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EFFECT OF DIFFERENT ADDITIVES ON THE ELECTROCHEMICAL BEHAVIOUR OF SODIUM BOROHYDRIDE ON Au ELECTRODE

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ABSTRACT

The paper presents results of the influence of different additives such as $NaBO_2$, $Na_2B_4O_7$ and ethylendiamine (EDA) to the oxidation of $NaBH_4$. On the basis of this research, a method for analyzing the concentration of mechano-chemically synthesized $NaBH_4$ from $NaBO_2$ and $Na_2B_4O_7$ compounds has been proposed. It has been shown that linear potentiodynamic (LPD) and cyclic voltamperometric (CV) methods are utilizable as easy, sensitive and accurate analyzing methods. It has been observed that EDA, $NaBO_2$ and $Na_2B_4O_7$ compounds do not contribute any obstacle for determining the $NaBH_4$ quantity.

Keywords: *Sodium borohydride, synthesis, determination, additives, cyclic voltammetry.*

INTRODUCTION

Depletion of fossil fuels, especially petroleum and their trigger and effect of global warming make hydrogen an important clean energy source of today and the future. For this reason its production, storage and utilization (especially for fuel cell applications) are some of the most important problems to overcome.
The storage of hydrogen is obtained by various methods such as by using pressurized tanks, by liquidification at low temperatures, by metal hydrides or with various chemicals. From these methods a safe and efficient method is storing hydrogen in chemicals such as sodium borohydride [1].

$NaBH_4$ includes approximately 10.57% hydrogen of its weight. To release hydrogen, $NaBH_4$ must be hydrolyzed with water. The following reaction takes place:

$$NaBH_4 + 2H_2O \xrightarrow{catalyst} 4H_2 + NaBO_2$$

As seen from the reaction, after the hydrolysis process, hydrogen from water is also captured, in other words $NaBH_4$ releases 21% of hydrogen by its weight. Also with the catalysts used for this process such as Ruthenium (Ru) or supported Cobalt (Co), it is possible to create mechanisms that can produce hydrogen on demand [1,2]. Consequently, with the hydrolysis of 1 g of $NaBH_4$, it is possible to produce approximately 2.4 liters of pure hydrogen. This is an important property which may be easily applied to vehicular [3] and many other applications related to fuel cells [4,5]. Other than its storage feature, $NaBH_4$ is used in various industrial applications such as paper, textile, ceramic, porcelain, drugs, perfume, rocket fuels and etc. Due to these mentioned properties above $NaBH_4$ is the most important of all commercially produced and utilized borohydrides. Recent studies on $NaBH_4$ is concentrated on its production methods.

1.1. Traditional Methods for $NaBH_4$ Production

Due to the expensiveness of present production methods, researches are mainly concentrated around this area. One of the production processes is done with the participation of NaH with $Na_2B_4O_7$ at elevated hydrogen pressure and temperature [6].

$$Na_2B_4O_7 + 16Na + 8H_2 + 7SiO_2 \rightarrow 4NaBH_4 + 7Na_2SiO_3$$

Another production method has multiple steps and includes the following reaction [7]:

$$4NaH + B(OCH_3)_3 \rightarrow NaBH_4 + 3NaOCH_3$$

Using $NaBH_4$ as reducing agent makes both of these processes expensive. Investigations are done to keep the synthesis costs minimum. This can be done by mechano-chemical methods with cheap reducing metals at elevated hydrogen pressures and temperatures [8,9]. This process includes $NaBO_2$ and $Na_2B_4O_7$ participation. Process is as follows:

$$NaBO_2 + 2Mg + 2H_2 \rightarrow NaBH_4 + 2MgO$$

Process is carried out with continuous stirring of $NaBO_2$ and powdered metal such as magnesium. Transformation of $NaBH_4$ is effected by temperature, hydrogen pressure, dimensions of metal powder and the dimensions of used metals for stirring process. Recent advances are synthesis at lower temperatures with decreased sodium or alkali metal requirements [10]. Today various companies, universities and research laboratories are working to put forward cheaper methods.

