



Short communication

Rotating ring-disc electrode (RRDE) investigation of borohydride electro-oxidation

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ABSTRACT

Rotating ring-disc electrode (RRDE) voltammetry is applied for the *in situ* determination of hydroxy borohydride ($\text{BH}_3(\text{OH})^-$) formation during borohydride (BH_4^-) electro-oxidation on a gold (Au) electrode in 6.0 M NaOH solution. The $\text{BH}_3(\text{OH})^-$ is detected at the ring electrode due to its further oxidation to $\text{BH}_2(\text{OH})_2^-$ by maintaining its potential in the range of -0.800 to -0.600 V vs. normal hydrogen electrode (NHE) while oxidizing BH_4^- on the disc electrode. The study reveals that the generation of $\text{BH}_3(\text{OH})^-$ increases if the anodic polarization of the disc electrode is increased. The RRDE ring-shielding experiments show that the electro-oxidation of BH_4^- occurs over a wide potential range of -0.500 to 0.400 V on the Au electrode under hydrodynamic conditions. Chronoamperometry is also used to study the $\text{BH}_3(\text{OH})^-$ oxidation in the potential range of -0.800 to -0.600 V with 0.33 M NaBH₄ in three different buffer solutions of pH 10.2, 11.0 and 11.70, respectively. The chronoamperometric studies indicate that the formation and stability of $\text{BH}_3(\text{OH})^-$ depends on the pH value.

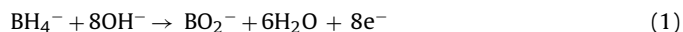
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1. Introduction

Existing battery technologies do not appear to demonstrate the required rate of improvement to match the ever increasing power demands of portable electronic devices in the near-future [1,2]. Various fuel cells are being developed as portable power sources to meet higher energy demands as well as to extend the operational hours of these devices [3–10]. Liquid fuel cells such as direct methanol fuel cells (DMFCs) are attractive due to the higher energy-density of the liquid fuel and their ease of integration with portable devices. But the widespread commercialization of DMFCs is delayed due to their low power output owing to sluggish electrode kinetics, methanol crossover, etc. [3]. Other liquid fuel cells such as direct ethanol fuel cell (DEFC) [4], direct formic acid fuel cell (DFAFC) [5], direct borohydride fuel cell (DBFC) [6–10], etc., are also being actively studied to try to meet the power demands of current and future portable electronic devices. Alkaline borohydrides, especially sodium borohydride (NaBH_4) which is used as the fuel in DBFC, have many advantages when compared with other liquid fuel cells. For example, NaBH_4 has higher volumetric (7314 Wh l^{-1}) as well as gravimetric (7100 Wh kg^{-1}) energy den-

sity than methanol (4800 Wh l^{-1} , and 6000 Wh kg^{-1} , respectively) [2]. Though energy density of the fuels, i.e., NaBH_4 solution in DBFC and methanol solution in DMFC will be less due to dilution, the difference is worth mentioning. Apart from this, alkaline BH_4^- solutions are also safer to transport and metabolize (BO_2^-), the final product of BH_4^- electro-oxidation is environmentally safe. Moreover, facile kinetics of the oxygen reduction reaction (ORR) under alkaline conditions could enable the use of non-precious electrocatalysts for the cathode. Because of these advantages, DBFC technology is being actively investigated by many research groups [6–10].

BH_4^- is reported to undergo an $8e^-$ oxidation as follows [11]:



Standard electrode potential (E°) of the above reaction is -1.24 V vs. normal hydrogen electrode (NHE). Since E° for oxygen reduction in an alkaline medium is 0.40 V vs. NHE, the DBFC should show a theoretical cell voltage of 1.64 V. However, BH_4^- is susceptible to catalytic hydrolysis on the electrode surface which generates hydroxy borohydride $\text{BH}_3(\text{OH})^-$ and H_2 as shown below [11]:

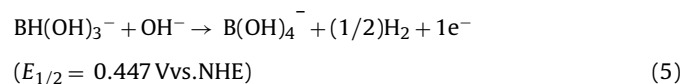
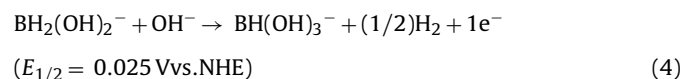
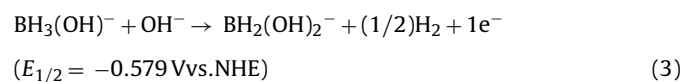


