

## **2006-354: STUDY OF SODIUM BOROHYDRIDE CATALYST FOR HYDROGEN GENERATION - PURDUE UNIVERSITY SURF PROGRAM**

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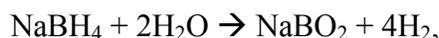
# Study of Sodium Borohydride Catalyst for Hydrogen Generation - Purdue University SURF Program

## Abstract

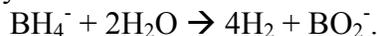
Proton exchange membrane fuel cells (PEMFC) need pure form of hydrogen for this metal hydride seems to be one of the best storage media. Amongst hydrides, sodium borohydride, NaBH<sub>4</sub> is desirable due to its high hydrogen storage efficiency of 10.80% and the excellent stability of its alkaline solutions. The alkaline borohydride solutions undergo hydrolysis in presence of various transition-metal catalysts to produce hydrogen. The hydrolysis product being borox it can be recycled. For the hydrolysis process of NABH<sub>4</sub>, various catalysts of Pt, Ru, Ni, Co etc., have been developed for hydrogen production from borohydride solutions and reported in recent years. However, implementation of these catalysts into the fuel cell is a challenge. A summer research project with an undergraduate was launched in developing catalyst for hydrogen generation in PEMFC fuel cell. Catalysts based on chlorides of Co, NI and Ru was developed and was directly deposited on metal foam. The resulting catalyst particles are nano-size and hence provide high catalytic activities in hydrogen generation from sodium borohydride solutions. Experiments were performed on the characterizing hydrogen generation rate as function of temperature and catalysts type. The project was carried under summer undergraduate research fellow (SURF) program.

## Introduction

Proton exchange membrane fuel cells (PEMFC) are on the verge of commercialization and expected to replace the internal combustion engine in transportation as well as residential power production<sup>1</sup>. However, efficient operation of the PEMFC needs hydrogen in pure form. In view of the above, on site hydrogen production from the chemical hydrides is attractive, since the hydrogen will be purer without any fuel cell poisons. Among the hydrides, sodium borohydride, NaBH<sub>4</sub> is desirable due to its high hydrogen storage efficiency of 10.80% and the excellent stability of its alkaline solutions. Schlesinger and Brown<sup>2</sup> disclosed a method of preparing alkali metal borohydrides and they noted that sodium borohydride was highly soluble in water, was stable in solution up to 400°C, and could be used to reduce metal salts to their metallic form, such as the reduction of nickel sulfate to nickel boride, Ni<sub>2</sub>B. Schlesinger *et al.*<sup>3</sup> have reported that the alkaline borohydride solutions undergo hydrolysis in presence of various transition-metal catalysts to produce hydrogen. Sodium borohydride reacts with water according to the following reaction:



alternatively, in an alkaline borohydride solution as:



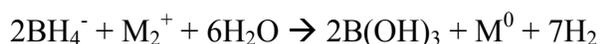
Schlesinger and Brown<sup>1</sup> realized that the formation of the metaborate ion (BH<sub>4</sub><sup>-</sup>) made the hydrolyzing solution basic and quickly slowed the reaction; however, they found that the use of metal salts acted as catalytic accelerators for the hydrolysis reaction. Mn(II)Cl<sub>2</sub>, Fe(II)Cl<sub>2</sub>,

Co(II)Cl<sub>2</sub>, Ni(II)Cl<sub>2</sub>, and Cu(II)Cl<sub>2</sub> were reduced with NaBH<sub>4</sub>(aq) and shown to produce black precipitates that also acted as catalyst to the hydrolysis reaction. Co(II)Cl<sub>2</sub> showed the greatest catalytic activity of the salts tested, in addition to forming a precipitate with the highest catalytic activity as compared to the other precipitates. For the hydrolysis process of NaBH<sub>4</sub>, various catalysts of Pt, Ru, Ni, Co etc., have been developed for hydrogen production from borohydride solutions and reported in recent years<sup>4-9</sup>. However, implementation of this catalyst into the fuel cell for in situ hydrogen generation is a challenge. The recycling of the spent products require energy source. For this nuclear heat is proposed to be used in recycling the products. Thus, the total cycle does not involve any green gas emission and makes use of nuclear reactor heat resulting in economic fuel cells usage. A research project with an undergraduate student was launched under summer undergraduate research fellow (SURF) program. The project involved in developing catalyst for hydrogen generation in PEMFC. Catalysts based on chlorides of Co, Ni and Ru was developed and was directly deposited on a metal foam and analysis of the hydrogen generation.

## Catalyst Development

The following procedure outlines the production of metal borides from the reduction of metal salts via combination of the salts with a solution of sodium borohydride. Figure 1 shows the test apparatus. The procedure calls for the addition of a salt solution to the solution of sodium borohydride. The metal salt and the metal boride produced act as catalysts for the hydrolysis reaction. Because of this, the mixing is usually performed at low temperatures to prevent aggressive hydrogen evolution. The metal boride precipitate produced during the reaction should be maintained in an environment where oxygen content is minimized to prevent oxidation of the metal or the formation of borate compounds. The metal boride must go through a rinsing procedure to remove residual ions. The precipitate is then heat-treated under vacuum or nitrogen to transition the material from an amorphous form to a crystalline form.

