

Review

# A Review of Electrochemical Reduction of Sodium Metaborate

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**Abstract:** The recycling of sodium borohydride poses a huge challenge to the drive towards a hydrogen economy. Currently, mechano-chemical, thermo-chemical and electrochemical are the only reported methods of recycling sodium metaborate into sodium borohydride. Much attention has been devoted to the mechano-chemical and thermo-chemical methods of reduction, but little focus has been devoted to electrochemical methods. This review describes the electrochemical behaviour of borohydride ( $\text{BH}_4^-$ ) and metaborate ( $\text{BO}_2^-$ ) anions in alkaline solutions. The  $\text{BH}_4^-$  is stabilized in highly concentrated alkaline solutions, while the electro-oxidation of  $\text{BH}_4^-$  is dependent on the type of electrode material. The attempts to electro-reduce the  $\text{BO}_2^-$  into  $\text{BH}_4^-$  is reviewed and the challenges, suggestions and future outlook of electro-reduction for the recycling of  $\text{BO}_2^-$  into  $\text{BH}_4^-$  is highlighted.

**Keywords:** sodium metaborate; sodium borohydride; electro-reduction; electro-synthesis



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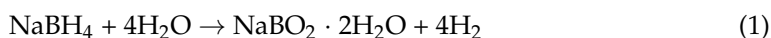
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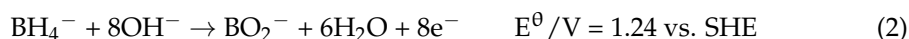
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## 1. Introduction

Sodium borohydride ( $\text{NaBH}_4$ ) is a hydrogen carrier with a high theoretical hydrogen storage capacity of around 10.8% w/w. In addition, the safe storage and fast kinetics of the release of gaseous hydrogen when in contact with water offers the storage and transport of hydrogen in solid form, which precludes the use of heavy high-pressurized gas storage containers and gas transport pipelines. The release of gaseous hydrogen at room temperature and pressure are described in the following equation:

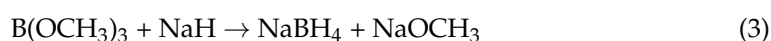


The release of hydrogen from concentrated alkaline solutions of  $\text{NaBH}_4$  necessitates the utilisation of  $\text{NaBH}_4$  as the active electrochemical reductant in direct borohydride fuel cell (DBFC):



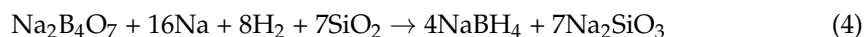
In both cases, the release of molecular hydrogen (Equation (1)) and the utilisation of the  $\text{BH}_4^-$  in DBFC (Equation (2)) release the sodium metaborate  $\text{NaBO}_2$  as the by-product. Therefore, successfully recycling the  $\text{NaBO}_2$  by-product into  $\text{NaBH}_4$  is the key for the utilisation of  $\text{NaBH}_4$  as a solid hydrogen storage material and as the electroactive reductant in DBFC.

The industrial production of  $\text{NaBH}_4$  developed in the 1950s, known as the Brown—Schlesinger process [1], which is highly inefficient, requires high temperatures, typically around 250 °C, and expensive chemical precursors, as given in the following equation:



Until now, there has not been much progress in increasing the efficiency of the production of NaBH<sub>4</sub>.

Another industrial process, known as the Bayer process, utilises the mineral borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) in powder form but reacted with sodium metal and hydrogen gas with the presence of silica, as given in the equation below:



The Bayer process also possesses low conversion efficiency in the production of NaBH<sub>4</sub>, in addition to being an energy-intensive process with operational temperatures of more than 400 °C [2].

All these factors render NaBH<sub>4</sub> an expensive chemical to be utilised even in DBFC and as a hydrogen carrier material. One solution is to recycle the NaBO<sub>2</sub> by-product into NaBH<sub>4</sub>. Among the methods for the recycling of NaBO<sub>2</sub> by-product into NaBH<sub>4</sub> are thermochemical [3–8], which involves the reaction of NaBO<sub>2</sub> in the presence of hydrogen gas at high pressures, and metallic Mg as the reducing agent at temperatures more than 500 °C.

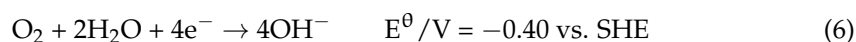
Another method for the recycling of the NaBO<sub>2</sub> by-product into NaBH<sub>4</sub> is by mechanochemical means, or by ball-milling powder of the NaBO<sub>2</sub> in a reactor in the presence of reductants, in the presence of steel balls, to facilitate the mechanical knocking process [9–19].

The electrochemical process, on the other hand, involves the electrochemical reduction of NaBO<sub>2</sub> into NaBH<sub>4</sub> with the passage of a reduction current. As mentioned in a recent review by Helder X. Nunes et al., 2021 [20], since the year 2000, the number of papers utilising electrochemical reduction for the recycling of NaBO<sub>2</sub> into NaBH<sub>4</sub> only constitutes around 18% of the total number of papers investigating the regeneration of NaBH<sub>4</sub>, whereas the bulk are dedicated to mechano-chemical (50%) and thermo-chemical (32%) methods of recycling. This mini-review focuses on the electrochemical behaviour of NaBO<sub>2</sub> and NaBH<sub>4</sub> in aqueous solution, the electrolytic reduction of NaBO<sub>2</sub>, and finally, the challenges and future outlook of the process.

Much information regarding the thermodynamics of the competing reactions against the electroreduction of BO<sub>2</sub><sup>−</sup> (Equation (2)) is available in the literature. The electroreduction of BO<sub>2</sub><sup>−</sup> should be performed in concentrated alkaline solutions, as the BH<sub>4</sub><sup>−</sup> is stabilized with the presence of the OH<sup>−</sup> in high concentrations. In concentrated alkaline solutions, there are few reactions which are competing reactions and are more thermodynamically favourable compared to Equation (2), which makes the electroreduction of BO<sub>2</sub><sup>−</sup> difficult in alkaline solutions. Among them are the hydrogen evolution reaction (HER) and reductions involving dissolved oxygen.



The presence of dissolved oxygen presents an avenue for the reduction of molecular oxygen into various ionic species in alkaline solution.



The reason for the thermodynamic feasibility of these reactions compared to Equation (2), is that these involve uncharged water and molecular oxygen in alkaline solutions, compared to the eight-electron reduction of a negatively charged BO<sub>2</sub><sup>−</sup> anion.

## 2. Analytical Methods of Detection of NaBH<sub>4</sub>

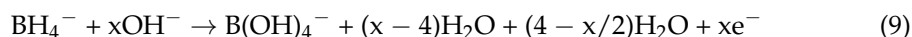
Several analytical methods have been used for the quantitative determination of BH<sub>4</sub><sup>−</sup>; among them are iodometry, hydrogen evolution, hydride hydrolysis, Fourier transformed

infrared spectroscopy (FTIR), and electrochemical methods. The reader is referred to the report by Biljana et al., 2013 [21], which discusses both the disadvantages and advantages of each technique.

