Disclaimer
This book contains paper abstracts that have received the Scientific Committee approval. The complete articles are included into the CD Collection of Articles attached to this book. Authors are responsible for the content and accuracy.

Information in the BIES'08 Symposium Abstract Book and the CD Collection of Articles is subject to change without notice. No part of this book or CD may be reproduced or transmitted in any form or any means, electronic or mechanical, for any purpose, without the express written permission of International Scientific Council except permission of BIES'08 Organisation Committee.

All Rights Reserved. Copyright© JIEAS and Blacksea International Environmental Symposium Organisation Committee, 2008.

Editors: S. Dursun, E. Esmeray, S. Dogan, F. Kunt, M. Karataş, E. Kalipci

Cover page and WEB page design: E Esmeray
Printed in Koza Press, Giresun, Turkey.
ELECTROCHEMICAL DEPOSITION, CHARACTERIZATION AND APPLICATION OF NICO COATINGS AS EFFECTIVE CATHODE MATERIALS FOR HYDROGEN PRODUCTION

R. Solmaz, A. Döner, G. Kardaş, B. Yazıcı, M. Erbil

Cukurova University, Science & Letters Faculty, Chemistry Department, 01330, Balcali Adana, Turkey

Email: rsolmaz@cu.edu.tr, gufeza@cu.edu.tr, Tlf: +90-322-3386081/16, Fax: +90-322-3386070

Abstract: In this study, the NiCo binary alloys in different metal ratios were electrochemically prepared on a copper electrode. Electrodeposited coatings were characterized by cyclic voltammetry, atomic absorption spectroscopy, scanning electron microscopy and atomic force microscopy techniques. Electrocatalytic activity of the coatings for the hydrogen evolution reaction (HER) was studied in 1 M KOH solution at 298 K using cathodic current-potential curves, electrochemical impedance spectroscopy and electrolysis techniques. The best Ni/Co metal ratio and thickness of the coating for effective cathode material for hydrogen gas production in alkaline medium was determined. It was found that, the NiCo coatings have a good electrocatalytic activity for the HER in alkaline media and the hydrogen evolution reaction activity of the coatings depends on the metal ratio of Ni/Co, deposition current density and the thickness of the coatings.

Keywords: NiCo coatings, atomic force microscopy, electrolysis, hydrogen production.

INTRODUCTION

Hydrogen is considered one of the most potential energy carriers due to its recyclable and nonpolluting nature as well as the fact that it is available in unlimited quantities (Lutfi & Veziroglu, 1991; Hu et.al., 2003). Hydrogen gas can be easily produced by water electrolysis in very high purity. In addition to its energy carriers, hydrogen of high purity needed in several industrial applications e.g. fuel cell, steel reel out, food industry, the refining of metals, etc. (Hu et.al., 2003; Giz et.al., 2003). However, this technique is quite expensive due to high energy consumption. The cost of hydrogen is directly proportional to the voltage of operation of electrolyser, which can be reduced by choosing an electrode material with low overpotential, good electrocatalytic activity and electrolyte conditions. The cost of electrode materials has to be consistent with the cost of technology being proposed. In addition, the electrode of choice must have high corrosion resistance (Solmaz and Kardaş, 2007). The cost of electrolytic hydrogen production can be reduced by reduction of the overpotential of the electrode reactions as well as selecting much cheaper electrode materials. The followings are the properties of an electrode for water electrolysis: A large active surface area, electrochemical stability, good electrical conductivity, and low overpotential, selectivity, low cost and ease of use (Yazici et.al., 1995). Recently several active electrodes have been developed for the hydrogen evolution reaction and the performance of nickel-based alloys is the best in all. Nickel has a high initial electrocatalytic activity towards the HER.
But, nickel losses its activity during alkaline water electrolysis. The HER can be enhanced by the formation of nickel alloys (Beiping et al., 2007). Several NiCo binary coatings have been prepared and characterized for the HER and reported to be good electrocatalysts for the HER in alkaline water electrolysis (Elumalai et al., 2002; Suffredini et al., 2000). Iron and cobalt binary alloys can be easily prepared by electrodeposition technique which is usually much cheaper and simpler than the other methods (Jafarian et al., 2007). The influence of alloy composition and the thickness of the coating have not been studied in detail.