A 200mL solution of 5-wt% NaBH<sub>4</sub> was prepared using DI water. All DI water used in the formation of solutions was purged with nitrogen prior to mixing with the solutes. 50mL of 6-wt% NiCl<sub>2</sub> was prepared and again purged with nitrogen after mixing. The metal salt reaction can be found by summing the equations for BH<sub>4</sub><sup>-</sup> reacting with M<sub>2</sub><sup>+</sup> and the reaction of BH<sub>4</sub><sup>-</sup> with H<sup>+</sup>:



This shows that if the reaction proceeds to completion, 2mol of NaBH<sub>4</sub> will be consumed for each mol of metal salt. The prepared solutions have a molar ratio of 11.1:1 NaBH<sub>4</sub> to NiCl<sub>2</sub>, providing ample excess of NaBH<sub>4</sub>. The solutions prepared were similar to the solution weight percents given by Hua, et al.<sup>7</sup>. The reaction test section is illustrated in Figure1.

The nickel chloride solution was added via an external 50mL syringe. The syringe needle as well as all tubing was used in conjunction with rubber stoppers to maintain an oxygen free environment in the reaction chamber. Nitrogen was bubbled through a flask containing DI water. The outlet tube could be raised or lowered to supply the reaction chamber with nitrogen or water.

The sodium borohydride solution was maintained near 0°C by placing the reaction chamber in an ice bath. Nitrogen and released hydrogen was off-gassed into a separate bubbler and released. Excess nitrogen was used to saturate the hydrogen gas being created for safety purposes. The bubblers were used to keep air from back flowing into the system. The sodium borohydride solution was kept well mixed during the drop wise addition of the nickel chloride via a magnetic stirrer. 25mL of nickel chloride was added in the span of one half hour. An additional 50mL of NaBH<sub>4</sub> solution was added before the final 25mL of NiCl<sub>2</sub> was injected. The final 25mL of NiCl<sub>2</sub> was also added over the course of 30 minutes.

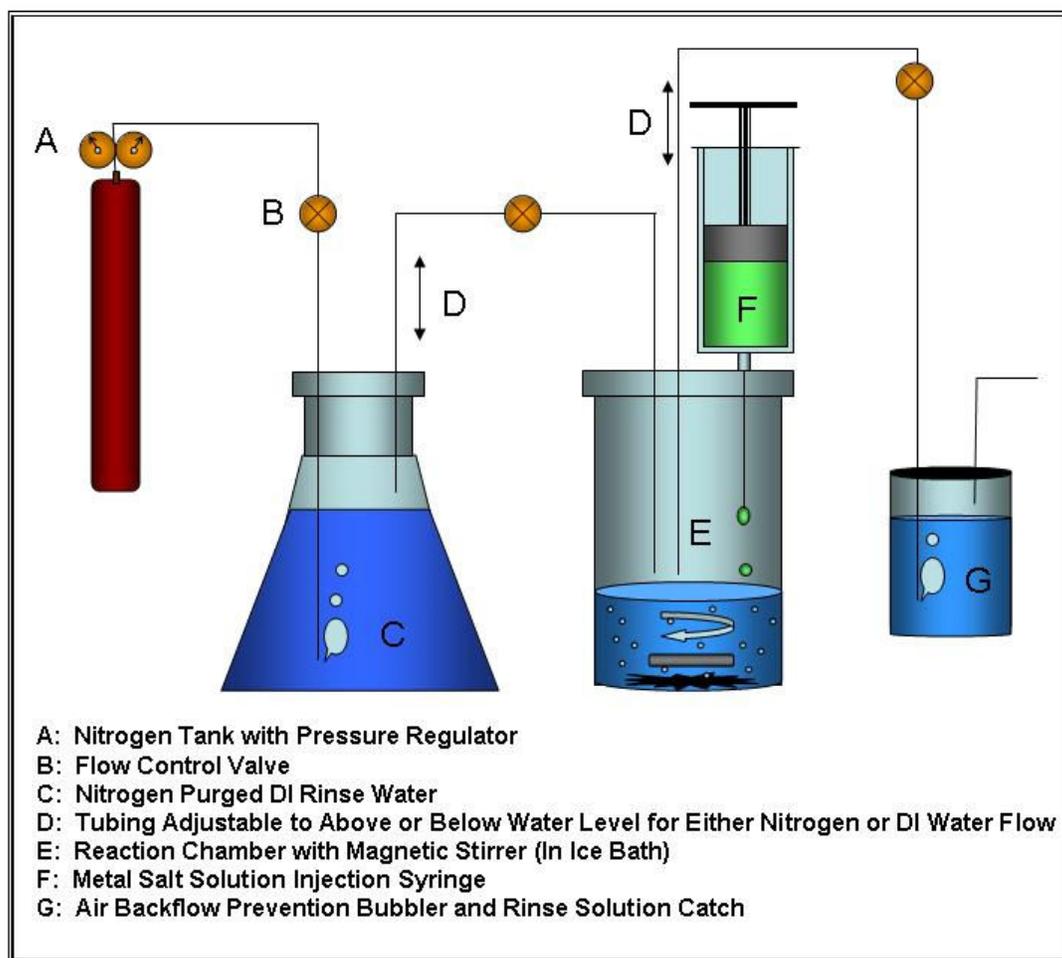


Figure 1: Schematic of experimental setup for catalyst production reactor.