### 2.1. Non-Iodometric Detection

Santos et al. [22] developed a hydride hydrolysis method based on the evolution of hydrogen gas upon decomposition of  $\text{NaBH}_4$ , where the volume of  $\text{H}_2$  is proportional to the amount of  $\text{NaBH}_4$ . It is important that the calibration process and the determination of the  $\text{NaBH}_4$  in the real sample are performed at same pressure and temperature. According to the authors, this method is simple in fabrication and operation, has high reproducibility but does not possess a low limit of detection (500 ppm) [22]. One suggestion for the improvement of this technique is to couple the setup with a gas chromatography mass spectrometer (GCMS) for the accurate determination of  $\text{H}_2$  gas, as seen in many photo-catalytic and photo-electrocatalytic water splitting experiments.

Voltammetric methods of detection of  $\text{BH}_4^-$  (Section 3), such as cyclic voltammetry (CV), linear scan voltammetry (LSV) and square wave voltammetry (SWV), are based on the electro-oxidation into  $\text{BO}_2^-$  and offer high sensitivity with a low limit of detection of 1 ppm [23].



If the  $n$  number of transported electrons is eight in highly concentrated alkaline solutions, then it conforms to the complete electro-oxidation into the  $\text{BO}_2^-$  without the hydrolysis reaction to release  $\text{H}_2$  gas [21]. The  $n$  number strongly depends on the electrode material and the concentration of the alkaline solution. The competition between hydrolysis (Equation (1)) and electro-oxidation (Equation (2)) of the  $\text{BH}_4^-$  determines the success of this method, in which the  $\text{BH}_4^-$  is stabilized in highly concentrated alkaline solutions. As will be explained in Section 3, the  $n$  value is usually lower than eight, which confirms that the hydrolysis of  $\text{BH}_4^-$  to release  $\text{H}_2$  cannot be completely avoided even in concentrated alkaline solutions.

Amendola et al. [24] reported a relatively simple potentiometric method for the analytical detection of the  $\text{BH}_4^-$  by measuring the open circuit potential (OCP) at a metal indicator electrode (IE) versus a reference electrode (RE), preferably mercury/mercury oxide ( $\text{Hg}/\text{HgO}$ ) in alkaline solutions. This method is based on the Nernstian relationship, where the OCP is proportional to the  $\log_{10}[\text{BH}_4^-]$  and only requires the potential measurement using a digital multi-meter without the use of a potentiostat/galvanostat, as seen in scanning techniques such as cyclic voltammetry (CV), linear scan voltammetry (LSV) or square wave voltammetry (SWV). By selecting a suitable IE, the concentration of  $\text{BH}_4^-$  was varied to obtain the linear regions. The linear regions depend on the type of IE material and the concentration of the alkaline solutions. For example, the linear range for the detection of  $[\text{BH}_4^-]$  is  $10^{-7}$ – $10^{-3}$  M for gold IE in 4 M KOH, while Pd IE shows a linear range of  $10^{-5}$ – $10^{-3}$  M in 4 M NaOH [22].

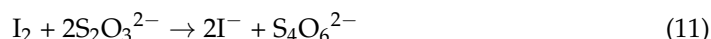
Spectroscopic detection of  $\text{BH}_4^-$  was reported by Elamin et al. [25], which is based on the reaction between the tri-nitrobenzenesulfonate anion with  $\text{BH}_4^-$  in alkaline aqueous solutions, which gives a UV absorption maximum at 460 nm [25]. The phosphotungstate anion,  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , can be reduced into a heteropoly blue species with the characteristic violet-blue colour upon reduction with  $\text{BH}_4^-$  in alkaline solutions with a UV absorption maximum at 680 nm and a lowest limit of detection of  $10^{-4}$  M [26]. However, the reduction of the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  is reversible; the heteropoly blue species can be oxidized into the colourless  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  in the presence of dissolved oxygen in the alkaline medium.

## 2.2. Iodometry

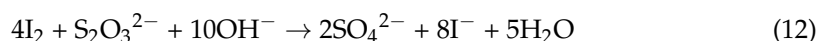
In iodometry, the oxidation of the  $\text{BH}_4^-$  with the addition of excess of the  $\text{IO}_3^-$  highly alkaline solution is shown below:



The released  $\text{I}_2$  is titrated with the  $\text{S}_2\text{O}_3^{2-}$  to obtain the amount of  $\text{I}_2$ :

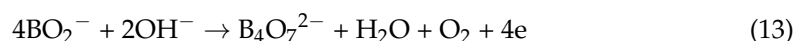


In highly alkaline solution, the presence of  $\text{OH}^-$  promotes the oxidation of the  $\text{I}_2$  with a different reaction pathway [26]:

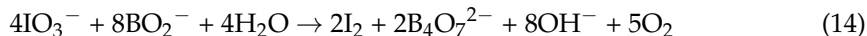


The errors associated with the iodometric method of analysis for the quantitative determination of the  $\text{BH}_4^-$  are due to two effects:

- the presence of high concentrations of  $\text{OH}^-$  enhances the reduction ability of the  $\text{S}_2\text{O}_3^{2-}$ . This effect shows that eight-times less  $\text{S}_2\text{O}_3^{2-}$  is required to reduce the  $\text{I}_2$  into  $\text{I}^-$  compared to Equation (2). This accounts for the erroneously higher values of the  $\text{BH}_4^-$  obtained from this method.
- in addition, the  $\text{BO}_2^-$  product can also be oxidized into the tetraborate anion  $\text{B}_4\text{O}_7^{2-}$  [27]:



and with the presence of excess  $\text{IO}_3^-$ , as follows:



This reaction (Equation (9)) also releases  $\text{I}_2$ , which accounts the erroneously higher amount of the  $\text{BH}_4^-$  in alkaline solutions.

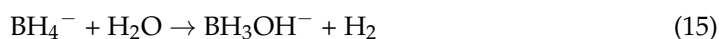
The iodometric method of analysis has been reported by few researchers in the ball-milling of  $\text{NaBO}_2$  for the conversion into  $\text{NaBH}_4$ , yielding high conversion efficiencies of nearly 76% [9], 80% [4,15,19] and even 90% [13]. Although the inaccuracies associated with the iodometric method of determination are described above, errors in such conversion efficiencies are easily reported when not confirmed by other methods of analysis. The iodometric method of quantitative detection should be abandoned as it provides an over-exaggeration of the amount of  $\text{BH}_4^-$  in the sample. Thus, the electroanalytical behaviour of the  $\text{BO}_2^-$  and  $\text{BH}_4^-$  should be investigated (Section 3), as it is becoming an important technique for the possibility of sensor fabrication for the quantitative detection of  $\text{BH}_4^-$ , especially in alkaline solutions.

