Chapter 6

Electrochemical Synthesis of Nanocomposite Films of Gold with Different Conducting Polymers and Their Applications in Electrocatalysis

Polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and poly(3,4-ethylenedioxythiophene) (PEDOT) are four most studied conducting polymers (CPs) for device applications and in preparation of different polymeric nanostructures. These polymers are very stable under ambient conditions, and also quite stable in contact with strong acidic and alkaline electrolytes, including nafion film, KOH and NaOH. This makes them as potential medium for the dispersion of electrocatalyst materials. The present chapter is focused on the electrocatalytic studies carried-out with gold and different conducting polymers nanocomposites.
6.1 Introduction

Gold is generally considered inert in bulk form. Interestingly it is a potent catalyst when used as nanoparticles [1]. Incorporating gold nanoparticles in CP matrix is an appropriate method of tapping the potential of gold nanoparticles as catalyst material. Among many advantages of using conducting polymers (CPs) as a matrix, the important one is its use as an alternative to the carbon powder normally used as a support in fuel-cell electrodes [2-10]. CPs possess the advantage of being able to accommodate large quantities catalytic of particles. The high porosity and extended structure of CPs allow electrocatalytic materials to properly disperse in a 3-dimensional structure. This makes maximum number of catalytic centers available for the reacting species and thus significantly improves the electrocatalytic performance.

There are two main methods of preparation of the CPs viz. chemical method and electrochemical method. For the chemical synthesis of polymer, ammonium peroxydisulfate, hydrogen peroxide etc., are among the most common oxidizing agents for monomer oxidation. Whereas acids such as sulfuric acid, hydrochloric acid and other strong acids are commonly used electrolytes for the electrochemical synthesis of the polymers. There are reports available on the use of gold tetrachloride as an oxidizing agent for the aniline oxidation [9,10]. Wang et al. have in their recent work prepared PANI nanofibers and gold nanoparticles simultaneously by using chloroaurate (AuCl₄⁻) as the oxidant [10,11]. But most of the methods available in the literature are solution based and multistep. In literature there is no report on single step electrochemical preparation of the Au-CP nanocomposites.

This chapter is essentially an extension of the last chapter except the main focus of study will be gold nanoparticles dispersed conducting polymers namely; polyaniline (PANI), polypyrrole (PPY), polythiophene (PTP) and polyethylenedioxythiophene (PEDOT). We present the electrochemical method similar to one described for Pd nanocomposite [12], to produce gold and CP nanocomposite films on the conducting surfaces. The unique method involves the in-situ polymerization of the monomer to yield the polymer nanocomposite with gold and subsequent deposition on cathode. PANI, PPY, PTP, and PEDOT were the polymers studied in this work.

The polymer and gold nanocomposites were formed in-situ during the galvanostatic deposition process in the presence of their respective monomers in HCl with Au wire as anode and another gold electrode as cathode. The conjugated polymer based metal nanocomposites are very useful electrocatalyst for the oxidation of small organic molecules.
as shown by the studies on the electro-oxidation of methanol on Pt-PANI and Pt nanoparticles dispersed PEDOT electrodes [13,14].

The present method is of particular significance due to the fact that it is a single step electrochemical method which avoids the extra steps of the preparation of CPs separately and subsequent mixing of polymer and gold. The prepared nanocomposite film can be directly used for further studying its properties such as electrocatalytic activity. The surface of the film was examined with SEM, EDAX, AFM and FTIR spectroscopy. The nanocomposite of Au and CPs modified surface was found to be exceptionally porous.

A high rate of electro-oxidation of ethanol in alkali media was observed for nanocomposite modified electrode. The electrocatalytic activity of all the nanocomposite films towards ethanol electro-oxidation was studied in alkaline medium and their electrocatalytic responses were compared. The high electrocatalytic activity of the nanocomposite films is attributed to the presence of additional active centers on gold nanoparticles dispersed in the conducting matrix of CP.