As the reaction proceeded, a black precipitate was formed in the reaction chamber. After all the nickel chloride solution was added, the system was left to sit over night, under nitrogen until the precipitate had settled to the bottom of the flask. DI water was then injected into the reaction chamber by lowering the outlet tube on the nitrogen bubbler below the water line. The reaction chamber (a 2L flask) was filled with DI water and stirred. After stirring for 5 minutes, the precipitate was allowed to settle. Nitrogen was then bypassed through the bubbler and into the reaction chamber, forcing out DI water from the reaction chamber after the outlet tube had been

lowered into the rinsing solution. Water was removed until the water level was just above the settled precipitate. Some water had to be left behind in order to prevent pushing the precipitate out of the reaction chamber. This procedure was repeated with nitrogen purged DI waters five times to facilitate adequate rinsing.

After the final rinsing, the precipitate was siphoned off the bottom of the reaction flask into a separate flask maintained under nitrogen. The flask was placed into an oven at 80°C with nitrogen bubbling through the water/precipitate mixture. The mixture was allowed to dry in this manner overnight. Upon complete drying, the oven temperature was raised to 150°C and held at that temperature for two hours. The now dry powder was allowed to cool to room temperature before exposure to air. Approximately 1.1gm of Ni<sub>x</sub>B was recovered from this process. The theoretical yield is 1.36gm. This difference likely arises from some precipitate being lost during rinsing. In addition, the dried precipitate had to be scraped from the drying flask and was not completely recoverable.

### **Deposition of Catalyst to Metal Foam**

Several methods were used to attach the catalyst to the metal foam. The prepared catalyst was mixed with Nafion® ion exchange resin and painted onto the foam. This resulted in a clumpy mixture with uneven catalyst distribution. This technique also clogged most of the pores of the metal foam. Another technique was to mix the metal chloride with the Nafion® resin solution and dry the coated piece. The dried piece was then submerged in a NaBH<sub>4</sub> solution to reduce the metal salt within the ion exchange resin. This process worked well, however the piece tended to lose its catalytic activity over time. The method of choice was determined to be etching the metal foam in an acid bath then placing the rinsed, dried piece into a solution of metal chloride. A vacuum was placed on the container with the submerged piece to allow the solution to deeply penetrate the metal crevices. The sample was then removed and placed into a cold NaBH<sub>4</sub> solution. A vacuum was immediately applied to the container. After the reduction was complete, the sample was removed and allowed to dry under nitrogen. Once dry the process was repeated. The process was carried out three times. Upon completion, the metal foam piece was placed into the oven under nitrogen at 150°C. A sample that was treated in this manner is shown in Figure 2. As is shown, the catalyst is thinly and evenly deposited on the metal surface. The pores of the metal foam remain open, which will allow for even flow of sodium borohydride solution through the flow field.

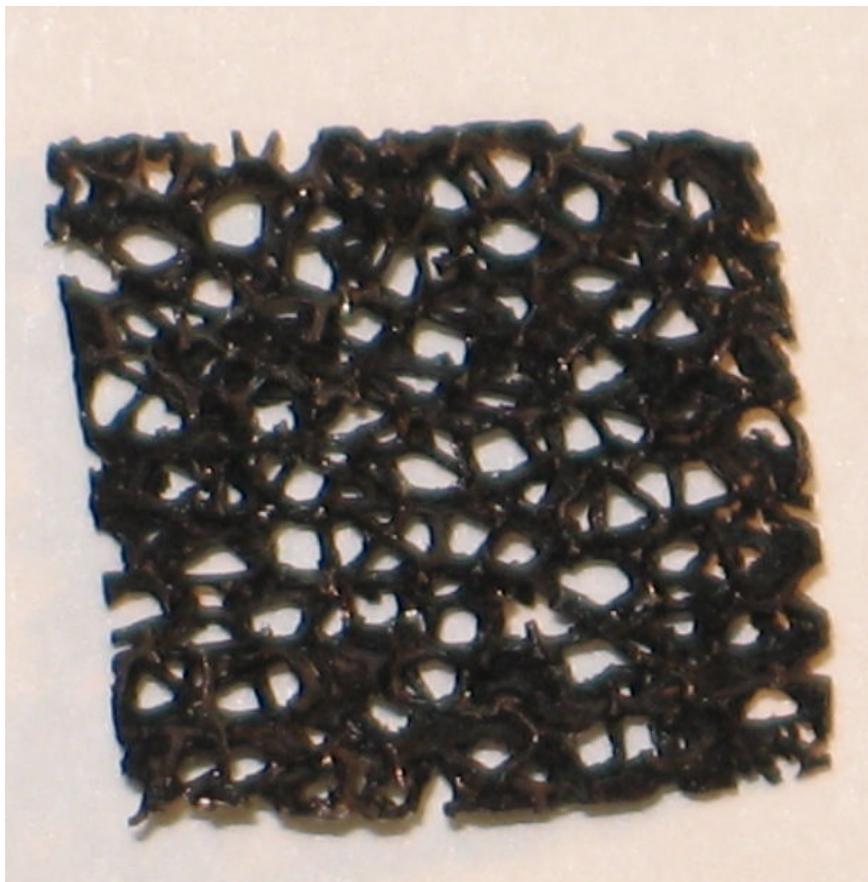


Figure 2: Catalyzed metal foam piece, 1cm x 1cm.

### Catalyst Analysis

Catalysts were produced and evaluated in terms of their effect on the hydrolysis of sodium borohydride solutions. Of primary interest are the catalysts  $\text{Ni}_x\text{B}$ ,  $\text{Co}_x\text{B}$ , and  $\text{Ru}_x\text{B}$ . Ru has the largest catalytic effect, followed by Co and Ni. It is understood that reaction rates will increase as temperature increases. It is necessary, however to optimize the rate of hydrolysis in terms of  $\text{NaBH}_4$  and base concentration. Both literature data and data obtained in the present study suggest that this characterization may be catalyst dependent, indicating additional complex mechanisms occurring during the reaction that are affected differently by different types of catalysts.