## 3. Electroanalytical Behaviour of $\text{NaBH}_4$

Mirkin et al.'s (1991) [28] was perhaps the earliest attempt to understand the electroanalytical behaviour of  $\text{NaBH}_4$ . They reported cyclic voltammetry of a series of  $\text{NaBH}_4$  in 0.2 M NaOH on gold disc working electrode (WE) with  $\text{RuO}_2$  counter electrode (CE) and mercury/mercury sulfate ( $\text{Hg}/\text{HgSO}_4$ ) reference electrode (RE). With five repetitive scans at 0.1 V/s, they reported a single peak at around  $-0.6$  V (vs.  $\text{Hg}/\text{HgSO}_4$ ) using 3.2 mM  $\text{NaBH}_4$ , which confirms the stable electro-oxidation behaviour of the gold electrode free from any irreversible changes. Linear plots of the current ( $I/A$ ) vs. the square root of scan rate ( $v^{1/2}$ ), and anodic peak current vs. borohydride concentration (mM) were obtained, confirming that the electro-oxidation of  $\text{BH}_4^-$  is mass transport controlled. In contrast, several overlapping peaks were found using Pt WE. They concluded that using voltammetric method on gold WE was more advantageous due to the stability and selectivity compared to iodometric method, which often yields an erroneously high concentration of  $\text{NaBH}_4$ . There

was no reverse peak obtained for the electro-reduction of  $\text{BO}_2^-$  to  $\text{BH}_4^-$ . The same authors investigated the electro-oxidation of  $\text{BH}_4^-$  on gold microelectrode and concluded that the electro-oxidation process involves an 8-electron electrochemical–chemical–electrochemical (ECE) mechanism [29].

They also reported that below pH 12,  $\text{BH}_4^-$  undergoes hydrolysis to release hydrogen gas, as follows [29]:

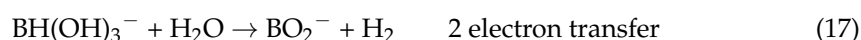


thus, the loss of  $\text{BH}_4^-$  should be avoided by storage in highly alkaline solution.

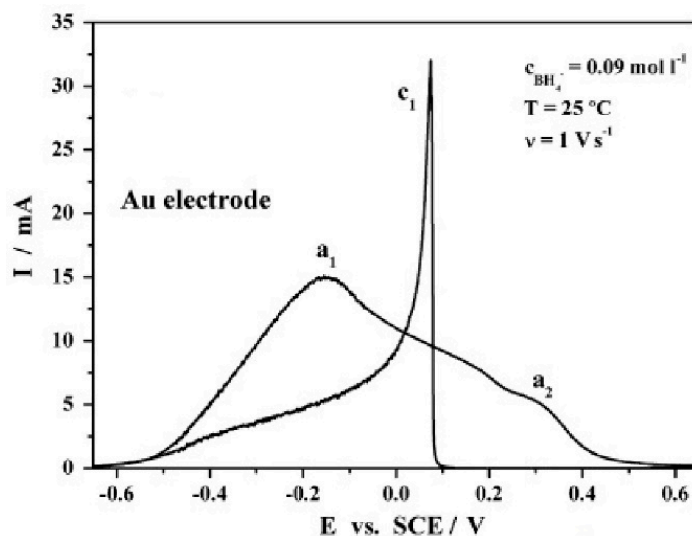
They also reported an  $n$  value of  $7.9 \pm 0.6$  electrons using the Levich equation in close agreement with the theoretical value of 8.

Sanli et al. [30] studied the electro-oxidation of  $\text{NaBH}_4$  in a three-compartment electrochemical cell separated with a Nafion cationic exchange membrane. The WE, CE and RE was Au disc, Pt wire and  $\text{Ag}^+/\text{Ag}$ , respectively. They reported a peak for  $\text{BH}_4^-$  oxidation at 0.3 V on a clean Ag surface but shifted to 0.1 V with an oxidized Ag electrode. It was obvious that the formation of silver oxides in alkaline solution had a catalytic effect on the electro-oxidation of  $\text{NaBH}_4$ . They also reported linear plots of peak current vs. borohydride concentration (M), confirming that the electro-oxidation is mass transport controlled. Coulometry at 0.45 V in 3M NaOH using 10 mM  $\text{NaBH}_4$  gave an  $n$  number of electrons around 6 for the electro-oxidation of  $\text{NaBH}_4$ . The same authors later investigated the electro-oxidation of  $\text{BH}_4^-$  on  $\text{Ag}_2\text{O}$  WE and obtained a  $n$  number of electrons almost of 6 [31].

Celikkan et al. [23] studied the electrochemical behaviour of  $\text{NaBH}_4$  in NaOH solution using several WE, such as Au, Pt, Pd and Ni. They reported a peak at  $-0.4$  V (vs. saturated calomel electrode, SCE) at lower scan rate, which shifted to  $-0.3$  V (vs. SCE) at higher scan rates using gold electrode. Linear plots of current (I/A) vs. the square root of scan rate ( $v^{1/2}$ ), and anodic peak current vs. borohydride concentration (mM) were also obtained, confirming the electro-oxidation of the  $\text{BH}_4^-$  is quasi-reversible with a slight shift in the peak potential of the oxidation currents. No reverse peak was obtained for the electro-reduction of  $\text{BO}_2^-$  to  $\text{BH}_4^-$ . The diffusion coefficient ( $D$ ) was determined from the Cottrell equation, which gave a value of  $4.02 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ , while rotating disc electrode (RDE) experiments gave an  $n$  number of electrons around 6 and 2, corresponding to the electro-oxidation of the  $\text{BH}_4^-$  as:

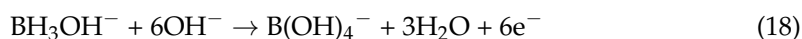


Santos et al. [32] investigated the electro-oxidation of  $\text{BH}_4^-$  on gold electrode in 2 M NaOH, using gold CE and SCE RE. Figure 1 shows the cyclic voltammetry of  $\text{NaBH}_4$  in 2 M NaOH solution. They reported the oxidation peak at  $-0.2$  V (vs. SCE) while a gold oxidation peak at higher potential of 0.3 V (vs. SCE). They obtained  $n$  values between 5 and 8;  $n$  values of less than 8 could be due the formation of boron oxides film on the gold electrode [33]. The  $a_1$  peak in Figure 1 is attributed to the 8-electron electro-oxidation of  $\text{BH}_4^-$ , while peaks  $a_2$  and  $c_2$  belong to the adsorbed  $\text{BH}_3\text{OH}^-$ , which is an intermediate in the electro-oxidation of  $\text{BH}_4^-$  on gold electrode [34].

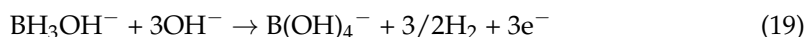


**Figure 1.** Cyclic voltammetry  $1 \text{ V s}^{-1}$  on Au electrode in  $2 \text{ M NaOH} + 0.09 \text{ M NaBH}_4$  solution at  $25 \text{ }^\circ\text{C}$ . Reproduced from ref. [32] with permission from the publisher.

