Study of Influence for Various Parameters to Electro-chemical Synthesis of Polyaniline Thin Film by Galvanostatic Method

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ABSTRACT
Electrochemical synthesis of Polyaniline films will be prepared by galvanostatic method for various supporting electrolytes which provides a constant oxidative current at the anode. The electrochemical deposition of aniline monomer and their copolymer films were carried out by using a galvanostatic technique at temperature 27 °C, after synthesis of the polymer coated film it will rinse thoroughly in deionized water and then dried in cold air then used for consequent characterization. The synthesized composite films will subjected to various characterizations such as FTIR, UV-Visible spectroscopy and SEM etc. and effect of influence of pH, current, monomer concentration and potential etc. these parameters are studied for optimization of the film formation.

Keywords: Electrochemical, Galvanostatic, Polymer. Aniline.

INTRODUCTION
Polymers have literally take charge as conductors by discarding their traditional role as electric insulator. Now a day polymers are being used for wide range of novel applications. Researchers from various subjects i. e. Physical science, Electronics, Chemistry, Biology etc are now coming together to study this organic materials, which show significant conducting properties.
A new class of polymers known as intrinsically conducting polymers or electro-active conjugated polymers has recently emerged. These materials exhibit excellent electrical and optical properties. Conducting polymers have attracted a lot of interest as a suitable matrix for the setup 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 polymer film is being used for various biosensor applications viz. Pesticides, Insecticides, Glucose, Cholesterol, Lactate, Urea etc. Pesticide is a term used in broad sense for organic toxic compounds used to control insects, bacteria, weeds, nematodes and other pests. The pesticide residues may enter into the food chain through air, water and soil. They have an effect on ecosystems and cause several health problems to animals and humans. Pesticides can be carcinogenic and cytotoxic. They can produce bone marrow and nerve disorders, infertility, and immunological and respiratory diseases [1]. The present research work deals with the optimization of process parameters i.e. concentration of monomer, various supporting electrolytes, pH of the electrolyte and current density etc. for the synthesis of conducting polymers. We have optimized process parameters of 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 [2-12]. 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. In modern material science, the synthesis of conducting polymer has been the point of research activity. This is an interdisciplinary and emerging research field. The specific objective of the work were optimization of process parameters viz. concentration of monomer and various supporting electrolytes such as HCl, NaCl, KCl (dopant), pH of the electrolyte, current density etc. for the synthesis of conducting polymer.

METHODOLOGY
The aniline monomer was double distilled before use. Hydrochloric acid (HCl) used as supporting electrolyte. All above reagents were obtained from Avra Chemical, Pune (India). An aqueous solution of 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 polymerization of polyaniline was carried out by galvanostatic technique in electrochemical cell. Platinum foil was used as a counter electrode, Indium tin oxide ITO (20 mm × 0.5mm) was used as a working electrode and Ag/AgCl was used as a reference electrode. 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 (0.05M, 0.1M, 0.2M), supporting electrolyte concentrations (0.1M, 0.3M, 0.5M), pH of the solution (1, 1.5, 3), and current density (0.5, 1, 2) mA/2cm² during synthesis of 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. Rookies).

RESULTS AND DISCUSSION

3.1 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 (aniline). The aqueous solution (80 ml) containing 0.1M aniline, 0.5M supporting electrolytes/dopants and deionized water with 2pH was prepared. It was subjected to electrochemical polymerization by galvanostatic method at 27 °C; with 2mA/2cm² applied current density. The chronopotentiogram recorded during electrochemical polymerization of PANI at various concentrations of supporting electrolyte solution viz KCl, NaCl and HCl with monomer of aniline at 2mA/2cm² current density at 3.0 pH are shown in Figure 3.1. The matrix with higher conductivity will be more useful for electron transfer process. Above fig: 3.1 indicate that HCl shows lower polymerization potential than KCl and NaCl. Dotted line indicates polymerization of KCl and NaCl, compound type line shows polymerization of aniline with HCl supporting electrolyte.

