Available online at www.sciencedirect.com

SCIENCE DIRECT®

Electrochimica Acta 49 (2004) 3097–3105

ELECTROCHIMICA Acta

www.elsevier.com/locate/electacta

Electrocatalysts for the anodic oxidation of borohydrides

Bin Hong Liu*, Zhou Peng Li, Seijirau Suda

Department of Environmental and Chemical Engineering, Kogakuin University, Hachioji, Tokyo 192-0015, Japan

Received 3 October 2003; received in revised form 19 January 2004; accepted 10 February 2004

Abstract

Anodic performances of alkali borohydrides on several electrocatalysts such as Ni, Raney Ni, Pd, Pt, Cu, Au have been studied in an effort to develop suitable electrode materials for a borohydride-fueled fuel cell. The open-circuit potentials (OCPs), polarization performances, and hydrogen evolution behaviors were examined in a three-electrode system. The open-circuit potential was found to be dependent on borohydride concentration and also influenced by the electrocatalyst. In concentrated borohydride solutions used in this work, electrode polarizations were less influenced by the fuel concentration. Borohydrides on different electrocatalysts showed different hydrogen evolution behaviors. The relation of hydrogen evolution rate with the anode current was found to change not only with the concentration of borohydride and but also with the electrode material. Comparison of anodic behaviors of borohydride on different electrodes implies that the anodic oxidation of borohydride, as a multi-step process, may take different reaction paths, depending on the electrocatalyst and reaction conditions such as the borohydride concentration.

Keywords: Borohydride; Anodic oxidation; Open-circuit potential; Polarization; Hydrogen evolution

1. Introduction

The increasing demand for efficient and clean power sources has greatly stimulated the research and development of fuel cells in recent years. Fuel cells are not only of interest in some large scale applications, but also being considered as power sources for portable machines such as lap-top computers and cellular phones. In these applications portable fuel sources are required. Currently the direct methanol fuel cell (DMFC) is attracting considerable attention as the fuel cell for portable applications [1]. However, it usually shows low cell voltage and power density. The poor anode performance of methanol requires heavy loading of noble metals like Pt or Pt–Ru alloy as the catalyst. On the contrary, aqueous solutions of alkali borohydrides (MBH_4, M: Li, Na, K) as another liquid-type fuel have high reactivity and non-precious materials like Ni and Cu are good enough to catalyze their anodic reactions [2,7]. In theoretical calculations, the standard potential of borohydrides is 0.43 V more negative than that of methanol in an alkaline environment. With similar energy densities as methanol, borohydrides are thus expected to provide higher cell voltage and power density.

Although the anodic oxidation of borohydrides is postulated as follows:

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e, \quad E^\circ = -1.24\,V \tag{1}$$

This reaction is barely found to happen in practice because the anodic reactions on electrodes have to compete with the hydrolysis reaction as follows:

$$BH_4^- + 2H_2O = BO_2^- + 4H_2 \tag{2}$$

The actual anodic reaction will be as follows:

$$BH_4^- + xOH^- = BO_2^- + (x-2)H_2O + (4 - \tfrac{1}{2}x)H_2 + xe \tag{3}$$

x here represents the actual number of the electrons released by each BH_4^- ion and it is called columbic number in following paragraphs.

It was reported by Indig and Snyder [2] that on a porous nickel electrode the anodic reaction was a 4e reaction, corresponding to $x = 4$ in the above formula. Kubokawa et al. [3] reported a 6e reaction on a Pd-coated carbon electrode.

---

* Corresponding author.
E-mail address: bp97002@ns.kogakuin.ac.jp (B.H. Liu).

0013-4686/$ – see front matter © 2004 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2004.02.023

Table 1
Details of the tested electrodes

Electrode	Ni	Raney Ni	Cu	Au	Pd	Pt
Powder	Inco type210 1.0 g	Raney Ni 0.01 g	Cu (10 μm) 1.0 g	Au (5 μm) 1.0 g	Pd/C (Pd 10 wt.%) 0.4 g (Pd 40 mg)	Pt/C (Pt 5 wt.%) 0.4 g (Pt 20 mg)
PTFE (g)	0.05		0.05	0.05	0.1	0.05
Area (cm^2)	5	1.5	5	5	5	5

Elder and Hickling [4] found that on a Pt electrode the columbic number is between 2 and 4. And Amendola et al. [5] reported a 7e reaction on an Au electrode.

In a previous paper, we made a detailed study on the anodic oxidation of borohydride catalyzed by a nickel electrode and also found a 4e anodic reaction [6]. In this work, we studied the electrochemical performances of borohydrides on several electrocatalysts including Ni, Raney Ni, Pd, Pt, Au, Cu in an effort to select proper anode material for a borohydride-fueled fuel cell. We also hope to clarify the reaction mechanism of borohydride oxidation by comparison of anodic behaviors on these electrodes.

2. Experimental

The electrodes were made by first thoroughly mixing and grinding metal or carbon-supported noble metal powders with polytetrafluoroethylene (PTFE) powder, then pasting the mixture on a nickel foam with a size of 2.5 cm × 2 cm and then enveloping it using a 100 mesh nickel net, and finally roller-pressing. A blank test showed that the effect of nickel foam and net supporter on electrochemical performance of electrodes was negligible. Metal powders used in the experiment had purities at least more than 99%. The Raney Ni electrode was made of a Ni foam on which a layer of Raney Ni was formed. The details of electrodes are described in Table 1.

