Dynamic Modeling of Hydrogen Generation via Hydrolysis of Sodium Borohydride

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This paper deals with the dynamic modeling of a hydrogen production system using *gPROMS*. The model includes mass balances, liquid-gas equilibrium relations, mass transfer laws and kinetic reaction equations. The initial reaction mixture is a sodium borohydride solution that reacts via a self-hydrolysis mechanism in the presence of water. The behavior of this system was measured in terms of produced hydrogen volume and solution *pH*. The kinetic parameters associated with each reaction mechanism step were estimated from experimental data. The validated model was then used to successfully predict the behavior of the system for different initial conditions.
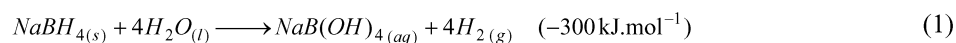
1. Introduction

Hydrogen usage as an alternative energy source to fossil fuels has been winning ground in the last few years. Its attractive advantages such as high energy density, abundant natural resources and environmental-friendly reaction products make this type of energy the key candidate for a future energy sustainable economy.

Borohydride, as a hydrogen-carrying molecule, enables the storage, transportation and on-site production of gaseous hydrogen. This production can be obtained by the hydrolysis of borohydride in the presence of water, and greatly enhanced by the presence of a catalyst and a strongly alkaline media. Experimental evidence has shown that the influence of these two factors on the H_2 production rate cannot be explained by a simple reaction mechanism. Recently, Guella et al. (2006) have proposed a mechanism for the Palladium-catalyzed and Shang and Chen (2006) a semi-empirical model for the carbon-supported ruthenium catalyzed hydrolysis. Although the self-hydrolysis has been deeply investigated since the 50's the reaction mechanism is still not fully understood. The study of self-hydrolysis is important in order to understand the changes that occur during the storage of borohydride solutions prior to its use. The current work proposes a 4-step reaction mechanism as the vital part of a theoretical model of the reaction system.

2. Self-hydrolysis reaction

In order to understand the changes that occur in a closed reaction system containing sodium borohydride in aqueous solution, it is essential to know which chemical transformations take place, to what extent and at which temperatures and pressures do

these modifications happen. In a hydrogen-producing reactor two main reactive paths can be taken: (i) the self-hydrolysis, a slower and spontaneous release of hydrogen from borohydride in the presence of water; (ii) and the catalytic hydrolysis, a faster reaction occurring in the presence of a catalyst. The self-hydrolysis can be described by the following reaction (Wee et al., 2006):

$$NaBH_{4(s)} + 4H_2O_{(l)} \longrightarrow NaB(OH)_{4\,(aq)} + 4H_{2\,(g)} \quad (-300\,\text{kJ.mol}^{-1}) \tag{1}$$

The reaction rate is not fast enough to ensure a viable and constant supply of H_2 to a Proton Exchange Membrane Fuel Cell (*PEMFC*), thus failing to act as a fuel-production reaction. However, the study of this reaction is very important as it can bring new insights to the prediction and avoidance of problematic hydrogen fuel losses, when using borohydride as a liquid fuel.

## 3. Proposed mechanism for self-hydrolysis

Experimental data has shown that H_2 formation through self-hydrolysis tends to decelerate as time passes. After a few hours there is hardly any hydrogen production while there is still plenty of unreacted borohydride. During this process the solution *pH* has increased significantly. It is well known (Pinto et al., 2006) that this spontaneous decomposition process can be inhibited if the borohydride solution is kept alkaline; as a result, there must be at least one intermediary compound that is difficult to form in such conditions.

The information on the reaction mechanism steps is given in Table 1. Step *1.1* corresponds to the sodium borohydride salt dissociation and its equilibrium constant can be easily obtained from general data tables. Steps *1.2* and *1.3* represent the hydrogen producing steps reported by Davis et al., 1962. Step *1.4* constitutes the borate formation step in alkaline media from Wee et al., 2006.

Table 1. Sodium borohydride self-hydrolysis reaction mechanism in water.

