# SECTION 4

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4. DEVELOPMENT OF NICKEL COATED GRAPHITE ELECTRODES

4.1. Introduction

Pure nickel electrodes and nickel coated electrodes find various applications in the field of electroanalytical chemistry. As discussed in section 1.3.5., nickel electrodes can be applied for electrochromic devices [61], alkaline batteries [62], and as electrocatalysts [63, 64]. Most of these applications are originated based on the redox pair system Ni(OH)\(_2\)/NiOOH [65,66]. The application of nickel based chemically modified electrode (Ni-CME) to detect aliphatic alcohols have been reported [67]. Electroless nickel coated electrodes can also be used as alcohol sensors [57]. But the concentration of reducing agent in electroless nickel plating bath affects the sensitivity of the electrodes. Nickel based thick film ethanol sensors has been developed by screen printing technology [91]. The sensing performance of these nickel electrodes is due to the oxidation of ethanol at a lower potential electrocatalyzed by the redox pair, a Ni(OH)\(_2\)/NiOOH which is formed on the nickel surface in alkaline medium [27, 86, 92]. But as reported in earlier studies [29], the background current of pure nickel electrode is unstable and there is low sensitivity in the electrochemical sensing system. According to the limiting current equation explained in section 1.4., the catalytic area of pure nickel electrode can be increased by using electrochemical deposition of nickel on the substrate material. The ease of immobilization on inert surfaces, good adherence, high corrosion resistance, lower impedance and feasibility to
control particle size are the merits of electrodeposition technique selected in the present study.

4.2. **Standardization of nickel plating system**

Several electroplating baths were applied during the preliminary stage of the present study. Watt's bath which contains least number of additives was selected for the present study. The composition and conditions adopted for the electrodeposition of nickel on graphite substrate was given in section 3.1.2.3.

4.3. **Evaluation of the developed electrodes**

4.3.1. **Evaluation of structural characteristics**

4.3.1.1. **Morphology**

The morphology of the electroplated nickel electrode was compared with that of pure nickel electrode. It showed that, the nickel plates on graphite substrates exhibited good adherence and reproducibility than the pure nickel electrode, even after subjecting them for repeated sensing measurements. The coating was uniform throughout the surface and only few pores were observed for the electrodeposited nickel electrode.

4.3.1.2. **Microstructure**

The microstructure of the nickel plated electrodes were analyzed using an optical microscope. The optical micrographs obtained showed very smooth surface finishing for the electroplated nickel electrode than that for the
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pure nickel electrode. The more clear and accurate microstructures of the
developed electrodes were obtained from scanning electron microscopic
(SEM) images. Figure 4.1. shows the SEM pictures of pure nickel electrode
and electroplated nickel electrode.

From the SEM pictures, it was clear that the uniformity and
homogeneity of the nickel plate is high for electroplated nickel electrode than
that of the pure nickel electrode. Better bonding was observed between the
matrix and nickel particles without any voids. The grain size of the
electroplated nickel electrode was very small and it gives better finishing of
the surface. The small grain size increases the effective electrocatalytic surface
area of the nickel plated electrode.

4.3.2. Evaluation of stability

4.3.2.1. Corrosion tendency

The corrosive nature of the electrode was identified from the polarization
study. The polarization study was carried out in 3% NaCl solution by
potentiodynamic technique. Tafel plots were drawn for both pure nickel electrode and electrodeposited nickel electrode (Figure 4.2.).