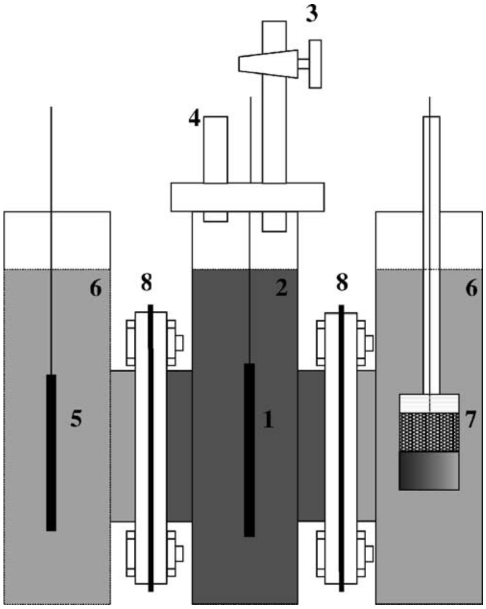


Fig. 1. Schematic diagram of the experiment set-up: (1) anode, (2) anolyte, (3) anolyte inlet, (4) H_2 gas outlet, (5) cathode, (6) 6 M KOH or 6 M NaOH electrolyte, (7) Hg/HgO reference electrode, and (8) Nafion 117 membrane.

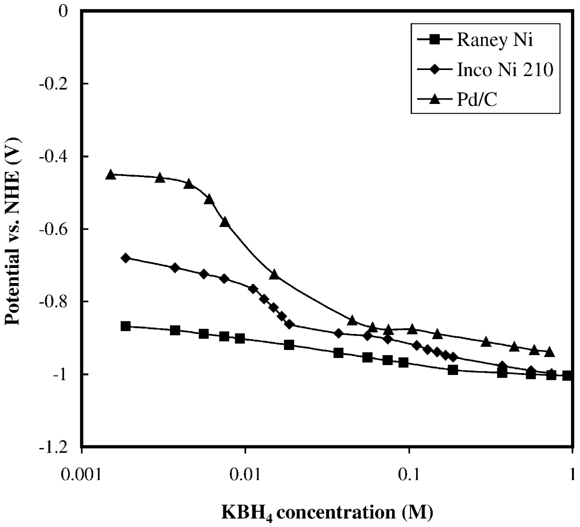


Fig. 2. Dependence of the open-circuit potential on the borohydride concentration for three electrodes at 293 K.

Anodic performances of borohydrides on the electrocatalysts were tested in a three-electrode system shown in Fig. 1. The anode was put in the middle compartment and the counter electrode and reference electrode were put in the outside compartments, respectively. The anode compartment was separated from other compartments by Nafion 117 membranes. The anode had a distance of 3.3 cm with the cathode and with the center of the reference electrode. The anolyte was prepared by dissolving $NaBH_4$ in 100 ml 6 M NaOH or KBH_4 in 100 ml 6 M KOH. The electrolyte in outside compartments was correspondingly 6 M NaOH or 6 M KOH.

Table 2
Open–circuit potentials exhibited on different electrodes at 293 K in a 2.4 M $NaBH_4$ solution

Electrode	OCP vs. NHE (V)
Ni	−1.03
Raney Ni	−1.03
Cu	−1.02
Au	−0.99
Pd/C	−0.91
Pt/C	−0.91

The cathode was a metal hydride electrode and a Hg/HgO electrode was used as the reference electrode. Open-circuit potentials (OCPs) of electrodes at different borohydride concentrations were measured by immersing the electrodes in the solution until the potential became stable within 10 min. Polarizations were recorded when anodic currents passed the electrode and at the same time hydrogen evolved from the anode was collected and the volume was converted into the value at the standard temperature and pressure (STP), then the hydrogen evolution rate was calculated.

3. Results

3.1. Open-circuit potentials

The open-circuit potentials of the anodes were found to depend on the concentration of borohydride in the solution. Fig. 2 shows the relation of OCP with the BH_4^- concentration in a KBH_4/6 M KOH solution for three electrodes. It can be seen that a step appeared in the OCP curve both for the Ni powder electrode and the carbon-supported Pd electrode while the Raney Ni electrode did not show such behavior and its OCP linearly changed with the logarithm of the borohydride concentration. We suppose the step in the OCP curves was related to a change in surface states. Below one certain level of BH_4^- concentration, the surface of electrodes remained in a passive state. When the concentration of borohydride was increased, the surface oxide or hydroxide was reduced by the borohydride and then activated. The potential then reflected the real anode potential of borohydride.

