A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst

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Abstract

A safe, simple, compact process generates high-purity hydrogen gas on demand from base-stabilized, aqueous solutions of sodium borohydride, $NaBH_4$, by using a ruthenium, Ru, catalyst. These $NaBH_4$-based solutions can store up to 7% hydrogen by weight. $NaBH_4$ solutions do not generate significant amounts of H_2 gas under ambient conditions. However, when in contact with Ru catalyst, $NaBH_4$ solutions spontaneously hydrolyze to form H_2 gas and sodium borate, a water-soluble, inert salt. When Ru catalyst is separated from the $NaBH_4$ solution, H_2 generation stops. This H_2 generator promises to be safer, have quicker response to H_2 demand, have a greater H_2 storage efficiency, and be more easily controlled than commonly used H_2 storage devices or generators. Nonflammable $NaBH_4$ solutions can be easily coupled to provide H_2 to internal combustion engines or fuel cell power systems. © 2000 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

H_2 gas is recognized as the environmentally desirable clean fuel of the future since it can be used directly in internal combustion engines or electrochemically oxidized efficiently ($> 50\%$) in Proton Exchange Membrane, PEM, or other types of fuel cells. H_2 is an ideal anodic fuel for PEM fuel cells that convert chemical energy of H_2 into electrical energy, heat and water in a clean, quiet manner with little or no environmentally harmful by-products. Until large PEM fuel cells become commercially available, internal combustion engines fueled with H_2 could represent a backup option for upcoming zero emission vehicle, ZEV, mandates for transportation applications. In internal combustion applications, H_2 can be considered more thermally efficient than gasoline primarily because it burns better in excess air, and permits use of higher compression ratios. H_2 can burn in lean as well as rich air mixtures; it can improve fuel use efficiencies in start–stop type city driving. Unlike hydrocarbon fuels, the only by-product of H_2 combustion in oxygen is water or water vapor. No pollutants or harmful emissions such as CO, unburned hydrocarbons, smoke, soot, odor, or the greenhouse gas CO_2 are produced. The small amount of NO_x, formed when H_2 is burned in air, can be minimized by reducing combustion temperatures through carefully designed lean fuel mixtures or by scrubbing the exhaust.

Using H_2 gas as a fuel presents its own unique set of

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challenges. The most daunting is the lack of efficient, low cost, safe, onboard storage technologies. Since H_2 is extremely energy rich on a weight basis but relatively poor (compared to gasoline) on a volumetric basis, large volumes of H_2 must be safely stored and transported. A primary technical challenge in developing H_2 fueled vehicles (and hand held PEM fuel cell devices) is to be able to safely generate, deliver and store adequate amounts of H_2.

This paper describes part of a study whose aim is to develop a new uncomplicated means of direct H_2 production from aqueous alkaline *solutions* of sodium borohydride ($NaBH_4$, tetrahydroborate). $NaBH_4$ has found wide usage as a powerful reducing agent and is extensively used in wastewater processing, paper bleaching, and pharmaceutical synthesis. Schlesinger et al. [1] found that aqueous alkaline $NaBH_4$ solutions in contact with selected catalysts hydrolyzes to H_2 gas and water-soluble, sodium metaborate, $NaBO_2$.

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} 4H_2 + NaBO_2 + HEAT \quad (300\,kJ)$$

$$(1)$$
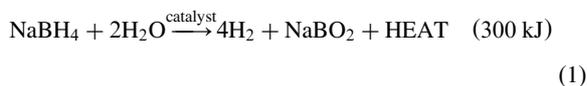
This reaction occurs to some extent even without a catalyst if the solution pH < 9. However, to increase the shelf life of $NaBH_4$ solutions (and to prevent H_2 gas from being slowly produced upon standing), $NaBH_4$ solutions are typically maintained as a strongly alkaline solution by adding NaOH. The key feature of using a catalyzed reaction to produce H_2 is that H_2 generation in alkaline (pH > 14) $NaBH_4$ solutions occurs only when these solutions contact selected heterogeneous catalysts. Without catalysts present, strongly alkaline $NaBH_4$ solutions do not produce appreciable H_2. This reaction is extremely efficient on a weight basis, since out of the 4 moles of H_2 that is produced, half comes from $NaBH_4$ and the other half from H_2O. Reaction (1) is exothermic, so no energy input is needed to generate H_2. Borohydride solutions essentially act as both the H_2 carrier and the storage medium. To generate H_2 at the point of use, this easily handled and air-storable *solution* containing dissolved $NaBH_4$ is simply allowed to contact a heterogeneous catalyst. This ensures rapid, dependable, and controlled H_2 generation in response to demand. In this system, H_2 generation by hydrolysis is directly proportional to the amount (surface area) of catalyst. One clear advantage of this method is that rapid (but carefully controlled) H_2 generation can be achieved at ambient temperatures (and even down to 0°C) without mechanical compression, addition of water, acid, or heat. In addition, since stabilized $NaBH_4$ solutions without catalyst produce very little H_2, and H_2 is only generated as needed, safety concerns about onboard storage of free H_2 are reduced.

