Electrochemical Synthesis of composite 4-Methyl Pyridine, Aniline as conducting Polymer by Galvanostatic Method

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Abstract

Polymer films will prepared by galvanostatic electrochemical synthesis, which provides a constant oxidative current at the anode. The electrochemical deposition of monomer and their copolymer films was carried out by using a galvanostatic technique at temperature 27 °C in a one-compartment, three-electrode glass cell. The ITO coated glass plate will have to use as a working electrode, platinum foil as a counter electrode and Ag/AgCl as a reference electrode. The electrolyte solution will prepare in deionized water with optimum parameter. After synthesis the polymer coated electrodes will rinsed thoroughly in deionized water dried in cold air and then used for subsequent characterization. The synthesized composite films will subjected to various characterizations viz. galvanostatic electrochemical techniques. The FTIR, SEM, X-RD etc methods use for characterization. The electrochemical, electrical, optical and morphological properties of composite 4-methyl pyridine and HCL (supporting electrolyte) at 1 mA/cm2 current density and pH 3.0 have been successfully studied. The characterization study reveals that the composite 4-methyl pyridine, aniline film provide uniform, porous and stable polymer matrix which is suitable for immobilization of bio component.. The composite 4-methyl pyridine, aniline film shows highest conductivity 2.412 x10-3 S/cm. with lower polymerization potential. The FTIR spectra of composite 4-methyl pyridine and aniline confirm the presence of organic groups as well as occurrence N-H.

Keywords*: Galvanostatic method; 4-methyl pyridine; polymer*

1. Introduction :

The demand for new polymeric materials that can be used as a matrix for the immobilization of biomaterials has been recently intensified. Among the various polymeric materials, the porous polymer matrix has been projected to have innumerable applications in biosensors and presently at the centre- stage of research and development. Conducting polymers have attracted a lot of interest as a suitable matrix for the entrapment of enzymes. Conducting polymers are used to enhance the speed, sensitivity and versatility of biosensors. Electrically conducting polymers have excellent flexibility in its chemical structure, which can be modified as per the requirement of specific application. Therefore, conducting polymers are being used for various biosensor applications viz. Glucose, cholesterol, lactate, urea etc.

Diabetes is one of the leading causes of death by disease. If we do not care, high levels of blood sugar associated with diabetes, can slowly damage both small and large vessels in the body, resulting in a variety of complications. With careful management, these complications can be prevented. The requirement of frequent and continuous monitoring of glucose in diabetics tempted the scientific community to work extensively in the field of glucose sensors and still it is essential to continue the research to provide sensor with better response.

The present research work deals with the optimization of process parameters viz concentration of monomer and various supporting electrolytes, pH of the electrolyte, current density etc for the synthesis of conducting polymers. We have optimized process parameters of 4-Methyl pyridine and aniline.

There are various active research groups worldwide working in the field of conducting polymer-based

biosensor since several years. Electrochemical polymerization is recognized as an effective technique for the synthesis of conducting polymers. It is widely reported, because it is simple and can be used as a one step method [1-12]. Polypyrrole family is suitable for various applications, such as solar cells, electrodes for rechargeable batteries, biosensors etc. [13-18]. It has been reported that the N-substituted polymers of pyrrole have low conductivity but large mechanical strength and relatively low production cost. The large mechanical strength of N-substituted polymers of pyrrole is very useful for biosensor applications [19-21]. It is well known that the dopant (i.e. anion or cation) used during synthesis causes the changes in the electrochemical, structural, morphological, optical, electrical and mechanical properties of the film [22-24]. The lifetime and stability of the enzymes determines the sensitivity and reliability of the biosensors signals. The good operational stability of the enzymes in the polymer matrix can be achieved by synthesizing the conducting polymers with polyelectrolyte [25-26].

The charge neutrality is an important factor for the immobilization of bio-components. It is reported that, the polymer film synthesized with polyelectrolyte gives good operational stability in the polymer matrix with increased growth rate and higher compactness. It is also useful for improving the conductivity [27]. The influence of dopants/supporting electrolytes on the synthesis of conducting polymers is being studied [28-30]. However, still it is essential to study the effect of process parameters and dopants/supporting electrolytes on the synthesis of conducting polymers, so that we will be possible to develop the biosensor with enhanced response, long lifetime and stability.