![Tafel plots](image)

Figure 4.2. The Tafel plots of nickel electrodes in 3% NaCl solution
A: Pure nickel electrode and B: Electroplated nickel electrode

The electrochemical parameters such as corrosion potential, corrosion current density and Tafel slope were calculated from the Tafel plot and are given in table 4.1.
Table 4.1. The electrochemical parameters of pure nickel electrode and electroplated nickel electrode observed in 3% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (V)</th>
<th>$i_{\text{corr}}$ (µA/cm$^2$)</th>
<th>Tafel slope V/(µA/cm$^2$)</th>
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<td>Pure nickel electrode</td>
<td>-0.520</td>
<td>0.600</td>
<td>0.163</td>
</tr>
<tr>
<td>Electroplated nickel electrode</td>
<td>-0.481</td>
<td>0.350</td>
<td>0.142</td>
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From the polarization study it was revealed that the corrosion potential changed from $-0.520$ V to $-0.481$ V, when pure nickel electrode was modified to electroplated nickel electrode. i.e., the corrosion of electroplated nickel electrode takes place at a higher positive potential than that of pure nickel electrode. This fact is also enhanced by the corrosion current density ($i_{\text{corr}}$) obtained from the Tafel plot of these two electrodes. The electroplated nickel electrode gives a corrosion current density of only $0.350$ µA/cm$^2$, whereas the pure nickel electrode gives a corrosion current density of $0.600$ µA/cm$^2$. The Tafel slope value of the electroplated nickel electrode was lower than that of the pure nickel electrode. All these factors enhanced the corrosion prevention tendency of the electroplated nickel electrode than that of the pure nickel electrode.

4.3.2.2. Long-term stability

The long-term stability of the electrodes was analyzed from the open circuit potential (OCP) decay study. The OCP decay study was carried
out in 3% NaCl solution, in 0.2M NaOH solution and in Ringer physiological solution. Figure 4.3. shows the open circuit potential decay study of pure nickel electrode and electroplated nickel electrode in 3% NaCl solution, in 0.2M NaOH solution and in Ringer physiological solution. From the graph it is clear that the potential became stable near their natural corrosion potential after about 200 hrs. From there, the corrosion became very less and it exhibited very minute tendency to corrode even when they were dipped in these solutions for about 700 hrs. The OCP values of electrodeposited nickel electrode in all the three solution taken for the present study are at lower negative potential region than that of the pure nickel electrode. From this study, it was clear that the corrosion tendency of the electroplated nickel electrode was lower than that of the pure nickel electrode.

From the open circuit potential decay study, it was also revealed that, the samples had lesser corrosion in 0.2M NaOH solution than in 3% NaCl solution. Similarly, the corrosion resistance of these samples in Ringer physiological solution was found to be higher than that in 3% NaCl and in 0.2M NaOH solutions. This is due to the difference in overall chloride concentrations in these solutions. The inhibiting action of some of the anionic components of the phosphate buffer used to maintain this solution at pH 7.4 is also the cause for the reduced corrosion in Ringer physiological solution [90].
Figure 4.3. The open circuit potential decay study of nickel electrodes in 3% NaCl solution, in 0.2 M NaOH solution and in Ringer physiological solution. A: Pure nickel electrode and B: Electroplated nickel electrode.
4.3.3. Evaluation of sensitivity

4.3.3.1. Identification of the redox species

The potential at which the redox pairs were formed was identified from the cyclic voltammetric studies, which were carried out as discussed in section 3.5.3.3. The cyclic voltammograms of pure nickel electrode and electroplated nickel electrode in 0.2 M NaOH solution are shown in figure 4.4.

![Cyclic voltammograms of nickel electrodes](image)

**Figure 4.4.** The cyclic voltammograms of nickel electrodes. Working electrode (nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), scan rate (10 mV/sec) and temperature (28°C). A: Pure nickel electrode and B: Electroplated nickel electrode.

From the wave form it is clear that, the forward scan produces a current peak for any analytes that can be reduced at that range of potential scan. The current increases as the potential reaches the reduction potential of the analyte, but then falls off as the concentration of the analyte is depleted.
close to the electrode surface. As the applied potential is reversed, it reached a potential that oxidizes back the product formed in the first reduction reaction, and produces a current of reverse polarity from the forward scan. The oxidation peak has the similar shape as that of the reduction peak. As a result, information about the redox potential and electrochemical reaction rates of the compounds are obtained. It can be inferred that in the system both redox reaction in the solution and solid-state electrochemical reactions over the electrode are happening.

