Anodic behavior of Ag metal electrode in direct borohydride fuel cells

Elif Sanlıa, Hüseyin Çelikkanb, B. Zühtü Uysalb, M. Levent Aksuc, *

a Department of Chemical Engineering, Faculty of Engineering and Architecture, Gazi University, Ankara, Turkey
b Department of Chemistry, Faculty of Science, Gazi University, Ankara, Turkey
c Department of Chemistry Education, Faculty of Education, Gazi University, Ankara, Turkey

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Abstract

The performance of alkaline borohydrides on Ag anode was tested in a three-electrode system in this research. The anode compartment was separated from other compartments by Nafion 117 membranes. It was observed that the cell potential increased with increasing BH$_4^-$ concentration. When CV graphs of clean and oxidized Ag surfaces were examined and it was determined that Ag oxide layers formed on the Ag surfaces in alkaline media had different catalytic effects on the oxidation of borohydride. The number of electrons transferred was found as 6 (5.55) after coulometric studies.

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1. Introduction

Fuel cells are batteries which convert chemical energy into electrical energy. They are the strongest candidates for alternative power generators of future. They can be used in diverse ways, as small portable models to constant power generators.

The potential of a fuel cell changes according to the anode material employed. The theoretical cell potential in hydrogen fuel cells is $E = -1.24$ V due to protide (H$^0$)–proton (H$^+$) conversion. In BH$_4^-$ fuel cells the theoretical cell potential goes up to $E = -1.64$ V due to protonium (H$^-$)–proton (H$^+$) conversion [1].

In aqueous media, the hydrolysis and oxidation reactions of BH$_4^-$ are in competition. The critical factor which determines the appropriate mechanism is the anode material. The anodic behavior of a metal and alloy is dependent upon its surface characteristics. Since
oxidation of borohydrides is carried out in highly alkaline media, the metal oxides and hydroxides formed upon the surface must also be taken into account [2]. There are numerous studies related to the formation of various oxides on Ag electrode in alkaline media. Pound et al. [3] claimed the formation of Ag$_2$O at lower (between +50 and 500 mV(SHE)) and Ag$_2$O$_2$ at higher anodic potentials (above 600 mV(SHE)) in 1 N KOH. Miller [4] reported that the surface is totally covered with Ag$_2$O as a result of the reduction of Ag$_2$O$_2$. Burstein and Newman [5] claimed that the surface is covered with a AgOH film between −600 and −500 mV (SHE) and this film is converted into Ag$_2$O starting from +50 mV (SHE) and above 500 mV(SHE) the film takes a multilayered nature. It was also claimed that Ag gives unstable oxides such as AgO$_3$ and Ag$_3$O$_4$ in the presence of oxy anions and unstable hydroxides such as Ag(OH)$_2$ in weak-alkaline and Ag(OH)$_4$ in strongly alkaline media [6,7]. Orozco et al. [8] reported that Ag(II) oxide was effective in the oxidation of methanol.

The electrocatalytic material for hydrogen evolution in borohydride fuel cells are generally noble metals such as Pt, Pd and Au and metal oxides such LiCoO$_2$, TiO$_2$, Ti$_2$O$_3$. The studies related to the use of Ag metal or its oxides in fuel cells are highly scarce [9].

In borohydride fuel cells, there are systems where different metal and metal alloy cathodes are used [10,11]. Ag is used also as cathode material [12]. However, there are no studies related to the use of Ag as anode material.

This study is related to the use of Ag metal as an anode material in alkaline borohydride fuel cells.

2. Experimental

A three-compartment cell was used for electrochemical measurements. The compartments were separated from each other by Nafion 117 membranes. The cell is depicted in Fig. 1.

Cyclic voltammograms were taken using Ag disc electrode by changing the concentration of NaOH and NaBH$_4$.

All the electrochemical measurements were taken by computer-controlled CH Instruments 660B potentiostat. The reference electrode was an oxidized Ag wire immersed working solution (pseudo-reference electrode). The counter and working electrodes were spiral Pt wire (BAS) and Ag disc electrode mounted in Teflon (BAS). The cyclic voltammograms were taken at a scan rate of 50 mV/s. The surface of the Ag working electrode was oxidized by scanning the electrode in a specified potential range.

The oxidized and clean Ag electrodes (polished with 1200 sand paper) were subjected to cyclic voltammetric potential scans using different NaOH and NaBH$_4$ concentrations.

The number of electrons transferred was determined coulometrically using 0.01 M NaBH$_4$ concentration at a potential of 0.45 V applied between the Ag pseudo-reference electrode and Ag spiral wire working electrode which is electrochemically oxidized at the same potential in NaOH solution before use. The use for the spiral wire working electrode was to increase the surface area since coulometric studies require enlarged surface area.

