

The investigation of the electrooxidation of sodium borohydride on various metal electrodes in aqueous basic solutions

Hüseyin Çelikkan^a, Mükerrerem Şahin^b, M. Levent Aksu^{c,*}, T. Nejat Veziroğlu^d

^aGazi University, Faculty of Science, Department of Chemistry, 06500 Teknikokullar, Ankara, Turkey

^bTurkish Mineral Research and Exploration Institute, 06520 Balgat, Ankara, Turkey

^cGazi University, Faculty of Education, Department of Chemistry, 06500 Teknikokullar, Ankara, Turkey

^dClean Energy Institute, University of Miami, Coral Gables, FL 33124, USA

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Abstract

This study is related to the electrochemical oxidation of NaBH₄ on Au, Pt, Pd and Ni electrodes by the use of cyclic and square wave voltammetry. The most effective metal for the oxidation of sodium borohydride was found to be Au. Pt and Pd electrodes also showed certain activity while Ni was not effective. The compound was observed to give two consecutive oxidation steps with 6 and 2 electron transfers. The experiments conducted while keeping the potential at -0.8 V showed that the resulting compound is adsorbed upon the electrode surface and gradually decrease its catalytic activity.

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1. Introduction

The search for the alternative form of energy has accelerated in recent years due to fact that the fossil forms are dangerously depleted and will not be sufficient to meet the worldwide demand in future. The research in this area is basically directed toward finding an environmentally benign, cost effective and efficient form of energy. The use of hydrogen gas in vehicles will greatly decrease the emission of harmful sulfur and nitrogen oxides and smog into the atmosphere. The only waste forms as a result of the combustion of hydrogen in engines is water. The biggest problem in the use of hydrogen as a fuel is the difficulty of its storage. The storage of liquid hydrogen in tanks is both difficult and expensive. The solution of this problem is the use of metal hydrides such as NaH, AlH₃, LiH, NaBH₄ [1], LiBH₄ [2] and NaAlH₄ or storing hydrogen in carbon nanotubes or active carbon [3]. The borohydrides which have high hydrogen storage capacity have an obvious advantage against other hydrogen storage compounds. There are already proto-

type vehicles with hydrogen fuels cells using NaBH₄ [4]. In the hydrolysis, half of the hydrogen comes from NaBH₄ and the other half comes from water. Under suitable conditions the amount of hydrogen obtainable from 1 g hydride are as follows: from NaBH₄ 0.213 g, from NaH 0.084 g and from LiH 0.254 g [5].

Sodium borohydride is highly sensitive against moisture and rapidly dissociates under moist conditions. However, in strongly basic aqueous solutions, sodium borohydride is highly stable and can be stored over prolonged periods. The reaction of sodium borohydride in the solution upon a suitable catalyst gives hydrogen gas and the hydride is converted into sodium metaborate (NaBO₂) [5–7]. The resulting metaborate can be reconverted into sodium borohydride [8]. There are numerous patents upon the production of NaBH₄ [9–11]. The investigation of these patents reveals us that the electrochemical production of NaBH₄ is the most economic and promising way [12].

The first step of the electrochemical synthesis of a compound is the determination of its electrochemical behavior. This study is concerned with investigation of the electrochemical behavior of NaBH₄ in alkaline media on different metal electrodes by

* Corresponding author. Tel.: +90 312 2126470x3758.

E-mail address: maksu@gazi.edu.tr (M.L. Aksu).

the use of cyclic (CV) and square wave voltammetry (SWV). Apart from these techniques the electrochemical parameters of the system were investigated by the use of rotating disc electrode (RDE) with 2 mm diameter Pt disc electrode.

2. Experimental

The studies were carried out in 0.5 M NaOH (aq) solution by the use of Teflon wrapped Au, Pt (2 mm in diameter) and 1.13 cm² Pd and Ni electrodes. The chronoamperometric studies were carried out using 10 μm diameter Pt ultramicro disc electrode (UME). The reference and counter electrodes were Ag/AgCl (3 M KCl) and Pt wire, respectively. All the solutions were prepared with deionized water and the electrodes were polished with 0.3 μm alumina and the solution was purged with purified nitrogen for 15 and blanketed there after prior to each experiment.

