

On-demand hydrogen generation by hydrolysis of sodium borohydride in batch reactors: effect of the buffer pressure

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Abstract

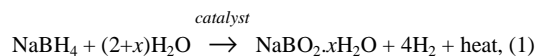
A study was undertaken in order to investigate the potential of hydrogen generation by hydrolysis of sodium borohydride in batch reactors, operating at moderate pressures, in the presence of a reused nickel-ruthenium based catalyst, to feed on-demand a proton exchange membrane fuel cell. The effect of the buffer pressure is explored and hydrogen generation rates are evaluated by changing catalyst amount, operating pressure and successive refueling.

Keywords: hydrogen generation, NaBH₄, PEM fuel cell, Ni-Ru based catalyst, batch reactor, buffer pressure

1 Introduction

Our planet faces serious and unprecedented energy challenges relating to sustainability and greenhouse gas emissions as well as energy security. Policies supporting the use of renewable energy sources are making manufacture and supply of renewable energy technologies more attractive as business opportunities. In recent years, the increasing demand for more portable electronic equipments leads to rapid developing of proton exchange membrane (PEM) fuel cells. PEM fuel cell is suited for pure hydrogen (H₂) fuel and it is primarily aimed at the telecommunication market and the transport market. In truth, the performance of PEM fuel cell dominantly depends on the stable supply of high purity H₂. Nevertheless, the methods of storing hydrogen using tanks, activated carbon or nanoscale materials cannot keep the long-term hydrogen storage. At present, the borohydrides have been proved as the new stable hydrogen-storage materials. High purity H₂ can be produced in the self-hydrolysis of the borohydrides. Among them, alkaline sodium borohydride (NaBH₄) solution is attracting more attention because it has many advantages, including high theoretical hydrogen content (10.6 wt%), stable self-hydrolysis process and friendliness to the environment. NaBH₄

reacts with water to generate molecular hydrogen according to the hydrolysis reaction:



where x is the hydration factor. Schlesinger *et al.* [1] recognized the particular striking catalytic effect of certain transition metals and their salts on NaBH₄ hydrolysis rate. Ideal hydrolysis is attained for $x = 0$ [1], but in practice excess of water is required to account for the fact that the solid by-product (NaBO₂· x H₂O) can exist with varying degrees of hydration [2]. At room temperature, however, the H₂ generation rate is not satisfactory without the presence of some catalysts. Several metal catalysts enhance hydrolysis of the alkaline NaBH₄ solution, giving high-performance H₂ generation rates. Demirci *et al.* [3] and more recently Liu *et al.* [4] reviewed the most used catalysts in reaction (1).

The present work investigates the possibility of simultaneously producing and storage H₂ to feed a PEM fuel cell, by using two batch reactors with different internal volumes, in the presence of nickel-based bimetallic catalyst, reused 235-238 times. The scenario of a sudden hydrogen on-demand is explored, by the quick opening reactor release valve (fixed on the outside lid of the reactor) for a few seconds, before reaction

completion. After then, the same valve is closed, and the hydrolysis reaction proceeds until its end. With this procedure, it is expected to accurately measure the H₂ generation rate, before and after the valve opening, and hence, studying the influence of an unexpected interruption on normal H₂ generation speeds. The effects of catalyst amount, operating pressure and successive refuelling on H₂ generation rate with one swift interruption, are also investigated. As the authors are aware, the subject *hydrogen buffer pressure* on hydrogen production (and storage) by catalytic hydrolysis of NaBH₄ in batch reactors is for the first time exposed on the present paper. Actually, the need of knowledge of the *working hydrogen buffer pressure* can shed new ways of constructing hydrogen generators and even containers and also improve control/safety of these systems for several applications.

2 Experimental procedure

2.1. Catalyst reutilization between 235-238 times

A nickel-based bimetallic catalyst of Ni-Ru, in the form of a finely divided powder and unsupported, was prepared in April of 2008 from a mixture of precursors, based on nickel salts (Riedel-de Haën), by chemical reaction with 10 wt% borohydride solution (Rohm and Haas) as the reducing environment. The catalyst, characterized by a large specific surface area, has been used since synthesis in many studies [5-6]. Aiming at studying the recyclability and aging of the catalyst – it is still running at the present work - the experiments reported in the current paper were performed with the catalyst reused between 235-238 times. Weighted amounts of catalyst in the proportion of Ni-Ru based catalyst/NaBH₄: 0.4 and 0.6 g/g (or 4.2 and 6.2 wt% of catalyst) were selected to study the influence of the amount of catalyst on H₂ generation rate, before and after one swift interruption in the gas cumulative production.