The OCP was also a little influenced by the electrocatalysts. Table 2 shows the OCPs in a 2.4 M $NaBH_4$ solution for different electrodes. It seems that the Ni and Raney Ni electrode exhibited the most negative potential, followed by

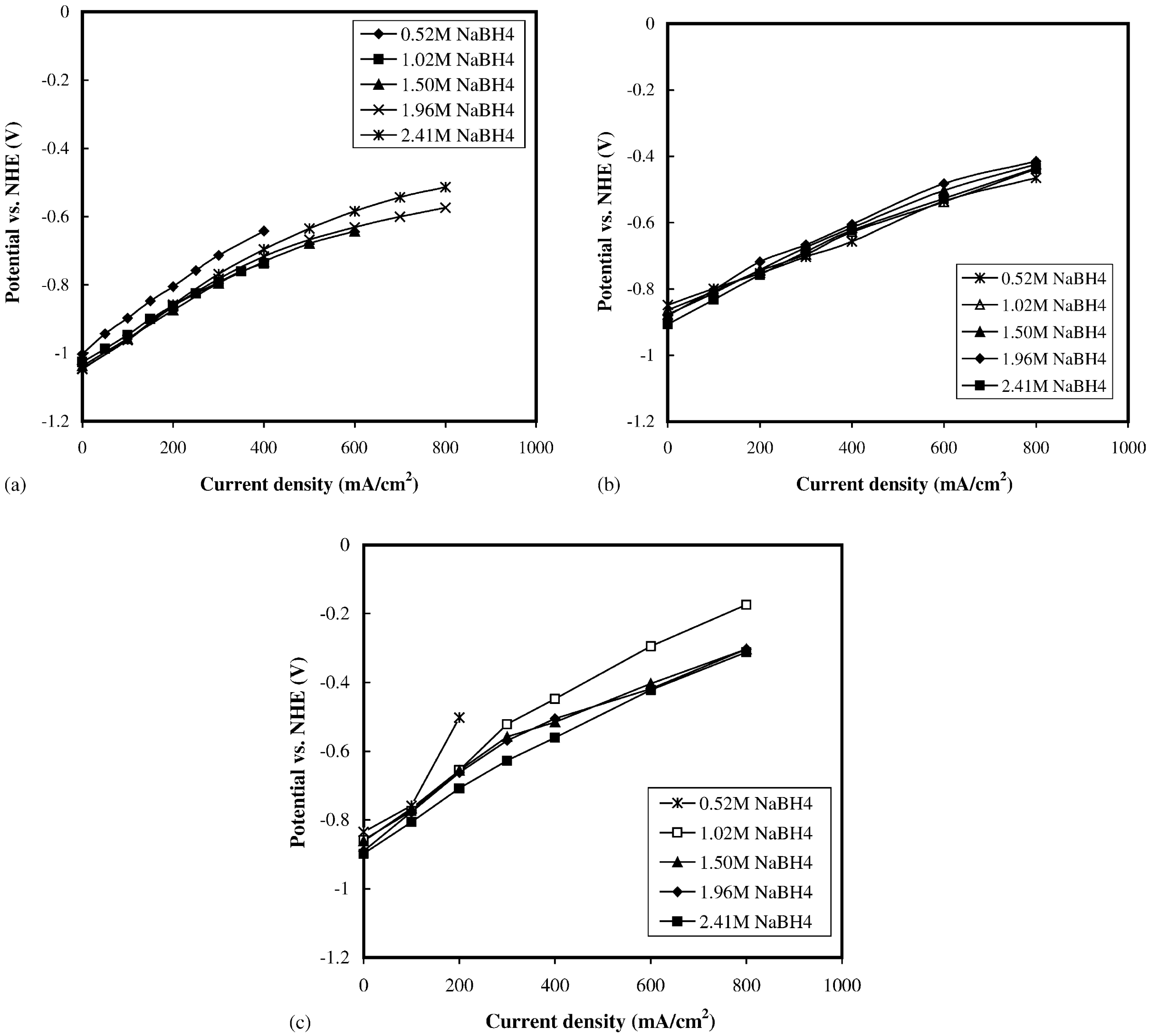


Fig. 3. Polarization curves for the (a) Ni electrode at different borohydride concentrations at 303 K; (b) Pd/C electrode at different borohydride concentrations at 303 K; and (c) Pt/C electrode at different borohydride concentrations at 303 K.

Cu, Au, Pt, and Pd. The observed OCPs were all less negative than the calculated standard potential of the reaction (1) but more negative than the hydrogen potential. The less negative potential is supposed to be caused by the presence of some intermediate oxidation products of BH_4^-, especially atomic hydrogen generated by the reaction (2). The carbon-supported Pd and Pt electrodes showed less negative potentials than other electrodes like Ni and Cu. The slight differences among the observed potentials on different electrocatalysts may be resulted from different anodic oxidation mechanisms, which will be discussed in the following section.

3.2. Polarization

Fig. 3 shows the polarization behaviors of borohydride on different electrodes. From the figure, it can be seen that the polarizations on these electrodes changed little with the increase of the borohydride concentration in the concentrated solutions. This result differs from our previous observation that in dilute solutions the polarization on the Ni electrode was largely dependent on borohydride concentration [6]. It seems that the polarization became stable when the borohydride concentration was increased to a certain level. This has a practical meaning because stable cell voltage can be achieved if the anode polarization is not so sensitive to the fuel concentration.

Although the polarization did not change much when the borohydride concentration varied from 0.5 to 2.4 M, maximum currents were observed at relatively low borohydride concentrations for the Ni, Cu, and also Pt electrode. The occurrence of maximum current behavior is usually attributed to the limitation of mass transfer. However, in this case it is also possible that the phenomenon was caused by a formation of oxide film on the electrode surface. When the potential goes into the range in which a surface oxidation reaction occurs, the surface will be oxidized and the anodic oxidation of borohydride could not continue without the active electrocatalyst. Therefore, there would not be stable anodic current beyond certain potential levels.

