

**DEVELOPMENT OF AN ON-BOARD H<sub>2</sub> STORAGE AND RECOVERY  
SYSTEM BASED ON LITHIUM BOROHYDRIDE**

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## Summary

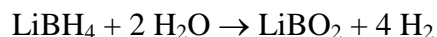
Alkali metal borohydrides based on sodium and lithium,  $\text{NaBH}_4$  and  $\text{LiBH}_4$ , have been evaluated as a potential hydrogen storage and recovery system for on-board vehicle use. The borohydride salts could be dissolved in water, followed by a hydrolytic reaction evolving hydrogen gas,  $\text{H}_2$ . It was found that pH of the aqueous solution, temperature, concentration of the borohydride salt, and exposure to catalytic surfaces all played a role in the rate of  $\text{H}_2$  evolution. The solution pH alone could vary the gas evolution rate over several orders of magnitude. However, without addition of external reagents, the solution left to itself would quickly rise into the pH 10-11 range and level out, due to the buffering capacity of the boric acid product. Therefore, it was decided to exclude secondary reagents and let the pH stay near the buffered value, and use other variables to control gas evolution rate. Varying temperature from ambient to 80 °C enabled a four-fold increase in reaction rate, enabling an effective means of control. Inserting plastic substrates bearing painted films of organic pigment catalysts such as pyranthredione into the borohydride solution could enhance gas evolution rates up to 40%. Better design of the mixing chamber could greatly improve this effect. In general,  $\text{LiBH}_4$  and  $\text{NaBH}_4$  evolved  $\text{H}_2$  at the same rate, but the lithium salt had a tendency to generate an initial surge upon contact with solution that could make it potentially problematic when mixing at high rates in tight spaces. As a proof of concept, a remote controlled, 1/10<sup>th</sup> scale monster truck was obtained and modified to run off of a proton-exchange membrane fuel cell supplied with  $\text{H}_2$  from a borohydride generator.

## Introduction

Our transportation infrastructure depends on the continuing discovery, drilling, and refining of crude petroleum. Nearly half of that petroleum presently comes from foreign sources, some of which are oftentimes openly hostile to the US. Domestic reserves are steadily becoming depleted, leaving only low-grade inaccessible deposits to be tapped. Identifying other types and sources of vehicular fuel is necessary.

Hydrogen fuel based on the simple molecular gas, H<sub>2</sub>, derived from natural gas, water electrolysis, or biomass processing, represents a domestic, environmentally “green” fuel that could be produced in sufficient abundance to largely supplant our 14 million barrels of oil per day transportation dependency. Its gravimetric energy density is unmatched at 51,590 Btu/lb; however, because it is a gas under standard conditions, it must be stored on-board in heavy pressurized cylinders. In plain language, it is difficult to carry enough H<sub>2</sub> on the vehicle to go very far.

One way to enable facile H<sub>2</sub> storage is to convert it to the solid state. Lithium borohydride, LiBH<sub>4</sub>, is a white crystalline solid that reacts spontaneously with water to generate H<sub>2</sub> and metaborate:<sup>1</sup>

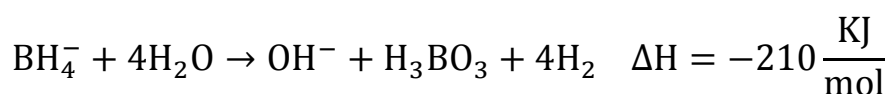


The storage density of H<sub>2</sub> in LiBH<sub>4</sub> is actually 69% greater than cryogenic liquid hydrogen itself! Just one gram of LiBH<sub>4</sub> liberates 4.11 liters of hydrogen gas at STP. One could envision developing an on-board “H<sub>2</sub> on demand” delivery system based on this reaction for either a fuel cell or a H<sub>2</sub>-burning internal combustion engine power train. The challenges are how to control the rate of H<sub>2</sub> generation and how to regenerate the borohydride from the metaborate. In both cases, the development of new catalysts to promote the respective processes is key. Most of the work reported in the following entails our effort in quantifying the rate of H<sub>2</sub> evolution as a function of pH, temperature, concentration, and catalyst implementation.

