CHAPTER 6

POLY (PYRROLE)/ MN NANOCOMPOSITE SUPPORTED Pd TOWARDS ALCOHOL ELECTROOXIDATION

6.1 INTRODUCTION

Small particles with large specific surface area are suitable as noble metal catalyst support for fuel cell and battery applications. The advantage of the conducting polymer over commonly applied carbon black materials is mainly due to its mixed electronic and ionic conductivity and its porous structure. Direct methanol fuel cells (DMFCs) are an attractive power source with potential applications in a variety of systems, ranging from automobiles to portable electronic devices (Arico et al 2009, Lamy 2009). Platinum and Nafion in particular have been identified as feasible anode catalyst layers for DMFCs. However, Pt electrocatalysts become poisoned by CO intermediate products of methanol oxidation. Additionally, both Nafion and Pt are expensive materials. Hence, much attention has been paid to develop less expensive materials with significantly better catalytic activity, proton conductivity, and reduced susceptibility to CO poisoning. The Palladium is the suitable alternative for Platinum (Bianchini and Shen 2009).

The use of conductive polymers improves the properties of the interface between the electrode and the electrolyte and facilitates the electrochemical oxidation of methanol on Pd. A number of polymeric films, such as polypyrrole (PPy) (Selvaraj and Alagar 2007), polyaniline (Pandey and Lakshminarayana 2009), and poly(3,4-ethylenedioxythiophene) (Pandey
and Lakshminarayana 2010) have been investigated as conducting catalyst supports for methanol oxidation. Among these films, PPy has been applied to serve against oxidative dissolution or/and passivation of active Pd catalyst by its redox property together with its conductive nature and stability (Seo et al 2010).

In order to improve the electrocatalytic activity and the stability, the Pd/PPy/MN nanocomposite electrode has been developed. The Pd/PPy/MN nanocomposite electrode was tested for its electrocatalytic activity towards methanol, EG, glycerol and xylitol in alkaline medium. The PPy/MN and Pd/PPy/MN were prepared by oxidative polymerization followed by reduction method described in the previous chapter.

6.2 EXPERIMENT

Pyrrrole and ammonium peroxosulphate were purchased from Sigma-aldrich. The PPy/ MN nanocomposite was synthesized by the oxidative polymerization method. In brief, about 1 ml of the pyrrol was added in 20 ml of distilled water and a 1-2 ml of 0.1 M hydrochloric acid was added. The whole reaction was performed in the ice cold bath. To this mixture about 100 mg of prepared MN was added and stirred well. After one hour freshly prepared (0.1 M) ammonium peroxosulphate was added drop wise. The resultant dark brown coloured material was separated by centrifugation, washed several times with water and dried in hot air oven at 80° C for 12 hrs (Munusamy et al 2013).

The Pd was coated on the PPy/MN was prepared by reduction method. Suitable quantity of PdCl₂ (10%wt Pd: with respect to PPy/MN) was added into PPy/MN nanocomposite (100 mg) in 10 ml isopropanol and stirred for two hours. 1 ml freshly prepared (0.1 M) NaBH₄ solution was added drop wise into the mixture and stirring was continued. After two hours, the resultant product was separated, washed with DD water and dried. The
prepared Pd/PPy/MN nanocatalyst was analyzed through FTIR, XRD, TEM and electrochemical techniques.

