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Article

The Catalyst Loading Effects on the Feed Rate of $NaBH_4$ Solution for the Hydrogen Production Rate and Conversion Efficiency

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Abstract: The research in this study focused on the operating parameters for a high efficiency hydrogen production rate system, with the aim to design a hydrolysis of the $NaBH_4$ hydrogen production module for lightweight and efficient hydrogen production and conversion. The experiment used a reactor, where the reaction volume was about 12 mL. The parameters on the feed rate of the $NaBH_4$ solution and the catalyst loading for the hydrogen production rate and conversion efficiency were investigated. The catalyst is sufficient to allow the release of hydrogen in the 1 g/min solution, but the efficiency of hydrogen production at high flow rates has been shown to be low in previous studies. Therefore, the aim is to increase the catalyst to improve the reaction efficiency in this study. The results show that at the high temperature reaction condition, solid $NaBO_2$ will not generate on the catalyst surface to influence the hydrogen production rate when using the five pcs catalyst. When the reaction temperature was 108 °C, the average hydrogen production rate was 1.72 L/min, and the conversion efficiency was 91.2%.

Keywords: $NaBH_4$; catalyst loading; $NaBO_2$; hydrogen production efficiency

1. Introduction

At room temperature, with no catalyst participation in the catalytic hydrolysis to produce hydrogen, the hydrogen generation efficiency is not ideal. The catalyst needs to be added to participate in the reaction. The catalysis includes Co-Rh/Ni foam [1], Pt/LiCoO2 [2], Co-powder [3], Co-P-B [4], etc.

Mancier et al. [5] propose a semi-theoretical explanation of the appearance of a second plateau during the discharge of overcharged nickel oxyhydroxide electrodes (NOHE), based on transmission line models of the charge–discharge processes of the active matter.

Yinghuai et al. [6] studied that boron compounds now have many applications in a number of fields, including Medicinal Chemistry. Although the uses of boron compounds in pharmacological science have been recognized for several decades, surprisingly few are found in pharmaceutical drugs.

Kim et al. [1] used a Co-Rh/Ni foam catalyst in a continuous dynamic reactor. Studies have shown that increasing the feed rate can also increase the hydrogen production rate. However, due to the lengthier sodium borohydride residence production time, the hydrogen conversion with the borohydride decreases relatively. The reactor can supply 6.5 L of hydrogen per minute, and with the addition of fuel cells, successfully supplies hydrogen to 400 W of proton exchange membrane fuel cells (PEMFCs).

Zhang et al. [7] added a heat exchange tube to the reaction chamber, and used the heat generated by the hydrolysis reaction of sodium borohydride to preheat the sodium borohydride solution that did not contact the catalyst. The reaction chamber is cylindrical and has a size of φ20.92mm × 152.4 mm. The catalyst is a mixture of metals such as Co-Rh, which is sintered on nickel. The reaction chamber contains a total of 33.1 g of catalyst. The experimental results show that there is a hydrogen production device using a heat exchange tube as a preheating mechanism. At each feed rate, the hydrogen production efficiency is more than twice that of a hydrogen production device without a heat exchange mechanism.

Gislon et al. [8] pressed sodium borohydride into a solid, installed in the interlayer of the reaction chamber, and added a solution containing a catalyst, thereby increasing the theoretical maximum hydrogen production of sodium borohydride. The size of the reaction chamber is φ44 mm × H55 mm, which contains solid sodium borohydride. The hydrogen generator can continuously produce 0.1–0.3 L/min of hydrogen for 20 h and can be used for about 10–30 W fuel cells.

Galli et al. [9] designed a tubular reactor with a total height of 150 mm, an outer tube diameter of 16 mm, and an inner tube diameter of 4 mm. It was filled with 1 g of the Co-powder catalyst for the continuous flow hydrogen production. The hydrogen production was about 0.5 L.

Kim et al. [10] designed a hydrogen-producing micro-reactor composed of three sheets of photosensitive glass, using a foam nickel-supported Co-PB catalyst. This micro-reactor had a reaction temperature of 40 °C. The hydrogen production rate was 15.6 ml/min, which is enough to operate 1.3 W PEMFC.