The competition between the electro-oxidation of  $\text{BH}_4^-$  and hydrolysis is present especially at pH lower than 12 as described in Equation (2). Thus a lower number of electrons (6) released for the electro-oxidation of  $\text{BH}_4^-$  compared to Equation (2) is due to the presence of the  $\text{BH}_3\text{OH}^-$ :



The peak  $a_1$  in Figure 1 could be due to the presence of  $\text{BH}_3\text{OH}^-$  [34]:



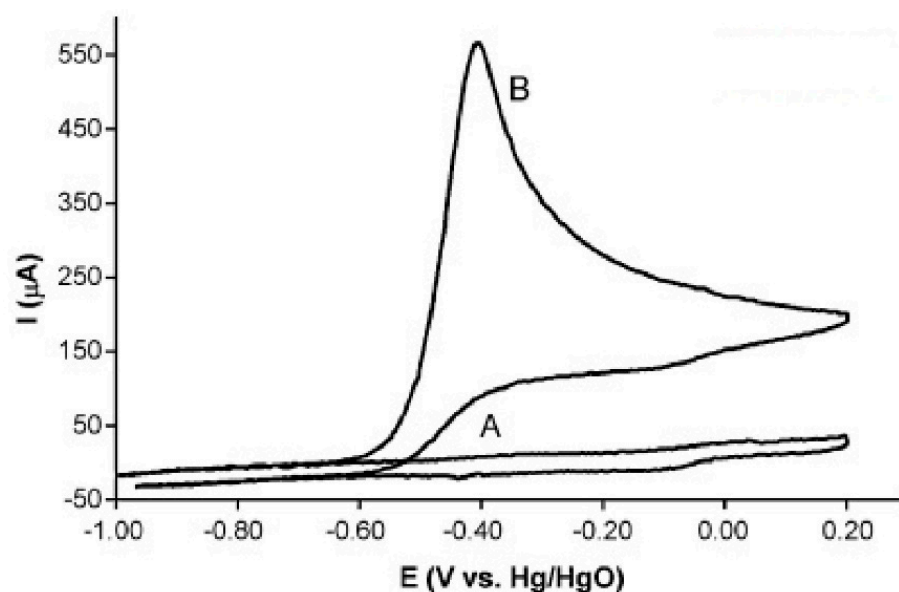
The detail oxidation behaviour of the  $\text{BH}_4^-$  on platinum anode is to date still largely unknown due to the platinum activity towards hydrogen adsorption and hydrogen evolution reaction (HER), which are the competing reactions towards the electro-oxidation of the  $\text{BH}_4^-$  [34,35]. Thus, the electro-oxidation of the  $\text{BH}_4^-$  on platinum does not involve eight electrons and the Faradaic efficiency is lower compared to gold electrode [34,36,37].

Thus, gold anode is generally the preferred electrode for the investigation of the electro-oxidation of  $\text{BH}_4^-$ , as it does not oxidize at positive potentials in alkaline solutions, and is inactive towards the heterogenous hydrolysis of the  $\text{BH}_4^-$  and the HER [29,38,39]. As previously confirmed, the electro-oxidation of the  $\text{BH}_4^-$  on gold electrode involves eight electrons (Equation (2)).

E. Gyenge [34] studied the voltammetry of  $\text{BH}_4^-$  and reported that the concentration of the hydroxide solution affects the oxidation potential of the  $\text{BH}_4^-$ . The standard potential for the reduction of the  $\text{BH}_4^-$  where the oxidation potentials of the  $\text{BH}_4^-$  on gold electrode has been reported to occur at positive potentials (vs. SHE) has been compared to the standard potential of the  $\text{BH}_4^-$  (Equation (2)). Thus, the kinetics of the oxidation of the  $\text{BH}_4^-$  are controlled by the concentration of the hydroxide solution, and the pH of 12 or less promoted the homogenous hydrolysis of the  $\text{BH}_4^-$ ; however, it is stable in concentrations of  $2 \text{ M OH}^-$  and above.

S. Colominas et al. [40] investigated the electrochemical behaviour of  $\text{NaBH}_4$  on gold electrode in  $2 \text{ M NaOH}$  solution. Figure 2 shows an oxidation peak around  $-0.4 \text{ V}$  (vs. mercury/mercury oxide,  $\text{Hg}/\text{HgO}$ ), which was obtained as reported by other researchers [34] with no reduction peak at the reverse scan.



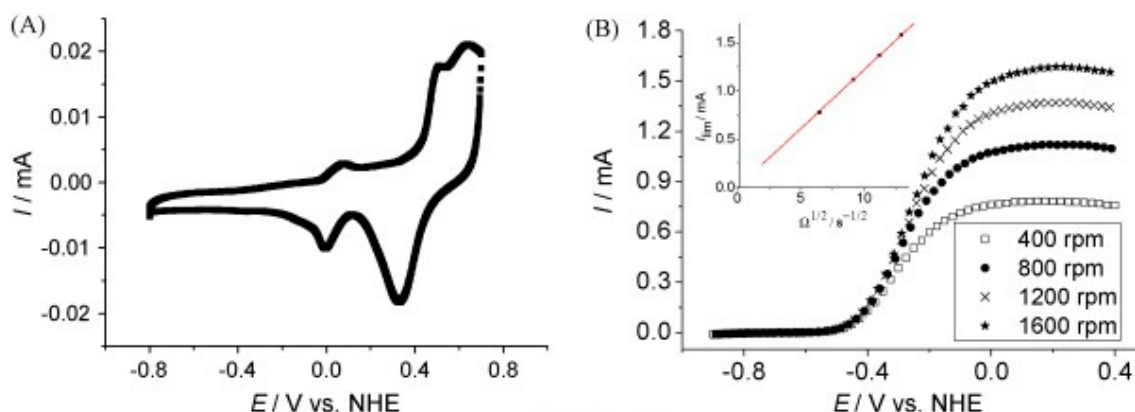


**Figure 2.** Cyclic voltammograms of (A) 2 M NaOH and (B) 1 mM NaBH<sub>4</sub> in 2 M NaOH at 6 mm Au disk at 0.100 V s<sup>-1</sup>. Reproduced from ref. [40] with permission from the publisher.

