

Effects of organic acid catalysts on the hydrogen generation from NaBH_4

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Abstract—Sodium borohydride has received much attention from fuel cell developers due to its high hydrogen storage capacity. In this study, organic acid solutions such as malic, citric, acetic acids were successfully utilized to accelerate and control hydrogen generation from stabilized sodium borohydride solutions. The generated hydrogen by malic acid was then continuously supplied to a PEMFC single cell. A power density of 168 mW cm^{-2} was achieved with a hydrogen flow rate of 0.050 L min^{-1} that was generated by adding 10 wt% aqueous malic acid to the stabilized sodium borohydride solution at an air flow rate of 0.11 L min^{-1} without humidification. Further increase of power density to 366 mW cm^{-2} is practicable by maintaining a precise hydrogen flow rate of 0.3 L min^{-1} . The current study focuses on the development of an instant hydrogen generation method for micro fuel cell applications. We successfully demonstrated that fast and direct generation of hydrogen could be achieved from stabilized borohydride using inexpensive organic acid solutions rather than expensive metal catalysts and a PEMFC single cell could be operated by generated hydrogen.

Key words: Sodium Borohydride, Malic Acid, Fuel Cell, Hydrogen, PEMFC, Hydrolysis

INTRODUCTION

Fuel cells are being extensively studied and developed throughout the world as one of the most feasible next-generation clean energy sources. There are many types of fuel cells; the proton exchange membrane fuel cell (PEMFC), which utilizes hydrogen as a fuel, has major applications in automobiles, residential uses, and portable devices. The automobile industry and city gas industry have been particularly motivated to develop PEMFC. Recently, portable applications have attracted the attention of the fuel cell industry. For example, the next generation of high bandwidth mobile devices, battery chargers and military applications are good niche markets for portable fuel cells since these applications require a supply of higher power density than existing batteries can provide. Consequently, the need for a better battery with a longer operating time is a top priority to the portable electronic device industry.

However, PEMFCs in portable applications have encountered several obstacles such as expensive and complicated fuel reformers and bulky hydrogen storage. Considering the mobile environment, the high cost and space limitations are inevitable. Thus, the direct methanol fuel cell (DMFC) has been studied extensively as an alternative for the battery. With fuel cartridge replacement, DMFCs are expected to provide real benefit based on their high energy density and instantaneous refueling time. However, high material costs due to high precious metal catalyst loading ($6\text{--}8 \text{ mg cm}^{-2}$), lower power density due to methanol crossover, and slower kinetic response than that of hydrogen-fuelled PEMFC are obstacles to the development of DMFC.

Recently, NTT and Hitachi Maxell announced micro fuel cell prototypes based on PEMFC technology [1,2]. An economical and efficient supply of hydrogen is critical for the success of PEMFC

in portable applications.

Generation of hydrogen from sodium borohydride (NaBH_4) solution is attractive considering the relatively high gravimetric storage efficiency as well as the possibility of on-site generation. However, there are also certain disadvantages to NaBH_4 that must be addressed, such as recycling of NaBO_2 byproduct, high cost of NaBH_4 , which is approximately $\$80 \text{ kg}^{-1}$, low energy efficiency due to heat loss from the exothermic reaction, etc.

Many studies have been dedicated to hydrogen generation from hydrolysis of NaBH_4 solutions [3]. Most studies have used metallic catalysts such as Ru [4,5], Pt on carbon [6] or metal oxide [7], Ni and Co [8,9], Co-B and Co-P [10,11] to accelerate hydrogen generation from stabilized NaBH_4 solutions. However, precious metal catalysts are not economical in light of the disposable cartridge concept in portable fuel cells. Zhang et al.'s study [12] newly adopted ethylene glycol for the generation of hydrogen by alcoholysis reaction, which might have better potential in the micro fuel cell applications.

In an early study, Schlesinger et al. [13] evaluated many acid accelerators in the hydrogen generation reaction and demonstrated that complete hydrolysis of NaBH_4 could be achieved rapidly by addition of acid. In particular, malic acid was recognized as a catalyst for rapid generation of hydrogen from NaBH_4 solutions [14].

