ABSTRACT

The initial steps of sodium borohydride oxidation are studied at PtAu alloy electrodes of Au bulk composition of 20, 40, 60 and 80 at. %. Linear sweep voltammetry is applied at low scan rates in 0.01 M NaBH$_4$ in 1.00 M NaOH. The experiments are performed at four temperature values in the range from 293.2 K to 323.2 K. The data obtained are compared to those referring to Pt and Au as well. The values of the exchange current density and the total number of electrons exchanged are determined following the effect of the temperature applied. The activation energy for the exchange current density is found dependent on the bulk composition of the alloys studied. The lowest value is expected for an alloy of Au bulk content of ca 50 at. %. The dependence on the surface composition is only a tentative one in view of the sensitivity of the reaction studied. Its proceeding requires the presence of four adjacent active centers on the electrode surface whose heats of adsorption are strongly affected by the alloying.

Keywords: borohydride electrooxidation, electrocatalysis, platinum, gold, PtAu alloys.

INTRODUCTION

Sodium borohydride (NaBH$_4$) has hydrogen content of 10.6 mass % and theoretical H-capacity of 10.8 mass % making it one of the most attractive compounds for chemical hydrogen storage [1]. Hydrogen is released through a hydrolysis reaction proceeding in correspondence with:

\[ \text{NaBH}_4 + 4\text{H}_2\text{O} \rightarrow \text{NaB(OH)}_4 + 4\text{H}_2 \] (1)

The reaction can take place in room conditions but it has to be catalyzed. Sodium borohydride can also be used as a direct fuel [2 - 5] whose hypothetical oxidation reaction is:

\[ \text{NaBH}_4 + 8\text{OH}^- \rightarrow \text{NaBO}_2 + 6\text{H}_2\text{O} + 8\text{e}^- \] (2)

It is worth noting that if the oxidation of hydrogen produced in reaction (1) is considered, the two processes are formally equivalent. But BH$_4^-$ poor anodic efficiency of the direct borohydride fuel cell (DBFC) is attributed to reaction (1) and which is why the underlying challenge is to find an electrocatalyst that is active towards oxidation while being inert towards hydrolysis.

A large number of fundamental electrochemical studies of BH$_4^-$ oxidation were carried out on Au [6-25] and Pt [7,8, 21, 22, 26-31] of various catalyst morphologies with the application of electrochemical, electroanalytical and surface techniques. Calculations and modeling based on the Density Functional Theory (DFT) were carried out as well. For several years the interest to Au as an anode material in DBFC was much greater.
than that to Pt as it was believed that it catalyzed predominantly the direct BH$_4^-$ oxidation reaction (BOR), while Pt favored the competition between this preferred reaction and the proceeding heterogeneous hydrolysis. It is well recognized that there are uncertainties regarding BOR mechanism on Au. Some of the schemes advanced suggest several EC steps [6, 8, 16], other focus on an overall CE pathway at low reaction overpotentials [11, 17, 22]. It is suggested [12, 22-24, 25] that BOR is limited at low overpotentials by the weak initial adsorption of the BH$_4^-$ ion resulting in a very low surface coverage of BH$_4^-$ and subsequent reactive intermediates.

There are some uncertainties in connection with BOR mechanism on Pt as well. They are determined by the competition between several electrochemical and chemical steps generating hydrogen as a by-product even at pH 14. It is assumed [21, 22, 26] that BOR at Pt starts with destructive chemisorption of BH$_4^-$ to the electrode followed by the ionization of the adsorbed surface hydrogen:

\[
\text{BH}_4^- + \text{Pt} \rightleftharpoons \text{Pt} - \text{BH}_4^- + \text{H}^+ + 2\text{e}^- \quad (3)
\]

This low potential direct oxidation at Pt precedes [22] the hydrolysis of BH$_4^-$, which follows CE-type [8] reactions, i.e. the complete oxidation of BH$_4^-$ follows stepwise mechanism. The comparative investigation of BOR on bulk Au and Pt electrodes [21] provides physical evidence of the intermediate species and H$_2$ formation as a function of the electrode potential advancing the knowledge that Pt can be Faradaic efficient, unlike Au, i.e. Pt will outperform Au as an anode material in DBFC.

