Cyclic voltammetry investigation of borohydride oxidation at a gold electrode

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ABSTRACT

Sodium borohydride ($NaBH_4$) is receiving increasing attention during the last decade regarding its possible application in energy systems. $NaBH_4$ has the dual potential of generating hydrogen on demand or being directly oxidised in a direct borohydride fuel cell (DBFC). Progress on DBFCs relies on the development of systematic studies to allow a more comprehensive characterisation of the borohydride (BH_4^-) oxidation process. In this paper, cyclic voltammetry (CV) is applied to study systematically the BH_4^- electrooxidation on a gold (Au) disc macroelectrode in $2\,mol\,l^{-1}$ NaOH solutions. Voltammograms are obtained for various $NaBH_4$ concentrations [$0.03–0.12\,mol\,l^{-1}$], working temperatures [$25–65\,°C$], and potential scan rates [$0.02–20\,V\,s^{-1}$], over a wide potential range [$−1.0–0.8\,V$ vs. SCE]. Modelling of CV data indicates that BH_4^- oxidation on Au electrode follows a first irreversible electrochemical pathway via the direct BH_4^- oxidation reaction, involving nearly 8 mol of exchanged electrons per mole of BH_4^-. A second pathway, at higher potentials, concerns a yet undetermined oxidation mechanism in the partially oxidised Au surface which, in a third pathway, is reactivated, allowing an electrochemical-adsorption mechanism to take place. Relevant parameters such as transfer coefficient, kinetic rate constant, standard rate constant, charge transfer activation energy, and number of exchanged electrons are estimated. The BH_4^- oxidation reaction on Au is found to be first order with respect to BH_4^-.

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1. Introduction

Recent studies in alkaline medium [1,2] and developments of hydroxyl ion conducting membranes [3–7] have increased the interest for alkaline fuel cells (AFCs) [8–10]. However, the decision on the right fuel to be used in these systems is still a key parameter. Pure hydrogen or hydrogen-rich gases allow high electric efficiency, but their production, storage and distribution are still constraints for a large scale development [11,12]. The electrooxidation of formic acid [13], methanol [14], ethanol [15] and other alcohols and polyols in AFCs led to achieve a few tens of $mW\,cm^{-2}$ as best cell performance [8–10]. This relatively low cell performance may be partially attributed to the fact that the oxidation reaction of alcohols and other liquid organic fuels is difficult to activate, even in alkaline medium. Sodium borohydride ($NaBH_4$) has then arisen as an attractive option because of its reactivity [16–18]. It has higher volumetric ($7314\,W\,h\,dm^{-3}$) as well as gravimetric ($7100\,W\,h\,kg^{-1}$) energy density than methanol ($4800\,W\,h\,dm^{-3}$ and $6000\,W\,h\,kg^{-1}$, respectively) [19], and it is stable in alkaline medium at pH > 12 [20]. Alkaline $NaBH_4$ solutions are also safer to transport and tetrahydroxyborate, $B(OH)_4^-$, the final product of BH_4^- electrooxidation, 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 composition. Because of these advantages, direct borohydride fuel cell (DBFC) technology is being actively investigated by many research groups [21–26], with electrical performances as high as $290\,mW\,cm^{-2}$ being reported [27]. Although the DBFC was first proposed in the early 1960s [28], further progresses suffered a hiatus of about 40 years due to lack of research on the understanding of the complex electrode kinetics of the BH_4^- oxidation reaction.

In highly alkaline conditions (pH = 14), BH_4^- may undergo an $8e^-$ oxidation described by Eq. (1).

$$BH_4^- + 8OH^- \rightarrow B(OH)_4^- + 4H_2O + 8e^- \quad (E^0 = -1.24\,V\,vs.SHE)$$

