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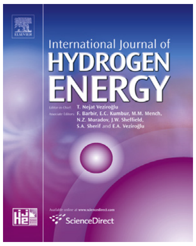

The development of a sodium borohydride hydrogen generation system for proton exchange membrane fuel cell

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This paper develops an on-demand hydrogen generation system, which can produce hydrogen from sodium borohydride ($NaBH_4$) solution, to operate proton exchange membrane fuel cell (PEMFC). We first build the hydrogen generation system, which hydrolyzes $NaBH_4$ in a batch reactor to provide a continuous supply of hydrogen to drive the PEMFC. We also discuss the impacts of solution concentration and batch volume. In addition, we develop a simulation model that evaluates the hydrogen generation and temperature responses of the system. Furthermore, we design a control strategy to adjust the batch intervals of $NaBH_4$ solution according to the PEMFC loads. We then implement the designed control on a microcontroller and integrate it with a PEMFC for experimental verification. The results confirm that the developed on-demand hydrogen generation system can hydrolyze $NaBH_4$ with a conversion rate of more than 90% so that it to continuously supplies hydrogen to drive a 3 kW PEMFC.

Introduction

Hydrogen is a potential energy carrier that can substitute for fossil fuels because of its high efficiency and free emissions. Among hydrogen applications, the proton exchange membrane fuel cell (PEMFC) is a promising alternative power source because it directly converts chemical energy to electrical energy with high efficiency, low noise, and zero air pollution. The PEMFC can therefore provide clean energy for transportation, stationary backup power, and personal electronic applications. However, the storage of hydrogen for PEMFC applications remains problematic. In some applications, hydrogen is stored in compressed containers, hydrogen-storing alloys, and carbon nanotubes. Nevertheless, the high transportation cost and low storage density of these methods may obstruct the development of PEMFC applications.

Chemical hydrides (e.g., $LiBH_4$, KBH_4, and $NaBH_4$) provide solutions for these obstructions, by virtue of their safety and high storage efficiency. Among these, sodium borohydride ($NaBH_4$) is a popular hydrogen storage material [1]. $NaBH_4$ was discovered by Schlesinger and Brown to produce uranium borohydride, and was later applied to generated hydrogen for signal balloons [2]. A $NaBH_4$ solution can rapidly produce hydrogen, especially with the use of catalysts and in low-pH

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states. Kreevoy et al. [3] discovered that the hydrolysis rate of $NaBH_4$ depends on the pH and temperature in the absence of a catalyst. In addition, the use of catalysts can significantly increase the hydrolysis rate, even in alkaline solutions. For example, Murooka et al. [4] proposed a hydrogen supply system fueled by $NaBH_4$ with nickel catalyst for 100 W PEMFC. Tomoda et al. [5] then applied a citric acid solution catalyst to improve the hydrogen generation rate at low temperature for vehicle applications.

Low-cost catalysts such as Co or Co–B [6] are favorable, compared with conventional catalysts such as Ru and Pt [7,8]. For instance, Kim et al. [9] applied a sputter Co–B catalyst to develop a hydrogen generation system that can supply hydrogen at a rate of 6.5 standard liters per min (SLPM) for 120 min to drive a 400 W PEMFC. For micro-PEMFC applications, Kim and Lee [10] developed a microreactor with Co–B catalyst with an average hydrogen generation rate of 15.6 ml/min. Kim [11] then used Co–P–B catalyst, because of its higher efficiency than Co–B for hydrogen generation, to supplied hydrogen to a micro fuel cell with a maximum power output of 157 mW at a current of 0.5 A. For vehicle applications, Kojima et al. [12] at Toyota Lab developed a $NaBH_4$ hydrogen generation system that can generate hydrogen at a rate of up to 120 SLPM to drive a 10 kW PEMFC. The generated hydrogen is of high purity and carbon free, which avoids PEMFC poisoning by carbon monoxide. Tomoda et al. [5] conducted experiments and discussed the advantages and disadvantages of fuel-cell electric vehicles powered by $NaBH_4$. In addition, the byproduct sodium metaborate ($NaBO_2$) is environmentally friendly.

