3 RESULTS AND DISCUSSION

3.1 Cyclic Voltammetry (Qualitative Observation)

3.1.1 Electropolymerization of Pyrrole in aqueous NaPSS solutions

In Figure 3.1.1, current versus potential characteristics for the electropolymerization of 0.1 M pyrrole (PPy) in aqueous 0.1 M NaPSS solutions are presented. Since the PSS did not undergo any electrochemical reduction or oxidation, it can be assumed that the oxidation peak from \(E=0\) mV to \(E=200\) mV was due to the PPy itself. The oxidation current decreased on the consecutive sweeps. This was probably due to the presence of a "hard oxidation" during the electropolymerization process\(^{[77]}\).

The charge compensation during the PPy/PSS\(^{-}\) film reduction involves incorporation of the sodium ions to balance the negative charges on permanently incorporated large PSS anions. Well defined cationic dynamics with Na\(^+\) cations uptake in the potential range from \(E= -600\) mV to \(E= -800\) mV was observed during the cathodic scan, as had been reported in the literature by others\(^{[44, 56]}\).
3.1.2 Electropolymerization of pyrrole in the presence of PVS

The composite PPy/PVS film (Figure 3.1.2) behaves very much like the PPy/PSS film (Figure 3.1.1). Figure 3.1.2 shows CV for the electropolymerization in aqueous solution of 0.1 M poly (vinylsulfonic acid, sodium salt) (PVS) and 0.1 M pyrrole (PPy). The oxidation peak at $E = -200 \text{ mV}$ was related to the monomer oxidation. It was observed that the current increased on the second sweep and became constant on the consecutive sweeps. This fact is reinforced by the overpotential decrease for the initiation of monomeric oxidation, as the oxidation current increased from the first to second sweep. Later, it became constant at following sweeps\cite{77}.

The charge compensation during the PPy/PVS film reduction involved incorporation of the sodium ions to balance the negative charges on permanently incorporated large PVS anions, as mentioned in the literature\cite{44}. Well defined cationic dynamics with Na$^+$ cation inserted from -500mV to -800mV was also observed during the cathodic scan\cite{44,56}.
Figure 3.1.1: Cyclic Voltammogram for a titanium electrode in aqueous solution containing 0.1 M pyrrole (PPy) and 0.1 M Poly (sodium 4-styrenesulfonate) (NaPSS), (potential versus Ag/AgCl at a scan rate of 50 mV/s).

Figure 3.1.2: Cyclic Voltammogram for a titanium electrode in aqueous solution of 0.1 M pyrrole (PPy) and 0.1 M Poly (vinylsulfonic acid, sodium salt) (PVS), (potential versus Ag/AgCl at a scan rate of 50 mV/s).
3.1.3 **Electropolymerization of pyrrole in the presence of PTS**

Figure 3.1.3 allows us to observe the electropolymerization process in 0.1 M p-toluenesulfonic acid monohydrate (PTS) and 0.1 M pyrrole (PPy) aqueous solution. The voltammogram results indicate the characteristics of the nucleation processes between 1000 and 1200 mV\[^{[78]}\]. The oxidation current increased from the first sweep to the consecutive sweeps. This was related to the overpotential decrease for the initiation of monomeric oxidation. As a result, the oxidation current increased with consecutive sweeps\[^{[77]}\].

![Graph showing cyclic voltammogram](image)

**Figure 3.1.3:** Cyclic Voltammogram for a titanium electrode in aqueous solution containing 0.1 M pyrrole (PPy) and 0.1 M p-Toluenesulfonic Acid Monohydrate (PTS), (potential versus Ag/AgCl at a scan rate of 50 mVs\(^{-1}\)).
3.1.4 **Electrochemical Incorporation/Release of Copper ions into/from the PPy/PSS film**

The composite PSS/PPy film with cation exchange properties was used for the removal of copper ions from aqueous solutions. Figure 3.1.4 shows the C.V. for a PSS/PPy film as the working electrode that was “cycled”, between -1200 mV to +1200 mV. The copper ions were deposited at a potential more negative than $E = -200$ mV. At the reversed potential sweeps, the copper ions were released from the PSS/PPy film at a potential more positive than $E = +600$ mV.

