



# Recovery of $\text{NaBH}_4$ from $\text{BH}_3\text{OH}^-$ hydrolyzed intermediate on the AgI surface treated with different electrochemical methods

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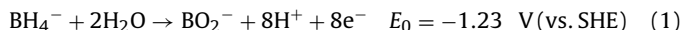
## ABSTRACT

This paper presents the investigation of the activity of silver electrode treated by cyclic voltammetric (CV) method with  $\text{H}_2\text{O}_2 + \text{KI}$  in aqueous solution on the oxidation of  $\text{NaBH}_4$ . Among the various treatment solutions investigated,  $\text{H}_2\text{O}_2 + \text{KI}$  solution shows the best performance with the maximum catalytic activity. CV treatment in  $\text{H}_2\text{O}_2 + \text{KI}$  on Ag electrode improves the catalytic activity more than bulk electrolysis (BE) due to increase in surface porosity. Apart from the catalytic effect of this surface in the oxidation of  $\text{BH}_4^-$  it was also observed that there is a formation of hydrolysis product of  $\text{BH}_3\text{OH}^-$  of  $\text{BH}_4^-$  during the anodic scan between  $-0.25$  and  $-0.45$  V which is seen to be converted back to  $\text{BH}_4^-$  during the cathodic scan.

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## 1. Introduction

$\text{NaBH}_4$  is a solid state metal hydride which stores hydrogen and does not releases it back hydrolyzing with water. That is why it is directly used as a fuel in fuel cells. It can theoretically be oxidized with 8-electron transfer [1,2].



Direct borohydride fuel cells have great use in air free media such as space studies, waterborne and portable applications. There are two types of direct borohydride fuel cells. One of them is Direct Borohydride/Air Fuel Cell (DBFC) which uses aqueous  $\text{NaBH}_4$  solution as a fuel. DBFCs have gained considerable popularity in recent years due to their high energy density, high cell voltage and environmental friendliness. In DBFCs  $\text{NaBH}_4$  oxidizes in an aqueous alkaline media to  $\text{BO}_2^-$  and water, generating eight electrons. The cell voltage of DBFC is 1.64 V [3,4]. This value is higher than those obtainable with PEM or methanol fuel cells. The cell reactions for DBFC are as follows:



In DBFCs it is important that  $\text{NaBH}_4$  be oxidized directly without hydrolysis. This is highly depended upon the development of a suit-

able anode material. This is one of the most popular topics in DBFC studies [5–7]. This can only be achieved with the selection of an anodic material that oxidizes  $\text{NaBH}_4$  in a most efficient manner without promoting the hydrolysis reaction. It is known that  $\text{NaBH}_4$  is oxidized with 4-electron transfer on Ni, 2e transfer on Pt-bulk, 5–8 electron transfer on Pt/C and 6 electron transfer on Pd and Ag electrodes. There are also La-, Zr- and Ni-based alloys used for the storage of hydrogen in borohydride fuel cells [5,8–14].

Another approach is the development of alloys with effectively prevents the hydrolysis of sodium borohydride. Au and Pt/C are the most suitable materials for the oxidation of  $\text{NaBH}_4$  with 8-electron transfer [6,11] followed by Ag with 6-electron transfer. Although Au is very effective its cost is a very big barrier. On the other hand Ag has very high hydrogen over voltage and oxidation of  $\text{NaBH}_4$  takes place at a lower potential than the hydrogen evolution potential and the hydrolysis reaction is largely obviated. The oxidation of  $\text{NaBH}_4$  on Ag surface takes place with 6e transfer [15]. Chatenet et al. calculated it as 7.2 [16]. Ag is used as an alloying material with other metals due to its hydrolysis preventive behavior [17–19].