The aim of this study was electrochemical preparation and characterization of the Ni-Co binary alloys of various compositions in view of their possible applications as electrocatalytic cathode materials for the hydrogen evolution reaction.

EXPERIMENTAL

The working electrode was a cylindrical disc cut from a copper rod in about 5 cm length. The copper specimen was coated with polyester block, aspect for measurement area of 0.283 cm² and the electrical conductivity was provided by a copper wire. Before electrodeposition, electrode surface was polished with emery paper (320-1000 grain size), then washed with distilled water, thoroughly degreased with acetone, followed washed with distilled water again and immersed in the bath solution. The electrodeposition was performed galvanostatically using Potentiostate-galvanostate (Princeton Applied Research Model 362) with a three-electrode configuration. A nickel electrode was used as counter and Ag/AgCl electrode was used as reference electrode, respectively. The bath compositions were as follow: a) Nickel plating bath: 30% NiSO₄·7H₂O, 1% NiCl₂·6H₂O, 1.25% H₃BO₃, b) Cobalt plating bath: 30% CoSO₄·7H₂O, 1% CoCl₂·6H₂O, 1.25% H₃BO₃, c) Nickel-Cobalt plating bath: Nickel and cobalt salts were fixed in different mole ratios (8:2 (NiCo(8 : 2)), 6:4 (NiCo(6 : 4)), 4:6 (NiCo(4 : 6)), 2:8 (NiCo(2 : 8)) which containing 1.25% H₃BO₃ whereas the total mole of nickel and cobalt were constant in all plating baths. The codeposition of NiCo was carried out at a constant current density of 50 mA cm⁻² at 298 K under stirring conditions. The thickness of the NiCo deposit was theoretically calculated as 50 μm by assuming an average alloy density and average atomic weight. (Stavanovic et al., 1998).

A CHI 604 model computer controlled electrochemical analyzer (serial number: 6A721A) was used for the cathodic current-potential curves and electrochemical impedance spectroscopy measurements. A double-wall one-compartment cell with a three-electrode configuration was used. A platinum sheet (with 2 cm² surface area) and Ag/AgCl electrode were used as the auxiliary and the reference electrodes, respectively. All potential values were referred to this reference electrode. During the polarization and impedance measurements, the counter electrode was separated from the main cell compartment by a glass tube using Nafion. The polarization curves were potentiodynamically obtained in the potential ranges between -1.8 V and respective open circuit potential with scan rate of 5 mVs⁻¹ after obtaining reproducible polarization curves. The electrochemical impedance spectroscopy experiments were conducted in the frequency range of 100 kHz to 0.01 f ≤1 Hz at different overpotentials by applying alternating current signal of 0.005 V peak-to-peak. Before the tests,
the working electrode was held at -1.80 V for 30 minutes in order to reduce the oxide film existence on the electrode surface and obtain a reproducible electrode surface. Cyclic voltammograms were recorded between hydrogen and oxygen evolution potential range started from negative direction with 100 mVs⁻¹ scan rate. In the electrolysis, two-electrode set-up, platinum as anode and working electrodes as cathode were utilized. A gradually increasing voltage was applied to the system starting from 0.00 V to 3.00 V, from a direct current source and current-voltage curves were obtained. A burette was filled with the same electrolyte and turned over the working electrode and a constant 5.0 V voltage was applied to the system. Hydrogen gas filling the burette was measured over 1 hour.

The HER activity of the working electrodes was performed in oxygen free 1 M KOH (Merck) solution which was achieved by purging of the cell electrolyte by hydrogen. During the electrolysis measurements the test solution was opened to air. All the test solutions were prepared from analytical grade chemical reagents in distilled water without further purification. For each experiment, a freshly prepared solution was used. The solution temperature was thermostatically controlled by Nuve BM 100 type thermostat.