All the electrochemical experiments were carried out by the use of CH Instruments 660B electrochemical analyzer and BAS C cell stand and BAS RDE with Pt electrode.

2.1. Methods

Cyclic voltammetry (CV) studies: The CV studies were carried out by the use of Pt, Pd, Au and Ni working electrodes in 0.5 M NaOH solution containing 1 mM NaBH₄. The change of peak current with NaBH₄ concentration was also investigated.

Square wave voltammetry (SWV) studies: The voltammograms of 1 mM NaBH₄ in 0.5 M NaOH solution on Au, Pt and Pd electrodes were taken. The system was kept at −0.8 V on Au electrode which gave the highest peak current density for certain periods and scanned in positive direction.

Chronoamperometry (CA) studies: The chronoamperometric Cottrell slopes of the 1 mM Ferrocyanide (which gave 1 electron reversible transfer) and 1 mM NaBH₄ on Pt UME were used to determine the diffusion coefficients and number electrons transferred.

Rotating disc electrode (RDE) studies: The RDE curves of 1 mM ferrocyanide reference solution (in 0.5 M aqueous KNO₃) and 1 mM NaBH₄ at a rotation rate of 1000 rpm were used to determine the D_o and n values.

3. Result and discussion

The cyclic voltammetric curves of sodium borohydride on Au electrode are depicted in Fig. 1. NaBH₄ is observed to be oxidized at −0.40 V on Au electrode at low scan rates (Fig. 1). This potential was observed to shift to −0.32 V at high scan rates (5 V/s). NaBH₄ which was observed to have a completely irreversible oxidation pattern at low scan rates showed a weak reduction peak around −0.42 V at high scan rates. This indicates that the completely reversible oxidation was not the case at high scan rates and the resulting metaborate was not reconverted into boron hydride. The potentials of borohydride oxidation were observed to shift towards the negative potentials as the scan rate was increased (Fig. 1). The small

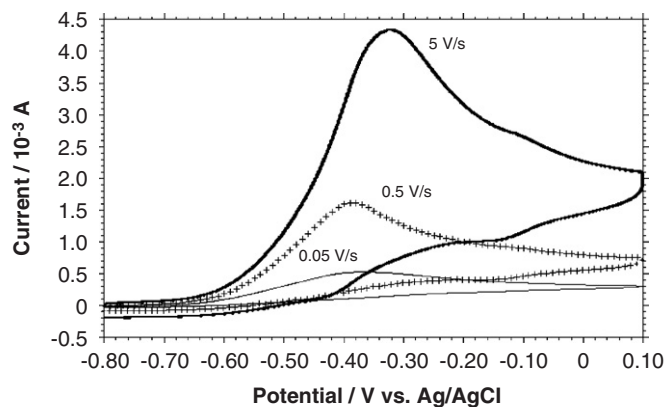


Fig. 1. The oxidation of 1.8×10^{-5} M NaBH₄ on Au electrode at different scan rates.

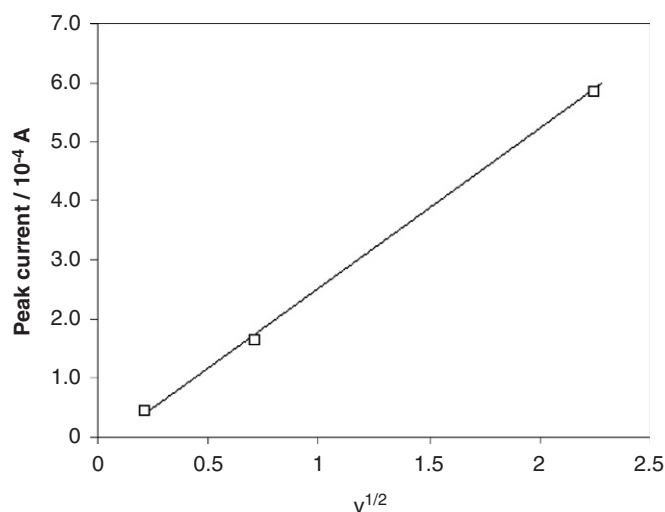


Fig. 2. $i_p - v^{1/2}$ plot of 1.8×10^{-5} M NaBH₄ on Au electrode.