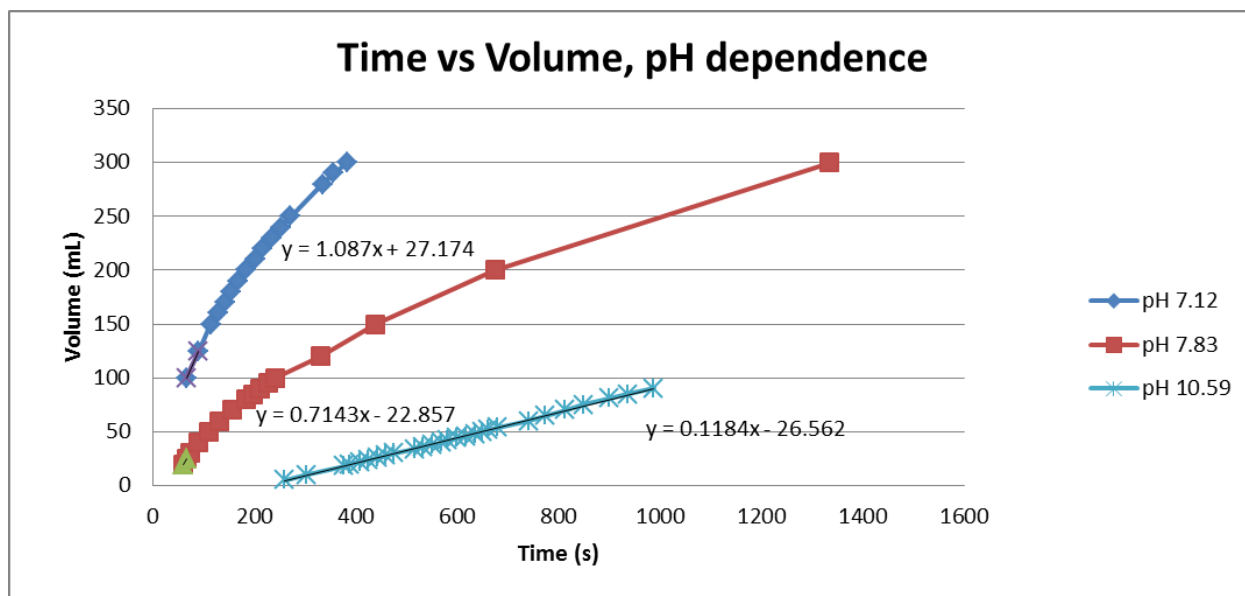
## Results

### pH dependence

Much of the kinetic studies were performed with sodium borohydride,  $\text{NaBH}_4$ , whose behavior was thought to be similar to that of  $\text{LiBH}_4$ . Sodium borohydride has also received much interest as a hydrogen storage method for hydrogen fuel cells, particularly for full size vehicle usage. One gram of sodium borohydride will produce 0.2132 g of hydrogen by the following reaction:

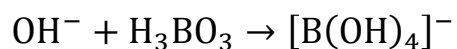


This leads to 8.064 g of  $\text{H}_2$  being produced from 109.892 g of reagents. This reaction likewise raises the pH of the solution, thus lowering its own reaction rate. This is shown below in Figure 1, where the rate of  $\text{H}_2$  evolution at pH 7.12 is considerably greater than at 10.59.

