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Recovery of $NaBH_4$ from BH_3OH^- 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 H_2O_2 + KI in aqueous solution on the oxidation of $NaBH_4$. Among the various treatment solutions investigated, H_2O_2 + KI solution shows the best performance with the maximum catalytic activity. CV treatment in H_2O_2 + 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 BH_4^- it was also observed that there is a formation of hydrolysis product of BH_3OH^- of BH_4^- during the anodic scan between −0.25 and −0.45 V which is seen to be converted back to BH_4^- during the cathodic scan.

1. Introduction

$NaBH_4$ 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].

$$BH_4^- + 2H_2O \rightarrow BO_2^- + 8H^+ + 8e^- \quad E_0 = -1.23 \text{ V (vs. SHE)} \quad (1)$$

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 $NaBH_4$ 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 $NaBH_4$ oxidizes in an aqueous alkaline media to 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:

$$BH_4^- + 2O_2 \rightarrow BO_2^- + 2H_2O \quad \Delta E_0 = 1.64 \text{ V (vs. SHE)} \quad (2)$$

In DBFCs it is important that $NaBH_4$ be oxidized directly without hydrolysis. This is highly depended upon the development of a suitable 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 $NaBH_4$ in a most efficient manner without promoting the hydrolysis reaction. It is known that $NaBH_4$ 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 $NaBH_4$ 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 $NaBH_4$ takes place at a lower potential than the hydrogen evolution potential and the hydrolysis reaction is largely obviated. The oxidation of $NaBH_4$ 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 $NaBH_4$ [15]. Theoretically the oxidation of $NaBH_4$ 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 $NaBH_4$ giving a $6e^-$ 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_2O_2 using both multicyclic 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^{-1} 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 $NaBH_4$ + 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 Kα 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 $NaBH_4$ 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_2O_2 increases the catalytic effect by the formation of nano-sized layers [20]. The surface was covered with AgI layer instead of Ag_2O 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_2O_2 + KI

The morphological structures of the surface of the electrodes covered with AgI by the use of H_2O_2 + 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_2O_2/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_2O_2 + 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_2O_2 + KI for the oxidation of $NaBH_4$ 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_2O_2 + KI solution using multi-CV method gives much higher current densities than that of treated with the BE method.

Another difference observed H_2O_2 + 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_2O_2 solutions. The insert shows the surfaces treated with H_2O_2 with and without KI. It is clearly obvious that the surface oxidized with H_2O_2 + 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_2O_2 + KI using CV method has an important effect on the oxidation of $NaBH_4$.

3.3. Kinetic analysis of the results obtained with the electrode treated with H_2O_2 + KI solution and multi-CV method

The electrochemical behavior of the electrode treated with H_2O_2 + KI, which gave the higher electrocatalytic activity, was investigated by the use of different $NaBH_4$ 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 $NaBH_4$ + 6 M NaOH. The most significant change observed with Ag surface oxidized with H_2O_2 + 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 $NaBH_4$ at 0.2 V (**I_a**), 0.1 V (**II_a**) and −0.25 V (**IIIa**). The first and the third peaks gave quasi reversible peaks at 0 V (**I_c**) and −0.45 V (**III_c**) in the reverse scan.

The peak at 0.2 V (**I_a**) exhibited a quasi reversible behavior (Fig. 5). This peak was not dependent upon the $NaBH_4$ concentration. Its reverse peak **I_c** was particularly apparent at the potential of 0 V. This peak corresponds to the potential where AgI/Ag_2O 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_a** got smaller probably due to adsorption effect. Zhang et al. in their galvanostatic study showed that the Ag_2O formation potential was 0.2 V (SCE) and the Ag_2O is converted to AgI at the reverse scan [21]. We can therefore conveniently claim the following reactions taking place in this region:

$$\text{Anodic reaction}: 2Ag + 2OH^- \rightarrow Ag_2O + H_2O + 2e^- \quad E = 0.2\,V/SCE \tag{3}$$

$$\text{Cathodic reaction}: 2AgI + 2e^- \rightarrow 2Ag + 2I^- \quad E = 0\,V/SCE \tag{4}$$

