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Title:	**Progress in the Catalysed Hydrolysis of Sodium Borohydride as a Hydrogen Source for Low Power PEM Fuel Cells**				
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EXPECTED CLASSIFICATION: (please, mark all the options that better define the research performed)

	MAIN SESSION
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	Supercapacitors
X	Hydrogen
	Other

	SUB-CLASSIFICATION
	Numerical simulation
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Progress in the Catalysed Hydrolysis of Sodium Borohydride as a Hydrogen Source for Low Power PEM Fuel Cells

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1 Introduction

Sodium borohydride ($NaBH_4$) is currently being studied as a promising hydrogen storage option due to its high gravimetric capacity (10.73 wt%), well within DOE targets for 2015. In spite of a no-go recommended by US DOE for sodium borohydride for on-board automotive hydrogen storage, interest continues to find solutions for portable applications [1]. Due to easy control of H_2 generation rate, moderate operation temperatures and environmentally benign hydrolysis by-products, sodium borohydride has prompted numerous research works contemplating catalysed hydrolysis as a means to produce meaningful reaction rates [2-10]. A critical issue in developing an efficient hydrogen generator is the limitation in terms of the amount of borohydride that can be dissolved in aqueous solutions and also the amount of water needed for reaction completion. The system looses efficiency of storage due to the fact that the reaction needs excess water to account for the solubility of sodium borohydride and the borate by-products; furthermore the capture water by the latter reduces even further the efficiency of the reaction, equation (1). In practice, four moles of water are necessary for full hydrolysis of 1 mol of $NaBH_4$ (equation 1).

$$NaBH_4 + (2+ x)\ H_2O \rightarrow NaBO_2.x\ H_2O + 4H_2\uparrow + \text{ heat} \quad (1)$$

where *x* is the excess hydration factor [11].

Ideal hydrolysis is attained for *x* =0 [12], but in practice excess of water is necessary to account for the fact that the solid by-product ($NaBO_2.xH_2O$) can exist with varying degrees of hydration [11]. In fact, most schemes for hydride hydrolysis require a large excess of water to pre-dissolve the hydride for storage or to keep the by-products in solution.

Most of the available research data focuses in the search for catalyst, their characterization and catalytic activity, with experiments generally performed under atmospheric conditions. In fact, work concerning $NaBH_4$ hydrolysis under pressure is scarce [13,14]. One of the most important works is that of Kojima *et al*. [13], who carried out sodium borohydride hydrolysis in a closed vessel at pressures up to 25 MPa, using a stoichiometric amount of water. Effective gravimetric and volumetric storage capacities yielded 9.0 wt% and 188 kgm^{-3}, respectively, attained using Pt-$LiCoO_2$ as a catalyst at 296K.

Ferreira *et al.* indicated that the gravimetric storage capacity of the system can be improved to over 6 wt% (material-only basis) by working in alkali free solutions and specific stoichiometric H_2O to $NaBH_4$ ratio under pressures up to 1.26 MPa [15].

In the present study, hydrogen was produced under moderate pressures in batch reactors (up to 70 bar) by hydrolysis of stabilized sodium borohydride solutions (10 wt% $NaBH_4$ and 3-10 wt% NaOH), in the presence of nickel-ruthenium (Ni-Ru) catalyst. Issues regarding the effect of hydrogen demand on generation rates are here explored. To this end, a sudden hydrogen demand is created and the consequent need to regulate the buffer H_2 pressure is investigated, by the opening the reactor release gas valve, at a pre-fixed pressure, and proceeding afterwards, till reaction is completed. The effects of catalyst amount, operating pressure and of successive loadings of reactant solution on H_2 generation rate, are studied. Data are thought to be important in the design and operation of reactors to be coupled to fuel cells in low power applications.

2 Experimental

A nickel-based unsupported catalyst containing 1.42 wt % Ru, in the form of a finely divided powder, was prepared from a mixture of precursors based on nickel and ruthenium salts (Riedel-de Haën), by a wet chemical route using 10 wt% $NaBH_4$solution (Rohm and Haas) as the reducing

environment. When the reduction was complete the catalyst was appropriately decanted, washed, filtered, dried and heat-treated at 110ºC. The catalyst was kept in a dessicator until use. The catalyst, characterized by a large specific surface area, has been reused since its synthesis in many of our studies [15-18]. The catalyst has been demonstrated to have been re-used by more than 300 times without significant degradation, fact already reported in previous publications [15,16].

Catalyst samples have been fully characterized and results published elsewhere, given account of BET surface area, morphology and elemental composition by SEM and EDAX. X-Ray Photoelectron spectroscopy (XPS) of the catalyst before use has indicated a Ru amount of 1.42 wt% [15,16].

A volume of 10 cm^3 of stabilized $NaBH_4$ aqueous solutions (the water being in excess: x= 16 or $H_2O/NaBH_4$: 18 mol/mol), with 10 wt% $NaBH_4$ (Rohm and Haas, ≥ 98% purity) and 7 wt% NaOH (Eka, ≥ 98% purity), was injected into the tested batch reactors.