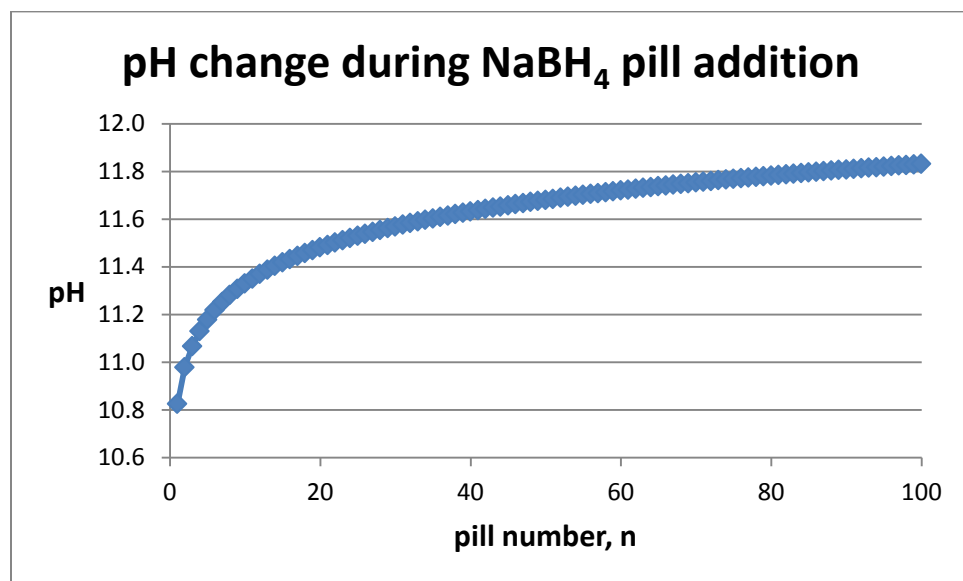


**Figure 1. pH dependence of  $\text{H}_2$  evolution from borohydride solution.**

However, as the solution pH rises,  $\text{OH}^-$  begins to be consumed by the reaction,



This slows the rise in pH, nearly halting it at ~11 pH. This self-buffering property makes running a system at this pH appealing, as a system designed to operate at a lower pH would have to combat the pH rise in some fashion. This is shown in Figure 2, where a theoretical development of solution pH was calculated based successive addition of 0.5 g tablets or “pills” to the solution and the  $\text{pK}_A$  of boric acid. It is seen that even after some 100 tablets were added, the change in pH would only cover a single unit.



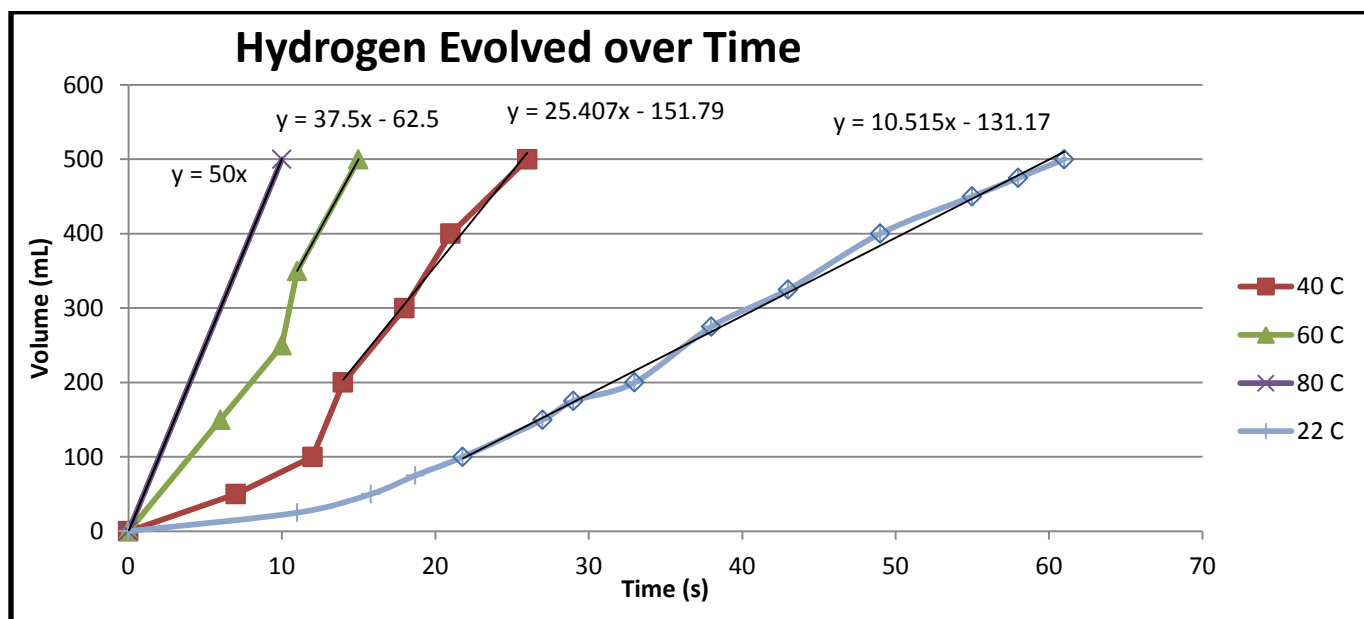
**Figure 2. Calculated growth of solution pH as cumulative borohydride concentration rises.**