The only other product of reaction (1), borate (in solutions with pH > 11 the predominant solution species is sodium tetrahydroxyborate, $NaB(OH)_4$), is water soluble and environmentally innocuous. Since reaction (1) is totally inorganic and does not contain sulfur, it produces virtually no fuel cell poisons such as sulfur compounds, CO, soot, or aromatics. Only H_2 and some water vapor are produced in the product gas stream. The presence of water vapor is beneficial for use in PEM fuel cells where the water vapor 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. Reaction (1) is considerably safer, more efficient, and easily controllable than producing H_2 by other chemical methods. Carrying $NaBH_4$ solutions onboard, a vehicle is far safer than carrying an equivalent amount of gasoline since aqueous $NaBH_4$ solutions cannot be easily ignited.

The heat generated by reaction Eq. (1), 75 kJ/mole H_2 formed, is considerably less than the typical > 125 kJ/mole H_2, produced by reacting other chemical hydrides with water [2]. This promises a safer, more controllable reaction. In vehicular applications, $NaBH_4$ solution can be carried onboard and stored in lightweight plastic tanks. Use of $NaBH_4$ solutions permits refueling similar to current gasoline stations, allowing tanks to be easily filled anytime. When H_2 is needed, $NaBH_4$ solution is allowed to flow to a catalyst chamber where H_2 is generated. This H_2, together with oxygen supplied from ambient air, flow separately to either PEM fuel cell stacks or H_2 combustion engine.

It must be admitted that true commercial success of this system will not be achievable without substantially reducing the current $80/kg cost of $NaBH_4$. This cost presently limits the use of this technology to small and medium scale H_2 sources. Our ongoing research has involved studying the possibility of recycling the sodium borate reaction product back to $NaBH_4$ starting material in an industrially attractive manner. This could eventually be performed at a central recycling facility thereby allowing for a recycling loop and lowering the user cost of consumed H_2. Fresh and spent borohydride solution could then be easily transported to and from distribution and recycling centers. If this method is successful, and $NaBH_4$ solution can be effectively recycled, $NaBH_4$ solutions could become a cost effective carrier of H_2 gas.

Generating H_2 catalytically from $NaBH_4$ solutions has the following advantages:

- $NaBH_4$ solutions are nonflammable
- $NaBH_4$ solutions are stable in air for months
- H_2 generation only occurs in the presence of selected catalysts
- The only other product in the gas stream is water

vapor
- Reaction products are environmentally safe
- H_2 generation rates are easily controlled
- Volumetric and gravimetric H_2 storage efficiencies are high
- The reaction products can be recycled
- H_2 can be generated even at 0°C

2. Using $NaBH_4$ solution as a transportation fuel

Since $NaBH_4$ solution is an easily handled liquid, it simplifies transportation, storage and delivery since in vehicles, $NaBH_4$ liquid can be refueled in a similar manner as gasoline at current filling stations. Spent borate waste products produced by the H_2 producing hydrolysis reaction can either be washed from onboard storage tanks during subsequent filling operations or collected at pumping stations and possibly regenerated or recycled back to $NaBH_4$ solution (utilizing various chemical processes with renewable resources) at a central processing plant.

3. Experimental

3.1. Catalyst preparation

In our system, high surface area ruthenium, Ru, catalyst was supported on ion exchange resin beads. We selected Ru based on results of Brown and Brown [3], who investigated various metal salts and found that Ru and Rh salts liberated H_2 most rapidly from $NaBH_4$ solutions. Ru has a lower cost and generates H_2 at faster rates than metallic Rh. We found that Co and Pt catalysts showed more modest H_2 generation rates.