Chatenet et al. [41] also reported  $n = 7$  as the number of electrons involved in the electro-oxidation of the BH<sub>4</sub><sup>-</sup> on gold electrode using the Levich equation in 1 M NaOH. As confirmed from previous studies [42], the  $n$  number of electrons in the electro-oxidation of BH<sub>4</sub><sup>-</sup> on gold electrode is controlled by the ratio of OH<sup>-</sup> to BH<sub>4</sub><sup>-</sup> ([OH<sup>-</sup>]/[BH<sub>4</sub><sup>-</sup>]) concentration. Smaller ratios inhibit the oxidation process and give smaller  $n$  values than eight, but higher ratios give  $n$  values slightly higher than eight. Different ratios of the [OH<sup>-</sup>]/[BH<sub>4</sub><sup>-</sup>] also gave different onset oxidation potentials at the voltammograms. For example, a unit ratio of the [OH<sup>-</sup>]/[BH<sub>4</sub><sup>-</sup>] gave an onset oxidation potential of around -1.2 V (vs. NHE) compared to -0.5 V (vs. NHE) at higher ratios. Thus, this ratio controls the overall oxidation kinetics of the BH<sub>4</sub><sup>-</sup> at gold electrode. They suggest a large excess of OH<sup>-</sup>, typically a ratio of [OH<sup>-</sup>]/[BH<sub>4</sub><sup>-</sup>] ≥ 100, for the sufficient oxidation of the BH<sub>4</sub><sup>-</sup>, for faster kinetics of oxidation of  $n$  values higher than 7, and for total suppression of heterogenous hydrolysis of the BH<sub>4</sub><sup>-</sup> anion.

On the other hand, we have the diffusion coefficient ( $D$ ) of the BH<sub>4</sub><sup>-</sup> oxidation current magnitude on gold electrodes. Other researchers [43] reported that high concentrations of alkaline solution decrease the diffusion coefficient of the BH<sub>4</sub><sup>-</sup>, as also predicted by the Stokes–Einstein equation.

M. Chatenet et al. [44] reported that the kinematic viscosity of the NaBH<sub>4</sub> in NaOH solution increases with higher concentrations of NaBH<sub>4</sub> and NaOH, which influences the diffusion coefficient value of the BH<sub>4</sub><sup>-</sup> from RDE experiments in different concentrations of NaBH<sub>4</sub> in alkaline solutions (Figure 3). The diffusion coefficient obtained using the rotating-ring disc electrode (RRDE) technique was nearly twice larger in a solution of 0.01 M NaBH<sub>4</sub> in 1 M NaOH at 25 °C, compared to the diffusion coefficient in 0.02 M NaBH<sub>4</sub> and 1 M NaOH at 30 °C obtained using chronoamperometry technique on gold microsphere electrode. They suggest the formation of boron oxide films on the gold surface and heterogenous hydrolysis releasing hydrogen gas in an insufficiently low concentration of NaOH solution could affect the value of the diffusion coefficients [44]. The presence of boron oxides and hydrogen gas bubbles yield diffusion coefficients smaller than expected compared to those obtained in their absence, as both phenomena hinder the mass transport of the BH<sub>4</sub><sup>-</sup> to the gold electrode [44].



**Figure 3.** Cyclic voltammetry (CV) at the gold disk ( $0.124 \text{ cm}^2$ ) of the RRDE in (A) supporting electrolyte (1 M NaOH) for  $\Omega = 0$  and in (B) 0.1 M NaOH +  $10^{-3}$  M NaBH<sub>4</sub> at 25 °C for several revolution rates ( $\Omega$ ) of the RDE. Reproduced from ref. [44] with permission from the publisher.

They reported that the  $D$  values were dependent on the concentration of both NaOH and BH<sub>4</sub><sup>−</sup>, which also influenced the  $n$  values of the number of electrons transferred [44]. At the same concentration of the BH<sub>4</sub><sup>−</sup> (0.001 M), higher concentration of NaOH (1 M) gave higher values of  $n$  (5.8–6.6), but lower values of  $D$  ( $2.26\text{--}3.71 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), compared to lower concentration of NaOH (0.1 M) with  $n$  (5.1–4.8) and  $D$  ( $2.78\text{--}4.49 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ), at all temperatures (10, 25 and 40 °C), though 1 M NaOH possesses slightly higher viscosity than 0.1 M NaOH [44]. With the same concentration of BH<sub>4</sub><sup>−</sup> but an increase in NaOH concentration to 4 M, the  $D$  values decreased further ( $1.41\text{--}2.31 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) and a slight decrease in the  $n$  values (5.3–6.0) was observed at all temperatures. The decrease in the  $D$  values in 4 M NaOH was due to the increase in the kinematic viscosity. With an increase in the BH<sub>4</sub><sup>−</sup> concentration (0.01 M) in 4 M NaOH, the  $D$  values were the smallest at all temperatures ( $0.74\text{--}2.21 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) due to the increase in the viscosity of the solution, while the  $n$  values did not show an obvious trend.

Previous measurements using polarography on dropping mercury electrode (DME) gave higher  $D$  values of  $2.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  in 0.11 M NaOH [45] and  $10^{-4} \text{ cm}^2 \text{ s}^{-1}$  in 0.1 M NaOH [46]. The higher  $D$  values could be due to the absence of boron oxide film formation and the formation of hydrogen bubbles on the mercury electrode surface.

An  $n$  value greater than 8 was reported by H. Cheng et al. [47] and Atwan et al. [48], 9.7 and 12, respectively, using the RDE method in 2 M NaOH at 25 °C. Therefore, these  $n$  values greater than 8 are not represented from a thermodynamic viewpoint, but the increase in the solution viscosity must be considered for more accurate calculation of the  $n$  values [44].

Thus, the  $D$  and  $n$  values are dependent on many factors, among which are the type of experimental technique involved and concentration of BH<sub>4</sub><sup>−</sup> and NaOH, together with the temperature. The importance of understanding the electrochemical behaviour of the BH<sub>4</sub><sup>−</sup> with regard to the  $D$  and  $n$  values is an important step in the quantitative electrochemical detection of the BH<sub>4</sub><sup>−</sup>, as seen in the Section 4.

#### 4. Electrolysis of BO<sub>2</sub><sup>−</sup> into BH<sub>4</sub><sup>−</sup>

A few patents describe the electro-reduction of BO<sub>2</sub><sup>−</sup> into BH<sub>4</sub><sup>−</sup> in an aqueous medium [49–51], but later reports [26] did not verify any viable conversion of BO<sub>2</sub><sup>−</sup> into BH<sub>4</sub><sup>−</sup> in an aqueous medium, although the current efficiencies of the conversion, 20–25%, were reported in those patents [49–51]. This could be due to the iodometric titration, which yields higher NaBH<sub>4</sub> formation, which was adopted by the patents [26].