The graph above does not accurately describe the rise of pH that would be observed in an actual H<sub>2</sub> generator, as the calculation assumes that each pill dissolves and the borohydride decomposes completely to H<sub>2</sub> before the next pill is added, i.e., there is no time dependence associated with the above graph. In reality, there would be a lag between the rate of tablet addition and the rate of H<sub>2</sub> evolution, so that the pH rise would be something less than indicated. Even so, this plays into the conclusion that the pH quickly levels off, so that the effect of pH on reaction rate will be restricted to within an order of magnitude. Our interpretation of this result is that pH should be

left alone and allowed to vary as it will, and compensate for the change in reaction rate with manipulation of other factors (temperature, concentration, and catalyst activity).

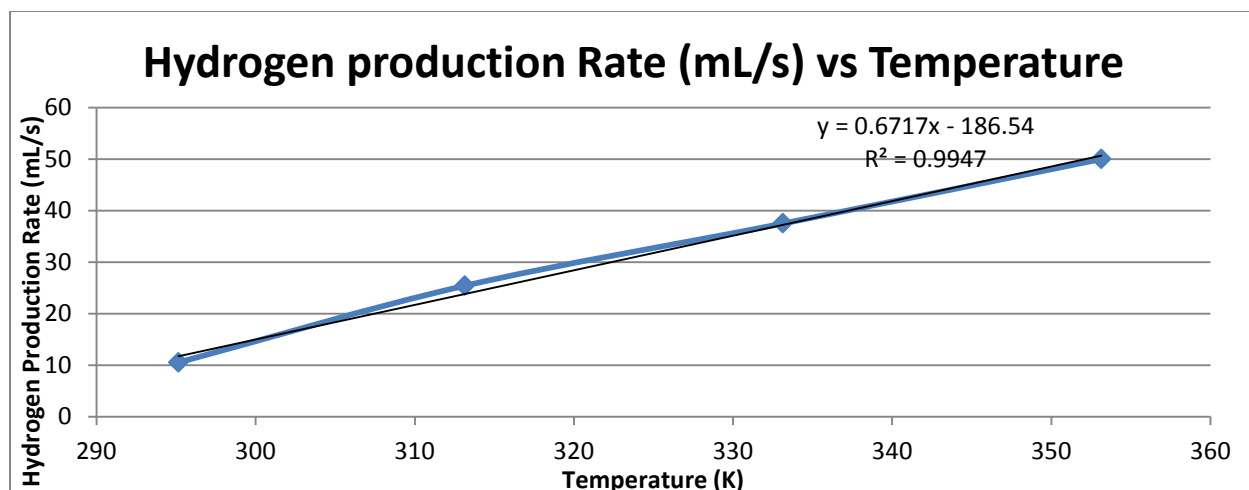
### Temperature dependence

To examine the temperature dependence of the hydrolysis of sodium borohydride, 0.5 g of sodium borohydride was placed into a stirred, 7.0 pH solution buffered by potassium dihydrogen phosphate and sodium hydroxide. This solution was preheated to a given temperature and maintained there with a heating mantle. The hydrogen gas formed was then measured by water displacement from a graduated cylinder.



**Figure 3. Hydrogen volume produced at various temperatures.**

It was found that there was a direct correlation between temperature and rate of gas evolution. At 80 °C, the H<sub>2</sub> evolution rate, as given by the slope of the least squares-fitted curve, was nearly four times greater than at the ambient temperature of 22 °C. Actually there was a linear correlation between temperature and gas evolution rate, as shown in Figure 4. Each degree Kelvin increase would increase the reaction rate by nearly 1.5 mL/min. The coefficient of determination was 0.9947, a very good fit.



**Figure 4. Hydrogen Production Rate vs Temperature.**

The data for the plot above is given in Table 1 below. The volume of working fluid in this case was large enough to dissipate the exothermicity of the reaction. However, with 210 kJ released per mole reacted, some form of heat control would be needed in large scale on-board designs where it would be necessary to conserve the volume and mass of liquid employed.<sup>1</sup>

**Table 1. Hydrogen Production and Borohydride Consumption at Various Temperatures**

Temperature (K)	Rate of H <sub>2</sub> evolution (mL/s)	Rate of borohydride consumption (mol BH <sub>4</sub> <sup>-</sup> / L-s)
295.15	10.515	0.000343035
313.15	25.407	0.000781219
333.15	37.5	0.001083836
353.15	50	0.001363273