1.2. Traditional Methods to Determine $NaBH_4$ Concentrations

As all known, syntheses of $NaBH_4$ with mechano-chemical means are generally produced with the addition of $NaBO_2$ and $Na_2B_4O_7$, with metals or metal hydrides at high hydrogen pressures and temperatures. After this process, $NaBH_4$ is taken from the reaction products with the help of various organics or NH_3. So, determination of $NaBH_4$ at the presence of these additives is extremely important.

Traditional methods to determine the efficiency of synthesized $NaBH_4$ are as follows:

- Titration: Analysis of $NaBH_4$ with titration gives correct results only at a specific pH interval (4-7) which is not the suitable pH alkali ambient that sodium borohydride is resistant to. A method introduced by Lyttle et al. [11] is based on the reaction:

$$3BH_4^- + 4IO_3^- \rightarrow 4I^- + 3H_2BO_3^- + 3H_2O$$

This involves the addition of sample sodium borohydride to the solution which requires a large amount of iodate.

- Process introduced by Brown et al. [12] is based on the reaction of Ag^+ ions with BH_4^- ions in 4% EDA and 40% NaOH solution forming Ag-EDA.

- The electrochemical oxidation of $NaBH_4$ by linear and cyclic voltammetric methods was introduced by Mirkin et al. [13] and was observed it is possible to determine $NaBH_4$ concentrations with the help of the oxidation of it on Au electrode.

These techniques have various disadvantages such as:

-Analysis can only be done with model concentrations of pure $NaBH_4$ and $NaBO_2$.

-The effect of side reactants such as $NaBO_2$, $Na_2B_4O_7$, metal etc. could not be understood.

-The effect of solvent which decomposes $NaBH_4$ from reactant mixture could not be understood.

1.3. Electrochemical Method to Determine $NaBH_4$ Concentration

As all known, ethylendiamine is a suitable material for the extraction of $NaBH_4$ from reactant products since it can dissolve $NaBH_4$ effectively whereas has little or no role to dissolve $NaBO_2$, $Na_2B_4O_7$, catalyst and metal used in the synthesis process. For this reason, to obtain the transformation degree of produced $NaBH_4$, it is necessary to obtain an accurate, fast and correct method to determine its concentration at the presence of EDA.

Literature researches have shown that electrochemical methods [14,15] can be utilizable as a fast and correct method for this process. But no fast and accurate analysis method at the presence of EDA has been put forward.

In this research, various electro-analytic methods have been used to analyze the mechano-chemically synthesized solid $NaBH_4$ concentration taken out from reaction products designated in EDA.

2. EXPERIMENTAL

The electrochemical tests were accomplished with IVIUM Stat mark potentiostat. All tests were made with commonly used electrochemical cell containing three electrodes. The temperatures of cells were controlled by thermostat and it was 26 ^oC. The operating electrodes with smooth active surface radius approximately 1 mm were prior mechanically cleaned (polishing using special polishing paste) and washed with alcohol and distilled water. Prior to the electrochemical experiments, the electrodes were electro activated in a specific potential region. All solutions were prepared in bidistilled water. $NaBH_4$ solutions which have standard concentrations were prepared using Merck mark chemicals. Used $NaBO_2$ and dry $Na_2B_4O_7$ were suitably prepared from the thermic treatment of $NaBO_2.4H_2O$ and $Na_2B_4O_7.10H_2O$. Cyclic voltammetery and linear sweep techniques were used with gold (Au) and platinum (Pt) indicator electrodes for this purpose. It was noted that the most effective measurements were done on Au electrode [16] since catalytic decomposition of $NaBH_4$ is possible at Pt electrode no such decomposition occurs on Au surface. Solutions of NaOH in bidistilled water were used as background electrolyte. Reference electrode was Ag/AgCl, KCl (saturated). To test the effect of additives, $NaBO_2$ and $Na_2B_4O_7$ quantities were kept close to $NaBH_4$ amount whereas EDA quantity was kept dominant in the test samples.