The studies presented here will be useful in understanding the formation of interesting nanocomposite structures from gold and also as an efficient substitute of Pt in direct ethanol fuel cells (DEFC). Ethanol can be obtained in large amount through a fermentation process from sources such as sugar cane, wheat, corn, etc. This kind of supply chain is already available for ethanol worldwide without the worry of fuel getting over. This is in sharp contrast to the use of fossil fuels. The use of ethanol would also help in overcoming both the storage and developing infrastructure challenge of hydrogen for fuel cell applications.

Although fuel cells based on acidic electrolytes (mainly Nafion) have received more attention in the literature than alkaline electrolytes based fuel cells yet there is plenty of room for alkaline electrolytes based fuel cells because fuel cells based on acidic electrolytes function mainly with Pt based catalysts. This dependency makes them more expensive [15,16]. However the alkaline fuel cells can function with cheaper metals such as Au, Ag and Ni too.

6.2 Methods and materials

Galvanostatic deposition was carried out using an EG&G potentiostat (model 263A) in chronopotentiometry mode and interfaced to a PC through a GPIB card (National Instruments). For Tafel slope calculations for ethanol electro-oxidation on different Au-CPs
systems, we have carried out chronoamperometry with a potential program similar to the one used in chapter 5 (Figure 5.13) with delay at negative and positive potentials.

6.2.1 Synthesis of the Au-CP nanocomposites on gold substrate

The method is similar to the synthesis of Pd-PEDOT and Pd-PANI nanocomposite films as described in previous chapter [17-20]. The nanocomposite preparation method can be summarized as following. A 10 ml beaker was used as an electrochemical cell for galvanostatic deposition, 5 mg of monomer (aniline for PANI, pyrrole, for PPY thiophene, for PTP and 3,4-ethylenedioxythiophene for PEDOT) solutions were prepared in 5 ml 0.1 M HCl, a current of 50 mA was used during the process of deposition. Au wire of 5 mm length and 0.5 mm diameter working as anode and an evaporated gold film electrode of 0.15 cm² area working as cathode were used. The deposition was also carried out at different currents, and it was observed that at lower currents (<50 mA) the electrocatalytic response of the film of coated material was comparatively low. At higher currents (>50 mA) the Au-CP nanocomposite was not adhering enough on the cathode surface during the gas evolution. However we found that the deposition at a current of 50 mA provides very good electrocatalytic activity and better adhesion. Therefore we have optimized the current value to 50 mA based on shorter time of deposition, improved electrocatalytic response and robust surface film. Therefore, for all the characterization studies of the film, all the specimens were deposited at a current of 50 mA unless otherwise stated.

The synthetic approach for all the Au-CP nanocomposite films are similar as described earlier for Pd dispersed PANI and PEDOT. We present below only the observation during the formation of the film.

**Au-PANI nanocomposite**

In the beginning of the experiment the aniline solution turned to light bluish color from the colorless solution which finally, at the end of experiment turned to reddish-pink. Simultaneously, a dark brown colored film was formed on the cathode surface.

**Au-PPY nanocomposite**

The pyrrole solution which was colorless in the beginning turned to black color soon after the start of the experiment, indicating of the formation of PPY in the solution. The electrode was coated with the film of black color, simultaneously during the experiment.
**Au-PTP nanocomposite**

The colorless thiophene solution turned to light yellow color in the beginning of the experiment which remained the same after the completion of the experiment. Simultaneously a light yellow-brown film was formed on the electrode surface.

**Au-PEDOT nanocomposite**

The 3,4-ethylenedioxythiophene solution turned blue in the beginning and finally into a dark blue colored solution at the end of the experiment. Simultaneously a black film was formed on the electrode surface.

6.2.2 Characterization of Au-CP nanocomposites with SEM, EDAX, AFM and FTIR spectroscopy

6.2.2.1 SEM analysis

Figure 6.1-6.4 show the SEM image of the Au-CPs nanocomposite deposited on the gold substrate. Figures 6.1a,b shows the SEM images of Au-PANI nanocomposite film. Figure 6.1a shows the spherical disc like features of diameter around 100-400 nm. In addition there are smaller features present on the surface of diameter around 50-100 nm. We observed similar kind of features at different locations on the modified substrate.