Zhen-Ming Huang [11] concluded that the higher the increase in catalysts, the hydrogen production performance gradually declines. The reason for the decrease in the hydrogen production rate is that the Ru particles on the carrier fall, and by-products of the reaction may cover the catalyst surface. This affects the catalytic reaction between the catalyst and the sodium borohydride hydrolysis solution.

In summary, hydrogen production via the use of NaBH4 is a new hydrogen production technology that is convenient, practical, and can effectively produce high-purity hydrogen. The sodium borohydride is configured as a solution, and liquid fuel allows the rate of hydrogen production to be easily adjusted. The recent development of the NaBH4-PEMFC system lies in the development of a sodium borohydride hydrolysis catalyst, the design of a hydrogen production device, and the optimization of the system performance.

This has resulted in sodium borohydride becoming the first choice of new hydrogen generation sources. However, the reaction rate of hydrogen production from hydrolysis is slow. In order to improve the hydrogen production rate, the catalytic capacity of the catalyst must meet the target requirements; therefore, the design of the hydrogen production system is one of the most important elements. Thus, the research related to the catalytic capacity and efficiency of the fuel feed reaction were both studied in this paper.

2. Hydrogen Production from the Hydrolysis of Sodium Borohydride

The basic reaction is Hydrolysis Reaction. The reaction formula is as follows [1]:

$$NaBH_4 + 2H_2O \rightarrow 4H_2 + NaBO_2 \quad (1)$$

The hydrolysis reaction of sodium borohydride to produce hydrogen is an exothermic reaction with an exotherm of 217 ± 11 kJ/mole. Because it is a self-heating reaction, it is not necessary to supply energy from the outside to continue to produce hydrogen, but the reaction speed is slow. The above reaction formula can also be carried out without a catalyst, and the reaction speed is related to both the pH value and temperature of the solution.

3. Results and Discussion

3.1. Effect of Fuel Feed Flow on Hydrogen Production Efficiency

During the process of sodium borohydride hydrolysis for the production of hydrogen, the output of hydrogen can be changed by adjusting the feed amount of the solution. In addition, the concentration of sodium borohydride can also be adjusted to change the hydrogen content of the solution. The feed rate of the sodium borohydride solution was set between 1–3 g/min, and each 1 g/min was a feed test to measure the hydrogen production at different feed rates in this experiment. In addition to adjusting the feeding amount of sodium borohydride solution, the values of other parameters are fixed at the same time. The concentration of sodium borohydride is 20 wt.%, the concentration of sodium hydroxide is 3 wt.%, the catalyst is a Ru/Ni foam catalyst, and the mass fraction of the Ru- is 4% of the entire foam. The area is a cylinder with a diameter of 10 mm.

From the hydrogen production line in Figure 1, it can be seen that the increase in the amount of feed increases the hydrogen production. However, the increase in hydrogen production decreases the reaction efficiency of the solution. The higher the feed rate, the lower the hydrogen conversion efficiency. At a feed rate of 1 g/min, the hydrogen conversion efficiency is as high as 96%, and at a feed rate of 3 g/min, the hydrogen conversion efficiency is 77%, which can decrease as much as 24.6%. Therefore, we can infer that the catalyst is sufficient to completely release the hydrogen contained in the 1 g/min solution, but for the 2 g/min and 3 g/min solutions, there is no way to completely release the hydrogen because the contact time with the solution is not long enough. That is, the hydrogen cannot be completely released, and the solution will be discharged out of the reactor with the hydrogen. Another more likely reason is that the amount of catalyst is not sufficient to ensure that the hydrogen content of the solution is completely released by the catalyst.

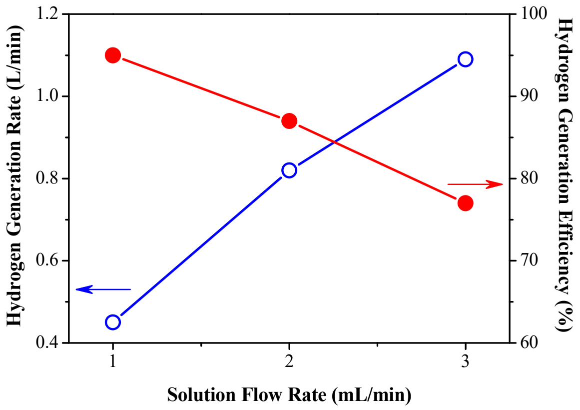

Figure 1. Effect of fuel feed flow on hydrogen production efficiency.

