The preparation and performance of high activity Ni-Cr binary catalysts for direct borohydride fuel cells

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Ni-Cr binary anode catalysts used in direct borohydride fuel cells (DBFCs) were prepared using a constant potential electrodeposition method. Compared with pure metal Ni catalysts, the electro-oxidation currents of borohydride ions (BH_4^-) more than doubled when using Ni-Cr binary catalysts under the same conditions. The enhanced activity of the Ni-Cr binary catalysts could be attributed to the change in distribution of BH_4^- ions on the surface of the Ni electrode. This is due to Cr electrodeposits, which allows a greater number of hydrogen atoms to catalyze from each tetrahedron BH_4^- ion. The performance of Ni-Cr binary catalysts could also be improved by optimizing the electrodeposition conditions. The results show that Ni-Cr binary catalysts are optimally prepared using an electrodeposition method of 1s with a Cr^{3+} concentration of 0.2 mol L^{-1} and a potential of -0.100 V .

Ni-Cr binary catalysts, borohydride ion, electro-oxidation, fuel cell

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Direct borohydride fuel cells (DBFCs) have been considered as an attractive energy supply. Particularly for portable applications due to its high theoretical cell voltage (1.64 V), specific capacity (5.67 Ah g^{-1}), theoretical conversion efficiencies (91%), non-toxic catalysts, and the convenient transportation of fuel [1]. These devices employ an alkaline solution of sodium borohydride (NaBH_4) as fuel and oxygen or hydrogen peroxide as the oxidant. The DBFC converts the chemical energy stored in the borohydride ion (BH_4^-) directly into electricity by redox processes. DBFCs not only overcome the disadvantages of production, storage and transportation issues related to the use of hydrogen gas, but also eliminate safety concerns regarding the use of hydrogen gas as fuel in traditional fuel cells. However, the degree of the direct electro-oxidation reaction of borohydride ions (BH_4^-) on the anode can be decreased owing to the hybrid electric potential resulting from the hydrolysis of BH_4^- ions during DFBC operation [2]. It has been widely reported that the oxidation rate of BH_4^- is increased by using anode electro-catalysts such as Ni, Au, Pt, or Pd despite their lower

fuel efficiencies [2–5] (e.g. 50% for Ni [6], 75% for Pd [7]). Although Au can catalyze the complete $8e^-$ oxidation of BH_4^- , its electrochemical activity is relatively low [8]. The hydrolysis and diffusion of BH_4^- ions through the separation membrane may be suppressed due to the addition of Thiourea (TU) into the alkaline electrolyte during the electrochemical oxidation of BH_4^- on the Pt electrode. This addition seems to reduce the operation potential of DBFCs [9].

To take advantage of the various benefits of different catalyst materials and to improve performance, many researchers have been engaged in developing composite anodic materials such as bi-metallic and multi-metallic materials. The activity and stability of bi-metallic catalysts are better than those of mono-metallic catalysts [10]. Considering the high cost of noble metals such as Au, Pt, and Pd, it is worthwhile to investigate non-precious metal catalysts for use as anode catalysts. Among non-precious metals, nickel is considered a promising candidate for the direct electro-oxidation of BH_4^- . Improved performance of DBFCs has been achieved by using anode loading Ni-based composite catalysts on nickel foams [11]. In this paper, Ni-Cr binary anode catalysts for DBFCs were prepared using a constant

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potential electrodeposition method. This method is considered simple and convenient. The catalytic activity of Ni-Cr binary catalysts on the electro-oxidation of BH_4^- ions was examined. The effects of the electrodeposition conditions on catalyst performance were also investigated.

1 Experimental

The preparation of Ni-Cr binary anode catalysts was carried out using a constant potential electrodeposition method with a three-electrode system. A nickel plate (2 cm^2) was used as a working electrode, a graphite rod as the counter electrode, and Ag/AgCl as the reference electrode. It should be noted that the nickel plate (2 cm^2) was polished, cleaned by ultrasonic wave, and washed with distilled water before use as an electrode material. Different Ni-Cr binary catalysts were prepared with different electro-deposition potentials. The concentration of the $\text{Cr}(\text{NO}_3)_3$ solution and the deposition time were also varied.

