

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/257173624>

# On the electrosynthesis of sodium borohydride

Article in *International Journal of Hydrogen Energy* · September 2010

DOI: 10.1016/j.ijhydene.2010.01.129

CITATIONS

24

READS

93

2 authors:



**D. M. F. Santos**

Universidade de Lisboa, Instituto Superior Te...

96 PUBLICATIONS 798 CITATIONS

[SEE PROFILE](#)



**César Sequeira**

Technical University of Lisbon

231 PUBLICATIONS 1,475 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



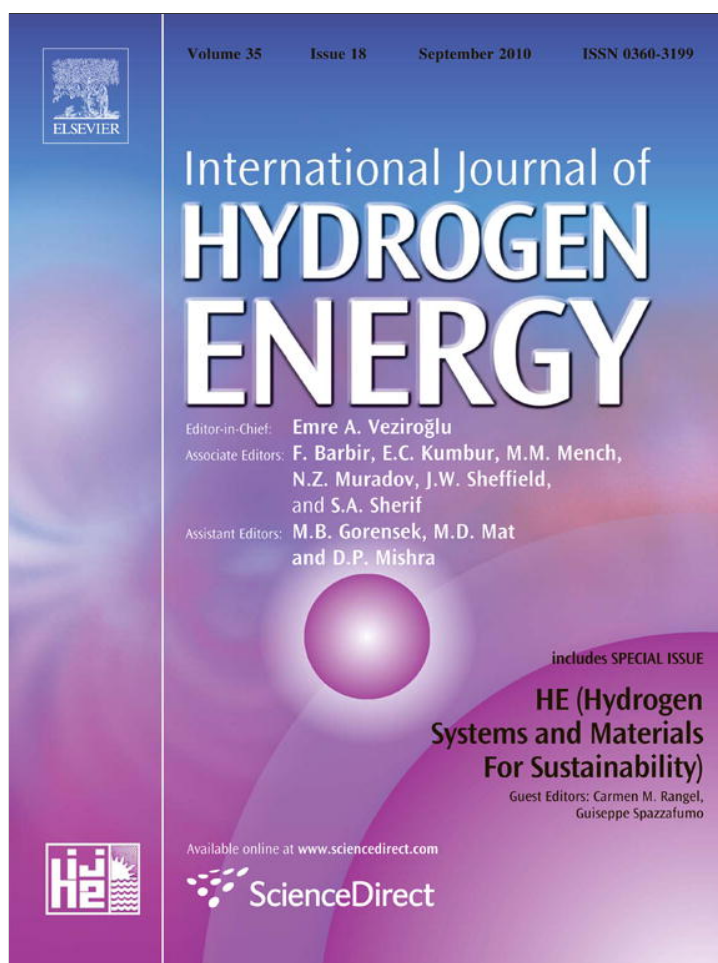
Synthesis and Electrochemical Characterization of Novel Organoborohydride Compounds

[View project](#)



Synthesis and Electrochemical Characterization of Novel Organoborohydride Compounds

[View project](#)



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

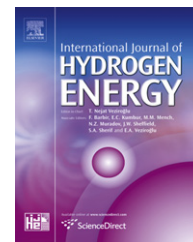
<http://www.elsevier.com/copyright>



Available at [www.sciencedirect.com](http://www.sciencedirect.com)



journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)



# On the electrosynthesis of sodium borohydride

D.M.F. Santos\*, C.A.C. Sequeira

Materials Electrochemistry Group, Instituto Superior Técnico, TULisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

## ARTICLE INFO

### Article history:

Received 20 June 2009

Received in revised form

11 December 2009

Accepted 26 January 2010

Available online 4 March 2010

### Keywords:

Sodium borohydride

Electrosynthesis

In situ monitoring

Potentiometry

Energy systems

## ABSTRACT

Sodium borohydride ( $\text{NaBH}_4$ ) is a versatile reducing agent used in many industrial processes. These include organic and pharmaceutical synthesis, wastewater treatment, and paper pulp bleaching. Additionally, it is a unique material in its ability to carry large amounts of hydrogen in a safe and innocuous form. In order for  $\text{NaBH}_4$  to serve as a valuable support of the hydrogen economy, it is estimated that its cost must be reduced by at least one order of magnitude from its present price. Therefore, considerable research is required on the development of innovative  $\text{NaBH}_4$  synthesis processes that have been reported in the open literature. It is anticipated that the most likely route to achieving the low-cost production of  $\text{NaBH}_4$  lies in the electrochemical methods. A process for synthesising a  $\text{NaBH}_4$  solution using a two-compartment electrolytic cell with conversion of metaborate to borohydride ions is described. Several cathode materials and electrolytic compositions are tested to select the most appropriate experimental conditions for the  $\text{NaBH}_4$  electrosynthesis. To avoid erroneous results leading to false conclusions, the electrolysed solutions were in situ monitored by a newly developed potentiometric technique, whose resulting data are explained by thermodynamic and kinetic considerations.

© 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Hydrogen, the most common element on earth, is widely seen as the ultimate form of clean energy. The proposition that hydrogen should be a sustainable medium has become known as the “Hydrogen Economy”. This term is thought to have been coined in 1970 by Neil Triner at the General Motors Technical Laboratory in Warren, USA. But the concept of using hydrogen have in fact been suggested much earlier in such diverse publications as Jules Verne’s science-fiction novel “The Mysterious Island” (1874) and J.B.S. Haldane’s paper “Daedalus, or, Science and the Future” (1923). It is further notable that Haldane proposed the use of wind power to produce hydrogen via electrolysis of water; the gas would be liquefied and stored in vacuum-jacketed reservoirs that would probably be sunk in the ground.

At current prices, hydrogen is used almost exclusively for the synthesis of ammonia, methanol and other petrochemicals – generally in a plant located in the same petrochemical complex as the reformer – and for petroleum refining. With the growing importance of fuel cells, there will be an increasing need for hydrogen. But, at present, the production of hydrogen as an all-purpose fuel is simply not economic, considering the variety of cheaper fossil fuels available. Moreover, the lack of a practical, affordable, and high-energy density hydrogen storage method is another barrier to the commercialisation of hydrogen fuel cells for automotive and other applications. The energy densities for state-of-the-art liquefied or compressed molecular hydrogen storage systems cannot meet the 2015 energy density targets (9 wt.%  $\text{H}_2$ ) set by the U.S. Department of Energy (DoE) Freedom Car Program [1]. Liquid hydrogen has very low density ( $70.8 \text{ g dm}^{-3}$ ) and requires a bulky cryogenic

\* Corresponding author. Tel./fax: +351 218417765.

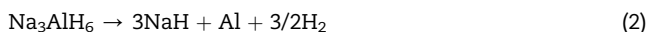
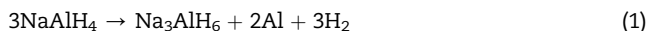
E-mail addresses: [diogosantos@ist.utl.pt](mailto:diogosantos@ist.utl.pt) (D.M.F. Santos), [cesarsequeira@ist.utl.pt](mailto:cesarsequeira@ist.utl.pt) (C.A.C. Sequeira).

0360-3199/\$ – see front matter © 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

doi:10.1016/j.ijhydene.2010.01.129

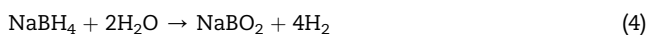
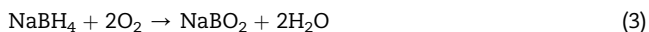
storage system, while compressed hydrogen (70 MPa) has even lower density and requires a heavy containment vessel [2].

Hydrogen may also be stored chemically in the form of the soluble ionic salts  $\text{Na}^+[\text{AH}_x]^-$ , where A represents boron or aluminium; such compounds are generally known as “complex hydrides”. Sodium and lithium borohydrides are well-known reducing agents commonly used in organic chemistry. For hydrogen storage, the aluminium salts  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$  (the so-called “alanates”) are the preferred agents. Thermal decomposition of  $\text{NaAlH}_4$  takes place in two steps.



However, sodium alanate ( $\text{NaAlH}_4$ ) and also magnesium hydride ( $\text{MgH}_2$ ) cannot meet the DoE's 2015 energy density targets, either having 4.7 and 7.6 wt.%  $\text{H}_2$ , respectively. Both require significant catalyst additions in order to desorb hydrogen with acceptable kinetics and are reactive towards moisture.

Sodium borohydride ( $\text{NaBH}_4$ ) is a complex hydride that meets the DoE's 2015 energy density targets for hydrogen storage materials. The  $\text{NaBH}_4$  complete oxidation (Eq. (3)) may be achieved through the  $\text{NaBH}_4$  hydrolysis (Eq. (4)) followed by electrochemical oxidation of the generated hydrogen (Eq. (5)).