symmetrical peaks observed at −0.2 V indicate the weak adsorption of the reactant. The fact that the cathodic and anodic peaks are not symmetrical indicates the presence of a quasi reversible reaction. The Randles–Ševčík equation given below is useful to determine whether the electrochemical reaction is diffusion controlled or not. The linearity of $i_p - v^{1/2}$ plot is the verification of a diffusion control (Fig. 2).

$$i_p = 2.69 \times 10^5 n^{3/2} D_o^{1/2} C_o v^{1/2}.$$

This relation shows that the peak potential changes linearly with the concentration of the electroactive compound. The fact that the peak at 0.4 V which belongs to the electrooxidation of sodiumborohydride changes linearly with the borohydride concentration indicates that it could conveniently be used in the electroanalytical determination of sodium borohydride (Figs. 3 and 4).

The investigation of the cyclic voltammetric curves NaBH₄ on Pt electrode in alkaline media reveals that NaBH₄ is mainly oxidized in the hydrogen desorption region of the Pt electrode (Fig. 5). The figure shows that catalytic surface oxides of Pt were not active toward the oxidation of NaBH₄.

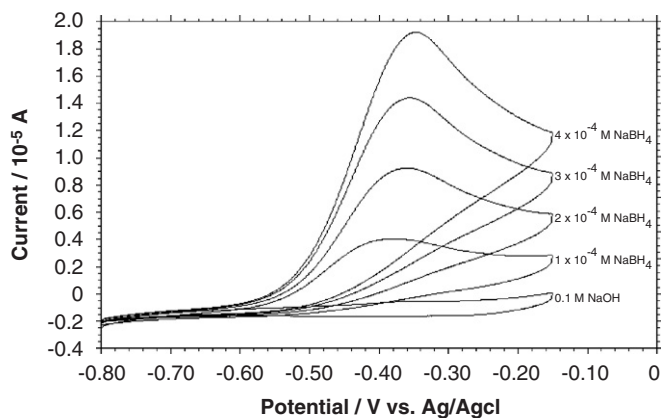


Fig. 3. The cyclic voltammometric oxidation curve of NaBH_4 on Au at different concentrations ($v = 50 \text{ mV/s}$).

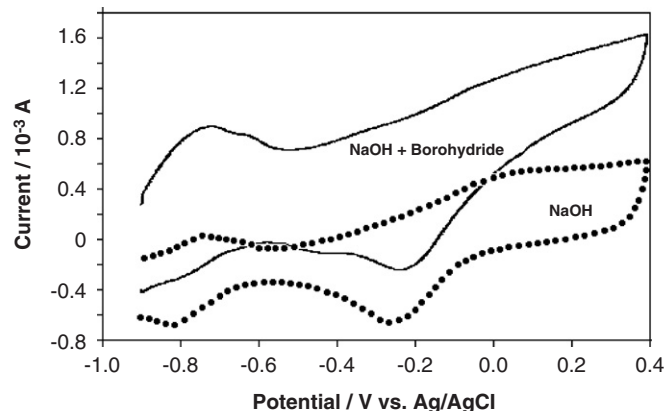


Fig. 6. The cyclic voltammograms 0.5 M NaOH and $0.5 \text{ M NaOH} + 1.8 \times 10^{-3} \text{ M NaBH}_4$ on Pd electrode at a scan rate of 50 mV/s .

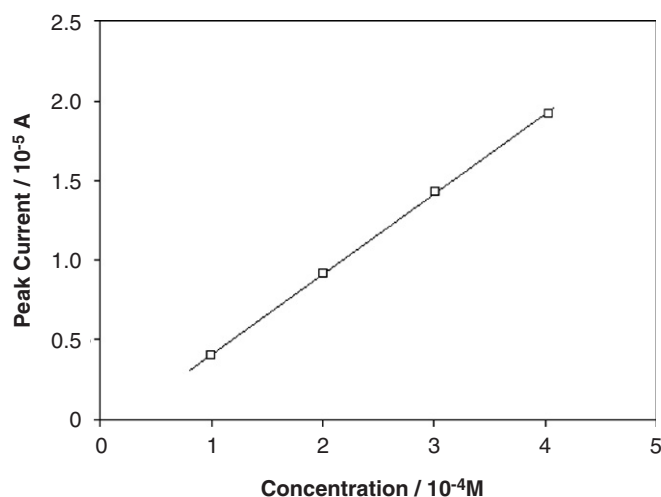


Fig. 4. The change of peak currents with NaBH_4 concentration on Au electrode.