Ion exchange resin beads were chosen because of their expected stability in strongly reducing aqueous $NaBH_4$ solution. Ru metal, supported/dispersed on ion exchange resin beads, was prepared by a two-step process (incipient wetness method). The first step involved ion exchange. $RuCl_3$–$3H_2O$ was dissolved in deionized water and acidified with HCl to convert $RuCl_3$ into $[RuCl_6]^{-3}$. This H_3RuCl_6 solution was added to IRA-400 ion exchange resin beads (Rohm and Haas, Philadelphia, PA) which had been previously washed and dried at 50°C. The ion exchange resin beads were 0.42 mm in diameter with ∼30 m^2/g surface area. The resulting slurry of H_3RuCl_6 solution impregnated into the ion exchange resin beads was allowed to stand at ambient temperature for 24 h with stirring at regular intervals to maintain uniformity. The slurry was then dried by evaporation at 50°C. The second step was to chemically reduce H_3RuCl_6, now impregnated in the ion exchange resin, by adding an aqueous $NaBH_4$ solution. Elemental analysis showed that our black cata-

lyst, as prepared, contained only metallic Ru (no borides). Ru coated resin beads were washed, dried, and separated with a 40 mesh sieve (420 μm).

3.2. Catalyst testing

In typical H_2 generation experiments, ∼30 ml of 1–25 wt% $NaBH_4$, and 1–10 wt% NaOH solution was placed in a sealed, thermostated flask fitted with an outlet tube for collecting evolved H_2 gas. Approximately 0.25 g catalyst (resin + Ru) was placed in a stainless steel screen container and dropped into the $NaBH_4$ solution to begin H_2 generation. $NaBH_4$ solution could contact the lightweight, Ru-coated, resin beads through the screen, H_2 could exit, while the catalyst, trapped inside the screen container, were prevented from floating to the top of the solution. The outlet tube exhaust from the reaction vessel was placed under an inverted, water filled, graduated cylinder situated in a water-filled tank. Generated H_2 volumes (∼1 l) were measured as a function of time by monitoring water displaced from the graduated cylinder as reaction Eq. (1) proceeded. Ion exchange resin beads not coated with Ru did not show any catalytic activity for generating H_2 from $NaBH_4$ solutions. Since it did not observe significant loss of catalytic activity when catalysts were used repeatedly, active catalytic sites were not being deactivated.

4. Results and discussions

$NaBH_4$ solutions are quite stable when maintained at a high pH. The rate at which $NaBH_4$ solutions undergo self-hydrolysis in water in the absence of catalysts depends on the pH and solution temperature. Based on the work of Kreevoy and Jacobson [4], this rate is empirically represented by:

$$\log t_{1/2} = \text{pH} - (.034T - 1.92)$$

Here, $t_{1/2}$ is the half-life (the time it takes for one-half of a $NaBH_4$ solution to decompose) in minutes, which is dependent on the solution pH and temperature, T, in K. At pH 14 and 25°C, for example, $NaBH_4$ solutions have a half-life of 430 days. In the presence of selected catalysts, however, the hydrolysis rate (and hence, H_2 generation rates) markedly increases even in high pH solutions at 25°C. We have investigated and optimized various catalyst formulations and operating parameters to give high H_2 generation rates.

Fig. 1 shows a typical plot of H_2 volumes generated as a function of time from a $NaBH_4$ solution catalyzed by Ru supported on ion exchange resin beads. In Fig. 1, a fast linear portion is followed by a slower,

more sloping, curve. Total H_2 yield obtained from this solution was $> 93\%$ of the theoretically expected value based on Eq. (1).

4.1. Effect of NaBH₄ concentration on H₂ generation rates

Initial H_2 generation rates as a function of weight percent $NaBH_4$ (for weight percent NaOH held constant at either 1, 5, or 10 wt%) and constant catalyst loading are shown in Fig. 2. As weight percent $NaBH_4$ is increased, initial H_2 generation rates increase and reach a maximum in the range $\sim$7.5–12.5 weight percent $NaBH_4$ (depending on weight percent NaOH). At higher weight percent $NaBH_4$, initial H_2 generation rates decrease. Greater H_2 generation rates at lower weight percent $NaBH_4$ are possibly due to reduced solution viscosity, i.e. reduced mass transport allows more $NaBH_4$ and H_2O to contact catalyst surfaces.

