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CHARACTERIZATION OF POLY(O-ANISIDINE) FILMS BY USING FOUR-PROBE TECHNIQUE

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ABSTRACT:

In the present investigation, poly (o-anisidine) thin films were synthesized with 0.2M monomer concentration, 1M concentration of H_2SO_4 electrolyte, 1.0 pH of the electrolyte solution and 2mA/cm^2 applied current density at room temperature on silver electrode by using electrochemical polymerization technique under galvanostatic conditions. The synthesized films were characterized by using electrochemical technique and four-probe technique. The poly(o-anisidine) sample was shown to have good conductivity. The effect of o-anisidine concentration decreases conductivity with increasing its concentration. The conductivity of each synthesized poly(o-anisidine) sample was determined by using four-probe technique. The I-V curve of synthesized sample indicates that it has an ohmic behavior. Experiments were carried out to establish the conductivity of synthesized sample from room temperature to 110^{0}C. The current was kept constant during the observation. It has been observed that at lower currents, conductivity of the synthesized sample is due to the impurities included by the H_2SO_4 electrolyte whereas at higher currents the conductivity is due to the electron transfer. This will be used for biosensor applications.

KEYWORDS: o-anisidine, electrolyte, ECP technique, Silver electrode, Four-probe technique.

1. INTRODUCTION

The use of conducting polymer as a coating material for biosensor applications have become one of the most exciting new research field [1]. There is a growing interest in the past two decades particularly to synthesize good quality conducting polymer films on a variety of substrates [2-5]. Among the various methods of synthesis of conducting polymers, most widely used method is electrochemical polymerization [6-9]. Many researchers in the world has been investigated that the polymers containing para and ortho-quinone groups acts as electron transfer relay systems for oxido-reductases and can effectively catalyze the electro-oxidation of glucose. The conducting polyaniline films are usually used for the fabrication of biosensors. Biosensors are usually developed by immobilizing the biological active components, directly into the conducting polymer matrix to form an enzyme electrode by which we can measure the related human fluid concentration [10].

Polyaniline has received a great deal of attention because of its electronic, electrochemical and optical properties and environmental and thermal stability in the past decades [11]. Polyaniline is composed of aniline repeated units connected to form a backbone of alternating nitrogen and benzene rings. A detailed systematic investigation on the influence of various supporting electrolytes, both inorganic and organic, on the electrochemical synthesis of polyaniline, poly(o-anisidine), poly(o-toluidine) and their co-polymer films was reported [12,13]. The polyaniline and its derivatives and their composite coating were characterized by UV-visible absorption spectroscopy. The choice of o-anisidine which is substituted derivatives of aniline with methoxy (-OCH_3) group, substituted derivative at ortho-position [14]. It consists in a variety of forms that differ in chemical and physical properties.

2. EXPERIMENTAL SET-UP

The o-anisidine monomer was distilled twice before use. All chemicals were obtained from Rankhem Ranbaxy New Delhi (INDIA). An aqueous solution of o-anisidine (99%) and H_2SO_4 electrolyte concentrations were prepared in distilled water. The electropolymerization of o-anisidine was carried out by galvanostatic method, in one compartment electrochemical cell. The reference electrode used was Ag/AgCl. All three electrodes were placed vertically in cell. The pH of the electrolyte was measured by a calibrated ELICO LI120 pH meter. These films were synthesized with 0.2M monomer concentration, 1M electrolyte concentration, 1.0 pH of the electrolyte solution and $2mA/cm^2$ applied current density at room temperature on silver electrode. After deposition the working electrode was removed from the electrolyte and washed with supporting electrolyte DMSO solvent. The poly (o-anisidine) sample was characterized by four-probe technique. The experimental circuit used for the measurement is illustrated in the Fig.1 and Fig. 2.

Fig.1 *The Four-Probe Apparatus.*

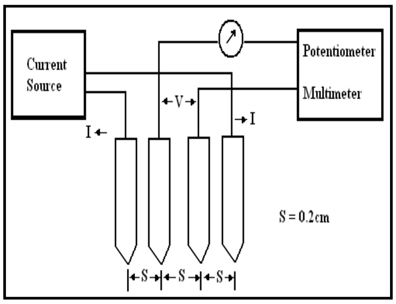

Fig.2 *Schematic diagram of Four-Probe.*

A nominal value of probe spacing, which has been found satisfactory, is an equal distance of 2.0 mm between adjacent probes. They permit measurement with reasonable current of n-type or p-type semiconductors. The current (I) was set to a constant and at the given condition, the temperature was varied from room temperature to 110^0C. The measured voltage was recorded with increasing temperature with an interval of 5^0C. The resistivity is then calculated at different temperatures using the formula.

$$\rho = \frac{1}{G_\tau(\omega/s)} \times \frac{V}{I} \times 2\pi s$$

Where, s is the distance between two probes, ω is the thickness of the sample which is 0.25mm and

$$G_\tau(\omega/s) = \frac{2s}{\omega} \times \log 2$$

Conductivity can be computed using the relationship,

$$\sigma = \frac{1}{\rho}$$

3. RESULTS AND DISCUSSION

It is essential that during polymerization the polymerization potential should be as lower as possible so that we can have higher conductivity of the synthesized polymer film [15]. The Fig.3 shows chronopotentiogram recorded during synthesis of POA film with H_2SO_4 for concentration ratio 0.2: 1M of monomer and electrolyte at 1.0 pH and $2mA/cm^2$ applied current density at room temperature. The lowest polymerization potential was recorded for H_2SO_4 electrolyte with 0.2M o-anisidine monomer concentration. This indicates that the synthesized POA film with H_2SO_4 electrolyte will have higher conductivity.

