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Palladium Coated Steel Electrode - Preparation, Characterization and Their Use of Borohydride Determination

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ABSTRACT

The purpose of this study is the fabrication of a cost effective palladium coated steel electrode (Pd-S) for the direct analysis of the sodium borohydride (BH_4^-). The electrode was prepared by the cyclic voltammetry. The electrode was observed to have a high catalytic effect on the oxidation of BH_4^-. The Pd-S surface was characterized with profilometry, scanning electron microscope, ferrocene test and electrochemical impedance spectroscopic technique. The effects of borohydride concentration, scan rate and pH upon the electrode reaction were examined. The concentrations of BH_4^- were found with an error of 0.35-0.53%. The interference of the cations and anions have been investigated.

Keywords: Palladium, borohydride, determination, surface characterization

1. INTRODUCTION

Sodium borohydride is a strong reducing agent widely used in the synthesis of the organic and inorganic compounds, pharmaceuticals, waste water treatment and pulp technology [1-3]. The depletion of the solid fuels and destructive effect of their side products on the atmosphere has made the use of clean and sustainable energy sources doubly important. Hydrogen is one of the cleanest energy sources. However hydrogen has inherent storage and transportation problems. The intermetallic compounds such as BH_4^-, AlH_4^- are widely employed to obviate these setbacks. These tetrahedral structured hydrides posses' very high hydrogen storage capacities (weight content of 10.60%). Borohydride has a very high hydrogen transport capacity of 5.67 $Ah \cdot g^{-1}$ which makes it highly attractive for hydrogen and direct borohydride fuel cell applications [4,5]. Borohydride is also a highly stabile and non-combustible fuel with a cell potential of 1.64 V which is higher than the potentials of the other fuel cells [6-8]. Borohydride fuel cells are particularly important for Turkey since she holds the 73 % of the world's total boron reserves [9].

The number of electrons transferred was reported as $2e^-$, $4e^-$, $6e^-$, and $7e^-$ according to the electrode used [3, 10-14]. In a study on a gold microelectrode it was found that 6.8±0.7 electrons transferred per BH_4^- ion [15]. The Pd coated electrodes were found to give $6e^-$ transfer. According to the literature Au electrode gives the best catalytic effect in alkaline media due to the formation of thick catalytic oxides. Au electrode was followed by Pt and Pd. The electrocatalytic activity of the Ni on the other hand is very low in alkaline media due to the formation of thick non-conducting nickel hydroxides [16]. Also Pd and Pt electrodes were

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[♠]Corresponding author, e-mail: kuddusi@gazi.edu.tr observed to give high hydrogen efficiencies at low concentrations under suitable conditions [3].

Using suitable electrodes the concentration of borohydride is readily calculated from the amount of hydrogen released during the hydrolysis of borohydride [1, 17, 18]. The determination of BH_4^- was also carried out by iodometric [21], titrimetry with hypocholoride [20] , voltammetric [21] and spectrophotometric methods [22, 23].

Ünal and Somer (2009) investigated the interference of Cr^{3+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+}, Cu^{2+} and Se^{2+}cations in the determination of borohydride and they found that only Cu^{2+} made an interference with borohydride which was eliminated by the formation of Cu-EDTA complex [24].

The purpose of this study is to develop a simple and a cost effective electrode for the determination of BH_4^- with a low detection limit. Also the surface characterization of the resulting Pd-S electrode was carried out by the use of surface techniques and electrochemical methods.

2. EXPERIMENTAL

2.1. Materials and Chemicals

All the materials used in this study were analytical grade and all the solutions were prepared by the use of ultra-pure de-ionized water (18.2 MΩ.cm). The substrate material used for the Pd coverage was 405 quality cheap ferritic steel with a medium corrosion and oxidation resistance. The ferritic steel contains 10-30% Cr and small amounts of austenitic forming metals such as carbon, molybdenum and nickel (Table 1).

