

Short communication

Feasibility study of hydrogen generation from sodium borohydride solution for micro fuel cell applications

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Abstract

This paper presents work on hydrogen generation from sodium borohydride (NaBH₄) solution that could have great application in micro fuel cells. A hydrogen test method has been developed, which is very effective for sustained measurement of the generation rate and yield of hydrogen. The hydrogen is supplied to a proton exchange membrane fuel cell. The discharged current is measured by a computer-controlled electronic load system connecting to the fuel cell where hydrogen generation rate and yield are calculated. The study is focused on the slow release of hydrogen. The results show that if the concentration of NaBH₄ solution is 10%, no solid substance is formed and the catalyst supported on the ion-exchange resin beads remains unchanged. The hydrogen generation can be controlled by inserting or removing the catalyst into/from the solution, which can be applied to a micro fuel cell. When the concentration of NaBH₄ solution is 20%, however, the catalyst beads are broken up and dispersed in the solution (probably by the NaBO₂ crystallization force) and give rise to uncontrollable generation of hydrogen.

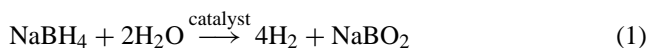
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1. Introduction

Hydrogen is recognized as an environment-friendly fuel for the future. Attention has recently been given to the generation of hydrogen by the hydrolysis of alkaline or alkaline earth metal hydrides [1]. Among these chemicals, sodium borohydride (NaBH₄) is a popular commercial material [2–7].

A stabilized aqueous solution of sodium borohydride is a safe, simple and compact source of high-purity hydrogen. The hydrolysis reaction is exothermic and proceeds according to:



Stabilized NaBH₄ solutions, which have a high pH, do not generate significant amounts of hydrogen under ambient conditions. Therefore, a catalyst is required and when this

is removed from the NaBH₄ solution, hydrogen generation ceases. Accordingly, this hydrogen generator promises a safe and fast response to hydrogen demand.

Recently, the use of micro technology for realizing power generation has been the focus of many research groups. In particular, micro fuel cells have attracted attention for application in electronic devices that require high power. Since the energy is stored as a ‘reservoir’ of fuel rather than as an integral part of the power source, fuel cells have numerous advantages over batteries. A miniaturized fuel cell can be realized through an approach that combines thin film materials with MEMS (micro-electromechanical system) technology. Micro fuel cells, which generally generate less than 5 W of electricity, can be developed by polymeric micro-machining with current collectors embedded in the flow channels [8].

This paper describes a feasibility study of hydrogen generation from sodium borohydride solution for micro fuel cell applications. Unlike the hydrogen generation system for large fuel cell stack applications, which can afford to have a fuel

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tank, pump, reactor, hydrogen separator, by-product tank, etc., the hydrogen generation system for micro fuel cell applications must be simple and small. The hydrogen generation behaviour of NaBH_4 is characterised in the presence of a ruthenium catalyst using an in-house proton exchange membrane fuel cell (PEMFC) serving as the hydrogen measurement instrument.

2. Experimental

Ruthenium catalyst particles with a high surface area were supported on ion-exchange resin beads. An appropriate amount of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (39.15 wt.% Ru, from Johnson–Matthey) was dissolved in deionized water to form 0.1 M RuCl_3 solution. The solution was acidified with HCl to convert RuCl_3 to $[\text{RuCl}_6]^{3-}$. The H_3RuCl_6 solution was added to ion-exchange resin beads (IRA-400, from Sigma–Aldrich). After drying, H_3RuCl_6 , which was impregnated on the surface of resin beads, was reduced by adding NaBH_4 solution.

In hydrogen generation experiments, 10 g of NaBH_4 solution was placed in a sealed bottle with an outlet tube. Then, 0.02 g of 5% Ru on ion-exchange resin beads, which contains 1 mg of Ru catalyst, was added into the solution. The generated hydrogen was fed to the anode of an in-house PEMFC. During the testing, the fuel cell was operated at a constant voltage of 0.1 V by means of an electronic load system (from Arbin) and the current, which reflects the hydrogen generation rate, was measured. A schematic of the experimental set-up is given in Fig. 1.