2. Chemicals and Experimental

The 4-Methyl pyridine and aniline monomer was double distilled before use. Sulphuric (HCl) acid used as supporting electrolyte. All above reagents were obtained from Avra Chemical, Pune (INDIA). An aqueous solution of 4MP/Aniline (99%) and various electrolyte concentrations were prepared in distilled water The reference electrode was kept in close proximity to the working electrode to minimize the electrolytic ohmic drop. The pH was adjusted by adding nitric acid or sodium hydroxide.

The electropolymerization of 4-MP/Aniline was carried out by galvanostatic technique, in one compartment electrochemical cell. Graphite Carbon was used as a counter electrode and another ITO (20 mm × 0.5mm) was used as a working electrode. The reference electrode was Ag/AgCl. All three electrodes were placed vertically in cell. An 80 ml solution was used for each reaction. The pH of the electrolyte was measured by calibrated ELICO LI120 pH meter.

We have varied the monomer concentrations (0.05 M, 0.1 M, 0.2 M,), supporting electrolyte concentrations (1 M,3 M, 5 M), pH of the solution (0.5, 1, 2), and current density (0.5, 1, 2) mA/2cm2 during synthesis of 4-MP/Aniline.

The electrochemical characterization was carried out by galvanostatic technique, which maintains a constant current throughout reaction. The optical absorption study was carried out in Analytic Jena specord 210 plus (Wavelength 200nm-800nm) UV- visible spectrophotometer. The conductivity was measured by using four-probe technique (S.E.S. Instrument Pvt. Ltd. Roorkee). A computer controlled Potentiostat/Galvanostat, indigenously designed and fabricated in the Materials Research Laboratory, Department of physics, ACS college Narayangaon.. (MS) India was employed for the electrochemical synthesis of 4-MP/Aniline-HCl film by using potentiometric (Galvanostatic) method.

3. Result and discussion

The optical absorption spectrum of synthesized poly 4-MP/Aniline films with optimized parameters with supporting electrolyte HCl are shown in Fig 1. The spectrums were recorded in directly without any solution on It was recorded using UV-visible spectrophotometer ,Analytic Jena specord 210 plus Wavelength (200 nm-800 nm). All spectra were recorded in the wavelength range of 300-800nm. The shoulder is appearing at 380 nm for HCl corresponds to the formation of ES phase irrespective of the inorganic supporting electrolyte. It shows very good resemblance with earlier reported work.

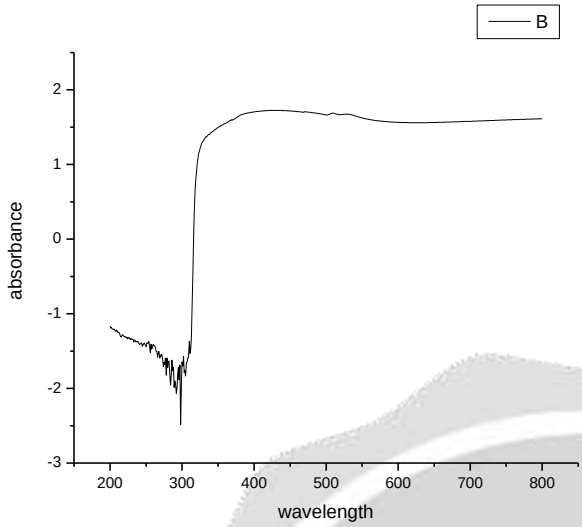

Fig 1. UV-vis of poly 4-MP/Aniline

FTIR :

The FTIR spectrum of synthesized poly 4-Methyl Pyridine is shown in Fig 2 spectrums showed the peak at 3100-3500 cm-1 corresponds to N-H stretching. The incorporation of the counter anion in the polymer is evidenced by the peaks. Further evidence of the presence of this anion in the polymer film is revealed by peaks at 1380 and 1600-1640 cm- 1 which may be assigned to SO2 stretch in sulphonates. The vibration bands are observed at 1728- 1784 cm-1 (C=O), 1527-1548 cm-1 (N-H bending). These bands correspond to the characteristic bands for 4MP/Aniline; it shows very good agreement with earlier reported work. Thus, the FTIR spectral results confirm the formation of poly 4- Methyl Pyridine.

