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The Electroanalytical Determination of Sodium Borohydride Using a Gold Electrode

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It was shown that square wave voltammetry, a technique with a much lower detection limit, could be successfully used in the detection of borohydride formed in alkaline medium. A Au electrode was found to be very suitable for this purpose. The detection limit was 3 x 10^{-5} M.

Key Words: Borohydride, square wave voltammetry, electrolysis.

Introduction

Sodium borohydride or sodium tetrahydroborate is used as a reducing agent in many organic and inorganic reactions. Therefore, the determination of sodium borohydride present in the system is of great importance. Borohydride releases hydrogen under appropriated conditions in the presence of a suitable catalyst. Since the amount of hydrogen emitted is proportional to the amount of borohydride, the measurement of the amount hydrogen emitted was the first method used for the determination of the borohydride present in the system[1]. This method is also employed in studies searching for suitable electrocatalysis for hydrogen generation from borohydride under different conditions[2-3]. Apart from the measurements of the hydrogen emitted, the amount of borohydride present in the system can conveniently be determined by the use of titrimetric methods. The most popular technique among these is the iodide method. In this method excess IO_3^- is added to the medium and the remaining IO_3^- after the reaction with BH_4^- is back titrated with buffered $S_2O_3^{-2}$ [4]. The semiquantitative silver-ethylenediamine (Ag-EDDA) is based upon the reaction of Ag (I) with BH_4^- in 4% EDA solution in 50% NaOH[5]. Crystal violet methods are particularly suitable in nonaqueous media [6]. The reduction of phosphotungstate can be conveniently used as a spot test for the determination of the presence of BH_4^- in the medium [7]. In addition to all these, although not used in the literature very commonly, it was determined that the addition of 0.1-0.05 M strongly basic solution of $NaBH_4$ to $KMnO_4$ results in the disappearance of the pink color of the solution. This method can be used

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as a spot test for the determination of BH_4^- in the medium. There are also other quantitative methods such as carmine reagents [8–9] and phosphomolybdic acid [10]. The spectrophotometric determinations are based on the reaction of the additive agent with borohydride, giving a colored product, and spectroscopic analysis of this product at a certain wave length. The polarographic [11] and voltammetric [12] techniques allow determinations at much lower detection limits. Gold was found to be the most suitable electrode material for the voltammetric determination of borohydride. The cyclic voltammetric peak current was found to show a linear change by the use of a standard addition method at a concentration level of 10^{-5} M BH_4^-. The reason that the Au electrode gave much more satisfactory results compared to Pt, Ni and Pd electrodes is the fact that Pt and Pd electrodes oxidizes the BH_4^- at the trans-passive oxide formation region and the electrocatalytic activity of the Ni electrode becomes very low as the medium is made more alkaline due to the formation of nonconducting nickel hydroxides. This study aimed to determine borohydride by the use of square wave voltammetry, which has a much lower detection limit than the spectrochemical and titrimetric methods and gives much sharper and better separated peaks compared to cyclic voltammetry and polarography. The working electrode was a Au electrode.

Experimental

All the electrochemical experiments were carried out by the use of a computer controlled CH Instruments 660 B model potentiostat and BAS C3 cell stand. The cyclic and square wave voltammetric curves were taken using a 2 mm diameter Au disk working, Pt coil counter and Ag/AgCl (3 M KCl) reference electrodes. The working electrode was polished with 0.5 μm alumina and thoroughly washed with de-ionized water prior to the experiments.

Test solutions

All the experimental solutions were prepared by the use of analytical grade reagents. NaOH and $NaBH_4$ were purchased from Merck, Germany. The experimental solutions were prepared on a daily basis.

Electrochemical experiments and determination of borohydride

All the electrochemical tests were carried out in a 10 mL cell. The cyclic voltammetric curves were recorded at a scan rate of 50 mV/s. Square voltammetric studies were performed using the same potential range but lower borohydride concentrations. The borohydride concentration was kept at 10^{-4} M in cyclic voltammetric and 10^{-5} M in square wave voltammetric experiments. The borohydride concentrations were made up by 100 μL additions from 10^{-3} M and 10^{-4} M stock solutions and the curves were presented as superimposed upon each other.

Results and Discussion

There are numerous studies related to the electrochemical oxidation of borohydride. This study is related to the electrochemical behavior of borohydride upon various electrodes. The electrocatalytic behaviors are important with regard to the hydrogen evolution reaction of borohydride in basic media. The first study related to the electroanalytic determination of borohydrides was carried out by Mirkin[12] in 1991. In this study a linear increase in the current peaks in linear sweep voltammetry was obtained by the standard addition of borohydride using a Au working electrode. The changes in peak currents by the standard addition of borohydride were also investigated by the use of square wave voltammetry.

The linear sweep voltammogram taken for standard borohydride additions is shown in Figure 1. Figure 2 gives the changes in peak currents with borohydride concentration. The R^2 of the line was 0.9990. The linear change of i_p with $v^{1/2}$ indicates that the electrochemical oxidation of borohydride on the Au electrode is a diffusion controlled process (Figure 3).

