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Design of a Hydrogen Gas Generator Using Aqueous Sodium Borohydride Solution for Portable Fuel Cell Applications

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1 Introduction

Due to increasing demand for power in portable electronic devices fuel cells attained considerable attention on replacement of lithium batteries. The last two century heavily depends on fossil fuels. Due to drawbacks of fossil fuels, researches have been concentrated on alternative energy sources. Hydrogen can be considered as ideal fuel for fuel cell. Since hydrogen can be stored, transported, and converted easily to other energy forms, there has been intense scientific, industrial, and governmental interest in the development of hydrogen based energy production technology [1,2]. Also it is considered as clean fuel but it has still a problem, storage that is crucial for the supply of hydrogen for portable fuel cells.

Hydrogen has been stored in tanks in compressed or liquefied form, in hydrogen-storing alloys, and on activated carbon or nanoscale materials such as carbon nanotubes but, none of these methods are suitable for portable applications due to the low volumetric and gravimetric efficiency of hydrogen storage as well as the associated safety issues. Instead of such hydrogen storage methods, liquid fuels (methanol, ethanol, gasoline, etc.) and chemical hydrides ($NaBH_4$, KBH_4, LiH, NaH, etc.) could be employed as hydrogen sources for portable PEMFC [2]. Among them, hydrogen generation from the hydrolysis reaction of an alkaline sodium borohydride solution ($NaBH_4$) has widely investigated due to its theoretically high hydrogen storage capacity (10.8 wt %). Also, because of the high purity of produced hydrogen, it can be used as hydrogen supplier for proton exchange membrane (PEM) fuel cells [3].

Hydrogen is produced from $NaBH_4$ according to the following irreversible, heterogeneous and highly exothermic, with the heat of reaction of 210kJ/mol:

$$NaBH_4(aq) + 2H_2O \underset{catalyst}{\rightarrow} 4H_2 + NaBO_2(aq) \qquad (1)$$

Catalytic generation of hydrogen from $NaBH_4$ solutions has several advantages listed below [4]:

- NaBH4 solutions are non-flammable and not toxic.
- NaBH4 solutions are stable in air for months.
- H2 generation only occurs in the presence of selected catalysts.

But this reaction can occur to some extent even without a catalyst if the solution pH < 9. However, to increase the shelf life of $NaBH_4$ solutions and to suppress the self hydrolysis of it, $NaBH_4$ solutions are typically maintained as a strongly alkaline solution by adding NaOH. According to the reactor type and amount of reactants, NaOH can be added in various amounts but generally in the range of 5-15 wt% of reactants. It must be noted that the excess amount of NaOH decreases the hydrogen yield. Mostly NaOH in the amount of 3-5% of reactant is thought to be sufficient to control hydrogen release. [4]

- The only other product in the gas stream is water vapour.

The presence of water vapour is beneficial for use in PEM fuel cells where the water vapour can be used to humidify the PEM membrane. The H_2 gas generated is sufficiently pure and it can be used directly in PEM fuel cells without further cleanup.

As a reactant, water is important since approximately 95% of the reactant mass is occupied by it. Furthermore fuel cell applications needs low weight hydrogen devices so, water content must be decreased as possible. [4]

- Reaction products are environmentally safe.

Since reaction (1) is totally inorganic and does not contain sulphur, it produces virtually no fuel cell poisons such as sulphur compounds, CO, soot, or aromatics.

- H_2 generation rates are easily controlled.

The heat generated by reaction Eq. (1), 75 kJ/mole H_2 formed, is considerably less than the typical > 125 kJ/mole H2, produced by reacting other chemical hydrides with water. This promises a safer, more controllable reaction.

Moreover, to generate H_2, $NaBH_4$ solution is allowed to contact catalyst either by dipping catalyst into a $NaBH_4$ solution or injecting $NaBH_4$ solution on catalyst. This ensures fast response to H_2 demand, i.e., H_2 is generated only when $NaBH_4$ solution contacts with catalyst. When H_2 is no longer needed, $NaBH_4$ solution is removed from catalyst and H_2 production ceases.

- Volumetric and gravimetric H_2 storage efficiencies are high.
- The reaction products can be recycled.
- H_2 can be generated even at 0°C.

Also hydrogen could be generated at temperatures below 0°C if water-methanol or water-ethylene glycol mixtures were used. [5]

2 Experimental

In this work, we construct a batch system for hydrogen production where hydrogen generating reactor is approximately 30mL three neck tube reactor that is stayed in a water bath. From one neck, alkaline $NaBH_4$ solution is introduced, from the other neck the reaction temperature is measured and recorded online. The generated gas that exits from reactor comes to the water displacement column that is filled with water. The scale is placed under the column for determining the change in the water amount and the scale is also connected to the computer for online recording the data. From that displacement of water the generated amount of hydrogen is determined. Figure 1 shows the experimental setup.