3.1.5 **Electrochemical Incorporation/Release of Copper ions into/from the PPy/PVS film**

In Figure 3.1.5, a PVS/PPy film acted as the working electrode. It was observed that the reduction of copper (II) ions to metallic copper occurred at the potentials more negative than -300 mV. It was also found that a second reduction peak appeared at the potential more negative than -700 mV, which probably corresponded to the reduction of $\text{Cu(L)}_2^{2+} + 2e^- \rightarrow \text{Cu}^0 + xL$ ($L = \text{composite polypyrrole film}$)\(^{[58]}\).

On the anodic sweeps, the copper ions were released from the PPy/PVS film at potential more than +600 mV.
Figure 3.1.4: Cyclic Voltammogram for a PPy/PSS film as the working electrode in a solution containing 0.01 M Cu\(^{2+}\), (potential versus Ag/AgCl at a scan rate of 50 mVs\(^{-1}\)).

Figure 3.1.5: Cyclic Voltammogram for a PPy/PVS film as the working electrode in a solution containing 0.01 M Cu\(^{2+}\), (potential versus Ag/AgCl at a scan rate of 50 mVs\(^{-1}\)).
3.1.6 **Electrochemical Incorporation/Release of Copper ions into/from the PPy/PTS film**

For the 0.01 Cu\(^{2+}\) on the anodic sweeps, two shoulders were obtained: the first one occurred at \(E = -200\) mV and the second at \(-400\) mV. The first reduction peak corresponded to the reduction of copper (II) ions to copper (I) ions. The second reduction peak is related to the reduction of copper (II) ions to copper metal.

Figure 3.1.6: Cyclic Voltammogram for a PPy/PTS film as the working electrode in a solution containing 0.01 M Cu\(^{2+}\), (potential versus Ag/AgCl at a scan rate of 50 mVs\(^{-1}\)).
3.1.7 **Electrochemical Incorporation/Release of Nickel ions into/from the PPy/PSS film**

Figure 3.1.7 shows the cyclic voltammetry behaviour of the PPy/PSS film in aqueous nickel sulphate solution. Figure 3.1.7 gives the CV for the PPy/PSS film as the working electrode. There were three cathodic peaks obtained. The first cathodic peak was found at the potential +600 mV, which corresponded to the reduction of the Ni$^{3+}$ ions to Ni$^{2+}$ ions.$^{79, 80}$ The second reduction peak initiated at -200 mV, which was attributed to incorporation of nickel ions into composite PPy/PSS film.$^{57}$ The third reduction peak at -800 mV was caused by the electrodeposition of nickel ions.$^{57}$

One of the anodic peak was observed at -600 mV. It corresponded to the electrodissolution of Ni$^0$ to nickel ions.$^{57, 58}$ The oxide layer (due to the passivation) was formed at potentials more positive than -300 to +700 mV.

3.1.8 **Electrochemical Incorporation/Release of Nickel ions into/from the PPy/PVS film**

From the cycling of the PPy/PVS film as the working electrode (Figure 3.1.8), it indicated that the PPy/PVS film has the same characteristic as compared to the PPy/PSS film. Three cathodic peaks were observed: the first centred at +600 mV, second started at -200 mV and the third initiated at -800 mV. It was found that the peaks corresponded to the reduction of Ni$^{3+}$ to Ni$^{2+}$ ions.$^{79, 80}$, incorporation of nickel ions into composite PPy/PVS film.$^{57}$, and electrodeposition of nickel ions.$^{57}$

On the anodic sweeps, it was observed that the Ni$^0$ was oxidized to nickel ions in the potential range from -400 to -600 mV.$^{57, 58}$ The oxide layer was formed at potentials more positive than -200 mV.
Figure 3.1.7: Cyclic Voltammogram for a PPy/PSS film as the working electrode in a solution containing 0.01 M Ni²⁺, (potential versus Ag/AgCl at a scan rate of 50 mV/s⁻¹).