At a polarization current density of 100 mA/cm^2, as can been seen in Fig. 3(a), the potential of the Ni electrode was still be more negative than the hydrogen potential, while this was not the case for the carbon-supported Pd and Pt electrode.

3.3. Hydrogen evolution

One of the most important features for selecting the electrode material for anodic oxidation of borohydrides is to decrease the evolution of gaseous hydrogen because hydrogen evolution not only reduces fuel efficiency but also cause other problems such as safety problem of the fuel. In this work, we made observations on how the hydrogen evolution rate changed with the anode current at different borohydride concentrations on these electrodes. Fig. 4(a) shows the relations of hydrogen evolution rate with anodic current at different $NaBH_4$ concentration levels on the Ni electrode. The hydrogen evolution rate first kept or a little decreased and then increased with increasing the anodic

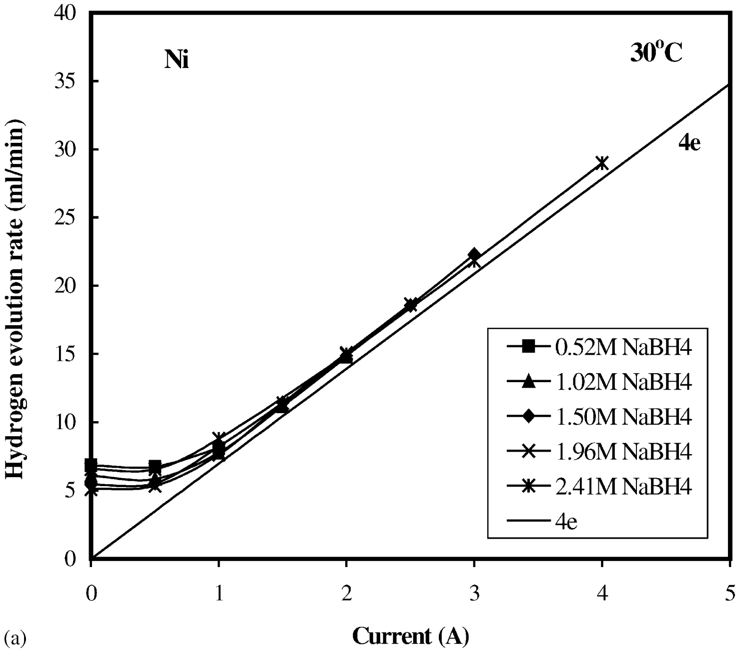
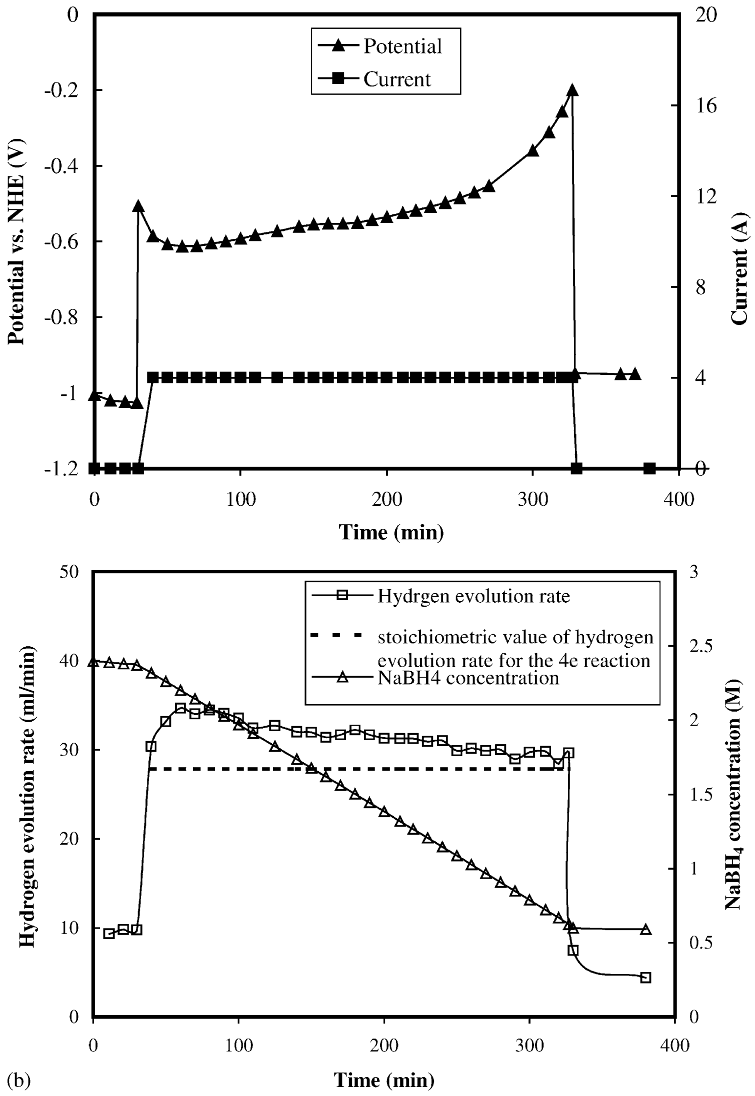


Fig. 4. (a) Relation of the hydrogen evolution rate with the anode current at different borohydride concentration levels for the Ni electrode at 303 K. (b) Changing of the potential, hydrogen evolution rate and borohydride concentration with the time when an anode current of 4 A was exerted on the Ni electrode in a 2.4 M borohydride solution at 303 K.