$\text{BH}_3(\text{OH})^-$ undergoes stepwise oxidations involving only $3e^-$ in total with the simultaneous generation of H_2 as described

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below [11]:



The generation of $\text{BH}_3(\text{OH})^-$ and its stepwise oxidation at the DBFC anode as written in Eqs. (3)–(5), would lower the expected fuel efficiency of an 8e^- oxidation by approximately 60%. In addition, the simultaneous evolution of H_2 poses problems in safety, system design, and the fabrication of durable membrane electrode assemblies (MEAs) [8]. Deeper understanding of $\text{BH}_3(\text{OH})^-$ formation at the anode will enable the development of selective catalysts for BH_4^- electro-oxidation where $\text{BH}_3(\text{OH})^-$ formation could be minimized or altogether eliminated. Therefore, it is critical to develop suitable techniques to study the formation of $\text{BH}_3(\text{OH})^-$ during BH_4^- electro-oxidation. Gardiner and Collatt [12,13] have carried out detailed studies of BH_4^- electro-oxidation on dropping mercury electrode (DME). They noticed two polarographic waves, a larger one at $E_{1/2} = 0.094 \text{ V vs. NHE}$, and a smaller one at $E_{1/2} = -0.396 \text{ V vs. NHE}$. The height of the smaller wave was only few percent of the larger one, and moreover, the height of the smaller wave first increased and then decreased after the solution was prepared. The wave at 0.094 V was attributed to the oxidation of BH_4^- , and the smaller wave at -0.396 V was attributed to the oxidation of $\text{BH}_3(\text{OH})^-$. They further carried out detailed investigations of $\text{BH}_3(\text{OH})^-$ in partially hydrolyzed NaBH_4 solutions containing the highest possible concentration of $\text{BH}_3(\text{OH})^-$. These studies date back to the 1960s with very little subsequent addition to the literature. One significant study in the meantime was by Bard and coworkers [14], who investigated BH_4^- electro-oxidation on a Au microelectrode and reported that BH_4^- oxidation is an overall 8e^- process involving many unstable intermediates.

There is renewed interest in BH_4^- electro-oxidation on solid electrodes mainly due to its application in DBFC, and a number of mechanistic studies have been recently reported [15–19]. Gyenge [15] studied BH_4^- oxidation on Pt and Au electrodes, and concluded that BH_4^- undergoes hydrolytic decomposition on Pt to generate H_2 which is oxidized in the potential range from -0.7 to -0.5 V , and direct oxidation of BH_4^- occurs between 0.05 and 0.150 V . He has also concluded that the catalytic hydrolysis of BH_4^- on Pt electrode could be avoided by adding strong adsorbents such as thiourea. Cheng and Scott [16] have studied BH_4^- electro-oxidation kinetics on Au rotating disc electrode and concluded that BH_4^- electro-oxidation is an 8e^- process at -0.350 V ; lower and higher electron counts were obtained at low and high potentials. Chatenet et al. [17] studied BH_4^- electro-oxidation on Au and Ag electrodes and observed it as a 7.5e^- reaction. Formation of $\text{BH}_3(\text{OH})^-$ at higher BH_4^- concentration and its oxidation at more negative potentials has also been discussed in the literature. Recently, Çelikkan et al. [18] studied BH_4^- electro-oxidation on Au, Pt, Pd and Ni electrodes and concluded that Au is the most effective, Pt and Pd show some activity, whereas Ni is not effective for BH_4^- electro-oxidation. Martins et al. [19] studied BH_4^- electro-oxidation on Pt electrode and reported that fuel efficiency in DBFC with Pt electrodes could be improved using thiourea. Although the formation and stepwise electro-oxidation of $\text{BH}_3(\text{OH})^-$ is discussed in many papers, *in situ* detection of $\text{BH}_3(\text{OH})^-$ during BH_4^- electro-oxidation is not

reported in the literature. In the present investigation, rotating ring-disc electrode (RRDE) voltammetric technique has been successfully employed for the *in situ* detection of $\text{BH}_3(\text{OH})^-$ formation during BH_4^- electro-oxidation. Results of cyclic voltammetric (CV) and chronoamperometric studies to support the RRDE investigations are also presented.