Figure 3.1.8: Cyclic Voltammogram for a PPy/PVS film as the working electrode in a solution containing 0.01 M Ni²⁺, (potential versus Ag/AgCl at a scan rate of 50 mV/s⁻¹).
3.1.10 **Electrochemical Incorporation/Release of Cobalt ions into/from the PPy/PSS film**

A composite PPy/PSS film with cation-exchange properties was used for the removal of cobalt ions from aqueous solutions.

During the cathodic sweeps in the Figure 3.1.10, two shoulders were obtained: the first one was initiated at +400 to +500 mV and the second was centred at -300 to -400 mV. The first reduction peak could be attributed to the reduction of Co\(^{3+}\) to Co\(^{2+}\). The second reduction was due to the insertion of cobalt ions.

During the anodic sweeps, an oxidation peak appeared at +800 mV, which could be assigned to the PPy/PSS mediated oxidation of Co\(^{2+}\) into Co\(^{3+}\)[81].

3.1.11 **Electrochemical Incorporation/Release of Cobalt ions into/from the PPy/PVS film**

For the PVS/PPy film used as the working electrode (Figure 3.1.11), two shoulders were obtained during cathodic sweeps. The first one was initiated at -800 mV and the second was centred at -300 to -400 mV. The first reduction peak could be attributed to the reduction of Co\(^{2+}\) to Co\(^{4+}\)[81]. The second reduction was due to the insertion of cobalt ions into the PPy/PVS film.

For anodic sweeps, two oxidation peaks appeared: the first one was initiated at +800 mV which related to the PPy/PSS mediated oxidation of Co\(^{2+}\) into Co\(^{3+}\)[81], while the second oxidation peak at the potential E= -200 mV was possibly attributed to cobalt ions being released from the PPy/PVS film.
Figure 3.1.10: Cyclic Voltammogram for a PPy/PSS film as the working electrode in a solution containing 0.01 M Co$^{2+}$, (potential versus Ag/AgCl at a scan rate of 100 mVs$^{-1}$).

Figure 3.1.11: Cyclic Voltammogram for a PPy/PVS as the working electrode in a solution containing 0.01 M Co$^{2+}$, (potential versus Ag/AgCl at a scan rate of 100 mVs$^{-1}$).
3.1.12 Electrochemical Incorporation/Release of Cobalt ions into/from the PPy/PTS film

From the cyclic voltammogram obtained in Figure 3.1.12, it did not show distinct peaks. As a result, no clear conclusion can be made for this cyclic voltammogram.

Figure 3.1.12: Cyclic Voltammogram for a PPy/PTS as the working electrode in a solution containing 0.01 M Co²⁺, (potential versus Ag/AgCl at a scan rate of 100 mVs⁻¹).
3.2 CONDUCTIVITY OF PPY/PVS FILMS

3.2.1 Surface Conductivity as a function of concentration of pyrrole used in the preparation of the film

In this experiment, different concentrations of pyrrole with constant concentration of 0.1 mole kg\(^{-1}\) poly (vinylsulfonic acid, sodium salt) (PVS) were used to prepare the composite films. The method of four point probe was used to determine the surface conductivity.

