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The development and evaluation of a flow-type reactor utilizing the thermal siphon effect to generate hydrogen

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ABSTRACT

For the first time, a highly energy efficient flow-type reactor supplying and generating hydrogen was developed utilizing of the thermal siphon effect. A novel cobalt oxide-based ceramic made it possible to construct this efficient flow-type reactor for generating hydrogen. The reactor itself not only plays a role in hydrolyzing $NaBH_4$ in an aqueous phase, but also transfers new fuel and by-products without requiring any mechanical means. Thus, this system equipped with a thermal siphon reactor, supplies hydrogen more stably and operates more quietly than ordinary hydrogen generation system coupled to a conventional pump for liquid transfer. In this study, we used various concentrations of $NaBH_4$ solution to investigate the impact of $NaBH_4$ concentration on several parameters such as reactor type as well as its size. The study elucidates that the conversion rate of the $NaBH_4$ hydrolysis is sensitively affected by concentration of $NaBH_4$ and reactor type as well as its size. We determined that the conversion rate of $NaBH_4$ hydrolysis was sensitively affected by both the concentration of $NaBH_4$ and the type and size of reactor type. The thermal siphon reactor was 5 cm in length, but the catalysts used inside of the reactors were tubular or rod-shaped porous ceramic catalysts. The maximum conversion rate of $NaBH_4$ hydrolysis that we recorded from the thermal siphon reactor was 96% at a 174-cc/min average hydrogen flow rate over the course of 1.79 h. We also report the reaction time, average hydrogen flow rate, and conversion rate in a variety of experimental conditions. Furthermore, we discussed a separation effect of by-products from the thermal siphon reactor, which yield overall improvements in the efficiency of the system. Finally, we determine the optimal design and operational factors for a system using the thermal siphon effect.

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Introduction

Hydrogen has gained much attention as a consequence of its numerous applications in the fields of energy, chemistry, and biotechnology. Although the conventional processes for its production and separation in large quantities have been relatively well established, small-scale production of hydrogen in a cost-effective and highly efficient way was has remained a challenge [1–3].

Recently, demand has increased for small consumer electronics with stronger power and longer operation times. Accordingly, many electronics manufacturers have pursued alternative solutions for power sources. One such alternative high density power supply is the fuel cell, which directly converts chemical energy to electrical energy without mechanical moving parts. Among the many fuel cell technologies, the polymer electrolyte membrane (PEM) fuel cell is the most attractive for small portable electronics in terms of efficiency and compactness. However, the hydrogen fuel supply system has become a bottleneck for the further development of PEM fuel cells for small electronic devices [4,5].

Recent progress has been made in the development of a hydrogen generation method that utilizes a catalyst-assisted hydrolysis reaction of sodium borohydride in an aqueous solution [6–11]. In this system, an efficient and durable catalyst is one of the most important components. Prior reports have successfully established a highly reliable ceramic catalyst for hydrogen generation through the catalytic hydrolysis of sodium borohydride [12]. Ceramic catalysts based on cobalt oxide exhibit high catalytic activity and robust durability in a variety of experimental situations and settings. Another critical issue in a hydrogen generation system based on chemical hydride technology is to accurately control the hydrogen generation rate through the catalytic hydrolysis of sodium borohydride in water. Conventionally, the catalytic hydrolysis reaction of sodium borohydride is carried out in either a batch-type reactor or an active flow-type reactor that uses a pump for fuel delivery. A major disadvantage of the batch-type reactor is the low conversion rate (usually less than 75%) because of mixing problems that result in by-products and reactant, even though its size can be compacted as a consequence of a smaller balance of plants (BOPs) and requiring no power source.

By contrast, an active flow-type reactor, having a higher conversion rate (over 80%), often requires larger BOPs and extra power consumption for the operation of a fuel pump. It also generates noise while operating. Consequently, these problems have given rise to many restrictions for the practical utilization of PEM fuel cells in portable electronic devices.

A recent report [14] showed that the hydrolysis product of sodium borohydride in water is $NaB(OH)_4$ rather than $NaBO_2$, had been widely cited in many reports. The basic chemistry of the new hydrolysis reaction of sodium borohydride is shown as follows:

$$NaBH_4\,(aq) + 4H_2O\,(l) \rightarrow NaB(OH)_4\,(aq) + 4H_2\,(g) \tag{1}$$

As shown in this equation, $NaB(OH)_4$ is a major by-product when the hydrolysis reaction is carried out in a high pH solution. The detailed mechanism and kinetic analyses of the hydrolysis reaction of sodium borohydride have been discussed elsewhere [14,15]. Based on the hydrolysis reaction indicated above, the anticipated stoichiometric concentration of sodium borohydride in water is 34.1 wt%. Practically, the use of over 30 wt% sodium borohydride solution has remained a challenge in the development of a hydrogen generation system using sodium borohydride.

Most fuel cells need to should be provided hydrogen by pressurization and required differential pressures to offset a pressure pump of pipe line that transports hydrogen to a fuel cell. Also, because a relatively lower concentration of product helps to improve the efficiency of hydrogen generation, the thermal siphon effect is effective for improving energy efficiency. Especially, for the commercialization of fuel cells, the energy required for hydrogen generation and transit should be minimized. However, the energy cost of a pump in a small fuel cell presents a significant obstacle for improving energy efficiency.

To maximize fuel utilization and compactness, the development of an innovative hydrogen generation system is highly desirable for the portable applications of PEM fuel cells. Herein, we first present the construction and role of highly efficient passive flow-type reactors, and describe their mechanism for generating hydrogen in a variety of concentrations of sodium borohydride solution. Additionally, the principles of the thermal siphon effect, which is a key concept for our new passive flow-type reactor, are discussed.

Principles of the thermal siphon effect

In general, a physical pump is a mechanical apparatus that allows fluid flow by increasing the pressure in an internal chamber. Unlike a physical pump, a thermal siphon induces fluid flow without mechanical movements. The operation of a thermal siphon results from a natural convection, which is defined as "any fluid motion that occurs by natural means, such as buoyancy," where "natural" indicates "heat transfer" [16–18].

The thermal siphon concept entails the utilization of energy from heat transfer. The movement of fluid occurs as a consequence of density differences resulting from fluid thermal gradients. In an example of a simple thermal siphon cooler, heated fluid rises because of its lighter density compared to the density of cooled fluid. Thus, as long as a heating source and condenser are present, fluid in a closed thermal siphon system continuously circulates without a mechanical device.

According to the second law of thermodynamics, heat transfer occurs when the hotter substance transfers energy to the cooler substance. In a plain thermal siphon system with a closed vertical tube, heat flow (q) can be expressed as follows:

$$q = m'(C_{PL})\Delta T_L \tag{2}$$

where m' is the mass flow rate [kg/s], C_{PL} is the heat capacity of liquid at constant pressure [kJ/kg·K], ΔT_L is the temperature difference of liquid between the inlet and outlet of the thermal siphon [K]. This expression of single-phase heat flow is based