

# An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst

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Received 10 May 1999; accepted 6 June 1999

## Abstract

A novel, simple, convenient, and safe chemical process generates high purity hydrogen gas on demand from stable, aqueous solutions of sodium borohydride, NaBH<sub>4</sub>, and ruthenium-based (Ru), catalyst. When NaBH<sub>4</sub> solution contacts Ru catalyst, it spontaneously hydrolyzes to form H<sub>2</sub> gas and sodium borate, a water-soluble, inert salt. When H<sub>2</sub> is no longer required, Ru catalyst is removed from the solution and H<sub>2</sub> generation stops. Since this H<sub>2</sub> generator is safer, has quicker response to H<sub>2</sub> demand, and is more efficient than commonly used H<sub>2</sub> generators, it is ideal for portable applications. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Ru catalyst; Sodium borohydride; Hydrogen gas

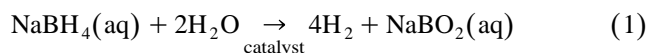
## 1. Introduction

PEM fuel cells are attractive alternative power sources for providing clean energy for transportation and personal electronics applications where low system weight and portability are important. For powering these systems, H<sub>2</sub> gas is the environmentally desirable anodic fuel of choice since only water is formed as a reaction product. A major hurdle is how to generate/store controlled amounts of H<sub>2</sub> directly without resorting to high temperature reformers with significant heat signatures.

## 2. Background of the borohydride H<sub>2</sub> generator

Our safe, portable H<sub>2</sub> generator overcomes these problems by using an aqueous, alkaline, sodium borohydride (NaBH<sub>4</sub>, tetrahydroborate) solution. This solution is extremely air stable. However, as found by Schlesinger et al. [1], in the presence of selected inexpensive metal (or metal

boride) catalysts, this solution hydrolyzes to yield H<sub>2</sub> gas and water-soluble, sodium metaborate, NaBO<sub>2</sub>.



This hydrolysis reaction occurs at different rates depending on the catalyst used and its preparation method. Levy et al. [2] and Kaufman and Sen [3] investigated cobalt and nickel borides as catalysts for practical, controlled generation of H<sub>2</sub> from NaBH<sub>4</sub> solutions. We studied ruthenium (Ru) based catalyst supported on ion exchange resin beads. Using Ru is based on the work of Brown and Brown [4], who investigated a series of metal salts and found that ruthenium and rhodium salts liberated H<sub>2</sub> most rapidly from borohydride solutions. We chose Ru because of its lower cost. Ru catalysts are not consumed during hydrolysis and are reusable. We have designed our system so that reaction (1) is self-regulating or carefully controllable. To generate H<sub>2</sub>, NaBH<sub>4</sub> solution is allowed to contact Ru catalyst either by dipping Ru catalyst into a NaBH<sub>4</sub> solution or injecting NaBH<sub>4</sub> solution on Ru catalyst. This ensures fast response to H<sub>2</sub> demand, i.e., H<sub>2</sub> is generated only when NaBH<sub>4</sub> solution contacts Ru catalyst. When H<sub>2</sub> is no longer needed, NaBH<sub>4</sub> solution is removed from Ru catalyst and H<sub>2</sub> production ceases. Based on molecular weights of NaBH<sub>4</sub> (38) and 2H<sub>2</sub>O (36), to form

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Table 1  
Comparison between generating H<sub>2</sub> by chemical hydrides and by aqueous borohydride

Parameters	Conventional chemical hydride	Borohydride solution
System	Water dripping on solid hydride	Borohydride solution contacting catalyst
Theoretical H <sub>2</sub> storage	< 10%	10.8%
H <sub>2</sub> contaminants	Possibly CO and CO <sub>2</sub> (from binders); possibly SO <sub>2</sub> or NO (from acids)	None expected
Heat generated	Excessive	Moderate
Components carried in generator	Water and dry hydride	Borohydride solution and catalyst
What limits H <sub>2</sub> generation rate?	Rate at which water drips on solid hydride	Surface area of catalyst
What determines total H <sub>2</sub> produced?	Amount of solid hydride	Amount of borohydride solution
H <sub>2</sub> source	Water + solid	Solution + catalyst
Is reactant moisture sensitive?	Yes	No
Technical roadblocks	Solids tend to cake Binders are needed to hold solids together	?
What happens if too much liquid enters cell	Violent reaction	Reaction rate is limited by catalyst surface area. Excess liquid cools and slows reaction

4H<sub>2</sub> (8), reaction (1) has a theoretical H<sub>2</sub> storage efficiency of  $8/74 = \sim 10.8\%$ .

