Short communication

Recovery of borohydride from metaborate solution using a silver catalyst for application of direct rechargable borohydride/peroxide fuel cells

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ABSTRACT

This study aims at the investigation of a suitable catalyst for the electrochemical reduction mechanism of metaborate into borohydride with the hope of the construction of rechargeable direct borohydride/peroxide fuel cell. A passive direct borohydride/peroxide fuel cell with Ag anode and Pt/C cathode was constructed. Its maximum power density was calculated as $7\,\mathrm{mW\,cm^{-2}}$ at a cell voltage of 0.5 and a current density of $11\,\mathrm{mA\,cm^{-2}}$. Recycling of the metaborate, the co-product of the borohydride oxidation, to the borohydride is the major issue in order to achieve the rechargeable borohydride fuel cells. Accordingly, the $NaBO_2$ solution was electrolyzed with the use of Ag electrodes for this purpose. The converted borohydride were determined by the cyclic voltammetry using Au and Ag electrodes which are highly selective for this purpose. The cyclic voltammetric curves revealed the peaks which indicated the conversion of $NaBO_2$ into $NaBH_4$. The presence of $NaBH_4$ was also verified iodometrically after the electrolysis. It was observed that there was 10% conversion after 24 h of electrolysis which reached up to 17% after 48 h. These data are very promising in the quest of the construction of a rechargeable direct borohydride fuel cell.

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1. Introduction

$NaBH_4$ is a metal hydride with strong reducing capacity and high hydrogen content. It releases its hydrogen as a result of hydrolysis. This is a rapid reaction at room temperature. Besides four moles of protide hydrogen coming from borohydride, four moles of protons come from water. This reaction takes place on the metal catalysts such as Pt, Pd, Ru, Ni and Co [1,2]. The mechanistic scheme can be summarized as

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \tag{1}$$
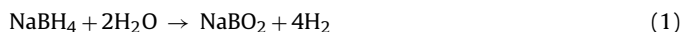
If we used $NaBH_4$ in this manner it acts as an indirect fuel. However, $NaBH_4$ can also be employed as a direct fuel as a result of electrooxidation with a mechanism given below:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-, \quad E_{cell}^\circ = 1.64\,\mathrm{V} \tag{2}$$
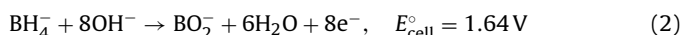
If we want use $NaBH_4$ as a direct fuel the hydrolysis reaction is highly undesirable. Therefore it is necessary to find a suitable anode material to prevent this reaction in direct borohydride/peroxide fuel cell (DBPFC). The use of peroxide solution as a catholyte in place of air increases the cell potential up to 2.1 V. That is why DBPFCs are much more advantageous.

As outlined above $NaBO_2$ is the end product of both the hydrolysis and electrooxidation of $NaBH_4$. Its reconversion into $NaBH_4$ is of great importance. There are some processes developed for this purpose such as ball milling [3] and high pressure hydrogenation at $650\,°C$ [4–9].

In addition there are methods for the electrochemical production of $NaBH_4$ [5]. Park et al. determined that there was a formation of borax hydride ($Na_2B_4O_7 \cdot 10H_2O$) in their conversion study they carried out with palladium, boron-doped diamond (BDD), gold and platinum electrodes; borax hydride was very active in the regeneration of $NaBH_4$ [10].

Gyenge et al. investigated the electrocatalytic hydrogenation and direct reduction of borates in basic media and determined that there was a measurable amount of $NaBH_4$ formed [11]. Copper also converted $NaBO_2$ into $NaBH_4$ by the use of hydrogenation catalysts such as Ni, Pt, Ph, Pd and Co [12].

In studies of methods recovering and synthesizing borohydride, one also needs a simple, rapid and accurate analytical method to monitor its concentration in the solution. The methods employed for the analysis of borohydride are as follows:

1. The iodate method is based on the reaction of BH_4^- with IO_3^- followed by back-titration of the remaining IO_3^- with the $I^-/I_2 - S_2O_3^{-2}$ system [13].
2. The spectrophotometric method is based on the reduction of phosphotungstate ($PW_{12}O_{40}^{3-}$) by BH_4^- [11,14].