Table 1. 405 stainless steel chemical composition (wt%)

Type	UNS number	Chemical analysis results %(w/w)								
		C	Mn	Si	Cr	Ni	P	Mo	S	Other
405	S40500	0.08	1.00	0.75	11.50 - 14.50	0.50	0.04	-	0.03	0.10-0.30 Al

The Pd electrode with a diameter 3.0 mm was purchased from BASi company (MF=2018). The reference electrode was Ag/Ag^+ in a non-aqueous medium for ferrocene experiments and saturated calomel electrode (SCE) for the rest. A Pt wire counter electrode was used throughout the study.

2.2. Preparation of Pd-S Electrode

1.00 cm^2 steel plates were thoroughly cleaned and covered with Pd in a 1 mM Pd solution in 0.01 M HCl solution taking 300 consecutive cyclic voltammetric scans between -0.4 and 1.0 V (SCE) at a scan rate of 50 $mV \cdot s^{-1}$ (not shown due to limited space). The reason for the use of cyclic voltammetry was to obtain more homogenous surface coverage by the gradual deposition of the Pd atoms on the electrode.

The profilometric measurements were made by the use of Dektak 150 brand apparatus. The resistance of the covered surface was determined by the use of an avometer. The SEM images were taken by JEOL JSM–6060 LV model equipment. All the electrochemical analyses were carried out by CHI 660B system.

3. RESULTS AND DISCUSSIONS

3.1. Investigation of BH_4^- Oxidation on Solid Pd Electrode

The first step was the investigation of catalytic activity of the solid Pd electrode on the oxidation of borohydride. The electrode surface was mechanically cleaned by alumina prior to the start of every experiment.

Figure 1 shows the CV curves of BH_4^- with increasing concentrations in 0.01 M NaOH supporting electrolyte on Pd electrode. The oxidation peak of borohydride appeared at -0.30 V.

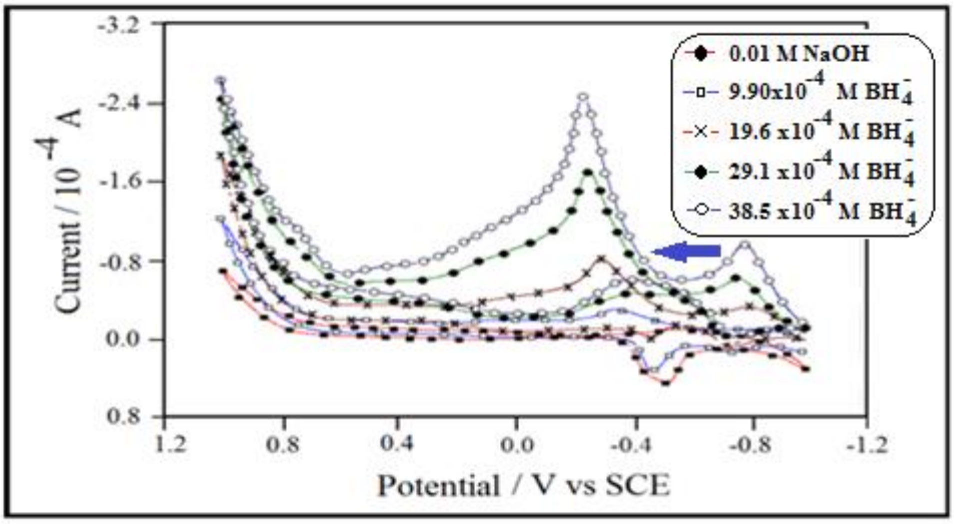

Figure 1. The cyclic voltammograms of $NaBH_4$ on solid Pd electrode (at 25 ^{0}C and scan rate 50 mV/s)

The observed peak current was proportional to the borohydride concentration as illustrated in Figure 1. The curves give a linear change with borohydride concentration which proves that the Pd is very a suitable electrode for the determination of BH_4^-.

The Pd deposition on steel substrate was carried out with 1.1 mM $PdCl_2$ solution in 0.01 M HCl supporting electrode at +0.15 V. The Pourbaix diagram of Pd showed that the deposition of Pd upon the surface as

$$Pd^{2+} + 2e^- \rightarrow Pd^0_{(k)} \qquad (1)$$

take place at +0.15V (SCE) at a pH value of 2 [25].

