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THE USE OF NI COATINGS FOR ALKALINE WATER ELECTROLYSIS

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Abstract: In this study, the Ni was electrochemically coated on a copper electrode at different deposition current densities and thicknesses. Electrodeposited coatings were characterized by cyclic voltammetry, scanning electron microscopy and atomic force microscopy techniques. Electrocatalytic activity of the coatings for hydrogen evolution reaction (HER) was studied in 1 M KOH solution using cathodic current-potential curves, electrochemical impedance spectroscopy and electrolysis techniques. It was found that, the nickel coated copper electrodes can enhance the electrocatalytic activity for the hydrogen evolution reaction in alkaline media when compared to bare copper. The hydrogen evolution reaction activity of the coatings depends on the deposition current density and the thickness of the coating.

Keywords: Ni coatings, electrolysis, hydrogen production.

INTRODUCTION

Fossil fuels are the major part of energy sources consumed on the world today. Because they cause environmental pollutions, irreversible effect on climate, and are fast approaching to an end and the efforts for scientist to find alternative sources have never been common (Barbir et al., 1990; Lutfi & Veziroğlu, 1991). Hydrogen gas could an alternative source of energy. An important technique of producing hydrogen is the electrolysis of water. However, this technique is quite expensive due to high energy consumption in electrolysis system and also the efficiency of this technique is low. In order to overcome these disadvantages and achieve cheap and effective hydrogen production by electrolysis, it is necessary to choose appropriate electrode and electrolyte conditions. 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 (Yazıcı et al., 1995). In addition, the electrode of choice must have a good electrocatalytic activity and high corrosion resistance (Solmaz and Kardaş, 2007). The electrocatalytic activity of the electrode materials can be considerably enhanced by the coating their surface with a thin metal film with higher catalytic activity. Recently several active electrodes have been developed for hydrogen evolution and the performance of nickel-based alloys is the best in all. A detail study on the effect of coating thickness and the deposition current density on the hydrogen gas production at the nickel coating has not been reported in detail.

The aim of this study was electrochemical preparation and characterization of the Ni coating on the copper electrode at different thicknesses and deposition current densities in view of their possible applications as
electrocatalytic materials for the hydrogen gas production.

EXPERIMENTAL

The electrodeposition of nickel was carried out on a copper electrode which was a cylindrical disc cut from a copper rod in about 5 cm length and coated with polyester block, aspect for measurement area of 0.283 cm$^2$. 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 carried out in a Wath bath with the chemical composition of 30% NiSO$_4$.7H$_2$O, 1% NiCl$_2$.6H$_2$O, 1.25% H$_3$BO$_3$. The electrodeposition was performed galvanostatically using Potentiosstate-galvanostate (Princeton Applied Research Model 362) with a three-electrode configuration. A nickel electrode was used as counter and Ag/AgCl electrode was used reference electrode, respectively. The thickness of nickel coating was theoretically calculated according to Faraday laws.

The coatings were characterized by cyclic voltammetry, 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.

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 and coated electrode was used. The solution temperature was thermostatically controlled at 298 K by Nuve BM 100 type thermostat.

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 cm$^2$ surface area) which was separated from the main cell compartment by a glass tube using Nafion and Ag/AgCl electrode were used as the auxiliary and the reference electrodes, respectively. All potential values were referred to this reference electrode. The cathodic current-potential 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$\leq f \leq$1 Hz at different overpotentials by applying alternating current signal of 0.005 V peak-to-peak. Before the tests, the working electrode was held at -1.80 V for 30 minutes in order to reduce the oxide film existence on the electrode surface and obtain a reproducible electrode surface. Cyclic voltammograms were recorded between -1.2 V and 0.5 V potential ranges started from negative direction with 100 mVs$^{-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.

RESULTS AND DISCUSSION

Characterization of the Coatings

The electrodeposited nickel coatings were characterized by cyclic voltammetry (CV), SEM and AFM techniques. The CVs of the 50 µm nickel coated copper electrode (Cu/Ni) at 50 mA.cm⁻² deposition current density was given in Figure 1. As can be seen from Figure 1 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).

$$\text{Ni} + 2\text{OH}^- \leftrightarrow \text{Ni(OH)}_2 + 2e^- \quad (1)$$
$$\text{Ni(OH)}_2 + \text{OH}^- \leftrightarrow \text{NiO(OH)} + \text{H}_2\text{O} + e^- \quad (2)$$

![Figure 1](image1.png)

**Figure 1.** The cyclic voltammogram of Cu/Ni recorded in 1 M KOH solution at 298 K (scan rate is 100 mVs⁻¹ and the potential was started from -1.1 V to positive direction)

In Figure 1, any peak related to copper did not appeared and well defined Ni peaks shows that, nickel was successfully electrodeposited on the copper surface.

![Figure 2](image2.png)

**Figure 2.** The SEM images of uncoated Cu (a) and nickel coated copper Cu/Ni (b) electrodes.
The SEM images of the 50 μm nickel coated copper at 50 mA.cm\(^{-2}\) deposition current density was given in Figure 2b. For a better comparison the surface SEM image of the uncoated copper was also given in Figure 2a. The surface image of the uncoated copper is smooth and the polishing stretches were visible on the surface. When a thick nickel film was electrodeposited on copper a compact and homogenous distributed pores were formed on the surface.