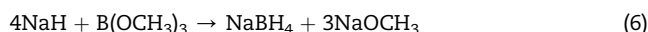


The  $\text{NaBH}_4$  hydrolysis reaction (Eq. (4)) is irreversible, but has the advantage that 50% of the resulting hydrogen comes from the water; in effect,  $\text{NaBH}_4$  is a “water-splitting” agent. Based on the mass of  $\text{NaBH}_4$ , the hydrogen released is 21 wt.%, which is a remarkably high figure. Of course this value can only be attained if the water required for hydrolysis exists at least in stoichiometric amounts (Eq. (4)), and if the hydrolysis reactor is pressurised [3]. Most of the research on the  $\text{NaBH}_4$  hydrolysis [4] has used base-stabilised  $\text{NaBH}_4$  solutions (3–7 wt.%  $\text{H}_2$ ). One approach to preparing the storage medium is to mix the  $\text{NaBH}_4$  with light mineral oil and a dispersant to form an “organic slurry”. The oil coats the  $\text{NaBH}_4$  particles and protects them from inadvertent contact with water, and also moderates the reaction rate of the  $\text{NaBH}_4$  with water, when desired. Naturally, by exposing this solution to catalysts, such as ruthenium, hydrogen can be released with good kinetics and conversion. The advantage of using complex hydrides is that the spent solution may be recycled to a processing plant for regeneration of the hydride. From the standpoint of mass, volume and cost, the system seems to be attractive as a hydrogen storage scheme for fuel cell vehicles. Daimler Chrysler has demonstrated that a  $\text{NaBH}_4$  system developed by Millenium Cell (USA) can provide a minivan, the “Natrium”, with a range of 480 km. Much will

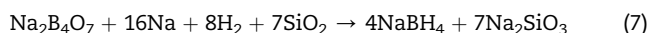
depend on the difficulty and cost of the reprocessing operation. At the service station, instead of refuelling with hydrogen gas, the vehicle would have its tank emptied and refilled with fresh  $\text{NaBH}_4$  slurry. This is similar to the procedure proposed for the zinc–air traction battery.

Many papers concerning the hydrogen generation from borohydride hydrolysis [5–18] and the borohydride direct oxidation on direct borohydride fuel cells (DBFC) [19–35] have been published in the last decade. However, when compared to the latter topics, only a short number of papers regarding borohydride synthesis were published [36–58]. The progresses on hydrogen generation from borohydrides and on the DBFC have been summarised in several review articles [59–61].

It is estimated that for  $\text{NaBH}_4$  be widely used in the context of the new hydrogen economy, the cost must be reduced by at least one order of magnitude from its present value ( $\sim 40$  €/kg). Therefore, it is imperative to find a suitable procedure for  $\text{NaBH}_4$  synthesis from  $\text{NaBO}_2$ . Schlesinger et al. [62] developed the  $\text{NaBH}_4$  present industrial synthesis (Eq. (6)), starting from sodium hydride ( $\text{NaH}$ ) and trimethyl borate ( $\text{B}(\text{OCH}_3)_3$ ). Unfortunately, this process is too expensive to be considered viable for the production of a commercial vehicular fuel [63].

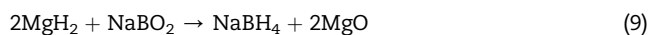
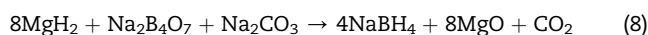


Another process that has been employed on a commercial scale to produce  $\text{NaBH}_4$  is the Bayer process [64,65], which is a one pot synthesis combining borax, metallic sodium, and hydrogen, in the presence of silica, to generate  $\text{NaBH}_4$  (Eq. (7)).



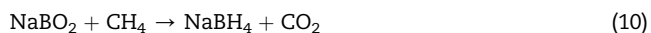
It would appear that if the cost of sodium was low enough, borohydride could be produced very cheaply, because all the other feedstocks are inexpensive materials. The Bayer reaction presents some explosion risk, mainly because it operates above the decomposition temperature of  $\text{NaBH}_4$ . Moreover, this process works in a batchwise mode in which raw materials are added to the reaction, processed into products and then sent on for separation.

There is currently an effort to modify the Bayer process by employing the less expensive reducing metal magnesium instead of sodium [36–38,66–70]. Eqs. 8 and 9 describe reactions that are promising modifications to the Bayer process, but have not been developed far enough to exhibit both high yield and fast reaction rates.



A different approach to the synthesis of  $\text{NaBH}_4$  might be to start by looking at the most desirable reactions and then examine their plausibility in terms of thermodynamics. One step process with interest is the direct conversion of borate raw material employing an exceptionally inexpensive

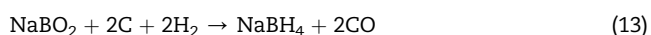
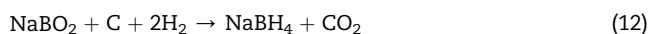
reducing agent, methane (Eq. (10)). However, between 0 and 1000 °C, the reaction free energy is always positive [71].



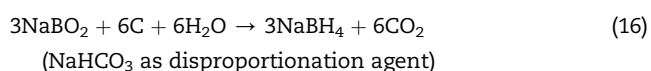
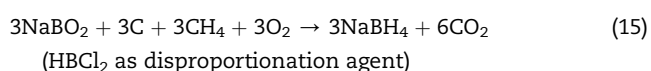
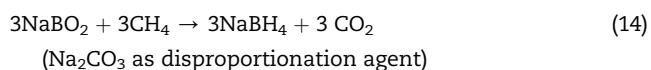
The same thermodynamic impossibility occurs with the direct thermal reduction of sodium metaborate with hydrogen [71]:



There is also no expectation that carbon reducing agents will prove any more effective than methane (Eqs. (12) and (13)) [71].



While developing an all-thermal synthetic process for NaBH<sub>4</sub>, Millenium Cell [72–75] proposed a family of processes which can be modified in various ways to optimise the trade-offs among energy efficiency, cost and greenhouse gas emissions. One example is based on the use of disproportionation, a classic reaction in the chemistry of boron compounds (Eqs. (14)–(16)) [76].



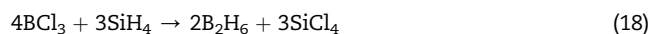
Another proposed carbon-based reduction method is based on formaldehyde as a reducing agent [77]. A different approach is to consider industrial processes used to manufacture other high-energy compounds, and determine whether they can be adapted to the NaBH<sub>4</sub> synthesis. For example, the “steel-making” process can be adapted for use with boron [78], according to Eq. (17):



The substantial cost reduction needed for NaBH<sub>4</sub> to become a low-cost fuel for the transportation market is unlikely to occur by implementing these multistep thermal reductions or similar processes, simply because of their complexity.

A number of metallic reducing agents can also be employed to convert the boron centres into B–H species. Additionally, many metals form hydrides with which boron compounds will exchange ligands. Magnesium, aluminium,

and silicon all exchange favourably with boron [79–83]. The conversion of BX<sub>3</sub> species to diborane (Eq. (18)) may be achieved by using silicon hydrides (silanes) [84].



At present, none of these processes is sufficiently simple to lower the cost of borohydride manufacture below its current level. Thus, using metallic reducing agents and their hydrides on alkyl derivatives suffer from the same weakness as the all-thermal routes described before.

An additional alternative for borates conversion into borohydrides was published in the early 1980s [85,86]. The reaction does not carry on readily via thermal methods, but microwave excitation allows it to proceed. This process is of interest to the synthesis of NaBH<sub>4</sub> because it makes use of a disproportionation reaction to transform dimethoxyborane to diborane and trimethylborate. To date there are no industrial syntheses that employ microwave irradiation as energy source, and ultimately very little is known about the economic effectiveness of the method.

A recent design for making NaBH<sub>4</sub> is being pioneered at the Idaho National Engineering and Environmental Laboratory (INEEL). Waste nuclear energy might be utilisable to produce NaBH<sub>4</sub> [87]. Preliminary results from INEEL show that gamma-irradiated NaBO<sub>2</sub> aqueous solutions can be converted to NaBH<sub>4</sub>. Much study remains to identify the mechanisms of borohydride formation, verify the efficiency of the reaction, and confirm the economic potential [88].

As done with the thermal reaction processes, it makes sense to envisage the most desirable electrochemical reactions for synthesising NaBH<sub>4</sub>, and then examine their flexibility. Cooper, Sharifian, Hale, Sun, Guilbault et al. [89–93] have reported the electrochemical conversion of borate to borohydride in aqueous media, but studies by Gyenge et al. [42] and by Calabretta and Davis [94] failed to verify that any borohydride was synthesised in the electrochemical systems used by Cooper, Sharifian and Hale. Aprotic organic media, molten salts, ionic liquids, and other reaction media are also being studied for the synthesis of borohydride, being anticipated that an alternative method of achieving NaBH<sub>4</sub> at a reduced cost is by an electrochemical route.