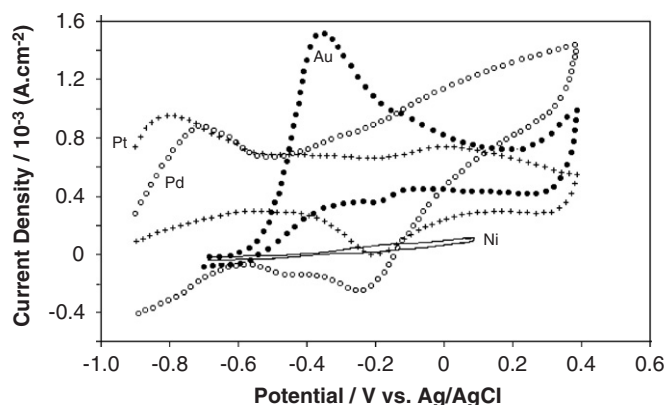


Fig. 7. The comparison of the oxidation of NaBH_4 on Au, Pt, Pd and Ni electrodes.

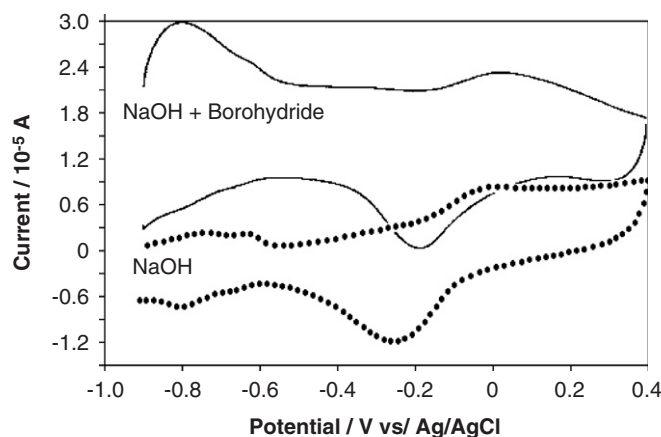


Fig. 5. The cyclic voltammograms 0.5 M NaOH and $0.5 \text{ M NaOH} + 1.8 \times 10^{-3} \text{ M NaBH}_4$ on Pt electrode at a scan rate of 50 mV/s .

The situation in Pd electrode is similar to that observed in Pt electrode. However, the double layer region is much more effective in the case of Pd electrode (Fig. 6).

The comparison of the catalytic activities of the Au, Pt, Pd and Ni electrodes reveal that Au shows the highest activity while Pt and Pd show similar behavior. Ni was observed to be inactive for the electrocatalytic oxidation of NaBH_4 (Fig. 7).

The square wave voltammograms of NaBH_4 taken in anodic and cathodic directions indicate that the Au electrode was the most active electrode towards the oxidation of the NaBH_4 . Pt and Pd showed certain activity in the hydrogen region while Ni had no activity at all (Figs. 8–10).

The oxidation potential of NaBH_4 was found to be -0.4 in all CV curves. The number of electrons transferred in the peaks observed in the voltammograms was determined by the use of UME, CA and RDE.

Figs. 11 and 12 show the chronoamperometric Cottrell curves and UME curves of ferrocyanide and borohydride in comparative manner.