3. Results and discussion

3.1. Methods for measuring rate of hydrogen generation

In the studies of Amendola et al. [2,3], hydrogen generation was measured by monitoring water displaced from a graduated cylinder as the reaction proceeded. Dong et al. [4] measured the volume of hydrogen evolved by displacement of water levels in a U-tube. The hydrogen generated in experiments by Kojima et al. [5,6] was collected and its volume was measured by the water trap method and the generation rate was calculated from the amount evolved during 3 min from the beginning of the test. In more recent work [7], the hydrogen generation rate was detected by a micro-motion flow meter.

There are drawbacks with these testing methods. The accuracy and sensitivity of recording the water level are not high, the gas volume will vary with temperature and pressure, and the water vapour in the hydrogen affects the accuracy of the flow meter.

In the present study, a method for measuring the rate of hydrogen generation has been developed. The hydrogen generated from the hydrolysis of NaBH_4 was fed to the anode

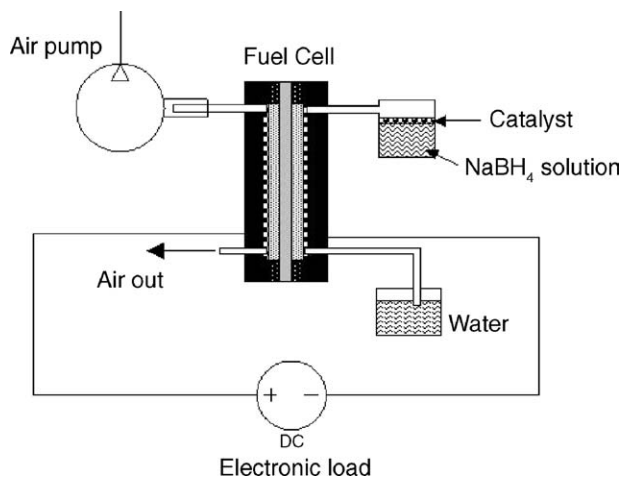


Fig. 1. Schematic of hydrogen generation testing system (in the single fuel cell, grey represents the electrolyte, dots the electrode, black with white dots gasket and black the flow channel plate).

of a PEMFC. The fuel cell has dimensions of $5\text{ cm} \times 5\text{ cm}$. The highest current that the fuel cell can discharge at $25\text{ }^\circ\text{C}$ is 3 A. The current that the fuel cell can discharge is more than sufficient (about 10 times) for determining the hydrogen generation rate in this study. The gas flow channel was designed to be serpentine to prolong the flow path. One end of the flow channel was connected to the hydrogen source, while the other was blocked by water. This ensures that all hydrogen generated would be consumed by the fuel cell to generate electrical current. During the initial period (about 10 min), the gases in the bottle and tubes, apart from hydrogen, were expelled. Bubbles in the water showed the expelled gases. After 10 min, no bubbles were observed and no water was sucked into the outlet tube for many hours. At the end of testing, when the reaction rate was very slow, the water started to be sucked into the outlet tube, at which time the test was terminated. The fuel cell was set at a constant voltage of 0.1 V and the current was measured and logged. Based upon the conservation of mass, the number of electrons and hence the current can be calculated. At conditions of standard temperature and pressure, 1 A of current corresponds to 7.6 ml min^{-1} of hydrogen. Knowing the current (correspond to the hydrogen consumption rate) as a function of time, the accumulated hydrogen can be determined by integrating the current curve over the entire measuring period.

This testing method has a number of advantages. First, the accuracy and sensitivity of recording the current are high. Second, since the number of electrons per unit time was measured, the temperature and other entrapped gases, such as water vapour, would not affect the results. Third, due to high accuracy and sensitivity of measurement, only small amount of catalyst was used, which results in a very low reaction rate. Thus, the reaction proceeds at constant temperature. Also, the pressure was always same as atmosphere pressure. The test data can be used to analyze the reaction kinetics.