Table 1: The comparison of the surface conductivity at the electrolyte and electrode sides

<table>
<thead>
<tr>
<th>Concentration of Pyrrole (mole kg(^{-1}))</th>
<th>Surface Conductivity /Scm(^{-1})</th>
<th>Percentage of Difference(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Electrolyte side: 0.0184</td>
<td>0.0184</td>
</tr>
<tr>
<td></td>
<td>Electrode side: 0.0184</td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>Electrolyte side: 0.0238</td>
<td>0.0239</td>
</tr>
<tr>
<td></td>
<td>Electrode side: 0.0239</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>Electrolyte side: 0.0411</td>
<td>0.0410</td>
</tr>
<tr>
<td></td>
<td>Electrode side: 0.0410</td>
<td></td>
</tr>
<tr>
<td>0.4</td>
<td>Electrolyte side: 0.0546</td>
<td>0.0545</td>
</tr>
<tr>
<td></td>
<td>Electrode side: 0.0545</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>Electrolyte side: 0.0621</td>
<td>0.0622</td>
</tr>
<tr>
<td></td>
<td>Electrode side: 0.0622</td>
<td></td>
</tr>
</tbody>
</table>

In Table 1, the electrolyte side refers to the side of polymer facing the solution during film formation. The electrode side refers to the side facing metal.

From the results given in Table 1, it is observed that there was no significant differences between the electrolyte sides and the electrode sides. This may be difficult to explain since the surface morphology of the two sides was found to be so different, unless the four point probe technique could not yield true surface conductivity data for conductivity polymers. One has to recall that this technique was originally designed for harder semiconductor solid film materials.
Table 2: The Correction Factor $C'$ used for the method of "four point probe"

<table>
<thead>
<tr>
<th>d/s</th>
<th>$C'$/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>2.2662</td>
</tr>
<tr>
<td>4.0</td>
<td>2.9280</td>
</tr>
<tr>
<td>5.0</td>
<td>3.3625</td>
</tr>
<tr>
<td>7.5</td>
<td>3.9273</td>
</tr>
<tr>
<td>10.0</td>
<td>4.1716</td>
</tr>
<tr>
<td>15.0</td>
<td>4.3646</td>
</tr>
<tr>
<td>20.0</td>
<td>4.4364</td>
</tr>
<tr>
<td>40.0</td>
<td>4.5076</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>4.5324</td>
</tr>
</tbody>
</table>

$C'$ = The Correction Factor  
$d$ = Diameter of the polymer films  
$s$ = The distance between probes  
(See section 1.7)

Figure 3.2.1: A plot of Correction factor ($C'$) versus d/s value
3.2.3 Effect of concentration of pyrrole on the surface conductivity or bulk conductivity of the composite PPy-PVS films

Figures 3.2.2 and 3.2.3 show the variation of the concentration of pyrrole with the surface conductivity and bulk conductivity with the concentration of PVS constant at 0.1 mol kg\(^{-1}\). It was found that surface and bulk conductivity increased with the increase in pyrrole (PPy) concentrations. The increase in PPy concentration probably increased the formation of more conjugated chains, which in turn increased the electrical conductivity of the polymer film. Hence, in this case, the conjugated system was the main factor in determining conductivity of the polymer film.

3.2.4 The relationship between density and surface conductivity or bulk conductivity

According to Figure 3.24, it appears that the densities of the films produced with the same constant current and period of the electropolymerization process, but with different starting concentrations of monomer of PPy, did not vary significantly.
Figure 3.2.2: Surface Conductivity of PVS/PPy films versus different concentration of Pyrrole

Figure 3.2.3: Bulk Conductivity of PVS/PPy films versus different concentration of Pyrrole
Figure 3.2.4: Density of PVS/PPy films versus Concentration of PPy monomer used
The differences in deposition colours were due to the copper ions and metallic copper (reddish colour)\textsuperscript{[82]}\textsuperscript{[82]}. Some of the metallic copper turned to greenish (hydroxocarbonate)\textsuperscript{[82]} due to oxidation or corrosion in air. The yellowish material was probably the cuprous oxide\textsuperscript{[82]} that was formed when the film was exposed to air.

The whole process could be described as:

\[
\text{Deposit (PPy-PVS)} \rightarrow \text{Stripping (PPy-PVS)} \rightarrow \text{Cu}^{2+} \text{ concentrates}
\]

Figure 3.3.1: A Diagram showing the steps in copper removal processes.

