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Kinetic and mechanistic evaluation of tetrahydroborate ion electro-oxidation at polycrystalline gold

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ABSTRACT

The anodic oxidation of tetrahydroborate ion is studied in NaOH at stationary and rotating polycrystalline Au disk electrodes. Linear sweep and cyclic voltammetry are applied varying the scan and rotation rate from 0.005 to 51.200 V s^{-1} and from 52.3 to 314.1 rad s^{-1}, correspondingly. The effects of variation of BH_4^- and NaOH concentrations as well as of the potential limits of the ranges studied have been initially followed. Most of the experiments have been carried out with 10.9 mM $NaBH_4$ in 1.04 M NaOH at 293 K in the potential range from −1.300 to 0.900 V (vs. Ag/AgCl). It is found that 6 electrons are exchanged in the overall oxidation transformation. The kinetic analysis of the processes determining the two anodic peaks recorded under static conditions at scan rates lower than 0.500 V s^{-1} shows that 1.4 electrons are exchanged in the potential range of the first one (at ca −0.5 V), while the rate of the second one (at ca +0.3 V) is determined by a quasi-reversible 1-electron transfer reaction. A kinetic evidence for the participation of surface bound intermediates in the electro-oxidation process is provided. Two additional well outlined anodic peaks are recorded in the aforementioned potential range under specific experimental conditions. A quasi-8 electron mechanism involving four oxidation and hydrolysis steps is advanced to explain the experimental results. It accounts for the involvement of borohydride oxidation species and the Au^+/Au^{3+} mediator couple.

1. Introduction

Sodium borohydride is attracting considerable attention [1–5] as a potential hydrogen source for fuel cells due to its capacity of 5.7 Ah g^{-1} and energy density of 9.3 Wh g^{-1} at 1.64 V. These values are much higher than those for other metal hydrides and most of the hydrogen storage alloys. $NaBH_4$ is easy to transport, while its alkaline aqueous solution is safe, non-toxic, and chemically stable. The products of $NaBH_4$ electro-oxidation are environmentally safe and can be recycled. The direct 8-electron oxidation [6,7] leads to the formation of $NaBO_2$ and H_2O in correspondence with:

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^- \quad (1)$$

Competitive hydrolysis [8,9] occurs to some extent in all $NaBH_4$ solutions:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2 \quad (2)$$

The catalytic hydrolysis of borohydride leads the incomplete oxidation process with lower total number of electrons exchanged. The relation of hydrogen evolution rate with the anode current observed is found to depend not only on the concentration of borohydride ion and the $[BH_4^-]/[OH^-]$ ratio but also on the applied potential and the electrode material as the multi-step process may take different reaction paths [10–12].

Gold anodes are considered selective for $NaBH_4$ direct oxidation [6,13,14]. The latter is usually carried out in strongly alkaline media [8] to eliminate the homogeneous hydrolysis proceeding. A cyclic voltammetry study [15] at an Au disc electrode reveals a single oxidation peak of well-defined shape. However when fast scan cyclic voltammetry is applied at an Au microdisc [6], a noticeable change of the voltammogram shape is observed—a new anodic peak appears at more negative potentials than the main wave. The investigation carried out suggests quasi-reversibility of the first electron transfer. The total number of electrons exchanged is found to be 1.8, which is in good agreement with $n = 2$, a value that has been proposed [9] for the first stage of borohydride oxidation. The digital simulation applied has provided better understanding of the reaction mechanism and especially of the stability and adsorption of the intermediates proposed. It is shown that this stage is in fact ECE sequence including two quasi-reversible steps and a coupled homogeneous chemical reaction. Monoborane is the 2-electron reaction

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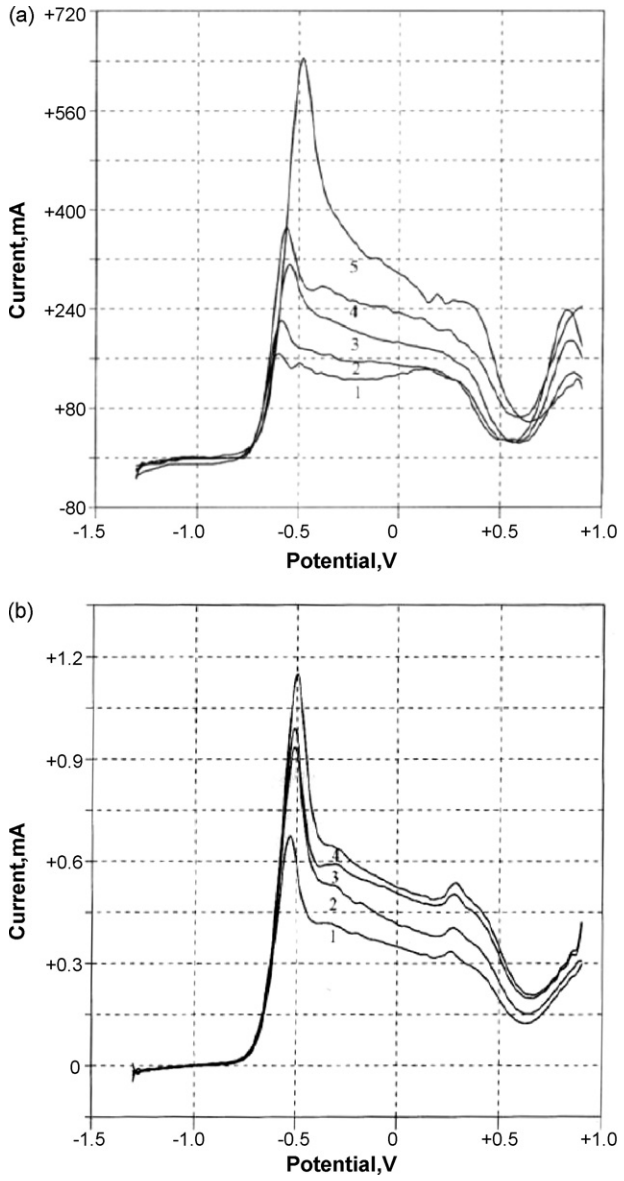