3.2. *Effect of Catalyst Dosage on Hydrogen Production Efficiency*

According to the experimental results on the influence of the fuel feed flow on the hydrogen production efficiency, it is apparent that the size of the catalyst is insufficient. Additionally, the contact time between the catalyst and the solution is not long enough, so that the hydrogen cannot be released completely and the solution is discharged out of the reactor with the hydrogen. Therefore, the reaction efficiency of hydrogen production was explored by increasing the amount of catalyst. The feed rate of sodium borohydride solution was set at 2 g/min as a test to measure the efficiency of hydrogen production at different amounts of catalyst in this experiment. Except for adjusting the amount of catalysts, the values of other parameters were fixed as follows: the concentration of sodium borohydride remained at 20 wt.%, the concentration of sodium hydroxide was fixed at 3 wt.%, the catalyst remained a Ru/Ni foam catalyst, the mass fraction of Ru loading was 4%, the area was always a cylinder with a diameter of 10 mm and the amount of catalysts used ranged from 1–5.

It is apparent that as the amount of catalyst increases, the output of hydrogen also increases from the hydrogen production line in Figure 2. As the amount of catalyst increases, the hydrogen conversion efficiency will also increase. The conversion efficiency of hydrogen using one catalyst was 87.6%, and the conversion efficiency of hydrogen using three catalysts was increased to 93.8%, and the increase rate was as high as 6.2%. However, the hydrogen conversion efficiency using four catalysts decreased slightly. As a test, a feed rate of 3 g/min of a sodium borohydride solution was used to measure hydrogen production efficiency at different catalyst dosages. Except for adjusting the amount of catalysts in the experiment, the values of other parameters were fixed again as follows: the concentration of sodium borohydride was 20 wt.%, the concentration of sodium hydroxide remained at 3 wt.%, the catalyst was a Ru/Ni foam catalyst, the mass fraction of the Ru- was 4% of the whole foam, the area was always a cylinder with a diameter of 10 mm and the amount of catalysts used ranged from 1–5.

It can be seen from Figure 2 that from one catalyst being tested to four catalysts being tested, all have a good hydrogen production rate, and, the hydrogen production rate gradually decreases with five catalysts tested. There are two possible reasons for this decrease in the rate of hydrogen production: firstly, the reaction of the same substrate has been completed and the reaction of raw materials must be added when the catalyst is used in multiple particles; secondly, the by-product sodium borate ($NaBO_2$) following the reaction may cover the surface of the catalyst, affecting the catalytic reaction between the catalyst and the sodium borohydride hydrolysis solution.

It is known from the formula (4) studied by Kim [5], that when the hydrogen generation rate (V) reaches nearly 100%, the increase in catalyst will decrease the hydrogen generation efficiency (η). Only when the feed rate (u) increases, can a new reaction mechanism be opened.

Kim-related [10] experimental studies have shown that increasing the feed rate can also increase the hydrogen generation rate, but the relative conversion rate of sodium borohydride decreases due to the retention time of sodium borohydride. That is, the feed rate and hydrogen generation rate will be mutually constrained.

Based on the above analysis, when multiple catalysts are used, the reaction under the same substrate has been completed. So, the main aim should be to increase the reaction of raw materials. That is, the optimal amount of catalyst used in this study should be a feasible target.