In basic solutions, nickel forms a redox pair Ni(OH)\textsubscript{2}/NiOOH which gives the catalytic activity to the surface of the electrode [60,65,66]. In the case of pure nickel electrode, the anodic peak appeared at 590 mV (vs. Ag/AgCl electrode), whereas in the case of electroplated nickel electrode, the anodic peak appeared at 570 mV (vs. Ag/AgCl). The anodic peak corresponds to the oxidation of $\alpha$ – Ni(OH)\textsubscript{2} to $\beta$ – NiOOH and $\gamma$ – NiOOH. The cathodic peak corresponds to the reduction of $\gamma$ – NiOOH and $\beta$ – NiOOH to $\alpha$ – Ni(OH)\textsubscript{2} and $\beta$ – Ni(OH)\textsubscript{2} [15,27,93,94]. The enhancement of current at a lower potential for the electroplated nickel electrode compared to pure nickel electrode was due to the greater surface area of the electroplated sample. The increase in surface area of the electrode increases the electron transfer between the nickel redox species and as a result, there is greater formation of the redox system on the electrode surface, which causes a current enhancement.
Figure 4.5. shows the cyclic voltammograms of pure nickel electrode and electroplated nickel electrode in the presence of acetylcholine.

The addition of 0.05µM acetylcholine to 0.2M NaOH solution caused a raise in anodic peak to more positive current region due to the enhancement of oxidation of $\beta - \text{Ni(OH)}_2$ to $\beta - \text{NiOOH}$. This occurs by the greater reduction of $\beta - \text{NiOOH}$ to $\beta - \text{Ni(OH)}_2$ during the oxidation of acetylcholine on the nickel electrode surface. This is in good agreement with other reports available in literature [15]. In the case of pure nickel electrode, the response current was raised by about 2 µA, whereas, in the case of electroplated nickel electrode, the response current was raised by about 2.5 µA.
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for addition of 0.05μM acetylcholine. The mechanism involved in the enhancement of response current by acetylcholine is similar to that reported elsewhere [15, 27].

**Step 1.** Nickel electrode gets oxidized to form Ni(OH)$_2$/NiOOH catalytic system in basic solutions.

\[
Ni + 2OH^- \rightarrow Ni(OH)_2 + 2e^-
\]

\[
Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^-
\]

**Step 2.** Acetylcholine molecules get hydrolyzed in basic solution to form acetate ion and choline molecules.

\[
CH_3OO(CH_2)_2 N^+ (CH_3)_3 + OH^- \rightarrow CH_3COO^- + (CH_3)_3 N^+ CH_2 CH_2 OH
\]

\[
\text{acetylcholine} \quad \text{acetate ion} \quad \text{choline}
\]

**Step 3.** The choline molecules get adsorbed on the nickel electrode surface and the alcohol groups of choline molecules get oxidized to corresponding carboxylic acid.

\[
(CH_3)_3 N^+ CH_2 CH_2 OH + NiOOH \rightarrow (CH_3)_3 N^+ CH_2 CH_2 \dot{O} + Ni(OH)_2
\]

\[
(CH_3)_3 N^+ CH_2 CH_2 \dot{O} + OH^- \rightarrow (CH_3)_3 N^+ CH_2 CH_2 O (OH)
\]

\[
(CH_3)_3 N^+ CH_2 CH_2 O(OH) + NiOOH \rightarrow (CH_3)_3 N^+ CH_2 COO^- + Ni(OH)_2 + H_2O
\]
The Ni(OH)$_2$/NiOOH redox system can oxidize the alcohol functional group to carboxyl group before the oxidation of water in aqueous solution [15, 28]. The current raise of the electroplated nickel electrode in presence of acetylcholine was found to be more than that of the pure nickel electrode. The increase in current by 0.5 µA for the electroplated nickel electrode was due to the presence of large number of active electrocatalytic surface area. The increased surface area enhances the reduction of acetylcholine molecules and it results in enhancement of current.