Step number	Reactions
1.	$NaBH_{4(s)} + 4H_2O_{(l)} \longrightarrow NaB(OH)_{4\,(aq)} + 4H_{2\,(g)}$ (global reaction)
1.1	$NaBH_{4(s)} \rightleftharpoons Na^+_{(aq)} + BH^-_{4(aq)}$ (sodium borohydride dissociation)
1.2	$BH^-_{4(aq)} + H^+_{(aq)} \rightleftharpoons BH_{3(aq)} + H_{2\,(g)}$ (intermediary borane formation)
1.3	$BH_{3(aq)} + 3H_2O_{(l)} \longrightarrow B(OH)_{3\,(aq)} + 3H_{2\,(g)}$ (boric acid formation)
1.4	$B(OH)_{3\,(aq)} + H_2O_{(l)} \rightleftharpoons B(OH)^-_{4\,(aq)} + H^+_{(aq)}$ (boric acid hydrolysis)

In the sequential reaction mechanism given in Table 1, it is to be noticed that the decrease in H^+ ions in solution ensures that the direct reaction of step *1.2* does not occur, making this step the limiting one in alkaline media. Nonetheless, this fact does not explain the increase in *pH* verified experimentally, as a function of reaction time. A simple explanation came up for this phenomenon: the reaction by-products, mainly tetrahydroxyborate *(B(OH)₄⁻)*, can, themselves, be a reactant to produce the tetraborate ion *(B₄O₇²⁻)*. This molecule can be formed by the *1.A* side reaction, where two protons are consumed, turning the reaction solution progressively more alkaline, as observed experimentally.

$$4B(OH)^-_{4\,(aq)} + 2H^+_{(aq)} \underset{\longleftarrow}{\overset{\longrightarrow}{}} B_4O^{2-}_{7\,(aq)} + 9H_2O_{(l)} \tag{1.A}$$
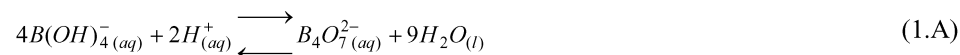
4. Experimental apparatus

The experimental apparatus used for the self-hydrolysis reaction of sodium borohydride enabled the measurement of the volume of gas produced through the displacement of water in an inverted burette, see Figure 1. Water and solid $NaBH_4$ were the reactants, with initial mass fractions of 10% $NaBH_4$ and 90% H_2O. The gas is produced in a reactor (test tube) immersed in a thermostatic bath, where the liquid phase occupies a fraction of the volume. It then leaves the reactor through the top, continues through the rubber tube and enters an inverted burette, initially filled with water. While the hydrogen accumulates at the top of the water column, pressure rises, and the water level decreases. Every time the reservoir fills up with gas, the rubber tube is directed to a new water-filled vessel, resulting in fluctuations on the gas pressure and consequently on the gas flow. This feature was implemented on the model with the creation of several identical reservoir units, and a routine command that ordered the switch to a new reservoir when it was needed.
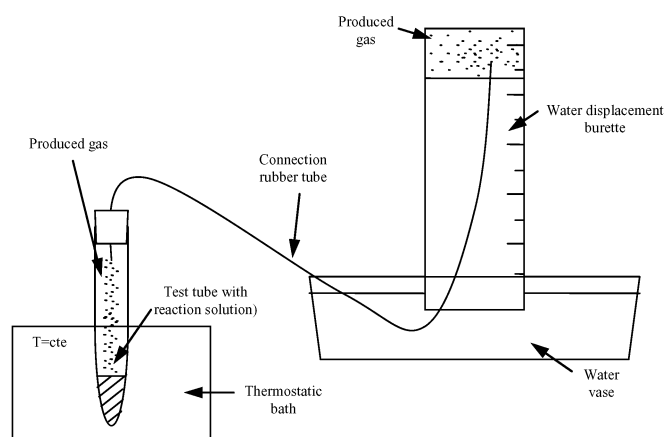

Figure 1. Schematic representation of the experimental apparatus used to measure the gas volume produced from self-hydrolysis of sodium borohydride (45°C).

Table 2. Equations distribution for the model of sodium borohydride self-hydrolysis.