Binary Pt-based electrocatalysts [32 - 40] are found to circumvent some of the major problems referring to borohydride oxidation transformation. All results obtained imply synergism in the electrocatalytic activity of PtAu bimetallic systems. The comparative study of the kinetics of borohydride oxidation in the range of the first anodic maximum at Pt, Au and PtAu bulk alloys [40] shows that two-step formation of adsorbed species containing BOH and H proceeds at the alloy surface. The electronic effect determining the performance observed is attributed to decrease of B-H bonding strength when compared to that of unalloyed Pt. In view of the perfect control [30, 31, 41] of the surface morphology, texture and structure required for the juxtaposition of the intrinsic activity of Pt and Au, it looks challenging to follow the effect of the alloys surface composition on the behavior of the alloys studied in the range of the first anodic maximum. This is in fact the aim of the present communication.

EXPERIMENTAL

The kinetic study envisaged was carried out following the procedure described in [40]. Linear sweep (LSV) voltammetry was applied varying the scan rate from 0.020 Vs$^{-1}$ to 0.100 Vs$^{-1}$ and the temperature within the interval from 293.2 K to 323.2 K. The electrochemical measurements were performed with an Autolab PGSTAT 30 with a FRA2 module driven by GPES 4.9 and FRA 4.9 software (EcoChemie, The Netherlands).

Stationary electrodes of PtAu alloy electrodes of Au bulk content of 20, 40, 60 and 80 at. % were used. Comparative investigations were carried out at polycrystalline Pt and Au electrodes as well. Pt or Au mesh counter electrodes and Ag/AgCl (KCl sat) reference electrode were used. The true electrode surface of the working electrodes was determined at room temperature prior to each experiment in a three-compartment cell containing 1.0 M aqueous solution of NaOH. The working electrode surface had to be pretreated because of the fouling observed [21, 42]. The procedure developed [40] was applied in a second cell of identical configuration and dimensions. The values of the alloys surface composition were within the error range of the method applied.

All experiments were conducted in 0.01M solution of NaBH$_4$ (Merck, p.a.) in 1.0 M NaOH (Merck, p.a.). Bi-distilled water was used. Each of the borohydride solutions was prepared prior to the corresponding experiment to exclude any homogeneous hydrolysis. A third three-electrode electrochemical cell was used.

RESULTS AND DISCUSSION

The comparative investigation of the electrodes catalytic performance is carried out on the ground of the exchange current densities observed following the effect of the alloys composition and the temperature applied. The exchange current density, $j_0$, is the product of the electrochemical specific rate constant and a concentration term containing the activities of the oxidizing and reducing species. It is introduced in electrochemical kinetics [43 - 45] by the rate equation of an electrode reaction:

\[
j = nFv = j_0 \left[ \exp \left( \frac{\beta F \eta / RT}{\beta F \eta / RT} \right) - \exp \left[ - (1 - \beta) F \eta / RT \right] \right]
\]

\[
(4)
\]
where \( \eta \) is the overpotential (\( \eta \) is the difference between the potential \( E \) and the reversible potential \( E_{\text{rev}} \)), \( \beta \) is the symmetry factor, \( v \) stands for the chemical reaction rate, while the rest of the symbols have their usual meaning.

At low values of the overpotential (\( |\beta F \eta / RT| \leq 0.1 \)) Eq. (4) can be put [44] into linear form by expanding the exponent and taking only the first two terms:

\[
j(\eta) = \frac{j_0 F}{\eta} \eta
\]

(5)

This relationship is found valid for a complex electrode reaction including intermediates adsorption. The derivation [44] is done considering the system at a steady state. When several consecutive reactions are involved and the system is at steady state, all steps occur at the same rate (\( v_1^1 A_1 = v_2^2 A_2 = v_3^3 A_3 \ldots = v_i^i A_i = \text{const} \)). In fact, although all steps in the sequence proceed at the same rate, the affinities of all steps, except the rate-determining one, are near zero, i.e. these steps are considered to be at equilibrium. The rate-determining step has an exchange rate, which is much lower than that of the other steps and affinity, which is much higher.

