Improvement of Energy Density of Hydrogen Generator System using Sodium Borohydride for Fuel Cell Hybrid Electric Vehicle

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***Abstract*—Fuel cell vehicle (FCV) or fuel cell hybrid electric vehicle (FCHEV) is very attractive as a zero emission vehicle. However, there are some barriers for the popularization of the vehicles. One of them is the construction cost of hydrogen gas station is very expensive. In addition, improvement of energy density of high-pressure hydrogen gas tank on vehicle is required. In this research, as a solution of the above problems, powder form sodium borohydride ($NaBH_4$) is used as the fuel for FCHEV. In addition, water-recycling system is introduced into the proposed hydrogen generator system to improve the energy density. Moreover, a prototype model of the proposed system was constructed. This paper describes the function of the proposed system and an experimental result that hydrogen could be generated continuously by the reactor of the prototype hydrogen generator system.**

I. Introduction

Fuel cell vehicle (FCV) or fuel cell hybrid electric vehicle (FCHEV) is very attractive as a zero emission vehicle. However, there are some barriers for the popularization of the vehicles. One of them is the construction cost of hydrogen gas station is expensive. In addition, high energy density hydrogen storage system on vehicle is required. Fig. 1 shows volumetric and gravimetric density of current key storage system[1]. In addition, the targets defined by US DOE (department of energy) are shown in the figure.

From several hydrogen storage systems, sodium borohydride $NaBH_4$ was selected as the fuel for FCHEV in this research since the energy density is high in theory. This material is a white powder and is soluble in water. Sodium borohydride reacts with water and generates hydrogen H_2 with sodium metaborate $NaBO_2$. This chemical reaction is expressed as the following equation[2], [3].

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 + 217kJ \qquad (1)$$

As the above equation, 4 moles of H_2 are generated from a mole of $NaBH_4$ with 2 moles of H_2O. Molecular weight of $NaBH_4$, H_2, and H_2O are 37.87g/mol, 2g/mol and 18.02g/mol, respectively. Consequently, the gravimetric density of this hydrolysis is calculated as the following equation.

$$4 \times 2 \div (37.87 + 2 \times 18.02) \times 100 = 10.8 \ \text{wt\%} \qquad (2)$$

On the other hand, the density of $NaBH_4$ and H_2O are 1.074g/mL and 1.0g/mL; thus, the volumetric density is calculated as following:

$$\frac{8}{(37.87/1.074 + 2 \times 18.02)} = 0.11 \ \text{kgH}_2/\text{L}. \qquad (3)$$

In this reaction, the theoretical hydrogen amount is 10.8wt% because hydrogen is contained in not only $NaBH_4$ but also H_2O. The gravimetric capacity of $NaBH_4$ is lower than that of compressed or liquefied hydrogen; however, the volumetric capacity is higher in theory.

Daimler Chrysler made an experimental fuel cell vehicle called *Natrium*, which used aqueous solution of sodium borohydride as the fuel. Since aqueous solution of sodium borohydride was used, the huge fuel tank, 53-gallon tank, was required in this experimental vehicle. As shown in the above, the volumetric density of *Natrium* and hydrogen storage systems shown in Fig. 1 is considerably lower than the theoretical value; thus, independent review panel of US DOE recommended "No-Go" decision for "Hydrolysis of Sodium Borohydride for On-Board Vehicular Hydrogen Storage" in 2007[4]. The reason why energy density becomes small is that an aqueous 24% or 30% solution of $NaBH_4$ containing

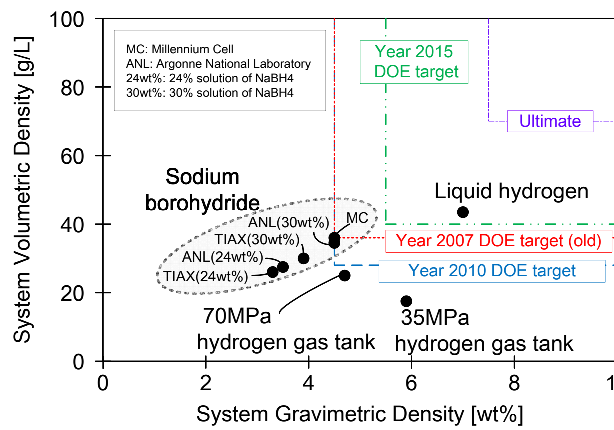

Fig. 1. DOE targets, and performance of current key storage system[1].

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3% sodium hydroxide NaOH as a stabilizer is used in the systems shown in Fig. 1.

As a solution of this problem, this research has proposed the following scheme[5]: (1) sodium borohydride is used in powder form, (2) recycling water that is generated by fuel cell (FC) is used for hydrolysis of $NaBH_4$.

This paper introduces a prototype proposed hydrogen generator system and reports experimental result that hydrogen could be generated continuously by the prototype model.