After covering some of the possible methodologies to synthesise NaBH<sub>4</sub>, electrochemical studies of its synthesis performed at our laboratory are described below. NaBH<sub>4</sub> electrosynthesis attempts in aqueous media, molten salts, and ionic liquids have been envisaged. Several problems were found, particularly in non-aqueous electrolytes but, on balance, the electrochemical avenues deserve further attention. Different methods to analyse the products of electrolysis were also studied, and an electrochemical technique was developed for the monitoring of the NaBH<sub>4</sub> electrosynthesis.

## 2. Electrosynthesis of NaBH<sub>4</sub>

In order to find an easy and economic route to produce NaBH<sub>4</sub> starting from NaBO<sub>2</sub>, the present work analysed the effectiveness of the NaBH<sub>4</sub> synthesis using electrochemical



methods. Three different reaction media, namely aqueous media, molten salts, and ionic liquids, were considered.

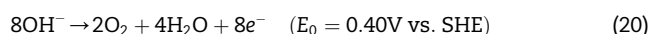
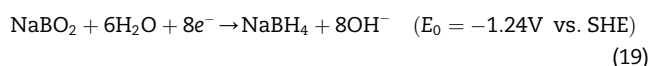
### 2.1. Aqueous media

Electrosynthesis of  $\text{NaBH}_4$  in aqueous media has been attempted in a two-compartment electrolytic cell using alkaline catholyte solutions containing sodium metaborate ( $\text{NaBO}_2$ ) or sodium tetraborate ( $\text{Na}_2\text{B}_4\text{O}_7$ ), with and without hydrogen poisons (thiourea), sodium hydroxide aqueous anolyte solutions, and Nafion 117 and other ion-selective membranes to separate the catholyte from the anolyte compartments.

Plate and fixed-bed cathodes of platinum, palladium, cadmium, nickel, gold, zinc, lead, mercury, graphite, stainless steel and other materials, were tested. As anode electrode materials, nickel, platinum, graphite and stainless steel were used. The working temperatures varied from 20 °C to 30 °C. The polarisation behaviour of the electrodes was controlled to guarantee that cathode potentials more negative than the discharge potential required for the borohydride production ( $\leq -1.7$  V vs. SCE reference electrode) were attained during the electrolytic operation.

Stepwise hydrolysis of the produced species with water leading to the generation of hydrogen was minimised by straight control of the solution pH, which was always kept close to 14. During bulk electrolysis the catholyte pH tends to increase with time, mainly due to  $\text{H}^+$  consumption in  $\text{H}_2$  evolution. On the other hand, the anolyte pH decreases with the  $\text{OH}^-$  anodic oxidation to  $\text{O}_2$ . Therefore, concentrated NaOH solution was added gradually to the anodic compartment to maintain the initial anolyte pH value.

The aqueous electrosynthesis of  $\text{NaBH}_4$ , starting from  $\text{NaBO}_2$ , is described by the reverse reaction of Eq. (3), being the cathodic and anodic partial reactions given by Eqs. (19) and (20), respectively.



Assuming that the applied cathodic overpotential is sufficient to achieve complete conversion of the  $\text{NaBO}_2$  into  $\text{NaBH}_4$  within the test solution, and there are no side reactions (e.g. hydrogen evolution, borohydride hydrolysis), the integrated charge is expected to rise asymptotically with time towards a value of  $znF$  ( $z$  is the number of moles of transferred electrons – 8 – per mole of  $\text{NaBO}_2$ ,  $n$  is the number of moles of  $\text{NaBO}_2$  present and  $F$  is Faraday's constant). Furthermore, if the cathodic reaction is diffusion controlled, it can be shown that

$$\ln i_t = \ln i_{t=0} - D_{\text{BO}_2} At / (\delta V) \quad (21)$$

where  $i_t$  and  $i_{t=0}$  are the currents at time  $t$  and  $t = 0$ ,  $D_{\text{BO}_2}$  is the diffusion coefficient of metaborate ion ( $\text{BO}_2^-$ ),  $A$  is the electrode area,  $\delta$  the thickness of the Nernst diffusion layer, and  $V$  is the solution volume.

This and other model approaches were used to characterise the system and to quantify the obtained results.

Additionally, the solution products resulting from the electrosynthesis tests were analysed by several different methods, including infrared spectroscopy [95,96], cyclic voltammetry [97], and open circuit potential measurements [98].

### 2.2. Molten salts

Analysis of the most suitable molten salts for the  $\text{NaBH}_4$  electrosynthesis reaction medium revealed that NaOH should be part of the molten electrolyte. NaOH provides  $\text{OH}^-$  ions for the oxidation at the anode and  $\text{Na}^+$  ions for the ionic conduction through the separator. It helps stabilising the produced  $\text{NaBH}_4$  in the catholyte and enables the preparation of low melting point eutectic compositions for the  $\text{NaBO}_2$  electrolysis. Accordingly, the following eutectic mixtures (in molar %) have been selected and tested: NaOH (49%) + KOH (41.5%) + LiOH (9.5%), NaOH (51%) + KOH (49%), and NaOH (27%) + LiOH (73%), whose melting points are 167, 170 and 210 °C, respectively. These compositions were derived from the phase diagrams shown in Fig. 1.

The presence of  $\text{Li}^+$  ions in the melts led to formation of Pt–Li alloys during electrolysis with platinum electrodes, which promptly promoted the borohydride hydrolysis. Therefore, LiOH–melts were abandoned and further tests were pursued with NaOH–KOH binary systems, which also showed problems concerned with electrodes stability, need for controlled atmosphere, nature of the metal electrocatalyst and separator material, and water contamination, among others.

### 2.3. Ionic liquids

Two ionic liquids (octa methylimidazolium and 1-butyl-1-methylpyrrolidinium trifluoromethanesulphonate) were selected and characterised as possible electrolyte medium for  $\text{NaBH}_4$  synthesis. Unfortunately, both ionic liquids displayed poor ionic conductivity. Moreover, the tested ionic liquids displayed good solubility for NaOH and  $\text{NaBH}_4$ , but high insolubility for  $\text{NaBO}_2$ . Experience gained with available ionic liquids does not make them particularly attractive for bulk electrolysis. Nevertheless, our group is developing ways to minimise present limitations, namely by: (i) increasing the working temperature to decrease the ionic liquid viscosity; (ii) using ultrasonication to assist mass transport; (iii) bubbling nitrogen gas through the solution to enhance mass transport; (iv) minimising the volume of the bulk electrolysis cell; (v) using a high area working electrode to optimise the area to ionic liquid volume ratio; (vi) using a flow cell or other hydrodynamic methods (e.g. stirring) to enhance mass transport; and (vii) employing a mixture of an ionic liquid and a low viscosity highly volatile organic solvent (e.g. dichloromethane) to lower the viscosity. The volatile organic solvent may then be removed under vacuum conditions after completion of the bulk electrolysis experiment. It is believed that the recent advances in the chemistry of ionic liquids [99] will soon render an effective electrolytic medium for  $\text{NaBO}_2$  conversion to  $\text{NaBH}_4$ .

### 2.4. $\text{NaBH}_4$ isolation and purification

Following borohydride electrosynthesis, either in aqueous, molten salt, ionic liquid, or in any other electrolyte medium, it

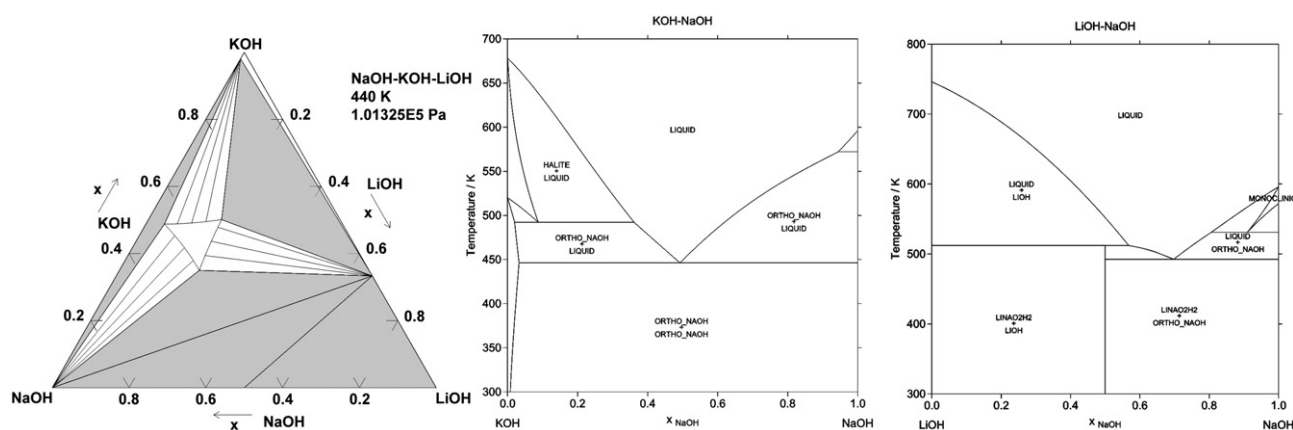


Fig. 1 – Calculated phase diagrams for the NaOH–KOH–LiOH ternary system at 440 K and for the NaOH–KOH and NaOH–LiOH binary systems.

is necessary to isolate the produced  $\text{NaBH}_4$  from other species present. It is known that the stability of  $\text{NaBH}_4$  solutions is dependent on the extent of its hydrolysis.  $\text{NaBH}_4$  can be very stable in solvents where there is no possibility of hydrolysis, such as solvents from the glymes family, namely tetraglyme ( $\text{C}_{10}\text{H}_{22}\text{O}_5$ ) and butyl diglyme ( $\text{C}_{12}\text{H}_{26}\text{O}_3$ ).