2. Experimental details

Sodium borohydride (NaBH_4) 99.0%, sodium hydroxide (NaOH) 99.50%, sodium bicarbonate (NaHCO_3) 99.50%, and disodium hydrogen phosphate (Na_2HPO_4) 99.0%, all from Fischer Scientific Inc., USA, were used as-received without further purification. Aqueous solutions were prepared with double-distilled water. Buffer solutions of pH 10.20 and 11.0 were prepared using 0.05 M NaHCO_3 and 0.10 M NaOH solutions, and a buffer solution of pH 11.7 was prepared using $0.05 \text{ M Na}_2\text{HPO}_4$ and 0.10 M NaOH solutions. The pH of the prepared buffer solutions was checked with a bench top pH meter (Accumet, AB15, USA). The CV and RRDE experiments were carried out in 6.0 M NaOH solution, and the chronoamperometric experiments were carried out in the buffer solutions as prepared above. All experiments were carried out at 25°C unless specified otherwise.

The cyclic voltammetry (CV) and chronoamperometry experiments (under stirring) were conducted in a conventional three-electrode jacketed electrochemical cell (250 ml capacity). An Au disc of 4 mm diameter (Pine Instruments, USA) was used as the working electrode in CV studies and an Au disc electrode of 1.6 mm diameter (BAS, USA) in chronoamperometric studies. The reference electrode was a classical mercury/mercuric oxide electrode (Hg/HgO) (Koslow Scientific Company, USA) in $20\% \text{ KOH}$, the standard potential of which is 0.098 V vs. NHE . All potentials are expressed against NHE and the potentials were not corrected for the electrolyte junction potential. A Pt spiral of relatively large area was used as the counter electrode. Rotating ring-disc electrode (RRDE) experiments were carried out using Au–Au ring-disc electrodes (AFMT28, disc radius $r_1 = 0.228 \text{ cm}$, ring inner radius $r_2 = 0.246 \text{ cm}$, and ring outer radius $r_3 = 0.269 \text{ cm}$) coupled with the RRDE MT28 series AFMSRX rotator, all from Pine Instruments, USA. The collection efficiency of the electrode system was 0.22. The RRDE experiments were carried out at the rotation rate of 1000 rpm.

The working electrodes were kept in a 50:50 volumetric mixture of H_2O_2 (30 wt%)– H_2SO_4 (3.0 M) for 5 min, rinsed, and then cleaned electrochemically by potential cycling [15]. The potential of the electrode was cycled at 0.1 V s^{-1} between 0 and 1.250 V vs. NHE in $0.10 \text{ M H}_2\text{SO}_4$ until reproducible CV was obtained [20]. The solutions were de-aerated by bubbling nitrogen (N_2) for at least 10 min prior to each experiment. A blanket of N_2 was maintained over the solution while conducting the experiments.

3. Results and discussion

3.1. Cyclic voltammetry

The cyclic voltammetry technique was employed to determine the possible potential window to investigate BH_4^- electro-oxidation and *in situ* detection of $\text{BH}_3(\text{OH})^-$ in 6.0 M NaOH . The CV recorded with the clean Au electrode in 6.0 M NaOH is plotted as solid lines in Fig. 1. In order to study the interference from H_2 which is likely to be present in the solution due to the hydrolysis of BH_4^- as well as the oxidation of $\text{BH}_3(\text{OH})^-$, H_2 was purged through the 6.0 M NaOH solution for 30 min and a voltammogram was again recorded (Fig. 1, dashed line). The CVs are similar to those reported in the literature for Au electrode in alkaline solution [21]. Steep

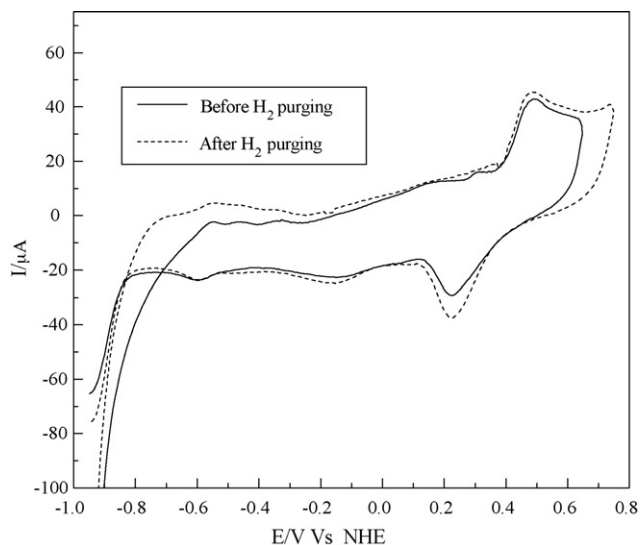


Fig. 1. Cyclic voltammograms of clean gold (Au) electrode. Solid line: 6.0 M NaOH; dashed line: after 30 min of H₂ purging.