3.2 Influence of concentration ratio of monomer and supporting electrolyte.
Fig 3.2 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 (2 AP and HCl) respectively has been successfully studied. The matrix with higher conductivity will be more useful for electron transfer process. We have synthesized polyaniline films with 0.1N, 0.2N, 0.5N concentration of supporting electrolyte HCl. The chronopotentiogram recorded during electrochemical polymerization of polyaniline with various concentrations of HCl. 0.1N concentration of monomer, 2mA/2cm² is current density and pH 3.0 is as shown in Figure (3.2) for HCl. This indicates that the synthesized polyaniline 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 aniline with 0.1N concentration of HCl was lower as compared with 0.2N concentration of HCl.

3.3 Influence of pH:
Below fig 3.3 shows the influence of pH (viz. 1, 1.5 and 3) has been studied on the galvanostatic deposition of Polyaniline film. We have recorded lowest polymerization potential for the synthesis of polyaniline films at 2mA/2cm² current density at 3.0 pH is compared to pH 1.5 and 1, which indicate higher conductivity. The synthesized films is uniform and adhesive at current density 2mA/2cm² and pH 3.0

3.4 Influence of current density:
Fig 3.4 show the influence of current density (viz. 0.5, 1, 2 mA/2cm²) has been successfully studied on the galvanostatic deposition of Polyaniline film. The chronopotentiogram shows lowest potential for the current 2mA/2cm² than the current 0.5 mA and 1mA. Current 2.0 mA/2cm² gives porous and uniform film.

3.5 UV-Visible spectroscopy (UV):
UV-Vis spectrum of synthesized PANI film is shown in Fig. 3.5 recorded using UV Visible 160 spectrophotometer, Shimadzu in the range of 400–1100 nm. This shows very good closeness with the polymerization potential. The absorption spectra observed for synthesized composite films gives good agreement with the earlier reported work. Fig 3.5 UV/Vis spectra of PANI film in aqueous solution at current density 2 mA/cm²and pH 3.0.

3.6 FTIR Studies of PANI-composite Film:
Transmittance versus Wavelength

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The FT-IR spectrum of synthesized composite PANI is shown in Fig.3.6 The FT-IR spectrum was verified using Shimadzu FT-IR-8400 series, using KB pellets in the region 350–4000 cm⁻¹. Spectrum show broad peak at 3623 cm⁻¹ corresponds to O–H stretching. Further evidence of the existence of this anion in the polymer film is revealed by peaks at 1382 and 1635 cm⁻¹ which may be assigned to SO₂ stretch in sulphonates. The trembling bands are observed at 1730 cm⁻¹(C=O), These bands correspond to the characteristic bands for Aniline; it shows very good agreement.

3.7 Scanning Electron Microscopy (SEM):
Fig 3.5 shows SEM images, at 5 micron. It clearly shows porous morphology of PANI Film. This nature of the thin film helps for the biosensor applications. 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 conical objective.

CONCLUSION

The influence of electrochemical process parameter on the surface morphology and the conductivity of polyaniline films were successfully studied. Process has been developed for the aqueous electropolymerization of PANI coating on ITO substrates. The 0.1:0.5 concentration ratios of Aniline and HCl for the synthesis of PANI film on ITO electrode are good combination for the deposition. The film shows good conductivity for current density 2 mA/2cm² at pH 3.
1. HCl is the best supporting electrolyte for synthesis of polyaniline film.
2. The concentration ratio 0.1N: 0.5N of aniline and hydrochloric acid is good combination on ITO electrode.
3. The pH 3 gives good conductivity and surface morphology for the film.
4. The aniline HCl film shows good conductivity for applied current density 2mA/2cm² at 27 °C.

The process parameters viz. type of supporting electrolytes/dopants, concentrations of monomer and supporting electrolytes/dopants, current density, pH of electrolyte solution etc for the synthesis of conducting polymers were optimized. It was found that the galvanostatically deposited conducting polymers viz. (Polyaniline)/HCl are very good matrices with excellent uniformity, porosity and stability for the immobilization of biocomponent.

Conflicts of interest: The authors stated that no conflicts of interest.

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