SUMMARY

The importance of the reduction of oxygen in water in fuel cell and metal/air batteries is well known. Platinum electrodes were the first choice for the use in fuel cells, but their high cost has necessiated the researches leading to preparation of low cost modified electrodes in which there is decreased oxygen reduction at lower potential. Hence the current interest lies in the utilization of carbon based modified electrodes and mediator. Over the last few years, the electrocatalysis of oxygen reduction on various conducting polymers/ceramic modified electrodes were studied. These materials are specially important owing to their bridging the world of conducting polymers and that of nanoparticles.

CHAPTER I
INTRODUCTION

This chapter deals with the basics, background and types of nanocomposites. The conductivity of conjugated polymer and conducting polymer-inorganic hybrid nanocomposites are discussed. Electrocatalysis of conducting polymer-inorganic hybrid nanocomposites oxygen reduction in Direct Methanol Fuel cells (DMFCs), electrocatalysis of Pt based nanocomposites, alternative cathode catalysts and applications of conducting polymer nanocomposites in electrocatalysis are presented here.
CHAPTER II
STATE OF THE ART AND SCOPE OF THE INVESTIGATION

This chapter gives details about the nanocomposites that are chosen for electrochemical analysis. The present status and earlier work carried out on those nanocomposites are also presented here. The necessity for the present investigation on electrochemical analysis of nanocomposites, and the scope of the present investigation are also presented.

Selected monomers are

- Aniline
- o-toluidine

Selected ceramics are

- TiO$_2$
- Al$_2$O$_3$
- SiO$_2$
CHAPTER III
EXPERIMENTAL DETAIL

Third chapter describes the instrumental aspects, methodology, materials and procedures employed during this investigation. Electrochemical workstation CHI650C (CH Instruments, USA) was employed for electrochemical and electroanalytical studies. For recording the UV-Vis absorption spectra, a computer controlled Jasco V-530 spectrophotometer was used. The FTIR spectra were recorded by SHIMADZU instrument in the frequency range of 400-4000 cm\(^{-1}\). The X-ray diffraction (XRD) patterns were recorded for the powdered materials using a BRUKER AXS (D8 ADVANCE) X-ray diffractometer in the scanning range of 20-80° (2\(\theta\)) using CuK\(\alpha\) radiation having a wavelength of 1.5405 Å. Thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) experiments were performed using Perkin-Elmer instruments. The morphology of the polymer and polymer-ceramic nanocomposites has been studied by Scanning Electron Microscopy (SEM) method. Scanning electron micrograms were obtained using Model: JEOL JSM 6360. TEM images were taken using PHILIPS model CM 200 in operating voltage 20-200 kV and with a resolution of 2.4 Å. These experimental methods for polymer and polymer-ceramic nanocomposites are studied in detail.

CHAPTER IV

Polyaniline

Intrinsically conducting polymer was synthesized from aniline along with oxidizing agent ammonium per sulphate by chemical oxidation method. It was characterized by UV-Vis, FTIR, XRD and SEM. As per TGA-DTA and DSC, PAni was found to be thermally stable. Cyclic voltammetric studies revealed the presence
of an adherent polymer film on the glassy carbon electrode and showed redox behavior of the polymer. At pH 1.0, PAni modified GCE showed high current value in normal condition and under N₂ and O₂ saturated buffer solution the current reduces and the reduction potential is shifted towards negative side. O₂ and N₂ gases interfere into the polymer layer to decrease the charge of reduction potential and it has been confirmed by cyclic voltammetry and chronoamperometric techniques. Methanol reduction was also observed at lower potential and enhancing the catalytic activity in N₂ saturated buffer.

**Polyaniline-Silica Nanocomposite**

The preparation of PAni-SiO₂ nanocomposites were carried out by bulk polymerization method with varying concentration of SiO₂. The composites were characterized by UV-Vis and FTIR spectroscopy. XRD studies revealed that 2θ values are broadened and the peak intensity increases due to the increase in concentration of SiO₂. The varying ceramic weights on polymer matrix are clearly shown by SEM study and rocky like morphology gradually changes into sea weeds. The nanoscale dimensions of the nanocomposites are confirmed by TEM and XRD studies. A good thermal stability was found in PAniSNCs by TGA-DTA and DSC studies. In cyclic voltammetric studies, the current density of PAniSNC6 modified GCE increased to a maximum at pH 1.0. The nanocomposite exhibits maxima current peak at lower potential. The ORR activity and diffusion coefficient value increases for O₂ saturated buffer than under normal condition and N₂ saturated buffer which were confirmed by chronoamperometry and chronocoulometry. PAniSNC6 modified GCE was found to have high electro catalytic current behavior for O₂ saturated buffer than
for PAni modified GCE towards methanol. EIS studies also predict a good conductivity of the nanocomposite with increasing compositions of SiO₂.