4.3.3.2. Identification of sensing potential

The sensing potential of the electrodes were identified by linear sweep voltammetric technique as described in section 3.5.3.3. Figure 4.6. shows the linear sweep voltammograms of the pure and electroplated nickel electrodes. The applied potential must be higher than that of both the redox and solid-state electrochemical reactions in the system. It was not only due to the redox reaction but also the electrochemical reaction involved in the system. These reaction occurred both at the interface of solution/electrode and inside the electrode [91]. The applied potential was swept from 450 to 700 mV (vs. Ag/AgCl). For the pure nickel electrode, the response current was found increased with increase in the applied potential upto 520 mV (vs. Ag/AgCl). In this region, the reaction was kinetically controlled. When the reaction reached the mass transfer control, the boundary layer approached a steady state and current remained almost constant at the potential range from
520 to 570 mV (vs. Ag/AgCl). Therefore the potential range of about 530 mV (vs. Ag/AgCl), a potential which gives maximum steady state current was chosen as the applied potential for the determination of acetylcholine concentration.

But in the case of electroplated nickel electrode, the response current was found increased with increase in applied potential upto 500 mV (vs. Ag/AgCl). Thereafter current remained almost constant in the potential range from 500 to 550 mV (vs. Ag/AgCl). Therefore potential of 510 mV (vs. Ag/AgCl), which corresponds to a maximum steady state current, was selected as the applied potential for sensing acetylcholine.

Figure 4.6. The linear sweep voltammograms of the nickel electrodes. Working electrode (nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), temperature (28°C) and scan rate (10 mV/sec). A: Pure nickel electrode and B: Electroplated nickel electrode.
As observed elsewhere [95], nickel exists at different mode of oxidation states including $\alpha$, $\beta$ and $\gamma$ – Ni(OH)$_2$/NiOOH, in alkaline solutions according to the available different potentials. Only $\beta$ – Ni(OH)$_2$/NiOOH has the features of electrochemical catalysis [28]. Therefore applying a higher potential can cause the nickel electrode to become over oxidized with a consequent loss of catalytic activity [15]. From the linear sweep voltammetric study, it was clear that, the electroplated nickel electrode can be applied for sensing acetylcholine at a lower potential than that of pure nickel electrode. This is due to the enhanced electrocatalytic nature of the electroplated nickel electrode than the pure nickel electrode.

4.3.3.3. Amperometric response

Amperometric response of the nickel electrodes was found out by chronoamperometric technique, which was described in section 3.6. The typical current response dependence on the acetylcholine concentration is shown in figure 4.7. The results indicated that the base line of pure nickel electrode approached the steady state at the beginning of a run at 530 mV (vs. Ag/AgCl) and the background current was 750 µA in the batch sensing system for about 300 seconds. After adding 0.05 µM acetylcholine in the test chamber, the response current was raised from 750 µA to 752 µA and the response time of the current, which reached 90% steady state current was 30 seconds. Whereas in the case of electroplated nickel electrode, the background
current was 800 $\mu$A at 510 mV (vs. Ag/AgCl) and the response current increased to 802.5 $\mu$A after adding 0.05 $\mu$M acetylcholine. The response time of this electrode was 23 seconds. This fast response of the electroplated nickel is due to the increase in the electrocatalytic surface area of the electrode during electroplating.

Figure 4.7. The amperometric response of nickel electrodes in sensing acetylcholine. Sensing conditions: working electrode (nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), temperature (28°C) and change in concentration of acetylcholine during each successive addition (0.05 $\mu$M). A: Pure nickel electrode at applied potential 530 mV and B: Electroplated nickel electrode at applied potential 510 mV.

Figure 4.8. shows the calibration curves of nickel electrodes showing the variation of response currents with concentration of acetylcholine,
which was based on the background current measured in blank electrolyte and passed through the zero point resulted in a straight line. The curve behaved in a good linear relationship with the acetylcholine concentration from 0 to 50µM. The results of linear fit was $y=40x + 750$ for pure nickel electrode and $y=50x + 800$ for electroplated nickel electrode.