**Fig. 6.1** (a) FESEM image of Au-PANI nanocomposite film (scale bar = 400 nm) and (b) high resolution FESEM image of Au-PANI nanocomposite showing the gold nanoparticles adhering on the surface (scale bar = 100 nm)
Fig. 6.2 (a) FESEM image of Au-PPY nanocomposite film scale bar = 400 nm and (b) high resolution FESEM image of Au-PPY nanocomposite showing the features in detail (scale bar = 100 nm)

Fig. 6.3 (a) FESEM image of Au-PTP nanocomposite film showing the dendritic growth of the nanostructures (scale bar = 400 nm) and (b) high resolution FESEM image of Au-PTP nanocomposite clearly shows the dendritic structures (scale bar = 200 nm)
Fig. 6.4 (a) FESEM image of Au-PEDOT nanocomposite film shows the cauliflowers like fractal growth of the nanostructures (scale bar = 400 nm) and (b) high resolution FESEM image of Au-PEDOT nanocomposite showing the flower like structures in detail (scale bar = 200 nm)

Figure 6.1 b is high resolution SEM image of the Au-PANI nanocomposite film. It shows clearly that the disc like features observed in Figure 6.1a are actually composed of smaller particles of 5-10 nm size embedded in it, which appear to be the gold nanoparticles embedded in the PANI matrix.

Figure 6.2a, b shows the SEM images of the Au-PPY coated surface. The images show features of irregular shapes with sharp edges. These features are 20-100 nm in size and spread throughout the surface. In addition to these features there are few cauliflower like structures present on the surface showing the fractal morphology of the Au-PPY nanocomposite in those regions. Figure 6.2b shows the high resolution SEM image of the Au-PPY nanocomposite film showing the nanostructured features with size of about 10-20 nm.

Figure 6.3a, b is the SEM images of the Au-PTP nanocomposite coated surface. Unlike the other Au-CPs nanocomposite the images show the presence of dendritic structure of the Au-PTP nanocomposite. These dendritic structures are more than a μm in length and from the high resolution SEM image (Figure 6.3b) of a single dendrite structure in much better resolution, we observe that the side branches of the dendritic structure have diameters of about 10-20 nm.

Figure 6.4a, b is the SEM images of the Au-PEDOT nanocomposite coated surface. The image shows the presence of cauliflower like nanostructures throughout the surface with sharp edges. These features resemble to the flower like structure with fractal growth. The size of these structures varies from 20 nm to 100 nm, which can grow as large as 500 nm as seen
in the figure. In high resolution Figure 6.4b, the fractal nature of growth is clearly visible and it shows that the flower like structures are composed of small 10-30 nm features.

The above SEM imaging analysis shows that the structure of the Au-CP nanocomposite coated surface varies for different CPs. This is an important observation as we can form varieties of nanostructures for various applications by this simple one step preparation method. However one common feature among these nanocomposite films is the fractal like growth, which indicates diffusion limited aggregation at high current densities employed for the film formation [21].

### 6.2.2.2 EDAX analysis

EDAX studies were also carried out on all Au-CPs coated surfaces. Tables 6.1-6.4 show the EDAX elemental analysis results for Au-PANI, Au-PPY, Au-PTP and Au-PEDOT nanocomposite films respectively. EDAX results show the presence of metallic Au and carbon in all the Au-CPs nanocomposite films along with nitrogen (Au-PANI and Au-PPY) and sulfur (in Au-PTP and Au-PEDOT). The Au-PEDOT nanocomposite film also shows the presence of O and Na (from SDS). The EDAX analysis confirms the presence of Au and respective CPs in all Au-CPs nanocomposite films.