Xia and Chan [15] studied the hydrogen generation behavior of NaBH_4 in the presence of Ru catalyst and calculated the amount of hydrogen generated from a PEMFC single cell by integrating the current curve over the entire measuring period. In another study [16], hydrogen was continuously generated from the Ru-loaded fixed bed reactor, and a PEMFC hybridized with a battery was successfully operated in the power range from 100 to 650 W.

In the current study, we investigated the behavior of hydrogen generation from NaBH_4 solution by adding aqueous organic acids such as malic acid, citric acid, and acetic acid. It is demonstrated that organic acids offer some advantages over expensive metal catalysts for the hydrogen generation in portable fuel cells. Especially

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malic acid is being illuminated in detail to a certain extent based on its high generation rate during the screening experiments. Malic acid is an organic dicarboxylic acid that is commonly found in apples and is the source of extreme tartness. Adequate amounts of malic acid solution were added to stabilized NaBH_4 solution to achieve the rapid and constant generation of hydrogen. In addition, generated hydrogen was directly fed to the anode side of PEMFC single cell to check the operation feasibility for application to portable fuel cells with power range of several watts.

EXPERIMENTAL

1. Materials

Sodium borohydride (NaBH_4) powder (98% purity) and NaOH powder (98% purity) were obtained from Daejung Chemicals & Metals Co., Ltd. Malic acid (99% purity), citric acid, and acetic acid were purchased from Junsei Chemicals.

2. Experimental Methods and Apparatus

A stainless-steel jacketed batch reactor was washed thoroughly with distilled water and dried (Fig. 1). A 100 g solution of 20 wt% NaBH_4 and 5 wt% NaOH was then placed in the bottom of the reactor. When the reactor and constant temperature water circulator had been prepared, the jacket was set to 20 °C to maintain a constant reaction temperature. 10–30 wt% organic acid solutions were then pumped into the reactor at a fixed rate with a micro pump.

When the hydrolysis reaction began, the mass flow meter valve was open to monitor the amount of hydrogen generated. The accumulated volume and generation rate of hydrogen were recorded by a computer connected to the mass flow meter.

The pumping period for the acid was carefully controlled by monitoring the rate of hydrogen generation in the mass flow meter. The generated hydrogen was saturated by flowing through a glass bubbler right before being fed to the anode of a single cell PEMFC. However, since the flow rate of hydrogen after the bubbler was not

consistent due to the pressure drop through the bubbler and the effect of the bubbler was negligible, the bubbler was later removed. The single cell PEMFC was connected to the electrical load and the performance was recorded by the computer connected to the load. The outlet of the anode was open to the air; thus unconsumed hydrogen was properly vented. Air to the cathode of single cell was also saturated in the glass bubbler at the rate of 0.06 L min⁻¹.

3. MEA Fabrication

The membrane electrode assembly (MEA) for a single cell operation was fabricated as follows. The electrodes consisted of uncatalyzed carbon papers; in other words, gas diffusion layers and catalyst layers were directly coated on the membrane. Gas diffusion layers were hydrophobized by soaking in liquid PTFE solution before coating the carbon layer. 50 wt% Pt/C catalyst was used for the anode catalyst layer, and 50 wt% Pt/C was used for the cathode catalyst layer. The catalyst solution was composed of polar solvents, water, catalyst and 30 wt% Nafion solution, which acts as a binder and an electron conductor in MEA geometry. It is widely accepted that Nafion binder is located on the electrode catalyst particles as a bridge among the active catalyst sites, as well as between the catalysts and the membranes in the interface. All components were mixed and thoroughly sonicated to ensure the complete dispersion of nanosized catalyst particles. The carbon and catalyst layers were deposited on the carbon paper and on the membrane, respectively, using the spraying method. The five-layer MEA was obtained by hot pressing the gas diffusion layers on both sides of Nafion 112 membrane at 120 °C. Catalyst was deposited at 0.3 mg cm⁻² for the anode and 0.4 mg cm⁻² for the cathode.

MEA prepared with an active area of 30.25 cm² was installed in the gold-coated single cell test fixture and then tested in the fully equipped lab test station, before being evaluated in the experimental setup to determine the hydrogen generated by malic acid.