**Polyaniline-Alumina Nanocomposites**

PAni-Al₂O₃ nanocomposites are synthesized with different weight ratio of Al₂O₃ by chemical oxidative polymerization method. Very smaller content of ceramic show a better results. UV-Vis, and FTIR revealed that increasing amount of ceramic content tend to eliminate with conducting polymer which was confirmed by morphological structure and element intensity ratio of EDAX. The SEM showed that small homogeneous small crystalline surface (PAniANC1) gradually changed to rather lumpy crystalline (PAniANC6). From the XRD data the grain size was calculated using Scherrer’s formula and it was found to be in nano range. That PAniANC1 has good thermal stability was found from TGA-DTA and DSC studies. For PAniANC1 modified GCE, electrochemical response depended significantly on the scan rate and pH. Oxygen reduction ability was enhanced in O₂ saturated buffer solution (pH 1.0) than when used at normal condition and N₂ saturated buffer. PAniANC1 modified GCE proves that there is enhancement of ORR activity in the presence of acidic MeOH under N₂ saturated buffer. EIS study showed that, PAniANC1 modified GCE has good conductivity and electron transfer limited process. From PAniANC1 to PAniANC6 were found to increase resistance with increase in ceramic concentration.

**Polyaniline-Titania Nanocomposites**

PAni-TiO₂ nanocomposites were synthesized by bulk polymerization method using K₂S₂O₈ as external oxidizing agent and varying the ceramic concentration.
UV-Vis and FTIR spectra revealed that the ceramics were strongly incorporated into the PAni matrix. Surface morphology and element ratio are confirmed by SEM and EDAX. SEM images showed that sponge like morphology gradually changes into granular flower like morphology. PAni-TiO$_2$ nanocomposites are in nanoscale, which is confirmed by XRD and TEM. PAniTNC1 was thermally stable up to 832°C and found from TGA-DTA. PAniTNC1 showed better results. At pH 1.0, PAniTNC1 modified GCE showed high electrocatalytic redox behavior under O$_2$ saturated buffer in electrochemical studies and methanol reduction was observed in acidic media. The diffusion coefficient value was high in O$_2$ saturated buffer solution. EIS study also showed that PAniTNC1 exhibits good conductivity.

**Poly (o-Toluidine)**

Synthesized PoT was characterized by UV-Vis, FTIR, XRD, SEM, TGA and DSC. UV and FTIR spectra confirm the polymerisation of o-toluidine. XRD patterns show that the 2θ value is broadened, due to PoT. SEM showed spongy ilke morphology. PoT was found to be thermally less stable by TGA-DTA and DSC studies. The prepared PoT modified GC electrode showed high current value under normal condition than in other gases (O$_2$ & N$_2$) saturated solution at pH 1.0. High electro catalytic reduction behavior was observed under N$_2$ saturated buffer solution in presence of acidic methanol.

**Poly (o-Toluidine)-Silica Nanocomposite**

Nanocomposites of PoT-SiO$_2$ were successfully synthesized with different amounts of SiO$_2$. FTIR, UV-Vis and XRD revealed that the ceramics were strongly incorporated into the PoT matrix. SEM showed that crystal layered morphology
gradually changed into lumpy crystalline structure. EDAX clearly showed the percentage of Si, N, C & O. The prepared polymer-ceramic composite were in nanoscale confirmed by TEM and XRD studies. TGA-DTA and DSC showed that PoTSNC6 had a good thermal stability. Higher concentration of SiO$_2$ showed good results. Use of PoTSNC6 modified GCE was highly sensitive and stable for electrochemical measurement at pH 1.0. The peak current and diffusion coefficient value were high PoTSNC6 modified GCE at normal condition than O$_2$ and N$_2$ saturated buffers, which was confirmed by chronoamperometry and chronocoulometry. This modified electrode was found to have high electro catalytic reduction behavior under O$_2$ saturated buffer solution than PoT modified GCE towards methanol reduction in pH 1.0. EIS studies predicted that PoTSNC6 has good conductivity.