II. Improvement of Energy Density

In order to improve the energy density, the proposed system uses sodium borohydride $NaBH_4$ in powder form and recycling water as fuel. Principle of energy density improvement by the proposed system, which uses water recycling is described as follows.

Fuel cell generates electrical energy by burning reaction of hydrogen. The reaction formula in FC is as follows:

$$2H_2 + O_2 \rightarrow 2H_2O. \qquad (4)$$

From the equations (1) and (4), the reaction formula in FC fueled by sodium borohydride becomes

$$NaBH_4 + 2O_2 \rightarrow NaBO_2 + 2H_2O. \qquad (5)$$

Thus, it is understood in theory that the sufficient water required for hydrolysis of $NaBH_4$ can be obtained when the recycling water is used because there is H_2O in right-hand side of the equation.

Using the water recycling, the volumetric- and gravimetric-density can be improved. The gravimetric- and volumetric-density of the hydrolysis in using water recycling can be calculated by the following equations.
Gravimetric density:

$$4 \times 2 \div 37.87 \times 100 = 21.1 \text{ wt\%} \qquad (6)$$

Volumetric density:

$$\frac{8}{37.87/1.074} = 0.23 \text{ kgH}_2\text{/L} \qquad (7)$$

In actual system, the water generated by FC is less than the theoretical amount; however, it has been verified that sufficient amount of the water required for hydrolysis of $NaBH_4$ could be obtained as a result of laboratory experiment in [5].

Energy density of hydrogen storage systems can be calculated by use of the following useful constants: 0.2778kWh/MJ and 33.3kWh/kgH_2. Using these constants, the energy density of $NaBH_4$ without water recycling is 13.7MJ/ℓ. On the other hand, the energy density can be improved up to 27.2MJ/ℓ by use of water recycling. Fig. 2 shows comparison of energy density among several hydrogen storage systems and fossil fuels. As shown in Fig. 2, considering the reaction calories, the energy density of $NaBH_4$ is almost same as gasoline. The value is higher than the other hydrogen storage systems such as compressed hydrogen.

III. Proposed Hydrogen Generator System

Fig. 3 shows the configuration of the proposed hydrogen generator system for FCHEV. The proposed system uses sodium borohydride $NaBH_4$ in powder form. In the proposed system, the influence of the causticity can be moderated because required amount of aqueous solution is prepared on demand by adding water to a sodium borohydride powder. In addition, water generated by FC at electric power generation is reused for the hydrolysis of $NaBH_4$ in the proposed system.

There is a problem that residual product $NaBO_2$ prevents hydrolysis in hydrogen generation by sodium borohydride. Thus, the reactor shown in Fig. 3 has not only a function of hydrogen generation system but also a function of centrifugal

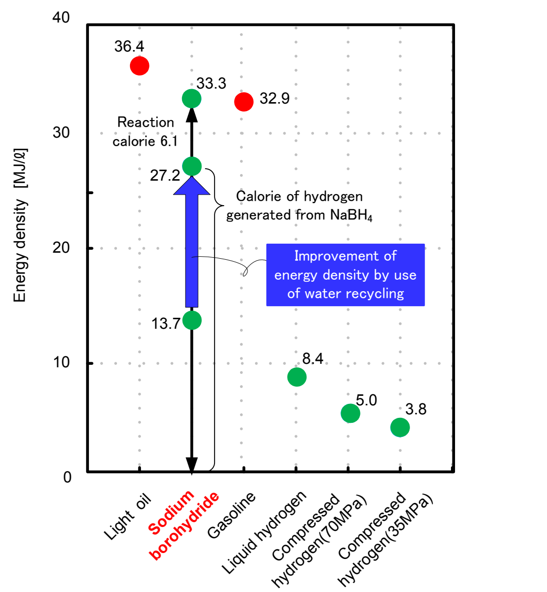


Fig. 2. Comparison of energy density.