The approach to the use of these two glymes is substantially different because of their different miscibility with water; tetraglyme is completely miscible with water, whereas butyl diglyme is completely immiscible. Another important feature of both these glymes is that although  $\text{NaBH}_4$  shows high solubility,  $\text{NaBO}_2$  and  $\text{NaOH}$  are insoluble. In this way, the solution product obtained in the electrosynthesis in aqueous medium, may be subjected to cold evaporation (preferably under vacuum) to remove the water, and then the dried solid product is added to tetraglyme, dissolving only the synthesised  $\text{NaBH}_4$ . As for the molten salt catholytes, the reaction product may be grinded and then mixed in the tetraglyme, once again dissolving just the  $\text{NaBH}_4$ . Alternatively, butyl diglyme can be used to perform a direct extraction of the  $\text{NaBH}_4$  present in the aqueous catholyte solutions, bearing in mind that water is completely immiscible with butyl diglyme and  $\text{NaOH}$  and  $\text{NaBO}_2$  are insoluble in the same. Whether using tetraglyme or butyl diglyme, these solvents must be further removed by evaporation under vacuum to isolate the  $\text{NaBH}_4$  product.

### 3. Monitoring of the $\text{NaBH}_4$ electrosynthesis

One of the main purposes of the present study was to develop an in situ method for continuous monitoring of the  $\text{NaBH}_4$  electrosynthesised from  $\text{NaBO}_2$ . Preliminary studies on the borohydride electrosynthesis had shown that a major difficulty of the work was based on the fact that the existing methods for borohydride monitoring were neither easy nor fast [100]. These include hydrogen evolution [101], acid-base titration [102], iodate [103], hypochlorite [104], and voltammetric procedures [97].

The development of faster  $\text{NaBH}_4$  monitoring methods would be helpful not only for research on borohydride synthesis but also for the whole scientific community working

in any applications using borohydride, e.g. in energy systems (direct borohydride fuel cells, hydrogen storage and generation), in electrodeposition, as reducing agent in organic synthesis, etc. The different studied analytical methods for borohydride monitoring are described in this section, as well as a simple and fast potentiometric technique developed for the in situ monitoring of  $\text{NaBH}_4$  concentrations.

#### 3.1. Non-electrochemical methods

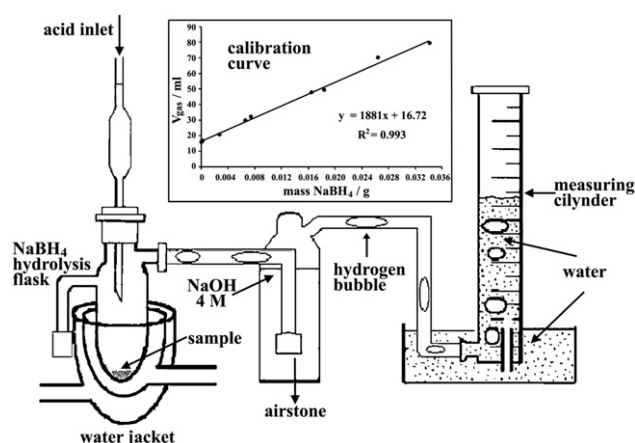
Following the electrosynthesis experiments, the reaction products were completely dried using cold evaporation and analysed using different methods.

The well-known iodate method [103] is based on the reaction of  $\text{NaBH}_4$  with  $\text{KIO}_3$ , followed by backtitration of the excess iodate with the  $\text{I/I}_2\text{-S}_2\text{O}_3^{2-}$  system. This volumetric method was extremely time-consuming and led to erroneous results, being promptly abandoned.

A new “hydride hydrolysis” test was developed based on the gasometric measurements (Fig. 2) of the hydrogen generated by the decomposable borohydride product resulting from the electrosynthesis experiments, which was assisted by a calibration curve for pure  $\text{NaBH}_4$ . This new method, although showing good reproducibility, does not have a low enough detection limit and, therefore, could not detect borohydride in the reaction samples.

Infrared spectroscopy analysis (Fig. 3) showed that the three B–H bond stretching vibration bands observed in the dried electrosynthesis reaction product are in good agreement to the ones obtained for pure  $\text{NaBH}_4$  and with the values found in the literature [96,105,106], as it is summarised in Table 1.

Although this method provided very encouraging results, suggesting the presence of borohydride in the electrosynthesis products, infrared spectroscopy analysis had the disadvantage of requiring full drying of the electrosynthesis reaction product and preparation of a KBr/sample mix pellet suitable for the used equipment. This procedure takes excessive time, especially when many parameters (temperature, current, potential, electrode material, electrode area, solution composition, separator) need to be changed and



**Fig. 2 – Experimental setup used for the gasometric measurements of the hydrogen generated on product sample hydrolysis and example of calibration curve used for NaBH<sub>4</sub> determination.**

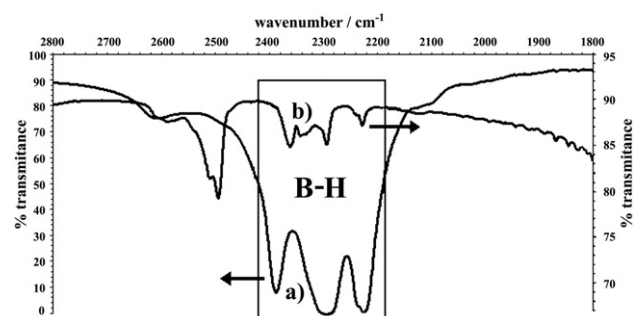
tested in order to find the best experimental conditions for the borohydride electro-synthesis reaction.

Considering the stated above, the ideal manner to monitor NaBH<sub>4</sub> electrochemical synthesis would be such that could be used in situ. Therefore, alternative methods that could follow the electro-synthesis reaction in situ were investigated.

### 3.2. Electrochemical methods

Experience on the monitoring of the borohydride electro-synthesis indicated that electrochemical methods should be appropriate to follow the reaction process.

To determine the most adequate cathode potential values to be used in the synthesis experiments, chronoamperometric measurements were performed in the electrolysis cell at several different applied electrode potentials. Chronoamperometry is a simple electrochemical method, where a constant potential is applied to the working electrode (vs. a reference electrode) and the cell current is recorded through time. This method is useful to follow the processes occurring



**Fig. 3 – Infrared spectra taken for NaBH<sub>4</sub>, p.a., (a), and for the electro-synthesis reaction product obtained in aqueous medium, (b).**

**Table 1 – B–H bond stretching vibration bands for NaBH<sub>4</sub>.**

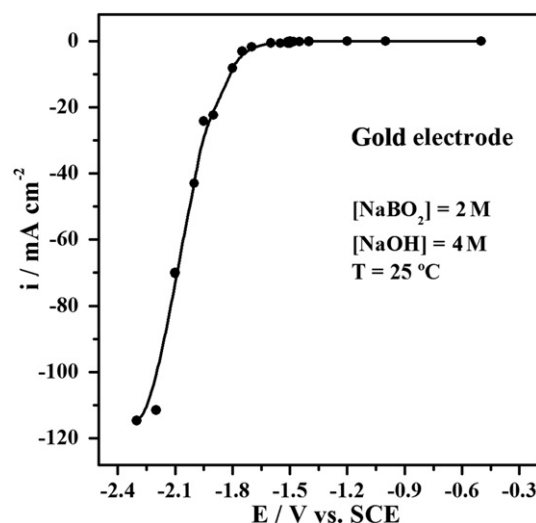
	$\nu$ (B–H)/cm <sup>-1</sup>
Electrosynthesis product	2225, 2293, 2359
NaBH <sub>4</sub> p.a.	2224, 2290, 2387
NaBH <sub>4</sub> [96]	2229, 2305, 2400
NaBH <sub>4</sub> [105]	2217, 2284, 2404
NaBH <sub>4</sub> [106]	2216, 2282, 2396
NaBH <sub>4</sub> ·2H <sub>2</sub> O [106]	2221, 2268, 2380

Data taken from the infrared spectra of the aqueous medium electro-synthesis product and of a sample of NaBH<sub>4</sub> p.a. The obtained values are compared to previous information available in the open literature.

at the working electrode surface during the chronoamperometric experiment timeframe. Fig. 4 shows the average cell current density obtained for each different potential applied to a gold working electrode.