Figure 3.3.5 shows the decrease of the copper concentration in a simulated dilute Cu\textsuperscript{2+} effluent solution.
Figure 3.3.2: A picture of Ppy-PSS surface after copper deposition using Leica Q500MC image Processing and Analysis system.

Figure 3.3.3: A picture of Ppy-PVS surface after copper deposition using Leica Q500MC image Processing and Analysis system.
Figure 3.3.4: A picture of Ppy-PTS surface after copper deposition using Leica Q500MC image processing and analysis system.
Figure 3.3.5: A plot showing the removal of copper ions using the PPy-PVS film
Density of the film: 0.8505 g/cm$^3$
The working electrode: PPy-PVS on Titanium
Voltage: -1000 mV  Current: -0.4$\rightarrow$ -0.7 mA
3.3.2 Nickel removal by alternately depositing/ ion-exchange and stripping using PSS-PPy and PVS-PPy films

The same method was used in reducing nickel ions by applying cathodic potential (-1000mV) to the PVS-PPy and PSS-PPy films. The nickel ions were reduced in 125 mL solution and deposited on the surface of the film. Then, the film was taken out from the solution and 10 mL of the solution were pipeted for determining the concentration of the nickel ions by using Atomic Absorption Spectroscopy. Then the film was dipped in 60 mL of 0.1 M H₂SO₄ solution and an anodic potential of +1000 mV was applied to it to allow nickel to re-dissolve.

The nickel ions were attracted to the surface of the film and deposited on the film. Further deposition was on the nickel itself. The colour of the film changed from black to blue before turning to brown. However, the deposition of the nickel ions were not distributed evenly on the surface of the film. The deposition of the nickel ions occurred more rapidly on the edges of the film due to the poor throwing power and uneven distribution on the surface of the working electrode.

The blue colour was probably caused by concentrating of nickel ions[83] at the surface of the film. In Figures 3.3.7, 3.3.8 and 3.3.9, the uneven deposition of nickel ions on the surface PPy-PSS, PPy-PVS and PPy-PTS films are shown. In Figure 3.3.7 (PPy-PSS surface), the deposition of the metallic nickel are shown in silver white colour[82]. Some of the metallic nickel changed from bright-yellow to dark green colour (hydrous nickel oxide)[82, 84]. The colour turned darker (black)[83, 85, 86] as the oxygen content increased. As shown in Figure 3.3.8, the PPy-PVS film was covered by the metallic nickel (silver white)[82] and the nickel oxide (green)[82, 84] on the surface. In Figure 3.3.9 (PPy-PTS film), the silver white[82] and bright-yellow[84]
colours were observed, which probably corresponded to metallic nickel and nickel oxide on the surface. The whole process could be summarised as:

![Diagram](image)

Figure 3.3.6: A diagram showing the steps in nickel removal processes.

Figures 3.3.10 and 3.3.11 show the decrease of the nickel concentration in sample solutions versus time.

According to Handbook of Preparative Inorganic Chemistry\(^{[84]}\), nickel oxide is a bright yellow powder, brown when heated. When the oxygen content is in slight excess, the colour is dark olive green, becoming darker as the oxygen content increases.
Figure 3.3.7: A picture of PPy-PSS surface after nickel deposition using Leica Q500MC image Processing and Analysis system.

