ELECTROCHEMICAL SYNTHESIS OF POLY 2-AMINO PYRIDINE 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 characterization viz. galvanostatic electrochemical technique. The FTIR, SEM, X-RD etc methods use for characterization.

Keyword - Galvanostatic, Monomer, Polymer

I. INTRODUCTION:

Polymers have literally take charge as conductors by discarding their traditional role as electric insulator. Nowadays polymers are being used for wide range of novel applications. Scientist from many disciplines viz. physics, electronics, chemistry, biology etc are now coming together to study this organic materials, which exhibit remarkable conducting properties. A new class of polymers known as intrinsically conducting polymers or electroactive-conjugated polymers has recently emerged. These materials exhibit excellent electrical and optical properties.

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 2 Amino Pyridine

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.

II. CONDUCTING POLYMERS

In the present era, polymers have been extensively investigated and being used in the daily life. Polymers are generally known for their insulating property. However, in the mid 1970’s, the first polymer capable of conducting electricity, polyacetylene was accidentally prepared by Shirakawa. The subsequent discovery by Heeger and MacDiarmid causes the polymer undergo an increase in conductivity of 12 orders of magnitude by oxidatively doping these polymers over the full range from insulator to metal. Alan MacDiarmid, Hideki Shirakawa and Alan Heeger were awarded “The Nobel Prize in Chemistry (2000)” “for the discovery and development of conducting polymers”. This was particularly exciting because they were able to create a new field of research and provided a number of opportunities to reduce the boundary between chemistry and condensed-matter physics. As the commonly known polymers are in general saturated and so insulators, these were viewed as uninteresting from the point of view of electronic materials. In conjugated polymers, the electronic configuration is fundamentally different, where the chemical bonding leads to one unpaired electron per carbon atom. Professor Bengt Ranby, in his lecture at the Nobel Symposium in the year 1991, designated it as electrically conducting polymers. Electrically conducting polymers are extensively conjugated in nature and therefore it is believed that they possess a spatially delocalized band electronic structure. These band stem from the splitting of interacting molecular orbitals of the constituent monomer units in a manner reminiscent of band structure of solid state semiconductor. It is generally agreed that mechanism of conductivity in these polymer is based on motion of charged defects within the conjugated framework. The charge carriers, either positive p-type or negative n-type, are the products of oxidizing or reducing the polymer respectively. Conducting 2 amino pyridine can be prepared by various method such as chemical, electrochemical etc.

Conducting polymer have recently emerged as a new class of electroactive materials between conductive oxidized (Doped) and the insulting reduced (Undoped) state is the basis of many application. Among others, the poly conjugated conducting polymer has been recently proposed for bio sensing application because of number of favorable characteristics such as 1. Direct and easy deposition on sensor electrode by electrochemical oxidation of monomer 2. Control of thickness 3. Redox conductivity.

They have widened the possibility of modification of surface of conventional electrode providing new interesting properties. They have been applied in electrocatalysis membrane separation and chromatography. They also create new technological possibilities in the design of chemical and biochemical sensor. A simple classification of conducting polymer on the basis of chain composition is representing in tree 1.1 Polypyrrole and the families are promising material for commercial application because of its good environmental stability, electrochemical preparation and bio-compatibility also. Aqueous electrochemical process is an environment friendly and efficient

1.1 Classification of polymers

Polymers can be having different chemical structures, physical properties mechanical behavior, thermal characteristics etc. Depending upon their origin, it is possible to classify polymers as natural, synthetic and conducting polymers.

1.1.1 Natural Polymers

Natural polymers such as rubber, wool, cellulose, starch etc. are produced from natural materials. These materials are extremely important in our daily life. Their physical properties are fixed by nature of the particular material and cannot normally be varied. Their supplies are limited by agricultural considerations. Thus, the materials are often expensive and subject to rapid fluctuations in price.