We should emphasize that $NaBH_4$ solution compositions having the highest initial H_2 generation rates (e.g. 1 wt% NaOH and $\sim$12.5 wt% $NaBH_4$) do not have the highest overall H_2 storage capacity, i.e. total amount of H_2 that can be delivered, or longest shelf life. Nevertheless, producing high initial H_2 generation rates is important in high power applications, such as vehicle acceleration.

4.2. Effect of NaOH concentration on H₂ generation rates

Fig. 2 further illustrates that as weight percent NaOH increases from 1 wt% (0.25 M) to 5 wt% (1.3 M), and then to 10 wt% (2.8 M), H_2 generation rates for a given weight percent $NaBH_4$ decrease. One possible explanation is the reduced activity of water at higher NaOH concentrations. This occurs primarily because the ions, especially OH^-, strongly com-
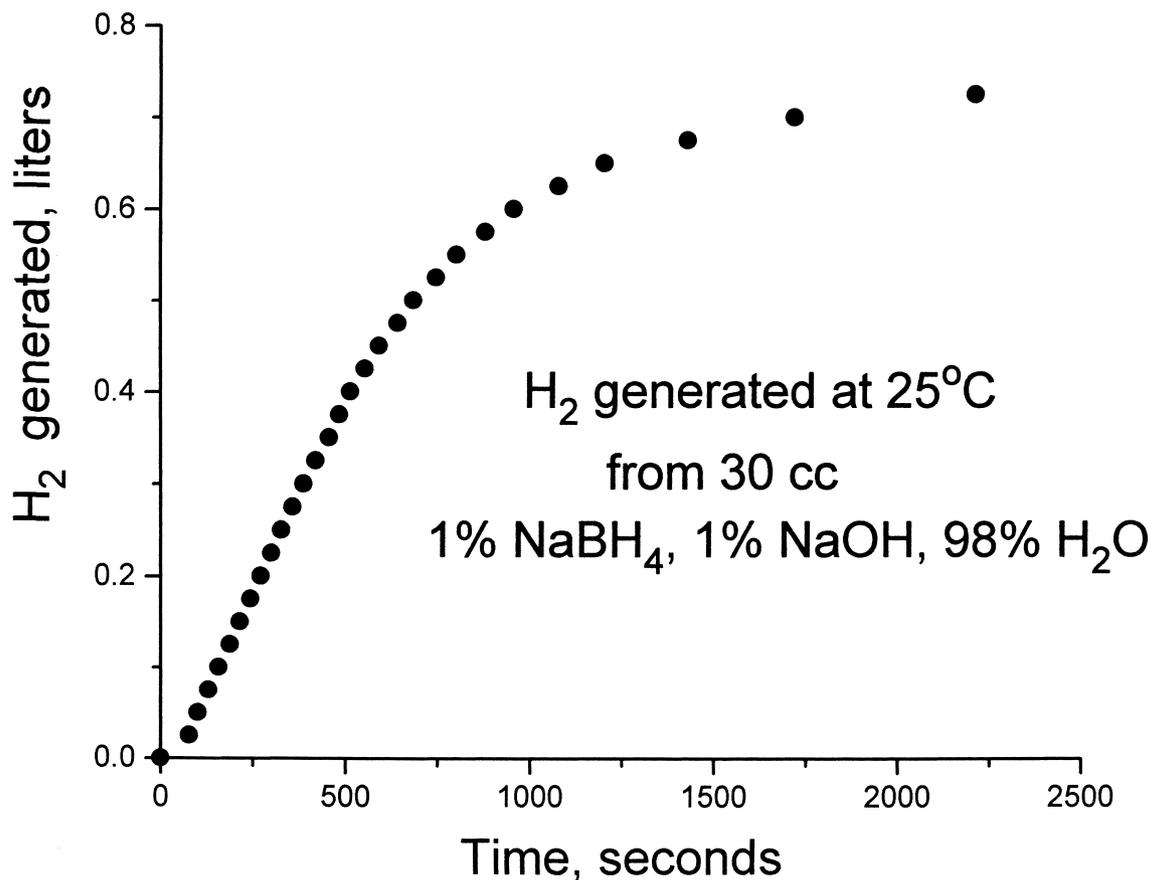

Fig. 1. H_2 volumes generated as a function of time with 5 wt% Ru supported on IRA-400 anion exchange resin in 1 wt% $NaBH_4$, 1 wt% NaOH, 98 wt% H_2O solution.

plex water, thus decreasing the available free water needed for $NaBH_4$ hydrolysis. Increased H_2 generation rates with decreasing wt% NaOH do not mean that NaOH is not needed. Without adding NaOH, $NaBH_4$ solutions would undergo slow, continual self-hydrolysis, and therefore, have a short useful shelf life. Thus, small amounts of NaOH must always be present to extend $NaBH_4$ solution shelf life.

