HYDROGEN PRODUCTION FROM SODIUM BOROHYDRIDE ON A Ni-Ru CATALYST: AN ELECTROCHEMICAL STUDY

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ABSTRACT

Previous work by the authors has demonstrated a high rate and high yield hydrolysis of sodium borohydride, in the presence of a Ni-Ru catalyst synthesized by wet chemistry. The catalyst has been fully characterized and utilized more than 300 times exhibiting high stability and durability. In this work, results of an electrochemical study are reported using the powder catalyst supported on a Ni foam in order to measure the open circuit potential during hydrogen production and to study the reaction using voltammetry and ac impedance. Production rates were as high as 10 $Lmin^{-1}g_{cat}^{-1}$ at 65ºC. Electrochemical studies indicated that the hydrogen evolution mechanism corresponds to a Volmer-Heyrovsky type, suggested by a Tafel slope of 117 $mVdec^{-1}$. Tafel region potentials are in agreement with values found for hydrolysis at the open circuit. The Langmuir-Hinshelwood mechanism explains the hydrolysis of sodium borohydride using a Ni-Ru catalyst. The role of Ni and Ru is briefly discussed.
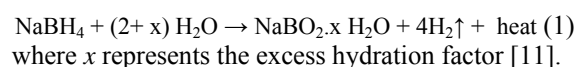
INTRODUCTION

Sodium borohydride emerges as potential hydrogen carrier and media for storage due to its high volumetric and gravimetric efficiency. Even though its storage capacity is well within DOE targets for 2015, limitations exist because hydrolysis is restricted by available water. Recycling cost of metaborates is another major drawback.

In spite of a no-go recommended by US DOE for $NaBH_4$ for on-board automotive hydrogen storage, interest continues to find solutions for portable applications [1]. Sodium borohydride good stability in alkaline solution, easy control of hydrogen generation rate, moderate operation temperatures and environmentally benign hydrolysis by-products has prompted numerous research works contemplating catalysed hydrolysis as a means to produce meaningful reaction rates [2-11].

Critical issue in the developing of an efficient hydrogen generator using $NaBH_4$ is the limitation of the amount of water needed for reaction completion given the amount of borohydride that can be dissolved in aqueous solutions. The system looses efficiency of storage because the reaction needs excess water to account for the solubility of $NaBH_4$

and the borate by-products; the captured 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 borohydride.

$$NaBH_4 + (2+ x) H_2O \rightarrow NaBO_2.x H_2O + 4H_2\uparrow + \; heat \; (1)$$
where x represents the excess hydration factor [11].

Ideal hydrolysis is attained for $x =0$ [12], where two moles of water are required to react with one mole of solid $NaBH_4$ to release four moles of hydrogen, 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.

The by-products species are alkaline and promote a low yield hydrolysis reaction. Inorder to take the reaction to full extent the presence of a catalyst is necessary.

Schlesinger et al. [13] recognized the striking catalytic effect of certain transition metals and their salts on $NaBH_4$ hydrolysis rate. Since the beginning of the last decade, efforts have been devoted to find stable metal catalysts appropriate for reaction (1) [1,2]. Most of the available research data focuses in their synthesis, characterization and catalytic activity. Actually, quite a variety of catalysts have been tested to accelerate the $NaBH_4$ hydrolysis. Demirci et al. [8], and more recently Liu et al. [10], reported an exhaustive list of the most used catalysts for sodium borohydride hydrolysis, which includes the catalyst based on Ru, Co and Ni.

Recent published works, carried out within our research group, have reported different approaches to tackle some of the mentioned critical issues such as the need for increasing the gravimetric storage capacity of the system. This is been done by using stoichiometric amounts of water in the hydrolysis or by using alkali free solutions [14,15]. The use of organic additives have been also put forward in an attempt to modify solution properties, creating conditions for the minimization of the amount of water capture by the by-products [16]. The synthesis and characterization of a non-noble catalyst with outstanding durability, which has been used more than 300X, has also been reported [17].

