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On the electrosynthesis of sodium borohydride

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ABSTRACT

Sodium borohydride (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 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 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 NaBH_4 lies in the electrochemical methods. A process for synthesising a 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 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.

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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.% H_2) set by the U.S. Department of Energy (DoE) Freedom Car Program [1]. Liquid hydrogen has very low density (70.8 g dm^{-3}) and requires a bulky cryogenic

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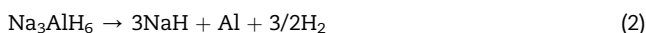
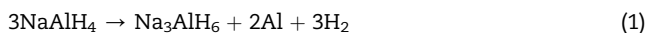
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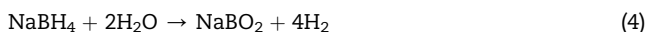
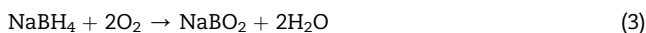
storage system, while compressed hydrogen (70 MPa) has even lower density and requires a heavy containment vessel [2].

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 NaAlH_4 and Na_3AlH_6 (the so-called “alanates”) are the preferred agents. Thermal decomposition of NaAlH_4 takes place in two steps.



However, sodium alanate (NaAlH_4) and also magnesium hydride (MgH_2) cannot meet the DoE’s 2015 energy density targets, either having 4.7 and 7.6 wt.% H_2 , respectively. Both require significant catalyst additions in order to desorb hydrogen with acceptable kinetics and are reactive towards moisture.

Sodium borohydride (NaBH_4) is a complex hydride that meets the DoE’s 2015 energy density targets for hydrogen storage materials. The NaBH_4 complete oxidation (Eq. (3)) may be achieved through the NaBH_4 hydrolysis (Eq. (4)) followed by electrochemical oxidation of the generated hydrogen (Eq. (5)).

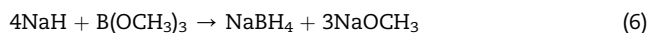


The NaBH_4 hydrolysis reaction (Eq. (4)) is irreversible, but has the advantage that 50% of the resulting hydrogen comes from the water; in effect, NaBH_4 is a “water-splitting” agent. Based on the mass of NaBH_4 , the hydrogen released is 21 wt.%, which is a remarkably high figure. Of course this value 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 NaBH_4 hydrolysis [4] has used base-stabilised NaBH_4 solutions (3–7 wt.% H_2). One approach to preparing the storage medium is to mix the NaBH_4 with light mineral oil and a dispersant to form an “organic slurry”. The oil coats the NaBH_4 particles and protects them from inadvertent contact with water, and also moderates the reaction rate of the 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 NaBH_4 system developed by Millenium Cell (USA) can provide a minivan, the “Natrium”, with a range of 480 km. Much will

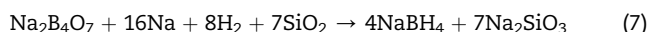
depend on the difficulty and cost of the reprocessing operation. At the service station, instead of refuelling with hydrogen gas, the vehicle would have its tank emptied and refilled with fresh NaBH_4 slurry. This is similar to the procedure proposed for the zinc–air traction battery.

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 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 (~ 40 €/kg). Therefore, it is imperative to find a suitable procedure for NaBH_4 synthesis from NaBO_2 . Schlesinger et al. [62] developed the NaBH_4 present industrial synthesis (Eq. (6)), starting from sodium hydride (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].

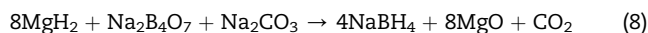


Another process that has been employed on a commercial scale to produce NaBH_4 is the Bayer process [64,65], which is a one pot synthesis combining borax, metallic sodium, and hydrogen, in the presence of silica, to generate NaBH_4 (Eq. (7)).



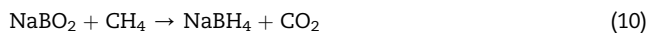
It would appear that if the cost of sodium was low enough, borohydride could be produced very cheaply, because all the other feedstocks are inexpensive materials. The Bayer reaction presents some explosion risk, mainly because it operates above the decomposition temperature of NaBH_4 . Moreover, this 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 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

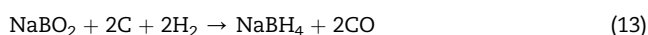
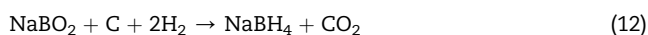
reducing agent, methane (Eq. (10)). However, between 0 and 1000 °C, the reaction free energy is always positive [71].