RESULTS AND DISCUSSION

1. Hydrogen Generation Behavior by Organic Acids

Three organic acids, malic acid, citric acid, and acetic acid, were

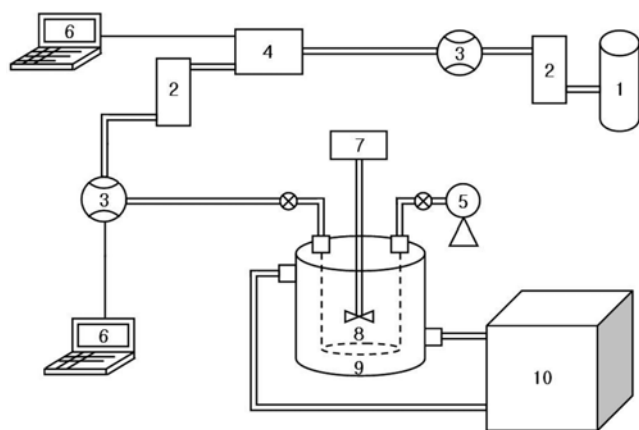


Fig. 1. Schematic for hydrogen generation from stabilized sodium borohydride solution and direct operation of a PEMFC single cell.

- | | |
|---------------|----------------------------|
| 1. Air bomb | 6. Data acquisition system |
| 2. Bubbler | 7. Motor |
| 3. MFC | 8. SUS reactor |
| 4. fuel cell | 9. Jacket |
| 5. Micro pump | 10. Circulator |

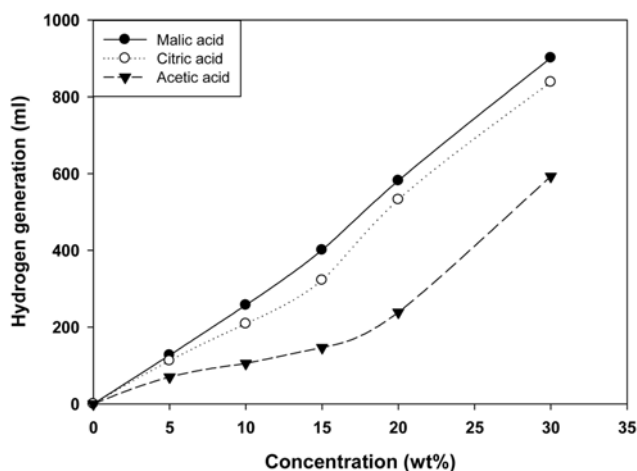


Fig. 2. Behavior of hydrogen generation according to the change of organic acid concentration at the reactor temperature of 20 °C.

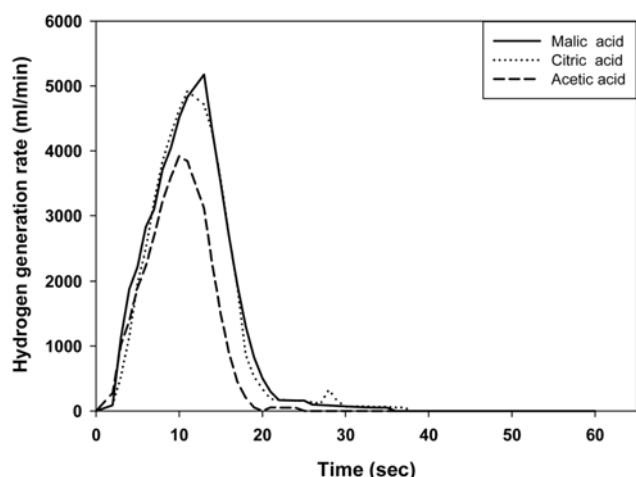


Fig. 3. Behavior of hydrogen generation rate via one dosage of 30 wt% acid solutions at the reactor temperature of 20 °C.

chosen and applied to the stabilized 10 wt% sodium borohydride solutions in order to catalyze the hydrogen generation reaction. Dependence of the hydrogen generation on the acid concentrations is shown in Fig. 2. Ten grams of acid solution prepared in various concentrations was injected into the reaction vessel each time and the amounts of generated hydrogen were measured. It was revealed that the amounts of hydrogen generated were proportional to the concentrations of malic and citric acids. However, proportionality between the concentration of acetic acid and the amount of hydrogen generated was less pronounced compared to those of the other two acids.