For work up to 70 bar, a type 316 stainless steel 300Parr pressure vessel equipped with several head fittings such as, a magnetic drive, a gas inlet valve, a thermocouple, a liquid sampling valve, a gas release valve, a safety rupture disc and a pressure gage was used, see figure1.

Fig. 1 A view of the reactor used in this work

Experiments were performed at room temperature and without stirring.

Special care was taken to correct the free varying volume of gas inside the reactor due to the consumption of water (it was assumed a consumption of 4 mole H_2O per mole of $NaBH_4$, the crystal structure of the classic hydrolysis by-product appears to be a preferential sodium metaborate dihydrate, $NaBO_2.2H_2O$ [17]).

3. Results

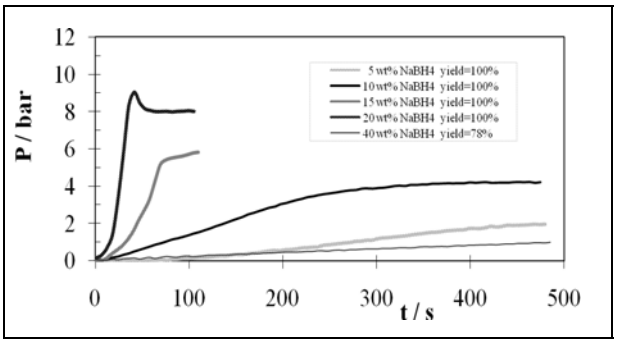
3.1 Catalytic activity

A NiRu catalyst was synthesized using small amount of Ru so to obtained Ru loads up to 1.42 wt%. It is considered that the strength of the NiRu catalyst for the hydrolysis of sodium borohydride lies in the activity of both of the chosen materials: nickel by its activity towards hydrogen evolution and ruthenium by its activity in water dehydrogenation reactions, which in this case play a complimentary role for an effective hydrogen delivery from borohydride.The catalyst has also been found to be sufficiently stable to allow extensive reutilization as already reported [16,18]. Typical rates of ~10000 $mLmin^{-1}g^{-1}$ have been attained for 10 wt% NaOH at 45ºC.

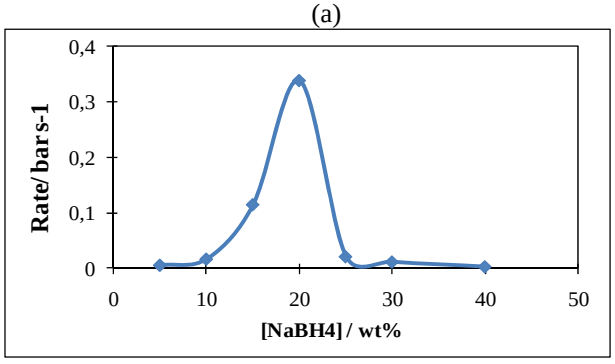
3.2. Hydrogen generation under pressure

The system NiRu/$NaBH_4$/NaOH in aqueous solutions was characterized as a function of the solution temperature and sodium borohydride concentration when the hydrolysis reaction was allowed to proceed under pressure.

At a fixed temperature, the effect of sodium borohydride concentration at 3 wt% NaOH on the hydrogen generation rate was ascertained, see figure 2. Reaction yields of 100% were associated to low concentration while for high concentrations, such as 40 wt% $NaBH_4$ only 78% was obtained..



(a)



(b)

Fig. 2 Effect of the concentration of sodium borohydride on the hydrogen generation rate (a). A maximum around 20 wt% is found

Regarding reaction rates, a maximum was found at 20 wt% $NaBH_4$, this value is higher than

the value found at atmospheric pressures which is between 10 and 13 %wt.

A set of experiments were designed to study the hydrogen generation under pressure using 10 wt% $NaBH_4$ stabilized solutions in various batch reactors to reach pressures between 2 and 70 bar.

The effect of pressure from 17 to 70 bar on the reaction rate and yield was carried out without temperature control for 10wt% sodium borohydride solution stabilized with 3 wt% NaOH, using different solution volumes and hence different initial sodium borohydride masses in order to maintained the same initial concentration of $NaBH_4$. The general trend of the curves, as evident in figure 3, is similar to those obtained at lower pressures, presenting also very high yields. Up to now high yields have only been reported for stoichiometric water to borohydride ratios from 2 to 8. Results presented here correspond to the case of hydrolysis in excess water (ratio 18).