1.1.2 Synthetic Polymers

These are manufactured from cheap and readily available petroleum fractions and the physical properties may be “tailor made” for almost any desired application. The examples of synthetic polymers are Poly ethylene, PVC, Nylon and Terylene. When we talk about polymers, conventionally it means synthetic or man-made polymeric substances. The first purely synthetic polymer was the Phenol Formaldehyde family of synthetic resins.
techniques being used for synthesis of conducting polymers. 2 amino pyridine and its family can often be used for biosensors, gas sensor, solid electrolytic capacitor, displays, packaging, polymeric batteries and functional membrane etc however conductive 2 amino pyridine is insoluble and infusible, which restricts its processing and application, this problem has been extensively investigated and new application field have been explored in the past several years for example 2 amino pyridine based polymer can be used to load and release drugs and biomolecules. It is preferably being used for biosensor application.

III. CONDUCTION MECHANISM

The electrical properties of any material are determined by its electronic structure. The theory that most reasonably explains the electronic structure of materials is band theory. However, it is difficult to explain the band theory of conducting polymers. In the solid state, the atomic orbital of each atom overlap with same orbital of their neighboring atoms in all directions to produce molecular orbital similar to those in small molecules. When this many orbital are spaced together in a given range of energies, they form continuous energy bands.

The energy spacing between the highest occupied and lowest uncoupled bands is called the band gap. The highest occupied band is called the valence band and lowest uncoupled band is the conduction band.

The electrical properties of conventional materials depend on how the bands are filled. When the bands are filled or empty, no conduction occurs. If the band gap is narrow, at room temperature thermal excitation of electrons from the valence band to the conduction band gives rise to conductivity. This is what happens in classical semiconductors. When the band gap is too wide, thermal excitation at room temperature is insufficient to excite electrons across the gap and become an insulator. The high conductivity of metals is due to partially occupied bands, a partially filled conduction band, a partially empty valence band or a zero band gap. Conductive polymers are peculiar in that they conduct current without having a partially empty or partially filled band. Typical conductive ranges of some conducting polymers are as shown in fig. 1.2

Conductive polymers show enhanced electrical conductivity by several orders of magnitude of doping. Conductivity in conducting polymers is influenced by a variety of factors including polaron length, the conjugation length and overall chain length and by the charge transfer to adjacent molecules. These are explained by large number of models based on inter soliton hopping, hopping between localized states assisted by lattice vibrations, intra-chain hopping of bipolaron, variable range hopping in 3-dimensions and charging energy limited tunneling between conducting domains. To explain some of the electronic phenomena in these organic polymers, concepts from physics that are new for chemists, including solitons, polarons and bipolarons have been applied to conducting polymers since early 1980’s. When an electron is removed from the top of the valence band of a conjugated polymer, such as polypyrrole, a vacancy (hole or radical cation) is created that does not delocalize completely, as would be expected from classical band theory. Only partial delocalization occurs, extending over several monomeric units and causing them to deform structurally. Moreover, π-bonding, in which the carbon orbitals are in the sp2pz configuration and in which the carbon orbitals of successive carbon atoms along the backbone overlap, leads to electron delocalization. This electronic delocalization provides the highway for charge mobility of the polymer chain. Therefore, the electronic structure in conducting polymers is determined by the chain symmetry i.e. the number and kind of atoms within the repeat unit with the result that such polymers can exhibit semi-conducting or even metallic properties.

The energy level associated with this radical cation represents a destabilized bonding orbital and thus has a higher energy than the energies in the valence band.

In other words, its energy is in the band gap. This rise in energy is similar to the rise in energy that takes place after an electron is removed from a filled bonding molecular orbital. In solid-state physics, a radical cation i.e. partially delocalized over some polymer segment is called polaron. It stabilizes itself by polarizing the medium around it.