6.3 RESULTS AND DISCUSSION

6.3.1 Physical characterizations of Pd/PPy/MN nanocomposite

The PPy/MN nanocomposite was prepared through oxidative polymerization. The MN and Pd were dispersed uniformly on the PPy polymer. The surface morphology of the Pd/PPy/MN nanocomposite was tested by SEM and TEM studies. Figure 6.1 a exhibits the needle like structure and Figure 6.1 (b–d) shows that the MN was uniformly dispersed (black colored small particles) in the PPy film and the Pd (JCPDS # 89-4897) nanoparticles were distributed in the composite. In higher magnification TEM image shows the presence of Pd nanoparticles in the PPy/MN nanocomposite. Figure 6.1 (e) shows the XRD profile for Pd/PPy/MN nanocomposite, the diffraction peak 2θ at 40.1 indicates the deposition of Pd (111) in the nanocomposite (Bianchini and Shen 2009). Other diffraction peaks exhibits simillar to the PPD/MN composite. The particles size of the Pd is 10–20 nm. The elemental analysis confirms the presence of Pd (9.7 %) on the nanocomposite film (Figure 6.2). Figure 6.3 shows the FTIR spectrum for PPy/MN nanocomposite at 3305 cm⁻¹ indicates the presence of –NH group. The bands at 780 and 927 cm⁻¹ indicate the polymerization of pyrrole (Selvaraj and Alagar 2007). Bands at 487 and 600 cm⁻¹ confirm the presence of Mn-O bonds.
Figure 6.1 (a) SEM image of PPy/MN nanocomposite, (b&c) Clusters of MN at the polymer matrix, (d) Pd nanoparticles on the PPy/MN nanocomposite, and (e) XRD profile for Pd/PPy/MN nanocomposite.
Figure 6.2 EDS of Pd nanoparticles on the PPy/MN nanocomposite

Figure 6.3 FTIR spectrum of PPy/MN nanocomposite
6.3.2 Electrochemical behaviour of Pd/PPy/MN nanocatalyst electrode

The electrochemical behaviour of Pd/PPy/MN nanocomposite electrode was tested in the 1 M KOH solution and the voltammogram was compared with Pd/MN and Pd/C electrodes. Pd/PPy/MN exhibits enhanced current response compared to Pd/C and Pd/MN electrodes were shown in Figure 6.4. The Pd/PPy/MN nanocomposite electrode shows the improved hydrogen adsorption and high current response towards PdO-Pd reduction process.

This phenomenon is due to the high surface area of Pd/PPy/MN nanocomposite. The Pd/PPy/MN nanocomposite electrode shows the ECAS of 43, which is higher than the Pd/MN and Pd/C. The electrooxidation of methanol at Pd/PPy/MN nanocomposite electrode was studied in alkaline medium; the result was compared with Pd/PPD/MN and Pd/MN electrodes.

Figure 6.5 shows the Pd/PPy/MN nanocomposite electrode exhibits higher current density values i.e., ~ 200 mA/cm² and which is higher than the Pd/PPD/MN electrode. The electrooxidation was initially very slow and for subsequent cycles it show improved density and reaches the maximum value at 300 mA/cm². This is due to gradual adsorption of methanol on the composite and reaches maximum in the 9th cycle (Figure 6.6). Upon increasing the number of cycle, the intermediate does not affect the catalytic activity of the Pd/PPy/MN catalyst. Because the active sites of Pd is separated by PPy film. Similarly the electro oxidation of EG, Gly and Xyl was studied at the Pd/PPy/MN electrode. This exhibits similar activity like methanol i.e., while increase the cycle the peak current density increases and reaches maximum at 9 or 10th cycle (Figure 6.7). Among the different alcohols, EG
show higher current density of 430 mA/cm$^2$. The glycerol and Xylitol exhibits current density of 380 and 315 mA/cm$^2$. The ESA for Pd/PPy/MN is 112 C g$^{-1}$.

The ratio between the forward oxidation peak current density and reverse or secondary oxidation peak current density reveals the effect of intermediate products on the catalyst (Pd/PPy/MN). The following table shows the ratio of different alcohols and their peak current densities for $O_f$ and $O_b$. The current density ratio such as $I_f/I_b$ is another useful index of the catalyst tolerance towards the accumulation of partially oxidized species on the surface of the active catalyst. The higher rate of index indicates most effective removal of poisonous formed during the reaction. The values listed in the table indicate that the Xyl and methanol shows higher catalytic tolerance compared to EG and Gly. The order of catalytic tolerance are Xylitol > methanol > Gly > EG.