(b)

Fig. 4. (*Continued*).

current. Finally they fell into the stoichiometric relation of the 4e reaction (corresponding to $x = 4$ in Eq. (3)). Increasing the initial concentration of borohydride led to an increase of limiting current but did not change the 4e relation. Fig. 4(b) shows the changing of hydrogen evolution rate with the time at a constant anode current of four ampere. Because of the limited volume of 110 ml for the fuel, the borohydride concentration decreased with the time. The actual borohydride concentration in the solution was calculated from the obtained electricity and collected hydrogen gas according to the reactions (1) and (2). Although the BH_4^- concentration continuously decreased from 2.4 M at the start to about 0.6 M at the end, the hydrogen evolution rate kept near the stoichiometric value of the 4e reaction. It can be concluded that the anodic oxidation of borohydride on the nickel electrode was essentially the 4e reaction within the concentrations of borohydride used in this work.

On the other side hydrogen evolution was more complicated on the Pd and Pt electrode. Fig. 5(a) shows the hydrogen evolution behavior on the carbon-supported Pd electrode. The hydrogen evolution rate first showed an obvious decrease but finally turned to increase again with the increase of the current. When the BH_4^- concentration was lower than 1.5 M, the hydrogen evolution rate and the current had a relation near to a 6e reaction. However, when the BH_4^- concentration became higher, the relation changed to a 4e reaction. Fig. 5(b) shows the changing of hydrogen evolution rate with the time at a constant current of 4 A on the Pd electrode. It can be seen that the hydrogen evolution rate decreased continuously with the time and did not show a definite stoichiometric relation with the current. It may rather be dependent on the actual concentration of borohydride in the solution as they showed a parallel relation in Fig. 5(b).

Fig. 6(a) shows the relation of hydrogen evolution rate with the current on a carbon-supported Pt electrode. Similar to the Pd electrode, the hydrogen evolution rate showed a changing relation with the current at different BH_4^- concentration levels. It is interesting to note that hydrogen evolution decreased and almost ceased at large currents when the BH_4^- concentration was less than 1.5 M. The anodic reaction appeared to be near the ideal 8e reaction. However, the electrode potentials at these large currents were not so negative. When the borohydride concentration was further increased to more than 1.5 M, a complete stop of hydrogen evolution did not happen before it turned to increase with increasing the current. Fig. 6(b) shows a prolonged anodic oxidation of 4 A on the Pt electrode. It can be seen that higher initial concentrations of BH_4^- led to larger hydrogen evolution rate, corresponding to Fig. 6(a). However, hydrogen was generated at the same rate during the period though the BH_4^- concentration kept decreasing with the time. It seems that in this case hydrogen generation rate depended on the initial BH_4^- concentration rather than the actual concentration at the time. Compared with that on the Pd electrode, the Pt electrode showed different behavior in this aspect.

Similar to the Ni electrode, the 4e reaction was found to happen on the Raney Ni and Cu electrode. In a 2.4 M borohydride solution, the Au electrode showed a 4.5e stoichiometric relation with the current.

4. Discussion

The electrochemical oxidation of borohydride is supposed to be a stepwise process [4], complicated by a stepwise hydrolysis reaction [8]. Therefore, there may exist several intermediates and different reaction routes for the oxidation of borohydride. For example, Elder and Hickling [4] proposed the following reaction scheme for the anodic behavior of borohydride on a smooth platinum electrode:

- initial step

$$BH_4^- + Pt - 2e \rightleftharpoons Pt\cdots BH_3 + H^+ \tag{4.1}$$

$$Pt\cdots BH_3 + OH^- \rightarrow Pt\cdots BH_3OH^- \tag{4.2}$$

- rate-determining step

$$Pt\cdots BH_3OH^- - 2e \rightarrow Pt\cdots BH_2OH + H^+ \tag{4.3}$$

$$Pt\cdots BH_2OH + H_2O \rightarrow Pt + BH_2(OH)_2^- + H^+ \tag{4.4}$$

- slow hydrolysis

$$Pt\cdots BH_3OH^- + H_2O \rightarrow Pt + BH_2(OH)_2^- + H_2 \tag{4.5}$$

- completion step

$$BH_2(OH)_2^- + H_2O \rightarrow BH(OH)_3^- + H_2 \tag{4.6}$$

$$BH(OH)_3^- \rightarrow H_2BO_3^- + H_2 \tag{4.7}$$

The overall reaction gives a columbic number between 2 and 4 for each BH_4^- ion. Mirkin et al. [9] suggested the first step of borohydride oxidation on a Au electrode was a 2e process with the BH_3-like intermediate rather than BH_3OH^-.