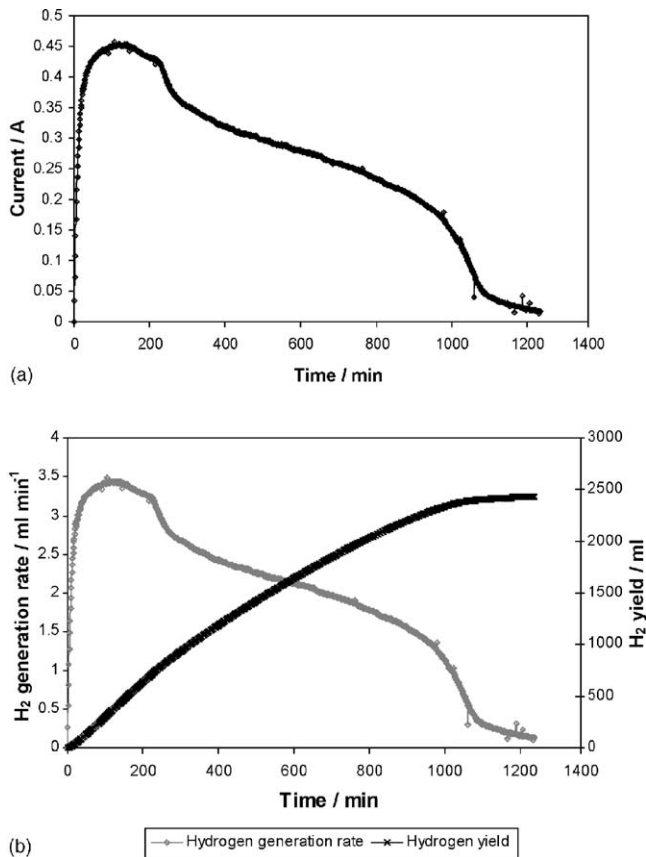


Fig. 2. Response of hydrogen generation from 10% NaBH_4 solution (solution: 10% NaBH_4 ; 10% NaOH ; 80% H_2O ; catalyst: 0.02 g; 5% Ru on IRA-400 ion-exchange resin beads, amount of Ru is 1 mg). (a) Raw current curve recorded by computer-controlled electronic load system. (b) Hydrogen generation rate and yield calculated from recorded current.

The raw current curve obtained during a total testing time of around 22 h is shown in Fig. 2a. The current was recorded at 1 min intervals. In this test, the solution contains 10% NaBH_4 , 10% NaOH and 80% H_2O (by weight). The results

show that the rate of hydrogen generation is not constant. By converting the units, the hydrogen generation rate was obtained. Integrating the rate of hydrogen generation over the entire period of testing gave rise to the accumulated hydrogen produced, as shown in Fig. 2b.

3.2. Analysis of hydrogen generation for a micro fuel cell

In the studies by Amendola et al. [2,3], 0.25 g catalyst containing 5% of Ru loaded on IRA-400 anion-exchange resin, which contains 12.5 mg of Ru, was added to ~30 ml of 20% NaBH_4 solution. Theoretical results showed that the NaBH_4 solution stored 16.5 l of hydrogen. From the published data for hydrogen generation at 25 °C, it took about 25 min to generate 1 l of hydrogen, i.e., only about 6% of stored hydrogen was measured. Data from further testing was not provided.

Since the present study is focused on micro fuel cell applications, the measurements are targeting a slow release of the hydrogen. In the experiment, only 1 mg of Ru in 10 g of solution was used. In this case, the solution temperature is almost unchanged as it equilibrated with the ambient at 25 °C. Unlike the data of Amendola, the experimental results (Fig. 2) show that the volume of hydrogen generated does not change linearly with time. It is considered that the linear change observed by Amendola et al. may be due to disregard of the heat generation effect in the measurement of the volume flow rate of the hydrogen.

The hydrogen generation rate with 20% NaBH_4 solution is presented in Fig. 3. The hydrogen generation curve can be divided into four stages. The first stage is from the starting time to 261 min (point 0 to A), during which the current increases with the time. In this stage, the activity of the catalyst increases and the change in NaBH_4 concentration does not have great influence on the rate of hydrogen generation. The second stage is from 261 to 1108 min (point A to B), where the current decreases with the time. In this stage, the NaBH_4 concentration decreases and causes a decrease in hy-