$$(1)$$
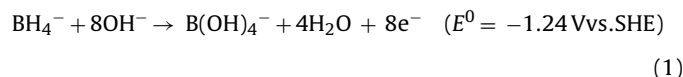
However, for pH < 12 or in the presence of certain electrocatalysts, BH_4^- is susceptible to catalytic hydrolysis on the electrode surface [20], which generates hydroxyborohydride (BH_3OH^-) and H_2 according to Eq. (2).
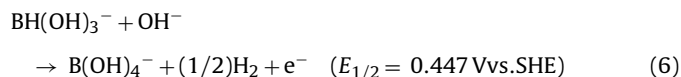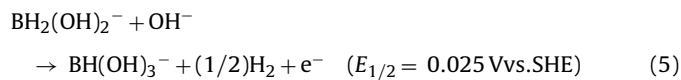
$$BH_4^- + H_2O \rightarrow BH_3OH^- + H_2 \quad (2)$$
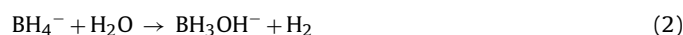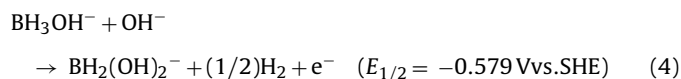
In fact, the competition between the BH_4^- oxidation and its hydrolysis reaction is always present. This means that both reactions can either be complete, or compete together, as reported by Dong et al. [29]. Therefore, the BH_3OH^- formed in Eq. (2) may be

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fully oxidised according to Eq. (3), yielding 6 electrons without any hydrogen release.

$$BH_3OH^- + 6OH^- \rightarrow B(OH)_4^- + 3H_2O + 6e^- \qquad (3)$$
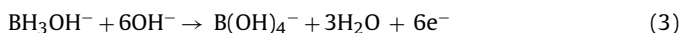
Alternatively, BH_3OH^- may undergo stepwise oxidations [30] involving only $3e^-$ in total with the simultaneous generation of H_2, as shown in Eqs. (4)–(6).

$$BH_3OH^- + OH^-$$
$$\rightarrow BH_2(OH)_2^- + (1/2)H_2 + e^- \quad (E_{1/2} = -0.579\,V\,vs.SHE) \qquad (4)$$

$$BH_2(OH)_2^- + OH^-$$
$$\rightarrow BH(OH)_3^- + (1/2)H_2 + e^- \quad (E_{1/2} = 0.025\,V\,vs.SHE) \qquad (5)$$

$$BH(OH)_3^- + OH^-$$
$$\rightarrow B(OH)_4^- + (1/2)H_2 + e^- \quad (E_{1/2} = 0.447\,V\,vs.SHE) \qquad (6)$$

The anodic wave for the oxidation of BH_3OH^- as written in Eqs. (4)–(6), that added give Eq. (7), appears at a potential about 0.5 V more negative than that of BH_4^-.

$$BH_3OH^- + 3OH^- \rightarrow B(OH)_4^- + (3/2)H_2 + 3e^- \qquad (7)$$
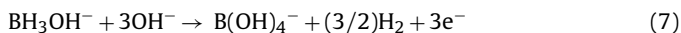
Part of the generated H_2 remains on the electrode surface and may be then oxidised through the reaction shown in Eq. (8).

$$(1/2)H_2 + OH^- \rightarrow H_2O + e^- \qquad (8)$$

The indirect oxidation reaction of BH_4^- via the oxidation of the BH_3OH^- intermediate involving H_2 evolution and its subsequent oxidation can then be described by Eq. (9), which corresponds to the addition of Eqs. (2), (7) and (8).

$$BH_4^- + 4OH^- \rightarrow B(OH)_4^- + 2H_2 + 4e^- \qquad (9)$$
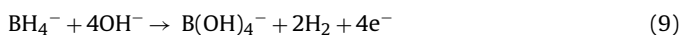
This process (Eq. (9)) is typically observed in metals like platinum, palladium, or nickel. These metals are known to be able to oxidise BH_4^- at low potentials [31], but have the drawback of being simultaneously catalysts for the BH_4^- hydrolysis.

The direct reaction pathway (Eq. (1)) has to be favoured in order to increase the efficiency of the DBFC. Gold (Au) is also known to be active for the BH_4^- oxidation, with the advantage of having virtually no catalytic effect on the hydrolysis reaction [20]. BH_4^- electrooxidation studies on Au particles have lead to 7.5 mol of exchanged electrons per mole of BH_4^- [32], against 2–4 with platinum [31]. However, recent findings [33–35] contradict this effect, claiming that Au also favours, at least to some extent, the catalytic decomposition of BH_4^-. Moreover, the onset of the BH_4^- oxidation wave in Au is shifted 0.3 V towards higher potentials when compared to platinum [36].

It is clear that much work still has to be done. In fact, higher fuel efficiency, adequate safety, system design, and durable membrane electrode assemblies (MEAs), require a deeper understanding of the BH_4^- oxidation at the DBFC anode [23]. Presently, the number of published works dealing with the DBFC anodic process is increasing exponentially [35–43] but systematic data collection on the BH_4^- oxidation reaction is still critical for the urgent quick development of this type of fuel cell. Recently our group has carried out detailed chronoamperometric, chronocoulometric, and chronopotentiometric systematic studies of BH_4^- electrooxidation on an Au macroelectrode [44,45]. Present paper concerns further investigations of BH_4^- oxidation on Au electrode employing the cyclic voltammetry (CV) technique.