In 2 amino pyridine, low doping concentrations create paramagnetic polarons, in which, as the degree of doping increases, it convert to spinless bi-polaron, which extend over about four pyrrole rings. Energy band diagram and the structure showing polaron and bi-polaron in 2 amino pyridine are shown fig.1.3 and 1.4. in the 2 amino pyridine, the pyrrole units have positive charges, which are balanced by a Variety of so called dopant anions. Anions are expelled from the polymer film (un doping) when a negative potential is applied to the films, thus reducing it to the neutral state. Conversely, when positive potential is applied to oxidize a neutral film, anions are taken up. During the
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doping process, the volume of the film changes as much as 50% depending on the specific volume of the dopant anion. When doped, it becomes black.

The heterocyclic polymer can be prepared either chemically or electrochemically. e.g. 2 amino pyridine prepared by two routes have different physical appearances. The chemical oxidation method usually leads to fine 2 amino pyridine powders, while the electrochemical method provides freestanding 2 amino pyridine films. However, size, shape and nature of electrodes restrict the use of the electrochemical method involves brittleness of the obtained film and difficulty in preparing thick films. The chemical route becomes the alternative for preparing large size conductive polymers.

The use of conducting 2 amino pyridine film is very attractive for sensor development, either as the sensing component or as the medium for immobilization of biomolecules such as enzymes and other important biological proteins. In particular the high stability of 2 amino pyridine at moderate temperature and in the presence of oxygen offers much promising for wider analytical utilization of biosensor. Future research of fundamental properties of the polymer and synthesis of functionalized 2 amino pyridine group will enable to develop highly sensitive biosensors. 2 amino pyridine films provide multi layered, dynamic properties coating which has three dimensional reaction zone at the electrode surface on which various chemistries such as, ion exchange, complexation, precipitation and enzymes reaction can be performed. The versatility of these conductive film enable to incorporation of wide variety of counter ion compared to the other heterocyclic polymer the performance of 2 amino pyridine is superior due to its ability to readily synthesized from a range of media. Furthermore it is convenient to directly incorporate a range of biologically active proteins from aqueous solution during polymerization of pyrrole to form 2 amino pyridine. This possible with more enzymes or proteins that contains amine functional group, as this ensure that the molecule has an overall negative charge.

IV. AIM/OBJECTIVE OF THE PRESENT RESEARCH WORK

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 (dopant) (potassium nitrate, sodium nitrate and nitric acid etc) pH of the electrolyte, current density etc. for the synthesis of conducting polymer.

V. EXPERIMENTAL

The 2-Amino Pyridine 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 2-Amino Pyridine(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 poly 2-AP 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 2-AP.

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, Shri Anand College, Pathardi, Dist. Ahmednagar, (MS) India was employed for the electrochemical synthesis of 2-AP-HCl film by using potentiometric (Galvanostatic) method.

VI. UV-VISIBLE SPECTROSCOPY

UV-visible spectroscopy- Analytic Jena specord 210 plus Wavelength (200 nm-800 nm) was used to study the oxidation state of synthesized poly 2-AP film. This facility was extended by DIAT, Pune.

VII. CONDUCTIVITY MEASUREMENT:

The four-probe set up (S.E.S. Instrument Pvt. Ltd. Roorkee) was used for the measurement of electrical conductivity of synthesized poly 2-AP films. The conductivity measurement was done in the Department of Physics, Shri Anand College, Pathardi, Dist. Ahmednagar, (MS) India.

The Four Probe Method is one of the standard and most widely used methods for the measurement of resistivity of semiconductors. The experimental arrangement is illustrated. In its useful form, the four probes are collinear. The method avoids the use of two extra contacts (probes) between the current contacts. In this arrangement the contact resistance may all be high compared to the sample resistance, but as long as the resistance of the sample and contact resistances are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or electronic voltmeter), the measured value remains unaffected. Because of pressure contacts, the arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample.

VIII. SCANNING ELECTRON MICROSCOPY (SEM):

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 lens.

The improved overall stability of the JSM-7500F enables you to readily observe your specimen at magnifications up to 1,000,000x with the guaranteed resolution of 1 nm. The energy filter (r-filter) makes it possible to observe the fine surface morphology of nanostructures.