It is clear that for applied potentials more positive than  $-1.7$  V vs. SCE the cell currents were practically negligible. For more negative applied potentials, the cell current starts to rise gradually due to an increase in the reaction kinetics of the borate species reduction and simultaneous hydrogen production through water electrolysis. Considering that the equilibrium potential for the metaborate conversion to borohydride reaction is  $-1.24$  V vs. SHE, i.e.  $\sim -1.48$  V vs. SCE, this result means that overpotentials of at least  $0.20$  V are required for any reaction to occur with significant kinetics.

Furthermore it was noticed that the gold working electrode open circuit potential (OCP) decreased from an initial value of  $-0.23$  V vs. SCE before the chronoamperometric experiments to a final value of about  $-0.90$  V vs. SCE after the experiments, and this value kept fairly constant even for relatively long periods of time. Moreover, when this electrode was removed from the solution, thoroughly washed, and put back in the same electrolysed solution, its OCP was again initially equal to  $-0.23$  V vs. SCE (the original value) and then gradually



**Fig. 4 – Effect of applied electrode potential on the electro-synthesis cell current density. Time step used to average the cell current density = 20 s.**



decreased to values around  $-0.34$  V vs. SCE. This suggests that the decrease on the gold OCP is mainly caused by the adsorption of reduced species on the electrode surface (although some portion should be in solution).

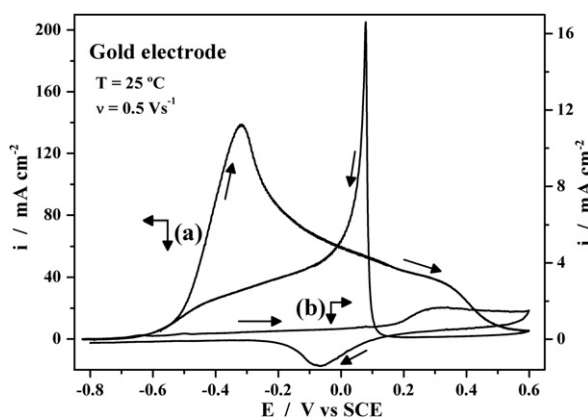
In order to identify the nature of the adsorbed species, cyclic voltammetry was used immediately after each chronoamperometric experiment. Cyclic voltammetry allows the characterisation of the species formed according to each potential applied to the gold working electrode.  $\text{NaBH}_4$  generally shows a well-defined cyclic voltammogram (CV) in alkaline solution (Fig. 5a).

However, the CVs for the electrolysed solutions (Fig. 5b) did not show the expected characteristic peaks for borohydride oxidation, which might be explained in part by the fact that the produced borohydride would be in quantities much below its detection limit for this method ( $\sim 10^{-4}$  M) [97].

In fact, the shapes of the CVs obtained after each chronoamperometric experiment were always basically the same, with the exception of two small oxidation peaks (at  $-0.65$  and  $-0.50$  V vs. SCE) that appeared following the chronoamperometric tests where potentials more negative than  $-1.7$  V vs. SCE were applied. These peaks might be attributed to the oxidation of boron intermediate species that were formed and adsorbed on the gold electrode surface during the chronoamperometric tests.

Despite the fact that cyclic voltammetry could not show the presence of borohydride in solution, explained by the fact that the detection limit was not low enough, the observation of the gold OCP decrease after the electrosynthesis tests was a clear assertion that changes in the solution composition had occurred. This change in the gold electrode OCP deserved a deeper study to find out if these OCP changes could be used to monitor borohydride concentrations in aqueous solution with detection limits lower than  $10^{-4}$  M.

In 1999, Amendola et al. [98] reported the non-destructive, in situ detection of relatively low  $\text{NaBH}_4$  concentrations by an undemanding method that is in essence a potentiometric titration technique. The method was simply based on the



**Fig. 5** – CVs obtained with a gold working electrode immersed in  $0.09$  M  $\text{NaBH}_4$  +  $4$  M  $\text{NaOH}$  solution, (a), and in  $2$  M  $\text{NaBO}_2$  +  $4$  M  $\text{NaOH}$  solution after being potentiostatically electrolysed at  $-1.8$  V vs. SCE during  $1$  h (b).  $T = 25$  °C; Scan rate =  $0.5$  V  $\text{s}^{-1}$ .

change of the OCP of a given metal with the borohydride concentration.

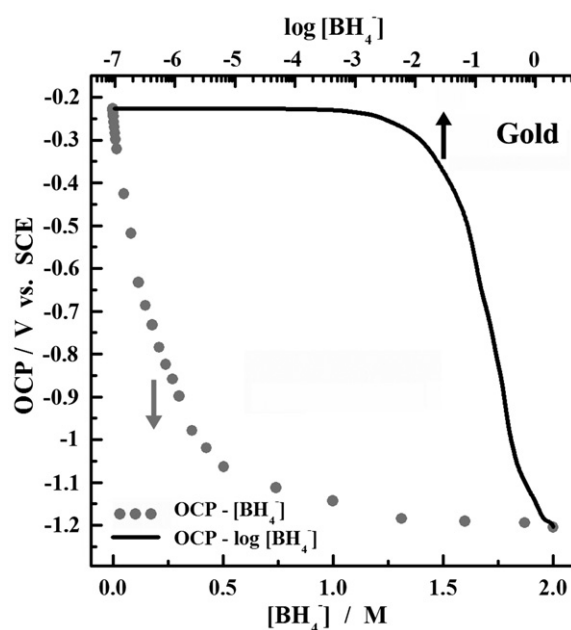
In the majority of potentiometric measurements the potential of one electrode is kept constant, being this electrode referred to as the reference electrode. The second electrode responds to the activity or concentration of the species contained in the solution under investigation and is referred to as the indicator electrode. Amendola et al. [98] used platinum, rhodium, and cobalt as metal indicator electrodes.

In order to develop the method originally proposed by Amendola et al. [98], we have tested several materials (e.g. Pt, Pd, Cd, Au, Cu, Ni, Fe, AISI 304 stainless steel, Zn, Mo, Nb, graphite, and Si) as indicator electrodes for  $\text{NaBH}_4$  monitoring. It was shown that those whose OCP is significantly different when immersed in  $\text{NaOH}$  supporting electrolyte with or without  $\text{NaBH}_4$  may be candidate indicator electrodes for application in a novel borohydride microelectrode sensor.

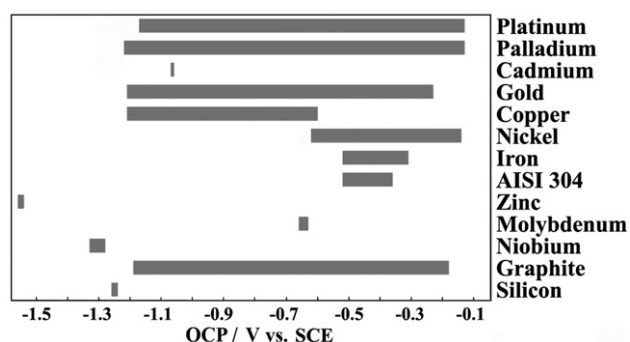
Available thermodynamic data [107–109] helped in the analysis of the obtained OCP- $[\text{BH}_4^-]$  plots, which was complemented by additional OCP measurements in hydrogen-saturated  $\text{NaBH}_4$ -free alkaline solutions. It is known that during the  $\text{NaBH}_4$  electrosynthesis tests there is a competitive simultaneous  $\text{H}_2$  evolution reaction in the cathode. These additional kinetics experiments in hydrogen-saturated  $\text{NaBH}_4$ -free alkaline solutions allowed the comparison of the single effects of  $\text{NaBH}_4$  and  $\text{H}_2$  in the OCPs of the indicator electrodes.

The potentiometric procedure for a gold indicator electrode led to the curve shown in Fig. 6.

Fig. 6 shows that the gold OCP starts to decrease for borohydride concentrations above  $10^{-2}$  M, with an OCP response range of about  $1$  V. Similar curves were recorded for the other tested indicator electrode materials and the corresponding OCP ranges are shown in Fig. 7.



**Fig. 6** – Gold electrode OCP change as a function of the  $\text{NaBH}_4$  concentration in  $4$  M  $\text{NaOH}$  solution at  $25$  °C.



**Fig. 7** – OCP values range displayed by the tested electrode materials at 25 °C in 4 M NaOH solution with various  $\text{NaBH}_4$  contents.

It is clear that from this group of thirteen indicator electrode materials, six showed an extended potential response range to the borohydride presence (Pt, Pd, Au, Cu, Ni, and graphite) and therefore may be used for borohydride monitoring.