The solubility of sodium metaborate reaction product was measured at various weight percent NaOH in water at 25°C. It was found that as the weight percent of NaOH decreased, $NaBO_2$ solubility increased. This indicates that in $NaBH_4$ solutions having low weight percent NaOH, not only will H_2 generation rates be faster (see above), but more of the reaction product will remain in solution. This will allow a greater stoi-

chiometric yield of H_2, i.e. greater H_2 storage efficiency.

4.3. Effect of temperature on H_2 generation rates

H_2 generation rates were measured in 7.5 wt% $NaBH_4$, 1 wt% NaOH, and 91.5 wt% water solutions at various temperatures in the 0–40°C range. It is noteworthy that H_2 could be generated from $NaBH_4$ solutions even at 0°C. The influence of solution temperature on H_2 generation rates is compiled in Table 1.

If the above data is represented in an Arrhenius type plot where log [H_2 generation rate] is plotted against reciprocal absolute temperature ($1/T$), an activation energy of 56 kJ/mole is calculated. This value com-
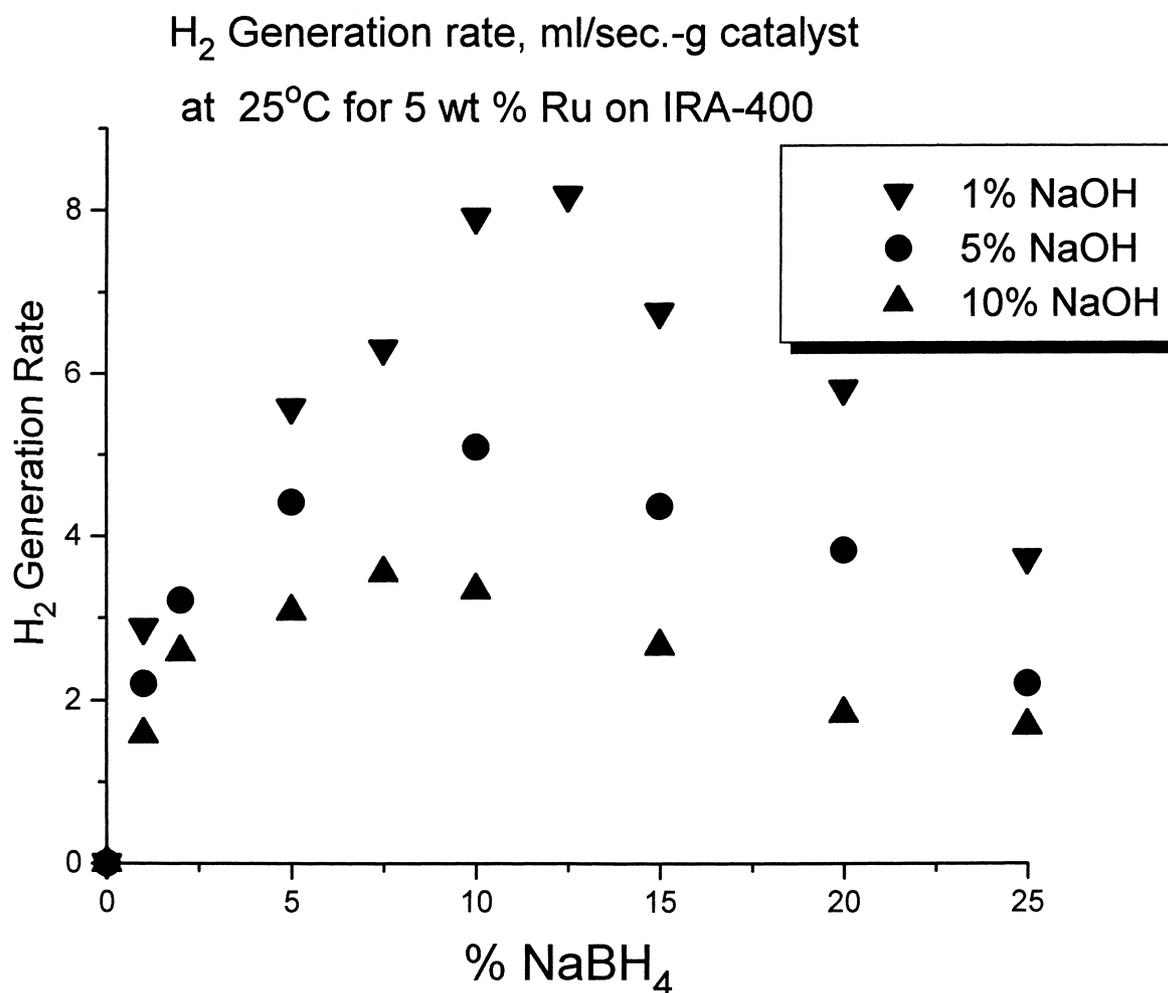