In addition to H<sub>2</sub>, the other reaction product, NaBO<sub>2</sub>, commonly found in laundry detergents, is safe. Unlike phosphates, borates are not environmentally hazardous in water supplies. Table 1 compares operational and safety features of generating H<sub>2</sub> via base-stabilized NaBH<sub>4</sub> solutions and via reactive chemical hydrides. Our generator is considerably safer/more efficient than producing H<sub>2</sub> via other reactive chemicals. The heat generated by our system 75 kJ/mol H<sub>2</sub> formed [5], is less than what is produced by other hydrides (> 125 kJ/mol H<sub>2</sub>), and ensures a safe, controllable chemical reaction.

The total amount of H<sub>2</sub> produced by reaction (1) depends on NaBH<sub>4</sub> solution volume, concentration and temperature. H<sub>2</sub> generation rates are primarily a function of Ru catalyst active surface area. H<sub>2</sub> pressure/flow rates can be accurately controlled and made self-regulating by numerous feedback mechanisms. An added attribute of our generator is that generated H<sub>2</sub> gas also contains water vapor. Since prehumidified H<sub>2</sub> is needed in PEM fuel cells, a NaBH<sub>4</sub> based H<sub>2</sub> generator should increase PEM fuel cell performance.

### 3. Experimental

Ru catalyst supported/dispersed on anionic exchange resin beads was prepared by ion exchange. Appropriate amounts of RuCl<sub>3</sub>·3H<sub>2</sub>O were dissolved in deionized water and acidified with HCl to convert RuCl<sub>3</sub> into [RuCl<sub>6</sub>]<sup>-3</sup>. This H<sub>3</sub>RuCl<sub>6</sub> solution was added to a weighed amount of anionic and cationic exchange resin beads which had been previously washed and dried at 50°C. The resulting slurry was allowed to stand at ambient temperature for 24 h while stirring at regular intervals to maintain uniformity. The slurry was then dried by evaporation at 50°C. After drying, H<sub>3</sub>RuCl<sub>6</sub>, now impregnated in the resin, was reduced by addition of 20% NaBH<sub>4</sub>, 15% NaOH, 65%

H<sub>2</sub>O solution. As prepared, our catalyst may be either metallic Ru or Ru boride of the form Ru<sub>2</sub>B. The black, Ru coated resin beads were washed, dried, and separated with a 40-mesh sieve. Ru loadings were  $\sim 5\%$  by weight.

In typical H<sub>2</sub> generation experiments,  $\sim 30$  ml of NaBH<sub>4</sub> solution containing 10% NaOH was thermostated in a sealed flask fitted with an outlet tube for collecting evolved H<sub>2</sub> gas. Ru coated resin beads were placed in a stainless steel screen container and dropped into the solution to begin H<sub>2</sub> generation. NaBH<sub>4</sub> solution could contact Ru catalyst through the screen, H<sub>2</sub> could exit, while lightweight resin beads were prevented from floating to the top of the solution. The outlet tube exhaust was placed under an inverted, water filled, graduated cylinder situated in a water-filled tank. Generated H<sub>2</sub> was measured by monitoring water displaced from the graduated cylinder as the reaction proceeded.

### 4. Results and discussions

We evaluated anionic and cationic exchange resin beads as catalyst supports for Ru catalyst. Table 2 lists normalized H<sub>2</sub> generation rates for the various ion exchange resin beads. Catalyst supports were evaluated based on their H<sub>2</sub> generation rates in liters of H<sub>2</sub> generated per second-gram catalyst. This is a convenient standard for meaningfully comparing various catalyst supports in our system because Ru catalyst performances are normalized with respect to catalyst weight. Table 2 illustrates that for catalytically generating H<sub>2</sub> from NaBH<sub>4</sub> solutions with  $\sim 5\%$  Ru supported on ion exchange resins, *anionic* resins are better than *cationic* resins. A-26 and IRA-400 (Rohm and Haas) anion exchange resins when used as supports for Ru gave the highest H<sub>2</sub> generation rates.