Characteristics of the generation rate of hydrogen by one dosage of each acid are shown in Fig. 3. The fastest generation was achieved by malic acid addition and similar result was also observed for the citric acid addition. The peak hydrogen generation was observed after 10 seconds of the acid injection and generation rates were drastically reduced after 20 seconds. It suggests that the hydrogen generation rate can be controlled to some extent by manipulating the type and injection amount of acid. Considering the portable fuel cell environments, it is also very important to have quick hydrogen generation from the fuel cartridge on demand. Quick generation of hydrogen can be achieved even without the mechanical stirring. Since malic acid demonstrated the highest generation rate and yield in this experiment, this material was adopted in the following controlled release and cell test experiments resultantly.

An interesting and promising result of hydrogen generation by organic acids was that a relatively constant amount of hydrogen could be generated by injecting the 10 g of 30 wt% organic acid catalyst solutions every 15 minutes as shown in Fig. 4. The amounts of hydrogen generated varied 1 to 2 liters depending on the type of organic acids; a slight increase of hydrogen generation was observed with each dosage of acid solution mainly due to the catalytic effect.

$$PV=nRT \quad (1)$$

According to Eq. (1), ideal gas law, the theoretical amount of hydrogen expected to be generated from the prepared borohydride solution is 25.43 liters. 83.5% of generation yield by malic acid was obtained compared to the theoretical value. It was then followed

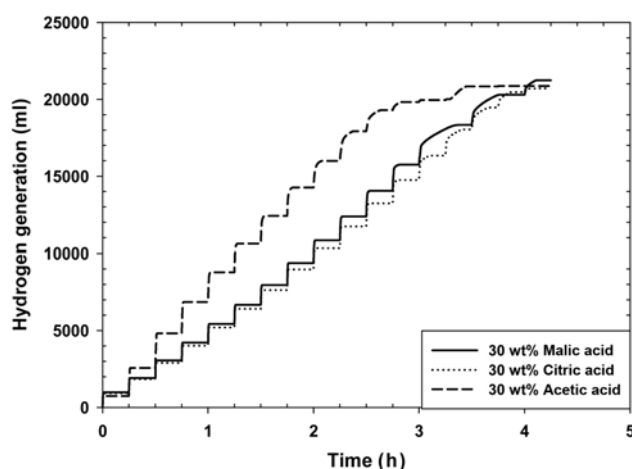


Fig. 4. Behavior of hydrogen generation according to the number of acid solution injections. 10 g of acid solution was injected every 15 minutes.

by 81.4% yield by acetic acid and 78.5% yield by citric acid.

It is critical to generate the exact amount of hydrogen on demand instantaneously in portable PEM fuel cell environment. In the real environment, hydrogen flow rate from the fuel cartridge to the fuel cell stack could be controlled by the on-off of precise pressure valve. However, by understanding and controlling the relationship between hydrogen flow rate and amounts of the organic acids, exact and safe generation of hydrogen could be achieved.

2. Hydrogen Generation by Malic Acid and a Single Cell Performance

The polarization behavior of a single cell PEMFC was tested by using hydrogen from a cylinder in the laboratory test station in order to optimize the electrochemical performance before installing a sin-

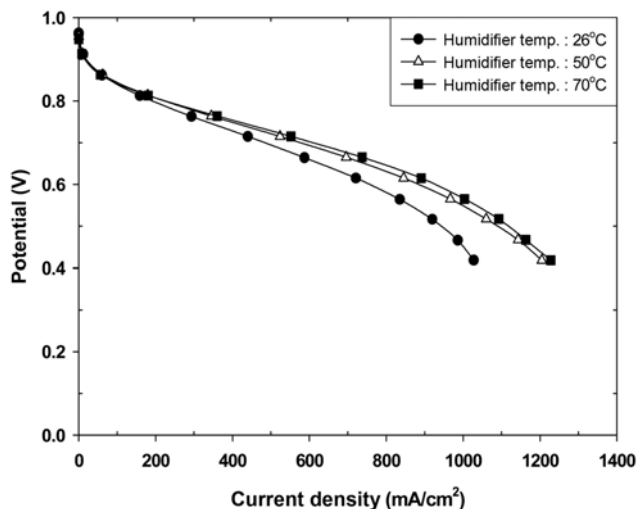


Fig. 5. Polarization curve of a PEMFC single cell according to changes in humidity by varying humidifier temperature (H_2 ; 0.3 L min^{-1} , Air 1.3 L min^{-1}); Humidifier temperature 70 °C (cell temperature 70 °C), Humidifier temperature 50 °C (cell temperature 50 °C), Humidifier temperature 26 °C (cell temperature 31 °C).

gle cell and testing it in the loop with on-site hydrogen generation by malic acid as shown in Fig. 1. The results are shown in Figs. 5 and 6. Before being fed to the anode in the lab test station, hydrogen from the cylinder was saturated by controlling the dew point humidifier temperature.