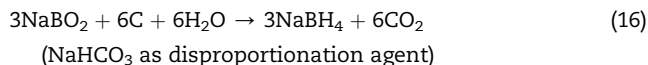
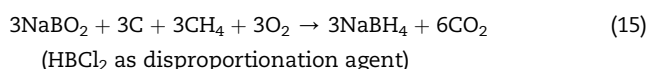
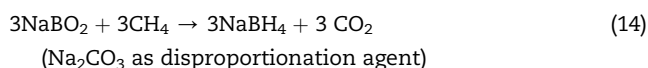
The same thermodynamic impossibility occurs with the direct thermal reduction of sodium metaborate with hydrogen [71]:



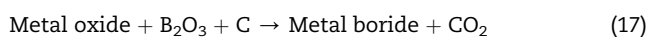
There is also no expectation that carbon reducing agents will prove any more effective than methane (Eqs. (12) and (13)) [71].



While developing an all-thermal synthetic process for NaBH₄, 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].



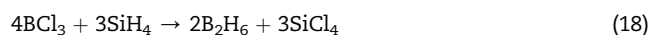
Another proposed carbon-based reduction method is based on formaldehyde as a reducing agent [77]. A different approach is to consider industrial processes used to manufacture other high-energy compounds, and determine whether they can be adapted to the NaBH₄ synthesis. For example, the “steel-making” process can be adapted for use with boron [78], according to Eq. (17):



The substantial cost reduction needed for NaBH₄ 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 BX₃ 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 NaBH₄ 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 NaBH₄ is being pioneered at the Idaho National Engineering and Environmental Laboratory (INEEL). Waste nuclear energy might be utilisable to produce NaBH₄ [87]. Preliminary results from INEEL show that gamma-irradiated NaBO₂ aqueous solutions can be converted to NaBH₄. 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 NaBH₄, 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 NaBH₄ at a reduced cost is by an electrochemical route.

After covering some of the possible methodologies to synthesise NaBH₄, electrochemical studies of its synthesis performed at our laboratory are described below. NaBH₄ 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 NaBH₄ electrosynthesis.

2. Electrosynthesis of NaBH₄

In order to find an easy and economic route to produce NaBH₄ starting from NaBO₂, the present work analysed the effectiveness of the NaBH₄ synthesis using electrochemical

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

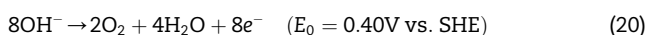
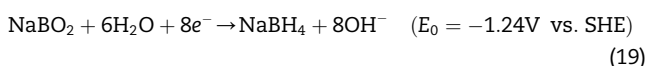
2.1. Aqueous media

Electrosynthesis of NaBH_4 in aqueous media has been attempted in a two-compartment electrolytic cell using alkaline catholyte solutions containing sodium metaborate (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 (≤ -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 H^+ consumption in H_2 evolution. On the other hand, the anolyte pH decreases with the OH^- anodic oxidation to O_2 . Therefore, concentrated NaOH solution was added gradually to the anodic compartment to maintain the initial anolyte pH value.

The aqueous electrosynthesis of NaBH_4 , starting from 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 NaBO_2 into 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 NaBO_2 , n is the number of moles of 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_{BO_2} is the diffusion coefficient of metaborate ion (BO_2^-), A is the electrode area, δ 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 NaBH_4 electrosynthesis reaction medium revealed that NaOH should be part of the molten electrolyte. NaOH provides OH^- ions for the oxidation at the anode and Na^+ ions for the ionic conduction through the separator. It helps stabilising the produced NaBH_4 in the catholyte and enables the preparation of low melting point eutectic compositions for the 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 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 NaBH_4 synthesis. Unfortunately, both ionic liquids displayed poor ionic conductivity. Moreover, the tested ionic liquids displayed good solubility for NaOH and NaBH_4 , but high insolubility for 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 NaBO_2 conversion to NaBH_4 .