3.2. Surface Characterization

3.2.1. Profilometric measurements

Profilometry is a surface technique, which uses needle contact method to determine the surface profile. A part of the surface of the steel substrate was covered with a Teflon band while the rest was exposed to the solution. Figure 2.a shows the profilometric picture of the coated and uncoated regions . The profilometric results showed that the surface of the steel electrode was covered with thick Pd film. The thickness of the surface coverage was found to be 950 nm after the profilometric studies (shown in Figure 2.b). The diameter of the palladium is 274 nm [26]. Assuming that the surface is perfectly smooth and each atom fits perfectly upon each other the number of the Pd atoms was found to be 3500. However, since these assumption are not realistic and this number is an approximate value.

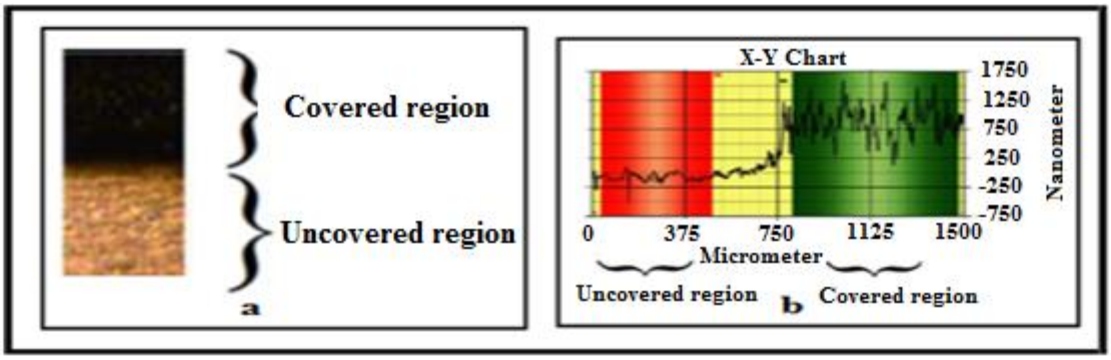

Figure 2. (a) The profilometric picture of Pd coverage upon steel electrode and (b) the change of coverage in profilometric curve

3.2.2. SEM studies

The SEM micrographs of the covered and uncovered surfaces taken at 10 kV and x2500 magnification were shown in Figure 3.

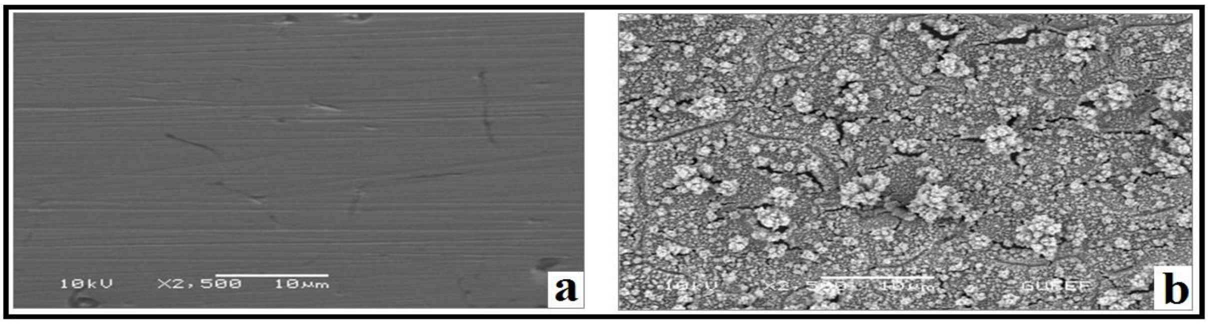

Figure 3. SEM micrograph of the (a) uncovered and (b) Pd covered steel electrodes (10kV, x2500)

The homogeneity and the coverage ratios of the Pd-S electrode were found to be 93.0% and 96.5 % by the use of least square method from the SEM pictures. The SEM picture of covered electrode was placed on a graph paper and the squares filled by Pd atoms were counted relative to the total number squares. Pd deposition was observed to take place as heaps on the surface due to the fact that active sites are not homogenously distributed over the surface.