The aim of this paper is to develop a stationary on-demand hydrogen generation system, and to integrate it with a PEMFC. We design the hardware structure and control strategies, and discuss the influences of $NaBH_4$ concentration and batch volume. We also consider the system dynamics and develop a simulation model that can correctly predict the system responses. The simulation model can then be applied to develop customized power systems in the future. The paper is organized as follows: Section 2 introduces the hydrogen generation system and designs a batch process for feeding the $NaBH_4$ solution. Section 3 tests the developed hydrogen generation system and discusses the effects of $NaBH_4$ concentration and batch volume. Section 4 builds a $NaBH_4$ hydrolysis model and tunes the parameters based on experimental data. The model successfully predicts hydrogen generation and temperature responses. Section 5 develops a control strategy to adjust the batch intervals according to PEMFC loads. We then implement the control algorithms on a microcontroller, and integrate it with a PEMFC for experimental verification. We then draw conclusions in Section 6.

The hydrogen generation system

The proposed hydrogen generation system consists of a 2.5 L stainless steel batch reactor, a heat exchanger with four 4 W fans, a 10 L buffer tank, a 5 L plastic fuel tank, and a control module, as shown in Fig. 1(a). We place the catalyst of cobalt oxide with nickel foam [13] at the bottom of the reactor. The system is designed to generate hydrogen at an average rate of 30 SLPM to drive a 3 kW PEMFC [14], with the schematic diagram as illustrated in Fig. 1(b). We install the push tank to pump $NaBH_4$ solution into the reactor. The solution is fed into the reactor by the following batch process:

1. Turn on valve 2 to drain the by-products out of the main reactor.
2. Turn on valve 3 to release the gas remaining in the push tank.
3. Turn on valve 5 and the extraction pump to add $NaBH_4$ solution into the push tank.
4. Turn off valve 3 and valve 5 when the $NaBH_4$ solution reaches the designed volume.
5. Turn off valve 2 when the by-products are released.
6. Turn on valve 4 to pressurize the push tank by the buffer tank.
7. Turn on valve 1 to push $NaBH_4$ solution from the push tank into the main reactor.
8. Turn off valve 1 and valve 4 when the pressure of the push tank and reactor is balanced.
9. $NaBH_4$ starts to react in the main reactor. The generated H_2 flows through the heat exchanger, cools down, and then passes through the check valve into the buffer tank.

Note that we use hydrogen to propel the $NaBH_4$ solution to prevent bubble formation in the pipes and blockage of the feeding flow, as usually happens when using chemical pumps.

Performance tests

This section integrates the hydrogen generation system for performance tests. The chemical reaction of $NaBH_4$ can be described as follows [2]:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 + 217\text{kJ} \tag{1}$$

That is, each mole of $NaBH_4$ can produce 4 mol of hydrogen and release about 217 kJ of heat [15]. We first fed the $NaBH_4$ solution of 10wt.% with a batch volume of 300 ml. The hydrogen generation rate $\dot{V}_{gen}$ and temperature responses are shown in Fig. 2 (a) (b). During the experiment, the generated hydrogen flowed into the buffer tank so that the pressure was increased. Therefore, we could measure the pressure change to estimate the hydrogen generation volume, V_{gen}, as follows:

$$V_{gen} = (\Delta P_{BT} \times F_{BT}) + V_{FC} \tag{2}$$

where ΔP_{BT} is the pressure change of the buffer tank, while F_{BT} is the volume-pressure coefficient of the buffer tank ($F_{BT} \approx 50.1$ L/Bar in our system) and V_{FC} is the hydrogen consumed by the PEMFC. For example, if the pressure change $\Delta P_{BT} = 1.29$ without PEMFC hydrogen consumption ($V_{FC} = 0$), then the generated hydrogen $V_{gen} = 64.8$ L.

On the other hand, the theoretical hydrogen generation volume can be calculated as follows:

$$V_{th} = \frac{V_{NaBH_4} \times \rho_{NaBH_4} \times W_{NaBH_4} \times 4 \times R \times T_{air}}{37.83 \times P_{air}} \tag{3}$$

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