Figure 3.3.8: A picture of Ppy-PVS surface after nickel deposition using Leica Q500MC image Processing and Analysis system.
Figure 3.3.9: A picture of Ppy-PTS surface after nickel deposition using Leica Q500MC image Processing and Analysis system.
Figure 3.3.10: A plot showing the removal of nickel ions using the PPy-PSS film
Density of the film: 0.8565 g/cm$^3$
The working electrode: PPy-PSS on the titanium
Voltage: -1000 mV   Current: -0.9→-3.0 mA

Figure 3.3.11: A plot showing the removal of nickel ions using the PPy-PVS film
Density of the film: 1.1223 g/cm$^3$
The working electrode: PPy-PVS on the titanium
Voltage: -1000 mV   Current: -0.5→-2.5 mA
3.3.3 Cobalt removal by alternately depositing/ion-exchange and stripping using PSS-PPy and PVS-PPy films

The same method and condition as discussed earlier were applied in removing cobalt ions from the solutions by using the PVS-PPy and PSS-PPy films under applied potentials. Cathodic potential was applied to the working electrode in 125 mL of cobalt ions solution and the reduced cobalt ions were deposited on the surface of the film. The film was taken out from the solution and a 10 ml of the solution were removed for determining the concentration of cobalt ions by using Atomic Absorption Spectroscopy. The film was dipped in 60 mL of 0.1 M H₂SO₄ solutions and an anodic potential of +1000 mV (versus Ag/AgCl reference electrode) was applied to it to allow the cobalt to re-dissolve.

A fixed -1000 mV potential was applied in reducing the cobalt ions. The cobalt ions were attracted to the surface of the film and deposited on the film. The colour of the film changed from black to blue before changing to brown. However, the deposition of cobalt was not evenly distributed on the surface of the film. Again, this was because the deposition of cobalt ions occurred more rapidly on the edges of the film.

The blue\(^{[85]}\) appearance was probably caused by the concentrating of cobalt ions on the surface of the film. However, the brown colour was probably due to the oxide layer (cobalt (II) oxide\(^{[84]}\) or cobalt (III) oxide\(^{[86]}\)) formed on the surface.

In Figures 3.3.13, 3.3.14 and 3.3.15, the uneven deposition of cobalt ions on the surface PPy-PSS, PPy-PVS and PPy-PTS films are indicated. In Figure 3.3.13 (PPy-PSS surface), the deposition of cobalt ions and metallic cobalt is shown in bluish white colour\(^{[82]}\). Some metallic cobalt changed to olive-green (cobalt oxide)\(^{[82]}\) due to oxidation in air. The colour of the cobalt (II) oxide became darker (brown to black
colour\textsuperscript{[84]} as the oxygen content increased. The brown colour material was probably due to the cobalt (III) oxide\textsuperscript{[86]} formed on the surface. As illustrated in Figure 3.3.14, the PPy-PVS film was covered by the metallic cobalt, cobalt (II) oxide\textsuperscript{[82]} and little bit of brown-colour cobalt (III) oxide\textsuperscript{[86]}. For PPy-PTS film in Figure 3.3.15, the pink colour layer was probably caused by the cobalt (II) chloride hexahydrate\textsuperscript{[85]} and the green colour layer was due to the cobalt (II) oxide\textsuperscript{[82]}. The whole process may be illustrated as:

![Diagram](image)

**Figure 3.3.12**: A diagram of showing the steps in cobalt removal processes

Figures 3.3.16 and 3.3.17 show the decrease of cobalt concentration in sample solutions versus time.
Figure 3.3.13: A picture of Ppy-PSS surface after cobalt deposition using Leica Q500MC image Processing and Analysis system.

Figure 3.3.14: A picture of Ppy-PVS surface after cobalt deposition using Leica Q500MC image Processing and Analysis system.
Figure 3.3.15: A picture of Ppy-PTS surface after cobalt deposition using Leica Q500MC image processing and analysis system.
Figure 3.3.16: A plot showing the removal of cobalt ions using the PPy-PSS film
Density of the film: 0.5304 g/cm³
The working electrode: PPy-PSS film on Titanium
Voltage: -1000 mV  Current: -0.7→2.0 mA

Figure 3.3.17: A plot showing the removal of cobalt ions using the PPy-PVS film
Density of the film: 0.7326 g/cm³
The working electrode: PPy-PVS film on Titanium
Voltage: -1000 mV  Current: -0.2→2.0 mA