3.2.3. Ferrocene test

Ferrocene ($Fe(C_5H_5)_2$, disiklopentadiphenylrone) is a compound which makes completely reversible $1e^-$ transfer. It is used to test the surface conductivity and determine the number of electrons transferred and the real surface area of the electrode. Ferrocene solution was prepared by dissolving 1.00 mM ferrocene in 0.10 M tetrabutylamonium tetrafloraborate (TBATFB). The cyclic voltamograms of the covered and uncovered steel electrodes are depicted in Figure 4.

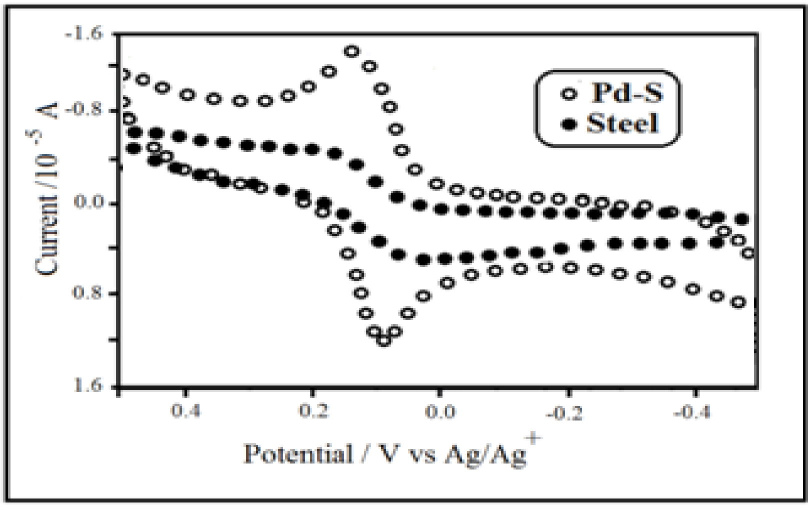

Figure 4. Electrochemical behavior of 1.00 mM ferrocene in 0.1 M TBATFB solution on Pd-S (o) and steel electrode (•) (scan rate: 0.1 $V \cdot s^{-1}$)

The voltamograms in Figure 4 show that the Pd deposition upon the steel surface greatly enhances the catalytic effect of the surface. There was also an appreciable increase in the conductance of the surface. The surface resistance of the covered and the uncovered electrodes were measured at a reliability of 95% with an avometer by taking five consecutive measures. The conductance of pure and Pd covered steel surface were calculated to be 1.07±0.02 and 3.25±0.03 S respectively. It was observed that the conductance of the coated surface was 3 times greater than the uncoated surface.

3.2.4. EIS

The EIS measurements were made by the use 1.00 mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ (1/1) mixture with a 0.10 M KCl supporting electrolyte adjusting the frequency range to 0.05 Hz and 100 kHz applying a 5mV amplitude direct current at a formal potential of 0.21 V at room temperature [27].

The Nyguist diagrams and the simulations of bare steel and the Pd-S electrodes are given in Figure 5 together with the related equivalent circuits.