The chemical composition of the alloy coatings was determined with the help of a Perkin-Elmer Atomic Adsorption Spectrophotometer model 3100 (AAS). The surface morphology of the electrodes was examined by high resolution SEM and AFM techniques. The SEM images were taken using a Carl Zeiss Evo 40 SEM instrument at high vacuum and 10kV EHT, AFM images were taken with Park SYSTEMS using non-contact mode.

RESULTS AND DISCUSSION

Characterization of the Coatings

After deposition, the composite coatings were mechanically removed from the surface of the electrodes and dissolved in dilute HNO₃ solution. The chemical composition of the alloys was analyzed by atomic absorption spectroscopy (AAS). The determined percentage metal ratios were as follow: NiCo(8 : 2) (28.3% Ni, 71.7% Co), NiCo(6 : 4) (16.5% Ni, 83.5% Co), NiCo(4 : 6) (5.8% Ni, 94.2% Co), NiCo(8 : 2) (3.1% Ni, 96.9% Co). The AAS results showed that the chemical composition of the alloy can be changed by changing the mol ratio of Ni⁺² and Co⁺² in the bath solution. The more cobalt ratio in alloy coatings indicate that the deposition rate of Co⁺² is higher than the Ni⁺² ions.

The cyclic voltammograms (CV) of working electrodes were presented in Figure 1a-f. Figure 1a shows the CV of the pure Ni coated copper electrode (Cu/Ni). It is clear from Figure 1a that, during forward scan two anodic peaks (A1 and A2) and two cathodic peaks (C1 and C2) were observed during reverse scan. The A1 peak corresponding to Ni/Ni(OH)₂, and the peak A2 to the Ni(OH)₂/NiO(OH) transitions as given in Equations (1-2).

\[
\begin{align*}
\text{Ni} + 2\text{OH}^- & \leftrightarrow \text{Ni(OH)}_2 + 2e^- \quad (1) \\
\text{Ni(OH)}_2 + \text{OH}^- & \leftrightarrow \text{NiO(OH)} + \text{H}_2\text{O} + e^- \quad (2)
\end{align*}
\]

The CV of the pure cobalt coated copper electrode was given in Figure 1b. As seen from this Figure, during anodic scan three well defined anodic peaks (A1, A2 and A3) were appeared. These peaks related to the Co/Co(OH)₂,
\[ \alpha-\text{Co(OH)}_2/\beta-\text{Co(OH)}_2 \quad \text{and} \quad \text{Co(OH)}_2/\text{CoO(OH)}, \text{respectively (Eq. 3-4)}. \]

![Graphs showing cyclic voltammograms for different systems](image)

**Figure 1.** The cyclic voltammograms of Cu/Ni (a), Cu/Co (b), Cu/NiCo(8 : 2) (c), Cu/NiCo(6 : 4) (d), Cu/NiCo(4 : 6) (e), and Cu/NiCo(2 : 8) (f) recorded in 1 M KOH solution at 298 K (scan rate is 100 mV/s and the potential was started from -0.9 V to positive direction).

\[
\text{Co} + 2\text{OH}^- \leftrightarrow \text{Co(OH)}_2 + 2e^- \quad (3)
\]

\[
\text{Co(OH)}_2 + \text{OH}^- \leftrightarrow \text{CoO(OH)} + \text{H}_2\text{O} + e^- \quad (4)
\]
The CVs of the composite coatings (Figure 1c-f) exhibited the behaviour of both nickel and cobalt.

![SEM images of Cu/Ni (a), Cu/Co (b), Cu/NiCo(8 : 2) (c), Cu/NiCo(6 : 4) (d), Cu/NiCo(4 : 6) (e), Cu/NiCo(2 : 8) (f) electrodes.](image)

Figure 2. The SEM images of Cu/Ni (a), Cu/Co (b), Cu/NiCo(8 : 2) (c), Cu/NiCo(6 : 4) (d), Cu/NiCo(4 : 6) (e), Cu/NiCo(2 : 8) (f) electrodes.

The surface images of the coated electrodes were analyzed by SEM and AFM and given in Figures 2 and 3, respectively. It is clear from these images that the coatings present a compact, uniform and porous structure.
on the surface. The images of the binary coatings show significant differences when compared to that of pure nickel and cobalt coatings.