2. Experimental

CV experiments were performed using a conventional three-electrode arrangement composed of a Metrohm 61204140 gold disc working electrode ($\phi = 0.2$ cm, $A = 3.14 \times 10^{-2}$ cm^2), a Johnson Matthey gold sheet counter electrode ($A = 2$ cm^2), and a Metrohm 60701100 saturated calomel reference electrode (SCE). The Au electrodes were cleaned by ultrasonication (Bandelin Sonorex Super RK 106) in acetone followed by 2 mol l^{-1} HNO$_3$ and finally, rinsing with deionised water. The supporting electrolyte was 2 mol l^{-1} NaOH (Fluka, 97 wt.%). The employed NaBH$_4$ (Fluka, 96 wt.%) concentrations varied between 0.03 and 0.12 mol l^{-1}. To prevent possible loss of BH$_4^-$, by hydrolysis during storage, the test solutions were prepared prior to measurements. The electrochemical cell, whose effective cell volume was 20 cm^3, had a thermostatic water jacket for controlling the solution temperature in the range 25–65 °C (± 0.1 °C) set by a recirculating water bath (Ultraterm 6000383 P-Selecta). A PAR 273A computer-controlled potentiostat (Princeton Applied Research Inc.) and the associated PowerSUITE package were employed for total control of the experiments, data acquisition, and treatment. Peak-shaped cyclic voltammograms were obtained by sweeping the working electrode potential from its open circuit potential ($E_i \cong -1.0$ V) to a potential of 0.8 V, at scan rates ranging from 0.02 to 20 V s^{-1}. All electrode potentials are reported with respect to SCE.

3. Results and discussion

A typical shape of the cyclic voltammograms obtained for the BH_4^- electrooxidation on the Au electrode in natural diffusion conditions exhibits the complexity of the system (Fig. 1a), being similar to the current–potential responses described in the open literature [34,46,47]. The voltammogram is basically composed of a well-defined anodic peak (a_1) around -0.2 V, followed by a broad oxidation hump (a_2) around 0.3 V, which is visible in the region of the Au oxides [32]. The Au electrode deactivates positive to peak a_2 above 0.35 V, which reveals that Au oxides are relatively inactive towards the BH_4^- oxidation reaction. On the reverse scan, a well defined, sharp, anodic peak (c_1), is observed around 0.1 V, a potential value where it is expected that the Au oxides are reduced and the electrode surface is reactivated. This peak tails off at about -0.1 V, as the potential is scanned into the range where the conversion, $BH_4^- \rightarrow B(OH)_4^-$, is no longer favourable.

Gyenge [46] associates peak a_1 to the direct electrooxidation of BH_4^- in an eight-electron process and proposes that waves a_2 and c_1 belong to adsorbed BH_3OH^- that could appear as an intermediate during the oxidation of BH_4^- on Au. Specifically, wave a_2 can be due to BH_3OH^- electrooxidation according to Eq. (7) and peak c_1 can also be due to the same process, but on the partially oxidised Au surface [46].

Analysis of Fig. 1a, b and f clearly reveals that peak a_1 is due to the oxidation of a species in solution, in agreement with the results from Gyenge [46].

A marked shift of the peak potential, E_p, with the potential scan rate, ν, is observed for peak a_1 (Fig. 1d), as expected for slow electron transfer irreversible processes. Therefore, assuming that peak a_1 corresponds to a single-step irreversible oxidation, i.e. a pure electrochemical (E) step, Eq. (10) applies [48]

$$E_p = E^0 + \left\{ \frac{RT}{(1-\alpha)n_aF} \right\}$$
$$\times \left\{ 0.78 + \ln\left(\frac{D_{BH_4^-}^{1/2}}{k_s} \right) + \ln\left[\frac{(1-\alpha)n_aF\nu}{RT} \right]^{1/2} \right\} \qquad (10)$$

where E_p is the peak potential (V vs. SCE), E^0 is the formal potential (V vs. SCE), R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature (K), α is the charge transfer coefficient for the oxidation step, n_a is the number of electrons involved in the rate determining step (being 1 the most likely value), F is the Fara-