Jeong et al.<sup>9</sup> performed tests with 0.05g Ru and Co prepared from  $\text{NaBH}_4$  reduction, and 0.25g of metallic Ni in a 20 wt%  $\text{NaBH}_4$  and 5 wt% NaOH solution at 20°C and is summarized in Figure 3. The rates were 74.5, 39.9, and 4.8 mL/min, respectively.

A similar test was performed using Co and Ru catalysts prepared and deposited in 1cm x 1cm nickel metal foam via reduction of the metal salt in a Nafion solution. The foam was placed in a 10 wt%  $\text{NaBH}_4$  and 5-wt% NaOH solution at 60°C. Heat treatment for the  $\text{Co}_x\text{B}$  catalyst and the  $\text{Ru}_x\text{B}$  were two hours at 100°C and 175°C, respectively. The hydrogen generation rate for these

samples is shown in Figure 4. The base case with an untreated sample of nickel metal foam is also shown.

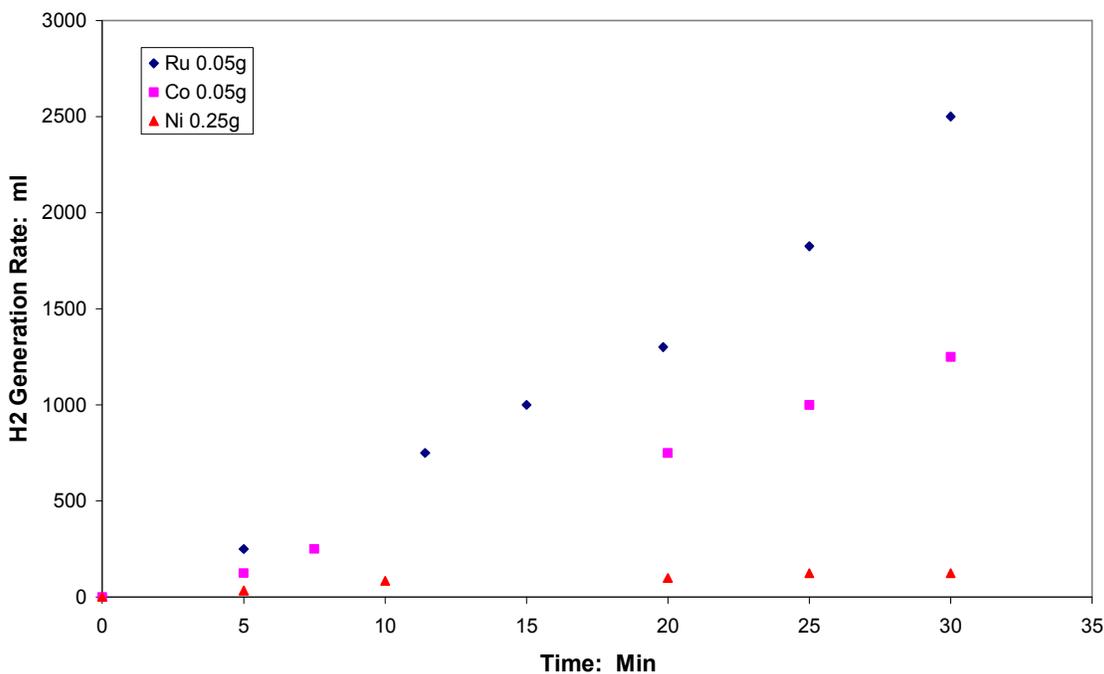


Figure 3: Hydrogen generation rate with 20 wt% NaBH<sub>4</sub> + 5-wt% NaOH at 20°C (Jeong et al<sup>9</sup>).