Results indicated that the gravimetric storage capacity of the system can be improved to over 6

wt% material-only basis) working in batch reactors under pressures up to 1.26 MPa.

In this work, voltammetry and ac impedance were used in an electrochemical study of a durable Ni-Ru catalyst, electroactive in the hydrolysis of sodium borohydride, in an attempt to better understanding the hydrogen evolution mechanism.

Even though advances have been made during the last 10 years, one of the drawbacks in the field is the lack of the kinetics and mechanism of the hydrolysis reaction that correctly describes the dependence on all involved species. Data availability in this context will be an important aid for the optimum design of hydrogen generators and thereby for the successful development of a borohydride-based hydrogen production/storage technology.

EXPERIMENTAL

A Ni-based catalyst, in the form of a finely divided powder, was prepared from nickel and ruthenium salts in a reducing environment. Full characterization is reported elsewhere [14-17].

Morphological aspects have been studied by scanning electron microscopy (Phillips Scanning Electron Microscope (SEM), Model XL 30 FEG, coupled to an Energy Dispersive Spectrometer (EDS), and Transmission Electron Microscopy (TEM) using a Tecnai F30 field emission gun instrument operated at an accelerating voltage of 300 kV. Typical experiments used 0.05 to 0.1g of catalyst in solutions containing 2 to 10 wt % sodium borohydride (Rohm and Haas) stabilised solution with 10 wt % NaOH. A study of the hydrolysis reaction was conducted in order to determine reaction rates at different conditions. The volume of generated gas was measured by a water displacement method rendering values at standard pressure and temperature. The produced gas volumes were measured as a function of time at controlled temperature till complete exhaustion of the reactant.

In order to conduct the electrochemical studies, the catalyst formulation was fixed on a Ni metallic foam

provided by INCO, with a density of 380 g.m^{-2} and a thickness of 1.6 mm, (figure 1a) shows the morphology of the as received foam). A modified "Doctor Blade" technique [6] was used to produce a supported catalyst with high surface area and activity. Because this technique does not use a complex equipment, it is a relatively cheap way to produce good supported catalysts. A slurry, containing the powder catalyst, was prepared and applied as a thin film to the support substrate. The slurry was uniformly applied over the foam in various successive loadings with drying periods between applications. When all the desired catalyst was deposited, a heat treatment was made at 423 K.

All the experiments were made in the stationary mode without magnetic stirring and under controlled temperature. In the case of the open circuit potential measurements, a simultaneous recording of the liberated hydrogen gas was made at all tested temperatures. The Ni-foam supported catalyst acted as the working electrode with an Ag/AgCl (KCl saturated electrode) as the reference electrode. Figure 1b) shows the typical experimental set-up used for the kinetic experiments with the supported catalyst. The set-up consisted of the reactor chamber, potential measurement, a computer data acquisition and a gas measurement system. For temperature control, a water bath provided with thermostatic control was used with the glass reactor partially immersed in the bath. A data logger from Fluke, model Hydra Series III was employed and the values were recorded using a computer data acquisition system.

Polarisation curves of the supported catalyst in stabilised sodium borohydride solutions were made using a potentiostat/galvanostat PARC Model 273. A three electrode conventional cell was used using a platinum wire as auxiliary electrode and a Ag/AgCl reference electrode.