In our previous studies Ag was proven to be a suitable anode material for the direct oxidation of  $\text{NaBH}_4$  [15]. Theoretically the oxidation of  $\text{NaBH}_4$  takes place with 8-electron transfer (Eq. (2)). It has been previously shown that the catalytic effect of silver oxides formed upon the electrode facilitates the oxidation of  $\text{NaBH}_4$  giving a 6e<sup>-</sup> transfer mechanism preventing the hydrolysis reaction. It was observed that electrochemical treatment of the surface and the

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methods of the treatment have a profound effect upon the kinetics of the oxidation.

## 2. Experimental

The experimental studies were carried with a classical three electrode system using Ag disc working, spiral wire Pt counter and SCE reference electrodes. The surface was treated by the use of different electrochemical techniques and the results were investigated in a comparative manner. The surface was treated with 6 M NaOH + 0.1 M KI with and without 3.5% H<sub>2</sub>O<sub>2</sub> using both multi-cyclic voltammetry (CV) and the bulk electrolysis (BE) techniques forming an AgI layer. The Ag disc electrodes were subjected to three CV scans between –0.8 and 0.8 V (Ag/AgCl) at a scan rate of 50 mV s<sup>-1</sup> and the bulk electrolysis was carried out potentiostatically at 0.45 V (Ag/AgCl) for 3 min.

The surfaces of the treated electrodes were then immersed into NaBH<sub>4</sub> + 6 M NaOH solutions for the characterization of their electrocatalytic activity. All the studies were carried out at room temperature.

The electrochemical studies were carried out with the use of CHI 660 B electrochemical analyzer. The crystal structure of materials was characterized by X-ray diffraction (XRD, Rigaku D/MAX-2200 H/PC, Cu K $\alpha$  radiation). Scanning Electron Microscopy (SEM) images were taken on JOEL Electron Microscopy.

## 3. Results and discussion

This study deals with the increase in the rate of NaBH<sub>4</sub> oxidation kinetics with the modification of Ag electrode surface. It is known from the previous studies that the treatment of the Ag surface with H<sub>2</sub>O<sub>2</sub> increases the catalytic effect by the formation of nano-sized layers [20]. The surface was covered with AgI layer instead of Ag<sub>2</sub>O by the addition of KI using multi-CV and BE techniques. The mode of electrochemical treatment is known to change the electrocatalytic effect of the surface.

### 3.1. Morphology of the electrode surface treated with H<sub>2</sub>O<sub>2</sub> + KI

The morphological structures of the surface of the electrodes covered with AgI by the use of H<sub>2</sub>O<sub>2</sub> + KI solution and multi-CV and BE techniques were determined by XRD analysis and SEM micrographs (Figs. 1–2). It is apparent that the physical method employed in the coverage process greatly affects the physical features of the resulting AgI layer. The formation of AgI layer was clearly apparent from both XRD spectra and SEM micrographs (Figs. 1–2). The SEM micrographs of the resulting AgI surface showed similarities with those obtained by Zhang et al. [21].

The differences of the surface morphology between the two oxidized Ag surfaces were shown by XRD patterns and SEM micrographs (Figs. 1a and b and 2a and b). According to the XRD results, silver iodide (AgI) was formed upon the both oxidized surfaces. However, comparing the intensity of the AgI peaks in Fig. 1a and b, it is seen that the peaks obtained with CV treated electrode were much more intense than the electrode oxidized with BE. This is due to the formation of a more homogenous layer upon the surface by the use of CV technique. The layer formed during the forward scan on the surface is partly removed during the reverse scan. This repeated deposition and removal process results in the formation of a much more homogenous layer. Indeed the crystals formed with BE in H<sub>2</sub>O<sub>2</sub>/KI solution were bigger than with CV.

This is an extremely important finding since this reversed peak, which resulted with Ag surface treated with H<sub>2</sub>O<sub>2</sub> + KI using CV may be the indication of a reversible mechanism. The reason that the surface treated with CV has a much intensive catalytic activity

than the surface treated with BE may be the result of gradual and more homogenous accumulation of AgI layer compared with the rapid deposition in the case of BE.