Fig. 2. H_2 generation rates with 5 wt% Ru supported on IRA-400 anion exchange resin in various weight percent $NaBH_4$ solutions. NaOH was held constant at 10, 5, or 1 wt%.

pares favorably with activation energies of 47 kJ/mole found by us [5,6] at higher $NaBH_4$ and $NaOH$ concentrations, and activation energies found by Kaufman and Sen [7] for $NaBH_4$ catalytically hydrolyzed with other metals, i.e. 75 kJ/mole for Co, 71 kJ/mole for Ni, and 63 kJ/mole for Raney Nickel.

4.3.1. Energy content of $NaBH_4$ solutions

Assuming 100% stoichiometric yield of H_2 in reaction Eq. (1), each mole of $NaBH_4$ (37.8 g/mole) produces 4 mole of H_2. At 25°C, 4 moles of H_2 occupies (4 moles H_2)(24.6 l H_2/mole) = 98 l. Therefore, assuming 100% conversion of $NaBH_4$, 1 l of 35 wt% $NaBH_4$ aqueous solution (containing 350 g/(37.8 g/mole) = 9.3 mole $NaBH_4$) will yield: (9.3 mole $NaBH_4$)(98 l H_2/mole $NaBH_4$) ~ 910 l H_2 = 74 g H_2 produced/l of 35 wt% $NaBH_4$ solution. Another way of expressing this storage efficiency is that 1 kg H_2 can be stored in only 14.2 kg of 35 wt% $NaBH_4$ solution (13.5 l of solution). This H_2 storage efficiency is comparable to (and in some cases exceeds) what can be obtained with other H_2 storage technologies. Although total H_2 storage efficiencies calculated here are based solely on $NaBH_4$ solution volumes, this is not an unrealistic estimate for a complete H_2 generation system. This is because nonpressurized $NaBH_4$ solutions will occupy most of the system volume; catalysts and lightweight plastic solution vessels will occupy negligible weight/volume.

The following summarizes the amounts of H_2 theoretically achievable from $NaBH_4$ solutions assuming negligible catalyst and container weights and volumes.

- Each mole of $NaBH_4$ reacted produces 4 moles of H_2 = 8 g H_2 = 98 l H_2 at 25°C.
- 1 l of 35 wt% $NaBH_4$ solution (1.05 kg) produces 74 g H_2 = 910 l H_2.

4.3.2. H_2 storage efficiencies for $NaBH_4$ solutions

The volumes required to store 5 kg H_2 in cryogenic

Table 1
H_2 generation rates[a]

Temperature (°C)	H_2 generation rate (ml H_2 s^{-1} g catalyst)$^{-1)}$
0	0.76
25	6.3
32.5	10.1
40	18.3

[a] In 7.5 wt% $NaBH_4$, 1 wt% $NaOH$, 91.5 wt% H_2O solution catalyzed by 5% Ru supported on IRA-400 resin.

containers, in pressurized tanks, and in $NaBH_4$ solutions can now be compared. For liquid H_2 stored cryogenically, 5 kg H_2 requires ~5000 g divided by 0.07 g/cm^3 (the density of liquid H_2) = 71 l H_2 if we neglect container and associated equipment volumes. Storing 5 kg H_2 in 34 MPa (5000 psi) pressurized containers requires ~180 l. Storing 5 kg H_2 in 35 wt% $NaBH_4$ solution requires only 65 l. These calculations show that $NaBH_4$ solutions are a convenient, nonpressurized way to store H_2. With $NaBH_4$ solution densities of ~1.05 g/cm^3, storing 74 g H_2 in 1 l of 35 wt% $NaBH_4$ solution (~1.05 kg) yields a H_2 storage efficiency of ~74/1050 = 7.0 wt%. This value is comparable to what is achievable by many reactive chemical hydrides.