A Frequency Response Analyser (model 1250, Solartron) connected to an Electrochemical Interface (model 1286, Solartron) was used to obtain the impedance spectra at pre-selected potentials.
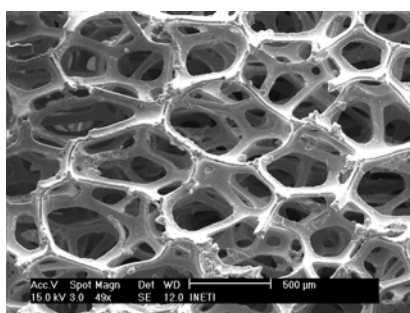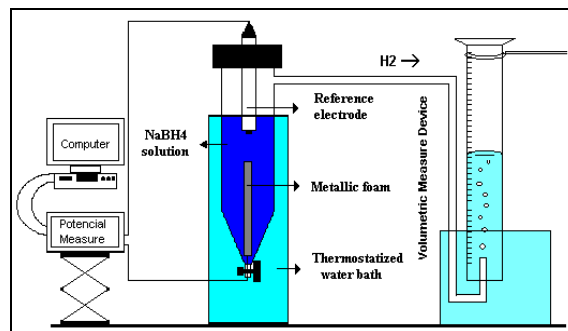

(a)   (b)

Fig 1: Scanning electron micrograph of the as-received nickel foam (a); experimental set-up used in electrochemical characterization of sodium borohydride hydrolysis (b).

RESULTS AND DISCUSSION

A Ni-Ru catalyst with a specific surface area of 54 m^2g^{-1} and negligible pore volume was synthesized with a Ru content of 0.74 at%. Full characterization is given elsewhere [15-17].

The effect of temperature on the reaction rate was studied and the activation energy of the process estimated for temperatures up to 338K. Typical data in the form of an Arrhenius type plot are given in figure 2 for a 10 and a 2 wt% solution of $NaBH_4$, stabilised with 10 wt% NaOH. Higher reaction rates are exhibited for the more concentrated solution. The plot shows the existence of two linear regions with slope changing at 318K. Activation energies of ~85 and 31 $kJmol^{-1}$ were found for temperatures lower and higher than 318K, respectively. This is adjudicated to a change in reaction mechanism.
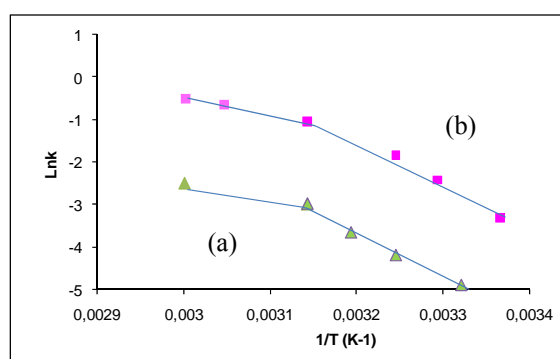

Fig 2: Arrhenius plots for sodium borohydride hydrolysis at temperatures from room temperature up to 338K, in aqueous solutions stabilized with 10 wt% NaOH and containing 2 wt% (a) and 10 wt% of NaBH4(b).

Most studies report only one slope but activation energies are generally estimated for temperatures up to 313K. In other cases, studies including temperatures over 318K, the observed tendency is similar to that found in this work, even though the authors do not acknowledge the existence of two slopes. It is only recently that the possibility of two slopes has been recognized, for example for the case of cobalt catalyst [18].

In order to have more information on the system, an electrochemical study was planned. The powder catalyst was supported on a nickel foam in order to be able to measure the open circuit potential and also to perform voltammetric and ac impedance experiments. In the latter case, potentials were selected taken into account the results obtained at the open circuit.

Figure 3a) shows a high resolution scanning electron micrograph of the powder catalyst particles. Contrast variation is observed due to atomic number differences between ruthenium and nickel particles. The lighter particles are ruthenium and the grey particles are nickel. Combined with transmission electron microscopy (TEM) results, it is suggested that Ru particles were not oxidized; the particle size is 30 to 50m, but the particles are clustered together. Ni particles are already oxidized and the particle size is 30 to 100 nm (not shown). Figure 3b) shows the morphological aspects of the supported catalyst as observed by SEM. A pore size of 597 µm was estimated.