increase of cathodic current at potentials more negative than -1.0 V is due to H₂ evolution. There is no anodic current corresponding to oxidation of H₂ in the voltammograms recorded before and after H₂ purging since it is well known that Au has no activity for H₂ oxidation [22]. Au oxide (Au₂O₃) formation occurs beyond 0.30 V during the forward sweep, and the Au oxide undergoes reduction around 0.20 V during the reverse sweep. Hence, electro-oxidation of BH₄⁻ as well as the formation of BH₃(OH)⁻ could be studied in the potential range of -0.900 to 0.200 V on Au electrode in 6.0 M NaOH solution and H₂, if present in the solution, will have no interference.

The cyclic voltammogram recorded using Au electrode with 0.020 M BH₄⁻ in 6.0 M NaOH solution at the potential scan rate of 0.100 V s⁻¹ is given in Fig. 2. The electro-oxidation of BH₄⁻ begins around -0.550 V during the forward sweep. A well-defined oxidation peak (a1) and a broad hump (a2) are observed during the forward sweep. A sharp anodic spike (c1) and a broad wave (c2) are observed during the reverse sweep. Peak a1 is attributed to

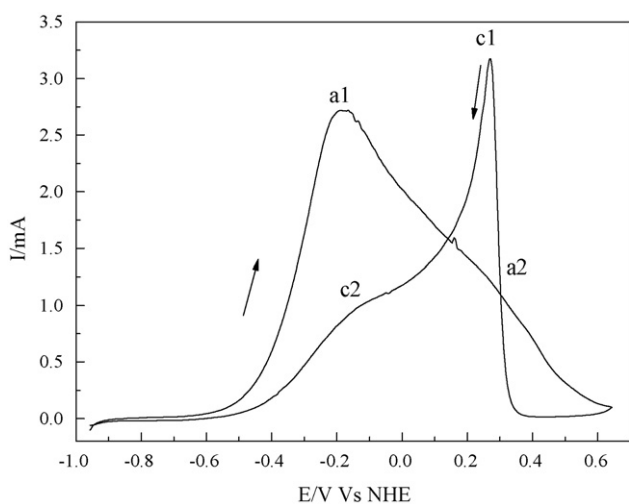


Fig. 2. Cyclic voltammogram recorded with 0.020 M NaBH₄ on Au electrode, with scan rate of 0.100 V s⁻¹. A well-defined oxidation peak (a1) and a broad hump (a2) are observed during the forward sweep. A sharp anodic spike (c1) and a broad wave (c2) are observed during the reverse sweep.

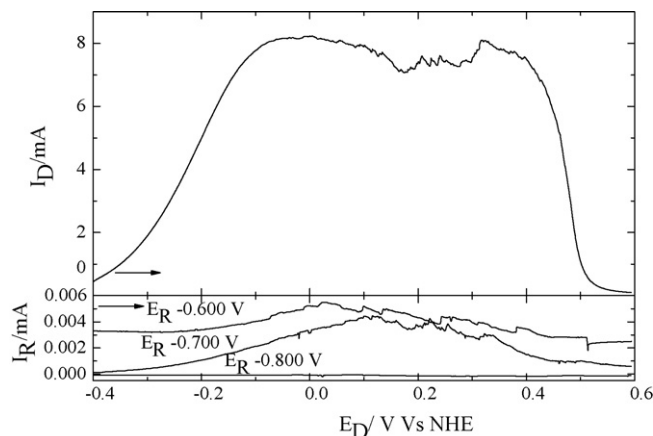


Fig. 3. Rotating ring disc electrode (RRDE) experiments on Au–Au by maintaining the ring electrode at different potential values. The NaBH₄ concentration is 0.005 M and the disc electrode scan rate is 0.005 V s⁻¹.

the direct $8e^-$ oxidation of BH₄⁻, and peaks a2, c1, and c2 are due to the oxidation of adsorbed intermediate oxidation products of BH₃(OH)⁻ [11]. Since the oxidation potential of BH₃(OH)⁻ is more negative than that of BH₄⁻ [11–13,23], BH₃(OH)⁻ could be detected *in situ* in the potential range -0.900 to -0.550 V using RRDE without interference from BH₄⁻ electro-oxidation. The results of RRDE investigations are discussed in the following section.