Fig. 1 plots H<sub>2</sub> volume generated as a function of time for  $\sim 0.25$  g combined weight of Ru supported on IRA-400 anion exchange resin beads immersed in 20% NaBH<sub>4</sub>, 10% NaOH, and 70% H<sub>2</sub>O (wt.%) solution at various

Table 2

Rate of H<sub>2</sub> gas generated catalytically per gram of catalyst (Ru + support resin) are compared for various anionic and cationic support resins in 20% NaBH<sub>4</sub>, 10% NaOH, 70% H<sub>2</sub>O solution at 25°C. All catalysts had ~ 5% Ru loading

Ru resin support	Time to generate 1-l H <sub>2</sub> gas (s)	Weight of Ru + support (g)	l H <sub>2</sub> s <sup>-1</sup> g <sup>-1</sup> catalyst × 10 <sup>-5</sup>
<i>Anionic resins</i>			
A-26	1161	0.2563	336
A-26	633	0.5039	313
IRA-400	1173	0.2565	332
IRA-400	773	0.4116	314
IRA-900	1983	0.2555	197
Dowex 550A	672	0.7692	193
Dowex MSA-1	791	0.7691	164
Dowex MSA-2	1028	0.7691	126
A-36	1415	0.2550	111
<i>Cationic resins</i>			
MSC-1B	2351	0.2592	164
Dowex HCR-W2	895	0.7631	146
MSC-1A	1382	0.5054	143
Amberlyst 15	2871	0.2563	136
Amberlyst 15	1324	0.5054	149
Dowex 22	1818	0.7678	72
Dowex 88	6163	0.2556	63

temperatures. Volumes of H<sub>2</sub> generated by Ru catalyzed NaBH<sub>4</sub> hydrolysis increased linearly with time:

$$-4d[\text{NaBH}_4]/dt = d[\text{H}_2]/dt = k \quad (2)$$

Under our experimental conditions,  $k$  is constant for a given temperature. This example of zero order kinetics implies that the first step in reaction (1) involves a surface reaction, most likely BH<sub>4</sub><sup>-</sup> adsorption on Ru catalyst. We have observed zero order kinetics for NaBH<sub>4</sub> hydrolysis

even at [NaBH<sub>4</sub>] as low as 0.1%. Catalyzed NaBH<sub>4</sub> hydrolysis ultimately depends on NaBH<sub>4</sub>. It would therefore not be surprising if diffusion controlled, first order kinetics dominates at very low [NaBH<sub>4</sub>] and/or high catalyst weights where catalyst sites are not totally occupied. From Fig. 1, an activation energy for Ru catalyzed hydrolysis of NaBH<sub>4</sub>, obtained by plotting log [H<sub>2</sub> generation rate] vs. reciprocal absolute temperature (1/ $T$ ) was computed to be 47 kJ/mol. This value compares favorably