2.4. NaBH_4 isolation and purification

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

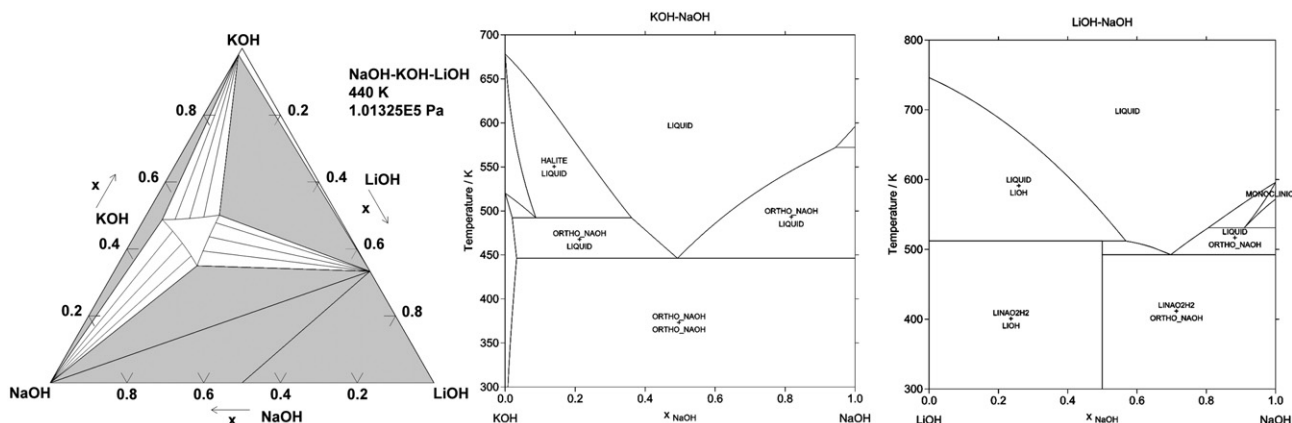


Fig. 1 – Calculated phase diagrams for the NaOH–KOH–LiOH ternary system at 440 K and for the NaOH–KOH and NaOH–LiOH binary systems.

is necessary to isolate the produced NaBH_4 from other species present. It is known that the stability of NaBH_4 solutions is dependent on the extent of its hydrolysis. 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 NaBH_4 shows high solubility, NaBO_2 and 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 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 NaBH_4 . Alternatively, butyl diglyme can be used to perform a direct extraction of the NaBH_4 present in the aqueous catholyte solutions, bearing in mind that water is completely immiscible with butyl diglyme and NaOH and 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 NaBH_4 product.

3. Monitoring of the NaBH_4 electrosynthesis

One of the main purposes of the present study was to develop an in situ method for continuous monitoring of the NaBH_4 electrosynthesised from 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 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 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 NaBH_4 with 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 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 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

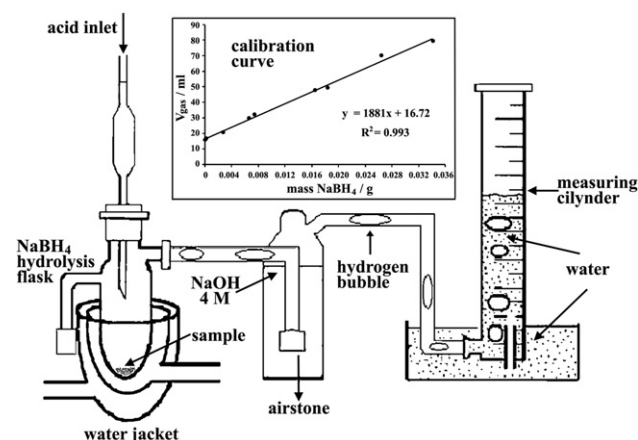


Fig. 2 – Experimental setup used for the gasometric measurements of the hydrogen generated on product sample hydrolysis and example of calibration curve used for NaBH_4 determination.

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_4 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

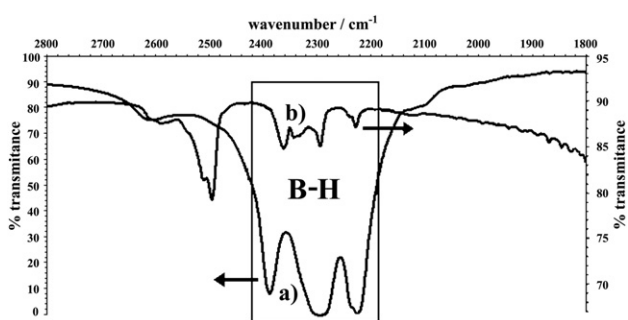


Fig. 3 – Infrared spectra taken for NaBH_4 , p.a., (a), and for the electro-synthesis reaction product obtained in aqueous medium, (b).