X-ray diffraction (XRD, BDX3200 X-ray diffractometer) was carried out to characterize the component that was electrodeposited onto the surface of Ni electrode. The catalytic activity of Ni-Cr binary catalysts on the electro-oxidation of BH_4^- ions was investigated using a standard three-electrode system, with $0.27\text{ mol L}^{-1}\text{ NaBH}_4$ in $2.0\text{ mol L}^{-1}\text{ NaOH}$ electrolyte solution. The nickel plate (2 cm^2) was prepared by electrodepositing Cr as a working electrode. A graphite rod was used as the counter electrode and Hg/HgO (MOE, $1\text{ mol L}^{-1}\text{ NaOH}$) was used as the reference electrode. Cyclic voltammetry tests were carried out by varying the voltage from -1.0 to -0.4 V vs. Hg/HgO with a scan rate of 10 mV s^{-1} .

Both the constant potential electro-deposition and the cyclic voltammetry (CV) tests were performed with an electrochemical analyzer (CHI660b).

2 Results and discussion

Figure 1 summarizes the XRD patterns of pure Ni and of Ni with Cr electrodeposited on surface under various times. Characteristic diffraction peaks of pure Ni were seen at 44.5° , 51.8° , 76.4° , 92.9° and 98.4° (Figure 1(b)). Ni-Cr prepared by electrodepositing over 1 s also possessed similar XRD patterns but the intensity of the diffraction peaks was significantly reduced (see Figure 1(c)). As the characteristic diffraction peaks of Cr metal were also not found, it was expected that Cr could have formed clusters and deposited sporadically on the surface of the Ni electrode [12]. Compared with pure Ni, the intensity of some of the diffraction peaks of the sample prepared by electrodepositing Cr over 30 min increased significantly (see Figure 1(d)). This was due to the diffraction peaks (110), (321) and (220) of Cr overlapping with peaks (111), (220) and (222) of Ni, sug-

gesting that the main component of the electrodeposited material was Cr.

N_{Cr} , the number of Cr atoms electrodeposited onto the Ni surface, can be calculated by the following formula:

$$N_{\text{Cr}} = \frac{Q}{zF} \times N_{\text{A}}, \quad (1)$$

where Q is the electric quantity passing through the Ni electrode during the electro-deposition process, z is the number of electrons transferred in the reaction, F is the Faraday constant and N_{A} is the Avogadro constant. In this case, $z = 3$, $F = 96500\text{ C mol}^{-1}$, and $N_{\text{A}} = 6.02 \times 10^{23}$.

Assuming that the Cr atoms were electrodeposited evenly on the Ni surface one layer at a time, the surface area (S) of the electrode that is covered by Cr can be given as follows:

$$S = \pi \times r_{\text{Cr}}^2 \times N_{\text{Cr}}, \quad (2)$$

where r_{Cr} represents the radius of the Cr atom and is equal to 140 pm. Characteristic values of the Ni electrode with electrodeposited Cr are listed in Table 1. The calculation results show that the area covered by electrodeposited Cr atoms was 0.05514 cm^2 , much less than the Ni electrode surface of 2 cm^2 . This coverage is only 2.75% of the surface. The Cr film may not have formed on the Ni surface but could have formed Cr atom clusters deposited sporadically on the surface. This would have caused the intensity of the XRD diffraction peaks to significantly decrease. However, the atom number and the area covered by Cr could increase with extended electro-deposition time. For example, the depositing area was found to be 124 cm^2 when the electro-deposition time was increased to 1800 s. As the electrode was almost covered with deposited Cr, the diffraction peaks (110), (321) and (220) of Cr appeared in the XRD pattern, which overlapped coincidentally with peaks (111), (220) and (222) of Ni metal, leading to increase of diffraction intensity of these peaks.

Figure 1 XRD patterns of a standard card of Ni metal (JCPDS No. 04-0850) (a), pure Ni (b), Ni with surface electrodeposited Cr over 1 s (c) and 30 min (d).