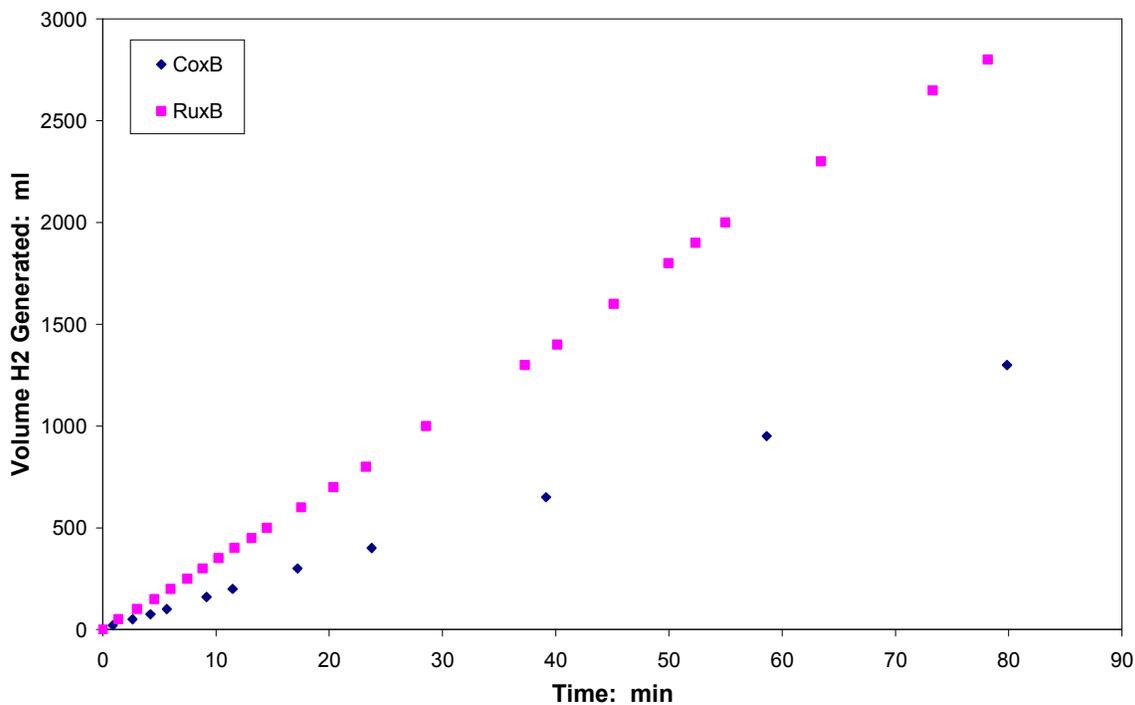


Figure 4: Hydrogen generation rate with 10 wt% NaBH<sub>4</sub> and 5-wt% NaOH at 60°C. Metal boride catalyst on Ni foam with Nafion Binder.

The amount of hydrogen generated on the piece of metal foam can be converted to a hydrogen power equivalent. This will give an estimate of the maximum amount of power that can be produced within the fuel cell from the sodium borohydride hydrolysis on the catalyzed metal foam per unit area. Catalyst loading on the metal foam is estimated at 0.01g. The power equivalent for  $\text{Co}_x\text{B}$  and  $\text{Ru}_x\text{B}$  bound to Ni metal foam with Nafion ion exchange resin along with the base case of untreated Ni foam is shown in Figure 5.

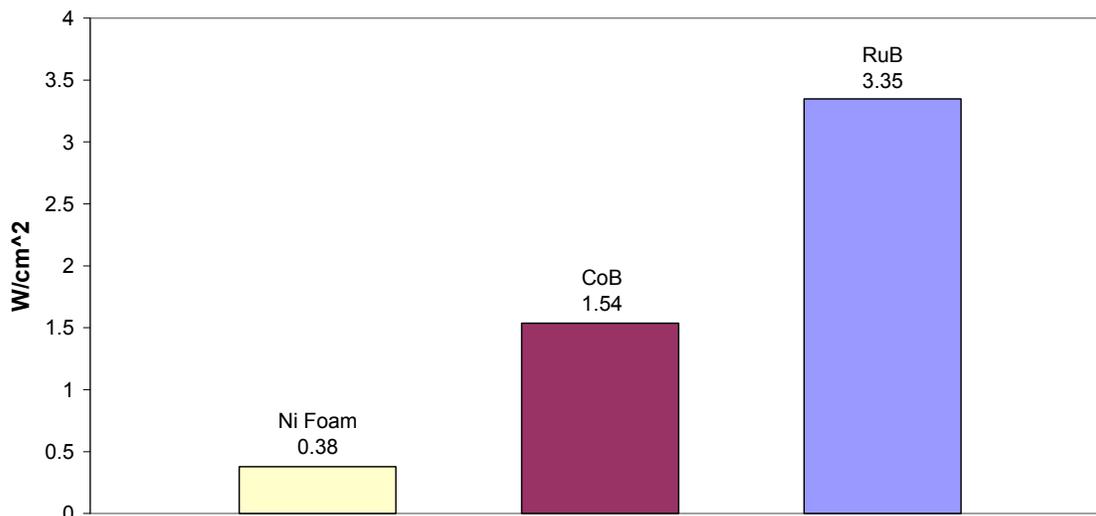


Figure 5: Hydrogen production power equivalent per unit area for 10 wt%  $\text{NaBH}_4$  and 5-wt%  $\text{NaOH}$  at  $60^\circ\text{C}$ .

The amount of hydrogen stored in a solution of sodium borohydride increases as the concentration of the hydride increases. The solution is base stabilized, indicating that as the pH increases, the rate of hydrolysis should decrease. Figure 6 shows hydrolysis rates obtained by Hua et al.<sup>7</sup> using both a  $\text{Ru/C}$  and a  $\text{Ni}_x\text{B}$  catalyst with different  $\text{NaOH}$  concentrations. The activity of the  $\text{Ru/C}$  catalyst decreases with increasing  $\text{NaOH}$  concentration while the  $\text{Ni}_x\text{B}$  activity increases. Hua argues that the hydroxide ions may be undergoing complicated surface reactions with the  $\text{Ni}_x\text{B}$  catalyst, which causes an increase in the reaction rate. Hua does not, however, comment on the differences in the way the catalysts are bound. The decrease in  $\text{Ru/C}$  activity with increasing  $\text{NaOH}$  concentration could be a result of reaction byproducts and excess  $\text{NaOH}$  blocking catalyst sites due to interactions with the carbon.

Figure 7 shows the reaction rate for various concentrations of sodium borohydride with 5-wt%  $\text{NaOH}$  concentration and Figure 8 shows the reaction rate for a constant  $\text{NaBH}_4$  concentration with varying  $\text{NaOH}$  concentrations. The data in Figures 8 and 9 illustrate results obtained by Jeong et al.<sup>9</sup>. Figure 10 and 11 show the results of a present test performed, in which 0.05g of  $\text{Ni}_x\text{B}$  catalyst was used in various solutions at a constant temperature of  $60^\circ\text{C}$ . In these cases, the catalyst was introduced to the hydrolyzing solution as a powder, which dispersed evenly across the bottom of the reaction chamber.