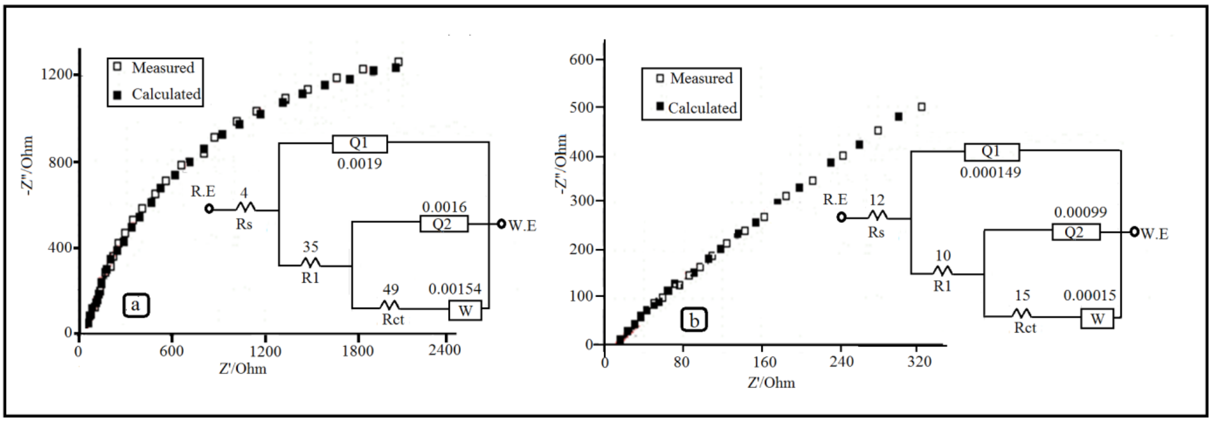

Figure 5. The measured and the simulated Nyguists diagrams and the equilibrium circuits of the uncovered (a) steel and (b) Pd-S electrode in 1.00 mM $[Fe(CN)_6]^{3-/4-}$ redox couple in 0.10 M KCl

The surface coverage ratio (Θ) of the electrode can easily be determined by the use of the following equation from the EIS data:

$$\Theta = 1 - \frac{R_{ct(steel)}}{R_{ct(steel)} + R_{ct(Pd)}} \qquad (2)$$

where R_{ct} signifies the charge transfer resistance

The charge transfer resistance of the both electrodes changed with the increased conductance of the electrode. The coverage ratio of the electrode was determined to be 97% which was very close to the value obtained by the SEM measurements.

3.2.5. The effect of pH upon the BH_4^- oxidation

The effect of the pH of the medium upon the oxidation of BH_4^- was investigated at pH 10, pH 12 and pH 13 and the optimum value for the reaction was found to be pH12. There was no peak observed for the oxidation BH_4^- at pH 10 since the competing hydrolysis reaction (2) prevails at this pH value (Figure 6.a).

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

The oxidation peak at the anodic direction is much more distinctive in pH 12 medium than ph 13 medium (Figure 6.b). That was why the pH of the medium was chosen as 12 throughout the study.

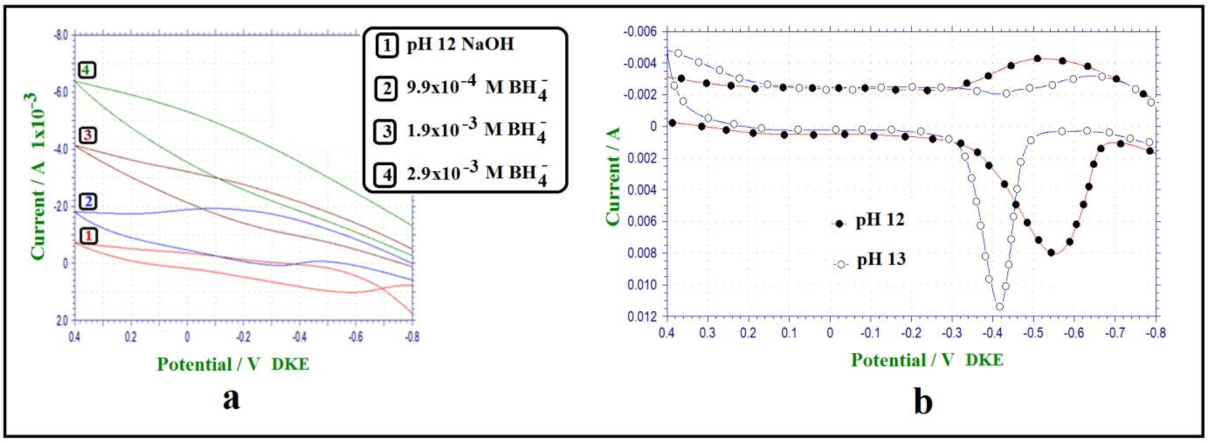

Figure 6. Borohydride oxidation in (a) pH 10 and comparison of pH 12 and pH13

3.2.6. The oxidation of sodium borohydride on Pd-S electrode

The oxidation was carried out in a highly basic media (pH 12) in order to obviate the hydrolysis of borohydride. The cyclic voltamograms obtained with different borohydride concentration on Pd-S electrode are depicted in Figure 7. The peak at -0.50 V at the anodic direction was found to show a linear increase with the borohydride concentration.