2.2. Hydrogen generation tests

A volume of 10 cm³ of stabilized sodium borohydride aqueous solutions (10 wt% NaBH₄ with 7 wt% NaOH) was injected into one of the two tested batch reactors – with internal volume of 0.646 L and 0.229 L (see Fig.1) – by means of a syringe.

More specific details of experimental rig and procedure are explained on earlier works [5, 7]. All experiments were performed at room temperature (19.5-22 °C) and without stirring. The temperature of the reactor medium was observed by a k-thermocouple and recorded simultaneously with a data acquisition system using LabView software. To monitor the rate of hydrogen generation, the gas

pressure inside the reactor was followed with an appropriate pressure probe.

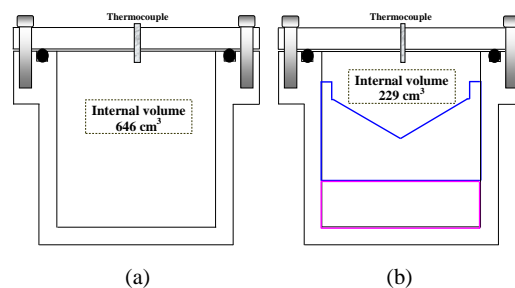


Fig. 1. Schematic view of the inside of the two batch reactors: (a) reactor LR/0.646 L and (b) reactor SR/0.229 L, with flat and conical bottom shapes, respectively.

The hydrogen yield in reaction (1) was calculated by the following equation

$$\text{yield}(\text{H}_2) = n(\text{H}_2)_{\text{exp}} / n(\text{H}_2)_{\text{theoretical}}, \quad (2)$$

where $n(\text{H}_2)_{\text{exp}}$ is the total number of moles of generated H₂ (before and during the reactor release valve opening and also after valve closing until hydrolysis completion) and $n(\text{H}_2)_{\text{theoretical}}$ is the theoretical amount of generated H₂ assuming 100% conversion of NaBH₄ by applying the ideal gas law. Special care was taken to correct the free varying volume of gas inside the reactor due to the consumption of NaBH₄ and water [5].

3 Results and discussion

As already referred, hydrogen was generated from catalyzed hydrolysis of 10 cm³ of the reactant solution (10 wt% NaBH₄, 7 wt% NaOH, 83 wt% H₂O) with Ni-Ru based catalyst/NaBH₄: 0.4 and 0.6 g/g. The effects of catalyst amount, system pressure and of two successive loadings of *fuel* on the hydrogen generation rate with one single sudden interruption (of a few seconds before reaction completion) were studied, and the results found are next presented and discussed.

3.1. Effect of catalyst amount on hydrogen rate

Figure 2 shows the influence of the amount of catalyst used in H₂ generation rate performed in batch reactor LR (646 cm³). As can be seen in the plot of Fig. 2, increasing the amount of the catalyst (catalyst/ NaBH₄: 0.4 g/g to 0.6 g/g) increases the dP/dt slope in the linear zone. Hence, in Fig.2(a), for catalyst/ NaBH₄: 0.4 g/g, the values of 0.004 bar/s or 0.3 L(H₂) min⁻¹ gcat⁻¹ before sudden valve opening and of 0.005 bar/s or 0.4 L(H₂) min⁻¹ gcat⁻¹ after valve closing till completion, were found. The same trend for one swift interruption was verified for the amount catalyst/ NaBH₄: 0.6 g/g, but with

higher values in H₂ rates: 0.011 bar/s or 0.6 L(H₂) min⁻¹ gcat⁻¹ before sudden valve opening and 0.006 bar/s or 0.3 L(H₂) min⁻¹ gcat⁻¹ after valve closing to reaction completion.