3.2. Rotating ring-disc electrode voltammetry

Since potentials of the disc and the ring electrodes can be controlled independently, RRDE is an ideal technique to detect and/or explore the behavior of unstable intermediates. Any such intermediate generated at the disc electrode is swept away to the ring electrode where it can be detected by maintaining the ring electrode potential at the desired value. Though it is well known that BH₄⁻ undergoes hydrolysis on metal electrodes such as Pt, Ni, Pd, Au, etc. to produce BH₃(OH)⁻, it is not known whether the rate of BH₃(OH)⁻ generation is affected by electrode polarization. The Au–Au RRDE is ideally suited for this study; while polarizing the disc electrode in the potential range of -0.500 to 0.500 V, BH₃(OH)⁻ if formed on the disc electrode will be swept away to the ring electrode due to convection where it could be detected by maintaining the ring electrode potential in the range of -0.900 to -0.550 V. At the ring electrode, the BH₃(OH)⁻ will undergo an $1e^-$ oxidation to BH₂(OH)₂⁻ as given in Eq. (3) above.

The disc voltammogram and the ring current response at various potentials are shown in Fig. 3. The disc potential was scanned from -0.400 to 0.600 V at the rate of 0.005 V s⁻¹, the ring potential was maintained at different values, and the ring current was monitored as a function of disc potential. There was almost no ring current when its potential was kept at -0.800 V. When the ring potential was maintained at -0.700 V, an oxidation current was detected at the ring electrode on initiation of BH₄⁻ oxidation at the disc. The oxidation current at the ring is obviously due to oxidation of BH₃(OH)⁻ which is generated at the disc and transported to the ring electrode by convective mass transfer. The ring current increased on continuing the disc potential scan towards more anodic values, attained a maximum value when the disc potential reached 0.100 V, and slowly decreased thereafter. The oxidation current density at the ring electrode was higher when it was maintained at -0.600 V probably due to better efficiency of BH₃(OH)⁻ oxidation at -0.600 V. These experiments are indeed the first to report on the *in situ* detection of BH₃(OH)⁻ during BH₄⁻ oxidation.

One concern directly related to DBFC is the continuous increase in $\text{BH}_3(\text{OH})^-$ formation at the disc electrode while scanning its potential from -0.400 to 0.100 V. Li et al. [7] recently reported that H_2 evolution in an operating DBFC increases when the current density of the cell is increased. H_2 is obviously generated along with $\text{BH}_3(\text{OH})^-$ due to the catalytic hydrolysis of BH_4^- on the electrode surface, and the rate of hydrolysis increases with increased polarization of the electrode. It is not clear if the increase in $\text{BH}_3(\text{OH})^-$ formation is only because of the increased catalytic hydrolysis of BH_4^- on the anodically polarized disc-electrode surface, or is also due to the chemical reaction of the primary products of BH_4^- electro-oxidation such as BH_3 with OH^- as postulated by Bard and coworkers [14]. Though the current density due to $\text{BH}_3(\text{OH})^-$ oxidation at the ring is less than the BH_4^- oxidation current at the disc, $\text{BH}_3(\text{OH})^-$ formation will obviously reduce fuel efficiency in DBFC by shifting the electrode potential to more negative values where direct oxidation of BH_4^- by an $8e^-$ process may not be possible, and oxidation of $\text{BH}_3(\text{OH})^-$ to $\text{BH}_2(\text{OH})_2^-$ at highly negative potentials is an effective $1e^-$ process [11,23]. It is quite possible that $\text{BH}_3(\text{OH})^-$ generated on the disc electrode could undergo further oxidation on the disc electrode itself; at the same time, it could be convected towards the ring where it could be detected.

Ring current shielding experiments were conducted to study the potential range of BH_4^- electro-oxidation. The result of shielding experiments is plotted in Fig. 4. The ring electrode potential was kept at -0.100 V in the first experiment (Fig. 4i) and 0.300 V in the second experiment (Fig. 4ii). The disc potential was scanned at 0.005 V s^{-1} from -0.400 to 1.300 V. When the disc electrode reaction was absent, the ring current remains at a constant value depending on the flux of BH_4^- . Once oxidation of BH_4^- begins at the disc electrode, the flux to the ring electrode is shielded due to the consumption of BH_4^- at the disc; as a result, the ring current starts to reduce. The ring current reaches a limiting value when the disc current also reaches a limiting value, i.e., around -0.100 V. Thereafter, both the disc and the ring currents stay at limiting values until the disc potential reaches 0.40 V. Beyond this potential, the disc current abruptly decreases because of Au oxide formation at the disc electrode (Fig. 1), and the ring current immediately increases to the initial value where there is no disc electrode reaction. The current-potential (I - V) curve of the disc electrode shows two small peaks overlaid on the limiting current plateau; these peaks are due to the oxidation of intermediate products of $\text{BH}_3(\text{OH})^-$ oxidation, i.e., $\text{BH}_2(\text{OH})_2^-$ and $\text{BH}(\text{OH})_3^-$ [11,23]. However, there was no noticeable change in the limiting current at the ring electrode due to these small peaks. It can be inferred from the above that BH_4^- is consumed at the electrode in the entire potential range of -0.400 to 0.400 V. However, the electrode process is not solely due to the oxidation of BH_4^- , but also due to the oxidation of the intermediate products of $\text{BH}_3(\text{OH})^-$ which also occurs along with BH_4^- [11,23].