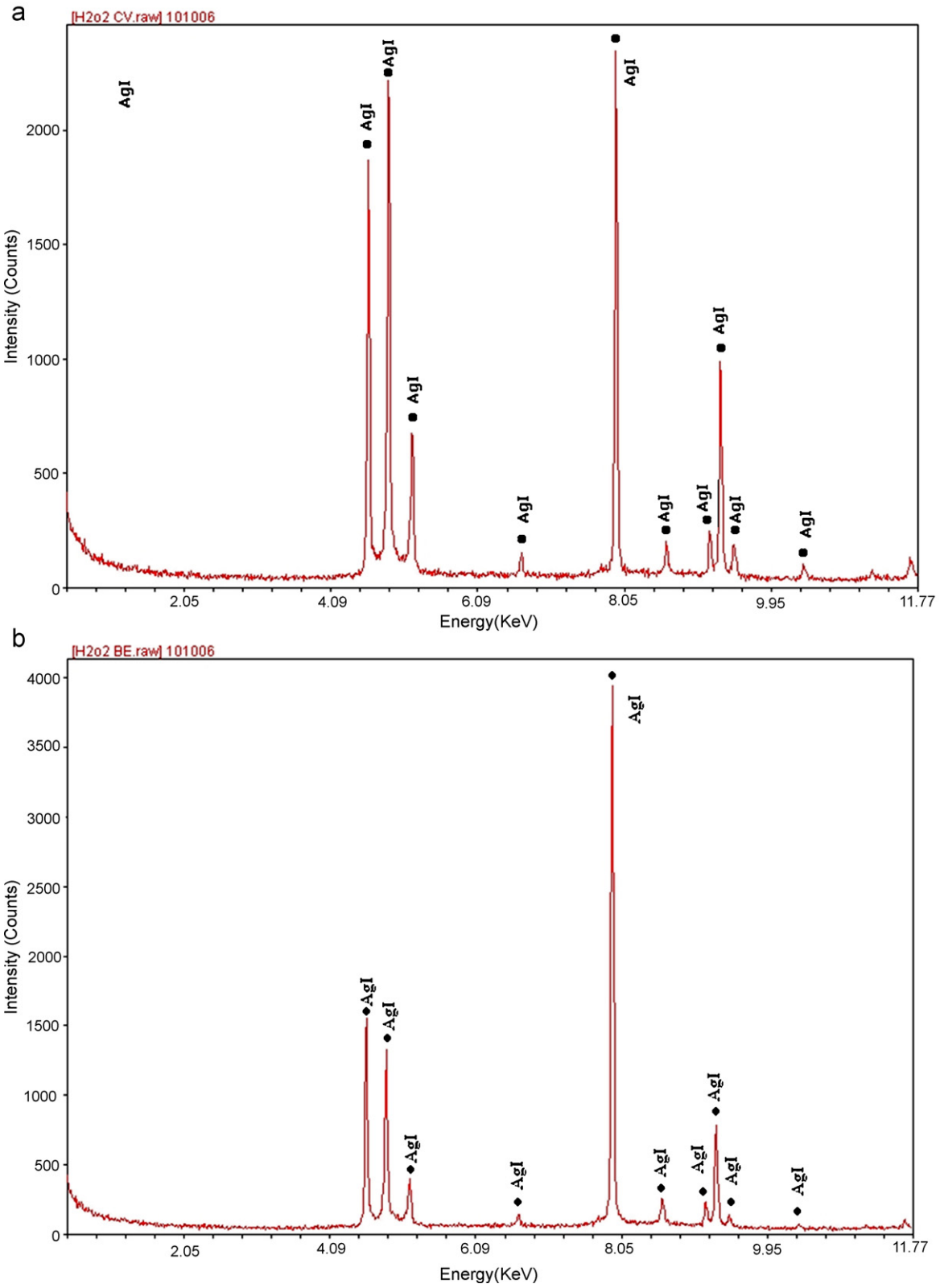

Fig. 1. The XRD patterns of the thick layer of AgI formed upon the surface with (a) CV method at between −0.8/0.8 V (50 mV s^{-1}) and (b) BE method at 0.45 V.