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3. The electrochemical method is based on the electrooxidation of borohydride on the Au electrode [15,16]. CV method is a very versatile technique to find whether there was any borohydride formation in the electrolyzed solution. Cyclic voltammetry at a gold electrode gives a well-defined sharp peak suitable for analytical determination.

In this study, the formation of NaBH$_4$ was determined by two different analytical methods namely cyclic voltammetry and iodometric titration. The CV analyses were carried out with the use of Ag gauze and Au electrodes. According to our previous papers Au and Ag electrodes are suitable anode catalysts for the oxidation and therefore the determination of borohydride [17,18]. The iodometric method was also used for determination of the amount of borohydride recovered.

Performance of a DBPFC constructed with Ag anode and Pt/C cathode was studied in our laboratory [19]. In this study, NaBO$_2$ was electrolyzed into NaBH$_4$ in a portable cell by the use of silver anodes. Achievement of electrochemical conversion of NaBO$_2$ into NaBH$_4$ will be an important milestone for DBFC technology and will pave the way for the construction of rechargeable DBFCs. The construction of a rechargeable fuel cell should be a priority task for the further study. The fact that the conventional means of production of NaBH$_4$ is highly cumbersome and expensive makes these studies doubly important.

2. Experimental

2.1. Electrochemical experiments

The studies were carried out with the use of Ag gauze working (Alfa Aesar, sized 3 mm × 3 mm and rolled), Pt wire counter (BASS) and saturated calomel (BASS) reference electrodes. The electrolyses were carried out in 1 M NaOH + 0.1 M NaBO$_2$ at 0.5 V for 24 and 48 h with Ag gauze electrode. The resulting solutions were analyzed for NaBH$_4$ with Ag and Au disc electrodes.

2.2. Iodometric titration

Reagents used in the titration are 4 N sulfuric acid, 0.25 N potassium iodate, 0.1 N sodium thiosulfate, and potassium iodide and starch indicator. 35 ml of standard potassium iodate solution was added into 10 ml sample of the electrolyzed NaBO$_2$ solution by stirring vigorously. 2 g potassium iodide was added followed by sulfuric acid. The flask was kept in dark for 5 min before the liberated iodine was titrated with 0.1 N thiosulfate with starch indicator [13].

3. Results and discussions

The cyclic voltammetric curve obtained with 0.1 M NaBO$_2$ + 1 M NaOH solution using Ag gauze electrode is given in Fig. 1. A reduction peak was observed at +0.5 V which attributed to reduction of BO$_2^-$ to BH$_4^-$. The oxidative peak appeared at −0.1 V upon the reversal of the scan is consistent with oxidation potential of the borohydride back to the metaborate. Metaborate solution was electrolyzed for 24 and 48 h using the Ag gauze electrode at 0.5 V. The temperature was maintained at room temperature throughout the electrolysis.

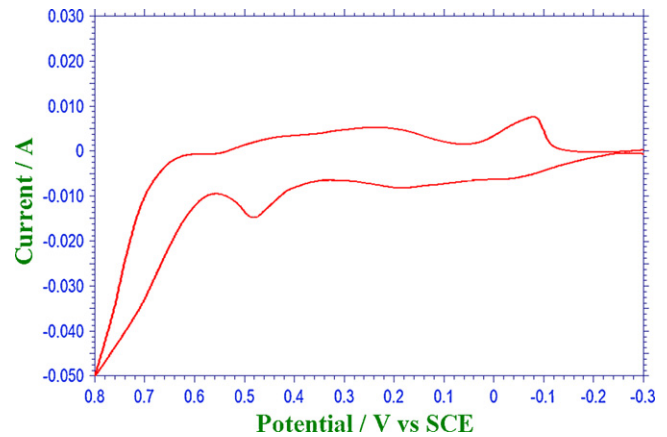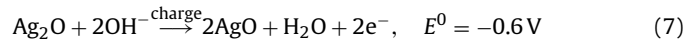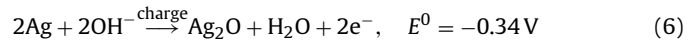The reactions which occur during the electrolysis are as follows:

$$BO_2^- + 4H_2 \Leftrightarrow BH_4^- + 2H_2O \tag{3}$$

$$2H_2O + 2e^- \Leftrightarrow 2OH^- + H_2 \tag{4}$$

$$2OH^- + 2H^+ \Leftrightarrow 2H_2O \tag{5}$$

Fig. 1. Cyclic voltammetric curve of 0.1 M NaBO$_2$ + 1 M NaOH with Ag gauze electrode.