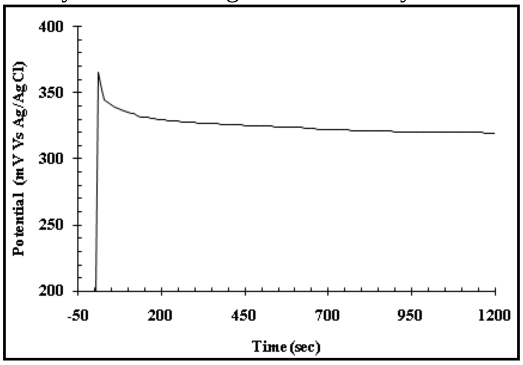

Fig. 3 *The chronopotentiogram recorded during synthesis of POA film.*

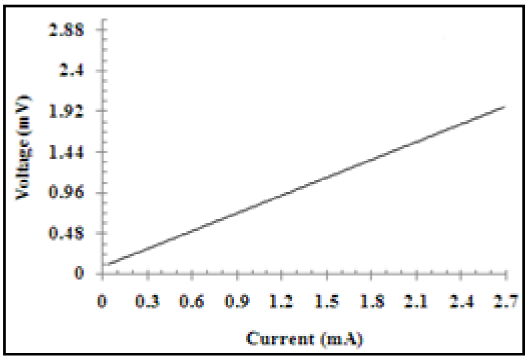

Fig. 4 *Characteristics of POA film.*

When current increases, voltage also increases and resistivity increases. Therefore, poly(o-anisidine) shows the ohmic behavior. It is shown in the Fig.4.

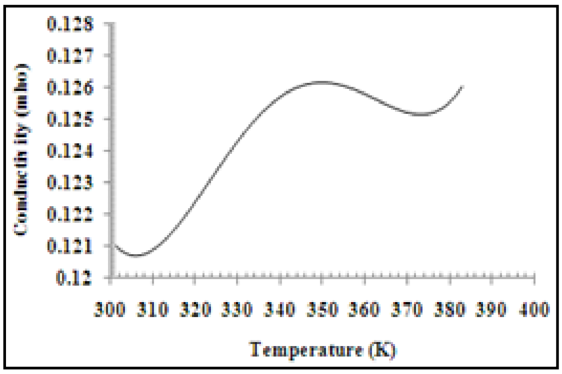

Fig. 5 *Relationship between T (K) and σ (mho).*

Fig.5 indicates the relationship between conductivity (σ) and temperature (T). The current (I) is set at 1mA. In conductors at room temperature there are some free electrons which exhibit small current. As we increase the temperature, more number of electrons will be detached from the nucleus of the atoms as a result we get a large amount of current. Our experimental result also exhibits that conductivity increases as the temperature increases, however at higher temperature the conductivity of the H_2SO_4 doped poly (o-anisidine) films slows down. The same thing can be confirmed from Fig.6. Electrochemically polymerized films of o-anisidine of the relevant monomer may be used for the immobilization of various enzymes for different applications as immobilization media.

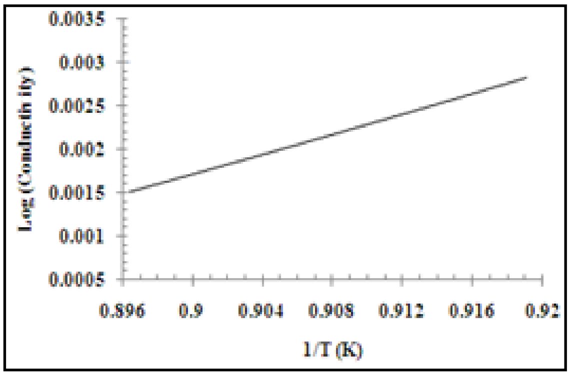

Fig. 6 *Plot of log(σ) against 1/T (K) at 1mA current.*

4. Conclusions

The poly(o-anisidine) films with 0.2M monomer concentration, 1M concentration of H_2SO_4 electrolyte, 1.0 pH of the electrolyte solution and $2mA/cm^2$ applied current density at room temperature by using electrochemical polymerization technique under galvanostatic conditions were successfully synthesized on silver electrode. These synthesized films were characterized by using electrochemical technique and four-probe technique. Using the four-probe technique the conductivity of H_2SO_4 doped poly(o-anisidine) films shows the good metallic behavior. This poly(o-anisidine) film sample is suitable for immobilization of biocomponent. This will be used for biosensor applications.

ACKNOWLEDGEMENT

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