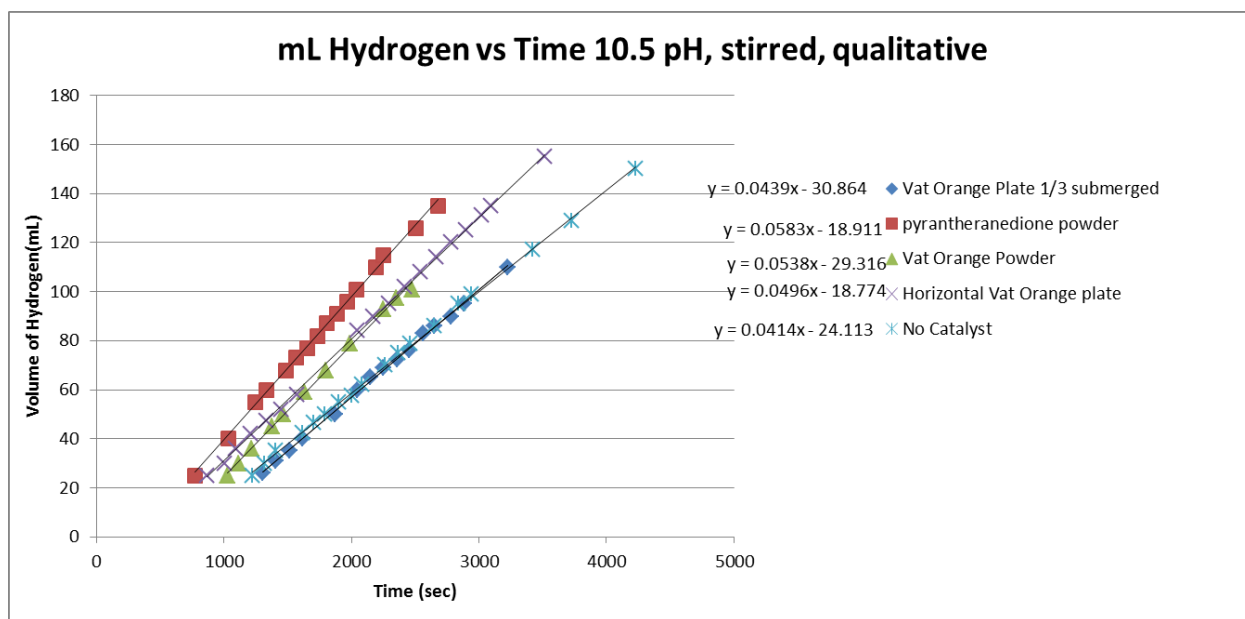
### Catalyst effect

Prior work by the PI in this area has shown that certain organic pigments are effective in catalyzing borohydride ion decomposition.<sup>3-5</sup> It was discovered that certain fused oxo-aromatic compounds such as pyranthredione and Vat Orange accelerate the rate of gas evolution. This effect was revisited in this project.



Commercial samples of pyranthredione and Vat Orange were obtained as powders, blended with 1,2-dichloroethane solvent, and painted onto acrylic plastic substrates. The solvent would soften the surface of the plastic, enabling us to feather in the pigment particles, so that once dry, the catalyst would be attached to the plastic surface. The effect of inserting the catalyst substrates into borohydride solution is shown below in Figure 5. From the slopes of fitted lines to the data, it was found that the best result was a pyranthredione film, evolving H<sub>2</sub> some 40% faster relative to the uncatalyzed case.

In order to fit the catalyst substrates through the 24/40 necks into the glass reaction flask, it was necessary to reduce their width down to 1.0-2.0 cm. This limited the exposed surface of catalyst to only a few square centimeters, and so it had limited effect on the overall gas evolution rate. Nevertheless, effervescence from the catalyst substrates was clearly visible, and so was indeed producing a catalytic effect. Future reaction vessels will be better optimized to contain a greater exposed catalyst area.