The shielding effect of disc electrode is given by the following equation [24]:

$$I_{R,1} = I_{R,1}^0 - NI_D \quad (6)$$

where $I_{R,1}^0$ is the limiting ring current when there was no disk current, I_D is the disk current, $I_{R,1}$ is the limiting ring current, and N is the collection efficiency. The factor NI_D is called the shielding factor. The collection efficiency N was calculated for the results of Fig. 4ii; the N value of 0.19 closely matches the theoretical N value of 0.22 for the electrode system. This agreement between the theoretical and experimentally determined N value indicates that at very low concentration (0.005 M) of BH_4^- in a highly alkaline solution (6.0 M NaOH), the process is mainly mass-transport-controlled; it is not greatly affected by the adsorption of stepwise oxidation products of $\text{BH}_3(\text{OH})^-$.

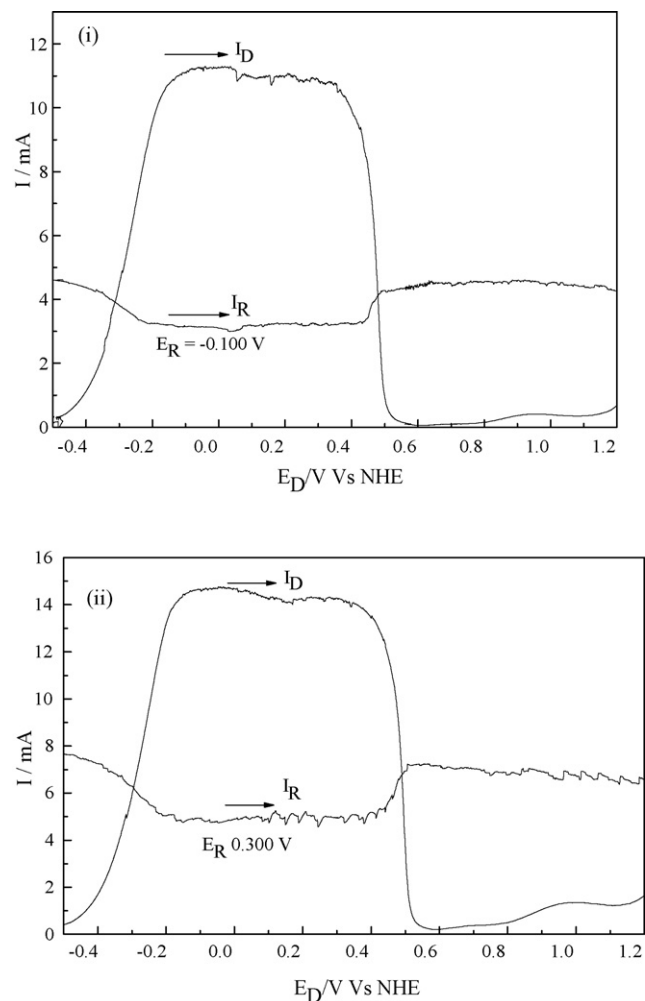


Fig. 4. Rotating ring disc electrode (RRDE) experiments on Au-Au by maintaining the ring electrode at different potential values. (i) $E_R = -0.100$ V; (ii) $E_R = 0.300$ V. The NaBH_4 concentration is 0.005 M and the disc electrode scan rate is 0.005 V s^{-1} .

3.3. Chronoamperometric studies

BH_4^- can also be subjected to controlled hydrolysis to generate $\text{BH}_3(\text{OH})^-$ by maintaining the pH of the BH_4^- solution in the range of 9 – 11 [12,13]. To determine $\text{BH}_3(\text{OH})^-$ in such hydrolyzing solutions, one must maintain the electrode potential in the range of -0.800 to -0.600 V. Since H_2 evolution in the hydrolyzing solutions disturbed the current measurement, the solutions were stirred using a magnetic stirrer, but some oscillations in current measurement could not be avoided even with stirring.

