

Anodic behavior of Ag metal electrode in direct borohydride fuel cells

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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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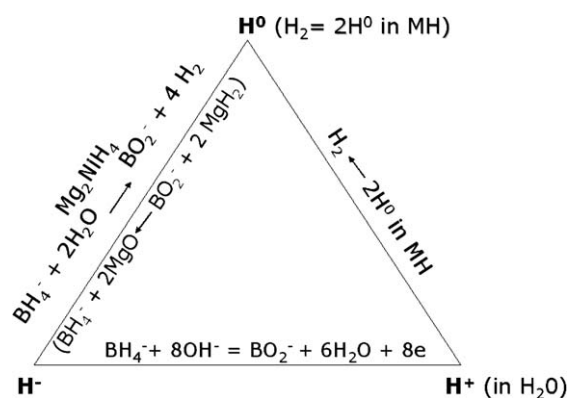
Keywords: Borohydride fuel cells; Ag anode; Catalytic effect

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 $E = -1.24 \text{ V}$ due to protide (H^0)–proton (H^+) conversion. In BH_4^- fuel cells the theoretical cell potential goes up to $E = -1.64 \text{ V}$ due to protonium (H^-)–proton (H^+) conversion [1].

The hydrogen energy conversion systems can be summarized as follows:



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

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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_2O at lower (between +50 and 500 mV(SHE)) and Ag_2O_2 at higher anodic potentials (above 600 mV(SHE)) in 1 N KOH. Miller [4] reported that the surface is totally covered with Ag_2O as a result of the reduction of Ag_2O_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_2O 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_3O_4 in the presence of oxy anions and unstable hydroxides such as $\text{Ag}(\text{OH})_2$ in weak-alkaline and $\text{Ag}(\text{OH})_4$ 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 fuels cells are generally noble metals such as Pt, Pd and Au and metal oxides such LiCoO_2 , TiO_2 , Ti_2O_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.

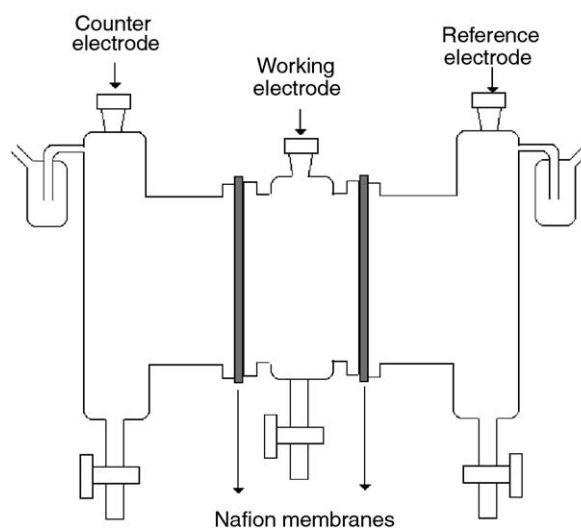


Fig. 1. The electrochemical cell used in the study.

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_2O .

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

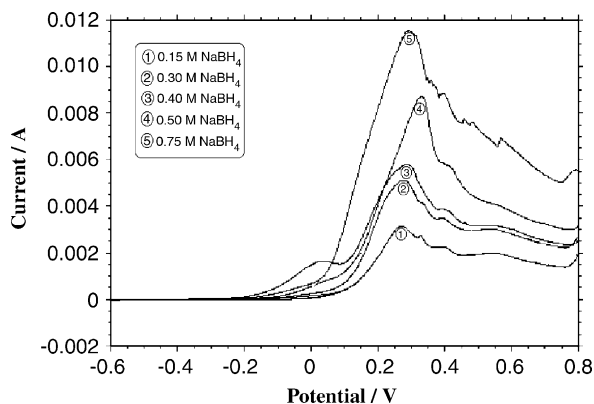


Fig. 2. The cyclic voltammograms of NaBH_4 at different concentrations taken at a scan rate of 50 mV/s in an alkaline media using Ag electrode.