<table>
<thead>
<tr>
<th>S.No</th>
<th>Alcohol</th>
<th>$I_f$</th>
<th>$I_b$</th>
<th>$I_f/I_b$</th>
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<tr>
<td>1</td>
<td>Methanol</td>
<td>315</td>
<td>130</td>
<td>2.423</td>
</tr>
<tr>
<td>2</td>
<td>EG</td>
<td>430</td>
<td>220</td>
<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>Gly</td>
<td>380</td>
<td>160</td>
<td>2.25</td>
</tr>
<tr>
<td>4</td>
<td>Xyl</td>
<td>250</td>
<td>65</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Table 6.1 Comparison of electrochemical performance of Pd/PPy/MN electrode towards electrooxidation of various alcohols in alkaline medium
Figure 6.4  CVs of (a) Pd/C, (b) Pd/MN and (c) Pd/PPy/MN electrodes in 1 M KOH

Figure 6.5  CVs of the electrooxidation of methanol at (a) Pd/MN, (b) Pd/PPD/MN and (c) Pd/PPy/MN electrodes in 1 M KOH/1 M CH$_3$OH solution
Figure 6.6  CVs of the electrooxidation of Methanol on Pd/PPy/MN electrode at (a) 4\textsuperscript{th} and (b) 9\textsuperscript{th} cycle in 1 M KOH/1 M CH\textsubscript{3}OH solution

Figure 6.7  CVs of the electrooxidation of EG on Pd/PPy/MN electrode at (a) 4\textsuperscript{th} and (b) 9\textsuperscript{th} cycle in 1 M KOH/1 M EG solution
During the methanol oxidation, the formation of Pd–CO$_{\text{ads}}$ is the major obstacle (Nishimura et al. 1989). The removals of these poisonous intermediates were highly difficult and it requires highly active oxygen to burn or oxidize these intermediates. This was supplied by the metal oxide supports. Figure 6.8 (a-d) shows the CVs for a Pd/PPy/MN nanocomposite electrode in 1M KOH/1 M CH$_3$OH in the (a) –1.1 to +0.2 V, (b) –1.1 to +0.4 V, (b) –1.1 to +0.6 V and (b) –1.1 to +0.8 V ranges. In all the CVs, an anodic oxidation peak appears in the –0.61 to + 0.7 V regions with vertex potential at –0.21 V and backward oxidation peak appears in the –0.37 to –0.6 V region. However, the –1.1 to +0.4 V range shows comparatively inferior current response with 40 mV negative shift in potential. While further increase in the potential the backward oxidation peak current was fewer and the forward oxidation peak potentials were remains same. Above +0.8 V, there is a possibility of formation of more PdO, which may reduce the catalytic activity. The availability of active oxygen is comparatively less at +0.2 V. However, further increase in the potentials lead to the supply of active oxygen by extracting active oxygen from the electrolyte and supplied to catalyst. Thus, the poisonous intermediates are oxidized more effectively.

The catalytic effect and the removal of poisonous intermediates were further studied using the $I_f/I_b$ ratio. For methanol oxidation the $I_f/I_b$ ratio are 2.14 (+0.2 V) and 2.6 (+0.4) V. A lesser amount of intermediate gets oxidized. On further increase in potential by + 0.6 V ($I_f/I_b$ 9.4), almost fifty percentages of intermediates were oxidized. When peak reaches by +0.8 V ($I_f/I_b$ 16.5), a drastic change was observed and about 95 percentages of the intermediates were oxidized. It is difficult to remove all the byproducts formed during the forward reaction. In all the CVs a smooth curves were
observed, which indicates the electrode possesses smooth surface. The forward peak potential remains same; the backward peaks were shifted in the negative direction with reduced peak current density. This behaviour is unique and it was due to the supportive material i.e., manganese oxide material and this kind of behaviour has not been observed in the carbon based supports.

In the EG electrooxidation (Figure 6.9), a similar behavior like methanol electrooxidation was observed. On increase of peak potential, the backward peak current density was decreased. The potential above +0.6 V, in the forward scan, a second oxidation peak was observed at +0.5 V. This was due to unoxidized intermediates formed during the forwards scan. EG electrooxidation requires little more oxidation potential i.e., -1.1 V to +1.0 V to oxidize the most of the intermediates. But in the case of +1.0 V, the possibility of formation PdO was observed, but almost 95% of intermediates were removed. The $I_f/I_b$ ratio also supports the above fact and the results were shown in the Table 6.2.