**Figure 5. Effect of catalyst on rate of H<sub>2</sub> evolution.**

## Lithium and sodium borohydride comparison

With a gravimetric hydrogen content of 18.5% compared to sodium borohydride's 10.65%, the use of lithium borohydride as the hydrogen storage medium for a hydrogen generator seems preferred. To test its usage in such a role, the hydrolysis of lithium borohydride was compared to that of sodium borohydride. Equimolar quantities of lithium borohydride and sodium borohydride were reacted separately with a boric acid buffer and the hydrogen gas production measured by displacement of water from an inverted graduated cylinder. The results are shown below in Figures 6 and 7.

Based upon the slopes of the linear parts of the curves, the lithium borohydride reaction proceeded scarcely 6% faster than the sodium borohydride reaction. This would be consistent with the idea that they are water-soluble salts, so that once dissolved, there is free  $\text{BH}_4^-$  ion separate from the alkali metal cation, and so the positive counterion has no effect. On the other hand, there was an obvious difference upon the initial contact with water. When the lithium borohydride tablets first contacted water, some of the borohydride quickly reacted to form a large quantity of gas and heat. Subsequently, the reaction rate slowed to approximately that of sodium borohydride. Unfortunately there was not enough time left in the project to investigate this phenomenon further. Certainly this initial flashing effect after each tablet hits the solution would have to be dealt with in a larger system.

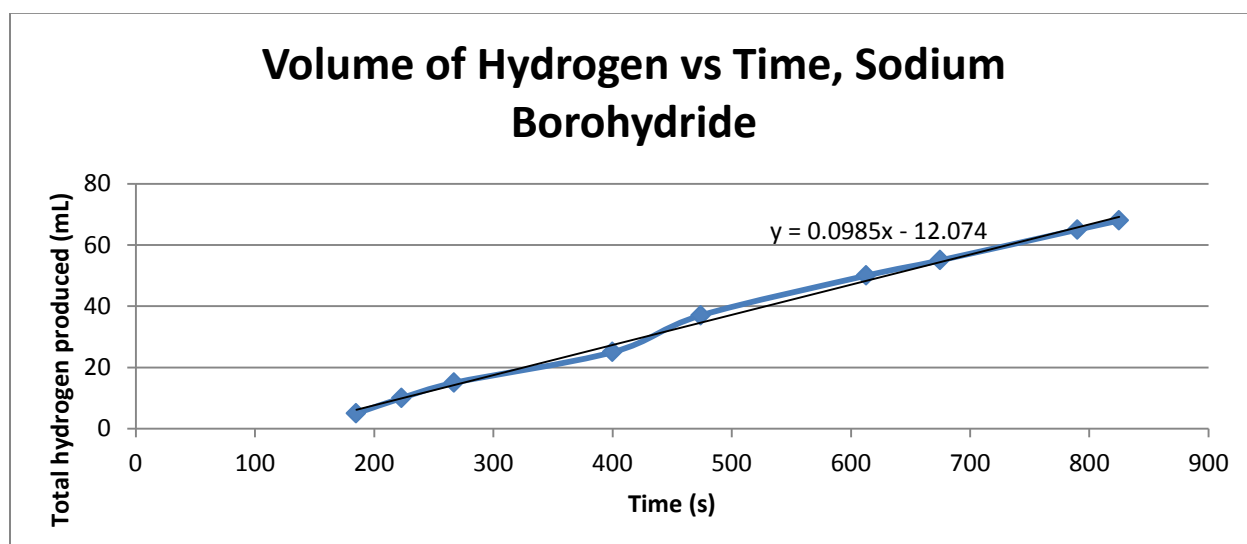
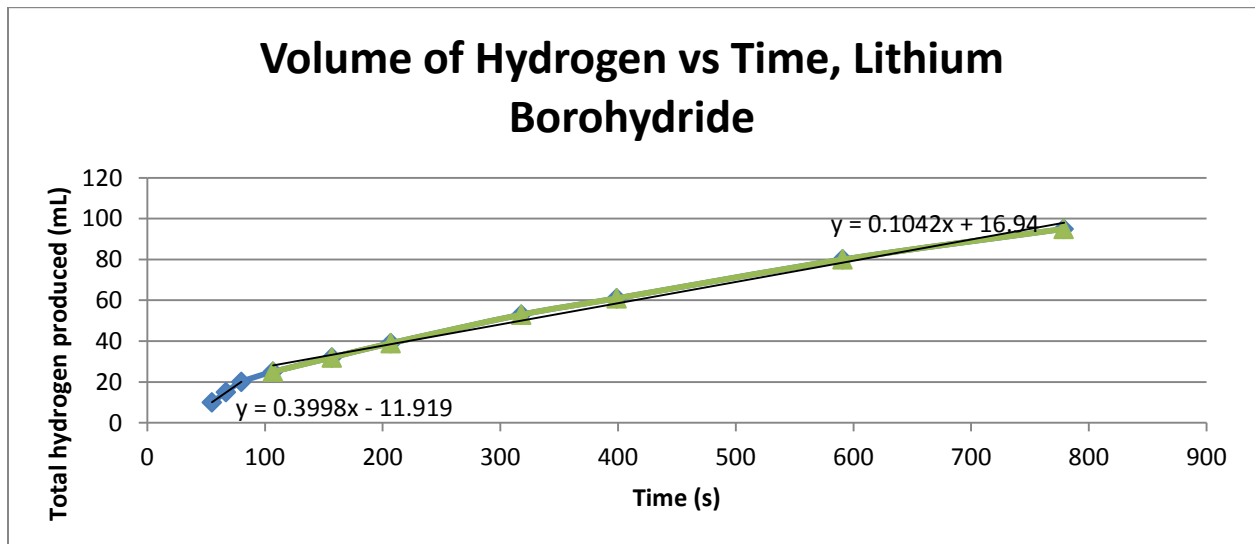