![Figure 4.8](image-url)

**Figure 4.8.** The calibration plots of nickel electrodes in sensing acetylcholine. Sensing conditions: working electrode (nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), scan rate (10 mV/sec), temperature (28°C) and change in concentration of acetylcholine during each successive addition (0.05 µM). Each point on the plot represents the mean ± S.D. of five experiments. A: Pure nickel electrode at applied potential 530 mV and B: Electroplated nickel electrode at applied potential 510 mV.

Different phases of NiOOH can lead to different response current during sensing. This is due to the existence of different structures of nickel hydroxides namely $\alpha - \text{Ni(OH)}_2$ and $\beta - \text{Ni(OH)}_2$ which are oxidized to $\beta$
- NiOOH and $\gamma$ - NiOOH. The oxidation state of nickel in $\gamma$ - NiOOH is higher than $\beta$ - NiOOH [86, 96]. The sensitivity obtained for pure nickel electrode was found to be 0.44 mA/(µM x cm$^2$) and that for the electroplated nickel electrode was found to be 0.56 mA/(µM x cm$^2$).

4.4. Evaluation of tolerance of the sensing system

The tolerance of the sensing system was tested by repeating the sensing experiments under same conditions after exposing the electrode in natural environment for different period of time. The developed electrode exhibited only slight variation in sensitivity even after 700 hrs. So these developed electrodes can be used as a cheap and fast response acetylcholine biosensor.

4.5. Variation of sensitivity with electrodeposition time

The sensitivity of the electroplated nickel electrodes varied with electrodeposition time, which is shown in figure 4.9. The electrode prepared from the bath providing a deposition time of 5 minutes exhibited the maximum sensitivity. As the electrodeposition time increased above 5 minutes, the thickness of the boundary layer over the electrode surface is increased. From the limiting current equation it is clear that increase in the boundary layer thickness reduces the limiting current. As a result, sensitivity of the electrode decreases. The decrease in sensitivity of the electrode obtained from the electrolytic bath providing greater electrodeposition time than 5
minutes was confirmed by the poor adherence of the nickel plate over the substrate material as observed through the optical microscope.

![Graph showing variation of sensitivity with deposition time.](image)

**Figure 4.9.** Variation of sensitivity of the electroplated nickel electrode with electrodeposition time. Sensing conditions: working electrode (nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), scan rate (10 mV/sec) and temperature (28°C).

### 4.6. Comparison with other similar reported systems

Electrodeposited nickel electrodes found an important place in the field of biosensing. The developed electrodes in this study showed greater sensitivity than that shown by other similar reported studies i.e., $6.53 \times 10^{-5}$ mA/(µM x cm$^2$) for nickel anode electrode [15] and $0.182 \times 10^{-3}$ mA/(µM x cm$^2$) for electrodeposited nickel from other plating bath [29]. All these results enhanced the application of electroplated nickel electrode for sensing acetylcholine.
4.7. Conclusions

- The application of nickel electrodes in the field the biosensors is an encouraging one.
- The biosensing nature of the electrodes can be improved by the electrodeposition technique.
- The suitable condition selected for the electrodeposition of nickel are pH: 3.5, temperature: 28°C, current density: 50 - 60 mA/cm² and deposition time: 5 minutes.
- The sensitivity of the electrodeposited nickel electrode is higher than that of the pure nickel electrode.
- The electrocatalytic nature and reproducibility of the electrodeposited nickel electrode is higher than that of the pure nickel electrode.
- The fast response time of electrodeposited nickel electrode makes it a very good acetylcholine sensor.

4.8. Scope for further study

Electrodepositon of nickel over a cheap substrate material like graphite finds immense applications in the field of electroanalysis. We can improve the electrocatalytic nature of the developed electrodes by applying a new approach such as process modification. No comprehensive report is available in this direction and hence it forms the next part of the present study (Section 5).