**Table 6.2  Comparison of $I_f/I_b$ towards the electrooxidation of alcohols at Pd/PPy/MN electrode in alkaline medium**

<table>
<thead>
<tr>
<th>S.No</th>
<th>Alcohol</th>
<th>$I_f$</th>
<th>$I_b$</th>
<th>$I_f/I_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
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<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>Gly</td>
<td>380</td>
<td>160</td>
<td>2.25</td>
</tr>
<tr>
<td>4</td>
<td>Xyl</td>
<td>250</td>
<td>65</td>
<td>3.85</td>
</tr>
</tbody>
</table>
Figure 6.8 CVs of electrooxidation of methanol on Pd/PPy/MN electrode in the scanning ranges -1.1 to (a) +0.2 V, (b) +0.4 V, (c) +0.6 V, and (d) +0.8 V at 1M KOH/1M CH$_3$OH solution.

Figure 6.9 CVs of electrooxidation of EG on Pd/PPy/MN electrode in the scan range of – 1.1 to (a) +0.2 V, (b) +0.4 V, (c) +0.6 V, (d) +0.8 V and (e) +1.1 V at 1 M KOH/1 M EG solution.
6.3.3 Electrooxidation of Glycerol and Xylitol at Pd/PPy/MN electrode

The electrooxidation of glycerol is an interesting one in the field of energy production (Yu et al 2010). The electrooxidation of glycerol at Pd/PPy/MN is shown in Figure 6.10. During the forward oxidation from –1.1 to +0.2 V, a strong forward oxidation peak was observed at –0.21 V and secondary oxidation peak at –0.34 V during the reverse scan. The peak current was increased with increase the number of cycles from 1 and reaches maximum at 9th cycle. In Figure 6.10 displays the CVs for the fourth and nineth cycle. In the first cycle the byproducts formation is low and while increasing the cycle more byproducts were formed. In the above reaction at Pd/PPy/MN nanocomposite electrode the electrode is more active.

Figure 6.10 CVs of electrooxidation of Glycerol on Pd/PPy/MN electrode at (a) 4th and (b) 9th cycle in 1 M KOH/1 M Gly solution
Figure 6.11 CVs of electrooxidation of Glycerol on Pd/PPy/MN electrode in scan range of \(-1.1\) to (a) \(+0.2\) V, (b) \(+0.4\) V, (c) \(+0.6\) V, (d) \(+0.8\) V and (e) \(+1.1\) V in 1M KOH/1 M Gly solution

Figure 6.12 CVs of electrooxidation of Glycerol on Pd/PPy/MN electrode at various concentrations of (a) 0.1 M, (b) 0.5 M, (c) 1 M and (d) 2 M Gly in 1 M KOH solution
Figure 6.13  CVs of electrooxidation of glycerol on Pd/PPy/MN electrode in (a) 0.5 M, (b) 1 M and (c) 2 M KOH/1 M Gly solutions

Figure 6.14  CVs of electrooxidation of Xylitol on Pd/PPy/MN electrodes at (a) 4th and (b) 10th cycle in 1 M KOH/1 M Xyl solution
Figure 6.15 CVs of electrooxidation of Xylitol on Pd/PPy/MN electrode at (a) 0.1 M, (b) 0.5 M , and (c) 1 M Xyl in 1 M KOH solution

Figure 6.16 CVs of electrooxidation of Xylitol at Pd/PPy/MN electrode in (a) 0.1 M, (b) 0.5 M , (c) 1 M KOH/0.1 M Xyl solutions
Figure 6.17 CVs of electrooxidation of Xylitol at Pd/PPy/MN electrode in scan range of –1.1 to (a) +0.2 V, (b) +0.4 V, (c) +0.6 V, (d) +0.8 V and (e) +1.1 V in 1 M KOH/1 M Xyl solution

Figure 6.18 Chronoamperometric studies for the electrode stability for various fuels at Pd/PPy/MN electrode
Figure 6.19 CVs of electrooxidation of EG at various scan rate (25 to 250 mV/s) in 1 M KOH/1 M EG at Pd/PPy/MN electrode

Figure 6.20 Long-term stability of Pd/PPy/MN electrode in 1 M KOH/1 M (CH₃OH, EG and 0.1 M Xyl)
The possible removal of the intermediates was achieved by the electrode materials through active oxygen atom extracted or supplied by the material. This was achieved by increase of scanning potentials. While increase the forward scan potential from +0.2 up to +1.0 V, a strong secondary oxidation of peak at +0.5 V was observed during the forward scan. The removals of intermediates were almost achieved at the scanning potential at +0.8 V (Figure 6.11).