The peak observed in region $\mathbf{II_a}$ was irreversible. The increase of the concentration of $NaBH_4$ caused a significant increase in the oxidation peak observed in this region. The previous studies indicate that $NaBH_4$ is oxidized approximately at 0.1 V (Ag/AgCl) [5]. This peak disappeared above BH_4^- concentration of 1 M. The proposed mechanism for this region is:

$$BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^- \quad (5)$$

Region $\mathbf{III_a}$ covers between −0.1 and −0.6 V. The peaks in this region are quasi reversible. The fact that the region is very close to the

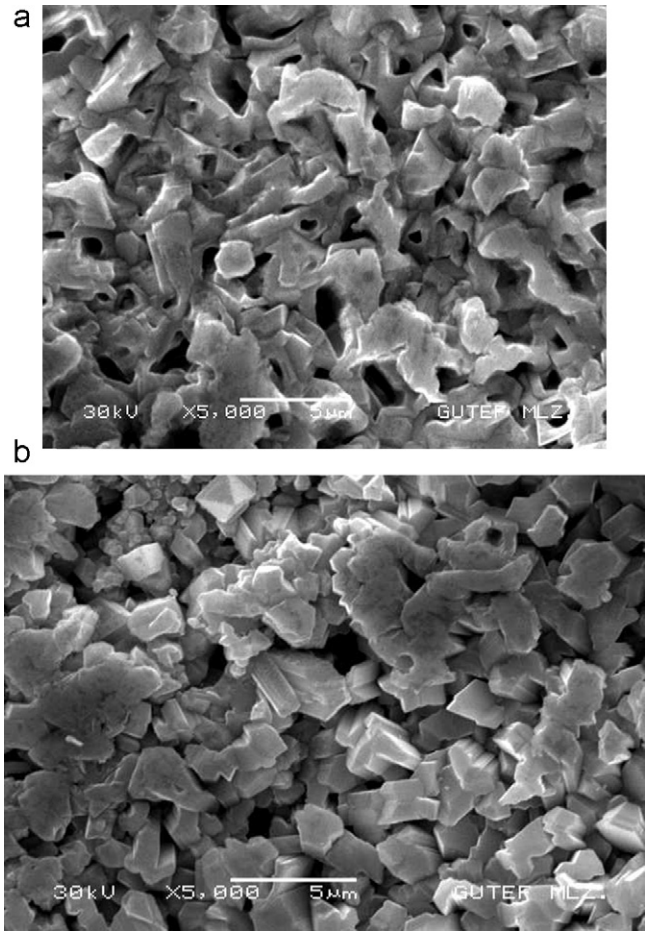

Fig. 2. The SEM micrographs of the thick layer of AgI formed upon the surface with (a) CV method at between −0.8/0.8 V (50 mV s^{-1}) and (b) BE method at 0.45 V.

hydrogen evolution potential supports the hypothesis that there is a formation of hydrolyzed by products of $NaBH_4$ in this region. Morris et al. explained the formation of BH_3OH^- on Pt surface as follows [22]:

$$BH_4^- + \text{Pt-}2e^- \rightleftarrows \text{Pt}\ldots BH_3 + H^+ \quad (6)$$

$$\text{Pt}\ldots BH_3 + OH^- \rightarrow \text{Pt}\ldots BH_3OH^- \quad (7)$$

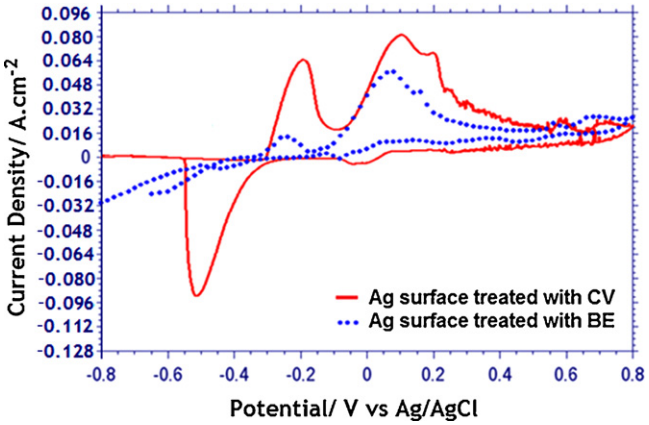

Fig. 3. The difference between Ag surfaces oxidized with 3.5% H_2O_2 + 0.1 M KI by CV method at between −0.8/0.8 V (50 mV s^{-1}) and BE method at 0.45 V.