The diffusion coefficients can easily be determined by the use of chronoamperometric Cottrell equation

$$i = \frac{nFAC_0D_0^{1/2}}{\pi^{1/2}t^{1/2}}$$

and ultramicro steady state current given by Baranski [13]

$$i_{ss} = 4rFnC_0D_0.$$

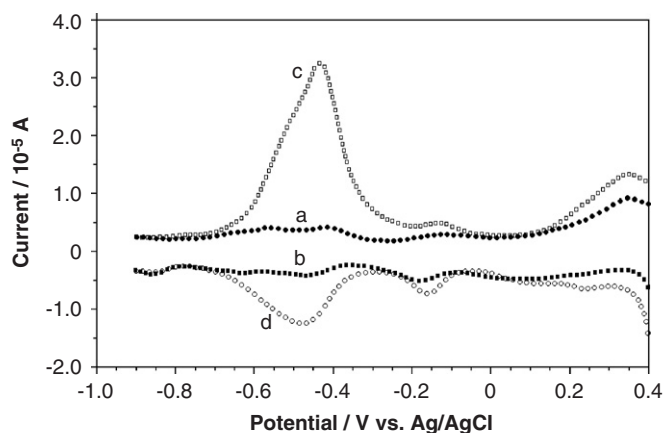


Fig. 8. The square wave voltammograms of NaBH₄ on Au electrode (Inc E . = 0,001 V, pulse amp. = 25 mV): (a) for NaOH in anodic direction; (b) for NaOH in cathodic direction; (c) for NaBH₄ in anodic direction; (d) for NaBH₄ in cathodic direction.

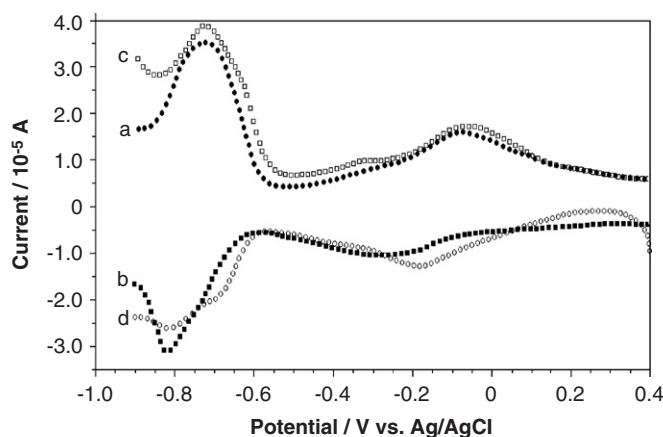


Fig. 9. The square wave voltammograms of NaBH₄ on Pt electrode (Inc E . = 0,001 V, pulse amp. = 25 mV): (a) for NaOH in anodic direction; (b) for NaOH in cathodic direction; (c) for NaBH₄ in anodic direction; (d) for NaBH₄ in cathodic direction.

Here A , r and D_0 signify the area of the working electrode, diameter of the UME and the diffusion coefficient of the compound. The D_0 values of the ferrocyanide and NaBH₄ were found as $4.20 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $4.02 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.

The principle of RDE method is fairly simple. The limiting current of one electron transferring (ferrocyanide in this case) is compared with the limiting current of the compound investigated. If the parameters such as the concentration, rotating rate, electrode area are kept constant and then the number of electron transferred will only be dependent upon the limiting current and the diffusion coefficients according to Lewich equation given below. The RDE curves of the NaBH₄ and ferrocyanide at a rotating rate of 1000 rpm are depicted in Fig. 13.

$$i_L = 0.29nFD_0^{2/3}\omega^{-1/2}v^{-1/6}C_0.$$

The limiting currents of the first and second oxidation waves were found as 225 and 87 μA , respectively. The limiting current for ferrocyanide is 40 μA (Fig. 13). By using the Lewich

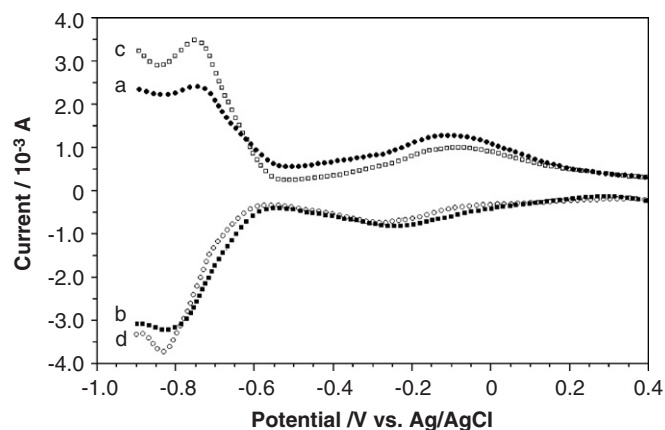


Fig. 10. The square wave voltammograms of NaBH₄ on Pd electrode (Inc E . = 0,001 V, pulse amp. = 25 mV): (a) for NaOH in anodic direction; (b) for NaOH in cathodic direction; (c) for NaBH₄ in anodic direction; (d) for NaBH₄ in cathodic direction.