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*Table 6.1 EDAX elemental analysis results for Au-PANI nanocomposite film*

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<td>S</td>
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<tr>
<td>Au</td>
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<td>47.95</td>
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*Table 6.2 EDAX elemental analysis results for Au-PPY nanocomposite film*
### Table 6.3 EDAX elemental analysis results for Au-PTP nanocomposite film

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<th>Atom %</th>
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<td>S</td>
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<td>7.93</td>
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<tr>
<td>Au</td>
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<td>47.95</td>
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</table>

### Table 6.4 EDAX elemental analysis results for Au-PEDOT nanocomposite film

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<td>Na</td>
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<td>21.78</td>
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</table>

#### 6.2.2.3 AFM analysis

The 3-dimensional nature and the roughness parameters of the Au-CP nanocomposite films were studied using an AFM, operating in tapping mode. Figure 6.5a-d shows the 5 μm x 5 μm AFM topographic images of Au-PANI, Au-PPY, Au-PTP and Au-PEDOT nanocomposite films respectively. Au-PANI and Au-PTP nanocomposite films were found to be very rough while the roughness of Au-PPY and Au-PEDOT nanocomposite films was considerably less.

The roughness parameters, i.e. the average and rms roughness calculated from the respective 5 μm x 5 μm AFM images are presented in Table 6.5. The average and rms roughness are maximum for Au-PTP surface followed by Au-PANI, Au-PEDOT and Au-PPY surface.
6.2.2.4 FTIR spectroscopy analysis

Infra-red spectroscopy was performed to check the chemical composition of the material in the film. Figure 6.6 shows the FTIR spectrum of the coated material in all the Au-CPs nanocomposite films.

Figure 6.6a shows FTIR spectra of Au-PANI nanocomposite, the distinctive infra-red peaks for the PANI are clear in the spectra. The peak at 1266 cm\(^{-1}\) is for the C-N stretch which is the characteristic infrared peak for the aromatic amines. The infra-red spectra of PANI show the characteristic peaks of benzenoid and quinoid form of the aromatic phenyl ring system. The two peaks at 1513 cm\(^{-1}\) and 1637 cm\(^{-1}\) are for the benzenoid and quinoid forms of the PANI respectively. The presence of the above mentioned infrared peaks confirms the presence of the polymer form of aniline in the coated material [12,22-26].
The integrated intensity of IR peaks at 1637 cm\(^{-1}\) (quinoid peak) and 1513 cm\(^{-1}\) (benzenoid peak) can be used to calculate the R value, which is the ratio of the area under the IR peaks at 1637 cm\(^{-1}\) and 1513 cm\(^{-1}\) [12,22].

![FTIR spectra of Au-CP nanocomposites](image)

**Fig. 6.6** FTIR spectra of Au-CP nanocomposites (a) Au-PANI nanocomposite showing the characteristic benzenoid and quinoid peaks for the PANI in the composite, (b) Au-PPY nanocomposite, (c) Au-PTP nanocomposite and (d) Au-PEDOT nanocomposite

In Au-PANI nanocomposite the R value was calculated to be 0.91. This shows that there are more benzenoid rings than quinoid rings in the PANI. With the help of R value which is often related with the oxidation state of the PANI, we have defined the following structure of PANI in the coated material.

![Structure of PANI](image)

Figure 6.6b shows the FTIR spectra of Au-PPY scraped out from the coated surface. The peaks at 1456 and 1377 cm\(^{-1}\) may be assigned to typical PPY ring vibrations. The peaks at 721, 770 and 1160 cm\(^{-1}\) is assigned due to the =C-H out of plane vibrations and C-N stretching vibrations respectively [27-29]. Figure 6.6c shows the FTIR spectra of the Au-PTP scraped out from the coated surface. It shows a C=C aromatic ring stretch at 1555, 1460 and
1374 cm\(^{-1}\) and in-plane C–H deformation at 1027 and 1072 cm\(^{-1}\). The spectra also show the C–S bending band at 850 cm\(^{-1}\) [28,30]. Figure 6.6d is the FTIR spectra of the Au-PEDOT nanocomposite. The spectra show the infrared peaks at 1374, 1462, 1520 cm\(^{-1}\) for stretching mode of C–C and C=C in the thiophene ring. The peaks at 770 and 720 cm\(^{-1}\) are associated with the C–S bending vibration. The peaks at 1650, 1700 and 1750 cm\(^{-1}\) may be assigned to the doped state of the polymer [31]. In all the above mentioned cases the slight shift in the peak positions is due to the presence of gold atoms which are attached to the polymer and cause the change in the electron density.