	Model units			For each…	
	Reactor	Reservoir	Connection	compound	reaction
Mass balance	X	X		X	
Liquid-vapor relation	X	X		X	
Kinetic reaction equation	X				X
Mass transfer equation			X	X	

5. Dynamic Model of the Reaction System

In order to realistically represent the experimental conditions verified for the self-hydrolysis of sodium borohydride (10% w/w, 50 ml), the *gPROMS* model consists of two independent units, the reactor and the gas reservoir, and the system unit, comprising the previous two. The model equations distribution along these units for every compound and reaction is shown in Table 2. The full DAE model is index 1 and consists of a total of 1044 equations and variables of which 153 are differential and 891 are algebraic.

The mass balance equation used in the model is given by eq 2, where m_i is the molar holdup of compound i (for a total of n compounds), rr_j is the reaction rate [mol.l^{-1}.s^{-1}] for the reaction j (for a total of m reactions), n_{ij} is the respective stoichiometric coefficient, V represents the solution volume [l], and $F_{out,k}$ is the reactor exit flow rate [mol.s^{-1}] to the reservoir k (for a total of p reservoirs). The liquid-gas equilibrium was modeled by eq 3, where P_t is the total pressure [Pa] of the gas phase, y_i and x_i are the molar fraction of i in the gas phase and aqueous solution phase, respectively, and K_i is a generic equilibrium constant [Pa] similar to the component vapor pressure or the Henry constant. The reaction order relative to every reactant was of one in all cases, being the kinetic equation for each reaction of the type shown in eq 4. Parameter k_j is the respective kinetic constant, M_i is the molarity of compound i in solution [mol.l^{-1}], and α_{ij} is the order of compound i related to the reaction j. If i is a reactant of reaction j, then α_{ij} is 1, otherwise it is 0.The gas flow rate from the reactor was calculated from the simplified Darcy equation (eq 5), where C_D is the Darcy constant [mol.s^{-1}.Pa^{-1})] and ΔP_k is the pressure difference [Pa] between the reactor and the k reservoir.

$$\frac{dm_i}{dt} = \sum_{j=1}^{m} \left(rr_j \times n_{ij} \right) \times V - \sum_{k=1}^{p} F_{out,k} \qquad ,i=1...n \qquad (2)$$

$$P_t \times y_i = K_i \times x_i \qquad ,i=1...n \qquad (3)$$

$$rr_j = k_j \times \prod_{i=1}^{n} M_i^{\alpha_{ij}} \qquad ,j=1...m \qquad (4)$$

$$F_{out,k} = C_D \times \Delta P_k \qquad ,k=1...p \qquad (5)$$

6. Results

The experimental results, obtained from the self-hydrolysis of aqueous sodium borohydride (10% w/w, 50 ml) at 45°C, in terms of gas volume produced and *pH* of the solution are shown in Figure 2. With these experimental data, the kinetic reaction

constants were estimated from successive simulations and correspond to the minimized square difference between the experimental and model predicted values. The estimated parameters are given in Table 3. It is clear that the proposed reaction mechanism successfully describes the experimental behavior, particularly for total gas production. Thus, with the estimated constants, the model can be used to predict the behavior of the system at 45°C for different initial conditions, as presented in Figure 3. For different temperatures, additional data need to be considered to determine the pre-exponential factor and the activation energy of the individual reactions, which is ongoing work.

Table 3. Kinetic reaction constants for each step of the self-hydrolysis mechanism of sodium borohydride (10% w/w) at 45°C.