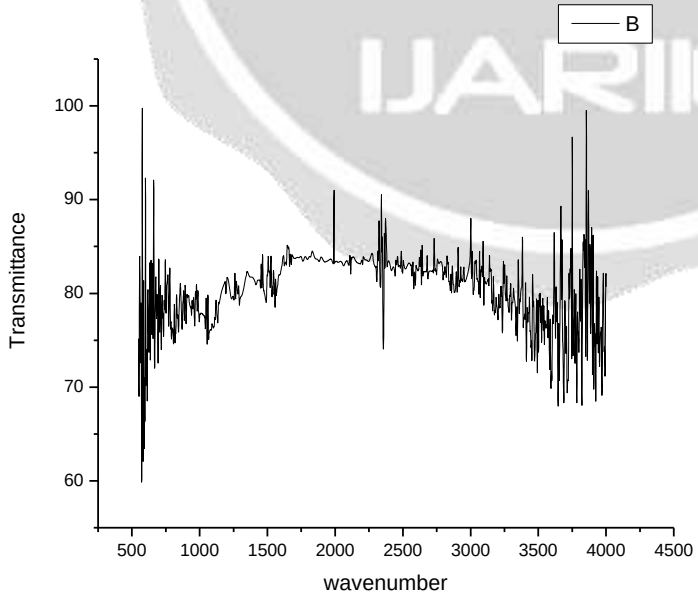

Fig. 2 FTIR of poly 4-MP/Aniline

Scanning Electron Microscopy (SEM)

Fig 3 shows SEM images, at 5 micron. It clearly shows porous morphology of 4-MP/Aniline Film. This nature helpful for the biosensor application of the film. This facility provided by Dept of Physics, University of Pune, India. The **JEOL JSM-7500F** is an ultra high resolution field emission scanning electron microscope (FE-SEM) equipped with a high brightness conical FE gun and a low aberration

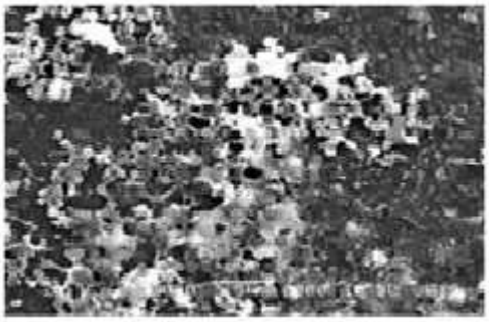

Fig.3 SEM of poly 4-MP/Aniline

INFLUENCE OF CONCENTRATION RATIO OF MONOMER AND SUPPORTING ELECTROLYTE.

Fig 4 shows the concentration ratio viz. 0.1: 0.1, 0.1: 0.2 and 0.1:0.5 for the monomer and the supporting electrolyte (4 M P/Aniline and HCl) respectively has been successfully studied.

The matrix with higher conductivity will be more useful for electron transfer process. We have synthesized poly 4-MP/Aniline films with 0.5N, 1N, 1.5M concentration of supporting electrolyte HCl. The chronopotentiogram recorded during electrochemical polymerization of poly 4-MP/Aniline with various concentrations of HCl. 0.1 N concentration of monomer, and 2mA/2cm2 current density at 3.0pH is as shown in Figure (3.2) for HCl, This indicates that the synthesized poly 4-MP/Aniline film shows highest conductivity for 0.5N concentration of HCl as compared with other concentrations 0.1N and 0.2N. This concentration is stable, porous and adherent to the surface. However, the polymerization potential recorded during synthesis of 4-MP/Aniline with0.1N concentration of HCl was lower as compared with 1.5N concentration of HCl.

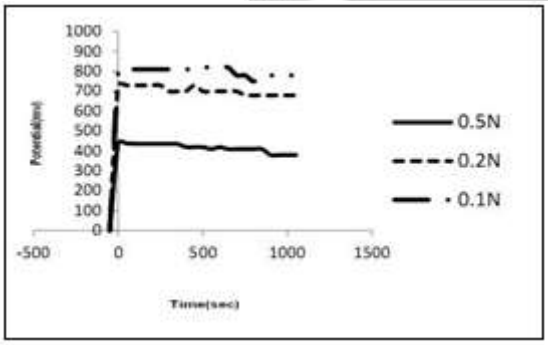

Fig 4. Concentration ratio of monomer

INFLUENCE OF SUPPORTING ELECTROLYTES

The study of different supporting electrolyte viz. type of electrolyte, electrolyte concentration and current density have been studied during polymerization of poly(4-MP/Aniline).The aqueous solution (70 ml) containing 0.1 M 4MP/Aniline, 0.5 M supporting electrolytes/dopants and deionized water with 2 pH was prepared. It was

subjected to electrochemical polymerization by galvanostatic method at 27 C; with 1 mA/2cm2 applied current density.