![SEM images of coated and uncoated copper](image)

**Figure 3.** The AFM images of uncoated Cu (a) and nickel coated copper Cu/Ni (b) electrodes.

AFM is a powerful technique to investigate the surface morphology at nano-to micro-scale and has become a new choice to study the surface morphology of the coatings. The surface AFM images of uncoated and 50 μm nickel coated copper electrodes were shown in Figure 3a-b, respectively. By comparing Figure 2 and Figure 3, there is a very good agreement between AFM and SEM images. As can be seen from Figure 3, the electrodeposited nickel film was homogeneously distributed pores were formed over the surface.

**Cathodic Current-Potential Curves**

In order to investigate the effect of deposition current density on the catalytic activity of the nickel coating for the HER, 10 μm thin nickel film was coated on the copper at different deposition current densities. The cathodic current-potential curves of the coated electrodes were shown in Figure 4 and the corresponding current densities which were determined at different overpotentials were given in Table 1. The comparison of the current densities at the same overpotential for the nickel coated electrodes and bare copper electrode suggested that nickel coatings exhibit better electrocatalytic activity for the HER in alkaline solution due to higher electrocatalytic activity of nickel (Petri & Tsirlina, 1994; Ndzebet & Savadogo, 1992; Hitz & Lasia, 2001; Choquette et. Al., 1990; Solmaz & Kardaş, 2007; Kardaş et. al., 2005; Solmaz et. al., 2007). As can be seen from Figure 4 and Table 1, the activity of the nickel coating depends on the deposition current density. At the same overpotential the higher current densities which directly proportional to hydrogen evolution reaction activity were obtained at 50 mA.cm\(^{-2}\) deposition current density. Because the electrochemical activity of an electrode material depends on the intrinsic activity of the metal and the surface porosity, at 50 mA.cm\(^{-2}\) deposition current density the most porous coating may be obtained.
Figure 4. Cathodic current-potential curves of 10 μm nickel coated copper electrodes at different deposition current densities recorded in 1 M KOH solution at 298 K.

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

<table>
<thead>
<tr>
<th>Working electrode</th>
<th>Coating thickness (μm)</th>
<th>Deposition current density (mA.cm⁻²)</th>
<th>I (mA.cm⁻²)</th>
<th>-0.100 V</th>
<th>-0.200 V</th>
<th>-0.300 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td></td>
<td></td>
<td>0.0656</td>
<td>0.3320</td>
<td>2.7095</td>
</tr>
<tr>
<td>10</td>
<td>30</td>
<td></td>
<td></td>
<td>0.1112</td>
<td>0.9509</td>
<td>8.2933</td>
</tr>
<tr>
<td>Cu/Ni</td>
<td>10</td>
<td>50</td>
<td></td>
<td>0.1216</td>
<td>1.4053</td>
<td>11.1060</td>
</tr>
<tr>
<td>10</td>
<td>75</td>
<td></td>
<td></td>
<td>0.1044</td>
<td>1.1618</td>
<td>9.6290</td>
</tr>
<tr>
<td>25</td>
<td>50</td>
<td></td>
<td></td>
<td>0.1454</td>
<td>1.6569</td>
<td>11.5053</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td></td>
<td></td>
<td>0.1465</td>
<td>1.6880</td>
<td>13.9329</td>
</tr>
</tbody>
</table>
At higher current densities the obtained coatings were not compact due to hydrogen evolution during the electrodeposition. The effect of the coating thickness for the HER activity was also investigated by cathodic current-potential curves at different thicknesses which were deposited at constant 50 mA cm⁻² deposition current density. The obtained current densities at different overpotentials were given in Table 1. It is clear from Table 1, among the studied nickel coatings the highest current densities were obtained at 50 μm coating.

**Electrochemical Impedance Spectroscopy**

The electrochemical impedance spectroscopy measurements of bare (Cu) and 50 μm nickel coated copper (Cu/Ni) electrodes which were carried out at 50 mA cm⁻² deposition current density were obtained at different over potentials and the representative Nyquist plots obtained at -0.200 V were presented in Figure 5. As seen from Figure 5, a slightly depressed semi circular shape was observed for both electrodes. The deviation from ideal semicircle was generally attributed the surface inhomogeneities of the coating (Elumalai et al., 2002; Rosalbino et al., 2005). Only one loop observing in Nyquist plots indicated 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. As can be seen from Figure 5a-b, the charge transfer resistance was reduced from 1000 Ω to 460 Ω when a thin nickel film was coated on the copper surface which indicate better electrocatalytic activity for the HER.

![Figure 5](image)

**Electrolysis**

In order to determine discharge potential and over potential of the electrolysis system, the current-potential curves obtained by two electrode set-up when platinum used as anode and nickel coated electrodes as cathode. For this purpose 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 (Figure 6). The curves are similar at beginning for all electrode pairs and up to a certain potential the current passing through the circuit is very small. After reaching discharge potential, the current densities were started to increase due to anodic oxygen evolution and cathodic hydrogen evolution.