(a)   (b)
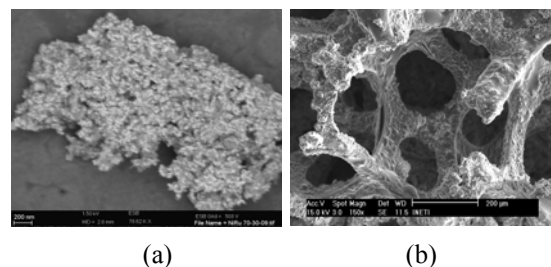
Fig 3: Morphology as observed by SEM of the powdered catalyst (a) and the supported catalyst (b).

Figures 4a) and 4b) shows the volume of gas produced as a function of time in a 2 wt % sodium borohydride solution, at 318 and 338K respectively, and the corresponding open circuit potentials which were simultaneously registered, using the supported catalyst. Three different regions were evident. A first region, where there was no hydrogen production (represents a reaction induction time, activated by temperature), was adjudicated to the adsorption of species. As temperature increases the transition between the first and the second region is less abrupt, suggesting that at sufficiently high temperatures the induction time will be even shorter. In the second region, a linear variation of the volume of produced gas with time is observed (zero order reaction regarding concentration of borohydride) corresponding to a potential plateau; and a third region where the rate of H_2 production decreases before it stops, due to total consumption of sodium borohydride. Rates for 65ºC were ~ 10 $Lmin^{-1}g^{-1}$. The foams were used up to 10 times without signs of deactivation. No loss of catalyst was observed.

The presence of an induction time for the reaction is justified in terms of an adsorption processes prior to the production of gas.

A study of the temperature effect conducted using the supported catalyst rendered an activation energy estimated in ~40 $kJmol^{-1}$. Only one region was observed in the Arrhenius plot, for the whole temperature interval used, with approximately the same value obtained for temperatures higher than

318K when using the powder catalyst. This suggest than temperatures higher than 318K and higher surface area may contribute to the observed change in activation energy.
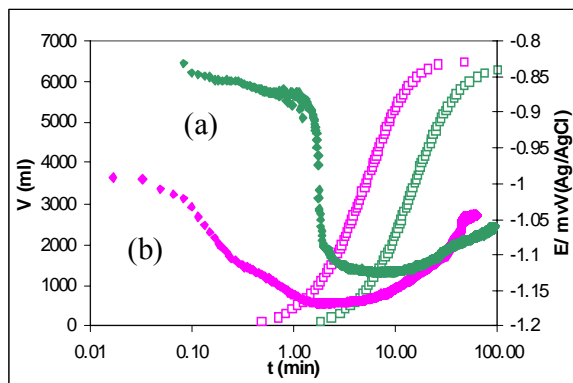
Fig 4: Gas volume produced with a Ni-based supported catalyst at 318(a) and at 338K (b) in a 2 wt % NaBH₄ solution stabilized with 10 wt% NaOH.

Figure 5 shows a typical cyclic voltammogram run at 100 mV.s^{-1},where the potential is plotted as a function of log of the current density, between -2 and 0 V vs Ag/AgCl. The voltammogram allows the identification of the cathodic domain for HER, represented by a linear region typical of a Tafel zone. A slope of ~117 mV/decade was estimated, which corresponds to a mechanism of the type Volmer – Heyrovsky [19]. It is also confirmed that, the potential range for the HER exhibited in the voltammogram falls within the values found in independent experiments where the open circuit potential was monitored.
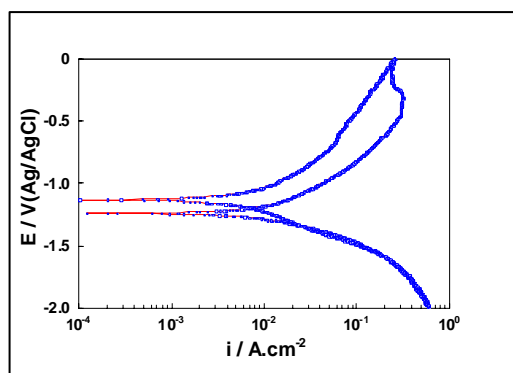
Fig 5: Typical polarization curves of the supported catalyst at a scan rate of 100 mVs^{-1}in a solution containing 10wt% of NaBH4 stabilised with 10 wt% of NaOH.