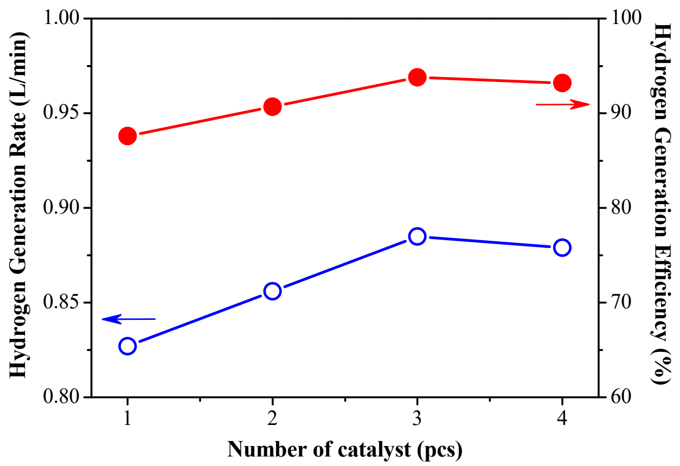

Figure 2. Effect of increasing catalyst dosage on hydrogen production efficiency (1). (Fuel 2g/min).

It can be found that the hydrogen conversion efficiency using one catalyst is 77.6% in Figure 3, and the hydrogen conversion efficiency using four catalysts is increased to 93%, an increase of 15.4%.

Results show that the hydrogen conversion efficiency of using three catalysts is 82.7%, and the hydrogen conversion efficiency of using five catalysts is increased to 90.5%, an increase of 7.8% as shown in Figure 4. When increasing the amount of catalysts to six, the hydrogen conversion efficiency dropped significantly by 5%. Therefore, it can be inferred that when the amount of catalyst is increased to ensure that the hydrogen content of the solution is completely released by the catalyst, it is necessary to pay attention to the concentration of the sodium borohydride solution in order to avoid the solid sodium metaborate ($NaBO_2$) generated on the surface of the catalyst in the high temperature reaction state. This affects the efficiency of the hydrogen production reaction.

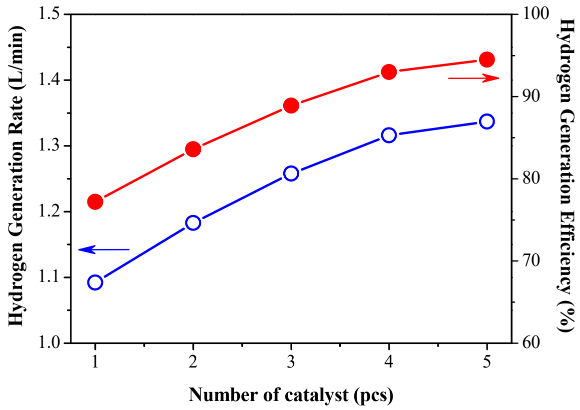

Figure 3. Effect of increasing catalyst dosage on hydrogen production efficiency (2). (Fuel 3g/min).

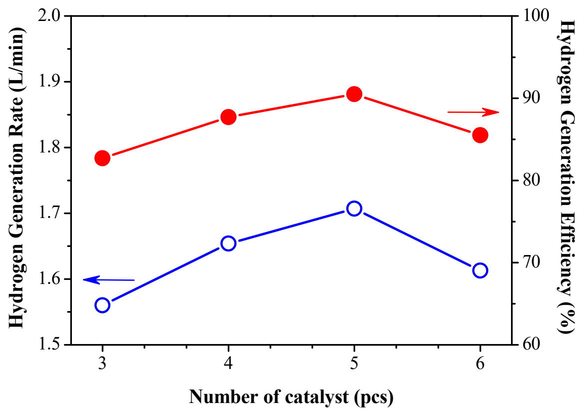

Figure 4. Effect of increasing catalyst dosage on hydrogen production efficiency (3). (Fuel 4g/min).

3.3. Long-Term Testing of Optimal Hydrogen Production Operating Conditions

In the process of sodium borohydride hydrolysis to produce hydrogen, tests involving the increase in the amount of catalysts ensure that the hydrogen content of the solution is completely released by the catalyst. They also pay attention to the concentration of the sodium borohydride solution to avoid solid metaboric acid. Sodium ($NaBO_2$) is formed on the catalyst surface under high temperature reaction, which affects the efficiency of the hydrogen production reaction. Therefore, the amount of catalyst and various operating conditions discussed are shown in Table 1. A long test is advised to see if solid sodium metaborate is formed on the catalyst surface. For the parameters, the catalyst was selected so that the mass fraction of Ru loading was 4%. The area was a cylinder with a diameter of 10 mm, and four were used. The concentration of sodium borohydride was 20 wt.%. The concentration of sodium hydroxide was 3 wt.%. The feed rate of the sodium borohydride solution was 3 g/min. Figure 5 demonstrates the hydrogen production test results after 2 h, where the reaction temperature is maintained at 101 °C, and the average hydrogen production per minute is 1.29 L. With five catalysts and a feed rate of 4 g/min, the reaction temperature was maintained at 108 °C. The average hydrogen production per minute was 1.72 L. The calculation formula of hydrogen generation efficiency η via hydrogen is [10]:

$$\eta = \frac{realH_2generation}{theoreticalH_2generation} = \frac{V}{u \times \frac{x}{38} \times 4 \times 22.4} \tag{2}$$

where V is the hydrogen generation efficiency (L/min), u is the flow rate of the solution (mL/min) and x is the concentration of sodium borohydride. The numerical values in the formula are: 38 representing the molecular weight of sodium borohydride, four is the number of moles of hydrogen generated by sodium borohydride per mole and 22.4 is the volume occupied by gas per mole.

Table 1. Operating parameter values for high-yield hydrogen production.

Concentration	$20wt.\%NaBH_4 + 3wt.\%NaOH$	
Flow rate (mL/min)	3	4
Catalyst(pcs)	4	5
Theoretical (L/min)	1.414	1.886
Real (L/min)	1.29	1.72
Efficiency (%)	91.5	91.2

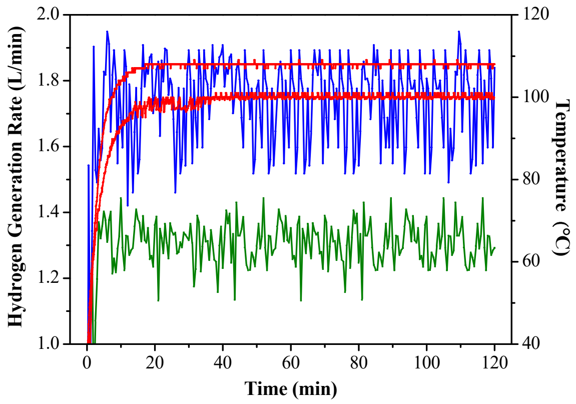

Figure 5. Long-term test results for optimal hydrogen production operating conditions.

According to the calculation formula, when using four catalysts and a feed rate of 3 g/min, the overall hydrogen production efficiency is as high as 91.5%. Similarly, the overall hydrogen production efficiency is 91.2% when using five catalysts and a feed rate of 4 g/min. After 2 h of testing, no solid sodium metaborate ($NaBO_2$) was formed on the catalyst surface.

The reactor used for the test can only hold up to six catalysts. Due to the limited reaction space for hydrogen production, a heat accumulation reaction may be formed to accelerate the precipitation of solid by-products. Therefore, the hydrogen production conversion efficiency of high feed hydrogen production is maintained above 90%.

4. Research Methods

4.1. Catalyst Preparation

The chemical substitution Ru plating reaction can be expressed as follows:

$$3Ni + 2Ru^{3+} \rightarrow 2Ru + 3Ni^{2+} \tag{3}$$

The prepared catalyst is a long sheet-shaped body of 20 mm × 30 mm, which is rolled into a cylinder with a diameter of about 10 mm. The catalyst entity is shown in Figure 6.

Figure 6. A picture of the catalyst.

The ruthenium catalyst prepared by the electrolysis plating method undergoes a substitution reaction via Ni and Ru. When the color of the plating solution changes from tan to blue-violet, and then to light green, once the color has stopped changing, the substitution reaction is complete.

The catalyst has a characteristic that, unlike the high-temperature reforming hydrogen production reaction of hydrocarbons and alcohols, the exothermic sodium borohydride hydrolysis reaction does not require additional energy to initiate and maintain the reaction. At the same time, the hydrogen can be generated at a normal temperature.

By controlling the amount of the $NaBH_4$ solution flowing through the catalyst or the amount of catalyst in contact with the $NaBH_4$ solution, the hydrogen production rate can be controlled. Therefore, it is an ideal on-site hydrogen production technology.