During the alkaline water electrolysis, the following anodic (A) and cathodic (C) reactions take place.

\[
\text{A: } 4\text{OH}^- \rightarrow \text{O}_2(g) + 2\text{H}_2\text{O} + 4e^- \\
E_A = 0.401 - 0.0592p\text{OH} \quad (\text{PO}_2 = 1.0 \text{ atm}) \quad (3)
\]

\[
\text{C: } 4\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- + 2\text{H}_2(g) \\
E_C = -0.828 - 0.0592p\text{OH} \quad (\text{PH}_2 = 1.0 \text{ atm}) \quad (4)
\]

\[
2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2 \\
E_{\text{theo}} = 1.229 \text{ V} \quad (5)
\]

According to equation 3, the theoretical discharge potential \(E_{\text{theo}}\) of water electrolysis is 1.229 V. But due to overpotentials existence in the electrolysis system, i.e., activation, solution, diffusion, ohmic overpotential etc., it must be applied higher potential to the electrolysis system more than 1.229 V in order to discharge oxygen and hydrogen evolution. For all the electrode couples, the experimental discharge potentials \(E_{\text{exp}}\) were determined by extrapolating two linear parts of the curves and over potentials were calculated from equation (6) and presented in Table 2.

\[
\eta = E_{\text{exp}} - 1.229 \quad (6)
\]

![Figure 6. Current-voltage plots determined by two-electrode set up.](image)
Table 3. Experimental discharge potentials and overpotentials for each electrode coupling determined from the current-voltage curves obtained by electrolysis technique.

<table>
<thead>
<tr>
<th>Cathode</th>
<th>( E_{\text{exp}} / \text{V} )</th>
<th>( \eta / \text{V} )</th>
<th>( V_{\text{H}_2} ) (mL.cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>2.46</td>
<td>1.23</td>
<td>52</td>
</tr>
<tr>
<td>Cu/Ni(10mA-10(\mu)m)</td>
<td>2.23</td>
<td>1.0</td>
<td>90</td>
</tr>
<tr>
<td>Cu/Ni(20mA-10(\mu)m)</td>
<td>2.25</td>
<td>1.02</td>
<td>92</td>
</tr>
<tr>
<td>Cu/Ni(30mA-10(\mu)m)</td>
<td>2.19</td>
<td>0.96</td>
<td>94</td>
</tr>
<tr>
<td>Cu/Ni(50mA-10(\mu)m)</td>
<td>2.21</td>
<td>0.98</td>
<td>121</td>
</tr>
<tr>
<td>Cu/Ni(75mA-10(\mu)m)</td>
<td>2.26</td>
<td>1.03</td>
<td>114</td>
</tr>
<tr>
<td>Cu/Ni(50mA-25(\mu)m)</td>
<td>2.06</td>
<td>0.83</td>
<td>133</td>
</tr>
<tr>
<td>Cu/Ni(50mA-50(\mu)m)</td>
<td>2.07</td>
<td>0.84</td>
<td>129</td>
</tr>
</tbody>
</table>

It is clear from Table 2 that, the overpotential was reduced when the surface of copper was coated with nickel. The electrocatalytic activity of the coatings depends on both coating thickness and the deposition current density and increasing with deposition current density and also coating thickness.

Hydrogen gas filling the burette turned over on the cathodes, which were working electrodes, measured over 1 hour by applying constant potential of 3.0 V. In these conditions measured volume is total of hydrogen gas and water vapor. Correct hydrogen volumes were calculated as described elsewhere (Kardag et. al., 2003) and determined the hydrogen gas volumes were given in Table 2. It can be seen from Table 2, the more hydrogen gas was produced at Ni coated electrodes.

**CONCLUSIONS**

The Ni was electrochemically coated on a copper electrode at different deposition current densities and thicknesses and characterized in view of their possible applications as cathode material for the electrochemical hydrogen production. The electrodeposited coatings were characterized by CV, SEM and AFM techniques. It was found that, the nickel coated copper electrodes can enhance the electrocatalytic activity for the hydrogen evolution reaction in alkaline media when compared to bare copper. The hydrogen evolution reaction activity of the coatings depends on the deposition current density and the thickness of the coating. The lowest overpotential and discharge potanetial values were obtained at 50 \(\mu\)m nickel coated copper electrode (Cu/Ni) at a constant current density of 50 mA.cm\(^{-2}\). The highest hydrogen volume was also obtained at this electrode. From the cathodic current-potential curves and the electrochemical impedance spectroscopy measurements it was found that, at the same over potential the 50 \(\mu\)m nickel coated copper electrode has the highest
current density which is directly proportional to the hydrogen production, and the lowest charge transfer resistance values were obtained. According to obtained results it can be said that when the surface of copper was electrodeposited by a thin nickel film, the lowest electrical energy will be consumed for the electrochemical hydrogen gas production.

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