3. RESULTS AND DISCUSSIONS

The periodic volt-ampere cycles of gold electrode used in experiments is shown in figure 1. At the potential range -1.0 / +0.8 V, oxide layer is formed at the surface in anodic half cycle and the desorption of oxygen from the electrode surface occurs at +0.4 / -0.7 V potential interval in cathodic half cycles. Generally, all the cycles taken after cycle number 1 fall closely together.

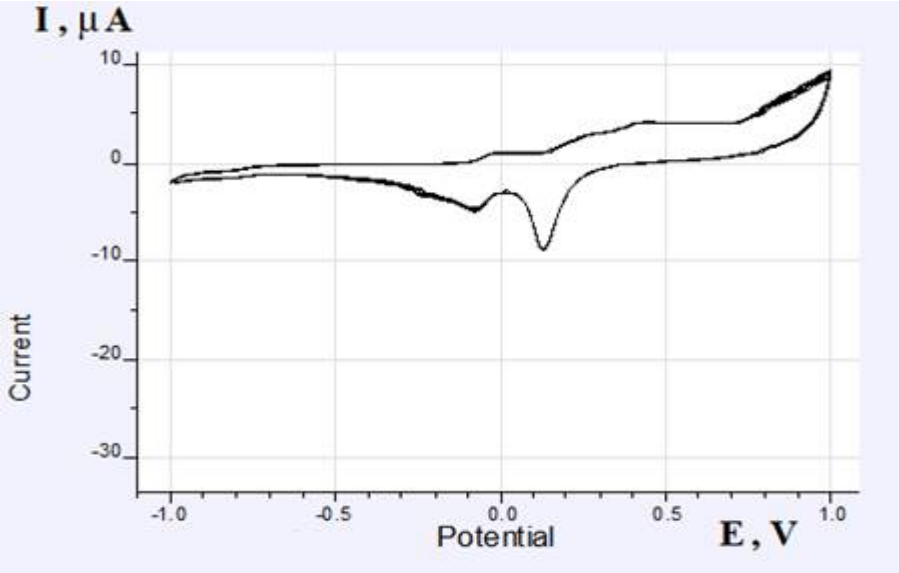

Figure 1. Periodic voltamperometric cycles on Au electrode in 1M NaOH solution (Potential region= -1.0/ +1.0 V, Scan rate: 0.050 V/s).

Mainly, the following reaction of $NaBH_4$ oxidation takes place at the Au electrode in alkali medium:

$$BH_4^- + 8\ OH^- \rightarrow BO_2^- + 6\ H_2O + 8\ e^-$$

Influence of scan rate to the maximum of oxidation of $NaBH_4$ is presented in fig.2

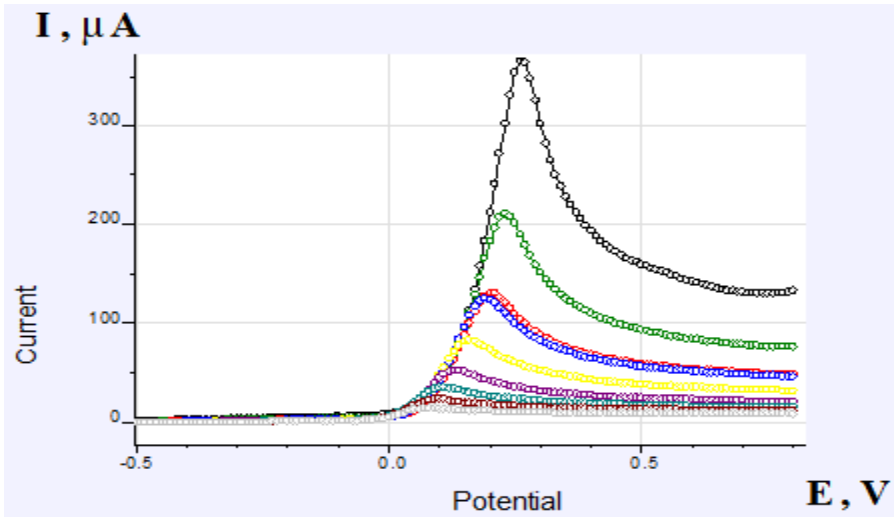

Figure 2. Linear potentiodynamic sweeps of various scan rate values at 2 M NaOH + 10^{-3} M $NaBH_4$ solutions

As is shown in figure 2, with the increase of scan rate, the height of peak maximum (i_p) is increased and shifting of the peak potential to more positive values is observed. The effect of EDA to the $NaBH_4$ concentration is shown in figure 3.

