## SECTION 5

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5. CO-ELECTRODEPOSITION AS A PROCESS MODIFICATION TECHNIQUE

5.1. Introduction

The application of nickel electrodes in sensing and estimating acetylcholine catch the attention of recent researchers due to the greater electrocatalytic performance of the nickel electrodes. The Ni(OH)$_2$/NiOOH catalytic system has been utilized to oxidize acetylcholine molecules in the enzyme-free system [15,27-29,57-59]. Due to the unstable nature of the background current and low sensitivity of the electrochemical system, pure nickel electrode was modified by electrodeposition of nickel on highly conducting graphite substrate. This increased the electrocatalytic surface area of the nickel electrode.

The process of electrodeposition can be modified by applying co-electrodeposition technique. There were similar studies showing co-electrodeposition of B$_4$C particles [97], nano Al$_2$O$_3$ whiskers [98], diamond powder [99] and electrodeposition of hydrophobic nickel [100]. But only few studies were reported on co-electrodeposition of nickel. Hence it forms part of the present study and the results are discussed in this section.

5.2. Characterization of the modified electrodes

As discussed in section 3.1.2.4., electroplated nickel electrodes were prepared. The co-electrodeposited nickel electrodes were prepared by double cell method according to the procedure discussed in section 3.2.1. The
characterization of the modified electrodes were discussed in the following part of this section.

5.2.1. Structural characterization

5.2.1.1. Study of surface roughness

The surface roughness of both electroplated and co-electrodeposited electrodes was examined thoroughly through optical microscope. The nickel plates obtained from the co-electrodeposition technique exhibited very good adherence with the substrate material than that of electrodeposited nickel. The surface roughness decreased due to the co-electrodeposition of nickel from the nickel plating bath. The decreased surface roughness showed the higher corrosion resistant nature of the co-electrodeposited electrode. The co-electrodeposition from the double cell system enhances the surface finishing of the electroplated nickel electrode. The depletion of Ni$^{2+}$ ions from the nickel-electroplating bath was overcome by the dissolution of nickel from the pure nickel electrode.

5.2.1.2. Growth of grain boundaries

The microstructure of the surface of the developed nickel plates was examined under optical microscope and it showed very good and smooth surface finishing for the co-electrodeposited nickel electrode than the electroplated nickel electrode. Very good samples obtained from the electrolytic bath were observed under scanning electron microscope. Figure 5.1. shows the SEM pictures of electroplated nickel electrode and co-
electrodeposited nickel electrode. The micrographs obtained showed clear
grain boundaries for the co-electrodeposited plate than that of electrodeposited
nickel plate. The voids between the particles were cleared by the co-
electrodeposition of nickel from the nickel bath. The grains were smaller in
size and gave uniform coverage throughout the surface of the co-
electrodeposited electrode. Smaller grains can also increase the active surface
area.

Figure 5.1. The surface morphology of A: Electroplated nickel electrode and B: Co-
electrodeposited nickel electrode.

5.2.2. Stability measurement

5.2.2.1. Polarizability

The polarizability of the developed electrodes was examined
according to the procedure discussed in section 3.5.3.1. This study was carried
out in 3% NaCl solution without any further treatment of the electrode surface.
Tafel plots of the developed electrodes were drawn and are given in figure 5.2.
The electrochemical parameters like corrosion potential, corrosion current density and Tafel slopes were calculated and the values are given in table 5.1. The corrosion potential value changed from -0.481 V to -0.282 V (vs. SCE) when the electrodeposition technique changed to co-electrodeposition. This indicated that corrosion of nickel starts only at higher positive potential region for the co-electrodeposited electrodes than that of the electrodeposited electrodes. In the same manner, Tafel slope changed from 0.142 to 0.130 V/(μA/cm²) indicating lower corrosion tendency of the co-electrodeposited electrode compared to electrodeopisted electrode.
Table 5.1. The electrochemical parameters of electrodeposited and co-electrodeposited nickel electrodes in 3% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (μA/cm$^2$)</th>
<th>Tafel slope V/(μA/cm$^2$)</th>
</tr>
</thead>
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<tr>
<td>Electroplated nickel electrode</td>
<td>-0.481</td>
<td>0.350</td>
<td>0.142</td>
</tr>
<tr>
<td>Co-electrodeposited nickel electrode</td>
<td>-0.282</td>
<td>0.150</td>
<td>0.130</td>
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The enhancement of corrosion prevention tendency of the co-electrodeposited nickel electrode than the electroplated nickel electrode was due to the greater surface coverage of nickel on the electrode surface by co-electrodeposition. Even a small break in the surface coating can induce the corrosive nature of the nickel electrode, which was overcome by co-electrodeposition. This increases the application of co-electrodeposited nickel electrode as corrosion resistant material.