4.2. Hydrogen Reactor

The reactor body of the test catalyst used in this experiment is shown in Figure 7. This reactor is a rectangular parallelepiped with a length of 70 mm, a width of 46 mm and a height of 20 mm. The internal reaction volume is 12 cm^3, and the catalyst is a cylinder with a diameter of about 10 mm. Fuel inlet is a 1/8 inch Teflon tube. The hydrogen and fuel outlets are 1/4 inch Teflon tubes.

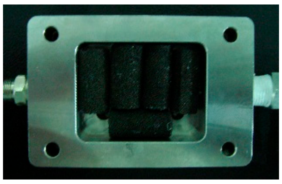

Figure 7. The hydrogen production reactor used for testing catalyst loading.

4.3. Chemical Hydrogen Production System

The hydrogen production parameter values and experimental frameworks discussed in this paper are shown in Table 2 and Figure 8, respectively. The fuel tank is filled with a certain concentration of sodium borohydride hydrolysis solution, and the fuel is sent to the reactor through the peristaltic pump to perform the hydrolysis hydrogen reaction with the ruthenium catalyst. The aqueous solution of hydrogen is recovered through a recovery bottle after the hydrogen production is started. The hydrogen is then cleared of alkaline substances via a self-made hydrogen washing bottle, followed by the measurement of the hydrogen production per min using a hydrogen mass flow meter. The temperature of the reactor is measured by a thermocouple, and its sensor is placed on the upper end of the cover plate of the reactor to monitor the temperature rise state of the reactor when the hydrogen-generating device is started.

Table 2. The best experimental values for hydrogen production by hydrolysis of sodium borohydride.

Concentration	**20wt.%$NaBH_4$ + 3wt.%NaOH**
Flow rate (mL/min)	1
Theoretical (L/min)	0.471
Real (L/min)	0.45
Efficiency (%)	96

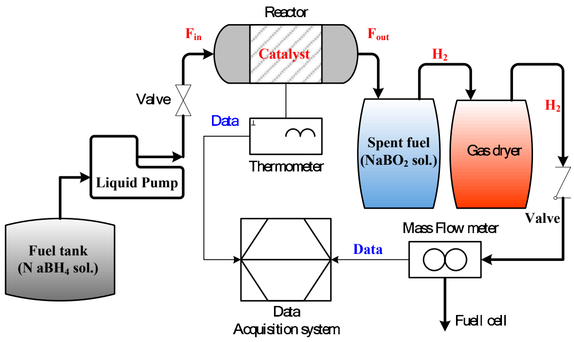

Figure 8. High-mobility hydrogen production system architecture diagram.

5. Conclusions

Using chemical hydride catalytic hydrolysis hydrogen production technology, the operating parameters of a high-mobility hydrogen production system were discussed in this study. These parameters were the catalyst amount and fuel feed flow in relation to hydrogen reaction efficiency. The experimental results show that:

(1) The hydrogen conversion efficiency using five catalysts was increased to 90.5%, and the increase was as high as 7.8%. After 2 h of testing, no solid sodium metaborate ($NaBO_2$) was formed on the catalyst surface. The reason for this is that the reaction under the same matrix has been completed when multiple catalysts are used. So, the addition of reactionary raw materials is the main factor. That is to say, the optimal amount of catalyst used in this study should be a highly feasible.

(2) Under the operating conditions of using five catalysts and a feed rate of 4 g/min, after a long-term hydrogen production test, the overall hydrogen production efficiency was as high as 91.2%, and the reaction temperature was maintained at 108 °C. The average hydrogen-yielding rate was 1.72 L per minute.

(3) The catalyst is sufficient to release the hydrogen contained in the 1g/min solution completely, but it is not efficient enough for high-flow hydrogen production. The experimental results show that increasing the amount of catalysts has a significant effect on improving the reaction efficiency and promoting hydrogen gas production.

(4) It is likely to be designed with a small volume, and therefore, the catalyst can evenly contact the solution for hydrogen production. Additionally, the length of time fuel spends in the reactor is prolonged to further aid the reaction with the catalyst. These are both advantageous and can be used as a reference for reactor design.

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