Meanwhile the oxidation mechanisms taking place on the surface of silver electrode are as follows:

$$2Ag + 2OH^- \xrightarrow{charge} Ag_2O + H_2O + 2e^-, \quad E^0 = -0.34\,V \tag{6}$$

$$Ag_2O + 2OH^- \xrightarrow{charge} 2AgO + H_2O + 2e^-, \quad E^0 = -0.6\,V \tag{7}$$

The first active layer form at the first charge was Ag$_2$O. However, it is further oxidized to AgO at the repetitive cycles.

Silver metal has been used as the catalyst at the Zn–AgO battery and Zn–Ag$_2$O accumulators with the highest power densities among the commercial rechargeable batteries by the charge–discharge cycling [20,21]. For example, in rechargeable lithium ion batteries, the discharge capacity increases by increasing the amount of the silver coated upon the electrode [22]. Taking all these into consideration the recovery of borohydride seems to be possible by the electrolysis with silver electrode.

3.1. CV analysis of electrolyzed solution using the Ag disc electrode

After the 24 h electrolysis at 0.5 V with Ag gauze electrode, the cyclic voltammetric curve of the electrolyzed solution reveals a second peak at −0.2 V which was not present before the electrolysis (Fig. 2).
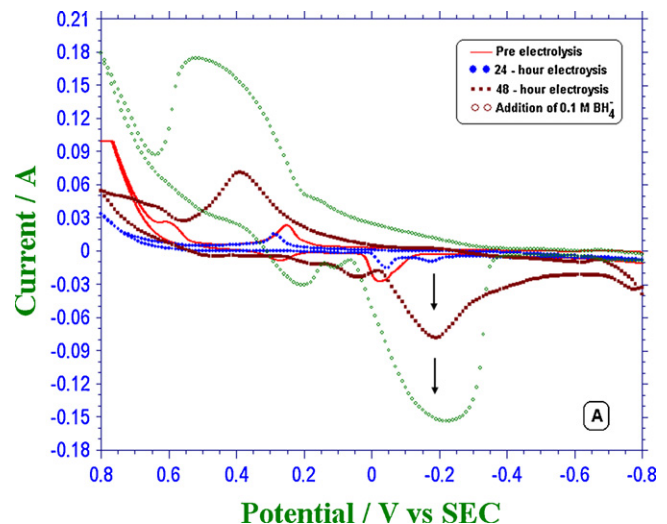

Fig. 2. The cyclic voltammetric curves of NaBO$_2$ electrolyzed with the use of Ag gauze electrode.
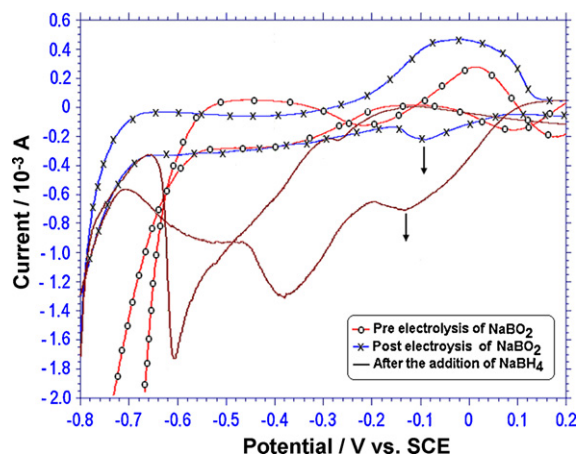
Fig. 3. The cyclic voltammetric curves of the electrolyzed $NaBO_2$ solutions by the use of Au electrodes.