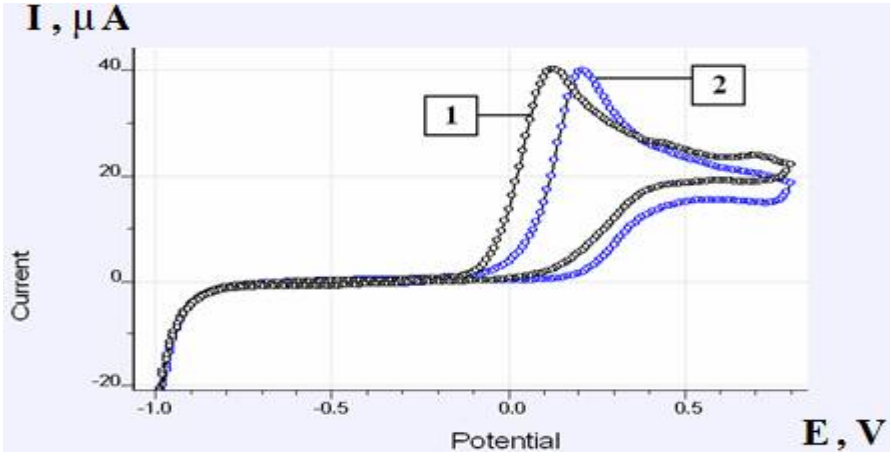

Figure 3. Periodic voltamperometric cycles of (1)10^{-3} M $NaBH_4$, (2) 10^{-3}M $NaBH_4$ + 0,29 M EDA in 2 M NaOH. (Scan Rate: 0.05 V/s)

Table 1. Numerical values of figure 3.

Cycle No	V_{peak} (V)	Current (A)	Charge (C)
1	0.13	3.19×10^{-5}	2.0×10^{-4}
2	0.21	3.02×10^{-5}	1.85×10^{-4}

From table 1, we can see that measured current and charge values slightly change after addition of EDA. The line of log(I) versus log(c) of various $NaBH_4$ concentrations is shown at figure 4. The line plotted with addition of ethylendiamine practically does not change. As seen from figure, with the increase of $NaBH_4$, linearly increase is observed at log scale.

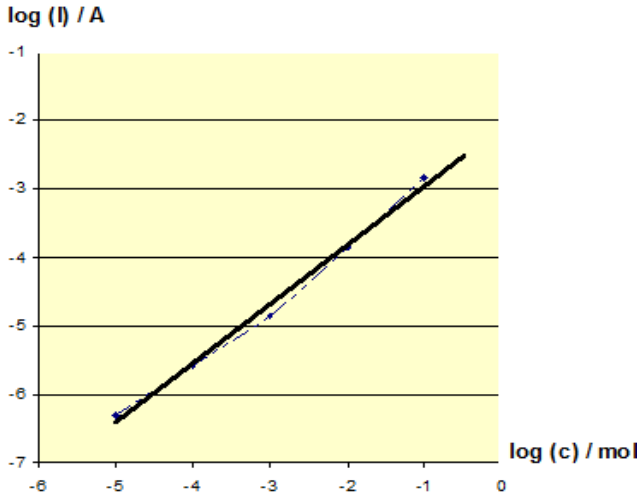

Figure 4. The line shows current values of $NaBH_4$ oxidations to the corresponding $NaBH_4$ concentrations. (Log I /Logc) in 1 M NaOH solution (Scan Rate: 0.05 V/s).