### 3.2. The effect of the solution and the mode of the surface treatment

The comparison of the Ag surfaces with H<sub>2</sub>O<sub>2</sub> + KI for the oxidation of NaBH<sub>4</sub> reveals some very important facts. Fig. 3 compares the catalytic effect of the surfaces treated by multi-CV and BE method. It is seen that the surface treated with H<sub>2</sub>O<sub>2</sub> + KI solution using multi-CV method gives much higher current densities than that of treated with the BE method.

Another difference observed H<sub>2</sub>O<sub>2</sub> + KI on Ag electrode treated with CV method was the quasi reversible behavior of the peak which appeared at –0.25 V. Also the peak observed at –0.25 V gave an almost reversible peak at –0.45 V at the reverse scan. The reversible peak at the potential of –0.45 V became extremely small with the BE method. The CV and BE conditions were adjusted to provide the same charge density on the surface.

Fig. 4 compares the catalytic behaviors of the surfaces treated with NaOH and H<sub>2</sub>O<sub>2</sub> solutions. The insert shows the surfaces treated with H<sub>2</sub>O<sub>2</sub> with and without KI. It is clearly obvious that the surface oxidized with H<sub>2</sub>O<sub>2</sub> + KI after the multi-CV scan gives a much higher current density than the surfaces treated without the use of KI. The peaks belonging to the surfaces treated with NaOH are given in Fig. 2 in a comparative manner. It is seen that the surface treated with NaOH solution gives no reversible peaks. It is obvious that the surface treated with H<sub>2</sub>O<sub>2</sub> + KI using CV method has an important effect on the oxidation of NaBH<sub>4</sub>.

### 3.3. Kinetic analysis of the results obtained with the electrode treated with H<sub>2</sub>O<sub>2</sub> + KI solution and multi-CV method

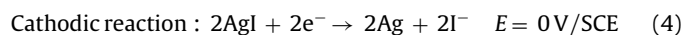
The electrochemical behavior of the electrode treated with H<sub>2</sub>O<sub>2</sub> + KI, which gave the higher electrocatalytic activity, was investigated by the use of different NaBH<sub>4</sub> concentrations (Fig. 5). In Fig. 5 the inner picture illustrates the electrochemical behavior of this electrode with the blank solution (6 M NaOH) and 0.1 M NaBH<sub>4</sub> + 6 M NaOH. The most significant change observed with Ag surface oxidized with H<sub>2</sub>O<sub>2</sub> + KI by the CV method was that it gave two peaks with significantly higher current densities with a quasi reversible peak at the reverse scan between –0.45 V and 0.0 V (Ag/AgCl) as seen in Figs. 3–5.

If we examine the voltammograms depicted in Fig. 5 there were three oxidation peaks belonging to NaBH<sub>4</sub> at 0.2 V (I<sub>a</sub>), 0.1 V (II<sub>a</sub>) and –0.25 V (III<sub>a</sub>). The first and the third peaks gave quasi reversible peaks at 0 V (I<sub>c</sub>) and –0.45 V (III<sub>c</sub>) in the reverse scan.

The peak at 0.2 V (I<sub>a</sub>) exhibited a quasi reversible behavior (Fig. 5). This peak was not dependent upon the NaBH<sub>4</sub> concentration. Its reverse peak I<sub>c</sub> was particularly apparent at the potential of 0 V. This peak corresponds to the potential where AgI/Ag<sub>2</sub>O conversion takes place as a result of the interaction of the AgI surface with concentrated NaOH bulk solution. This peak also appeared with the bulk solution alone which verified this hypothesis. At higher concentrations the peak I<sub>a</sub> got smaller probably due to adsorption effect. Zhang et al. in their galvanostatic study showed that the Ag<sub>2</sub>O formation potential was 0.2 V (SCE) and the Ag<sub>2</sub>O is converted to AgI at the reverse scan [21]. We can therefore conveniently claim the following reactions taking place in this region:



$$E = 0.2 \text{ V/SCE} \quad (3)$$



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