McLafferty et al. [52] also performed experiments to verify several patents [52–54] that claim the successful electrochemical reduction of BO<sub>2</sub><sup>−</sup> into BH<sub>4</sub><sup>−</sup>. They performed electrolysis of boric acid on mercury pool cathode in a divided electrolysis cell with cationic



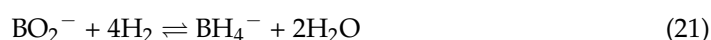
exchange membrane with sulfuric acid as the anolyte and  $\text{BO}_2^-$  in 2 M NaOH as the catholyte. Since mercury has high overpotential for the hydrogen evolution reaction (HER), it was selected as the cathode in this study, and the potential of the mercury cathode was maintained between  $-2.16$  and  $-2.60$  V (vs. Hg/HgO). The authors found no presence of the  $\text{BH}_4^-$  using cyclic voltammetry of alkaline solution even after two days of electrolysis. The same results were obtained with the hydrolysis of  $\text{BO}_2^-$  in the catholyte at gold and Cu electrodes, to reproduce the work of Jiang et al. [55], but no traces of the  $\text{BH}_4^-$  were detected using CV of the catholyte after electrolysis. Gold cathode was used again in pulsed potential electrolysis and there was no presence of any  $\text{BH}_4^-$  detected using CV. Titanium, Ag and Pb, which possess high overpotentials of HER, also did not show any conversion into  $\text{BH}_4^-$  in the alkaline reduction of the  $\text{BO}_2^-$  in the divided electrolysis cell. The authors used tetraalkylammonium hydroxide (TAAH) to increase the overpotential of the HER. All experiments concluded that the  $\text{TAA}^+$  cation was ineffective in absorbing at the cathode surface due to the replacement of water molecules at higher negative potentials, which promoted the HER. The authors also tried to modify the cathode surface using a chelating compound or a cationic polyelectrolyte to coat the gold electrode surface, forming a self-assembled monolayer (SAM), which promotes the attraction of the  $\text{BO}_2^-$  at small distances from the gold electrode surface. The chelating agent utilised for this purpose was 1-thioglycerol, which consists of a thiol group, which strongly bounds to the gold surface, and a diol group, which could bind with the  $\text{BO}_2^-$ , while a quaternized poly(4-vinylpyridine) was selected as the cationic polyelectrolyte. The electrolysis was repeated as with the high overpotential metal cathode, but no presence of the  $\text{BH}_4^-$  ion was detected in the CV.

Sanli et al. [56] carried out electrolyses in 1 M NaOH + 0.1 M  $\text{NaBO}_2$  at 0.5 V for 24 h and 48 h with Ag gauze cathode at room temperature and atmospheric pressure in an undivided electrochemical cell. The authors performed iodometric titration for the determination of the conversion efficiency of sodium metaborate into sodium borohydride. It was observed that there was 10% conversion after 24 h of electrolysis, reaching 17% (by iodometric titration) after 48 h. It was obvious that the low conversion efficiency was due to the HER at the cathode, which is a strong competing reaction with the electro-reduction of metaborate into borohydride.

The hydrogen is produced in situ at the cathode:

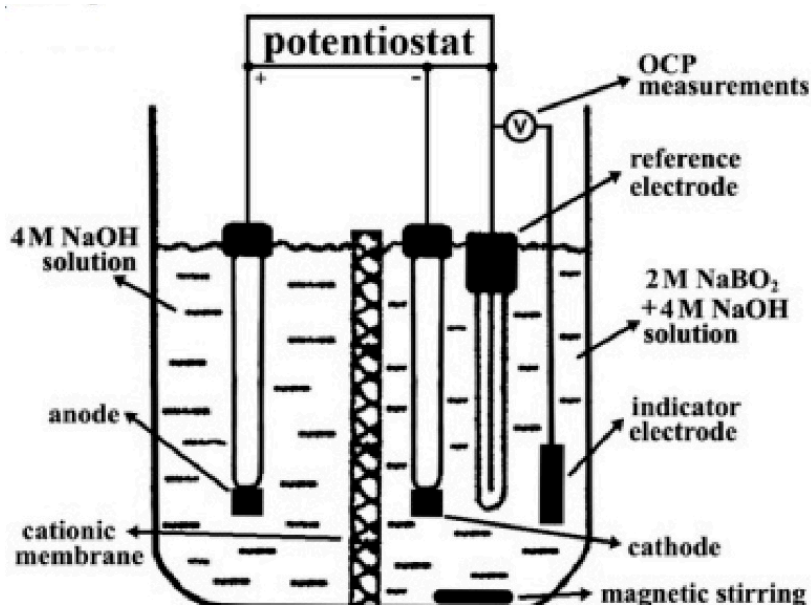


which was used to reduce the borate into borohydride:



The authors performed cyclic voltammetry of  $\text{NaBO}_2$  in 1 M NaOH and found that the electro-reduction of  $\text{BO}_2^-$  occurred at 0.5 V (vs. SCE) and the corresponding electro-oxidation of  $\text{BH}_4^-$  into the  $\text{BO}_2^-$  at 0.1 V (vs. SCE). They also reported that gold electrode is the most effective for the reduction of  $\text{BO}_2^-$  compared to Pt, Pd and Ni electrodes.

Santos et al. [22] performed controlled potential (1.8 V) bulk electrolysis for the electroreduction of 2 M  $\text{NaBO}_2$  at cadmium cathode in 4 M NaOH in a divided electrochemical cell with a cationic exchange membrane (CEM), as shown in Figure 4. The cathodic compartment consists of an indicator electrode connected to a high impedance voltmeter for the potentiometric monitoring of the concentration of the sodium borohydride. However, the authors did not report any conversion efficiency for this electrochemical method. Upon completion of electro-reduction, the  $\text{NaBH}_4$  can be isolated from aqueous solution by freeze-drying to eliminate water, leaving the  $\text{NaBO}_2$ , NaOH and  $\text{NaBH}_4$ . Then, the solid free water is dissolved in tetraglyme. The  $\text{NaBH}_4$  is only solubilised in tetraglyme, leaving the  $\text{NaBO}_2$  and NaOH undissolved. Tetraglyme is removed by thermal evaporation, leaving the  $\text{NaBH}_4$ , tetraglyme ( $\text{C}_{10}\text{H}_{22}\text{O}_5$ ) is also known as tetraethylene glycol dimethyl ether, butyl diglyme ( $\text{C}_{12}\text{H}_{26}\text{O}_3$ ) or diethylene glycol dibutyl ether.

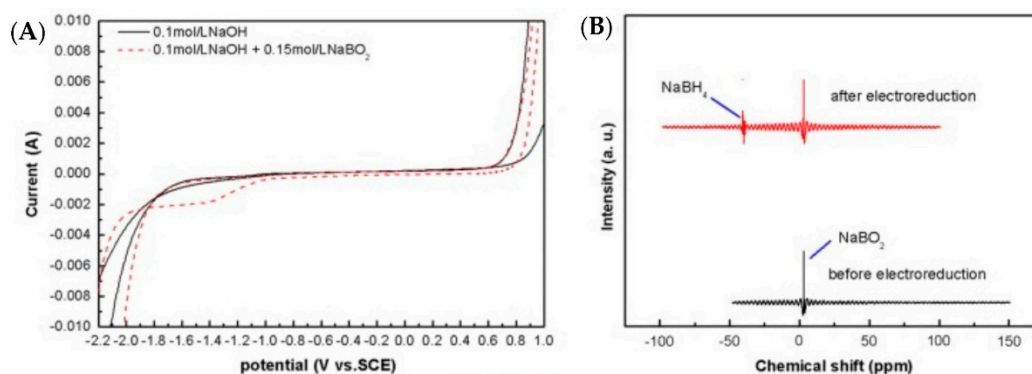


**Figure 4.** Electrochemical cell for bulk electrolysis of  $\text{NaBO}_2$  and open circuit potential (OCP) measurements in alkaline solution at 25 °C. The  $\text{NaBO}_2$  is reduced at the cadmium cathode while a high impedance voltmeter prevents current to flow into the circuit between the indicator and reference electrodes for the OCP monitoring. Reproduced from ref. [22] with permission from the publisher.