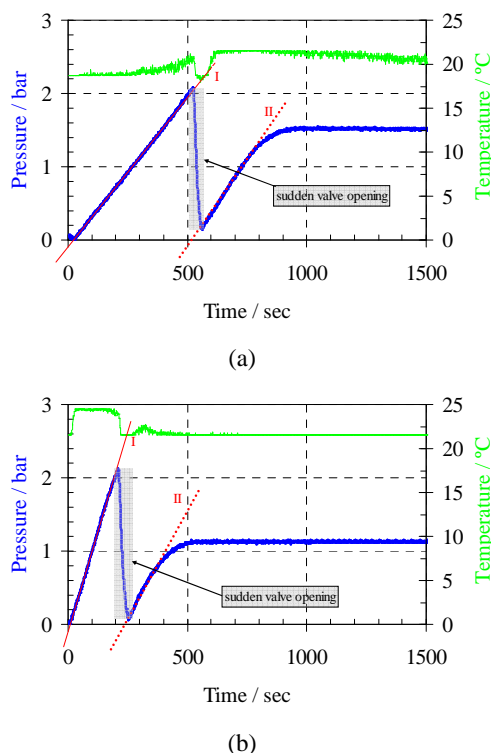


Fig. 2. Influence of the amount of catalyst on H₂ generation rate with one swift interruption performed in batch reactor LR (646 cm³): (a) catalyst/NaBH₄: 0.4 g/g and (b) catalyst/NaBH₄: 0.6 g/g.

The plot in Fig.2(a), for a single fuel injection, also show the tendency of the studied system to maintain practically constant the H₂ generation rate before and after one swift interruption. These rates differs by a factor of 2 in case of the experiment with catalyst/NaBH₄=0.6 g/g. In fact, in the plot of Fig.2(b), after valve closing, the H₂ generation rate decreases gradually from 0.6 L(H₂) min⁻¹ gcat⁻¹ to 0.3 L(H₂) min⁻¹ gcat⁻¹. This may be caused by some H₂ adsorption at the surface of the porous catalyst (due to its higher amount in the system) and thus reducing its catalytic reactivity.

3.2. Effect of pressure on H₂ generation rate

Figure 3 shows the rate of hydrogen generation in terms of H₂ pressure as a function of time, for one single injection of 10 cm³ of reactant solution, performed in the batch reactors LR and SR (Fig.3(a) and Fig.3(b), respectively), using a proportion Ni–Ru based catalyst/NaBH₄: 0.4 g/g.

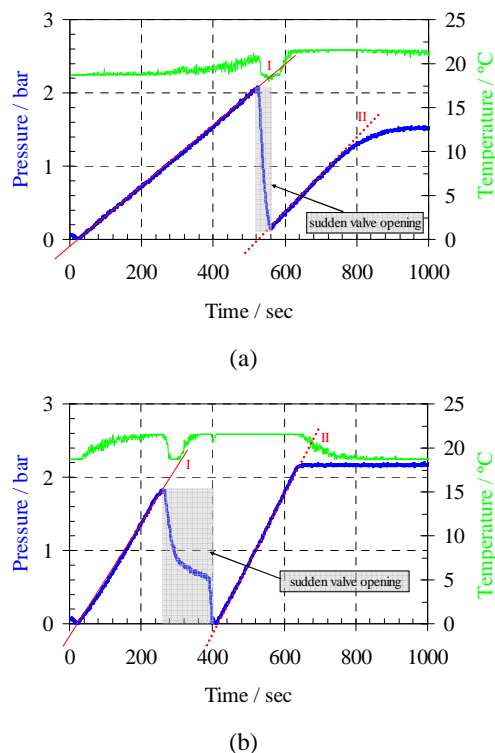


Fig. 3. Influence of pressure on H₂ generation rate for one swift interruption performed in the: (a) batch reactor LR (646 cm³) and (b) batch reactor SR (229 cm³), with a proportion of Ni-Ru based catalyst/NaBH₄: 0.4 g/g.

As can be seen from the plots of Fig. 3 the effect of pressure on H₂ rates is considerable. In truth, we may conclude that increasing the pressure, by changing the reactor vessel from LR to SR, significantly increases H₂ rates from ~0.0045 bar/s to ~0.0085 bar/s.