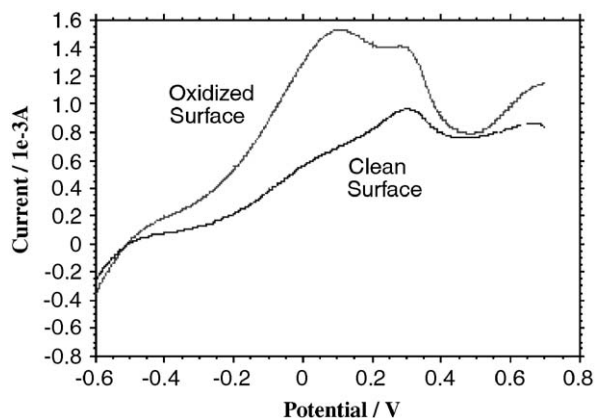


Fig. 5. Cyclic voltammograms of 0.1 M NaBH_4 in 6 M NaOH taken with oxidized and clean Ag electrode.

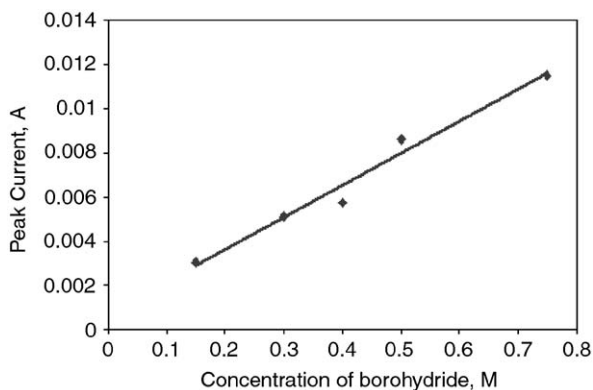


Fig. 3. The change of peak currents against NaBH_4 concentration.

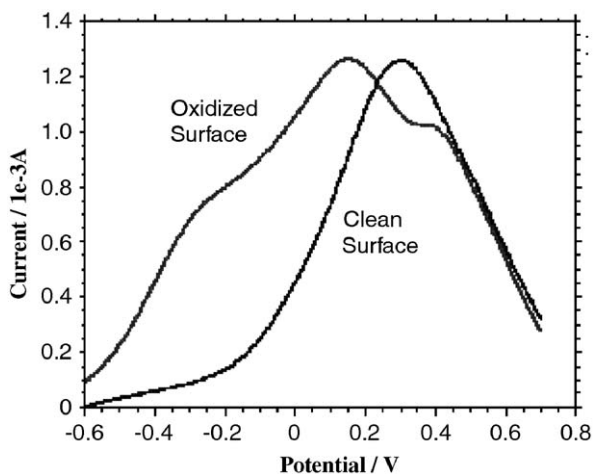


Fig. 4. The cyclic voltammograms of 0.1 M NaBH_4 in 3 M NaOH taken with oxidized and clean Ag electrode.

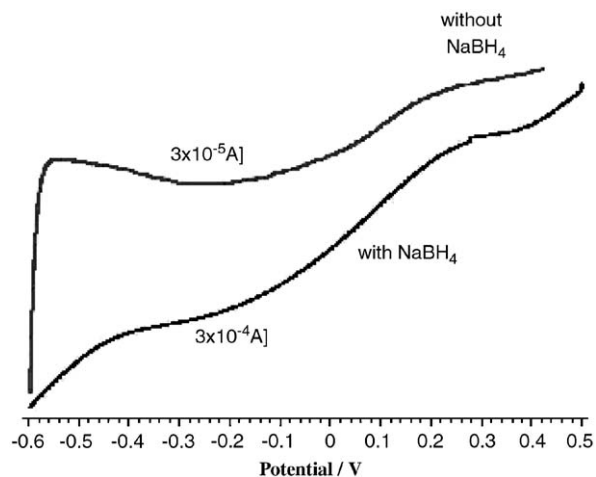


Fig. 6. The cyclic voltammograms with and without 0.1 M NaBH_4 in 0.1 M NaOH .

oxides. 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 NaBH_4 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.