Fig. 1. Subsequent LSV anodic profiles recorded at a stationary Au electrode in 10.0 mM $NaBH_4$ + 0.995 M NaOH at 293 K with a sweep rate of (a) 0.005 V s^{-1} (1), 0.010 V s^{-1} (2), 0.020 V s^{-1} (3), 0.050 V s^{-1} (4) and 0.100 V s^{-1} (5); (b) 0.200 V s^{-1} (1), 0.300 V s^{-1} (2), 0.400 V s^{-1} (3) and 0.500 V s^{-1} (4).

product which reacts with water or OH^- and dimerizes to diborane to give products which are oxidized further to produce the total 8-electron wave.

A picture very close to that described above is presented in Ref. [[7], Fig. 1]. The voltammogram recorded at a stationary Au RDE shows an anodic peak and a prewave. It is found that in case of 0.27 mol dm^{-3} $NaBH_4$ + 2.5 mol dm^{-3} NaOH solution the current is totally determined by electron transfer kinetics at low potentials and the mass transport has no effect on the current, i.e. the disc current is independent on the rotation rate. A further increase in the rotation rate causes a current increase, although the curves do not level off as expected. It is assumed that borohydride oxidation is affected by other factors, such as side reactions involving oxygen evolution, and/or adsorbed intermediates (BH_3 or B_2H_6) interactions, which cause deviation from the Levich's equation.

Gyenge [14] observes two anodic peaks (*a2* and *a3*) in the cyclic voltammogram of tetrahydroborate (THB) ion at Au electrode. He attributes *a2* to the direct, potentially 8-electron oxidation of THB ion, while peak *a3*—to the oxidation of reaction intermediates on the partially oxidized Au surface.

It is evident that the factors just discussed affect the shape of the observed electrochemical response, i.e. a single peak, a peak and a prewave, or two peaks of THB ion oxidation are distinguished. Because of the uncertainty regarding the nature of partial oxidation products some recent studies [16–18] focus on the application of RRDE, *in situ* infrared reflectance spectroscopy and DFT methods aiming to contribute to the understanding of the oxidation mechanism. Thus the presence of $BH_3(OH)^-$ as an intermediate product is experimentally verified [16], $BH_{3,ads}$ and $BH_3OH_{ads}{}^-$ are proposed to explain FTIR data [17] concerning the band in the B–H bond region, surface bound $B(OH)_2{}^*$and $BOOH^*$ intermediate species are reported [18] as stable intermediates in the oxidation reaction at Au(1 1 1). However, there is no evidence of the consecutive reactions pathway of THB ion oxidation and the resulting products accounting for the total number of electrons exchanged and the fact that the complete oxidation occurs on the Au surface. Moreover the effect of redox mediators whose presence is crucial for the anodic processes taking place at Au has not so far been considered. Therefore a revision of THB ion oxidation mechanism at Au seems justified. This is the aim of the present paper.

2. Experimental

Linear sweep (LSV) and cyclic voltammetry (CV) were applied at a stationary and a hydrodynamic polycrystalline Au electrode of a geometric area 0.0707 cm^2 (the real electrode surface was checked prior to each series to give a roughness factor of ca 1.7; the pretreatment included polishing on a moist polishing cloth with 0.3 μm alumina (Buehler), sonication in distilled water for 15 min and cathodic polarization for 5 min at −1.300 V). The ranges of the scan and rotation rate were from 0.005 to 51.200 V s^{-1} and from 52.3 to 314.1 rad s^{-1}, correspondingly. The curves used for illustration in this paper were recorded in the potential range from −1.300 to 0.900 V vs. Ag/AgCl (KCl_{std}, i.e. from −1.1 to 1.1 V vs. NHE) although the effect of the corresponding potential limits was thoroughly followed. The voltammetry studies were undertaken with a BAS100B electrochemical workstation combined with a Metrohm 628-10 rotating disk electrode (RDE) assembly. All experiments were performed in a 25 mL two-compartment cell equipped with a Pt gauze counter electrode and an Ag/AgCl (KCl_{std})reference electrode. Solutions of $NaBH_4$ in NaOH of varying concentrations were studied. The results reported here refer mainly to 10.9 mM $NaBH_4$ in 1.04 M NaOH. All chemicals were commercially available and used as supplied (from Analar and Ajax Chemicals, respectively). The solution in the working electrode compartment was degassed by nitrogen prior to each series of experiments. The study was carried out at 293 K.

3. Results and discussion

Prior to the discussion of the experimental data obtained it is important to visualize the respond of the stationary working electrode which undergoes anodic oxidation in presence of $NaBH_4$. Fig. 1 presents subsequent linear sweep voltammograms recorded with a scan rate varying from 0.005 to 0.500 V s^{-1} (the composition of the solution is identical to that used in Refs. [6,10]). The profiles recorded at lower scan rates (0.005–0.100 V s^{-1}, Fig. 1a) show a peak (*peak 1*) at ca −0.5 V and a wave in the range between 0 and 0.4 V. The further scan rate increase (illustrated in Fig. 1b) leads to the transformation of the wave into a peak (*peak 2*), while a new wave starts to outline (curves 3 and 4 in Fig. 1b) immediately after *peak 1*.

Regarding the process responsible for *peak 1*, conclusions could be drawn evaluating the number of electrons involved, *n*. This can be done by fitting the data presented in Fig. 1b to Eq. (3), i.e. by