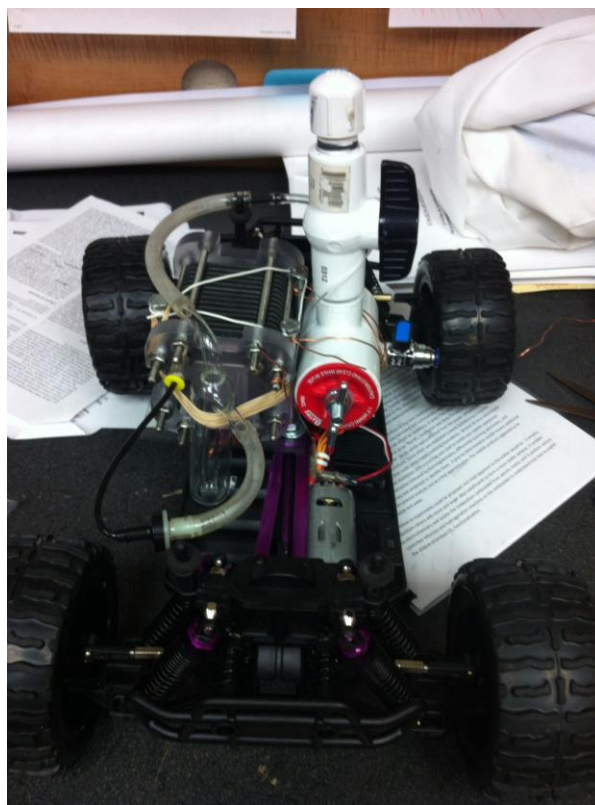
Figure 6. Hydrogen Production vs Time with Sodium Borohydride



**Figure 7. Hydrogen Production vs Time with Lithium Borohydride**

### Remote controlled (RC) car prototype

To test out using the fuel cell to move a vehicle, a Redcat Volcano EPX electronic car had its 27T 540 brushed motor powered by a 15 cell TDM PEM fuel cell stack. The 256.88 g, 7.2 V, 2000 mAh NiMH<sub>x</sub> battery was replaced with the 670.86 g fuel cell and a 356 g storage and reactor vessel created from PVC pipe. The modified vehicle is shown in Figure 8. The reactor and fuel cell were purged with nitrogen or argon before trials. Sodium borohydride pellets were stored above a 10.6 pH solution and released into it by a ball valve to create a 10 wt % solution and a 2 mL/sec hydrogen flow rate. Functionality of the car remained intact; however, the added weight from the reactor and fuel cell limited car speed and continuous drive time.



**Figure 8. Hydrogen-powered fuel cell car.**

### **Scale-up issues**

For a larger, automobile sized system, an assumed operating condition was a delivery rate of 1.6 g of hydrogen per second to the fuel cell. Using the same data gathered for the RC car, it can be simply calculated that a delivery rate of 1.6 g of hydrogen per second would require 611.9 L of 10 wt% sodium borohydride, 10.6 pH solution, not catalyzed and at room temperature. This amount is far above the maximum of 75.55 L of water that could be used to maintain a hydrogen gravimetric content of at least 5.5%, and that is neglecting the system weight. It is clear then, that the reaction rate must be increased, either through increasing the temperature, lowering the pH, or use of a catalyst.