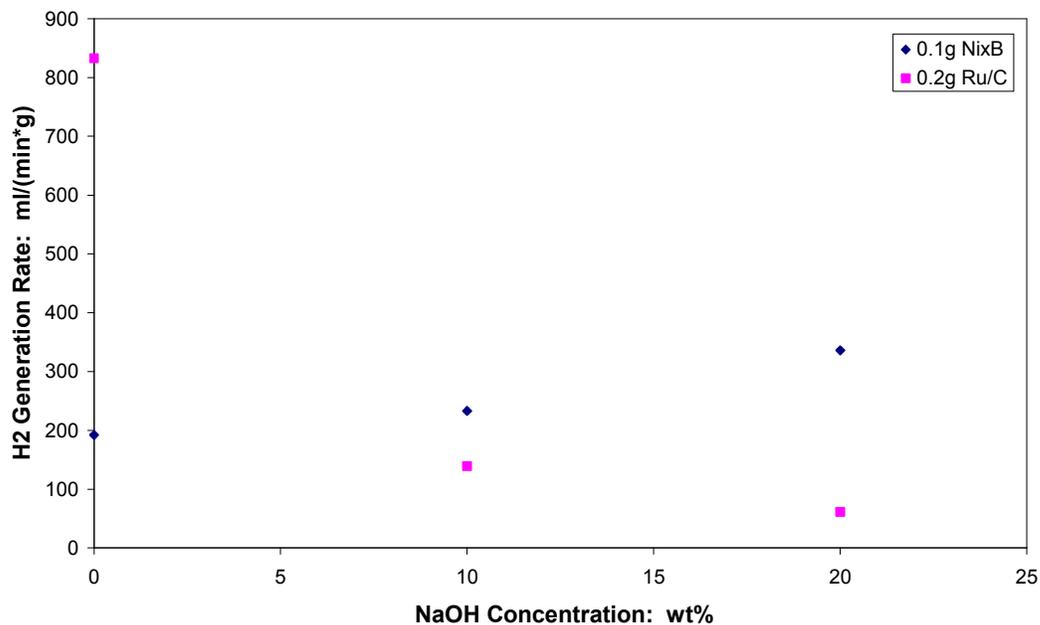


Figure 6: Hydrogen generation rate at room temperature with 0.1g Ni<sub>x</sub>B and 0.2g Ru/C in 20ml of 1.5 wt% NaBH<sub>4</sub> solution at various NaOH concentrations.

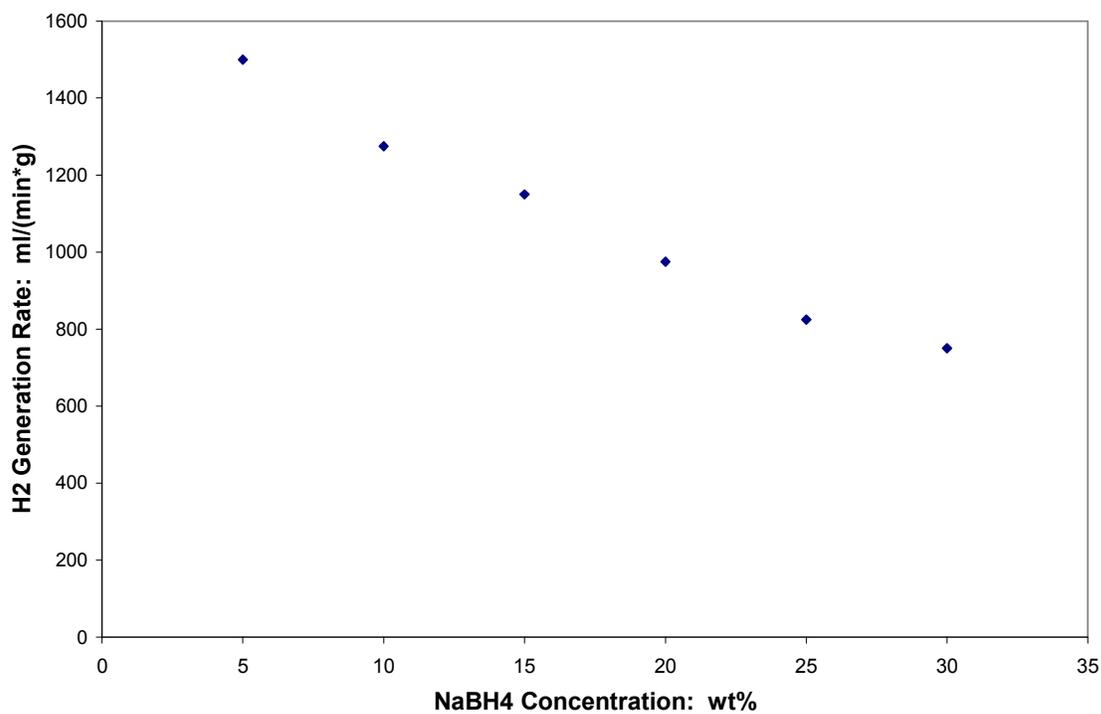


Figure 7: Hydrogen generation rate with X wt% NaBH<sub>4</sub> + NaOH using 0.05g CoB at 20°C.