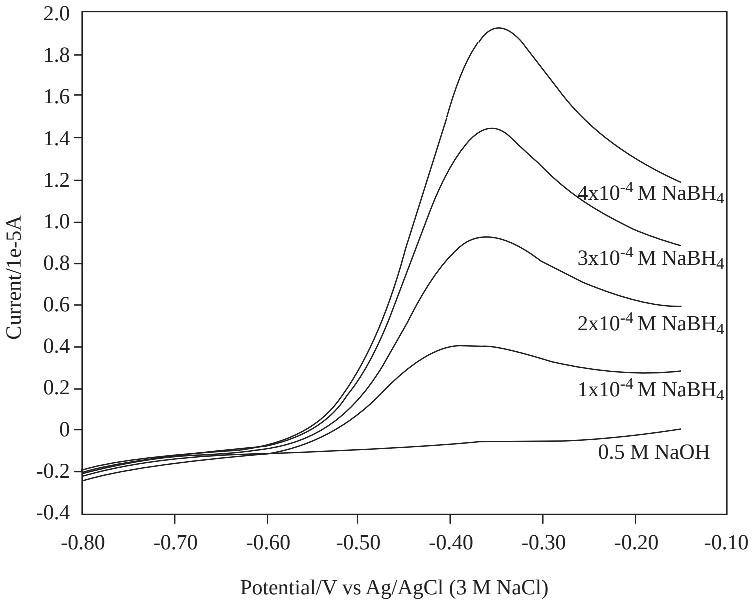

Figure 1. The cyclic voltammetric oxidation curve of $NaBH_4$ on Au at different BH_4^- concentrations (v = 50 mV/s).

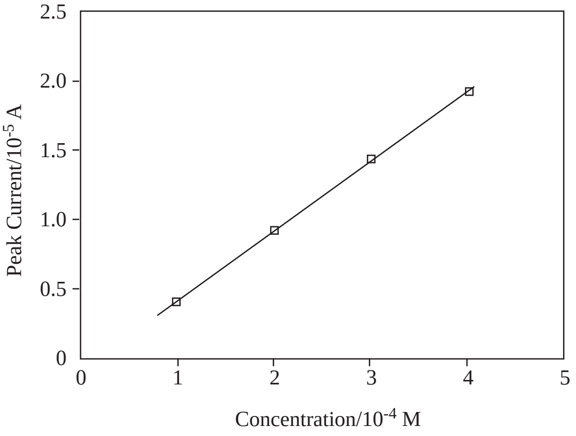

Figure 2. The changes in peak currents with $NaBH_4$ concentration on a Au electrode.

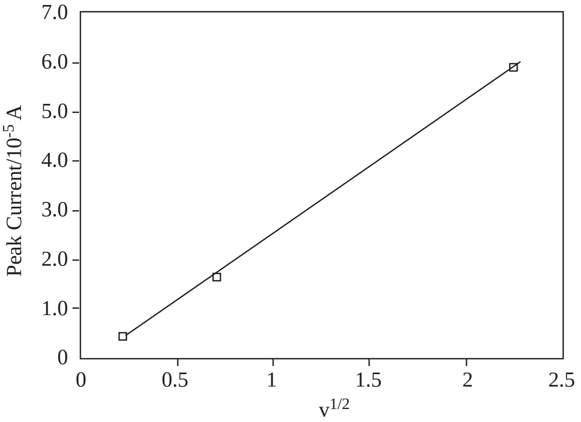

Figure 3. $i_p - v^{1/2}$plot of 1.8 x 10^{-5} M $NaBH_4$ on a Au electrode.

The square wave voltammograms obtained with the standard addition of borohydride are presented in Figure 4. The peak currents corresponding to various borohydride concentrations are plotted in Figure 5. The graph gives a linear line with a correlation of 0.9992.

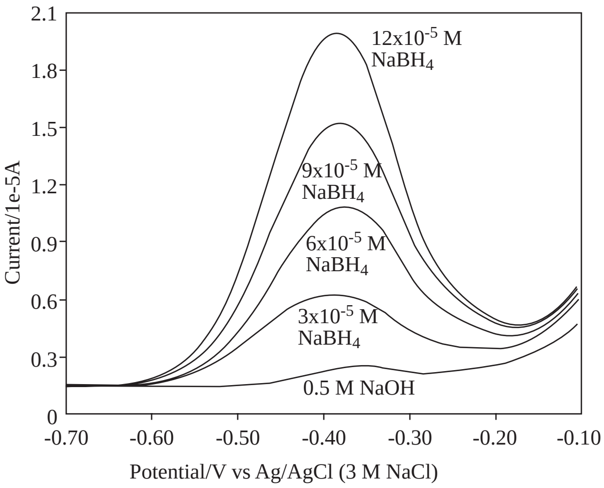

Figure 4. The square wave voltammetric curves of $NaBH_4$ on a Au electrode.