Table 1 Characteristic values of Ni electrode surface electrodeposited Cr

Electrodepositing time (s)	Electric quantity (C)	N_{Cr}	Area covered by Cr (cm ²)
1	4.31×10^{-5}	8.96×10^{13}	0.05514
1800	9.75×10^{-2}	2.03×10^{17}	124

Figure 2 shows the CV curves of BH_4^- using the Ni catalyst. There was an obvious oxidation peak representing BH_4^- at approximately -0.7 V and at a current of ~ 6.5 mA when Ni was used as a catalyst. This peak was absent from the CV curve in the NaOH solution. This indicates that Ni can catalyze the electro-oxidation of the BH_4^- ions. Boron atom with a valence electron configuration of $2s^2 2p^1$ is sp^3 hybridized and forms a tetrahedral BH_4^- ion with four hydrogen atoms. Nickel is a group VIII B element in the fourth row of the periodic table [13], and has a valence electron configuration of $3d^8 4s^2$. There are three lone pairs of electrons in the 3d orbital, so BH_4^- can be strongly adsorbed onto the Ni surface and form coordinate bonds between the nickel and hydrogen atoms on the BH_4^- ions. So the electro-oxidation reaction of BH_4^- ion is occurred.

However, there were more BH_4^- ions than catalytic activity points and only one hydrogen atom from each BH_4^- ion tetrahedron could be oxidized (see the inset in Figure 2). This leaves three other hydrogen atoms to be hydrolyzed [14].

Thus, the electro-oxidation of BH_4^- was reduced and the electrode reaction was hindered by hydrogen gas from hydrolysis.

From Figure 3, it was found that the electro-oxidation of BH_4^- ions could also be catalyzed by Ni-Cr binary catalysts. With electro-deposition of 1 s, the oxidation current increased by approximately 2.5 times. The enhanced electro-oxidation of BH_4^- ions by the Ni-Cr binary catalysts could

Figure 2 CV curves of BH_4^- with Ni catalyst in (a) 2 mol L^{-1} NaOH solution, (b) 0.27 mol L^{-1} $NaBH_4$ in 2 mol L^{-1} NaOH solution with a scan rate of 10 mV s^{-1} . **Figure 3** CV curves of BH_4^- with (a) Ni and (b) Ni-Cr catalyst in 0.27 mol L^{-1} $NaBH_4$ solution with a scan rate of 10 mV s^{-1} .

be attributed to the change in the distribution of BH_4^- ions on the surface of the electrode from the electrodeposited Cr. As the element Cr is in the fourth row of the periodic table [13], its valence electron configuration $3d^5 4s^1$ is in a half-filled stable state, and coordinate bonds between Cr and H atoms in the BH_4^- ion could not form easily. With electrodeposited Cr on the surface of Ni electrode, the adsorbance of BH_4^- ions on the electrode surface decreased significantly, leading to an increase in space between the BH_4^- ions. Therefore, two or more hydrogen atoms of the tetrahedron BH_4^- ions could be oxidized, and the catalyst activity was subsequently enhanced significantly (the inset in Figure 3).

Figure 4 displays the CV curves of BH_4^- using Ni-Cr catalysts prepared with various electro-deposition times. It can be seen that the electro-oxidation of BH_4^- ions was enhanced significantly by electrodepositing Cr on the nickel electrode.

Figure 4 CV curves of BH_4^- with Ni-Cr catalysts prepared in different electro-deposition time. (a) 1 s, (b) 1 min, (c) 10 min, (d) 30 min, (e) 1 h.

However, this decreased gradually and the oxidation potential slowly shifted to the positive with extended electro-deposition time. With an electro-deposition time of 1 h, the oxidation peak disappeared in the CV curves of BH_4^- . This suggests that Cr could not catalyze on the electro-oxidation of BH_4^- ions. With electro-deposition times of more than 1 s, the catalytic activity points of Ni were occupied by more Cr atoms, resulting in the reduction of the catalytic activity of Ni-Cr. Therefore, it is suitable to prepare Ni-Cr catalysts with a deposition time of 1 s.