6.2.3 Electrochemical activity of Au-CP nanocomposite films for ethanol oxidation

The electrocatalytic oxidation of small chain alcohols has been intensively studied as it is the anodic reaction in direct alcohol fuel cells (DAFCs). The CP nanocomposites with gold have the potential to emerge as a very good catalytic material due to the high porosity, conducting nature and easy access of reacting species to the electrocatalytic centers.

![Fig. 6.7 200 cycles, voltammogram for the electro-oxidation of 1.0 M ethanol in 0.5 M NaOH at different Au-CP nanocomposite film](image)

(a) Au-PANI nanocomposite film, (b) Au-PPY nanocomposite film, (c) Au-PTP nanocomposite film and (d) Au-PEDOT nanocomposite film
We have evaluated the electrocatalytic activity of different Au-CP nanocomposite coated electrodes by studying ethanol electro-oxidation as a model system in alkaline medium of 0.5 M NaOH.

Figure 6.7a-d shows the ethanol electro-oxidation voltammogram for the different Au-CP modified electrodes (a-Au-PANI, b-Au-PPY, c-Au-PTP and d-Au-PEDOT) in 1 M ethanol in 0.5 M NaOH. In all the cases we have carried out 200 potential cycles experiment in order to determine the reproducibility of the electrocatalysis results and stability of the nanocomposite modified electrode. All the current values are corrected to the respective effective catalytic surface area (ECSA). ECSA of all Au-CP nanocomposite films was measured from the gold oxide stripping analysis carried out in 0.5 M sulfuric acid solution [32].

Table 6.6 shows the CV results obtained for different Au-CP nanocomposites in terms of onset potential, peak potential and peak current. Among the four systems we have studied, the Au-PTP system was found to be the best in terms of onset potential for ethanol oxidation. The Au-PTP modified electrode shows the lowest onset potential of -0.40 V followed by Au-PEDOT (-0.36 V), Au-PPY (-0.35 V) and Au-PANI (-0.34 V) modified electrodes. The onset potential was constant in all the four systems even after the 200 potential cycles.

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Onset Potential / V</th>
<th>Peak Potential / V</th>
<th>Peak Current / mAcm^-2</th>
</tr>
</thead>
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<tr>
<td></td>
<td>1st cycle</td>
<td>200th cycle</td>
<td>1st cycle</td>
</tr>
<tr>
<td>Au-PANI</td>
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<td>0.314</td>
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<td>Au-PPY</td>
<td>-0.35</td>
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<tr>
<td>Au-PTP</td>
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<tr>
<td>Au-PEDOT</td>
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<td>0.118</td>
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</tbody>
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Table 6.6 The ethanol electrocatalysis results obtained for different Au-CP nanocomposites in terms of onset potential, peak potential and peak current

The Au-PANI nanocomposite modified electrode was found to be the best in terms of peak current. The peak current, 3.36 mAcm^-2 of Au-PANI electrode was found to be the maximum among the four systems studied, which was closely followed by Au-PEDOT (2.93 mAcm^-2), Au-PPY (2.02 mAcm^-2) and Au-PTP (1.68 mAcm^-2). The peak currents of Au-PANI, Au-PPY and Au-PTP modified electrodes were unchanged after 200 potential cycles. The decline in the peak current was observed in Au-PEDOT modified electrode from 2.93 mAcm^-2 to 1.80 mAcm^-2.
During the reverse potential scan there is a secondary peak in all the Au-CP nanocomposite systems. This reverse anodic peak behavior can be explained as follows. The oxide film forms during the forward scan and it gets removed from the surface during the reverse scan, this process exposes fresh gold surface and the exposed Au atoms are not in equilibrium with the metallic lattice and therefore these high energy sites possess excellent catalytic activity [33].

6.2.3.1 Mechanism of electro-oxidation

The established mechanism for the electro-oxidation of ethanol in alkaline medium involves the oxidation of ethanol to acetate ions at the anode. The reaction can be summarized as following [34-37].