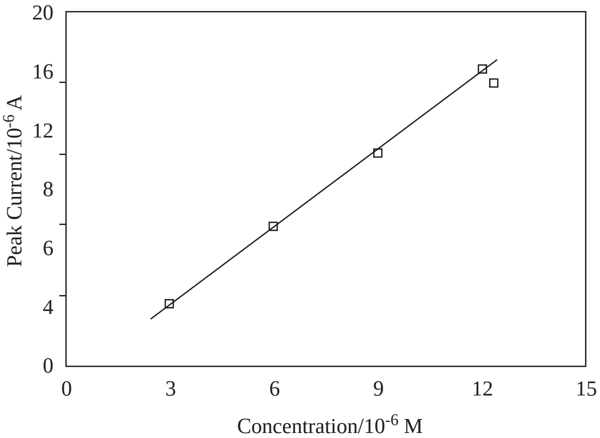

Figure 5. The changes in peak currents with $NaBH_4$ concentration on a Au electrode.

Based upon all these data one can conveniently claim that Au is the most suitable electrode material for both the electrochemical investigation and the analytical determination of borohydride. The lowest detection limit in Mirkin's study was 8 x 10^{-5} M borohydride. It was found in this study that this limit may well be reduced to 3 x 10^{-5} M borohydride concentration by the use of square wave voltammetry.

The purpose of the present study was to develop a suitable technique for the determination of borohydrides formed as a result of the electroreduction of borates. It was not possible to obtain a sufficient amount of borohydride from the electroreduction of borates for analytical determination by semiquantative techniques such as the iodate method. Therefore, the presence of borohydride was investigated by the use of square wave sweep voltammetry during the electrolysis of borates. Figures 6 and 7 show SW voltammograms and the changes in peaks currents found at different electrolysis times. It was found that square wave voltammetry is the best method to detect the product formed upon the electrode surface.

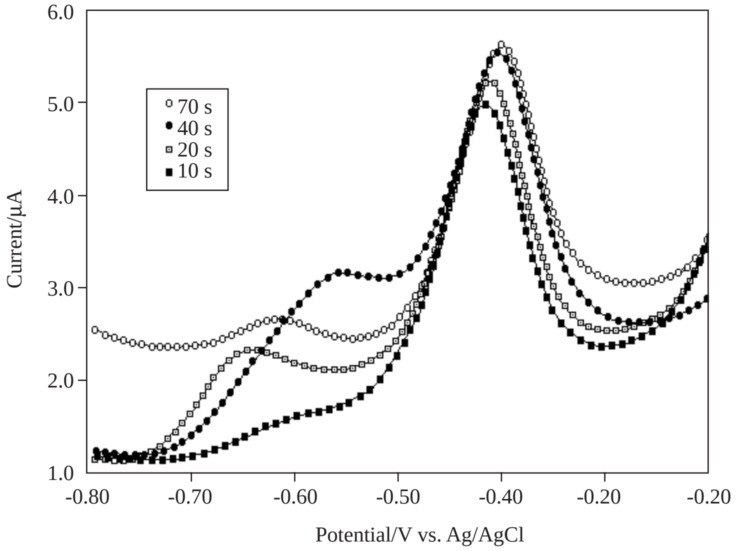

Figure 6. The SWV behavior of $NaBH_4$ kept at -0.8 V for different electrolysis periods.

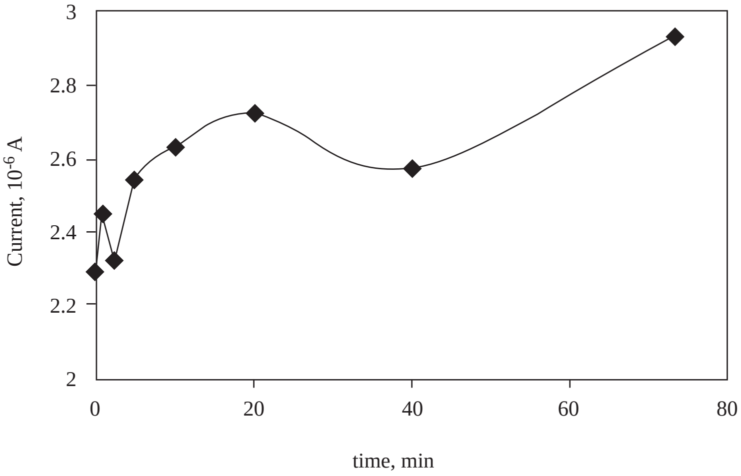

Figure 7. The changes in current values of $NaBH_4$ against the waiting period at 0.8 V.

Conclusion

It was shown that square wave voltammetry can be successfully employed for the determination of borohydride in alkaline media. The detection limit of square wave voltammetry is approximately 3 x 10^{-5} M, which is well below the values reported in the literature[12]. The method can be conveniently used in mechanistic studies of the formation of borohydrides.

Acknowledgments

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