An equivalent circuit describing the HER was put forward in order to explain impedance data. The circuit includes the solution resistance Rs in series

with a parallel (R_{ct}C)W circuit, integrating the contribution of the charge transfer resistance (R_{ct}) and double layer capacity and the mass transfer processes by introducing a finite length diffusion Warburg element, W. The non-homogeneity of the electrode was taken into account by substituting the capacitance C by a CPE element. In figure 6 it is shown a Nyquist plot of the impedance data at selected potentials, taken from figure 4. The equivalent circuit used to model the data is shown in the inset.

The resistance to charge transfer was calculated and plotted against the applied potential, see figure 7, covering the range from adsorption to hydrogen evolution according to data in figure 4. R_{ct} shows a sharp decrease in the second region where hydrogen evolution occurs.

Exchange current densities estimated from R_{ct} values provided from impedance data are of the order of 1×10^{-3} Acm^{-2} at near room temperature, which is in good agreement with values extracted from typical voltammograms as that shown in figure 5.

The results are interpreted in the light of the general mechanism for the HER in alkaline solutions, proceeding via three steps. These involve atomic hydrogen adsorbed on the electrode surface namely by water reduction with hydrogen adsorption (see reaction 2, known as the Volmer step), followed by two parallel competitive steps, the Heyrovsky and Tafel steps, i.e electrochemical and chemical desorption[19].
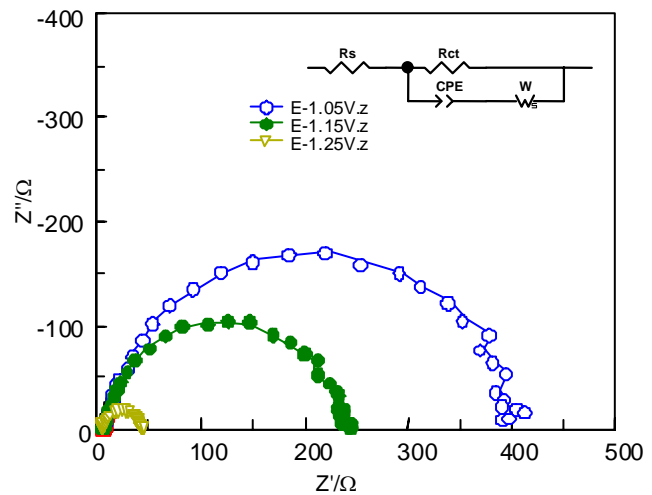

Fig 6: AC impedance spectra obtained at different potentials within the range exhibited by the supported catalyst in 2 wt% NaBH₄ solution stabilised with 10 wt% NaOH at the open circuit. The equivalent circuit used to model data is shown in the insert.
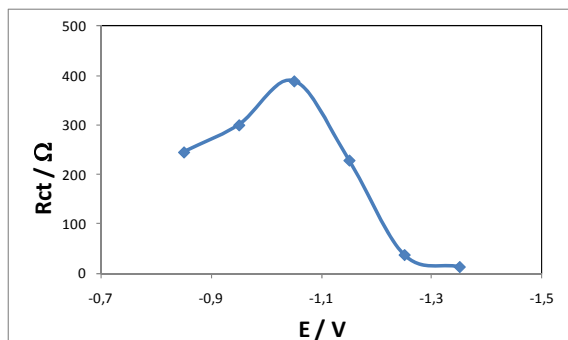
Fig 7: The resistance of charge transfer as a function of potential for the hydrogen evolution reaction from a 2 wt% $NaBH_4$ solution, stabilised with 10 wt% NaOH, using a Ni-Ru catalyst at near room temperature.