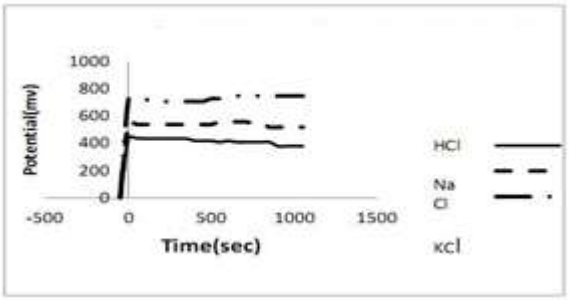

Fig 5 Influence of supporting electrolyte.

INFLUENCE OF PH

Below fig.6 shows the influence of pH (viz. 1, 1.5 and 3) has been studied on the galvanostatic deposition of 4MP/Aniline film. We have recorded lowest polymerization potential for the synthesis of poly 4-MP/Aniline films at 2mA/2cm2 current density at 3.0 pH as compared to other pH 1.5 and pH 1, which indicate higher conductivity. The synthesized films is uniform and adhesive at current density 2mA/2cm^2 and pH3.0

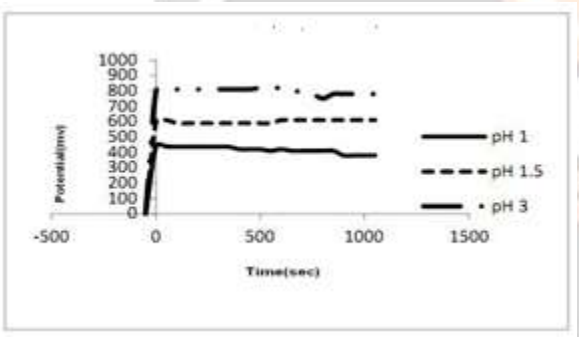

Fig 6 Influence of pH

Polymerization of 4-MP and Aniline with HCl

The chronopotentiogram recorded during electrochemical polymerization of 4MP and aniline at various concentrations of supporting electrolyte solution HCl with monomer of 4MP and Aniline at 2mA/2cm^2 current density at 3 pH are shown in Fig.7 The matrix with higher conductivity will be more useful for electron transfer process. Above fig:7 indicate that HCl shows lower polymerization potential 4-MP/Aniline with HCl supporting electrolyte.

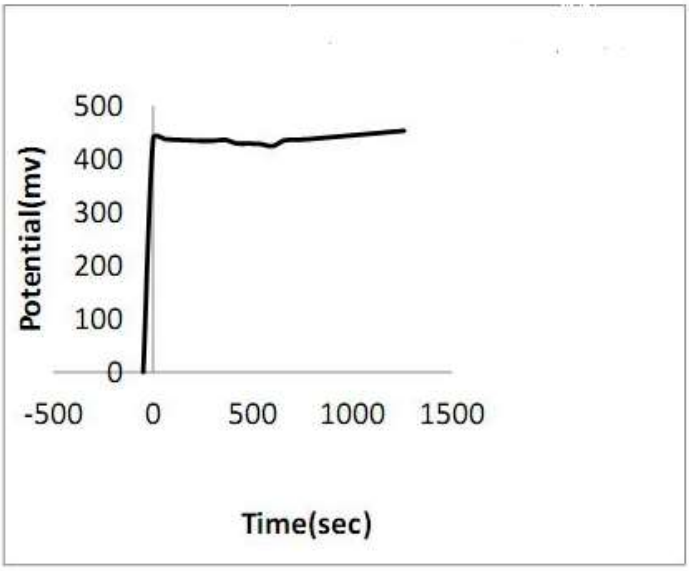

Fig.7 Polymerization of 4-MP and Aniline with HCl

CONCLUSIONS

The influence of electrochemical process parameter on the surface morphology and the conductivity of poly 4MP/Aniline film were successfully studied. Process has been developed for the aqueous electro-polymerization of N-4MP/Aniline coating on ITO substrates. The concentration ratio of 0.1: 0.5 of N-4MP/Aniline and HCl for the synthesis of P (4-MP/Aniline) film on ITO electrode are good combination for the deposition. The film shows good conductivity for current density 2 mA/2cm^2 at pH 3.

1. HCl is the best supporting electrolyte for synthesis of poly 4MP/Aniline.
2. The concentration ratio 0.1N:0.5N of 4MP/Aniline and Hydrochloric acid is good combination on ITO electrode.
3. pH 3 gives good conductivity and surface morphology for the film.
4. The 4MP/Aniline-HCl film shows good conductivity for applied current density 2mA/2cm2 at 27^{o}C.

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