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + 3\text{OH}^- & \rightarrow \text{CH}_3\text{CO}_{\text{ads}} + 3\text{H}_2\text{O} + 3\text{e}^- \quad (1) \\
\text{OH}^- & \rightarrow \text{OH}_{\text{ads}} + \text{e}^- \quad (2) \\
\text{CH}_3\text{CO}_{\text{ads}} + \text{OH}_{\text{ads}} & \rightarrow \text{CH}_3\text{COOH} \quad (3) \\
\text{CH}_3\text{COOH} + \text{OH}^- & \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad (4)
\end{align*}
\]

In the above mentioned reaction scheme reaction 3 is the rate limiting step. An in-situ FTIR spectroscopy studies by de Lima et al. shows that the acetate ions are the primary product of ethanol electro-oxidation on gold in alkaline medium [36].

In all the nanocomposite systems the onset potential is more negative and the current is more than the previous reported values for ethanol electro-oxidation on porous gold nanoparticles film [36,37]. This shows that the combination of CP and gold in the form of nanocomposite serves as a better electrocatalyst for ethanol oxidation than gold nanoparticles alone. Except in Au-PEDOT system which shows a 38% decline in the catalytic current, 200 cycles, voltammetry experiment in Au-CP nanocomposite films shows no decline in the electro-oxidation current of ethanol. This shows that there is negligible poisoning of the catalytic surface due to any of the reaction products of ethanol oxidation and a high CO tolerance. This is an important advantage of Au-CP nanocomposite electrodes as the electrode poisoning is a major problem in electro-oxidation reactions of alcohols.
6.2.4 Kinetics of ethanol electro-oxidation

6.2.4.1 Activation energy (Eₐ) determination

Figure 6.8 shows the CVs for ethanol oxidation at different temperatures for all Au-CP nanocomposite films. In all the Au-CP nanocomposite films it is clear from the figure that the ethanol electrocatalysis currents have increased with the temperature and also the onset potentials have become more negative.

The change in the onset potential at higher temperature is attributed to the low activation energy requirement at higher temperatures. This can be due to the fact that the increase in the temperature accelerates the adsorption of OH⁻ ions to form OHads and the presence of OHads is in fact helpful in achieving higher electro-oxidation current. It also helps in suppressing the formation of poisoning species, like CO which is converted to CO₂ rapidly at higher temperatures [38-41]. The adsorption of hydroxyl ions on gold has been a well established fact in the literature [42-44]. The adsorption plays a key role in determining the catalytic properties of gold electrode for electro-oxidation of small organic molecules [45].

At high temperatures we also observe an increase in the anodic current of reverse potential scan. This current eventually becomes higher than the anodic current of the forward potential scan.

The plots between log I vs. 1/T (Arrhenius plot) for ethanol oxidation on all Au-CP electrodes at different potentials, near the foot of the CV (-500 mV to -100 mV) are shown in Figure 6.9. A very good linear relationship can be seen from these plots. This shows that the essential mechanism of ethanol electro-oxidation remains the same at all the temperatures. The apparent activation energies were calculated from the slope of those curves (slope = -Eₐ/2.3R), R being the gas constant. The activation energy values are labeled adjacent to their respective plots. The average Eₐ values for different Au-CPs films in the potential range studied are 37.5 kJ mole⁻¹, 56.7 kJ mole⁻¹, 54.1 kJ mole⁻¹ and 56.9 kJ mole⁻¹ for Au-PANI, Au-PPY, Au-PTP and Au-PEDOT nanocomposite films respectively. It is clear that the Eₐ required for the Au-PANI system is the lowest among all the Au-CPs, this is followed by Au-PTP system. While for Au-PPY and Au-PEDOT the activation energies required are almost the same. The lower Eₐ value in the case of Au-PANI system than other Au-CPs systems can be accounted due to the small size particles present on the surface as seen in the SEM image (Figure 6.1b). The values obtained of Eₐ are comparable to the values observed for Pt, Pd and Au [46-48], based catalytic materials.
Fig. 6.8 Cycle voltammograms for the electro-oxidation of 1.0 M ethanol in 0.5 M NaOH at different Au-CP nanocomposite film at different temperatures (a) Au-PANI nanocomposite film, (b) Au-PPY nanocomposite film, (c) Au-PTP nanocomposite film and (d) Au-PEDOT nanocomposite film
Fig. 6.9 Log I vs. 1/T (Arrhenius plots) for different Au-CP nanocomposite film at different potentials, corresponding activation energy values are labeled adjacent to the curves. (a) Au-PANI nanocomposite film, (b) Au-PPY nanocomposite film, (c) Au-PTP nanocomposite film and (d) Au-PEDOT nanocomposite film