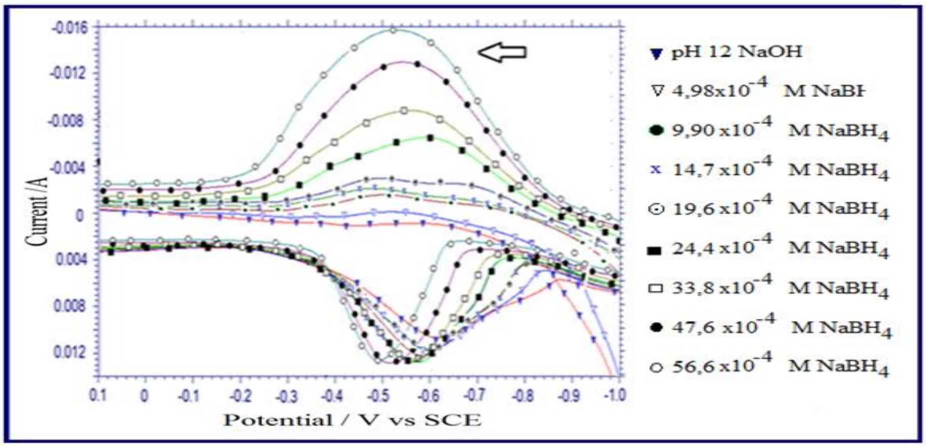

Figure 7. Cyclic voltammetric curves of $NaBH_4$ at various concentrations on Pd-S electrode in a pH 12 NaOH supporting electrolyte (v:50 mV·s^{-1}).

The voltamograms revealed that Pd has a good catalytic effect upon the oxidation of BH_4^- and it imparts its catalytic affect to steel when the steel substrate is coated with Pd (the Pd-S electrode) . In a study of Celikkan et al. the oxidation peak has appeared at -1.40 V [29].

Also when the scan rate was varied between 5 to 1000 mV·s^{-1} it was observed that the peak current increased up to 100 mV s^{-1} decreased thereafter (Figure 8) .This was attributed to the fact that the electron transfer rate became slower compared to the scan rate as the scan rate was increased. That was why the scan rate used through this study was 50 mV·s^{-1}.

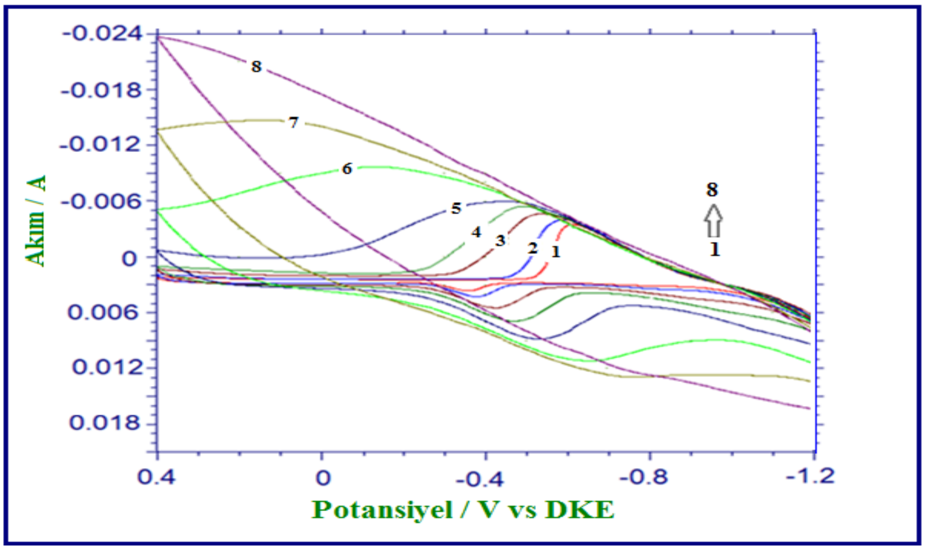

Figure 8. The CV curves of 1mM BH_4^- in pH12 supporting electrolyte at various scan rate on Pd-S electrode (1) 5 mV/s, (2) 10 mV/s, (3) 25 mV/s, (4) 50 mV/s, (5) 100 mV/s, (6) 250 mV/s, (7) 500 mV/s, (8) 1000 mV/s