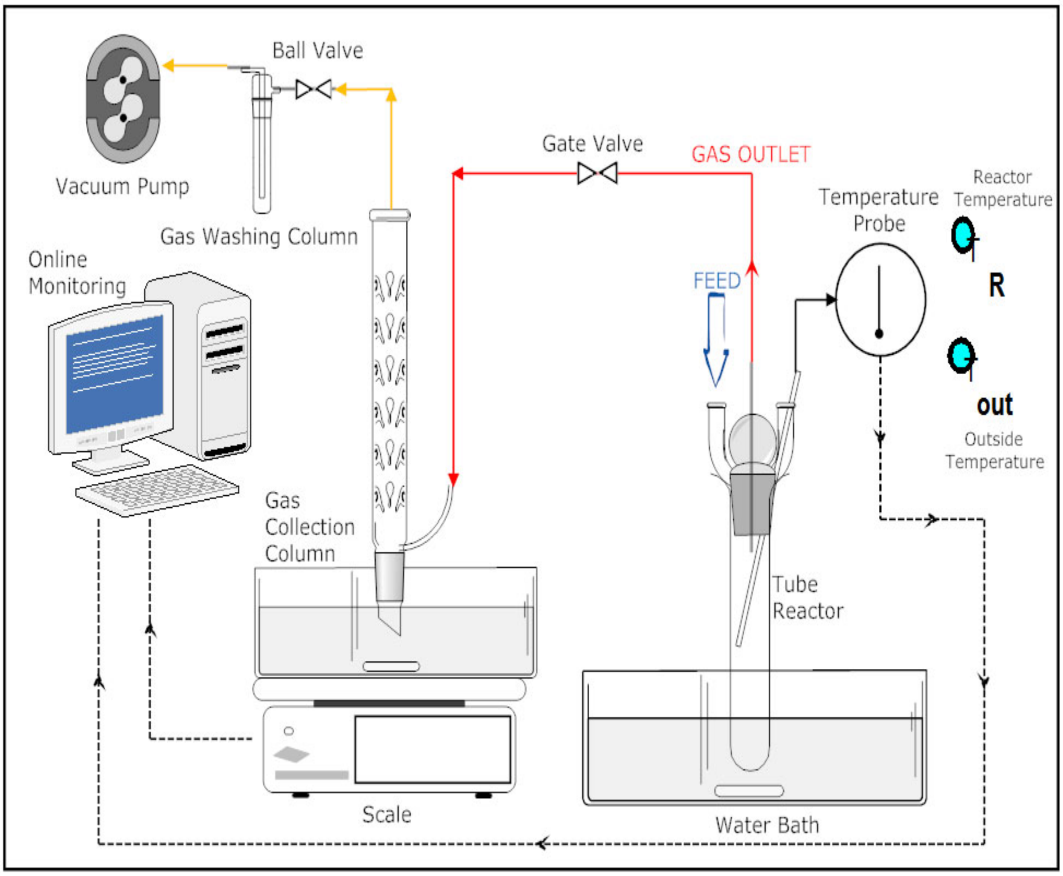

Figure 1: Experimental setup for hydrolysis of sodium borohydride.

In experiments first, water displacement column is filled with water by the help of vacuum pump. In order to prevent the water leakage to the pump, there is a gas washing column for collecting coming water. Then the solutions are prepared. Since $NaBH_4$ spontaneously reacts with water, while the spontaneous hydrolysis can be depressed in alkaline solutions, we prepared solutions on sodium hydroxide (NaOH) medium. The commercial catalyst that is 20% HP Pt on Vulcan XC-72 (ETEK®) is used in powder form to initiate the reaction. The desired amount of catalyst is weighted and placed into the reactor. Some amount of deionized water (1-2mL) is added on the catalyst to wet and introduce a homogenous medium. Then necessary amount of NaOH is weighted and dissolved in 14mL of deionized water. When alkaline medium is established the $NaBH_4$ is added to finish the solution preparation. During the set of experiments amount of water used is fixed. For the high temperature experiments this prepared solution is heated until it reaches to the reaction temperature before adding to the reactor. After that the solution is introduced to the reactor. When it comes to contact with catalyst the hydrogen is started to be generated. The generated gas comes to the water displacement column from the bottom. After it enters the column the water level reduces and this pressurizes the scale under it. The change in the scale is measured at every 0.2s. Also the temperature of the reaction and the ambient temperature are recorded at every 0.2s.

3 Results

There are mainly four parameters that are affecting the hydrogen generation such that $NaBH_4$ concentration, catalyst amount, NaOH concentration and temperature. To investigate the order of magnitude of their effects the controlled experiments were carried out. The effect of $NaBO_2$ is not considered in this work.

To analyze the effect of $NaBH_4$ concentration on H_2 generation rate three sets of experiment were prepared. In these sets, the only parameter that was changing is $NaBH_4$, others were kept as constant. These three experiments were carried out at constant temperature of 20□C. The pressure of system was 0.94atm. It was found that as $NaBH_4$ concentration increases the amount of hydrogen increases. The initial hydrogen generation rates are nearly the same for all these three experiments but, through the completion of reaction the rates were changing. This shows that the reaction rate is dependent of concentration of sodium borohydride solution catalyzed with Pt/C.