6.2.4.2 Tafel plot analysis for ethanol electro-oxidation

As pointed out in the previous chapter the current–potential plots and the Tafel slopes derived from them have different connotation in the case of alcohol oxidation reaction in which the surface active sites are blocked by adsorbed intermediates. However the values of Tafel slopes provide meaningful information on the surface blocking by adsorbed intermediates.

Figures 6.10 to 6.13 show the Tafel plots for the different Au-CP systems Au-PANI (Figure 6.10), Au-PPY (Figure 6.11), Au-PTP (Figure 6.12) and Au-PEDOT (Figure 6.13). The values of the slopes for all the Au-CP systems are given in Table 6.7.
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<td>449.0</td>
<td>223.0</td>
<td>360.0</td>
</tr>
<tr>
<td>45°C</td>
<td>118.1</td>
<td>184.8</td>
<td>447.0</td>
<td>-</td>
<td>269.0</td>
<td>445.0</td>
</tr>
<tr>
<td>55°C</td>
<td>132</td>
<td>211.8</td>
<td>479.0</td>
<td>-</td>
<td>319.3</td>
<td>650.0</td>
</tr>
</tbody>
</table>

Table 6.7 The Tafel slopes for ethanol electrocatalysis obtained at different temperatures for different Au-CP nanocomposites

Fig. 6.10 Tafel plots (Overpotential (η) vs. log I (mAcm<sup>-2</sup>)) for Au-PANI nanocomposite at different temperatures and the fitting for two slopes
Fig. 6.11 Tafel plots (Overpotential ($\eta$) vs. log $I$ (mA cm$^{-2}$)) for Au-PPy nanocomposite at different temperatures and the fitting for first slope at 7°C, 15°C two slopes at 25°C and 35°C and linear curve at 45°C and 55°C.

Fig. 6.12 Tafel plots (Overpotential ($\eta$) vs. log $I$ (mA cm$^{-2}$)) for Au-PTP nanocomposite at different temperatures and the fitting for two slopes.
Fig. 6.13 Tafel plots (Overpotential ($\eta$) vs. log $I$ (mA cm$^{-2}$)) for Au-PEDOT nanocomposite at different temperatures and the fitting for a straight line

It can be seen that the Tafel slopes are unusually large for all systems except Au-PANI electrode. This shows that the extent of contamination and surface blocking by adsorbed intermediates are minimum in the case Au-PANI compared to other polymers. The plots of Au-PANI and Au-PTP systems fit for the two slopes at lower and higher overpotentials, having the first slope value lower than the second slope as can be seen from the Figure 6.10 and 6.12. The values of both first and second slopes increase steadily with the temperature. The higher slope values at higher temperatures indicate the enhanced adsorption of carbonaceous species, formed after the ethanol electro-oxidation reaction, on the electrode surface at elevated temperatures. These adsorbed species may block the available active sites and can only be oxidized at very high overpotentials. The values of the first slope (at lower overpotentials) can be compared to those of the second slopes (at higher overpotentials). It can be seen that second slope values are always higher than the first slope, which again shows that as the reaction progresses the impurities get adsorbed on the surface, which can only be removed at very high anodic overpotentials. The higher slope values of both the slopes (first and second) in Au-PTP system than that of Au-PANI system indicate that the reaction is more favored in the case of Au-PANI system than Au-PTP system.