As seen from the related voltamograms there is a net shift of potential towards the positive direction as the scan rate is increased. The scan rate is linearly proportional to peak current according to Randles-Sevcik equation (I_p=k$\nu^{1/2}$) in diffusion controlled systems. The logarithmic equation between the scan rate and the peak current is given as log I_p=log k + xlog ν. Here the x value is 0.50 in diffusion controlled systems. After a scan rate of 100 mV s^{-1} the current started to decrease with the shift of potential and it was totally disappeared after 500 mV s^{-1}. The slope was calculated to be 0.48 (Figure 9). This value shows that although the reaction is diffusion controlled there was a significant adsorption effect upon the reaction.

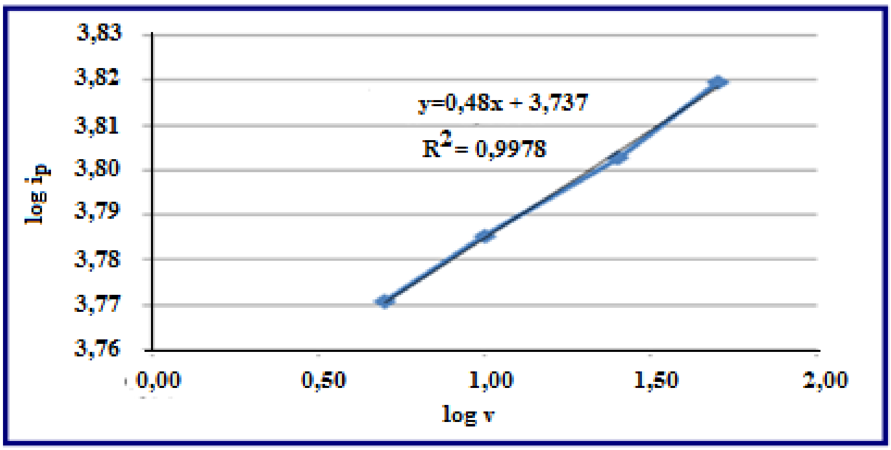

Figure 9. The log(i_p)-log(v) of 1mM BH_4^- in pH12 supporting electrolyte at various scan rate on Pd-S electrode

The fact that the current function decreases with the scan rate and the oxidation potential shifts towards the anodic values indicates that the electrochemical reaction is EC type [29].

3.3. The quantitative analysis of borohydride

The quantitative analysis of borohydride was carried out by the square wave voltammetry at the optimum conditions determined above (pH 12 and at a scan rate of 50 $mV \cdot s^{-1}$) and the electrode was calibrated against a sample with known concentration (Figure 10).