Results from chronoamperometric experiments carried out in a bicarbonate buffer solution of pH 10.2 are presented in Fig. 5. At first, the electrode potential was maintained at -0.600 V and an i vs. t curve was recorded; a constant cathodic current of about $12 \mu\text{A}$ was obtained under stirring, the current was due to H_2 evolution. In the next experiment, an i vs. time curve was recorded in the blank for about a minute; then, a precisely weighed quantity of NaBH_4 was added to obtain 0.33 M solution of NaBH_4 in the buffer. The current started to increase in the anodic direction immediately upon adding NaBH_4 and reached a value of about $100 \mu\text{A}$ and remained more or less constant. The Au has no activity for H_2 [22], and moreover, oxidation of BH_4^- commences beyond -0.550 V, therefore, the oxidation current at -0.600 V is obviously due to oxidation of $\text{BH}_3(\text{OH})^-$ generated by hydrolysis. To further ascertain

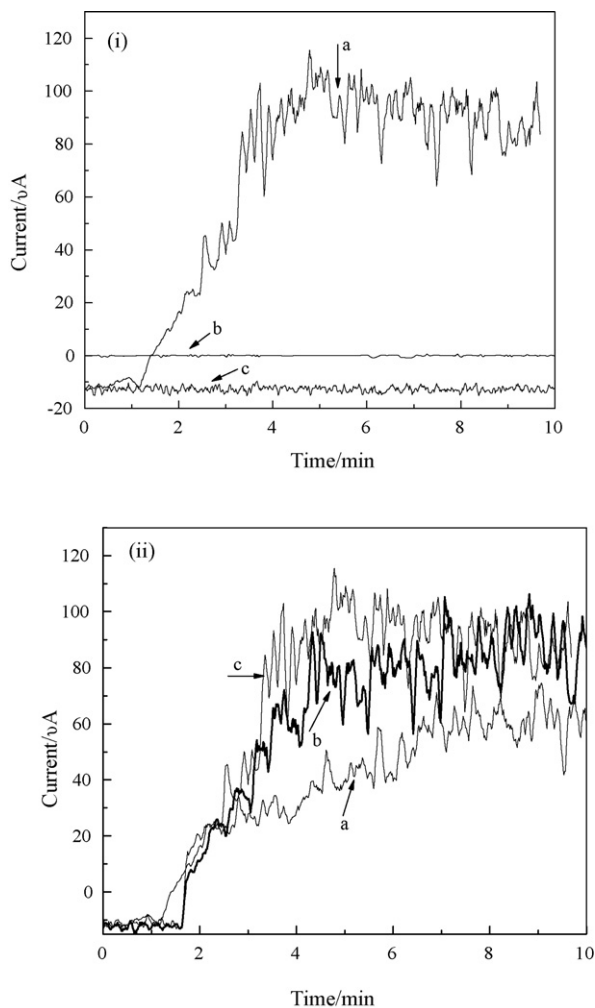


Fig. 5. Chronoamperometric ($i-t$) curves (i) at -0.600 V in different solutions: (a) pH 10.2 buffer; (b) 0.33 M NaBH_4 in 6.0 M NaOH; (c) 0.33 M NaBH_4 in pH 10.2 buffer; (ii) at different potentials in 0.33 M NaBH_4 in pH 10.2 buffer solution: (a) -0.800 V; (b) -0.700 V; (c) -0.600 V.

this fact, 0.33 M NaBH_4 in 6.0 M NaOH was prepared and an i vs. time curve was recorded at -0.600 V; the current was almost zero since $\text{BH}_3(\text{OH})^-$ generation is negligible in 6.0 M NaOH solution. Further experiments were conducted by maintaining the electrode potential at different values and the results are given in Fig. 5ii. It could be noted that the current due to $\text{BH}_3(\text{OH})^-$ oxidation increased on moving the potential towards more positive values from -0.800 V and maximum oxidation current is obtained at -0.600 V. These results confirm the conclusions drawn during the RRDE studies (Fig. 3).