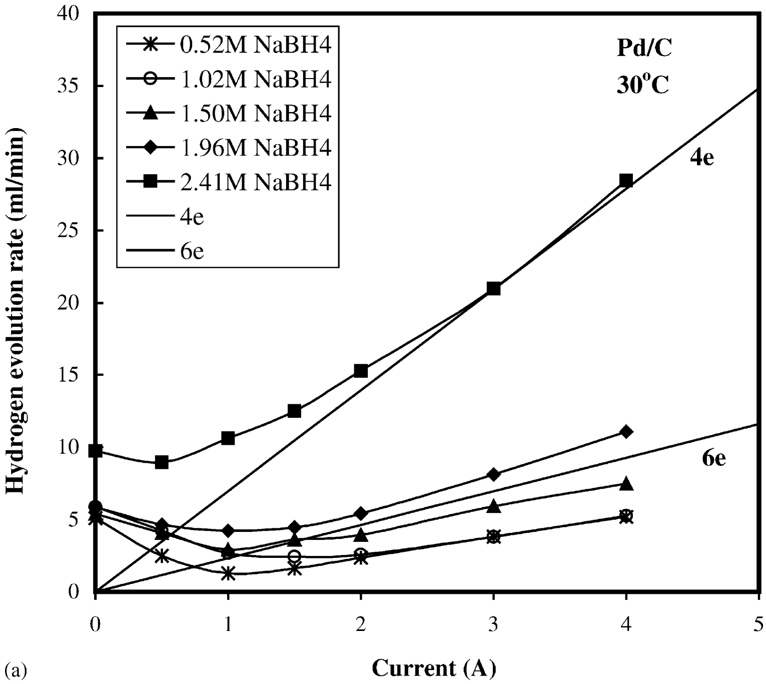


Fig. 5. (a) Relation of the hydrogen evolution rate with the anode current at different borohydride concentrations for the Pd/C electrode at 303 K. (b) Changing of the hydrogen evolution rate and borohydride concentration with the time when the Pd/C electrode was under a current of 4 A at 303 K ((I) initial borohydride concentration 1.5 M; (II) initial borohydride concentration 2.4 M).

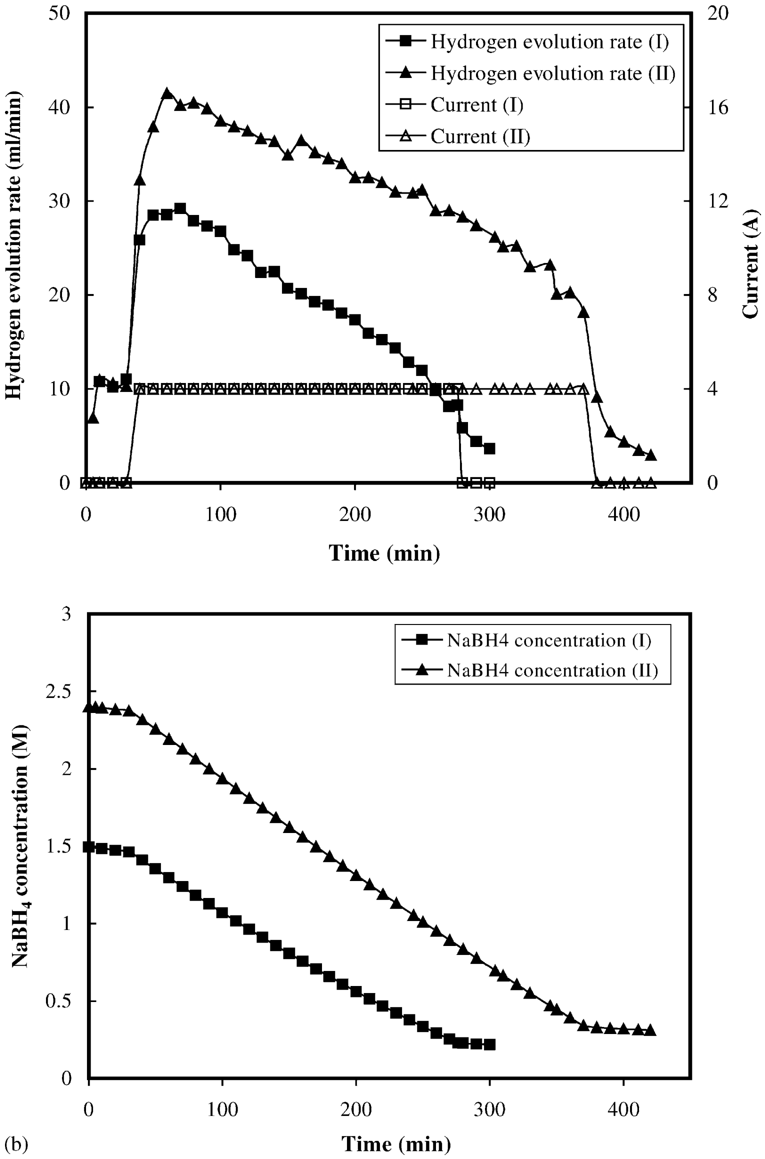


Fig. 5. (*Continued*).

Our results shown above demonstrate changing columbic numbers, depending not only on borohydride concentration but also on electrode materials. Although it is too early for us to deduce reaction mechanisms without more detailed analyses, we may get some clues to understand the reaction mechanism by comparing the anodic behaviors of borohydride on these electrodes. Three major differences can be concluded based on the experimental results. First, the OCP of the Ni electrode was observed to be more negative than those of Pd and Pt, which was also reported by others [3,7,10]. Second, the potential at 100 mA/cm^2 on the Ni electrode was still more negative than that of atomic hydrogen, while this was not the case for the carbon-supported Pd and Pt electrode. Third, the anodic reaction on the Ni was primarily a 4e process within the tested BH_4^- concentrations and current densities. On the contrary, the columbic number changed on the Pd and Pt electrodes with changing current density and BH_4^- concentration.