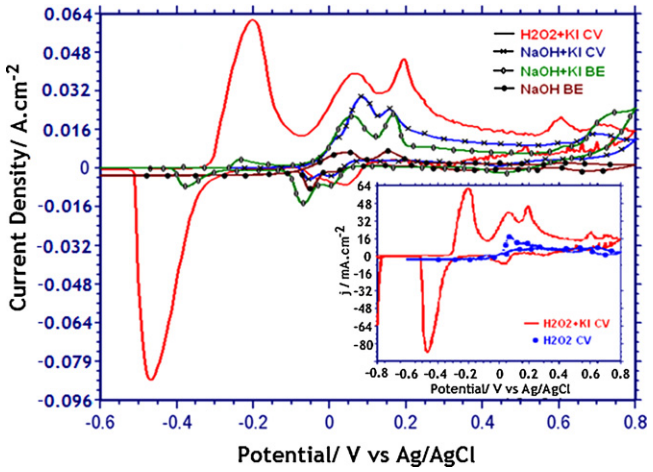

Fig. 4. Comparison of CV graphs of the Ag surfaces treated with (—) 3.5% H_2O_2 + 0.1 M KI by CV, (×) 6 M NaOH + 0.1 M KI by CV, (Θ) 6 M NaOH + 0.1 M KI by BE and (•) 6 M NaOH by BE.

This mechanism involves the hydrolysis of BH_4^-. The hydrolysis product of borohydride is BH_3OH^-. This reaction was proven to take place at −0.45 V/SCE by Morris et al. [22].

On the other hand Santos et al. found that BH_4^- is susceptible to catalytic hydrolysis on the Au surface, which generates the hydroxyborohydride (BH_3OH^-) according to the following equation:

$$BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \quad (8)$$

There is a continuous competition between the oxidation and hydrolysis of borohydride. BH_3OH^- appears as an intermediate during the oxidation of BH_4^- [23,25,26]. Chatenet et al. showed that the oxidation of BH_3OH^-, the by product of the hydrolysis of BH_4^-, took place at 0.25 V/SCE [11]. Therefore the peak **III_a** observed at −0.25 V in our voltammogram was attributed to the formation of product of BH_3OH^-.

The reactions of the borohydride seem to proceed through the direct oxidation of BH_4^- and the partial hydrolysis of BH_4^- into BH_3OH^-. This is followed by the oxidation of BH_3OH^- that is much faster than that of BH_4^-.

At higher potential, the direct and complete borohydride oxidation reaction (BOR) becomes more likely and BH_3OH^- and hydrogen are generated at low potentials. It is known that plat-

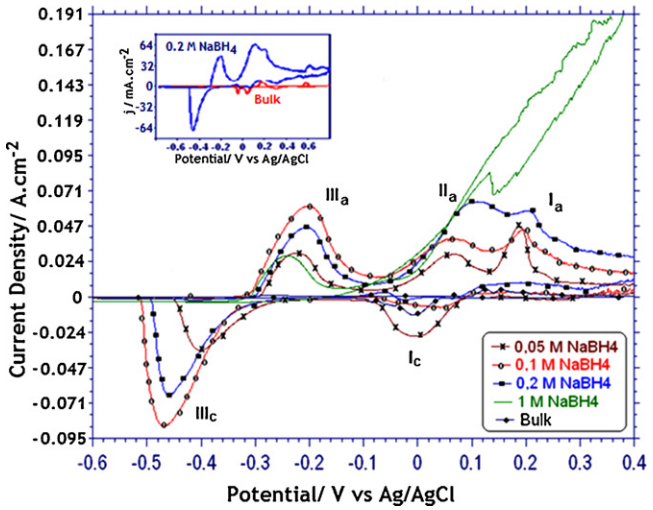

Fig. 5. The voltammograms of the Ag electrode treated with 3.5% H_2O_2 + 0.1 M KI obtained in 6 M NaOH solutions at different $NaBH_4$ concentrations.

inum, palladium and nickel generate the hydrogen and show poor Faradaic efficiency for the borohydride oxidation at lower overpotentials. Alternatively gold and silver are believed to be an effective catalysis for borohydride oxidation and non-catalytic to its hydrolysis, and uniquely capable of producing eight electrons per BH_4^- molecule [16,23,24].