Table 1 – B–H bond stretching vibration bands for NaBH_4 .

	ν (B–H)/ cm^{-1}
Electrosynthesis product	2225, 2293, 2359
NaBH_4 p.a.	2224, 2290, 2387
NaBH_4 [96]	2229, 2305, 2400
NaBH_4 [105]	2217, 2284, 2404
NaBH_4 [106]	2216, 2282, 2396
$\text{NaBH}_4 \cdot 2\text{H}_2\text{O}$ [106]	2221, 2268, 2380

Data taken from the infrared spectra of the aqueous medium electro-synthesis product and of a sample of NaBH_4 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. ~ -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

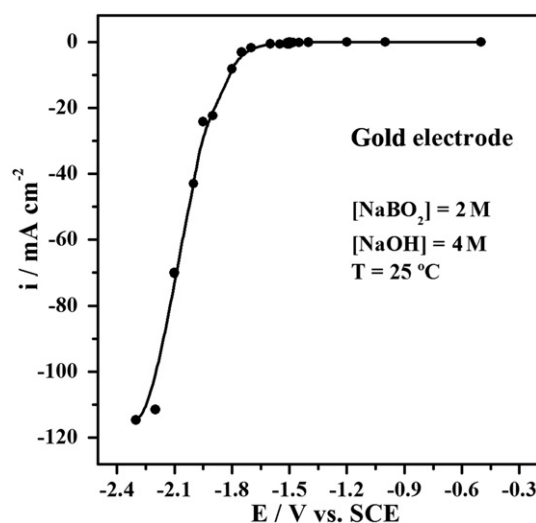


Fig. 4 – Effect of applied electrode potential on the electro-synthesis cell current density. Time step used to average the cell current density = 20 s.

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. 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 NaBH_4 concentrations by an undemanding method that is in essence a potentiometric titration technique. The method was simply based on the

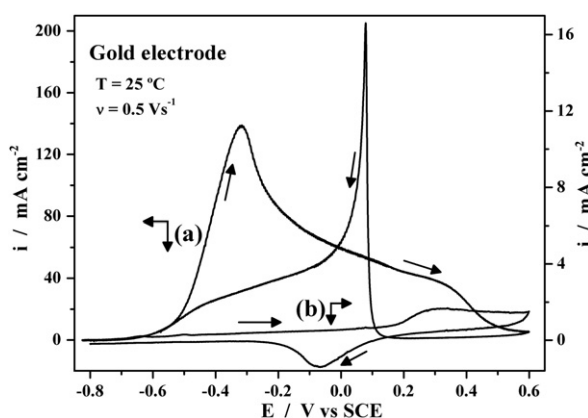


Fig. 5 – CVs obtained with a gold working electrode immersed in 0.09 M NaBH_4 + 4 M NaOH solution, (a), and in 2 M NaBO_2 + 4 M NaOH solution after being potentiostatically electrolysed at -1.8 V vs. SCE during 1 h (b). $T = 25$ °C; Scan rate = 0.5 V s^{-1} .

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 NaBH_4 monitoring. It was shown that those whose OCP is significantly different when immersed in NaOH supporting electrolyte with or without 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 NaBH_4 -free alkaline solutions. It is known that during the NaBH_4 electrosynthesis tests there is a competitive simultaneous H_2 evolution reaction in the cathode. These additional kinetics experiments in hydrogen-saturated NaBH_4 -free alkaline solutions allowed the comparison of the single effects of NaBH_4 and 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.