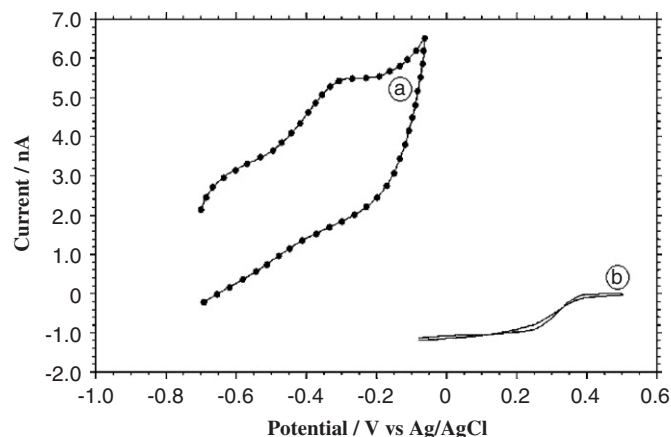


Fig. 11. The behaviors of NaBH₄ (a) and ferrocyanide (b) on gold UME.

equation and assuming the kinematic viscosity of water does not change, these limiting currents can be written as

$$\frac{(i_L)_{\text{Ferrocyanide}}}{(i_L)_{\text{Borohydride}}} = \frac{1 \times (D_{\text{Ferrocyanide}}^0)^{3/2}}{n \times (D_{\text{Borohydride}}^0)^{3/2}}.$$

Using this equation the number of electrons transferred in these waves were found as 6.01 and 2.32, respectively. Therefore, one can write the following mechanism for the oxidation of NaBH₄ in basic media.



The previous literature states that the 2e transfer takes place first [13]. The RDE data indicate that there were two consecutive electron transfer first with 6e hydrolysis reaction followed by a 2e as shown above comparing the peak currents with that of ferrocene which is known to give a completely reversible 1e transfer wave. The fact that 6e transfer is seen as a single wave

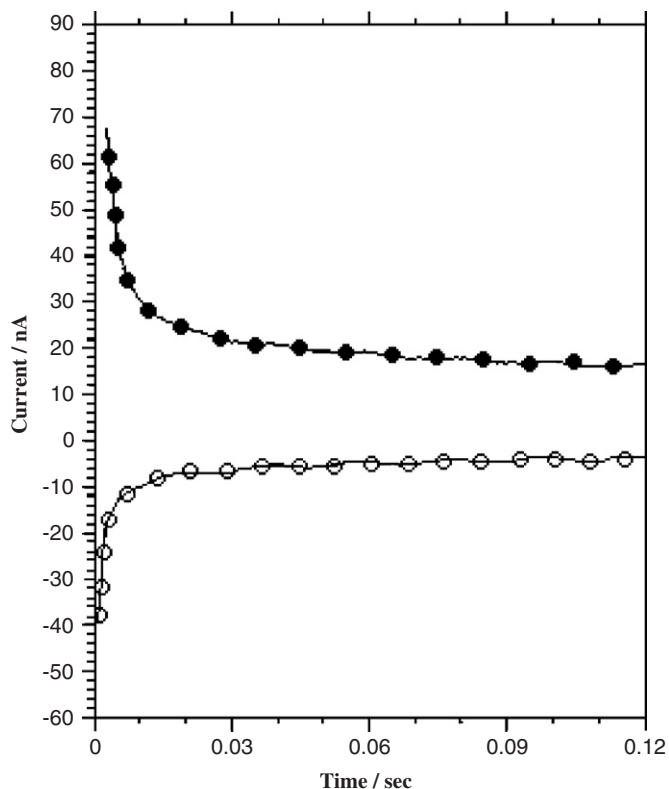


Fig. 12. The chronoamperometric curves for NaBH_4 (●) ve ferrocyanide (○).