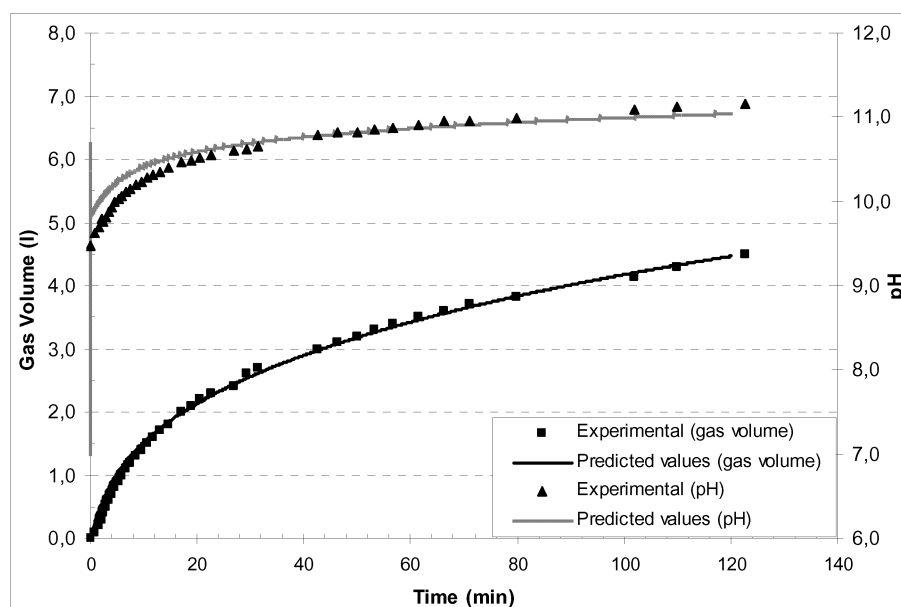| Step number	Direct reaction kinetic constant	Indirect reaction kinetic constant
	$[s^{-1}]$	$[l.mol^{-1}s^{-1}]$
1.1	4.0×10^2	1.8
	$[l.mol^{-1}s^{-1}]$	$[l.mol^{-1}s^{-1}]$
1.2	2.8×10^6	1.1×10^8
1.3	1.0×10^8	-
1.4	9.8×10^7	1.7×10^{17}
1.A	2.1×10^5	5.0×10^{-9}

Figure 2. Graphical comparison between the experimental data and the model predicted values for the produced gas volume and solution pH through the self-hydrolysis of sodium borohydride (10% w/w) at 45°C, for a 50 ml initial solution.
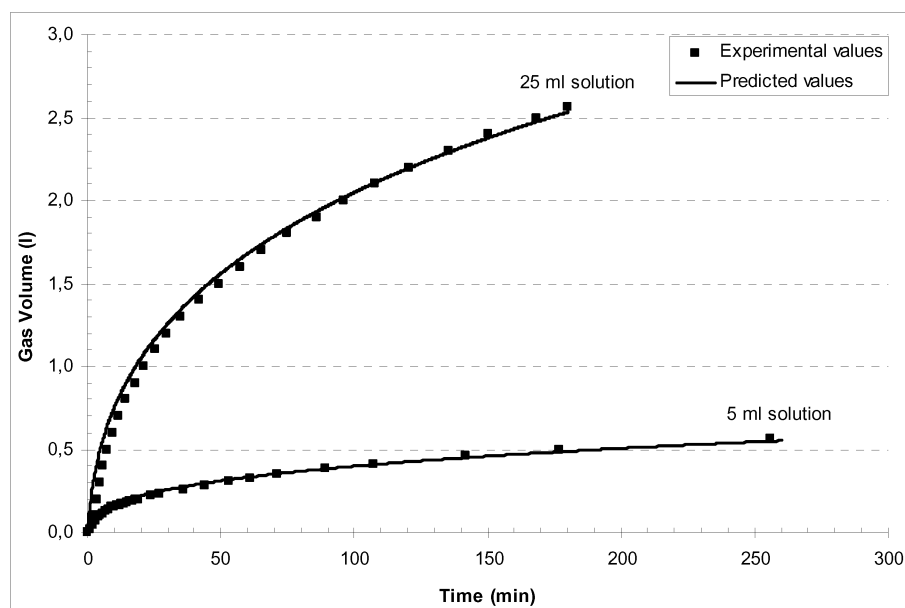
Figure 3. Graphical comparison between the experimental data and the model predicted values for the produced gas volume during the self-hydrolysis of sodium borohydride (10% w/w) at 45°C, for 5 and 25 ml solutions.

7. Conclusions

The results have revealed that the proposed reaction mechanism together with the system model can adequately describe the experimental data obtained for the self-hydrolysis of sodium borohydride. Furthermore, it was confirmed that this reaction is self-inhibited and its rate, in alkaline media, is controlled by the borane formation step, dependent on the H^+ ion concentration. Other preponderant factors are the subject of future work, such as: the identification of all self-hydrolysis reaction products and their fractions, the effect of borates precipitation on the reaction rate and the more important catalyzed hydrolysis process.

8. References

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