**Poly (o-Toluidine)-Alumina Nanocomposite**

Nanocomposites of PoT-Al$_2$O$_3$ were successfully synthesized with varying ceramic concentration. The varying concentration of Al$_2$O$_3$ tends to eliminate the PoT matrix, which is confirmed by UV-Vis and FTIR spectra and XRD patterns. The surface morphology of crystal like structure gradually changed to rough and broken surface by SEM study. Al$_2$O$_3$ nanofibres are encapsulated by PoT clearly as shown in nanoscale by TEM analysis. TGA-DTA and DSC showed that the PoTANC1 had a good thermal stability. PoTANC1 modified GCE increased to a maximum current density, after which it declined with increase in Al$_2$O$_3$ composition in acidic media. This modified electrode enhanced electrocatalytic reduction behavior in O$_2$ saturated buffer than in the normal and N$_2$ saturated buffer. The catalytic reduction behaviour was high in methanol in acid solution in O$_2$ saturated buffer which is confirmed by
LSV. Diffusion coefficient value was high in O$_2$ saturated buffer which is studied by chronoamperometry and chronocoulometry. EIS study revealed that PoTANC1 modified GCE has a good conductivity and electron transfer limited process. PoTANC1-PoTANC6 were found to increases with increased in ceramic concentration which shows greater resistance to conduction.

**Poly o-Toluidine-Titania Nanocomposites**

Nanocomposites of PoT-TiO$_2$ were synthesized with different compositions of TiO$_2$ and characterized by UV-Vis, FTIR, XRD, SEM, EDAX, TEM, TGA and DSC. When ceramic content is increased there is strong incorporation in polymer, which is confirmed by FTIR and UV-Vis studies. Very low concentration of the ceramic exhibits a better result. A typical fibrous morphology is gradually changed to granular particle (Marigold flower like structure) morphology and this change is observed in the conducting polymer matrix and it is due to the incorporation of higher amount of ceramic concentration, which is confirmed by SEM. TiO$_2$ encapsulated by PoT matrix in nanoscale is confirmed by TEM analysis. A good thermal stability was found in PoTTNC1 from TGA-DTA and DSC studies. At pH 1.0, the current density of PoTTNC1 modified GCE increased to a maximum and gets decreased with increase in TiO$_2$ composition in cyclic voltammetric studies. Oxygen reduction ability is observed at very low potential in case of O$_2$ saturated buffer. The methanol reduction ability in PoTTNC1 is higher in acidic media, which was studied by LSV. EIS studies exhibits a good resistance of the nanocomposite with increases of TiO$_2$ and higher conductivity is observed in PoTTNC1 modified GCE.
Fig. 5.1. Bar diagram of peak current vs. electrodes at optimum experimental conditions (Cathodic reaction in pH 1.0 solution)

Fig. 5.2. Bar diagram of peak current vs. electrodes at optimum experimental conditions (Cathodic reaction in acidic methanol solution)
CONCLUSIONS

Various conducting polymer and polymer-ceramic nanocomposites were synthesized by chemical polymerization method. Regarding electrochemical studies, it was found from the bar diagram 5.1 and 5.2 that electrocatalytic Oxygen reduction ability is maximum for PAniTNC1 modified GCE at pH 1.0 in O2 saturated buffer solution and methanol reduction enhanced in PAniANC1 modified GCE in acidic medium.

The increasing order of ORR activities towards methanol reduction potential as follows:

PAniTNC1<PoTANC1<PoT<PoTSNC6<PoTTNC1<PAni<PAniSNC6<PAniANC1

The increasing order of ORR activities towards methanol reduction current as follows:

PoT<PAni<PoTSNC6<PoTANC1<PoTTNC1<PAniANC1<PAniTNC1<PAniSNC6

Comparison results of thermal stability and C_{dl} values are given below

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Samples</th>
<th>TGA/DTA (°C)</th>
<th>EIS-C_{dl} (Fcm^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PAni</td>
<td>500</td>
<td>5.6844 x 10^{-10}</td>
</tr>
<tr>
<td>2</td>
<td>PAniSNC6</td>
<td>800</td>
<td>7.0934x10^{-9}</td>
</tr>
<tr>
<td>3</td>
<td>PAniANC1</td>
<td>800</td>
<td>1.033x10^{-8}</td>
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<tr>
<td>4</td>
<td>PAniTNC1</td>
<td>832</td>
<td>3.442x10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>PoT</td>
<td>520</td>
<td>1.5948x10^{-10}</td>
</tr>
<tr>
<td>6</td>
<td>PoTSNC6</td>
<td>510</td>
<td>3.5198x10^{-9}</td>
</tr>
<tr>
<td>7</td>
<td>PoTANC1</td>
<td>550</td>
<td>1.9175x10^{-8}</td>
</tr>
<tr>
<td>8</td>
<td>PoTTNC1</td>
<td>590</td>
<td>1.447x10^{-7}</td>
</tr>
</tbody>
</table>
The salient feature about this investigation is

- Facile route for the synthesis and characterisation of polymer and polymer-ceramic nanocomposites
- Good thermal stability
- Enhanced electrocatalytic reduction behaviour
- Moderate conductance behaviour nanocomposites.