As mentioned before, the solutions of $NaBH_4$ were prepared in NaOH in order to prevent self hydrolysis of sodium borohydride. To investigate the effect of NaOH concentration again three sets of experiments were conducted that had 1ww% NaOH, 5ww%NaOH and 10%NaOH. It was found that the amount of hydrogen produced is same within 3 cases as expected since the $NaBH_4$ amount did not changed. Also, as NaOH concentration increases the H_2 generation rate decreases accordingly. So we conclude that for high production rates we have to optimize the amount of NaOH that also stabilize the solution.

When catalyst amount and temperature was considered as expected it is seen that the hydrogen production rate increases with increase of catalyst and temperature whereas the maximum amount of hydrogen produced does not changes.

To determine the kinetic model of hydrolysis reaction on commercial Pt/C catalyst, method of excess is used. After the experiments we concluded that the reaction rate depends on concentration of $NaBH_4$ and NaOH, catalyst amount and temperature. By using power law we propose a model:

$$r_{H_2} = f(T, C_{NaOH}, C_{NaBH_4}, C_{cat})$$

$$r_{H_2} = ke^{-E_a/RT} C_{NaBH_4}^{\alpha} C_{NaOH}^{\beta}$$

After calculations the rate model proposed is of the form that:

$$r_{H_2}' = 5.2 \times 10^{-3} \times \frac{C_{NaBH_4}^{0.235}}{C_{NaOH}^{0.405}} \qquad \text{for } 20^0\text{C and } 0.048\text{gPt/C with } \text{R}^2 = 0.994$$

For the temperature analysis Arrhenius plot is drawn shown in Figure 2.

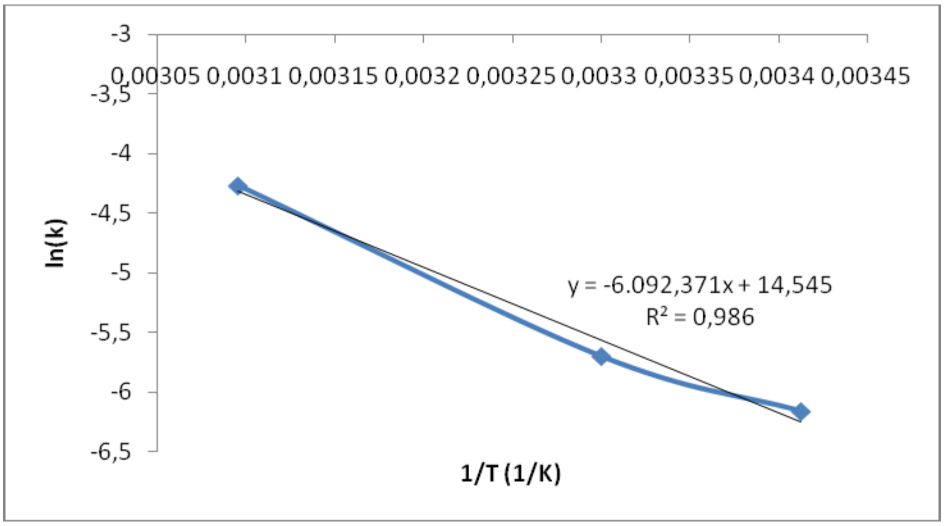

Figure 2: Arrhenius plot.

From Figure 2, the pre-exponential factor and activation energy are found as

$2\times10^{6}\dfrac{mol}{L.\min}$ and 50.65 kJ/mol respectively.

So the rate expression takes the form:

$$r_{H_2}' = 2\times10^{6}\times e^{-\frac{50.65}{RT}}\times\frac{C_{NaBH_4}^{0.235}}{C_{NaOH}^{0.405}} \qquad \text{for 0.048g Pt/C with } R^2 = 0.986$$

The catalyst effect must be introduced to the model in the activation energy but this is not investigated through this work.

4 Conclusions

Hydrogen generation from the hydrolysis of stabilized sodium borohydride solution offers a convenient, practical and effective way for portable fuel cell applications. Using $NaBH_4$ solutions reduces inherent safety concerns associated with long-term gaseous H_2 storage. H_2 production occurs on demand and reaction products are not toxic. Even the presence of water vapour is beneficial for use in PEM fuel cells where the water vapour can be used to humidify the PEM membrane. The H_2 gas generated is sufficiently pure and it can be used directly in PEM fuel cells without further cleanup.

In the present work, hydrogen generation system for portable applications has been studied and developed. The 20% Pt/C catalyst was utilized in the form of powder to initiate the hydrolysis reaction. The four parameters that are affecting the H_2 generation rate such as amount of catalyst, $NaBH_4$concentration, NaOH concentration and temperature has been widely investigated. It was seen that under Pt catalyst reaction behaves nearly zero order with respect to the $NaBH_4$. Also, the increase in NaOH concentration which is used to prevent self hydrolysis of $NaBH_4$ results decrease in the rate. The catalyst amount and temperature significantly affect the H_2 generation rate in a positive manner as expected. At the end of controlled experiments the rate equation for hydrolysis reaction has been derived. Moreover, at ambient conditions the generation rate was estimated as 2.14L/min.g Pt catalyst for 0.23M $NaBH_4$-0.27M NaOH solution.

This indicates that our generator system is suitable for portable applications of PEM fuel cells.

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