad (2)$$

The first member of the right hand side of formula (2) (＝$\eta_1 \times \eta_2$) shows the efficiency of the hydrogen which is produced by a primary energy and is stored in SBH. Likewise, the second member (＝η_2) shows the efficiency of the proliferated hydrogen. According to the result of the trial calculation shown in Fig. 5, it is obvious that the total efficiency is more effectively heightened by the efficiency of the energy of the proliferated hydrogen shown as ＋100% (＋1.0 in formula (2)).

6. Effect exerted on electric power storage

From now on, as commercial power sources are required to be of low carbon, the ratio of carbon-free power sources including nuclear power will definitely be increased. Consequently, this causes the increase of fixed base powers, particularly night–time powers. Increase of power storage, therefore, has to be studied more seriously as a measure of this situation. Let us take a look of the authors' system in view point of power storage. Calculation of input and output are as written hereinafter if the power is generated by a fuel cell of which fuel is SBH produced by the authors' system where the hydrogen used is produced by electrolysis of water with the energy efficiency of 80 percent.

The input to the electrolysis of water

$$= 1 / 0.8 = 1.25 \quad \cdots \quad (3)$$

Taking the power generating efficiency of the fuel cell as 0.65:

The output of the fuel cell when the 'proliferated hydrogen' is used

$$= 2 \times 0.65 = 1.3 \quad \cdot \cdot \cdot \quad (4)$$

As the quantity of output (1.3) is more than that of input (1.25), the efficiency of electric power storage in the system can be evaluated as 100 percent. This means that it is much effective to use the power generated by fuel cells in daytime and to produce hydrogen for SBH in nighttime by means of the authors' method.

The method that uses hydrogen produced by electrolysis of water shown in Fig. 5 can achieve as high total energy efficiency as 71 percent. This is lower than that uses hydrogen produced by reforming of methane gas as shown in Fig. 5. However, from the view point of low-carbon power generation, the method that uses electrolysis of water is more advantageous.

7. Supply of high-density hydrogen energy

As stated above, SBH is well known as one of the high-density hydrogen storing materials. By using SBH as a hydrogen carrier and by using the 'hydrogen proliferation' function, the authors have achieved hydrogen energy level of 32.3 MJ / liter (HHV). This is almost comparable to gasoline as shown in Fig. 6 [7]. It should be noted that water (H_2O) is capable of having about 1.5 times higher hydrogen storing capability than that of liquid hydrogen. The authors' system effectively utilizes this fact and, as a whole, makes it possible to supply the high density hydrogen of which density is 2,500 times higher than that of hydrogen gas in normal conditions.

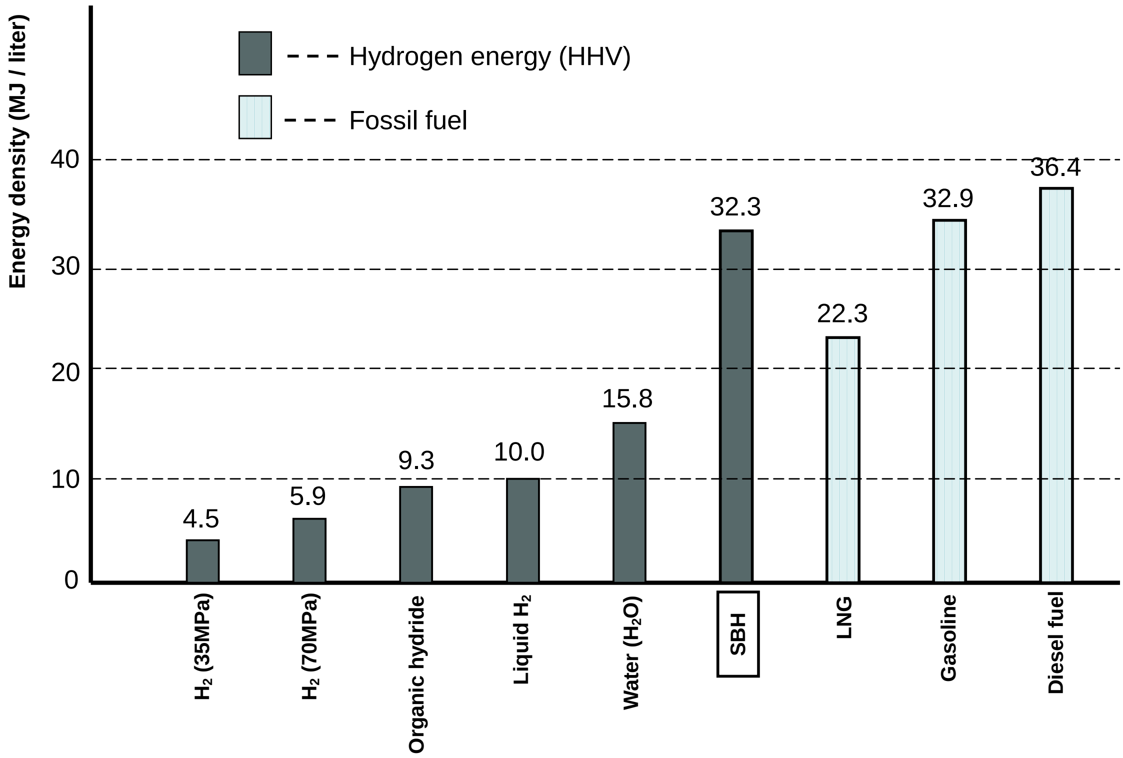

Fig. 6 Energy density of various fuels which consist of hydrogen compound

8. Power generating capability of borohydride fuels

When hydrogen energy, of which amount is expressed in chemical energy (kJ) (LHV basis), is converted to electric energy (kW) by a fuel cell, these two amounts are the same. The actual power generated by a fuel cell is obtained by multiplying the amount by the efficiency of the fuel cell. A trial calculation of the power generated from 1 kg of SBH fuel produced by the authors' system is as follows:

Amount of hydrogen produced from SBH
＝ 2,370 N liter / 1 kg of fuel
Heat of combustion (LHV) ＝ 10.78 kJ / N liter
Efficiency of fuel cell ＝ 65 percent (LHV)
The power generated from 1 kg of fuel is as follows:
Power generated ＝ 2,370 × 10.78 × 0.65
＝ 16,606.59 kJ / 1kg of fuel
16,606.59 / 3,600 sec ＝ 4.6 kWh / 1 kg of fuel

Therefore, if an average family is connected to a distributed generation for household use which uses the authors' system and consumes power of 10 kWh a day, the amount of SBH fuel necessary for the power is calculated as follows:
Necessary amount of SBH ＝ 10 / 4.6
＝ 2.2 kg (volume of SBH : approximately 2 liters)
As the conclusion, the necessary amount of SBH is reasonably small.

9. Compact hydrogen storing system

The size of a hydrogen storing system depends on how to store hydrogen. The following features enable the authors' system to be more compact and light weight than any other systems.

1) Less load capacity of the fuel due to high hydrogen mass density (＝ 21.2 wt %)
2) The system is operated under normal ambient temperature and atmospheric pressure; that makes the hardware of the system compact and light weight.
3) No outer water supply is needed as the water necessary for the hydrogen generation can be obtained by the recycling process inside the system; that results in the provision of a simpler and lighter construction.

It has been officially discussed about the capacity and the weight of systems which are mounted on a car and are able to store 5 kg hydrogen. Also this issue has been put on the road map officially with a target. That is, at present, the capacity and the weight of the storage are estimated to be 280 liters and 110 kilograms [8] respectively for a high pressure hydrogen system of 35 MPa. These dimensions are aimed to be 100 liters and 100 kilograms in future.

The authors have made a trial calculation by using the outstanding features of the system and the result of the experiments. The result shows that the system can clear the future target stated above and can provide such a possibility as 70 liters and 60 kilograms that is even much more compact storage than the future target stated above.

10. Expectation of low-carbon society

The reduction of greenhouse gas is one of the most important matters of concern as it is essential for the prevention of global warming. Studies aiming to accomplish this have been worked on. Such studies as supply-demand optimization and efficient utilization of the available energies are effective for realizing low-carbon societies. This will be carried out by introducing renewable energies backed by modern information technologies. Thus, smart grids and smart cities are under examination for realizing low-carbon societies.

However, at the supply-demand optimization of power, there will be a limit of introducing renewable energy powers if their instability is kept unimproved in future. In order to solve this, the authors propose to add a fuel cell system to a renewable energy power system. Namely, to use controllable distributed generation systems, which are controlled by modern information technologies to optimize the supply-demand of the power within the area, is the most effective way to stabilize the renewable energy power and to compensate its instability. The authors' proposal can realize the minimization of the instability of the system effectively without any additional cost or impelled load limitation. And the proposal is a positive plan that promotes power generation rather than power storing; therefore, it is effective to solve a power shortage that is now becoming a more serious problem in this country. If the control of the system is incorporated in the daily power generating plan of a power company, it can surely stabilize the whole power system of the company.

Hydrogen energy used as the driving energy of a fuel cell can be efficiently converted into electric energy and so, it can be directly connected to the present high-energy consuming societies. This tells that the fuel cell system which utilizes hydrogen energy is a potential basic resource to realize the energy in low-carbon society.

11. Conclusion

Above mentioned technology makes it possible to realize a safe and inexpensive hydrogen storing system as mechanical containers to store a large amount of high-pressure hydrogen are not needed. This is because the hydrogen is stored in a solid chemical compound and so, it is easy to transport it from one place to the other. As for the transportation and distribution of the hydrogen, inexpensive structures which utilize granular material conveyance via pipe lines or ordinary transportations are taken into consideration. Also the 'proliferated hydrogen' makes the efficiency of the hydrogen energy double and results in the saving of primary energies.

The realization of the proposed hydrogen energy means the realization of the high-density energy equivalent to fossil fuels with such outstanding features as environmental conservation (no fear for exhaustion of resources), energy security (security itself and self-support), and economy together with prevention of global warming. This energy can be developed to a ubiquitous energy as it has a great advantage of safe and easy handle under normal conditions. Furthermore, the fuel cells, which use the energy stated above, can stabilize the renewable energies for smart grids or smart cities. In other words, this fuel cell system can be so recognized as the most fundamental system for realization of low-carbon society.

From now on, the authors look forward to realizing a practical system for the hydrogen fuel recycling and, for this purpose, welcome any suggestions or advices from related fields.

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