**Figure 3.** The AFM images of Cu/Ni (a), Cu/Co (b), Cu/NiCo(8 : 2) (c), Cu/NiCo(6 : 4) (d), Cu/NiCo(4 : 6) (e), Cu/NiCo(2 : 8) (f) electrodes.

**Cathodic Current-Potential Curves**

The cathodic polarization curves of the both pure metal coatings and binary nickel-cobalt coatings were given in Figure 4. In order to better compare the electrocatalytic activity of the coatings, the current densities were determined at different cathodic overpotentials and collected in Table 1. As can be seen...
from Figure 4 and Table 1, comparison of the current densities at the same overpotential suggested that the binary alloy coatings exhibited better electrocatalytic activity for the HER in alkaline solution deposited in Ni:Co(6:4) bath solution by cathodic current-potential curves. The determined current densities for the thicknesses were given Table 2. The decrease in activity of the electrodes at 75 and 100 μm may be related to the increasing cobalt percentage in the alloy whose deposition rate is higher than nickel.

Figure 4. Cathodic current-potential curves of working electrodes in 1 M KOH solution at 298 K.

Table 1. The current density values determined from cathodic current-potential curves at different overpotentials for the bare and nickel coated electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>I / mA.cm⁻²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.100 V</td>
</tr>
<tr>
<td>Cu/Ni</td>
<td>0.15</td>
</tr>
<tr>
<td>Cu/Co</td>
<td>0.056</td>
</tr>
<tr>
<td>Cu/NiCo(8:2)</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu/NiCo(6:4)</td>
<td>0.94</td>
</tr>
<tr>
<td>Thickness</td>
<td>I / mA.cm²</td>
</tr>
<tr>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td>10 μm</td>
<td>0.26</td>
</tr>
<tr>
<td>25 μm</td>
<td>0.67</td>
</tr>
<tr>
<td>50 μm</td>
<td>0.94</td>
</tr>
<tr>
<td>75 μm</td>
<td>0.60</td>
</tr>
<tr>
<td>100 μm</td>
<td>0.69</td>
</tr>
</tbody>
</table>

**Table 2.** The current density values determined from cathodic current-potential curves at different overpotentials in 1 M KOH solution for the NiCo(6 : 4) electrode at different thicknesses.

*Electrochemical Impedance Spectroscopy*

In order to get information about electrocatalytic activity of the coated electrodes, electrochemical impedance spectroscopy measurements were performed at different cathodic overpotentials. The obtained data were presented in Figure 5 in Nyquist representation. As seen from Figure 5a-f, a slightly depressed semi circular shape was observed for all electrodes, while their radius is different. The deviation from ideal semicircle indicated the surface inhomogenities of the coatings (Elumalai et.al., 2002; Rosalbino et.al., 2005). Only one loop observing in Nyquist plots indicates that the hydrogen evolution reaction is mainly controlled by charge transfer process (Navarro-Flores et.al., 2005). In the evaluation of Nyquist plots, the difference in real impedance at lower and higher frequencies is commonly considered as charge transfer resistance. The charge transfer resistance values were determined from Figure 5a-f and given in Table 3. From Figure 5 and Table 3, it can be seen that the Cu/NiCo(6 : 4) electrode has the lowest charge transfer resistance and the highest electrocatalytical activity for the HER.

**Electrolysis**

In order to determine discharge potential and over potential of the electrolysis system, the current-potential curves were obtained by two electrode set-up when platinum used as anode and working electrodes as cathode. Both the experimental discharge potentials and overpotentials were calculated as described elsewhere (Solmaz ve Kardas, 2007) and given in Table 4. It is clear from Table 4, the hydrogen evolution activity can be enhanced by alloying nickel and cobalt. The lowest discharge
potential was obtained at Cu/NiCo(6 : 4) electrode.