Assuming that the rate-determining step occurs \( \nu \) times per act of the overall reaction, its affinity is given by \( A_i = A / \nu \). This provides to express the net rate, \( v \), of the reaction close to equilibrium through:

\[
v = v_{\text{rds}}^\nu \left( \frac{A}{\nu RT} \right)
\]

(6)

where \( v_{\text{rds}}^\nu \) is the exchange rate of the rate-determining step. Since the affinity \( A \) of an electrode reaction is equal to the electrical energy per mole which is applied to remove the system from its equilibrium, the rate of the overall reaction is given [44] by:

\[
j = \frac{j_0 n F \eta}{\nu RT}
\]

(7)

It is seen that Eq. (7) is in fact identical with Eq. (5) derived for a simple one-electron reaction. Furthermore it can be used in this study as the system behaves reversibly at low scan rates. Eq. (7) is applied in the form:

\[
\hat{j}_p = -\frac{j_0 n F}{RT} E_{p,\text{rev}} + \frac{j_0 n F}{RT} E_p
\]

(8)

assuming that \( \nu = 1 \). Eq. (8) shows that \( \hat{j}_p \) depends linearly on the peak potential \( E_p \) providing to estimate \( j_0 \) from the slope obtained.

The calculations carried out with the application of Eq. (8) are based on LSV profiles recorded at scan rates varying in the range between 0.020Vs\(^{-1}\) and 0.100Vs\(^{-1}\) at several temperature values. Fig. 1 illustrates some of the scans recorded. It is evident that the peak current density increases, while the peak potential value shifts in positive direction with scan rate increase at any of the temperature values set. Fig. 1 shows as well that the curves cross each-other at potentials prior to that of the peak. It is worth noting that this behavior is observed only in absence of electrode surface fouling which in turn leads to the suggestion that it can be assigned to a non-negligible hydrolysis of BH\(_4\) in correspondence with findings [21, 22]. The latter refer to the behavior of Pt rotating disc electrodes. The fit of the experimental data to Eq. (8) is illustrated in Fig. 2.

The estimation of \( j_0 \) requires the introduction of...
the value of \( n \). The latter gives the total number of electrons exchanged in the process investigated. It is determined on the ground [40 and references therein] of the rate dependence of the peak current density. Much higher scan rates are required. They have been applied and some of the values obtained were reported [40]. The temperature effect on \( n \) is followed on the ground of the temperature dependence of the diffusion coefficient \( D \). Theoretically it is given by an exponential equation of the type \( D = D_0 \exp \left( - \frac{E}{RT} \right) \), where \( D_0 \) is the maximum diffusion coefficient, while \( E \) is the activation energy for diffusion usually given varying from 12.6 \( \text{kJ mol}^{-1} \) to 28.1 \( \text{kJ mol}^{-1} \). The values of \( D \) reported in [19], i.e. 2.42x10^{-5} \( \text{cm}^2 \text{s}^{-1} \) at 298 K and 5.00x10^{-5} \( \text{cm}^2 \text{s}^{-1} \) at 338 K, provide to calculate \( E \) in case of \( 4BH \) diffusion. The value found is equal to 15.2 \( \text{kJ mol}^{-1} \), i.e. it falls within the range pointed above. The calculations referring to \( n \) show that the value for Pt changes from 0.9 at 299.2 K to 1 with temperature increase, while that of the alloy containing 60 at. % is 0.8 and changes to 0.9 at the highest temperature applied. The values found for the alloys containing 40 at. % and 80 at. % of Au stay constant with temperature variation. They are 0.4 and 0.6, correspondingly. That obtained for the alloy of Au bulk content of 20 at. % changes from 1.3 to 1.8 with temperature increase. In fact this is the only electrode material studied whose \( n \) value is close to the expected value of 2. It should be added that all values obtained are lower than 1 and 2, correspondingly, because of hydrolysis proceeding [21, 22], but they are in accord with the mechanistic concepts of borohydride oxidation on Pt(111) and Au(111) [23, 24, 29]. They are based on DFT calculated energy diagram of the reactions taking place. Further support is given by investigations [46 - 51] focused on the relation between the surface electronic structure and the reactivity of transition on noble metals and alloys. It is assumed that in case of Pt [29] and most of the alloys studied [40] the anodic peak is determined by the proceeding of:

\[
\text{BH}_4^{-aq} + 4^+ \rightarrow \text{BH}^+ + 3\text{H}^+ + e^- \quad (9)
\]

where the symbol (*) denotes adsorption sites or adsorbed species. The potential range of reaction (9) proceeding is obviously too low for most of the electrodes to provide the occurrence of the second step of the 2e-process, i.e.