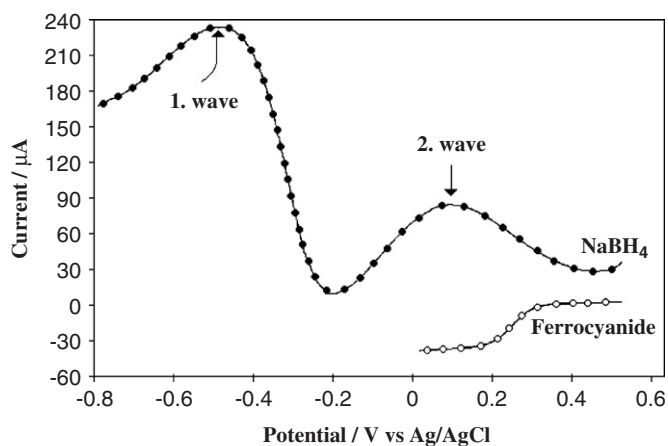


Fig. 13. The RDE curves for NaBH_4 (●) and ferrocyanide (○).

shows that there were fast electron transfer reactions following each other.

NaBH_4 was kept at -0.8 V , a value well above its oxidation potential, for different periods Fig. 14. The currents were found to increase and the potentials were observed to shift towards more positive values with the increasing period. The graph of the waiting time against the peak current values increases in an exponential manner (Fig. 15). This shows that the compound is adsorbed upon the surface and decreases its electrocatalytic capacity.

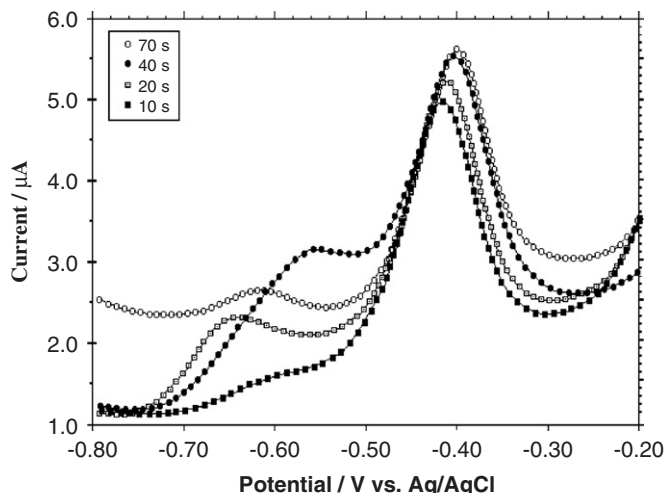


Fig. 14. The SWV behavior of NaBH_4 kept at -0.8 V for different periods.

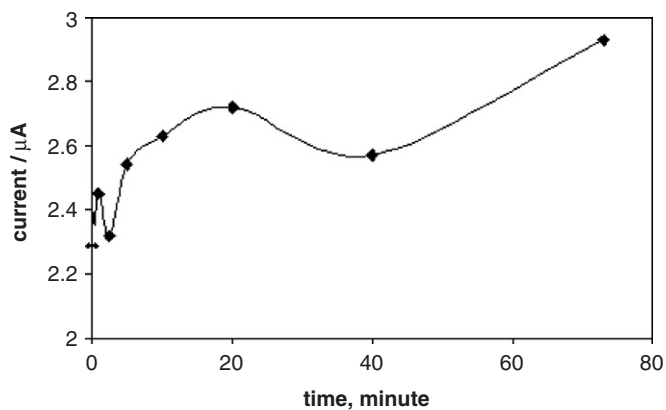


Fig. 15. The change of current values of NaBH_4 against the waiting period at 0.8 V .

4. Conclusion

The most effective metal for the oxidation of sodium borohydride was found to be Au. Pt and Pd electrodes also showed certain activity while Ni was not effective. The compound was observed to give two consecutive oxidation steps with 6 and 2 electron transfers. The experiments conducted keeping the potential at -0.8 V showed that the resulting compound is adsorbed upon the electrode surface and gradually decreased its catalytic activity.

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