Fig. 5 shows the effects of humidifier temperature on the single cell performance in the fuel cell test station. Since the humidity of the tested single cell is expected to be quite low in experiments using malic acid, as expected for micro fuel cell systems in real environments, it is beneficial to determine the performance at both low and high humidity conditions in the lab test station. However, hydrogen generated from the NaBH_4 solution is believed to be saturated to a certain extent, which is helpful for proton transport through the proton exchange membranes in the portable environments.

The current density was 720 mA cm^{-2} at a potential of 0.6 V with humidifier temperature at 26°C and cell temperature at 31°C , which is close to the humidity conditions of a cell in the portable environment. The current density increased from 720 mA cm^{-2} to 930 mA cm^{-2} as the humidifier temperature was increased from 26°C to 70°C .

Since this experiment relies on the on-site hydrogen generation in micro fuel cell to power portable electronics, the volume of the micro fuel cell system should be as small as possible and efficient utilization of hydrogen from a limited-volume fuel cartridge is highly recommended. Thus, we also evaluated the effect of hydrogen flow rates on the electrochemical performance in the lab test station before evaluating cell performance with on-site hydrogen generation using malic acid. Fig. 6 shows that the current densities in scan voltage mode varied from 680 to 830 mA cm^{-2} at the potential of 0.6 V as the hydrogen flow rate was changed from 0.05 L min^{-1} to 0.30 L min^{-1} for the anode; the air flow rate was 1.3 L min^{-1} for the cathode, the humidifier temperature was 26°C and the cell temperature ranged from 31 to 35°C . This result suggests that cell performance is not significantly affected by changes in hydrogen flow rate at an air flow rate of 1.3 L min^{-1} .

In Figs. 7 and 8, hydrogen was generated by controlling the amount of malic acid solution added to the NaBH_4 solution. Using organic

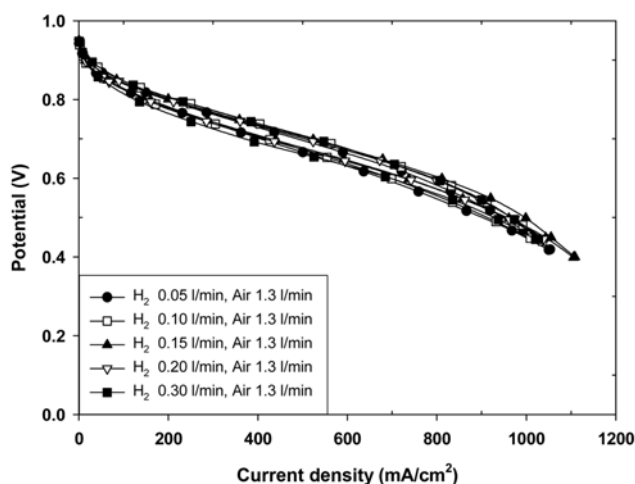


Fig. 6. Polarization curve of a PEMFC single cell according to changes in hydrogen flow rate in the feed stream (humidifier temperature 26°C , cell temperature $31\text{--}35^\circ\text{C}$, Air 1.3 L min^{-1}).