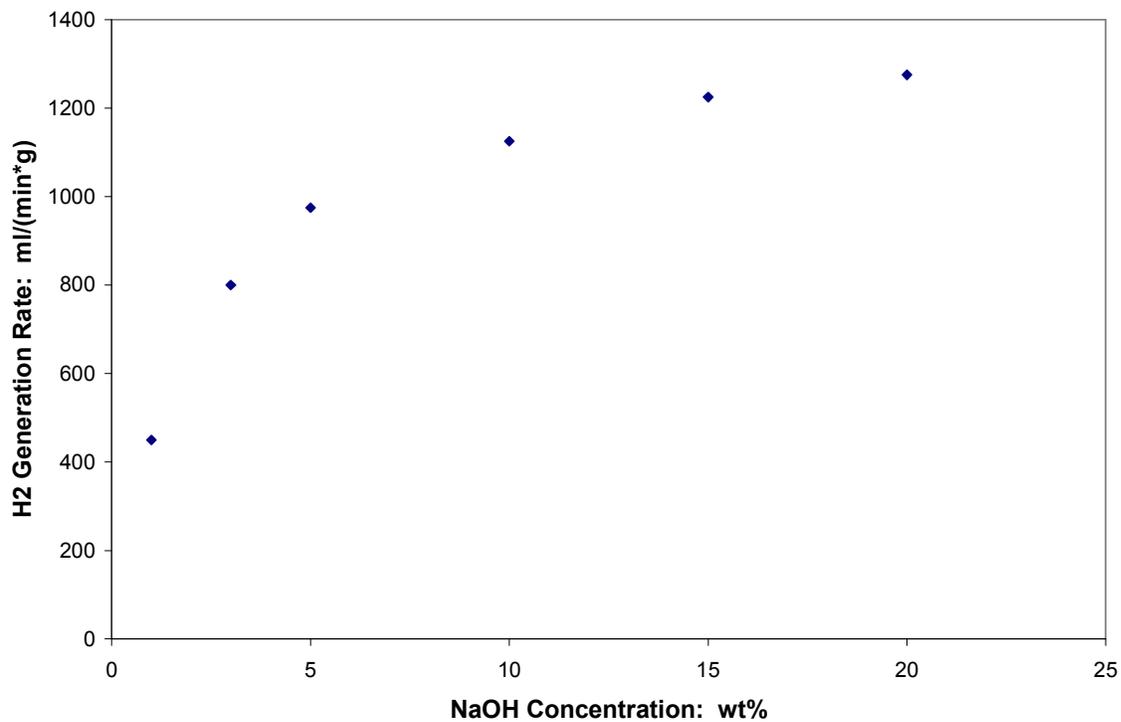


Figure 8: Hydrogen generation rate with 20-wt% NaBH<sub>4</sub> + X wt% NaOH using 0.05g CoB at 20°C.

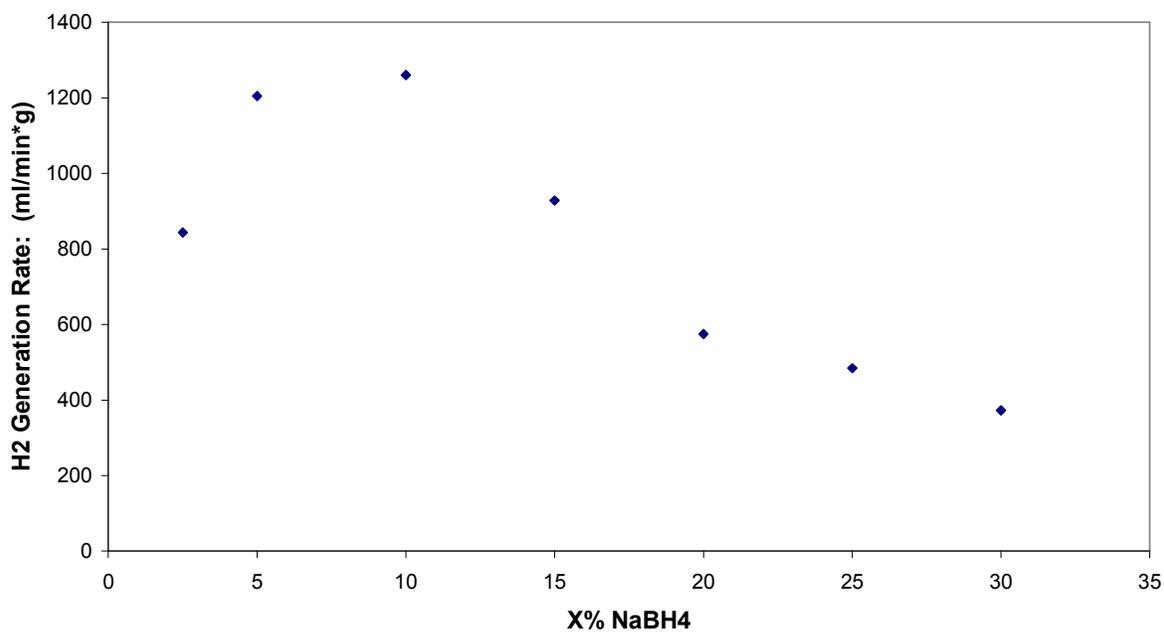


Figure 9: Hydrogen generation rates using 0.05g Ni catalyst in 15ml of X wt% NaBH<sub>4</sub> solution with 5-wt% NaOH. Solution held at 60°C.