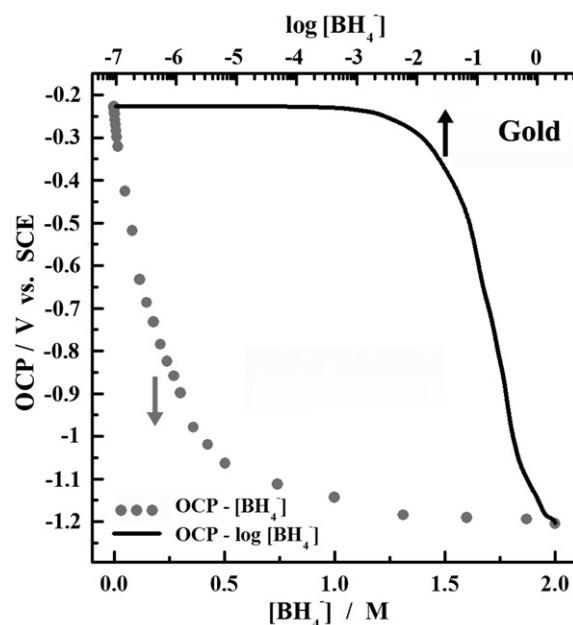


Fig. 6 – Gold electrode OCP change as a function of the NaBH_4 concentration in 4 M NaOH solution at 25 °C.

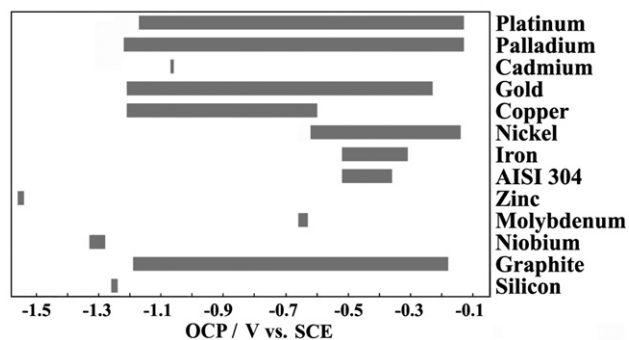


Fig. 7 – OCP values range displayed by the tested electrode materials at 25 °C in 4 M NaOH solution with various NaBH_4 contents.

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.

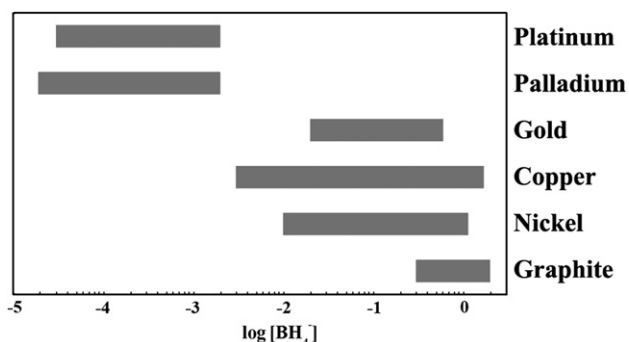


Fig. 8 – Top materials displaying steeper OCP changes for specific borohydride concentrations.

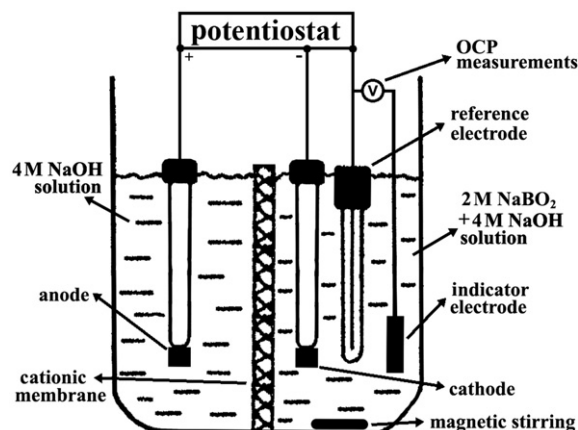


Fig. 9 – Electrochemical cell for bulk electrolysis of NaBO_2 and OCP measurements in alkaline solution at 25 °C. NaBO_2 is reduced at the cadmium cathode; simultaneously the high impedance voltmeter prevents current to flow in the circuit between the indicator and reference electrodes, allowing its 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 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
OCP_i	-0.23	-0.15	-0.59	-0.18
OCP_f	-0.36	-1.10	-0.63	-0.32

OCP_i stands for the initial electrode OCP; 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, 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 NaBH_4 as a clean fuel.

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 NaBH_4 does not already find extensive use as a fuel. A different future in which 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 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 NaBH_4 are described and a newly developed potentiometric technique is applied for in situ monitoring of small NaBH_4 concentrations.

From the present study, it seems that the short-term prospects for electrolytic 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 NaBH_4 energy. That should include intensive research aimed at increasing the efficiency of NaBH_4 production from selected electrocatalysts and electrolytic media, improving methods for its monitoring, and perfecting electricity generation from NaBH_4 in fuel cells, and all at reduced cost.

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