Based on the reaction scheme proposed by Elder and Hickling [4] and our observations on different electrocatalysts, we suppose that the anodic oxidation of BH_4^- on the electrodes may take different reaction paths, depending on electrocatalysts and reaction conditions. On the Ni electrode, we suppose that the reaction may be initiated by the electrochemical reactions of BH_4^- and BH_3OH^- shown as (4.1) and (4.3), and then followed by the hydrolysis reaction of the derived intermediates $BH_2(OH)_2^-$ and $BH(OH)_3^-$ shown as (4.6) and (4.7). The overall reaction gives a columbic number of four. On the other side, the anodic reaction on the Pt and Pd electrode may be more complicated as shown in Figs. 5 and 6. In less concentrated solutions, the electrochemical reaction predominating on the Pd or Pt electrode may be the ionization of atomic hydrogen, the product of the hydrolysis reaction. Then we can explain why the OCPs on Pt and Pd were less negative than that on the Ni electrode and were near to that of atomic hydrogen. The gradual decrease and final cease of hydrogen evolution on Pt electrode with the increase of anode current may be described as a gradual consumption of the atomic hydrogen produced by the hydrolysis reaction. When the concentration of BH_4^- increases, the direct anodic oxidation of BH_4^- or $BH_3(OH)^-$ becomes more favorable. The anodic reaction may be predominated by the direct anodic oxidation of borohydride ions and hydrogen tends to evolve out. The columbic number then decreases down at concentrated solutions. Although hydrogen evolution behaviors on Pd and Pt showed some similarities, they also showed differences. In the prolonged test shown in Fig. 5(b), the hydrogen evolution rate on the Pd electrode changed continuously with the time, while that on the Pt electrode kept the same value during the period. It suggests that the reaction path might change during the test on the Pd electrode but the reaction path kept the same on the Pt electrode and it only depended on the initial reaction condition.

More experiments and analyses are needed to clarify the reason why borohydride shows different anodic behaviors on different electrocatalysts. We suppose the difference in reaction mechanism on the Ni and Pt or Pd electrode may be mainly due to their different catalytic abilities towards the electrochemical and hydrolysis reaction of borohydride ions, boron-containing intermediates and atomic hydrogen.

Although hydrogen evolution was decreased or even ceased on carbon-supported Pd and Pt electrodes, it only took place at limited conditions when the concentration of BH_4^- and the temperature were not very high and the current was large enough. At these conditions, the polarizations were large. It may have little practical meaning because the very negative potential of borohydride was not obtained and therefore there was a large energy loss. It may not be more advantageous than an indirect oxidation process which means that borohydride is first catalytically hydrolyzed to hydrogen gas and then hydrogen is used as the fuel to feed fuel cells.

Borohydride is a promising fuel considering its high reactivity that results in a high open-circuit potential and good anode performance. However, hydrogen evolution is still a problem. Our results above show that the Ni electrode is cheap and has good performance but it ends up with the 4e reaction. Although it is possible to achieve higher fuel efficiency on a Pd or Pt electrode under certain conditions, the process may not be so advantageous compared with an indirect process via hydrogen. One more problem is how to deal with the metaborate, the oxidation product of borohydride. If these two problems are solved, borohydride may serve as a suitable fuel for a portable purpose.

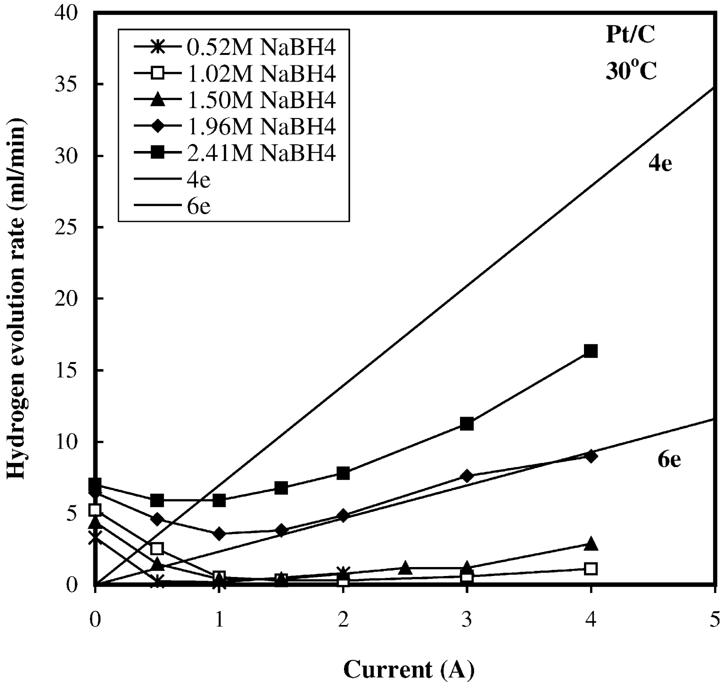


Fig. 6. (a) Relation of the hydrogen evolution rate with the anode current at different borohydride concentrations for the Pt/C electrode at 303 K. (b) Changing of the hydrogen evolution rate and borohydride concentration with the time when the Pt/C electrode was under a current of 4 A at 303 K ((I) initial borohydride concentration 1.5 M; (II) initial borohydride concentration 2.4 M).