The linear potentiodynamic sweeps of sodium borohydride, $NaBO_2$, and EDA bearing 1 M NaOH solution is shown in figure 5.

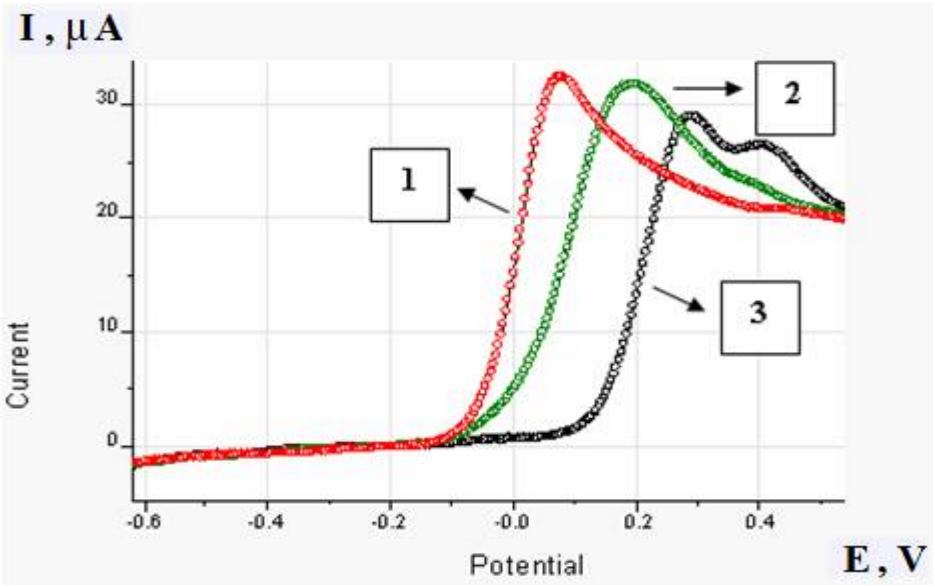

Figure 5. Potentiodynamic sweeps of Au electrode in (1) 10^{-3} M $NaBH_4$, (2) 10^{-3} M $NaBH_4$ + 10^{-3} M $NaBO_2$ and (3) 10^{-3} M $NaBH_4$ + 10^{-3} M $NaBO_2$+ 0.29 M EDA in 1M NaOH (Scan Rate: 0.050 V/s)

Table 2. Numerical values of figure 5.

Cycle No	V_{peak} (V)	Current (A)	Charge (C)
1	0.076	$2.72x10^{-5}$	$1.63x10^{-4}$
2	0.196	$2.40x10^{-5}$	$1.50x10^{-4}$
3	0.288	$1.27x10^{-5}$	$0.278x10^{-4}$

From the values of table 2, we can see that $NaBO_2$ addition to the $NaBH_4$ sample has a slightly decreasing effect on current and charge values.

Also with the addition of $Na_2B_4O_7$ we can see that the oxidation potential of $NaBH_4$ has a slight increase (fig 6). Their values are given in table 3.