Shen Y. et al. [57] carried the desulfurization of dibenzothiophene with a potential difference 3.5 V and an electrolytic time 4 h in 0.025 M NaOH using Pb cathode in an undivided cell for the regeneration of the  $\text{NaBH}_4$ . Pb cathode was selected due to the large overpotential for the HER, which could not have interfered with the electroreduction of  $\text{BO}_2^-$  to  $\text{BH}_4^-$ . The authors reported that the desulfurization efficiency was increased with the amount of added  $\text{NaBO}_2$ , due to the increased regeneration of the  $\text{BH}_4^-$  with the presence of  $\text{BO}_2^-$ ; however, no efficiency conversion of the  $\text{BO}_2^-$  into  $\text{BH}_4^-$  was reported in this study.

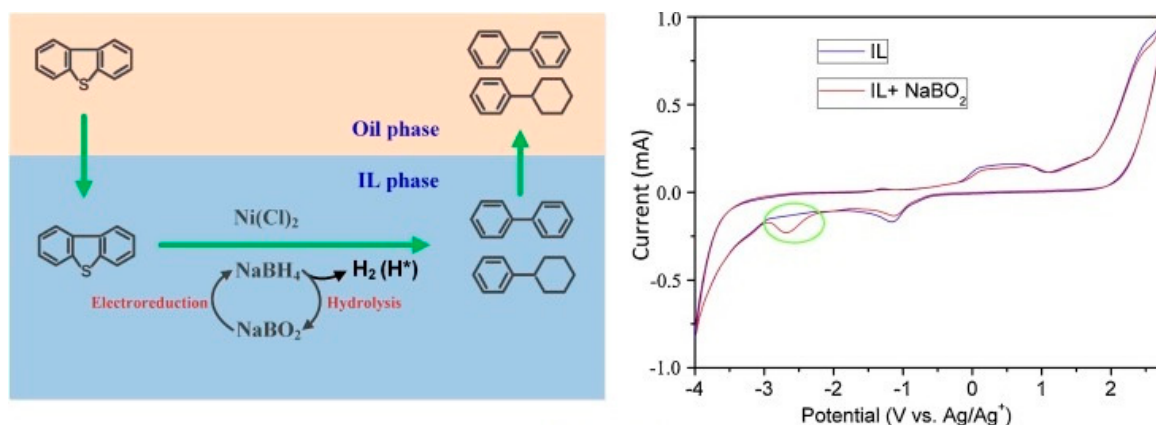
Zhu et al. [58] performed cyclic voltammetry at Cu cathode and Ni counter electrode (CE) and reported that the cathodic peak at 1.2 V (vs. SCE) was due to the formation of the  $\text{BH}_4^-$ . In addition, they reported a conversion efficiency of 15% from electrolysis using an undivided electrolysis cell, with a potential difference of 1.7 V, in 1 M NaOH as the catholyte, at Cu cathode.

Chenhua et al. [59] used  $\text{NaBH}_4$  for the de-sulfurization of fuel and regenerated the  $\text{NaBH}_4$  through electroreduction of the  $\text{NaBO}_2$ . The  $\text{NaBO}_2$  was converted into sodium borohydride ( $\text{NaBH}_4$ ) through electroreduction on boron doped diamond (BDD) cathode. The authors used a divided cell, using a cationic exchange membrane (CEM) to separate the CE from the WE and RE and used a pulsed current for the electro-reduction of the  $\text{BO}_2^-$  into  $\text{BH}_4^-$ . The negatively charged  $\text{BO}_2^-$  experiences repulsion at the cathode. Thus, a pulse cycle of positive followed by negative potential facilitated the electro-reduction of the  $\text{BO}_2^-$ . When the WE was charged positive, the  $\text{BO}_2^-$  was attracted to the WE surface, and reduced into the  $\text{BH}_4^-$ , as the potential was pulsed into the negative potential. The BDD showed the onset potential for the HER is at  $-1.8$  V (vs. SCE), while the onset potential for the oxygen evolution reaction (OER) is around  $+0.6$  V (vs. SCE), as shown in Figure 5. The negative pulse is more positive than  $-1.8$  V to avoid the HER but more negative than  $0.6$  V to avoid the OER. The electro-reduction of  $\text{BO}_2^-$  into  $\text{BH}_4^-$  showed a peak at  $-1.4$  V (vs. SCE). The authors did not report any conversion efficiency for the electro-reduction of the  $\text{BO}_2^-$  into borohydride  $\text{BH}_4^-$ . The  $\text{BH}_4^-$  was used as an intermediate for the desulfurization by supplying hydrogen for the reductive de-sulfurization of the gasoline samples. Upon reductive desulfurization, the  $\text{BH}_4^-$  is oxidized into  $\text{BO}_2^-$ .



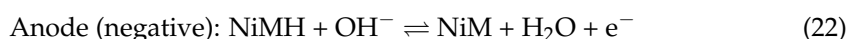
**Figure 5.** (A) Cyclic voltammogram of a BDD electrode in 0.1 M NaOH and 0.1 M NaOH + 0.15 M NaBO<sub>2</sub> at 0.100 V s<sup>-1</sup>; and (B) 11 boron NMR spectrogram of electrolytes before and after electroreduction, reaction conditions: 1.5 V forward pulse voltage, 0.3 V reverse pulse voltage, 1.5 s forward pulse duration, 0.5 s reverse pulse duration, 0.15 M NaBO<sub>2</sub> concentration, 0.1 M NaOH, 1.5 h of electrolytic time. Reproduced from ref. [59] with permission from the publisher.