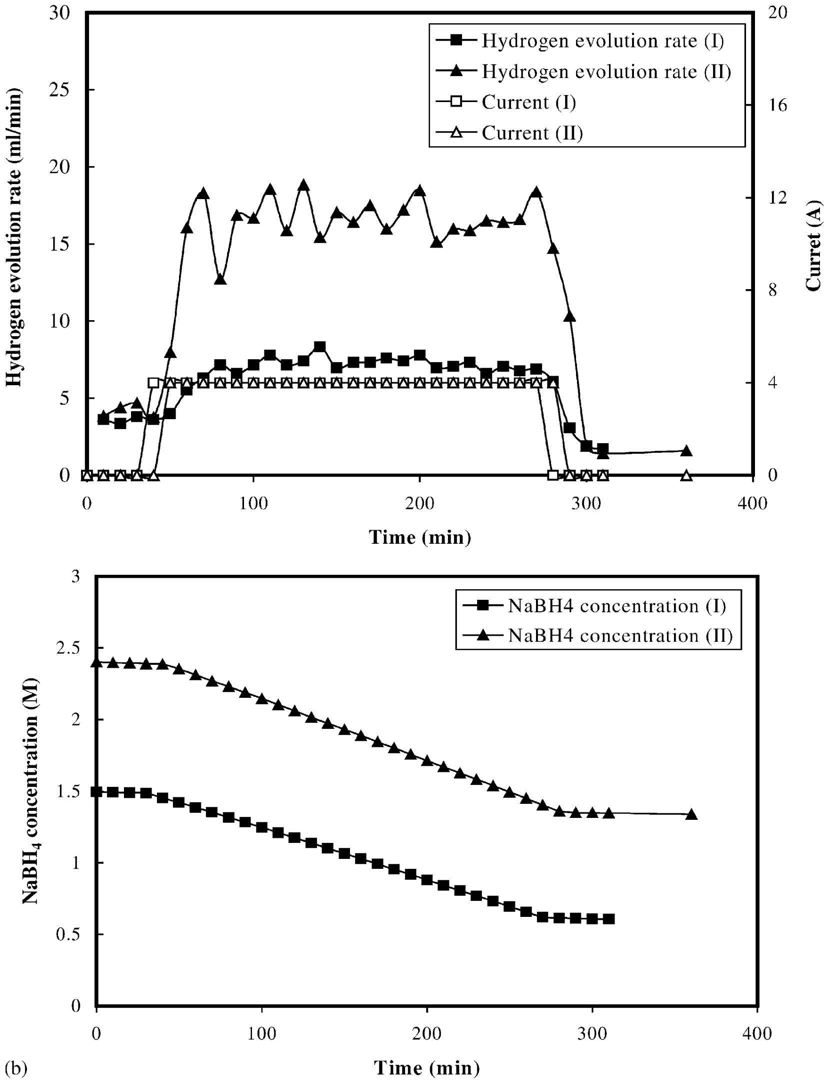


Fig. 6. (*Continued*).

5. Conclusions

Anodic oxidation of alkali borohydrides on several electrocatalysts was studied in this work. The open-circuit potentials shown on electrodes were less negative than the theoretical value but more negative than the hydrogen potential at high borohydride concentrations. The Ni electrode showed good anode performance with more negative open-circuit potential and small polarizations but the reaction was a 4e reaction where half of borohydride turned into hydrogen gas. Higher efficiency can be achieved on Pd and Pt electrode at some special conditions such as relatively low borohydride concentration and large anode current. An almost cease of hydrogen evolution was found on the carbon-supported Pt electrode at certain conditions. We suppose that the anodic reaction of borohydride may change its path depending on reaction conditions and the nature of electrocatalysts.

References

[1] J. Larminie, A. Dicks (Eds), Fuel Cell Systems Explained, second ed., Wiley, 2003, p. 157.
[2] M.E. Indig, R.N. Snyder, J. Electrochem. Soc. 109 (1962) 1104.
[3] M. Kubokawa, M. Yamashita, K. Abe, Denki Kagaku 36 (1968) 788.
[4] J.P. Elder, A. Hickling, Trans. Faraday Soc. 58 (1962) 1852.
[5] S.C. Amendola, P. Onnerud, M.T. Kelly, P.J. Petillo, S.L. Sharp-Goldman, M. Binder, J. Power Sources 84 (1999) 130.
[6] B.H. Liu, Z.P. Li, S. Suda, J. Electrochem. Soc. 150 (2003) A398.
[7] I. Ono, O. Wakabayashi, S. Haruyama, J. Electrochem. Soc. 132 (1985) 2323.
[8] J.A. Gardiner, J.W. Collat, J. Am. Chem. Soc. 87 (1965) 1692.
[9] M.V. Mirkin, H. Yang, A.J. Bard, J. Electrochem. Soc. 139 (1992) 2212.
[10] R. Jasinski, J. Electrochem. Technol. 3 (1965) 40.