3. Results

The cyclic voltammetric curves of NaBH$_4$ at different concentrations taken at a scan rate of 50 mV/s in an alkaline media using Ag disc electrode are depicted in Fig. 2. It is seen that the peak currents increase with the increasing borohydride concentration. The oxidation mainly takes place upon multilayered Ag$_2$O.

Plotting peak currents against borohydride concentration gives a straight line (Fig. 3). This shows that cyclic voltammetry is a versatile technique to determine the borohydride concentration in the solution.

Fig. 4 shows the cyclic voltammetric curves of 0.1 M NaBH$_4$ in 3 M NaOH taken with oxidized and clean Ag electrode. It is obvious that the oxidation behavior of borohydride is markedly different on these electrodes. The peak observed at around 0.15 V belongs to the oxidation of borohydride on multilayered catalytic Ag.
Fig. 2. The cyclic voltammetric curves of NaBH₄ at different concentrations taken at a scan rate of 50 mV/s in an alkaline media using Ag electrode.

Fig. 3. The change of peak currents against NaBH₄ concentration.

Fig. 4. The cyclic voltammograms of 0.1 M NaBH₄ in 3 M NaOH taken with oxidized and clean Ag electrode.

Fig. 5. Cyclic voltammograms of 0.1 M NaBH₄ in 6 M NaOH taken with oxidized and clean Ag electrode.

Fig. 6. The cyclic voltammograms with and without 0.1 M NaBH₄ in 0.1 M NaOH.

The hunches observed at −0.2 and 0.4 V are most probably the pre- and post-peaks due to adsorption of product and the reactant.

The increase in NaOH concentration also caused significant changes in the oxidation behavior of borohydride on clean and oxidized electrodes (Fig. 5). This may be due to the increase in the thickness of the catalytic Ag oxides.

Fig. 6 shows the electrochemical behavior of NaBH₄ at low NaOH concentration (0.1 M). If we compare this figure with the ones taken at higher NaOH concentrations (Figs. 7 and 8), the effect of low NaOH concentration upon the oxidation of borohydride is minimal (Fig. 6) due to the lack of the formation of catalytic Ag oxides.
However, the increase in pH, i.e., NaOH concentration causes incredible change in the rate of the oxidation of NaBH\(_4\) (Figs. 7 and 8). The oxidation takes place around 0.2 V against pseudo-Ag reference electrode which corresponds to the formation of multilayered Ag oxide.

The number of electrons was calculated by the use of coulometry and Faraday law as 6 (5.55) (Fig. 9). The following reaction can thus be suggested.

\[
\text{Ag}_2\text{O} + \text{BH}_4^- + 6\text{OH}^- \rightarrow 2\text{Ag} + \text{BO}_2^- + 5\text{H}_2\text{O} + 6\text{e}^-
\]

4. Conclusions

It is obvious that the oxides formed upon Ag surface have catalytic effect on the oxidation of borohydride. The coulometric analysis gave the number of electrons during the electrolysis reaction as 5.55 (~6e). It is clear that Ag is a highly suitable material as an anode material for direct borohydride fuel cells.

Based on the number of electron transferred, we can propose the following mechanism for the oxidation of sodium borohydride.

\[
\text{Ag}_2\text{O} + \text{BH}_4^- + 6\text{OH}^- \rightarrow 2\text{Ag} + \text{BO}_2^- + 5\text{H}_2\text{O} + 6\text{e}^-
\]

According to this mechanism the high hydroxide concentration oxidizes the metal to Ag\(_2\)O again and there is no loss of catalytic Ag\(_2\)O on the surface. This reaction takes place at 0.1–0.2 V.

When the effect of Ag as an anode material for the electrooxidation of organic compounds was investigated by the use of CV data, it was found that the way the electrode was prepared, number of scans, scan rate and the structure of the organic compounds had different effects on the electrooxidation process, as also reported elsewhere [13–16].

The operation of direct methanol fuel cell (DMFC) with the use of Ag anode is similar to the oxidation of NaBH\(_4\). It is observed that the oxidation takes place at the positive potential where Ag oxide is formed. This verifies the electrocatalytic properties of Ag oxides reported by Orozco et al. [8].

The most appropriate NaOH concentration was found to be 6.0 M. The oxidation reaction of NaBH\(_4\) seems to be promoted at high pH values due to formation of multilayered oxide film (Ag\(_2\)O) upon the surface which is also in good accordance with the literature [17].

References