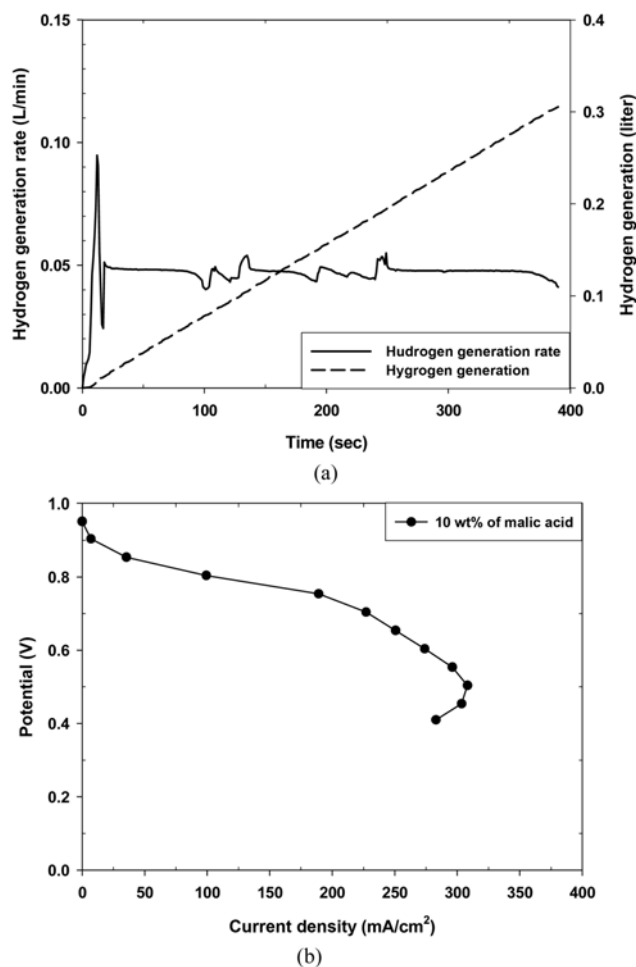


Fig. 7. (a) Hydrogen generation rate and volume of hydrogen generated; (b) I-V curve; 10 wt% malic acid was added to the 20 wt% NaBH_4 solution stabilized with 5 wt% NaOH . Hydrogen flow rate was 0.05 L min^{-1} at the anode and air flow rate was 0.11 L min^{-1} at the cathode.

malic acid as a catalyst to promote hydrogen generation from NaBH_4 is quite unique compared to the precious metal catalysts typically used in the hydrogen generation from stabilized NaBH_4 solutions, particularly when a cheap and disposable cartridge is needed for micro fuel cell applications. Hydrogen generation is easily controlled by adding aqueous malic acid. The two solutions, i.e., aqueous malic acid and NaBH_4 solution, are easily mixed by designing a channel in the fuel cartridge. The low cost and environmentally benign properties are also advantageous.

In Fig. 7(a), 9 mL of 10 wt% malic acid solution was added during the 380-second cell operation, so that the hydrogen generation was maintained at approximately 0.05 L min^{-1} . When malic acid solution was added to NaBH_4 solution, the temperature immediately rose from 20°C to 35°C and was recorded. A hydrogen flow rate of 0.05 L min^{-1} was assumed to be reasonably acceptable for the micro fuel cell environment. The total amount of hydrogen generated was 0.3 L (Fig. 7(a)). Note that the theoretical amount of hydrogen stored in 20 wt% NaBH_4 solution is 51.04 liters according to the ideal gas law.