5.2.2.2. Long-term stability

The long-term stability of the electrodes was examined as per the procedure discussed in section 3.5.3.2. The stability behaviour of electrodeposited and co-electrodeposited electrodes in different environments is explored by monitoring the OCP decay of both the electrodes (Fig. 5.3.)
Figure 5.3. 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: Electroplated nickel electrode and B: Co-electrodeposited nickel electrode.
Due to the greater reinforcement by nickel in the co-electrodeposited nickel sample, it exhibited lower decay tendency than that of the electrodeposited nickel electrode. Among 3% NaCl, 0.5 M NaOH and Ringer physiological solution, the co-electrodeposited electrode showed the least potential variation in Ringer physiological solution. This indicated the more suitability of the co-electrodeposited electrodes in body fluids. The least potential variation of the co-electrodeposited nickel electrode than electroplated nickel electrode in all these solutions enhanced the extra stability of the co-electrodeposited nickel electrode in the corroding environments. This is mainly attributed to the greater adhesion of the nickel plate with the substrate material in the case of the co-electrodeposited nickel electrodes.

5.2.3. Sensitivity measurement

5.2.3.1. Exploration of redox nature of the electrode

The redox nature of the developed electrodes were found out by the procedure discussed in section 3.5.3.3. The cyclic voltammetric studies of the modified electrodes in 0.2 M NaOH solution showed the presence of Ni(OH)$_2$/NiOOH catalytic system at the expected potential region. The anodic peak of the co-electrodeposited sample appeared at potential 570 mV (vs. Ag/AgCl). But the response current of the co-electrodeposited nickel electrodes is higher than that of electrodeposited sample. i.e., the response current changed from 800 µA to 1000 µA for the co-electrodeposited electrode
indicating the presence of greater amount of nickel having definite structure. Nickel can exist in different phases as explained in previous studies [91]. They are, $\alpha$, $\beta$ and $\gamma$ phases. $\alpha$ - phase, is a phase with a formulation of $\text{Ni(OH)}_2 \cdot x\text{H}_2\text{O}$, where $x$ ranging from 0.5 to 0.7, $\beta$ - phase is a phase of $\text{Ni(OH)}_2$ and $\text{NiOOH}$ with definite structure and $\gamma$ - phase is a phase of $\text{NiOOH}$ derived from $\alpha$ - $\text{Ni(OH)}_2$ or $\beta$ - $\text{Ni(OH)}_2$ with a turbostatic structure. Among all these structures, $\beta$ - form of nickel is the most catalytically active species [28]. The high electrocatalytic activity of the developed electrode shows the existence of $\beta$ - form of nickel in alkaline medium. Figure 5.4. shows the cyclic voltammetric response of the co-electrodeposited nickel electrode without and with the presence of acetylcholine.

![Cyclic voltammograms](image)

**Figure 5.4.** The cyclic voltammograms of co-electrodeposited nickel electrode with and without the presence of acetylcholine. Working electrode (co-electrodeposited nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.02 M), scan rate (10 mV/sec) and temperature (28°C). A: Without the presence of acetylcholine and B: With the presence of acetylcholine (0.05 µM).
Addition of 0.05 µM acetylcholine raised the response current to 1003 µA. This showed greater oxidation of Ni(OH)₂ on the nickel electrode surface by the acetylcholine molecules. The enhancement of current at lower potential shows the increased electrocatalytic surface area of co-electrodeposited electrode. As a result, greater reduction of acetylcholine molecule on the surface of the electrode occurs and hence response current increases.

5.2.3.2. Finding out of suitable potential range for sensing

The linear sweep voltammetric analysis carried out as per the procedure discussed in section 3.5.3.3., revealed same behaviour for the co-electrodeposited electrode as that of the electrodeposited sample (Figure 5.5.).