IX. RESULTS AND DISCUSSION

We have polymerize and studied various combination of monomer and supporting electrolyte through entire work, viz, (Di-methyl Amino Pyridine-H2SO4), (Immedozol-HCl) and composite film (Pyridine + Aniline-HCl), (2 Amino Pyridine-HCl) etc. It was found that during the work 2-Amino Pyridine film shows the lowest potential i.e. higher conductivity than other monomer-electrolyte pair, so we focused 2Amino Pyridine as monomer for my work. Below chronopotentiogram [fig A, B, C and D] indicates the various monomers and supporting electrolyte polymerization process. Among them fig D shows is good for further characterization process.

![Fig A: Polymerization of DMAP-H2SO4](image)
The chronopotentiogram recorded during electrochemical polymerization of 2 AP at various concentrations of supporting electrolyte solution viz KCl, NaCl and HCl with monomer of 2AP at2mA/2cm2 current density at 3.0 pH are shown in Figure3.1.

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 2 Amino Pyridine with HCl supporting electrolyte.

XI. 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 poly 2-AP films with 0.5N, 1N, 1.5M concentration of supporting electrolyte HCl. The chronopotentiogram recorded during electrochemical polymerization of poly 2-AP with various concentrations of HCl. 0.1 N concentration of monomer, and 2mA/2cm2 current density at3.0pH is as shown in Figure (3.2) for HCl,This indicates that the synthesized poly 2-AP 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 2-AP with0.1N concentration of HCl was lower as compared with 1.5N concentration of HCl.

XII. 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 P(2-AP) film.
We have recorded lowest polymerization potential for
the synthesis of poly 2-AP films at 2mA/2cm² current
density at 3.0pH 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/2cm² and pH 3.0.

XIII. 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 P (2-AP) film. The
chronopotentiogram shows lowest potential for the
current 2mA/2cm² than the current 0.5 mA and 1mA.
Current 0.2 mA/2cm² gives porous and uniform film.

XIV. CHARACTERIZATIONS

The synthesized P (2-AP) films were characterized
using electrochemical method, conductivity
measurement, UV-spectroscopy, FTIR spectroscopy
and SEM.

XV. UV-VISIBLE STUDIES

The optical absorption spectrum of synthesized poly
2-AP films with optimized parameters with
supporting electrolyte HCl are shown in Fig 3.5. 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 480 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.

XVI. FTIR:

The FTIR spectrum of synthesized poly 2-Amino
Pyridine is shown in Fig. 3.6 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 2-AP; it shows very good
agreement with earlier reported work. Thus, the FTIR
spectral results confirm the formation of poly 2-
Amino Pyridine.
CONCLUSIONS

The influence of electrochemical process parameters on the surface morphology and the conductivity of poly 2-Amino Pyridine film were successfully studied. Process has been developed for the aqueous electro-polymerization of N-2AP coating on ITO substrates. The concentration ratio of 0.1:0.5 of N-2AP and HCl for the synthesis of P(2-AP) 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 poly 2-Amino Pyridine film.
2. The concentration ratio 0.1N:0.5N of 2-Amino pyridine and Hydrochloric acid is good combination on ITO electrode.
3. pH 3 gives good conductivity and surface morphology for the film.
4. The 2AP-HCl film shows good conductivity for applied current density 2mA/2cm² at 27°C.

CONCLUDING REMARKS

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. P(2-AP)/HCl are very good matrices with excellent uniformity, porosity and stability for the immobilization of biocomponent.

FUTURE SCOPE

In very near future, the biosensors for detection of Cholesterol, Lactate, Urea, Hemoglobin etc will be developed with some more alterations and additional characterizations dealing with the mentioned system. Efforts are also directed to develop mobile equipment for the uniquely designed for biosensors.

REFERENCES

Electrochemical Synthesis Of Poly 2-Amino Pyridine As Conducting Polymer By Galvanostatic Method