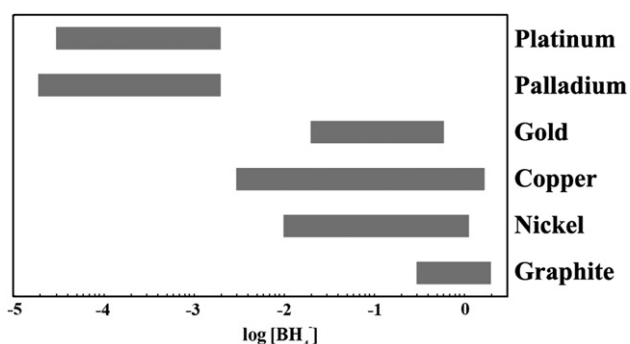
According to the borohydride concentration ranges where the OCP changes take place (Fig. 8), the six selected materials can be classified as the top materials for each specific borohydride concentration range.

This fast and relatively precise potentiometric titration technique based on the OCP response of different indicator electrode materials, that was recently developed at our laboratory [110], is being improved, with a microelectrode array borohydride sensor being expected.

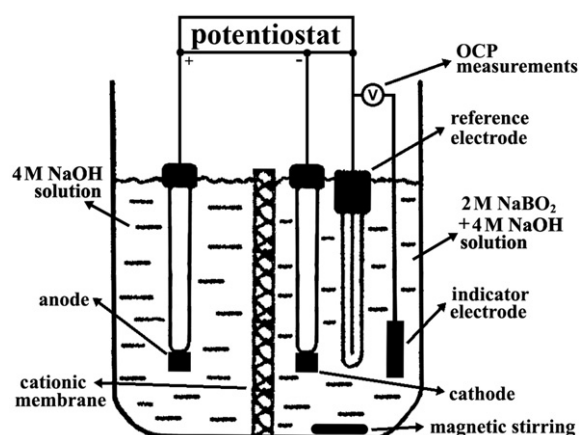
### 3.3. Continuous in situ electrochemical monitoring

The potentiometric method described in previous section allows that by simply using the calibration curves obtained for each indicator electrode material we may find with relatively high accuracy the borohydride concentration in any given alkaline aqueous solution.

Therefore, this method was applied to our electrosynthesis experiments by inserting an indicator electrode inside the cell and by continuously monitoring its OCP during electrolysis. The experimental electrolysis cell with integrated monitoring system is schematically shown in Fig. 9.



**Fig. 8** – Top materials displaying steeper OCP changes for specific borohydride concentrations.



**Fig. 9** – Electrochemical cell for bulk electrolysis of  $\text{NaBO}_2$  and OCP measurements in alkaline solution at 25 °C.  $\text{NaBO}_2$  is reduced at the cadmium cathode; simultaneously the high impedance voltmeter prevents current to flow in the circuit between the indicator and reference electrodes, allowing its OCP monitoring.

Several electrosynthesis experiments were performed using chronoamperometry to record the cell current with time, for each different potential applied to a cadmium foil working electrode. Cadmium was chosen for the working electrode material due to its high overpotential to the hydrogen evolution reaction. Gold, platinum, copper, and graphite were used as indicator electrodes for the continuous in situ monitoring system.

Table 2 shows the initial and final OCPs observed for the four tested indicator electrodes used in the electrosynthesis experiments.

Considering that the concentration of borohydride generated in the electrosynthesis tests should be relatively low, platinum could be used as indicator electrode (Fig. 8). However, platinum also responds to the hydrogen presence and, therefore, the OCP of  $-1.10$  V during the electrosynthesis test must be attributed to the hydrogen saturation on the cell. The slight decrease on the gold OCP during the experiment indicates a change in the solution composition but does not clearly show the borohydride presence. Copper and graphite also showed minor decreases in their OCP value.

These results indicate that only traces of  $\text{NaBH}_4$  could be detected in the electrolysed solutions. It is clear that it is necessary to improve the electrolytic cell as well as the proposed integrated monitoring system in order to reach our technical goal.

**Table 2** – OCP responses of the tested indicator electrodes.

	Gold	Platinum	Copper	Graphite
$\text{OCP}_i$	$-0.23$	$-0.15$	$-0.59$	$-0.18$
$\text{OCP}_f$	$-0.36$	$-1.10$	$-0.63$	$-0.32$

$\text{OCP}_i$  stands for the initial electrode OCP;  $\text{OCP}_f$  corresponds to the final electrode OCP measured at the end of the electrosynthesis tests; OCP values are shown in V vs. SCE reference electrode.

#### 4. Conclusions

Apart from its established use for hydrogenation and reduction processes in the chemical industry,  $\text{NaBH}_4$  is being, particularly in the present decade, converted to electricity in fuel cells and other energy systems. This is particularly evidenced by specialist journals, like the International Journal of Hydrogen Energy, that are devoting much attention to the subject of  $\text{NaBH}_4$  as a clean fuel.

$\text{NaBH}_4$  can be produced by many ways, as discussed in the present paper, and has many attractive features to generate electricity directly. However, there are many practical engineering and economic considerations that explain why  $\text{NaBH}_4$  does not already find extensive use as a fuel. A different future in which  $\text{NaBH}_4$  is produced by electrolytic means seems to be not too much away, and this paper reports some steps towards this direction. Traces of  $\text{NaBH}_4$  were detected in the products resulting from the electrosynthesis in aqueous media and it is suggested that this embryonic study should be pursued. Methods to analyse  $\text{NaBH}_4$  are described and a newly developed potentiometric technique is applied for in situ monitoring of small  $\text{NaBH}_4$  concentrations.

From the present study, it seems that the short-term prospects for electrolytic  $\text{NaBH}_4$  production as an option for the renewable energies scenario are not very enthusiastic. However, preliminary results indicate that it is expedient to continue the development of  $\text{NaBH}_4$  energy. That should include intensive research aimed at increasing the efficiency of  $\text{NaBH}_4$  production from selected electrocatalysts and electrolytic media, improving methods for its monitoring, and perfecting electricity generation from  $\text{NaBH}_4$  in fuel cells, and all at reduced cost.

#### Acknowledgments

The authors would like to thank Alan Dinsdale (NPL Materials Centre) for providing the phase diagrams calculation. D.M.F. Santos acknowledges the financial support from FCT (Portuguese Foundation for Science and Technology) for PhD grant no. SFRH/BD/24772/2005.