Since the rate of $\text{BH}_3(\text{OH})^-$ generation as well as its stability highly depends on the pH, the current due to $\text{BH}_3(\text{OH})^-$ oxidation in the chronoamperometric experiments could be a function of pH as well [25]. In order to investigate this, further experiments were carried out in buffers of pH values of 11 and 11.7. The blank $i-t$ curve in these buffers was also similar to those presented in Fig. 5 and hence is not presented here. The $i-t$ curves for the 0.33 M NaBH_4 solution at -0.600 V in pH 11 and 11.7 buffer solutions are given in Fig. 6. It is interesting to note that the $\text{BH}_3(\text{OH})^-$ oxidation current at -0.600 V has increased about eightfold on increasing the pH from 10.2 to 11.0 (Figs. 5 and 6). In fact, the rate of $\text{BH}_3(\text{OH})^-$ generation would obviously decrease with increasing the pH; this dramatic increase in $\text{BH}_3(\text{OH})^-$ oxidation current is due to the increased sta-

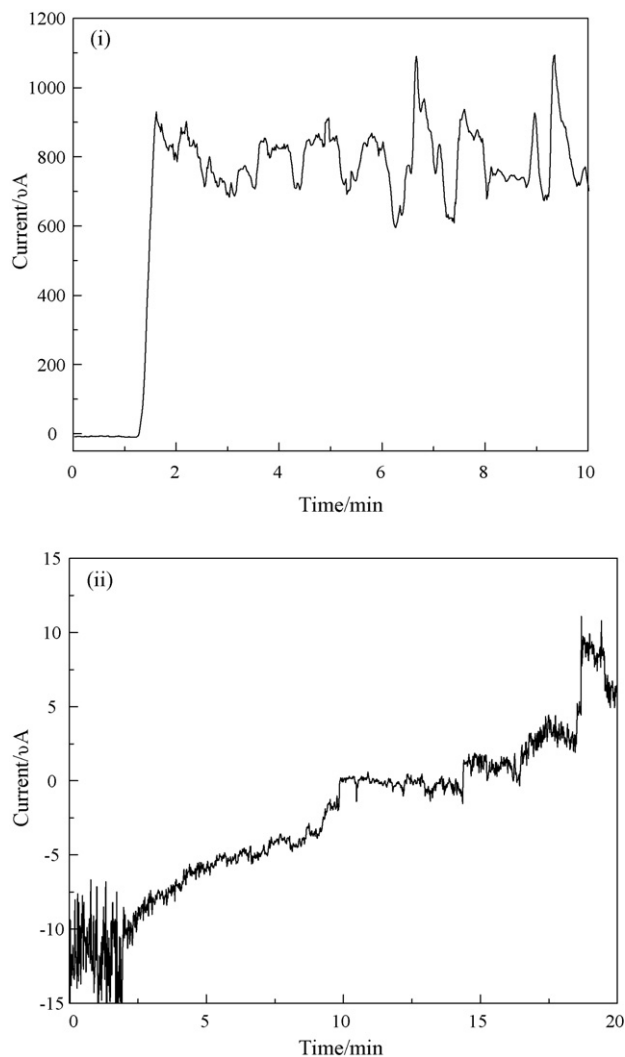


Fig. 6. Chronoamperometric ($i-t$) curves of 0.33 M NaBH_4 at -0.600 V in buffer solutions of different pH values: (i) pH 11.00; (ii) pH 11.70.

bility of $\text{BH}_3(\text{OH})^-$ at pH 11. On increasing the pH to 11.70, the rate of $\text{BH}_3(\text{OH})^-$ generation has significantly dropped resulting in very low anodic current. However, the $i-t$ profile is significantly different from the others; the $\text{BH}_3(\text{OH})^-$ oxidation current continuously increases with time due to enhanced stability of $\text{BH}_3(\text{OH})^-$ in the pH 11.70 solution. Thus, the chronoamperometric experiments nicely complement the results of RRDE studies with respect to the detection of $\text{BH}_3(\text{OH})^-$ in the potential range from -0.800 to -0.600 V.

4. Conclusions

The *in situ* formation of $\text{BH}_3(\text{OH})^-$ during the electrochemical oxidation of BH_4^- was determined for the first time, by the application of the RRDE technique. The extent of $\text{BH}_3(\text{OH})^-$ formation increased with increased polarization of the electrode which is a concern with respect to fuel efficiency in DBFC. This method could be employed as a useful tool to study the extent of $\text{BH}_3(\text{OH})^-$ formation while developing suitable anode electro-catalysts as well as to identify the optimum operational parameters for DBFC. The ring shielding experiments showed that BH_4^- electro-oxidation occurs over a wide potential range from -0.400 to 0.400 V. The chronoamperometric studies have further confirmed that the generation as

well as the stability of $\text{BH}_3(\text{OH})^-$ depend strongly on the pH of the medium.

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