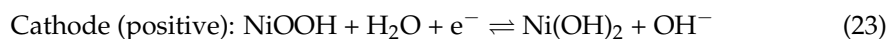
The same authors also used the same method of pulsed potential to re-generate BH<sub>4</sub><sup>-</sup> from BO<sub>2</sub><sup>-</sup> but applied a larger negative pulse potential (-2–2 V to -3.0 V) compared to the positive pulse potential (0.1 V to 0.9 V) [60]. From the CV in ionic liquids (IL), the reduction of the BO<sub>2</sub><sup>-</sup> occurred at -2.5 V vs. Ag/Ag<sup>+</sup> using glassy carbon electrode (GCE) as the WE, where the HER was ineffective in providing competition against the electroreduction of the BO<sub>2</sub><sup>-</sup> as it occurred beyond -3 V vs. Ag/Ag<sup>+</sup>, is shown in Figure 6. The whole regeneration of BH<sub>4</sub><sup>-</sup> from BO<sub>2</sub><sup>-</sup> and desulfurization of a model fuel oil was carried out in an IL, 1-ethyl-3-methylimidazolium bis (trifluoromethanesulfonyl) imide (EMI[TFSI]) in an undivided electrochemical cell. A higher reverse pulse towards the positive potential was avoided due to the effect of oxygen evolution reaction (OER) and the oxidation into borax (sodium tetraborate). The time duration for the negative and positive pulse increased (0.1 s to 1.0 s) the desulfurization efficiency of the model oil; however, the conversion efficiency of the BO<sub>2</sub><sup>-</sup> into BH<sub>4</sub><sup>-</sup> was not calculated.



**Figure 6.** Left: The schematic diagram of the novel desulfurization process. Right: Cyclic voltammogram of IL and IL + NaBO<sub>2</sub> on a glassy carbon electrode at 0.100 V s<sup>-1</sup>. The green arrows show the movement of the molecule. Reproduced from ref. [60] with permission from the publisher.

Hydrogen carrier electrode materials are also hydrogen release materials, as seen in rechargeable nickel metal hydride battery electrodes, such as NiMH and Ni(OH)<sub>2</sub> in alkaline solutions.





Both forward reactions are discharge reactions at the anode (-ve electrode) and cathode (+ve electrode) which takes place in rechargeable NiMH batteries in highly alkaline solutions. Both electrodes involve the hydride in the electrochemical redox at both electrodes, which is similar to the sodium borohydride; thus, it could be utilised in the electroreduction of the  $\text{BO}_2^-$  into the  $\text{BH}_4^-$  (Section 5).

## 5. Conclusions and Future Outlook

Electrochemical reduction of sodium metaborate is still an expanding field of research and not many papers report the successful conversion of sodium metaborate into sodium borohydride. Research reports which mention the in situ electrochemical reduction of sodium metaborate into sodium borohydride are available in the literature, though they fail to investigate the conversion efficiencies of such techniques. In all the papers reviewed, electrochemical reduction takes place in an alkaline aqueous solution where water is the reductant but the same water molecules promote the hydrolysis of sodium borohydride releasing hydrogen gas when the pH reaches 12. Several patents report the successful electrochemical reduction of sodium metaborate into sodium borohydride, but research reports investigating the electrochemical reduction of sodium metaborate fail to reproduce and substantiate even trace amounts of sodium borohydride, as claimed by the patents. In alkaline aqueous solutions, there are a few reasons for the failure of such electrochemical conversion:

- (a) the metaborate anion  $\text{BO}_2^-$  is a negative ion which is repelled by the cathode surface. In addition, in the large presence of the  $\text{OH}^-$  ions, the HER in alkaline solutions (Equation (5)) is thermodynamically more favourable than the electro-reduction of the  $\text{BO}_2^-$  anion.
- (b) the  $\text{BH}_4^-$  is stabilized in alkaline solutions with pH of more than 12. Attempts to reduce the  $\text{BO}_2^-$  into  $\text{BH}_4^-$  require the presence of  $\text{OH}^-$  in concentrated solutions. However, in concentrated alkaline solutions with the presence of large amounts of  $\text{OH}^-$ , the effect of the HER becomes more prominent.
- (c) the presence of dissolved oxygen promotes the oxygen reduction reaction (OER, Equations (6)–(8)). In addition, the presence of dissolved carbon dioxide ( $\text{CO}_2$ ) also promotes the electroreduction of  $\text{CO}_2$ . In all the papers reviewed, there were no mention of eliminating dissolved  $\text{O}_2$  and  $\text{CO}_2$  by nitrogen or argon gas bubbling prior to the electroreduction of  $\text{BO}_2^-$ . The analytical detection of  $\text{BH}_4^-$  using iodometric titration must be abandoned altogether as it gives erroneously high concentrations, as high as eight times higher than the actual concentration of  $\text{BH}_4^-$  in the samples. More accurate methods of detection, such as based on the hydrolysis of the  $\text{BH}_4^-$  to release  $\text{H}_2$ , and electrochemical methods of detection should be given priority.

Given are a few examples from the literature and suggestions to improve the efficiency of the electrochemical reduction of the  $\text{BO}_2^-$  into  $\text{BH}_4^-$ . As reported in the literature, a pulsed potential of the cathode could be implemented in a divided electrochemical cell using a cationic exchange membrane (CEM). The initial positive pulse attracts the  $\text{BO}_2^-$  towards the electrode surface, and immediate negative pulse reduces the  $\text{BO}_2^-$  immediately into  $\text{BH}_4^-$ . This method was adopted [59,60] for the in situ regeneration of  $\text{BH}_4^-$  from the  $\text{BO}_2^-$ .

The second approach is to utilise electrode materials which could reduce the  $\text{BO}_2^-$  instead of relying on water in alkaline electrolyte as the reductant, as explained in Equations (14) and (15).

The only drawback is the presence of the smaller and more mobile  $\text{OH}^-$  in large concentrations compared to the  $\text{BO}_2^-$ , which could decrease the conversion efficiency of the  $\text{BO}_2^-$  into  $\text{BH}_4^-$ . Even at larger negative potentials, the presence of the HER in alkaline solutions should provide another competition for the electro-reduction of  $\text{BO}_2^-$  into  $\text{BH}_4^-$ .

One possible solution of the problems of electro-reduction in alkaline aqueous solution is to perform the electro-reduction in organic solvents and molten salts such as ILs or deep

eutectic solvents (DES) with the presence of such hydrogen carrier electrode materials, or with the presence of stronger chemical reductant such as hydrazine. Before attempting such procedures, preliminary investigation of the electro-reduction behaviour must be studied using cyclic voltammetry to ascertain the onset of the reduction wave and RDE to determine the  $D$  and  $n$  values in such medium.

The electro-reduction of  $\text{BO}_2^-$  could be the “next big thing” after the electro-reduction of dissolved carbon dioxide, as both are by-products formed from the release of energy and the recycling into their precursors is non-spontaneous with positive free energies.

Boron and carbon are in the same row and are neighbours in the periodic table, and both oxides are difficult to reduce. There are hundreds of papers reporting the photocatalytic and photo-electrocatalytic reduction of dissolved  $\text{CO}_2$  into short chain molecules, such as methane, methanol and formic acid, using semiconductor materials such as titanium  $\text{TiO}_2$  and  $\text{ZnO}$ , but there is yet to be a single paper on the same subject devoted to the reduction of  $\text{BO}_2^-$ . Nevertheless, both are important processes in the drive towards decreasing global warming and climate change, and the utilisation of hydrogen energy to replace fossil fuels.

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