5. Description of prototype H_2 generators

We have successfully constructed and tested two prototype designs for a H_2 generator using $NaBH_4$ solutions. Design #1, similar to a Kipp Generator, uses pressure differentials to force quiescent $NaBH_4$ solutions from a storage tank into a tube containing supported catalyst. Borohydride solution enters the bottom of the column and reacts with catalyst to generate H_2. The generated H_2 rises to the top of the column, where it is removed through a control valve. The level of $NaBH_4$ solution in the column, and hence, H_2 generation rates, are controlled by the pressure exerted by H_2 over the column. When sufficient H_2 has been generated, resulting pressure differentials force $NaBH_4$ solution away from the catalyst bed thereby stopping H_2 generation. No complicated control systems are needed to ensure proper and safe operation of this reactor. Although this simple, low cost, compact, self-regulating design has no moving parts, it must remain in an upright position for the H_2 generation reaction to remain controllable.

Design #2, which has extremely rapid response to H_2 requirement and is direction insensitive, uses a small mechanical pump to meter $NaBH_4$ solution onto a tubular catalyst bed to generate H_2. These designs were easily able to provide sufficient H_2 to continually power large highway traffic signs using >75 W H_2/air PEM fuel cells for operation. Construction details of these H_2 generator prototypes, and their performance characteristics (H_2 generation rates, pressures, and overall system efficiencies) have been described [5,6].

6. Conclusions

Stabilized, aqueous $NaBH_4$ solutions are a convenient, practical, and effective source of high purity H_2. Using $NaBH_4$ solutions reduces inherent safety concerns associated with long-term gaseous H_2 storage.

H_2 production occurs on demand, near ambient temperature (H_2 can be produced even at $0°C$), and reaction products are not toxic. This H_2 generator can be easily recharged (refueled) by adding fresh $NaBH_4$ solution. Catalysts are reusable. Since this system is uncomplicated ($NaBH_4$ solution simply contacts Ru catalyst to produce H_2), it can be used, for numerous applications where H_2 gas is used e.g. PEM fuel cells or as a direct fuel in internal combustion engines. For long-term operation, using $NaBH_4$, based H_2 generators is more advantageous than using either pressurized tanks or reactive chemical hydrides. Rapid H_2 generation rates have been achieved from $NaBH_4$ solutions with 5 wt% Ru supported on anion exchange resin beads.

References

[1] Schlesinger HI, Brown HC, Finholt AE, Gilbreath JR, Hoekstra HR, Hyde EK. Sodium borohydride, its hydrolysis and its use as a reducing agent and in the generation of hydrogen. Journal of the American Chemical Society 1953;75:215.

[2] Davis WD, Mason LS, Stegeman G. The heats of formation of sodium borohydride, lithium borohydride and lithium aluminum hydride. J Am Chem Soc 1949;71:2775.

[3] Brown HC, Brown CA. New, highly active metal catalysts for the hydrolysis of borohydride. Journal of the American Chemical Society 1962;84:1493.

[4] Kreevoy, MM Jacobson, RW The rate of decomposition of $NaBH_4$ in basic aqueous solutions. Ventron Alembic. 15, 1979. 2–3.

[5] Amendola SC, Sharp-Goldman SL, Janjua MS, Kelly MT, Petillo PJ, Binder M. A safe portable hydrogen generator using aqueous borohydride solutions (II). Presented at the Fall 1999 Electrochemical Society Meeting, Honolulu, Hawaii, Oct. 22. 1999.

[6] Amendola, SC, Sharp-Goldman, SL, Janjua, MS, Kelly, MT, Petillo, PJ, Binder, M. A safe hydrogen generator using aqueous borohydride solutions. Journal of Power Sources 2000; 85:186.

[7] Kaufman, CM, Sen, B. Hydrogen generation by hydrolysis of sodium tetrahydroborate: effects of acids and transition metals and their salts. Journal of the Chemical Society, Dalton Trans 1985:307.