The electrolysis time was prolonged to 48 h in order to investigate the further reconversion of BH_4^- in the solution. In a similar way, the current of the peak observed at −0.2 V increased after the electrolysis as expected. There was 10 ml of $NaBH_4$ added to electrolyzed solution in order to verify to formation of borohydride. The peak at −0.2 V showed a distinctive increase which proved that the peak was attributable to $NaBH_4$.

3.2. CV analysis of the electrolyzed solution using the Au electrode

Similarly the cyclic voltammetric curves of the solutions after and before electrolysis were taken with the use of Au electrode in order to determine the presence of $NaBH_4$ formed. According to the literature, the comparison of the catalytic activities of the Au, Pt, Pd and Ni electrodes reveal that Au is the most effective metal catalyst towards the oxidation of borohydride [16]. Since the peak which belongs to the electrooxidation of BH_4 changes linearly with the borohydride concentration, it is suggested that Au could be used in the electroanalytical determination of BH_4^-.

After the electrolysis of 24 h, a new peak appeared at −0.1 V which was not present before the electrolysis. This voltammetric peak was then analyzed by means of standard addition. The voltammograms obtained before and after the addition of $NaBH_4$, are depicted in Fig. 3. The fact that the new peak appeared at −0.1 V increased after the addition of $NaBH_4$ solution verified the presence of borohydride in electrolyzed solutions.

3.3. Analysis of the electrolyzed solution by iodometric titration

This method has been developed as a volumetric method in which borohydride is oxidized with excess potassium iodate. Unreduced potassium iodate is determined by the usual iodometric procedures. The method is reproducible, fast and can be carried out with simple volumetric equipment. The method is based on the following equation:

$$3BH_4^- + 4IO_3^- \rightarrow 4I^- + 3H_2BO_3^- + 3H_2O \quad (8)$$
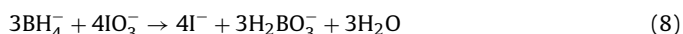
The weight of sodium borohydride can be calculated as [13]:

$$\text{mg of NaBH}_4 = (\text{ml of KIO}_3 \times \text{normality} - \text{ml of Na}_2S_2O_3$$
$$\times \text{normality}) \times 4.731$$

The samples of 10 ml taken from 24 h (S.1; sample 1) and 48 h (S.2; sample 2) electrolyzed solutions were titrated with the use of thiosulfate. Based upon the equation above the amount of $NaBH_4$

Table 1
The amount and percentage conversions of $NaBH_4$ according to iodometric titration results.

		% Conversion
Amount of potassium iodate added into S.1 and S.2	35 ml	
Amount of thiosulfate consumed for S.1.	83.4 ml	
Amount of thiosulfate consumed for S.2.	94.4 ml	
Theoretical amount of $NaBH_4$ expected	18.9 mg	
Amount of $NaBH_4$ after 24 h electrolysis	1.609 mg	9%
Amount of $NaBH_4$ after 48 h electrolysis	3.230 mg	17%

was calculated according to the amount of thiosulfate used. The results are tabulated in Table 1.

4. Conclusions

1. It is concluded that as well as Au electrode, Ag is also a suitable catalyst for determination of $NaBH_4$.
2. The electrochemical reconversion of $NaBH_4$ with the use of Ag gauze electrode is a completely new, simple and inexpensive process. $NaBH_4$ was formed by electrochemical techniques at room temperature and the atmospheric pressure.
3. It is apparent that reverse electrolysis of $NaBO_2$ with the use of Ag gauze electrode results in the reformation of $NaBH_4$. The amount of conversion was found to be 10% after 24 h of electrolysis. This value was almost doubled and reached to 17% after 48 h of electrolysis. The conversion of 17% is highly promising.
4. It was reconfirmed that Ag is a very suitable anode material for direct borohydride/peroxide fuel cells as verified previously [17–19] and it gives a great promise for rechargeable direct borohydride/peroxide fuel cells.
5. The electrochemical data reveal that the use of Ag anode would pave the way for the construction of "rechargeable DBFCs". However, the studies should be extended to various Ag alloys to increase the conversion. This study is hoped to be a guide for future studies.

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