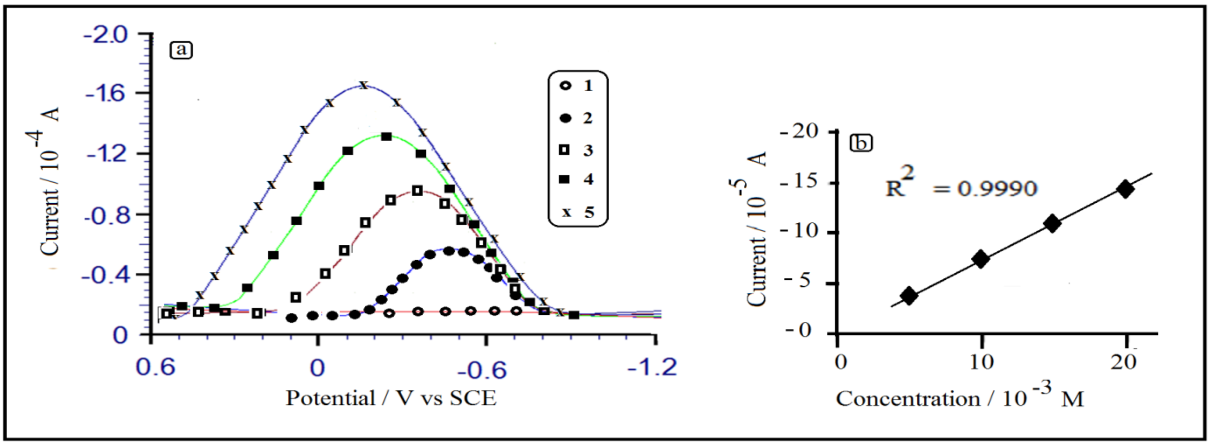

Figure 10. (a) The square wave voltamograms of BH_4^- oxidation at different concentrations upon Pd-S electrode, (1) with a supporting electrolyte of 0.01 M NaOH at pH 12, (2) 4.97x10^{-5} M BH_4^-, (3) 9.90 x10^{-5} M BH_4^-, (4) 14.8 x10^{-5} M BH_4^-, (5) 19.6 x10^{-5} M BH_4^- (b)Resulting calibration curve

The analysis of the samples with known concentrations was repeated five times using the same electrode and freshly prepared samples every time. The data are tabulated in Table 2. The table shows that the quantitative determination of sodium borohydride involves very small error and standard deviation.

Table 2. The statistical evaluation of the oxidation of BH_4^- at different concentrations

No of experiments	Concentration of BH_4^- added ($M \times 10^{-5}$)	Calculated mean concentration ($M \times 10^{-5}$)	Error %	Reliability range* ($M \times 10^{-5}$)
1	6.00	5.97	0.43	5.97±0.08
2	9.00	8.96	0.35	8.96±0.07
3	12.00	11.93	0.53	11.93±0.08

The LOD and LOQ values were found to be 1.24×10^{-6} M and 3.72×10^{-6} M respectively. The LOD value of 1.24×10^{-6} M is lower than 3.00×10^{-5} M reported by Çelikkan et.al [16] and 10^{-4} M and reported by Mirkin and Bard [21]. This shows that the Pd-S electrode prepared in this study is very suitable for the determination of borohydride at extremely small concentrations.

3.4. Interference Studies

There is a very high probability that the media used with borohydride contain Cr^{3+}, Fe^{3+} and Cu^{2+} anions introduced by the steel walls of the reactor where borohydride was synthesized. Therefore the interference of borohydride with cations such as Cr^{3+}, Cd^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Fe^{3+} and Cu $^{2+}$ $^{-}$ and anions such as CO_3^{2-} and BO_2^- with BH_4^- have been investigated. The metal hydroxides precipitate when they reach to their K_{sp} values causing the turbidity and changing the conductivity of the medium. However even under these extreme conditions there was no deviation in the oxidation peak of borohydride. It was found that none of the cations listed above showed any interference with borohydride.

The interference of BO_2^- and CO_3^{2-} anions upon the Pd-S surface was investigated by adding these ions in increasing concentrations in the presence of 1 mM borohydride in the same medium (pH 12 NaOH). There was a %5 decrease in peak current when the concentration of added BO_2^- and CO_3^{2} ions reach the 1.9 mM and 2.9 mM, respectively. However there was no deformation in the shape of the peak or any shift in its potential.

The interference of CO_3^{2-} and BO_2^- anions have been destroyed when the borohydride concentration increased (Table 3).

Table 3. The data obtained by the standard addition method is used to prevent oxidation of borohydride interference effect, borate and carbonate

Concentration (mM)			Error (%)
BH_4^-	**BO_2^-**	**CO_3^{2-}**	
0,5	2	3	12,3
1	2	3	9,2
2	2	3	4,5
3	2	3	1,3
4	2	3	0,8
5	2	3	0,8

3. CONCLUSION

The Pd-S sensor developed in this study emerges as a good alternative for the determination of borohydride due to its low detection limit, very good stability, cost effectiveness and simplicity. The concentration of the supporting NaOH electrolyte is about 0.01 M which is much lower than the concentrations (5-6 M) employed in the literature [4-7, 9, 15].

CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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