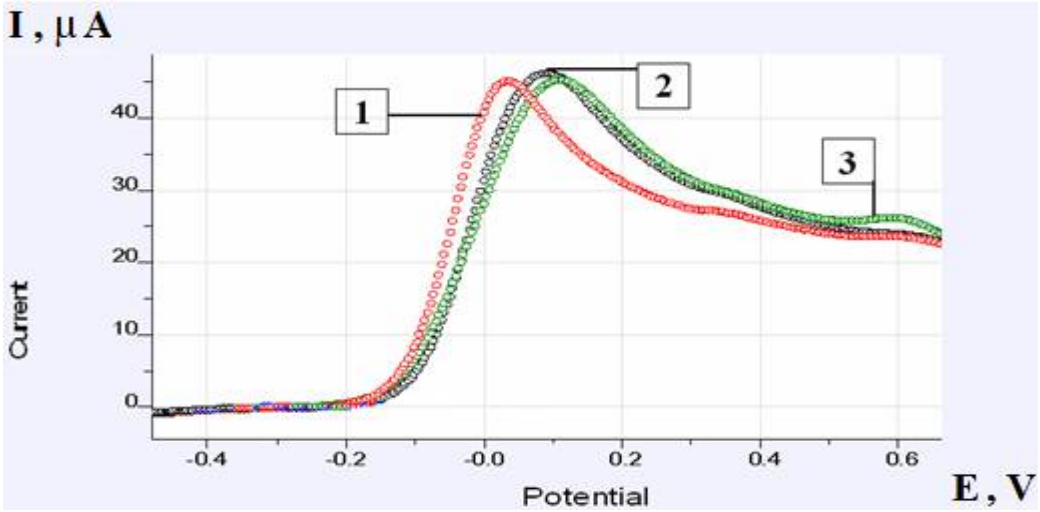

Figure 6. Linear potentiodynamic sweeps of (1) 10^{-3} M $NaBH_4$, (2) + 10^{-3} M $Na_2B_4O_7$, (3) + 0.29 M EDA in 2 M NaOH. (Scan Rate v:0.05 V/s

Table 3. Numerical values of figure 6.

Cycle No	V_{peak} (V)	Current (A)	Charge (C)
1	0.036	3.76×10^{-5}	2.2×10^{-4}
2	0.092	3.93×10^{-5}	2.87×10^{-4}
3	0.112	3.45×10^{-5}	2.14×10^{-4}

4. CONCLUSIONS

Proceeding from our measurements, we can conclude the followings:

Au electrode gives repeatable results on the oxidation of $NaBH_4$;

Presence of $NaBO_2$ and $Na_2B_4O_7$ compounds have small effect on the electro-oxidation of sodium borohydride on Au electrode but this does not create an obstacle to determine $NaBH_4$ concentrations even at very low values such as 10^{-4} M.;

The difference in the molarity of the background electrolyte particularly has a small effect on the V_{peak} values but does not contribute any obstacle to observe the effect of additives and consequently the concentration of $NaBH_4$;

This method is effective when ethlendiamine is used as solvent to remove $NaBH_4$ from reaction products.

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ВЛИЯНИЕ РАЗЛИЧНЫХ ДОБАВОК НА ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ БОРОГИДРИДА НАТРИЯ НА ЗОЛОТОМ ЭЛЕКТРОДЕ

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В настоящей статье представлены результаты исследования влияния различных добавок, таких как $NaBO_2$, $Na_2B_4O_7$ и этилендиамин (EDA) на окисление $NaBH_4$. По результатам проведенного исследования предлагается метод определения концентрации механохимически синтезированного $NaBH_4$. Показано, что линейный потенциодинамический (LPD) и циклический вольт-амперометрический (CV) методы можно применять в качестве простых, чувствительных и точных методов анализа. Отмечается, что соединения EDA, $NaBO_2$ и $Na_2B_4O_7$ не мешают количественному определению $NaBH_4$.

***Ключевые слова**: борогидрид натрия, синтез, определение, добавки, циклическая вольтамперометрия.*

NATRİUM BOROHİDRİDİN QIZIL ELEKTROD ÜZƏRİNDƏ ELEKTROKİMYƏVİ ÇEVRİLMƏSİNƏ MÜXTƏLİF ƏLAVƏLƏRİN TƏSİRİ

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Natrium borohidridin qizil elektrod üzərində elektrokimyəvi oksidləşməsinə $NaBO_2$, $Na_2B_4O_7$ və etilendiamin kimi əlavələrinin təsiri öyrənilmişdir. Tədqiqatın nəticələrinə əsaslanaraq göstərilib ki, $NaBH_4$ miqdarını xətti potensiodinamik və tsiklik voltampeometrik metodları ilə təyin etmək olar və bu zaman $NaBO_2$, $Na_2B_4O_7$ və etilendiamin natrium borohidridin təyininə mane olmur.

***Açar sözlər:** natrium borohidrid, sintez, əlavələr, tsiklik voltampeometrik metodu.*

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