Proton discharge electrosorption, step generally accepted for the HER in alkaline solutions, is suggested as the rate determining step:

$$M + H_2O + e^- = MH_{ads} + OH^- \qquad (2)$$
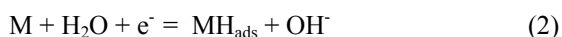
The reversible adsorption of borohydride ion on the catalyst surface, forming two metal complexes (equation 3) is also suggested:

$$2M + BH_4^- = MH_{ads} + MBH_3^- \qquad (3)$$

The hydrogen evolved during the complete hydrolysis partially originates from the solvent and another part from the borohydride ion. Holbrook and Twist [20], when studying the $NaBH_4$ hydrolysis used D_2O over cobalt and nickel boride catalysts, proved that approximately half the evolved gas comes from the solvent. The mechanisms suggest two different adsorption sites.

The Langmuir - Hinshelwood (L-H) model, commonly used to describe reaction kinetics in catalytic reactions, explains the hydrolysis of sodium borohydride over the Ni-Ru catalyst used in this work.

The model combines zero- and first-order kinetic models in two equation terms (equation 4), with the adsorption coefficient K_a determining the relative weight of each term. k_L is the reaction rate constant.

$$(C_{NaBH_4,0} - C_{NaBH_4}) + \frac{1}{K_a}\ln\left(\frac{C_{NaBH_4,0}}{C_{NaBH_4}}\right) = k_L t \qquad (4)$$

K_a decreases with increasing temperature and as a result, at sufficiently high temperatures, K_a is very low and the contribution from the second term of the left hand side of equation (4) dominates the reaction kinetics, thus becoming first-order. On the other hand, at lower temperatures, the K_a magnitude increases, contributing for a zero-order reaction kinetics.

Data obtained conform to the LH model when using the powder and supported catalyst. Typical curves, plotting equation (4) left hand side term as a function of time, are shown in Figure 8.
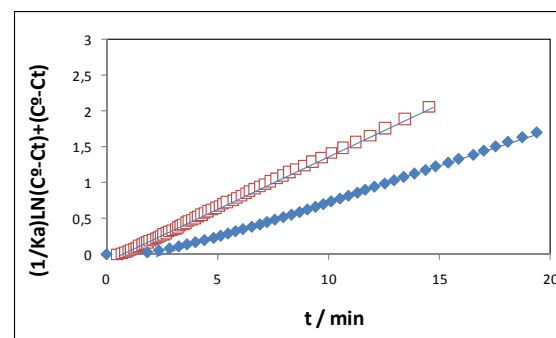
Fig 8: The hydrogen evolution reaction from a 2 wt% $NaBH_4$ solution, stabilised with 10 wt% NaOH, using a Ni-Ru catalyst at 318 and 338K conforms to the Langmuir-Hinshelwood model.

High surface area Ni-Ru catalyst has been shown to be an active electrocatalyst for the HER in alkaline media in the presence of sodium borohydride. Even though the amount of Ru is very small, it is provided the catalyst with outstanding activity and chemical stability and durability. It is considered that the strength of catalyst 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.

CONCLUSIONS

A Ni-Ru catalyst synthesized by wet chemistry, was used for sodium borohydride hydrolysis with excellent catalytic activity and durability. Production rates were as high as 10 $Lmin^{-1}g_{cat}^{-1}$ at 338K. An activation energy change was observed at temperatures higher than 318K.

Supported catalysts were investigated in this work as materials for hydrogen production systems using sodium borohydride and use to conduct an electrochemical characterization of the system. The open circuit potential at which the reaction occurs was identified. Electrochemical studies indicated that the hydrogen evolution mechanism corresponds to a Volmer-Heyrovsky type suggested by a Tafel slope of 117 $mVdec^{-1}$.

The Langmuir-Hinshelwood mechanism explains the hydrolysis of sodium borohydride using a Ni-

Ru catalyst according to results obtained in this work.

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