Tafel plot analysis of Au-PPY system (Figure 6.11) shows completely different behavior with temperature. At lower temperatures (7 and 15°C) the Tafel plot which is linear in the beginning (lower overpotentials) deviates to become nonlinear at higher overpotentials.
The plots fit well for two slopes at intermediate temperatures (25 and 35°C) and again deviate at elevated temperatures (45 and 55°C).

Unlike Au-PANI and Au-PTP systems the Tafel plots of Au-PEDOT system can be fitted for the straight line at all the temperatures as can be seen from Figure 6.13. Au-PEDOT system also shows the trend of higher slope values with increasing temperature. The slope values are much higher than those of Au-PANI system. The presence of a linear curve and higher slopes values perhaps indicate the significant electrode poisoning and the adverse effect of impurities adsorption, which does not vary much as the reaction progress.

Au-PANI system shows the lowest slope values among all the Au-CP systems studied in this work. The smaller slope values even at elevated temperatures in the case of Au-PANI indicate that the adverse effect of the carbonaceous species is the lowest in this case. All these observations suggest that Au-PANI has the potential to emerge as the best catalyst for the ethanol oxidation research. This is also in conformity with the low activation energy values measured for ethanol electro-oxidation in Au-PANI system.

### 6.2.4.3 Reaction order calculation

The reaction order with respect to ethanol was also calculated by plotting the log I vs. log c (ethanol concentration) for all Au-CP nanocomposite films as shown in Figure 6.14. The order was calculated by using the following equations:

\[ I = nFkc^m \]

\[ \log I = \log nFk + m \log c \]

where, F is the Faraday’s constant, k is the reaction rate constant, c is the ethanol concentration and m is the apparent reaction order with respect to ethanol.

The slope of the log I vs. log c plot, at any constant temperature gives the apparent reaction order (m) of ethanol electro-oxidation reaction with respect to the ethanol concentration [46,49,50]. We have calculated the reaction order at two different potentials - 0.2 V and 0.0 V. The values of reaction order are shown in Table 6.8. In all the Au-CP systems except the Au-PANI system there is a change in the reaction order at different potentials. Reaction order of Au-PANI remains the same at both the potentials with a value of 0.57. This shows that the reaction mechanism for ethanol oxidation essentially remains same at different potentials.
Fig. 6.14 Log I vs. log c plots for different Au-CP nanocomposite films at two different potentials (a) Au-PANI nanocomposite film, (b) Au-PPY nanocomposite film, (c) Au-PTP nanocomposite film and (d) Au-PEDOT nanocomposite film

The slight change in the reaction order in Au-PPY, Au-PTP and Au-PEDOT systems can be seen from the Table 6.8, the reaction order is more at lower overpotentials (-0.2 V) and less at higher overpotentials (0 V).

<table>
<thead>
<tr>
<th>Nanocomposite</th>
<th>Reaction order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.2 V</td>
</tr>
<tr>
<td>Au-PANI</td>
<td>0.57</td>
</tr>
<tr>
<td>Au-PPY</td>
<td>0.77</td>
</tr>
<tr>
<td>Au-PTP</td>
<td>0.92</td>
</tr>
<tr>
<td>Au-PEDOT</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Table 6.8 The calculated reaction order with respect to ethanol concentration for different Au-CP nanocomposites

6.3 Conclusions

In conclusion a novel one step electrochemical method to prepare gold and different CP namely PANI, PPY, PTP, PEDOT nanocomposites in ambient conditions is proposed. The nanocomposites were then subjected to ethanol electrocatalysis experiment and found to be
very efficient catalysts for ethanol electro-oxidation reaction. Based on the electrocatalysis experimental results we can conclude that Au-PANI nanocomposite is the best electrocatalyst material among all the nanocomposites studied in this work in terms of the activation energy required, electro-oxidation current and lower Tafel slopes. The other Au-CP nanocomposites although show a low onset potential value for ethanol electro-oxidation yet require relatively higher activation energy. We believe that the analysis of Au and CP nanocomposites towards ethanol electro-oxidation carried out in this work, may have useful implication in the development of anode catalyst in direct alkaline alcohol fuel cells.
Bibliography