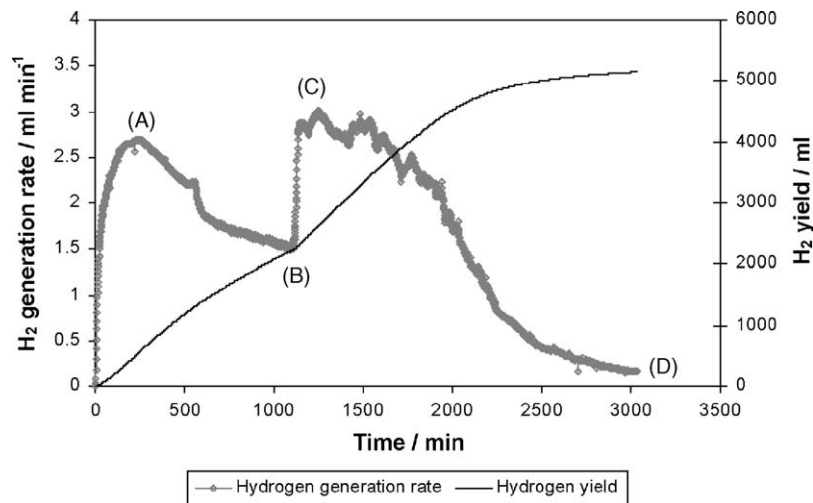


Fig. 3. Response of hydrogen generation from 20% NaBH_4 solution (solution: 20% NaBH_4 ; 10% NaOH ; 80% H_2O ; catalyst: 0.02 g; 5% Ru on IRA-400 ion-exchange resin bead, the amount of Ru is 1 mg).

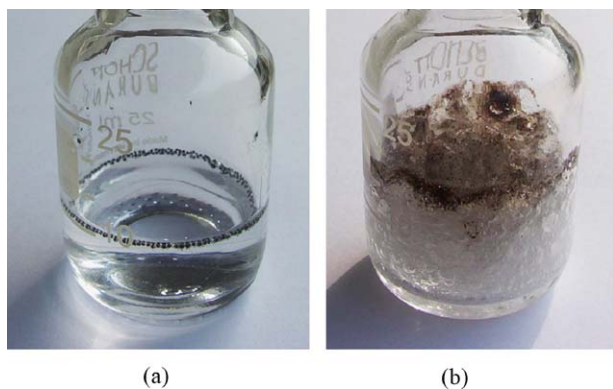


Fig. 4. Photographs of solutions taken after the tests. (a) 10% NaBH_4 ; (b) 20% NaBH_4 .

drogen generation. It is also noted that solid NaBO_2 is not formed and the solution is still clear. The third stage is from 1108 to 1148 min (point B to C), during which the current increases significantly with time. In this stage, The Ru impregnated ion-exchange resin beads are broken up into fine particles probably under the action of the NaBO_2 crystallization force. The Ru particles are displaced from the resin beads and this increases the surface of the active catalyst surface. At the end of this period, no resin beads are found in the solution, but solid NaBO_2 starts forming. The last stage is from 1148 min to the end (point C to D) The current decreases with the time and, hydrogen generation slows down with decrease in the NaBH_4 concentration. A large amount of solid NaBO_2 is produced and retards the hydrolysis reaction. The accumulated hydrogen is 5149 ml, which is 98.9% of the theoretical stored hydrogen in the solution.

A photograph of the solution taken after the test is shown in Fig. 4. There is no change in appearance of the 10% NaBH_4 solution (Fig. 4a) before and after test. No solid substance is formed and the catalyst supported on ion-exchange resin beads remains unchanged. In this case, the hydrogen generation can be controlled by inserting or removing the catalyst into/from of the solution, which can be applied to the micro fuel cells. With 20% NaBH_4 solution, the reaction products (white solid) displace the original solution (Fig. 4b). The catalyst beads (black powder on the surface) are broken up to form fine particles. Therefore, when a high concentration of NaBH_4 is used, the catalyst beads are disintegrated by the NaBO_2 crystallization force and dispersed in the solution, to cause uncontrollable hydrogen generation.

4. Conclusions

A technique has been developed for measuring the flow rate of hydrogen generated from sodium borohydride solution. The hydrolysis of sodium borohydride is characterised with the help of a fuel cell connected to an external electronic load system and the current is measured at constant voltage. The variation of the discharged current with time is an indication of the rate of hydrogen generation. The results show that if the concentration of NaBH_4 solution is 10%, no solid substance is formed and the catalyst supported on the ion-exchange resin beads remains unchanged. In this case, hydrogen generation can be controlled by inserting or removing the catalyst into/from the solution. The catalyst beads are broken up into fine particles during the course of hydrogen generation when a high concentration of NaBH_4 (20%) is used. Repeated experiments provide consistent findings. Though we do not have any explanation for this phenomenon at the moment, we suggest that the disintegration of the catalyst beads could be due to the crystallization force of NaBO_2 . Subsequent to the breaking up of the catalyst beads, hydrogen generation increases abruptly and causes uncontrollable hydrogen generation. Finally, the rate of hydrogen generation rate slows down and the accumulated gas approaches the theoretical amount of hydrogen stored in the NaBH_4 .

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