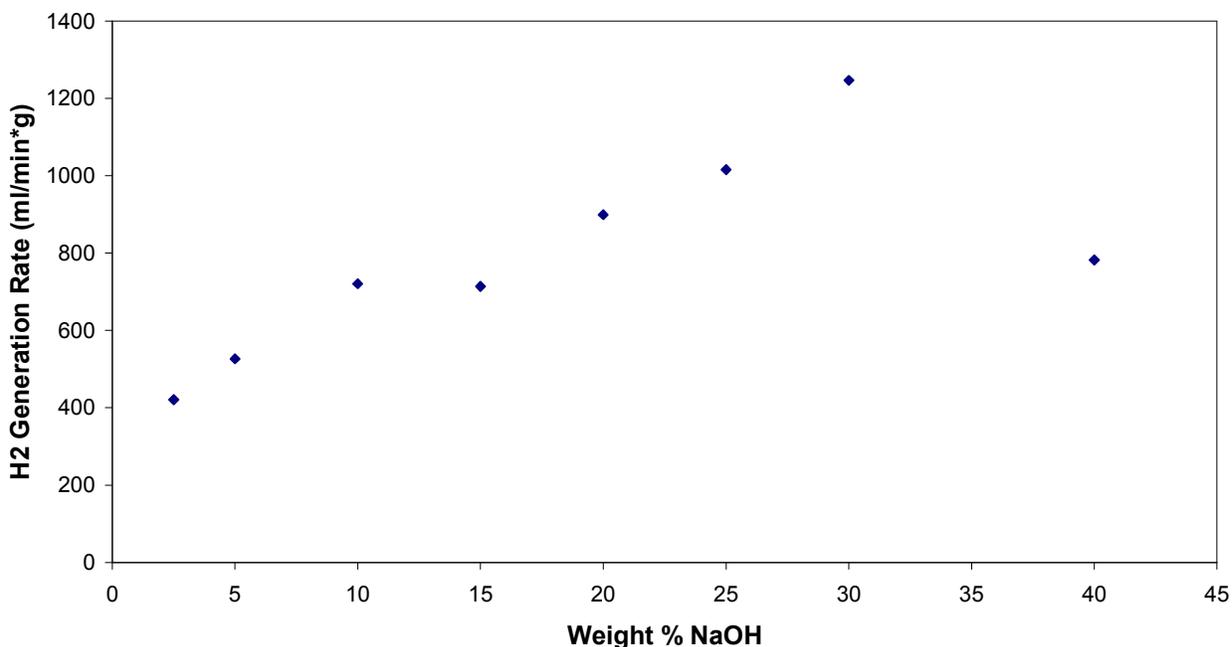


Figure10: Hydrogen generation rates using 0.05g Ni catalyst in 15ml of 20-wt% NaBH<sub>4</sub> solution with X wt% NaOH. Solution held at 60°C.

Figure 7 compared to Figure 9 and Figure 8 compared to Figure 10 show differing trends in the effect of the various solution constituent concentrations on the hydrolysis rate. Figure 7 shows a consistently decreasing hydrolysis rate with increasing NaBH<sub>4</sub> concentration. Similar experiments by Amendola et al. (2000) show the same trend when using a Ru catalyst and attribute the decrease to an increasing solution viscosity. Figure 9 shows a peak in the hydrolysis rate near 10-wt% NaBH<sub>4</sub> concentration. This likely stems from a small viscous effect at lower concentrations, which becomes more prominent at concentrations above 10-wt%. The data obtained at Purdue and by Hua for the Ni<sub>x</sub>B catalyst as well as the Co<sub>x</sub>B obtained by Jeong show an increase in reaction rate with increasing NaOH concentration. The data in Figure shows a steady, constant increase in the rate as the NaOH concentration increases until the solution becomes saturated at above 30-wt%.

Hua et al.<sup>7</sup> showed that the maximum amount of reacted NaBH<sub>4</sub> occurs in solutions containing 5-10 wt% NaOH and that the hydrogen storage capacity of the solution decreases linearly with increasing NaOH concentration. In a solution of 34-wt% NaBH<sub>4</sub> + 5-wt% NaOH, a 6.75 wt% H<sub>2</sub> storage capacity was achieved. Applying the data from Figure to the power density produced from the Co<sub>x</sub>B catalyzed metal foam, roughly half of the reaction rate would result, giving 0.77 W/cm<sup>2</sup>. As reaction temperature is increased above 25°C, the total amount of NaBH<sub>4</sub> reacted becomes nearly constant for the 34 wt% NaBH<sub>4</sub> case, with 92% of the initial NaBH<sub>4</sub> being hydrolyzed<sup>7</sup>. This provides validation for reaction characteristics shown in Figure 7 to be applied to the catalyzed metal foam tests, which were performed at 60°C. It should be possible to increase the equivalent metal foam hydrogen production capacity by increasing the amount of catalyst being deposited onto the foam. A level of 1W/cm<sup>2</sup> is sufficient for high performance H<sub>2</sub>/O<sub>2</sub> fuel cells.

## Conclusions

Increased NaOH concentration results in increased rates of hydrolysis for the sodium borohydride solution. Since, however, increased NaOH concentration decreases the amount of hydrogen stored in the solution, development of a detailed understanding of the mechanism is not necessary to achieve the desired objective. The catalyst type, catalyst loading, and sodium borohydride concentration can be adjusted to reach the needed hydrolysis rates. The decrease in catalytic activity with increasing NaOH concentration in the case of the Ru/C catalysts should be examined. If the lower rate is obtained through solution viscosity effects, then this can be avoided by using the metal foam as the catalyst support as opposed to carbon.

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