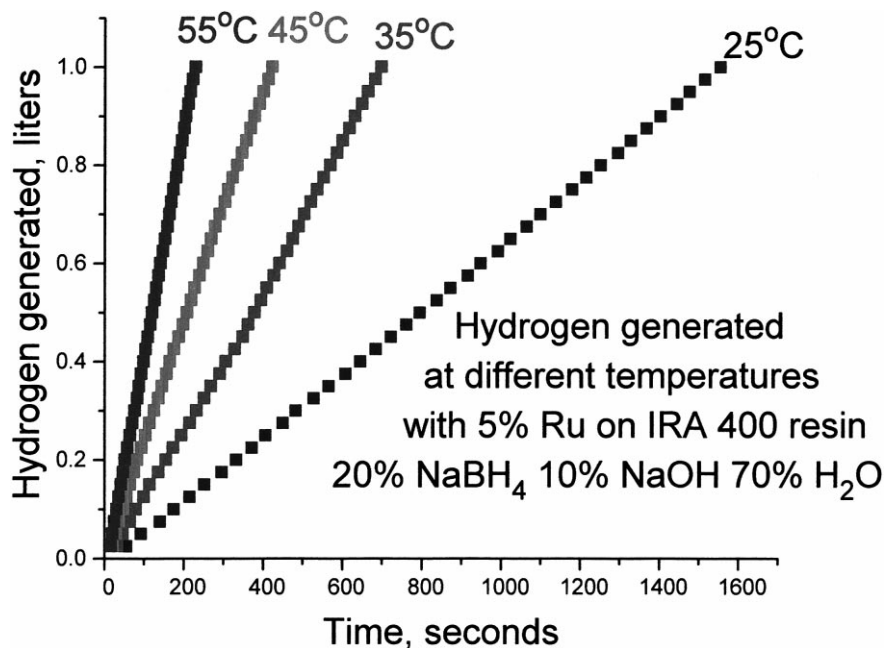


Fig. 1. Volume of H<sub>2</sub> generated as a function of time by ~0.25 g catalyst consisting of 5% Ru loading supported on IRA 400 anion exchange resin in 20% NaBH<sub>4</sub>, 10% NaOH, 70% H<sub>2</sub>O solution at various temperatures.

with activation energies found [3] for  $\text{NaBH}_4$  hydrolysis catalyzed with other metals: 75 kJ/mol for Co, 71 kJ/mol for Ni, and 63 kJ/mol for Raney Ni.

As reaction (1) proceeds,  $\text{NaBO}_2$  eventually exceeds its solubility limit and precipitates out of solution. We were concerned that this solid may block catalyst sites thereby affecting subsequent  $\text{H}_2$  generation rates. To test this, 5 g of  $\text{NaBH}_4$  solution were allowed to catalytically hydrolyze to completion and the total generated  $\text{H}_2$  measured. Although  $\text{H}_2$  generation rates slowed as the reaction proceeded, nevertheless, > 70% of the stoichiometric amount of  $\text{H}_2$  was generated based on the amount of  $\text{NaBH}_4$  in solution. This indicated that reaction (1) is quite efficient and that  $\text{NaBO}_2$  precipitation at these concentrations/conditions does not seriously interfere with catalyst operation. If water generated by PEM fuel cells could be returned to  $\text{NaBH}_4$  solutions, additional  $\text{H}_2$  could be generated because  $\text{NaBO}_2$  would remain in solution.

We can estimate achievable power levels from our  $\text{H}_2$  generator. Assuming a standard PEM fuel cell operates at  $\sim 0.7$  V, generating 1 g  $\text{H}_2$ /min is equivalent to 26.8 A h  $\times$  60 min/h  $\times$  0.7 V  $\times$  1/min = 1125 W, i.e., 1-l  $\text{H}_2$ /min can power a 100-W fuel cell. Since  $\sim 5\%$  of the 0.25 g of our total catalyst weight was active Ru, Fig. 1 illustrates that our  $\text{H}_2$  generator produced the equivalent of  $\sim 0.3$  kW/g Ru catalyst at 25°C and  $\sim 2$  kW/g Ru catalyst at 55°C. Greater  $\text{H}_2$  generation rates (and power levels) are expected for higher Ru loadings.

Prototypes of our  $\text{H}_2$  generator have been used to power a commercial 35 W  $\text{H}_2$ /air PEM fuel cell and an internal combustion engine (1 kW) running on hydrogen. For applications requiring long-term operation,  $\text{H}_2$ /air PEM fuel cells together with a  $\text{NaBH}_4$ -based  $\text{H}_2$  generator is considerably more advantageous than using rechargeable batteries. Our  $\text{NaBH}_4$  generator can be quickly refueled by simply filling the reservoir with fresh  $\text{NaBH}_4$  solution (the Ru catalyst is reusable).

## 5. Conclusions

Stabilized  $\text{NaBH}_4$  solutions have been demonstrated to be an effective source for producing  $\text{H}_2$ . Due to system simplicity ( $\text{NaBH}_4$  solution simply contacts Ru to produce  $\text{H}_2$ ), it can be used in applications where  $\text{H}_2$  gas is used, e.g., PEM fuel cells. High  $\text{H}_2$  generation rates have been achieved from  $\text{NaBH}_4$  solutions with tiny amounts of Ru supported on anion exchange resins. Optimizing catalyst loading, supports, and  $[\text{NaBH}_4]$ , should lead to catalysts capable of quickly generating large amounts of  $\text{H}_2$ .

## Acknowledgements

We thank Mike Strizki of the NJ Department of Transportation for constant encouragement and enlightening technical suggestions. Kudos to Martin M. Pollak and Jerome I. Feldman of GP Strategies for their unfailing enthusiasm and support throughout this effort. This work was partially supported by the State of New Jersey Commission on Science and Technology for which we express our gratitude.

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