As expected, the H₂ rates or the dP/dt slopes in the linear zone of the plots outlined in Fig.3, remain almost constant before sudden valve opening and after closing it (~0.3 L(H₂) min⁻¹ gcat⁻¹). However, looking at the end of the reaction curve, after the reactor release valve was closed, i.e., before H₂ generation curve reaches the “plateau” (~100% conversion), the aspect of the curves in that specific zone are quite different. In Fig.3(b), for the batch reactor SR with 229 cm³, a sharp edge was found. In its place, a round edge was sketch for the same experiment performed in reactor LR (with 646 cm³). A possible explanation could be related to the fact of the two batch reactors having different bottom geometries: the SR reactor has a conical bottom shape, which enhances the contact between the catalyst and the reactant solution [6]. The LR batch reactor has a flat bottom shape, which could rise to some mass transfer limitations between the reacting solution and the by-products.

It is worth to notice that the results presented in Figs.2-3 were achieved using Ni–Ru based powdered catalyst reused about 235-237 times. After separation from the reaction medium and rinsing with deionised water, the used Ni–Ru based catalyst was re-evaluated and almost the same catalytic activities were obtained during the studied cycles (for reproducibility).

3.3. Effect of two successive loadings of reactant solution on hydrogen generation rate

Figure 4 shows the hydrogen generation rates of two successive loadings of 10 cm³ of reactant solution, using a proportion Ni–Ru based catalyst/NaBH₄= 0.6 g/g.

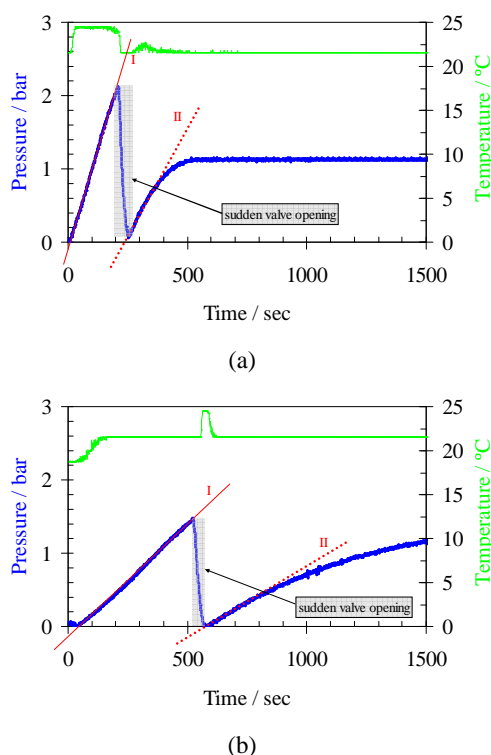


Fig. 4. Hydrogen generation in batch reactor LR (646 cm³) of two successive loadings of 10 cm³ of reactant solution, with Ni–Ru based catalyst/NaBH₄= 0.6 g/g: (a) 1st loading and (b) 2nd loading (performed after 15 days).

The plots in Fig.4 show that the tendency to keep almost constant the hydrogen generation rates, before and after one swift interruption, differs from the experiments performed by one single loading (see Figs.2-3). With two successive refuellings, and for the same reactor bottom geometry, a reduction by an half of H₂ generation rate value were observed, not only before and after the sudden H₂ release but also between the two successive loadings. Hence, in Fig.4(a), values of 0.6 L(H₂) min⁻¹ gcat⁻¹ before

sudden valve opening and 0.3 L(H₂) min⁻¹ gcat⁻¹ after valve closing (till completion) were attained. In Fig.4(b), 0.2 L(H₂) min⁻¹ gcat⁻¹ and 0.1 L(H₂) min⁻¹ gcat⁻¹ were, respectively, found. It can be conclude that the effect of refuelling on H₂ generation rates put forward the importance of considering diffusion limitations between the fresh reacting solution and the remaining reused catalyst, which was kept at the bottom of the reaction vessel.

4 Conclusions

The hydrogen generation rates found in present studies are within the range of values reported in the open literature [3, 4], for catalyst metals with ruthenium. The need of defining a hydrogen buffer pressure, for example, to satisfy a sudden hydrogen demand, was explored. To achieve this goal, the reactor release valve (fixed on the outside lid of the reactor) was quickly opened for a few seconds. Then after, the valve was closed and the H₂ generation continues until hydrolysis completion. The results have shown the tendency of the studied systems to maintain constant the H₂ generation rates for single fuel injections. This trend is broken in the experiments with successive refuelling, probably due to mass transfer limitations. To conclude, the analysis reported on the present paper provides a framework for predicting the performance of a reused powdered catalyst on H₂ generation rate via hydrolysis of NaBH₄ in batch reactors for on-demand portable fuel cell applications.

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