#### REFERENCES

- [1] [http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/hydrogen\\_storage\\_roadmap.pdf](http://www1.eere.energy.gov/vehiclesandfuels/pdfs/program/hydrogen_storage_roadmap.pdf).
- [2] Zuttel A. Materials for hydrogen storage. *Mater Today* 2003; 6:24–33.
- [3] Kojima Y, Kawai Y, Nakanishi H, Matsumoto S. Compressed hydrogen generation using chemical hydride. *J Power Sources* 2004;135:36–41.
- [4] Zhang Q, Smith G, Wu Y, Mohring R. Catalytic hydrolysis of sodium borohydride in an auto-thermal fixed-bed reactor. *Int J Hydrogen Energy* 2006;31:961–5.
- [5] Kong VCY, Foulkes FR, Kirk DW, Hinatsu JT. Development of hydrogen storage for fuel cell generators. I: hydrogen generation using hydrolysis hydrides. *Int J Hydrogen Energy* 1999;24:665–75.
- [6] Aiello R, Sharp JH, Matthews MA. Production of hydrogen from chemical hydrides via hydrolysis with steam. *Int J Hydrogen Energy* 1999;24:1123–30.
- [7] Amendola SC, Sharp-Goldman SL, Janjua MS, Kelly MT, Petillo PJ, Binder M. An ultrasafe hydrogen generator: aqueous, alkaline borohydride solutions and Ru catalyst. *J Power Sources* 2000;85:186–9.
- [8] Amendola SC, Sharp-Goldman SL, Janjua MS, Spencer NC, Kelly MT, Petillo PJ, et al. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. *Int J Hydrogen Energy* 2000;25:969–75.
- [9] Liu BH, Li ZP, Chen LL. Alkaline sodium borohydride gel as a hydrogen source for PEMFC or an energy carrier for  $\text{NaBH}_4$ -air battery. *J Power Sources* 2008;180:530–4.
- [10] Suda S, Sun YM, Liu BH, Zhou Y, Morimitsu S, Arai K, et al. Catalytic generation of hydrogen by applying fluorinated-metal hydrides as catalysts. *Appl Phys A Mater* 2001;72:209–12.
- [11] Kojima Y, Suzuki K, Fukumoto K, Sasaki M, Yamamoto T, Kawai Y, et al. Hydrogen generation using sodium borohydride solution and metal catalyst coated on metal oxide. *Int J Hydrogen Energy* 2002;27:1029–34.
- [12] Hua D, Hanxi Y, Xiping A, Chuansin C. Hydrogen production from catalytic hydrolysis of sodium borohydride solution using nickel boride catalyst. *Int J Hydrogen Energy* 2003;28(10):1095–100.
- [13] Wu C, Zhang H, Yi B. Hydrogen generation from catalytic hydrolysis of sodium borohydride for proton exchange membrane fuel cells. *Catal Today* 2004;93–95:477–83.
- [14] Kim J-H, Kim K-T, Kang Y-M, Kim H-S, Song M-S, Lee Y-J, et al. Study on degradation of filamentary Ni catalyst on hydrolysis of sodium borohydride. *J Alloys Compd* 2004; 379(1–2):222–7.
- [15] Zaluska A, Zaluski L. New catalytic complexes for metal hydride systems. *J Alloys Compd* 2005;404–406:706–11.
- [16] Kim J-H, Lee H, Han S-C, Kim H-S, Song M-S, Lee J-Y. Production of hydrogen from sodium borohydride in alkaline solution: development of catalyst with high performance. *Int J Hydrogen Energy* 2004;29(3):263–7.
- [17] Liu BH, Li ZP, Suda S. Nickel- and cobalt-based catalysts for hydrogen generation by hydrolysis of borohydride. *J Alloys Compd* 2006;415(1–2):288–93.
- [18] Ay M, Midilli A, Dincer I. Investigation of hydrogen production from boron compounds for PEM fuel cells. *J Power Sources* 2006;157(1):104–13.
- [19] Amendola SC, Onnerud P, Kelly MT, Petillo PJ, Binder M. A novel, high energy density aqueous borohydride battery. In: *Proc. Electrochem. Soc.* 98–15 (1999) 47–54 (selected Battery Topics), 194th Meeting of the Electrochemical Society, Boston, MA; November 1–6, 1998.
- [20] Amendola SC, Onnerud P, Kelly MT, Petillo PJ, Sharp-Goldman SL, Binder M. A novel high power density borohydride-air cell. *J Power Sources* 1999;84(1):130–3.
- [21] Amendola SC, Petillo PJ, Kelly MT, Sharp-Goldman SL, Binder M. A safe, self-regulating, hydrogen generator using aqueous borohydride solutions. In: *Proc. 195th Meet. Electrochem. Soc.*, Seattle, WA; May 2–6, 1999.
- [22] Li ZP, Liu BH, Arai K, Suda S. A fuel cell development for using borohydrides as the fuel. *J Electrochem Soc* 2003; 150(7):A868–72.
- [23] Liu BH, Li ZP, Suda S. Anodic oxidation of alkali borohydrides catalyzed by nickel. *J Electrochem Soc* 2003; 150(3):A398–402.
- [24] Mirkin MV, Yang H, Bard AJ. Borohydride oxidation at a gold electrode. *J Electrochem Soc* 1992;139:2212–7.
- [25] Gyenge EL. Electrooxidation of borohydride on platinum and gold electrodes: implications for direct borohydride fuel cells. *Electrochim Acta* 2004;49(6):965–78.

- [26] Santos DMF, Sequeira CAC. Determination of kinetic and diffusional parameters for sodium borohydride oxidation on gold electrodes. *J Electrochem Soc* 2009;156:F67–74.
- [27] Liu BH, Li ZP, Suda S. Electrocatalysts for the anodic oxidation of borohydrides. *Electrochim Acta* 2004;49(19):3097–105.
- [28] Dong H, Feng R, Ai X, Cao Y, Yang H, Cha C. Electrooxidation mechanisms and discharge characteristics of borohydride on different catalytic metal surfaces. *J Phys Chem B* 2005;109(21):10896–901.
- [29] Kim J-H, Kim H-S, Kang Y-M, Song M-S, Rajendran S, Han S-C, et al. Carbon-supported and unsupported Pt anodes for direct borohydride liquid fuel cells. *J Electrochem Soc* 2004;151(7):A1039–43.
- [30] Li ZP, Liu BH, Arai K, Asaba K, Suda S. Evaluation of alkaline borohydride solutions as the fuel for fuel cell. *J Power Sources* 2004;126(1–2):28–33.
- [31] Li ZP, Liu BH, Arai K, Suda S. Development of the direct borohydride fuel cell. *J Alloys Compd* 2005;404–406:648–52.
- [32] Santos DMF, Condeço JAD, Franco MAW, Sequeira CAC. An improved borohydride–H<sub>2</sub>O<sub>2</sub> laboratory fuel cell. *ECS Trans* 2007;3(32):19–30.
- [33] Santos DMF, Sequeira CAC. Zinc anode for direct borohydride fuel cells. *J Electrochem Soc* 2010;157:B13–9.
- [34] Santos DMF. Studies on sodium borohydride for energy systems. Ph.D. thesis, TULisbon, Portugal; 2009.
- [35] Santos DMF, Sequeira CAC. Chronopotentiometric investigation of borohydride oxidation at a gold electrode. *J Electrochem Soc* 2010;157:F16–21.
- [36] Li ZP, Morigasaki N, Liu BH, Suda S. Preparation of sodium borohydride by the reaction of MgH<sub>2</sub> with dehydrated borax through ball milling at room temperature. *J Alloys Compd* 2003;349:232–6.
- [37] Kojima Y, Haga T. Recycling process of sodium metaborate to sodium borohydride. *Int J Hydrogen Energy* 2003;28:989–93.
- [38] Li ZP, Liu BH, Morigasaki N, Suda S. Preparation of potassium borohydride by a mechano-chemical reaction of saline hydrides with dehydrated borate through ball milling. *J Alloys Compd* 2003;354(1–2):243–7.
- [39] Suda S, Iwase Y, Morigasaki N, Li Z-P. Advanced materials for energy conversion II. TMS; 2004. 123.
- [40] Suda S, Morigasaki N, Iwase Y, Li ZP. Production of sodium borohydride by using dynamic behaviors of protide at the extreme surface of magnesium particles. *J Alloys Compd* 2005;404–406:643–7.
- [41] Jeon E, Cho Y. Mechanochemical synthesis and thermal decomposition of zinc borohydride. *J Alloys Compd* 2006;422:273–5.
- [42] Gyenge EL, Oloman CW. Electrosynthesis attempts of tetrahydridoborates. *J Appl Electrochem* 1998;28:1147–51.
- [43] Sequeira CAC, Parda TCD, Santos DMF, Condeço JAD, Franco MAW, Gonçalves MCMR. Studies on sodium borohydride for energy systems. *ECS Trans* 2007;3(18):37–47.
- [44] Hsueh C-L, Liu C-H, Chen B-H, Chen C-Y, Kuo Y-C, Hwang K-J, et al. Regeneration of spent-NaBH<sub>4</sub> back to NaBH<sub>4</sub> by using high-energy ball milling. *Int J Hydrogen Energy* 2009;34:1717–25.
- [45] Li ZP, Liu BH, Zhu JK, Morigasaki N, Suda S. NaBH<sub>4</sub> formation mechanism by reaction of sodium borate with Mg and H<sub>2</sub>. *J Alloys Compd* 2007;437:311–6.
- [46] Çakanyıldırım Ç, Gürü M. Production of NaBH<sub>4</sub> and hydrogen release with catalyst. *Renew Energ* 2009;34:2362–5.
- [47] Piskin MB. Investigation of sodium borohydride production process: “Ulexite mineral as a boron source”. *Int J Hydrogen Energy* 2009;34:4773–9.
- [48] Liu BH, Li ZP, Zhu JK. Sodium borohydride formation when Mg reacts with hydrous sodium borates under hydrogen. *J Alloys Compd* 2009;476:L16–20.
- [49] Liu BH, Li ZP, Suda S. Influences of alkali in borates on recovery of sodium borohydride. *J Alloys Compd* 2009;474:L6–9.
- [50] Liu BH, Li ZP, Suda S. Improving MgH<sub>2</sub> formation kinetics and its effect on NaBH<sub>4</sub> synthesis. *J Alloys Compd* 2009;474:321–5.
- [51] Zhang H, Zheng S, Fang F, Chen G, Sang G, Sun D. Synthesis of NaBH<sub>4</sub> based on a solid-state reaction under Ar atmosphere. *J Alloys Compd* 2009;484:352–5.
- [52] Çakanyıldırım Ç, Gürü M. Hydrogen cycle with sodium borohydride. *Int J Hydrogen Energy* 2008;33:4634–9.
- [53] Nakamori Y, Li H-W, Matsuo M, Miwa K, Towata S, Orimo S. Development of metal borohydrides for hydrogen storage. *J Phys Chem Solids* 2008;69:2292–6.
- [54] Liu BH, Li ZP, Morigasaki N, Suda S. Kinetic characteristics of sodium borohydride formation when sodium metaborate reacts with magnesium and hydrogen. *Int J Hydrogen Energy* 2008;33:1323–8.
- [55] Kantürk A, Pişkin S. Innovation in sodium borohydride production process from borosilicate glass with sodium under hydrogen atmosphere: “high pressure process”. *Int J Hydrogen Energy* 2007;32:3981–6.
- [56] Park EH, Jeong SU, Jung UH, Kim SH, Lee J, Nam SW, et al. Recycling of sodium metaborate to borax. *Int J Hydrogen Energy* 2007;32:2982–7.
- [57] Kemmitt T, Gainsford GJ. Regeneration of sodium borohydride from sodium metaborate, and isolation of intermediate compounds. *Int J Hydrogen Energy* 2009;34:5726–31.
- [58] Soloveichik GL, Andrus M, Gao Y, Zhao J-C, Kniajanski S. Magnesium borohydride as a hydrogen storage material: synthesis of unsolvated Mg(BH<sub>4</sub>)<sub>2</sub>. *Int J Hydrogen Energy* 2009;34:2144–52.
- [59] Li ZP, Liu BH, Arai K, Morigasaki N, Suda S. Protide compounds in hydrogen storage systems. *J Alloys Compd* 2003;356–357:469–74.
- [60] Ponce de Leon C, Walsh FC, Pletcher D, Browning DJ, Lakeman JB. Direct borohydride fuel cells. *J Power Sources* 2006;155:172–81.
- [61] Wee J-H. A comparison of sodium borohydride as a fuel for proton exchange membrane fuel cells and for direct borohydride fuel cells. *J Power Sources* 2006;155(2):329–39.
- [62] 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. *J Am Chem Soc* 1953;75:215–9.
- [63] Wu Y. Annual EERE progress report. U.S. Department; 2003.
- [64] Broja G, Schlabacher W. Process for the production of alkali metal borohydrides. DE Patent 1108670; 1959.
- [65] Schubert F, Lang K, Schlabacher W. Process for the production of borohydrides. DE Patent 1067005; 1959.
- [66] Haga T, Kojima Y. Method for manufacturing metal borohydride. JP Patent 2002-241109; 2002.
- [67] Kojima Y, Haga T, Suzuki K, Hayashi H, Matsumoto S, Nakanishi H. Method for manufacturing metal borohydride. JP Patent 2002-193604; 2002.
- [68] Nakamura M, Nakao H, Tsuchiyama K, Suda S. Method for separating metal hydrogenated complex compound and its oxidant and membrane separation apparatus. JP Patent 2002-126458; 2002.
- [69] Nakao H, Nakamura M, Tsuchiyama K, Suda S. Separation method and separation apparatus for complex compound metal hydride and its oxide. JP Patent 2002-137906; 2002.
- [70] Suda S. Method of manufacturing metal hydrogen complex compound. JP Patent 2002-173306; 2002.