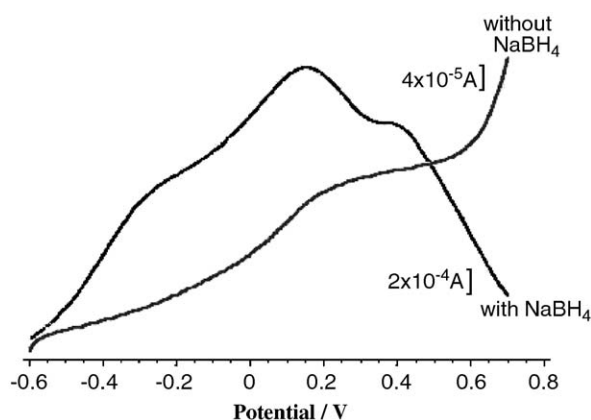


Fig. 7. The cyclic voltammograms with and without 0.1 M NaBH₄ in 3.0 M NaOH.

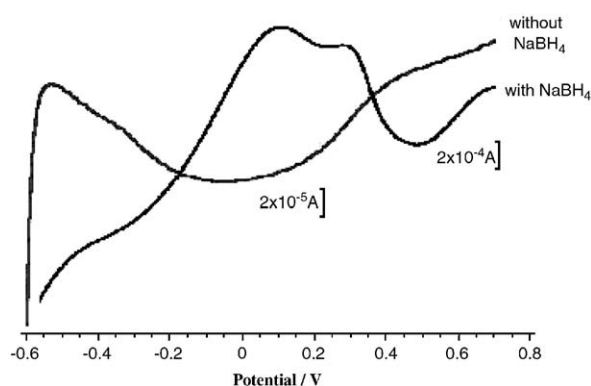


Fig. 8. The cyclic voltammograms with and without 0.1 M NaBH₄ in 6.0 M NaOH.

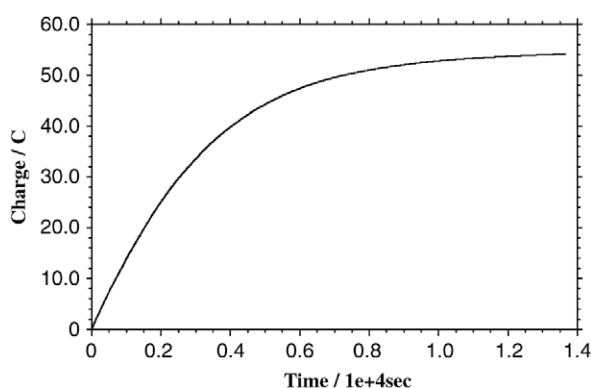
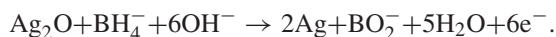


Fig. 9. The coulometric curve taken at 0.45 V for 0.01 M NaBH₄ in 3.0 M NaOH.

However, the increase in pH, i.e., NaOH concentration causes incredible change in the rate of the oxidation of NaBH₄ (Figs. 7 and 8). The oxidation takes place around 0.2 V against pseudo-Ag reference

electrode which corresponds to the formation of multi-layered Ag oxide.

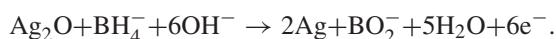
The number of electrons was calculated by the use of coulometry and Faraday law as 6 (5.55) (Fig. 9). The following reaction can thus be suggested.



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 ($\approx 6\text{e}$). 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.



According to this mechanism the high hydroxide concentration oxidizes the metal to Ag₂O again and there is no loss of catalytic Ag₂O 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 NaBH₄. 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 NaBH₄ seems to be promoted at high pH values due to formation of multilayered oxide film (Ag₂O) upon the surface which is also in good accordance with the literature [17].

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