It can be seen from the temperature dependence section that increasing the temperature to 80 °C from 22 °C increased hydrogen production rate by approximately a factor of four. However, vaporization of the alkaline solution could damage further systems downstream, most notably the fuel cell. Filters would have to be in place to prevent this alkaline vapor from

reaching the cell at any temperatures, but it is likely that this problem would increase with higher temperatures.

Lowering the pH of the solution would provide another route to accelerate the rate of reaction, whether by having a lower pH buffer solution in place of water or by addition of acid as borohydride is added. Lowering the pH is certainly capable of increasing the reaction rates by orders of magnitude very quickly. Unfortunately, the acid or buffer solution would be used up with each tank of gas and thus would have to be replaced, further adding to the cost of the fuel. Also, the remnants and conjugates of the buffer or acid could complex recovery and recycle of the spent borohydride solution. This may remain a viable route, however, and is certainly not to be entirely dismissed.

The final available option for increasing the reaction rate would be use of a catalyst. Current research has shown cobalt, ruthenium, and platinum based catalysts all to be quite effective at increasing reaction rates. Use of such heterogeneous catalysts could be extremely useful in controlling the rate of reaction to match hydrogen demand. One issue with such catalysts would be their cost, especially considering the low lifespan many seem to currently have of less than 10 uses.<sup>2</sup> However, use of a catalyst should be enough to produce the flow rate desired.

The hydrogen gas would be generated in the reactor by reaction of borohydride with water. To maintain a 5.5% gravimetric content of hydrogen in reagents alone, the tank would need to be no larger than 75.55 L. Borohydride would be added according to readings from a pressure sensor, which will also control depth and immersion of movable catalysts to control the rate of reaction. Temperature sensors can be linked with coolant flow to prevent the reactor liquid from vaporizing. With a density of 1.0740 kg/L and a desired storage capacity of 5.6 kg, the storage tank for the sodium borohydride has to be at least 5.2 L. The borohydride is recommended to be stored as small pellets or balls for simple addition, as powder can become extremely sticky with contact to any moisture.

The hydrogen gas produced proceeds first through a filter or condenser to separate the hydrogen gas from any vaporized alkaline solution that could damage further downstream systems, such as the fuel cell. The gas would then continue to the air fed fuel cell, where it will produce the electricity to power the vehicle. The water formed from the fuel cell is cooled and condensed before being added back into the reactor.

One major issue is the accumulation of the product of the hydrolysis reaction,  $\text{NaBO}_2$ . The build-up of this substance in solution may slow reaction rates, and the precipitation of it may interfere with catalysts and methods to empty the tank. Flushing the tank with water or some other solution may function to dissolve any  $\text{NaBO}_2$  for removal and recovery. The borohydride container should be able to be refilled with little difficulty.

## References

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<sup>1</sup> J. Zhang, T. S. Fisher, J. P. Gore, D. Hazra, P. V. Ramachandran, *Int. J. Hydrogen Energy* 2006, 31, 2292.

<sup>2</sup> Demirci, U. B., Akdim, O., Andrieux, J., Hannauer, J., Chamoun, R. and Miele, P. (2010), Sodium Borohydride Hydrolysis as Hydrogen Generator: Issues, State of the Art and Applicability Upstream from a Fuel Cell. *Fuel Cells*, 10: 335–350. doi: 10.1002/fuce.200800171

<sup>3</sup>C.A. Linkous, D.K. Slattery, and D.D. Nangle, "Catalysts for the Evolution of Hydrogen from Borohydride Solution," U.S. patent #7,842,276, November 30, 2010.

<sup>4</sup>C.A. Linkous, D.K. Slattery, and D.D. Nangle, "Catalysts for the Evolution of Hydrogen from Borohydride Solution," U.S. patent #7,722,853, May 25, 2010.

<sup>5</sup>C.A. Linkous, D.K. Slattery, and D.D. Nangle, "Catalysts for the Evolution of Hydrogen from Borohydride Solution," U.S. patent #7,591,864, September, 22, 2009.