- [71] Roine A. HSC chemistry: v5.0. Pori: Outokompu Research Oy; 2004.
- [72] Amendola SC, Kelly MT. Compositions and processes for synthesizing borohydride compounds. US Patent 6433129; 2002.
- [73] Amendola SC, Kelly MT, Ortega JV, Wu Y. Process for synthesizing borohydride compounds. US Patent 6670444; 2003.
- [74] Amendola SC, Kelly MT, Wu Y. Process for synthesizing borohydride compounds. US Patent 6524542; 2003.
- [75] Ortega JV, Wu Y, Amendola SC, Kelly MT. Processes for synthesizing alkali metal borohydride compounds. US Patent 6586563; 2003.
- [76] Holzmman RT, editor. Production of the boranes and related research. New York: Academic Press; 1967.
- [77] Glemser O. Process for the complete or partial replacement of halogens from group 3, 4, and 5 halides using hydrogen and/or organic reducing agents. DE Patent 949943; 1956.
- [78] King AJ, Russell VA. Preparation of borohydrides. US Patent 2942935; 1960.
- [79] Hurd DT. Preparation of boron compounds. US Patent 2469879; 1949.
- [80] Hurd DT. Preparation of boron compounds. US Patent 2596690; 1952.
- [81] Hurd DT. The preparation of boron hydrides by the reduction of boron halides. *J Am Chem Soc* 1949;71:20–2.
- [82] Jenkner H. Process for the production of boron hydrides. DE Patent 1095797; 1960.
- [83] Jenkner H. Improvements in or relating to the manufacture of boron hydrides and boron hydrides containing organic substituent radicals. GB Patent 907462; 1960.
- [84] Van Dyke CH, MacDiarmid AG. Formation of diborane by the interaction of disilane with boron trichloride. *J Inorg Nucl Chem* 1963;25:1503–6.
- [85] Jeffers PM, Bauer SH. Partial reduction of trimethoxyborane: an old reaction in a new reactor. *Inorg Chem* 1981;20:1698–701.
- [86] Jeffers PM, Bauer SH. Disproportionation of dimethoxyborane. *Inorg Chem* 1981;21:2516–7.
- [87] Bingham DN, Wilding BM, Klingler KM, Zollinger WT, Wendt KM. Method of forming a chemical composition. US Patent Appl. 2005/0077170 A1; 2005.
- [88] Demirci UB, Akdim O, Miele P. Ten-year efforts and a no-go recommendation for sodium borohydride for on-board automotive hydrogen storage. *Int J Hydrogen Energy* 2009;34:2638–45.
- [89] Cooper HBH. Electrolytic process for the production of alkali borohydrides. US Patent 3734842; 1973.
- [90] Sharifian H, Dutcher JS. Production of quaternary ammonium and quaternary phosphonium borohydrides. US Patent 4904357; 1990.
- [91] Hale CH, Sharifian H. Production of metal borohydrides and organic onium borohydrides. US Patent 4931154; 1990.
- [92] Sun Y, Liang Z. Electrochemical process for preparing borohydride. CN Patent Appl 1396307A; 2003.
- [93] Guilbault LJ, Sullivan EA, Sullivan NM, Weinberg NL. Electrolytic method for producing borohydride. US Patent Appl 2005/0224364 A1; 2005.
- [94] Calabretta DL, Davis BR. Investigation of the anhydrous molten Na–B–O–H system and the concept: electrolytic hydriding of sodium boron oxide species. *J Power Sources* 2007;164:782–91.
- [95] Ketelaar JAA, Schutte CJH. The borohydride ion ( $\text{BH}_4^-$ ) in a face-centred cubic alkali-halide lattice. *Spectrochim Acta* 1961;17:1240–3.
- [96] Schutte CJH. The infra-red spectrum of thin films of sodium borohydride. *Spectrochim Acta* 1960;16:1054–9.
- [97] Mirkin MV, Bard AJ. A voltammetric method for the determination of borohydride concentration in alkaline solutions. *Anal Chem* 1991;63:532–3.
- [98] Amendola SC, Onnerud P, Kelly MT, Binder M. Inexpensive, in-situ monitoring of borohydride concentrations. *Talanta* 1999;49:267–70.
- [99] Sequeira CAC, Santos DMF. Electrochemical routes for industrial synthesis. *J Braz Chem Soc* 2009;20:387–406.
- [100] Santos DMF. Analysis of boron compounds present in the electrosynthesis of sodium tetrahydridoborate, M.Sc. thesis. TULisbon, Portugal; 2006.
- [101] Krynsky JA, Johnson JE, Carhart HW. Determination of lithium aluminum hydride in solution. *Anal Chem* 1948;20:311–2.
- [102] Davis WD, Mason LS, Stegeman G. The heats of formation of sodium borohydride, lithium borohydride and lithium aluminum hydride. *J Am Chem Soc* 1949;71:2775–81.
- [103] Lytle DA, Jensen EH, Struck WA. A simple volumetric assay for sodium borohydride. *Anal Chem* 1952;24:1843–4.
- [104] Chaikin SW. Direct volumetric assay of sodium borohydride and potassium borohydride. *Anal Chem* 1953;25:831–2.
- [105] Renaudin G, Gomes S, Hagemann H, Keller L, Yvon K. Structural and spectroscopic studies on the alkali borohydrides  $\text{MBH}_4$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ). *J Alloys Compd* 2004;375:98–106.
- [106] Filinchuk Y, Hagemann H. Structure and properties of  $\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{NaBH}_4$ . *Eur J Inorg Chem* 2008;3127–33.
- [107] Pourbaix M. Atlas of electrochemical equilibria in aqueous solutions. 2nd ed. Houston, TX: NACE International; 1974.
- [108] Bard AJ, Parsons R, Jordan J, editors. Standard potentials in aqueous solution. NY: Marcel Dekker; 1985.
- [109] Chase Jr MW. NIST-JANAF thermochemical tables. *J Phys Chem Ref Data*; 1998. Monograph 9, American Chemical Society and American Institute of Physics, Washington, DC.
- [110] Santos DMF, Sequeira CAC. Sodium borohydride determination by measurement of open circuit potentials. *J Electroanal Chem* 2009;627:1–8.