Hydrogen gas filling the burette turned over on the cathode measured over 1 hour by applying constant potential of 3.0 V to the electrolysis system. In these conditions measured volume is total of hydrogen gas and water vapor. Corrected hydrogen volumes were calculated as described elsewhere (Kardaş et al., 2003) and determined hydrogen gas volumes were given in Table 4. It can be seen from Table 4, the most hydrogen gas was produced at Cu/NiCo(6 : 4) electrode.
Figure 5. The Nyquist plots of Cu/Ni (a), Cu/Co (b), Cu/NiCo (8 : 2) (c), Cu/NiCo (6 : 4) (d), Cu/NiCo (4 : 6) (e) and Cu/NiCo (2 : 8) (f) electrodes at -0.200 V overpotential in 1 M KOH solution at 298 K.

Table 3. The charge transfer resistance values determined from Nyquist plots at different potentials in 1 M KOH solution for the bare and binary NiCo alloy coated electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>R / Ω</th>
<th>-0.200 V</th>
<th>-0.300 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni</td>
<td>6000</td>
<td>460</td>
<td>67.8</td>
</tr>
<tr>
<td>Cu/Co</td>
<td>5500</td>
<td>800</td>
<td>190</td>
</tr>
<tr>
<td>Cu/NiCo(8 : 2)</td>
<td>2225</td>
<td>370</td>
<td>91,4</td>
</tr>
<tr>
<td>Cu/NiCo(6 : 4)</td>
<td>2000</td>
<td>335</td>
<td>68.3</td>
</tr>
<tr>
<td>Cu/NiCo(4 : 6)</td>
<td>3000</td>
<td>435</td>
<td>115</td>
</tr>
<tr>
<td>Cu/NiCo(2 : 8)</td>
<td>2850</td>
<td>1325</td>
<td>260</td>
</tr>
</tbody>
</table>

Table 4. Experimental discharge potentials, overpotentials and hydrogen gas volumes for each electrode coupling determined from the current-voltage curves obtained by electrolysis technique.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>E_{exp} / V</th>
<th>η_{H₂} / V</th>
<th>V_{H₂} (mL·cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Ni</td>
<td>2.07</td>
<td>0.84</td>
<td>129</td>
</tr>
<tr>
<td>Cu/Co</td>
<td>2.17</td>
<td>0.94</td>
<td>110</td>
</tr>
<tr>
<td>Cu/NiCo(8-2)</td>
<td>2.17</td>
<td>0.94</td>
<td>134</td>
</tr>
<tr>
<td>Cu/NiCo(6-4)</td>
<td>2.16</td>
<td>0.93</td>
<td>138</td>
</tr>
<tr>
<td>Cu/NiCo(4-6)</td>
<td>2.19</td>
<td>0.96</td>
<td>119</td>
</tr>
<tr>
<td>Cu/NiCo(2-8)</td>
<td>2.20</td>
<td>0.97</td>
<td>120</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The pure nickel, pure cobalt and nickel-cobalt binary alloys of various compositions were electrochemically
prepared on a copper electrode and characterized in view of their possible applications as electrocatalytic materials for the hydrogen production. The following points can be emphasized:

1) The nickel-cobalt binary electrodes were successfully electrodeposited on copper electrode. The chemical composition of the coatings can be changed by changing the bath composition.

2) The alloying nickel with cobalt enhances the electrocatalytic activity of the coating for the HER when compared to pure nickel and pure cobalt coatings.

3) The lowest overpotential and discharge potenatial values were obtained at Cu/NiCo(6 : 4) electrode. The highest hydrogen volume was also obtained at this electrode at a constant 3.0 V potential over 1 hour by electrolysis technique.

4) At the same over potential the Cu/NiCo(6 : 4) electrode has the highest current density which is directly proportional to the hydrogen production, and the lowest charge transfer resistance were obtained.

5) When the Cu/NiCo(6 : 4) electrode was used for the electrochemical hydrogen gas production, the lowest electrical energy will be consumed.

ACKNOWLEDGMENTS

This study has been financially supported by Cukurova University research fund (Project Number: FEF2006D8) and The Scientific and Technical Research Council of Turkey (TUBITAK) (Project Number: TBAG106TS42). The authors are greatly thankful to Cukurova University research fund and TUBITAK.

REFERENCES


Jafarian M., Azizi O., Gobal F., Mahjani M.G. 2007. Kinetics and electrocatalytic behavior of nanocrystalline CoNiFe alloy in