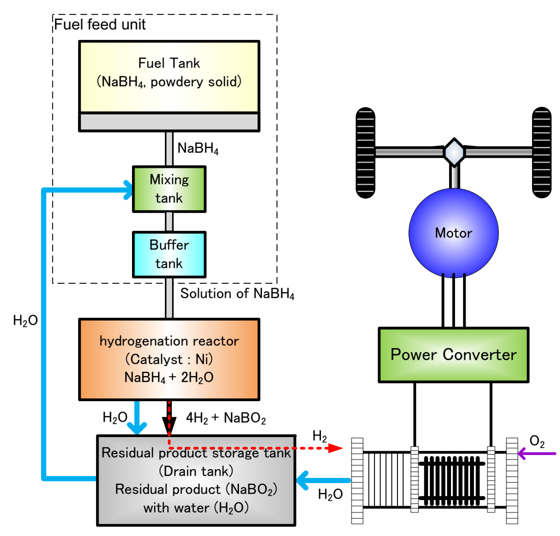
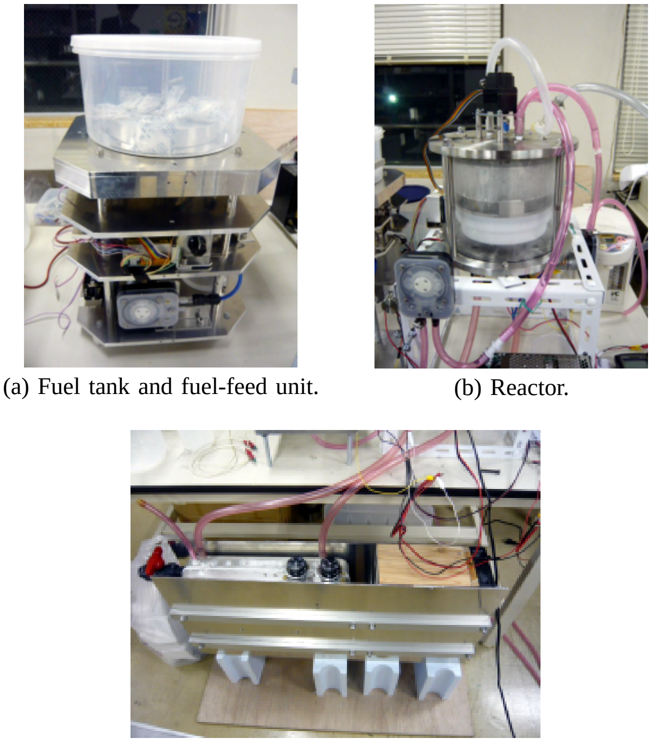


Fig. 3. Configuration of the proposed hydrogen generator system.



(a) Fuel tank and fuel-feed unit.

(b) Reactor.

(c) Residual product storage tank (drain tank).

Fig. 4. Photo of a prototype of the proposed hydrogen generator system under construction.

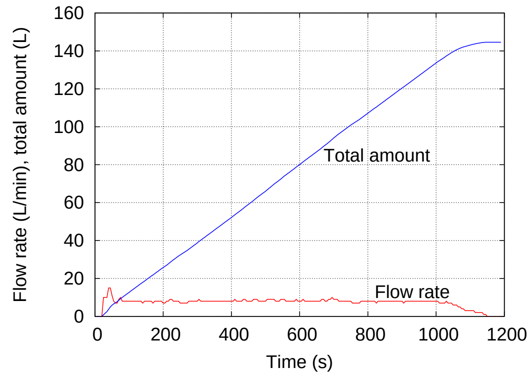


Fig. 5. Flow rate and total amount of hydrogen generated by the prototype reactor.

separator for residual product. By the centrifugal separator function, the residual product can be removed and hydrogen can be generated continuously in constant flow rate. The residual product is sent to the residual product storage tank, and collected.

In the proposed system, the hydrogen gas generated by the reactor includes water vapor. Thus, the hydrogen gas is sent to the FC after the gas is sent to the residual product tank and is dehumidified by cooling.

Fig. 4 shows photo of the prototype model of the proposed hydrogen generator system. Fig. 4 (a) is fuel tank and fuel-feed unit. Sodium borohydride in powder form is put in the see-through bottle on the top of this unit. In this unit, aqueous solution of $NaBH_4$ is made according to the following procedure: (1) Specific amount of $NaBH_4$ is put into stirred tank in the same unit from the top bottle. (2) In the stirred tank, specific amount of the water from the drain tank shown in Fig. 4 (c) is added with $NaBH_4$, and the tank is stirred. (3) The well stirred solution is sent to the buffer tank in the same unit.

The aqueous solution that is liquid fuel is sent from the buffer tank to the reactor shown in Fig. 4 (b) at on-demand flow rate. In the reactor, hydrogen gas with vapor is generated; and the residual product $NaBO_2$ is removed by use of centrifugal separation method. The gas with vapor and the residual product are sent to the residual product storage tank shown in Fig. 4 (c). In this tank, the residual product is collected and the hydrogen gas is sent to FC after dehumidifying by cooling.

IV. Experimental Verification

Controller of the proposed hydrogen generator system is now under construction. Thus, experiment in the reactor was conducted in order to confirm the hydrogen gas could be generated at constant flow rate from the proposed hydrogen generator system. In the experiment, aqueous solution of $NaBH_4$ as fuel is injected into the reactor shown in Fig. 4 (b) at a constant rate; and then hydrogen gas with vapor is generated. After desiccant dehumidification, flow rate of hydrogen gas was measured by a flow sensor. Fig. 5 is measured flow rate and total amount of hydrogen generated by the prototype reactor. As shown in Fig. 5, it is confirmed that the hydrogen gas could be generated at almost constant flow rate from the proposed reactor.

V. Conclusions

This paper proposed a novel hydrogen generator system which uses sodium borohydride $NaBH_4$ in powder form and recycling water as fuel. In addition, it was confirmed that the reactor of the proposed system could generate hydrogen gas at constant flow rate continuously. Experimental verification of total system will be reported in future work.

Acknowledgment

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