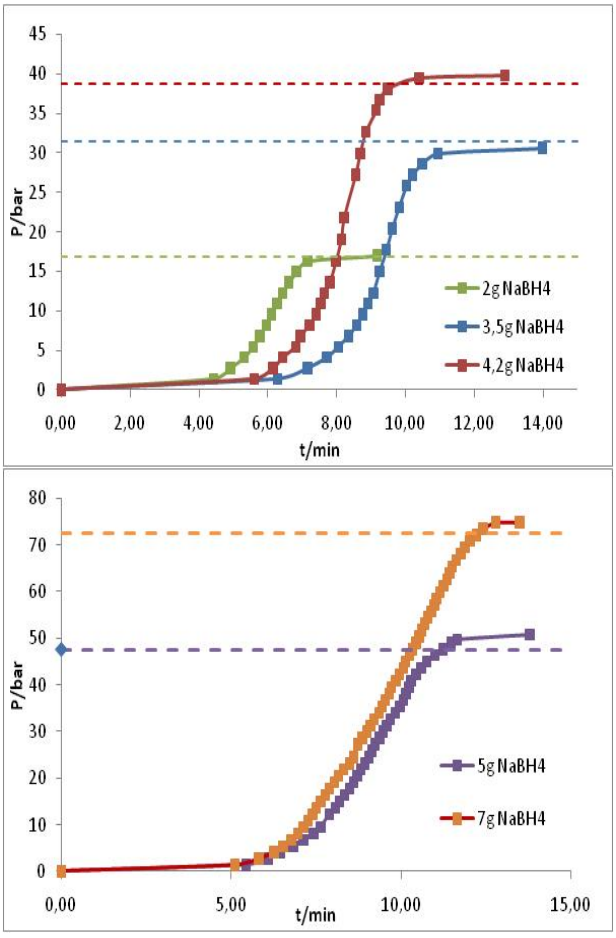


Fig.3 Hydrogen generation from sodium borohydride expressed as the reactor pressure vs reaction time, for various initial amounts of $NaBH_4$ compliant with 10wt% in the working solution using a NiRu catalyst. Final pressures varied from 17 to 70 according to the initial amount of sodium borohydride. Theoretical expected hydrogen pressures are indicated by a horizontal broken line for each case.

Another critical issue when working with batch reactors is the requirement for on-demand hydrogen. In this work this is simulated by opening the reactor valve before reaction completion. The effect was studied programming a cycle of valve openings after hydrogen production has reached a pressure of near 20 bar. The effect of catalyst concentrations is also presented and discussed.

Figure 4 shows the hydrogen generation rate, without temperature control, for a 10wt% sodium borohydride solution stabilized with 3 wt% NaOH after the reaction is left to proceed up to the first 19 bar of pressure. Following swift opening of the reactor valve for hydrogen release, the valve is closed again so that reaction can proceed up to the same pressure before he valve is again opened. The cycle is repeated up to completion of the reaction with the exhaustion of the all the borohydride initially loaded into the reactor. Figure 4 shows typical hydrogen generation profiles as a function of reaction time, where it is evident that it is possible to act in the on-demand fashion without altering the rate of hydrogen delivery. Efficiency of the reaction is very high, nearly 100%. When the catalyst mass was doubled, the tendency is maintained but the reaction time is brought down by half, for a corresponding increase in reaction rate of 2x.

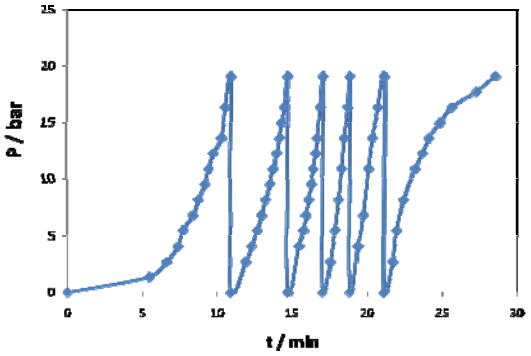


Fig. 4 Hydrogen generation profile as a function of reaction time for the hydrolysis of a 10 wt % sodium borohydride solution stabilized with 3 % NaOH. A pressure of 19 bar was pre-fixed for hydrogen release.

To summarize, the catalytic abilities of Ni-Ru based catalyst in H_2 generation rates are within the range of the largest values reported so far in the open literature.

After successive loadings of reactant solution the by-product identified is a sodium metaborate dehydrated ($NaBO_2.2H_2O$), as reported elsewhere [18].

4. Conclusions

Promising results with potential to overcome some of the critical issues of catalytic hydrolysis of sodium borohydride in batch reactors were tackled and discussed in this paper.

- The H_2 generation rates found using a NiRu catalyst with 1.42wt % Ru, are within the range of values reported in the open literature, for catalysts containing higher Ru concentrations.
- The need to define a hydrogen *buffer pressure* was attempted, to satisfy a specific hydrogen demand was explored; taking into consideration that completion of hydrolysis for high yields is required, with excellent results.
- The results have shown the tendency of the studied systems to maintain constant H_2 generation rates, after swift interruption for fuel injections and also after pressure release.

Research continues along these lines with the search for optimum conditions for the hydrolysis of $NaBH_4$ in batch reactors that might be connected to fuel cells as well as to obtain larger H_2 storage capacities and strategies with impact on recyclability and dehydration kinetics of by-products.

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