This was further supported by the $I/I_b$ ratio shown in Table 6.2. Above +0.6 V there is a possibility of PdO formation, but this does not affect the reaction rate.

Figure 6.12 shows peak current densities for different concentrations of Gly. The peak current increased from 0.1 M to 2 M Gly. 1 M and 2M Gly exhibits almost similar peak current. It was observed that the higher concentrations of KOH were required to dissociate Gly molecules. The effect of glycerol and supporting electrolyte was studied for the electrooxidation of Gly at Pd/PPy/MN nanocomposite electrode. The electrocatalytic activity of alcohols was increased or altered with the supporting electrolytes, in the case of alkaline medium. Initial adsorption of OH$^-$ on the electrode surface facilitates the electrocatalytic reaction. By increasing the concentration of KOH from 0.5 M to 2 M KOH (Figure 6.13), the peak current increases and at the same time a shift in peak position was also observed. After 2 M KOH the peak current density attains a constant value. this is due to the complete coverage of active surface area of the catalyst (Pd/PPy/MN) by OH$^-$ ions.

The electrooxidation of poly hydric alcohol such as Xylitol was studied at Pd/PPy/MN nanocomposite electrode in 1M Xyl in 1 M KOH
solutions (Figure 6.14). The forward anodic oxidation peak centered at – 0.21 V and secondary oxidation peak centered at – 0.38 V. Xyl electrooxidation was also exhibits similar kind of electrooxidation behaviour like glycerol i.e., the peak current increase with increasing the cycle and reached maximum at 9th cycle (Figure 6.15). When increase the Xyl concentrations from 0.01 to 1M (Figure 6.16), the maximum current was observed at 0.1 M, which was due to the better dissociation of Xyl molecule. Hence, the higher catalytic activity was observed, which was further analyzed by changing the KOH concentrations, the maximum peak current density was observed at 1 M KOH/0.1 M Xyl. Thus, further studies were carried out at this concentration. The removal of poisonous intermediates were studied by increasing the peak potential, but the reduction in backward peak current was very slow or minimum up to +0.6 V. At +0.5 V a secondary oxidation peak was also observed, hence after +0.6 V, the peak current density was decreased and reached almost 90 % and the potential reaches to +1.0 V.

The electrocatalytic stability was tested by Chronoamperometry, which displays in Figure 6.18, the Pd/PPy/MN nanocomposite electrode shows higher stability at glycerol electrooxidation and order of stability shown as Glycerol > Ethylene Glycol > Methanol, Xylitol. The electrode stability was further analyzed by varying the scan rate in the EG electrooxidation reaction. The peak current density against square root of scan rate displays the electrode is highly surface controlled one (Figure 6.19). The long term stability of Pd/PPy/MN electrode was tested upto 500 cycles, the current densities were decreased by 9% (EG) and 5-6 % (CH₃OH, Gly) (Figure 6.20).
6.4 CONCLUSION

The Pd/PPy/MN nanocomposite electrocatalyst was studied for the electrooxidation of alcohols in alkaline medium. The uniform distribution of Pd in PPy/MN composite was confirmed through physical characterizations. The electrooxidation of methanol, EG and xylitol were tested in alkaline medium (KOH) at Pd/PPy/MN electrode. Methanol and EG electrooxidation exhibits excellent activity and poly hydric alcohol i.e., Xylitol shows improved and exceptional electrocatalytic activity in Pd/PPy/MN electrode. As a whole the PPy/MN would act as an excellent support material for Pd for alcohol electrooxidation in alkaline medium.