Figure 5.5. The linear sweep voltammogram of the co-electrodeposited nickel electrode. Working electrode (co-electrodeposited nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), scan rate (10 mV/sec) and temperature (28°C).
In this case also when the potential swept from 450 to 500 mV (vs. Ag/AgCl), the response current increased and it remains almost constant up to 550 mV (vs. Ag/AgCl) and then it rapidly raises. Since the maximum steady state current was observed at 510 mV, the sensing potential of the developed electrode was taken as 510 mV (vs. Ag/AgCl). In this region, the electrode maintained its maximum redox nature, above that potential it loses its catalytic nature.

5.2.3.3. Variation of response current with acetylcholine concentration

Figure 5.6. The amperometric response of the co-electrodeposited nickel electrode in sensing acetylcholine. Sensing conditions: working electrode (co-electrodeposited 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).
Figure 5.6. shows the chronoamperometric response of the developed electrodes in 0.2 M NaOH solution. From the chronoamperometric study it was revealed that the background current reached a steady state of 1000 µA at 510 mV (vs. Ag/AgCl). After the addition of 0.05 µM acetylcholine solution, the response current increased to 1003 µA and remains steady after sometime. The response time shown by the co-electrodeposited electrode was only 5 seconds which was far better than the conventional nickel electrodes [15, 29].

The calibration curve of co-electrodeposited nickel electrode indicating the current response with acetylcholine concentration in 0.2 M NaOH solution is shown in figure 5.7. The curve behaved in a good linear manner with acetylcholine concentration from 0 to 50 µM. The results of linear fit was \( y = 60x + 1000 \) and sensitivity of the co-electrodeposited electrode was 0.67 mA/(µMxcm\(^2\)) which was greater than that of pure nickel electrode and electroplated nickel electrode discussed in section 4. The enhanced performance of the co-electrodeposited nickel electrode can be attributed to the improved nature of the nickel plate due to synergistic structural control of the simultaneous and secondary plating. In this case, the plating of nickel from the electroplating bath is influenced by the anodic
dissolution also. Existence of parallel co-plating system can act as that of presence of a complexing agent.

Figure 5.7. The calibration plot of co-electrodeposited nickel electrode in sensing acetylcholine. Sensing conditions: working electrode (co-electrodeposited 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.

5.3. Influence of co-electrodeposition time on variation in sensitivity

The sensitivity depends largely on the electro-deposition time. Figure 5.8. shows the variation of sensitivity of the nickel electrode with co-electrodeposition time. The sensitivity first increased with deposition time which reached a maximum value at 5 minutes and then decreased. This is due to the fact that at the initial stage, co-electrodeposition helps to increase the electrocatalytic surface area of the electrode; but after five minutes multiple growth of nickel takes place over the electrode surface, which causes its poor
adherence on the substrate material. As observed in the previous section (Section 4), the increase in the boundary layer thickness caused by providing greater electrodeposition time decreases the limiting current. The decrease in limiting current induces lower sensitivity and lower response time for the co-electrodeposited electrode. Hence better sensitivity was obtained for the co-electrodeposited sample with electrodeposition time of 5 minutes.

Figure 5.8. Variation of sensitivity of the co-electrodeposited nickel electrode with time. Sensing conditions: working electrode (co-electrodeposited nickel), counter electrode (platinum), reference electrode (Ag/AgCl), electrolyte (NaOH 0.2 M), scan rate (10 mV/sec) and temperature (28°C).

5.4. Conclusions

The surface morphological and electrochemical studies reveals the high corrosion resistance and stability of co-electrodeposited nickel electrode compared to electrodeposited nickel.
Nickel plates with excellent structural and electrochemical characteristics can be obtained by co-electrodepositing of nickel along with plating of nickel directly from a pure nickel anode.

The prepared electrodes exhibited low response time and better sensitivity as evidenced by chronoamperometric studies.

The sensing procedure, calibration and accuracy of the present case of nickel electrodes were found to be reliable and reproducible.

The sensing performance of the electrodes developed from optimized bath was found to be superior than that of other nickel electrodes being reported in the literature currently.

5.5. Scope for further study

The major aim of the present study was to prepare a more sensitive and fast response nickel electrode through process modification. The developed electrodes exhibited better sensitivity. This indicated that, the electrocatalytic performance of the nickel electrodes can be improved in many ways. There are a lot of other studies like composite addition for improving the performance of the nickel electrodes [100, 101]. But studies regarding the application of composite modified nickel electrodes in sensing acetylcholine are only few. Hence compositional modification of the nickel electrodes was carried out in the next section of the present study.