On platinum borohydride ion first hydrolyses to BH_3OH^- as a stable intermediate, which undergoes partial oxidation (rate determining step) and subsequent hydrolysis. The silver and gold electrodes are presented in the literature as non-catalytic materials with respect to BH_4^- hydrolysis, but these materials nevertheless show some catalytic activity toward the BOR [9]. We know from our previous studies for silver electrode silver oxides on the surface plays an important role in the borohydride reaction [15,16]. It was also shown that the pristine silver surface does not exhibit a good activity on borohydride oxidation reaction, contrary to silver oxides (Ag_2O and AgO) [9]. On the contrary, this effect is not observed for gold (Au) electrodes. Au oxides are reduced and the electrode surface is reactivated. Therefore Au oxides are relatively inactive towards the BH_4^- oxidation reaction [23]. However, BH_3OH^- is not generated on the silver or silver oxide surface. That is why the positive currents are not observed in CV graphs of the Ag electrode at the cathodic scan.

Chatenet et al. showed that the oxidation of BH_3OH^- the by product of the hydrolysis of BH_4^- took place at a low potential [11,22,23]. Therefore, the peak **III$_a$** observed at a lower potential (−0.25 V) in our voltammogram (Fig. 5) was attributed to the formation of product of BH_3OH^- [16,23,24]. Unlike the silver electrode, BH_3OH^- is generated on the AgI surface at a lower potential. Moreover, it is reduced to borohyride rather than oxidized to the metaborate on the AgI electrode unlike to Pt and Au at the cathodic scan. It is a new result and has not been published in the literature. It is envisaged that with the use of a suitable electrode the first hydrolysis product of BH_3OH^- could be electrochemically oxidized back to borohydride. It is known that both BH_4 and its first hydrolysis product BH_3OH^- are adsorbed upon the electrode with irreversible hydrogen bonds [22]. It is possible that the highly reactive I^- is converted into IO_3^- at −0.45 V/SCE during the cathodic scan and facilitates the reduction of the hydrolysis products adsorbed upon the surface.

According to the study of Anderson et al., iodite is oxidized to iodine in acidic medium (sodium nitrate and H_2SO_4) and iodate (IO_3^-) is reduced to iodide (I^-) with $NaBH_4$ in basic medium (6 M NaOH) [27]. We can therefore conveniently propose the following mechanism for the reaction of AgI with basic $NaBH_4$ at −0.45 V/SCE (**III$_c$**) [23].

$$4IO_3^- + 3BH_4^- \rightarrow 4I^- + 3BH_3OH^- + 3H_2O \quad (9)$$

4. Conclusions

The results obtained in this study can be summarized as follows:

1. The treatment of the surface with H_2O_2 + KI and CV results in much higher current densities. This may be the result of more homogeneous and granulated surface layer compared to that obtained with BE.
2. The addition of KI into the medium results in the coverage of the silver electrode with AgI giving a much higher electrocatalytic effect with an enhanced current density and a quasi reversible behavior may be the indication of the reduction of the first hydrolysis product $BH_3(OH)^-$. This effect was attributed to the formation of thick AgI layer upon the electrode.
3. The possible anodic reactions are:

I$_a$ in the anodic region : $2Ag + 2OH^- \rightarrow Ag_2O + H2O + 2e^-$ (10)

It is highly probable that AgI is formed at the same potential according to [21]

$$Ag_2O + H_2O + 2I^- \rightarrow 2AgI + 2OH^- \quad (11)$$

II$_a$ in the anodic region : $BH_4^- + 8OH^- \rightarrow BO_2^- + 6H_2O + 8e^-$ (12)

III$_a$ in the anodic region : $BH_4^- + 2OH^- \rightarrow BH_3(OH)^- + H_2O + 2e^-$ (13)

4. The possible cathodic reactions are the recovery of BH_4^- from $BH_3(OH)^-$ and dissociation of AgI:

The quasi reversible peak **I$_c$** in the cathodic region : $2AgI + 2e^- \rightarrow 2Ag + 2I^-$ (14)

The quasi reversible peak **III$_c$** in the cathodic region :

$$I^- + 3BH_3(OH)^- \rightarrow IO_3^- + BH_4^- \quad (15)$$

Although the conversion of the metaborate to borohydride has not been very successful, the conversion of $BH_3(OH)^-$ intermediate given above is very promising for the future of the rechargeable direct borohydride fuel cells.

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