Figure 5 shows the CV curves of BH_4^- using Ni-Cr catalysts prepared with different concentrations of Cr^{3+} while the other conditions of the electro-deposition process were maintained as constants. The electro-oxidation current of BH_4^- increased with the Ni-Cr catalysts, but decreased gradually with the increase in Cr^{3+} concentration. As the Ni catalyst was enhanced by the Cr deposits, more Cr atoms occupying the electrode surface resulted in a reduction of the BH_4^- adsorbance and also reduced the number of catalytic activity points of Ni, decreasing the activity of the Ni-Cr binary catalyst. It should also be noted that the peak potential of BH_4^- electro-oxidation slowly shifted towards the positive with increased Cr^{3+} concentration in the electrolyte solution. Some studies have reported [9,11, 15,16] that the peak potential of BH_4^- electro-oxidation may vary with different anode catalysts. For example, the peak potential was at approximately -0.40 and 0.20 V (two continuous oxidation peaks) on Pt, -0.25 V on Au, -0.40 V on Cu and -0.70 V on Ni catalyst in alkaline mediums, respec-

tively.

When using Ni-Cr catalysts prepared with different concentrations of Cr^{3+} , the potential of BH_4^- ion electro-oxidation could shift. However, it has been previously demonstrated [9] that a positive shift of BH_4^- electro-oxidation potential is not advantageous in increasing the operation potential of DBFCs. The electro-oxidation current of the BH_4^- ions were maximized and the positive shift of potential were indistinctive when concentrations of Cr^{3+} was 0.2 mol L^{-1} , suggesting that 0.2 mol L^{-1} was the optimum concentration for Ni-Cr catalysts prepared by electro-deposition.

Figure 6(a) presents the CV curves of BH_4^- using the Ni catalyst and Figure 6(b)–(d) shows Ni-Cr catalysts prepared at deposition potentials of 0.100 , -0.100 , and -0.300 V respectively, while other preparation conditions were maintained as constant. It was found that the electro-oxidation current of BH_4^- ions using Ni-Cr catalysts was considerably increased. The current reached approximately 22 mA using the catalyst prepared by deposition at -0.100 V, which was almost 3 times that achieved using pure Ni catalysts. However, the electro-oxidation current decreased slowly with a decrease in deposition potential. As the potential approached -0.522 V, the content of Cr in the Ni-Cr catalysts was found to increase with the potential shifted to the negative due to easy electro-deposition of Cr on Ni. This led to a reduction in the number of catalytic activity points on the Ni surface and a reduced electro-oxidation current of BH_4^- . The optimum deposition potential found for preparing Ni-Cr bimetallic catalysts was -0.100 V.

Figure 5 CV curves of BH_4^- using Ni-Cr catalyst prepared with different Cr^{3+} concentration and a scan rate of 10 mV s^{-1} . (a) 0.0 mol L^{-1} , (b) 0.1 mol L^{-1} , (c) 0.2 mol L^{-1} , (d) 0.3 mol L^{-1} .

Figure 6 CV curves of BH_4^- (a) with Ni catalysts; with Ni-Cr catalysts prepared at different electrodeposition potential: (b) 0.100 V, (c) -0.100 V, (d) -0.300 V with a scan rate of 10 mV s^{-1} .

3 Conclusion

Ni-Cr binary catalysts were prepared by a simple and convenient electro-deposition method. The electro-oxidation performance of BH_4^- was enhanced significantly using Ni-Cr binary catalysts. The improvement of BH_4^- electro-oxidation could be attributed to the increase in the number of hydrogen atoms that each tetrahedron of BH_4^- ion adsorbed onto the electrode surface, which could then be oxidized directly. The performance of Ni-Cr binary catalysts was also found to be influenced by electro-deposition conditions. The results indicate that optimum conditions for the preparation of Ni-Cr binary catalysts using this electro-deposition method were to use a Cr^{3+} concentration of 0.2 mol L^{-1} , with a depositing potential of -0.100 V over 1 s . This work demonstrates an exciting opportunity to effectively improve the catalytic abilities of Ni.

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