I-V performance is shown in Fig. 7(b). The current density ob-

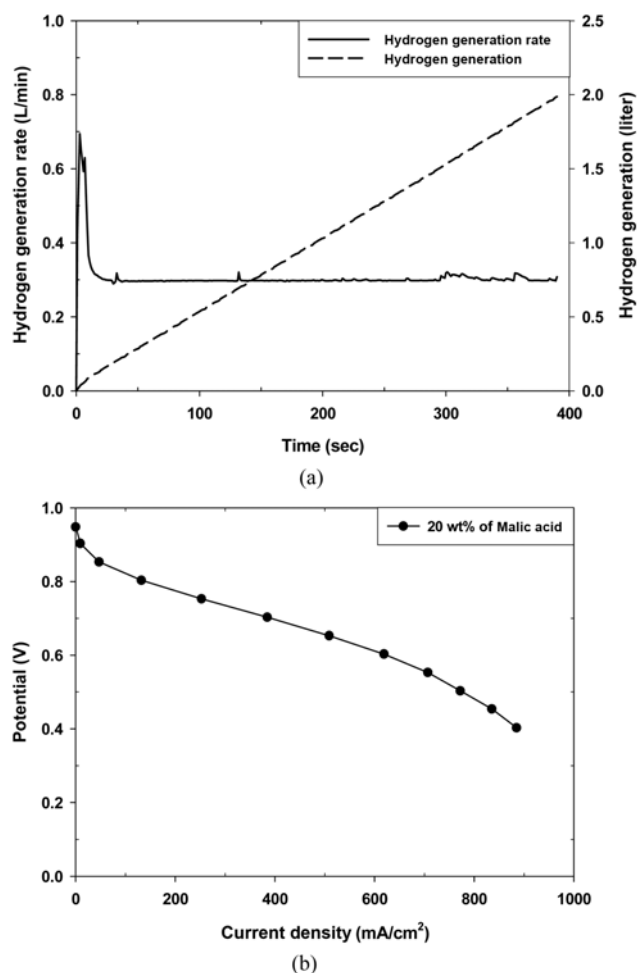


Fig. 8. (a) Hydrogen generation rate and volume of hydrogen generated; (b) I-V curve; 20 wt% malic acid was added to the 20 wt% NaBH_4 solution stabilized with 5 wt% NaOH . Hydrogen flow rate was 0.3 L min^{-1} at the anode and air flow rate was 0.06 L min^{-1} at the cathode.

tained was 280 mA cm^{-2} at the potential of 0.6 V , which is significantly lower than that obtained in the lab test station for the same single cell. Note that a current density of 680 mA cm^{-2} was achieved at the potential of 0.6 V for a single cell accommodated in the test station with feed conditions of hydrogen (0.05 L min^{-1}) and air (1.3 L min^{-1}). The difference between the experimental conditions of the standard lab test station and those of Fig. 7(b) was the air flow rate and humidity level, which were much lower in Fig. 7(b). In particular, a low air flow rate of 0.11 L min^{-1} was used since 1.3 L min^{-1} of air flow rate can only be achieved with a high flow rate micro compressor in a real micro fuel cell system, which consumes a high amount of energy generated by the fuel cell. Thus, it is highly recommended that hydrogen and air in a micro fuel cell system be supplied passively in order to increase the power density and to reduce the system volume. The experimental concept of the current study can be applied for the fabrication of a micro PEM fuel cell which is expected to power the portable electronic gadgets consuming around 2 W such as DMB phone.

The result obtained is quite promising considering the operating conditions of no external humidification and low fuel flow rate. The

hydrogen and air fuel stoichiometries at 0.6 V were only 0.85 and 0.8 , respectively, whereas typical stoichiometries for PEMFC are approximately 1.5 and 2.5 . The current density also decreased slowly from 0.75 V and dropped rapidly at 0.5 V due to the lack of fuel at high current densities since the fuel flow rate was fixed at approximately 0.05 L min^{-1} of hydrogen and 0.110 L min^{-1} of air.

In Fig. 8(a), the hydrogen flow rate increased significantly by adding 5 mL of 20 wt\% malic acid solution, which resulted in a precise hydrogen flow of 0.3 L min^{-1} . The air flow rate was reduced to 0.06 L min^{-1} , but was saturated by passing through the bubbler. The total recorded volume of hydrogen was around 2 L . In Fig. 8(b), the current density was 610 mA cm^{-2} at the potential of 0.6 V , which is considered excellent performance if it can be realized in micro fuel cells.

In summary, we successfully demonstrated that organic malic acid could be utilized as an economic hydrogen generation accelerator for stabilized NaBH_4 solution with the aim of applying this method to micro fuel cell systems. Further experiments are needed to clarify the methods of controlled hydrogen generation, such as the relationship between hydrogen flow rate and the concentration and dosage of malic acid. But several benefits of using malic acid as an accelerator in a NaBH_4 cartridge for a micro fuel cell are its low cost, easy control of hydrogen generation and chemically benign properties in the portable environment.

CONCLUSIONS

Inexpensive organic acids like malic, citric, and acetic acids instead of traditional metal catalysts were utilized to generate hydrogen in a controllable manner with the aim of the portable fuel cell applications.

Feasibility tests of PEMFC were successfully carried out by supplying hydrogen from NaBH_4 hydrolysis reaction for micro fuel cell applications. The hydrogen generation was controlled by adding a small amount of organic acid solutions to stabilized NaBH_4 solution. A current density of 280 mA cm^{-2} at the potential of 0.6 V was achieved under experimental conditions of 0.05 L min^{-1} hydrogen generated by the addition of malic acid and 0.11 L min^{-1} air without any external humidification. That is, a power density of 168 mW cm^{-2} was achieved in harsh operating conditions.

When the operating condition was further optimized with higher hydrogen flow rate and saturated air supply, a power density of 366 mW cm^{-2} was obtained. The operating conditions may be further optimized by future studies.

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