\[
\text{BH}^+ + \text{OH}_2^- * \rightarrow \text{BOH}^+ + \text{H}^+ + e^- \quad (10)
\]

The concepts just outlined are in accord with the first peak potential values reported in [40]. For the alloys of Au bulk content less than 80 at. % they are lower than this for Pt, which in turn is lower than that for Au [8, 19, 21, 22]. These findings are valid for all temperature values studied. They are in correspondence with the data referring to PtAu bimetallic systems examined [2, 32 - 40].
The values of \( j_0 \) determined depend on the surface composition of the electrode materials. Fig. 3 outlines this dependence. It is seen that \( j_0 \) for three of the alloys is close to and slightly less than that for Pt at lower temperatures (Fig. 3a). These values are much smaller than that for Pt at higher temperatures (Fig. 3b). The exchange current density referring to the alloy of Au surface content of 30 % is the highest among those obtained in this study at all temperatures applied.

The results just reported determine the interest towards the temperature effect on \( j_0 \). It can be described [52] by:

\[
j_0 = A \rho \pi kT \exp \left( -\frac{E_S}{4kT} \right)
\]

where \( A \) is the frequency factor, \( c \) is the concentration of the reacting ion, \( \rho \) is the density of the electrode material’s electronic states, \( k \) is the Boltzmann constant, while \( E_S \) is the reorganization energy, characterizing the ligands’ charging. In fact \( E_S/4 \) is the activation energy [52] for the exchange current density. Eq. (11) shows that it can be estimated on the ground of the slope of the linear dependence of \( \ln j_0 \) vs. \( 1/T \). Some of the lines obtained in correspondence with Eq. (11) are presented in Fig. 4. The values of the activation energy are calculated. They are found dependent on the bulk as well as on the surface composition of the alloys investigated. The corresponding dependences are illustrated in Figs. 5 and 6. It is worth pointing out that the dependence on the bulk composition is of the form obtained in [40]. The curve presented in Fig. 5 goes through a minimum at Au bulk content of ca 50 at. %. Besides, the activation energy obtained for two of the alloys is less than that of Au. The effect of the surface composition is not so well outlined. Fig. 6 illustrates the relation’s tentative character. The curve shown goes through a minimum at Au surface content of 30 %. The latter value is attracting attention as the highest exchange current densities as well as the highest value of the total number of electrons exchanged are found for this particular surface content. The generalization of all facts obtained provides to conclude that the adsorption sites required for the proceeding of reaction (9) are most favorably distributed in case of Au surface presence of ca 30 %. The requirement of four adjacent...
adsorption centers on the electrode surface combined with the alloying effect on the heats of adsorption of these cites can explain the sensitivity of the oxidation reaction studied and hence the scattering of the points around the tentative curve in Fig. 6.

CONCLUSIONS

The comparative kinetic investigation of the process determining the first anodic peak of borohydride oxidation at Pt, Au and Pt-Au alloys of Au bulk content of 20, 40, 60 and 80 at. % provides the determination of the corresponding exchange current density taking into consideration the total number of electrons exchanged in the peak’s potential range and the temperature applied. The latter is varied in the range from 293.2 K to 323.2 K. The activation energy for the exchange current density is estimated and the effect of the alloys composition is followed. It is found that the alloys activation energy is lower than that of Pt. The lowest value is expected at Au bulk content of ca 50 at. %. The dependence on the alloys surface composition is only tentatively outlined most probably because of the sensitivity of the surface reaction studied. Its proceeding requires the presence of four adjacent active centers whose heats of adsorption are strongly affected by the alloying.

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