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The influence of electrochemical process parameters on the conductivity of poly(*N*-methylpyrrole) films by galvanostatic method

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Abstract

The influence of electrochemical process parameters viz. type of electrolyte, electrolyte concentration and current density have been studied during polymerization of poly(*N*-methylpyrrole) (P(NMP)). The changes in the conductivity of synthesized P(NMP) film for different electrolytes were noticed by chronopotentiograms recorded during the electrochemical polymerization and it was confirmed by measuring it using two probe technique. The current density used during the polymerization has a considerable influence on the conductivity of the film. The P(NMP) film was synthesized on the platinum substrate by electrochemical polymerization with different electrolytes such as potassium nitrate, sodium nitrate, nitric acid, oxalic acid, sodium salicylate, hydrochloric acid, potassium chloride, and sodium chloride under galvanostatic condition over a wide range of pH of the reaction medium and applied current density. The concentration ratio of *N*-methylpyrrole (NMP) and sodium nitrate were taken as 0.02 : 0.1, 0.05 : 0.05 and 0.1 : 0.02 respectively. It has been observed that, the polymerization potential increases with the pH and applied current density. A good quality P(NMP) film was formed by controlling the electrochemical process parameters. The characterization of synthesized P(NMP) film was done by electrochemical techniques, solubility test, FTIR and the scanning electron micrograph (SEM).

Keywords: Electropolymerization; Poly(*N*-methylpyrrole); Platinum; Galvanostatic

1. Introduction

Electrochemical polymerization is recognized as an effective technique for the synthesis of conducting polymers. It is widely reported [1–4], because it is simple and can be used as a one step method. Polypyrrole family is suitable for various applications, such as solar cells, electrodes for re-chargeable batteries, biosensors etc. [5–10]. 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 [11–13]. The galvanostatic (constant current) method of synthesis of conducting polymers on platinum electrode offers an efficient and effective control of the properties of synthesis as well as to control the reactivity of electrochemical species. In order to have uniform and reproducible results, the process parameters of electrochemical polymerization have to be optimized. The parameters 1) type of electrolyte, 2) concentration ratio of monomer and electrolyte, 3) pH of the electrolyte and 4) current density will affect the conductivity and morphology of the synthesized P(NMP) film [14–16].

In the present investigation, we have taken the monomer NMP and synthesized conducting polymer P(NMP) by electrochemical polymerization using galvanostatic method. We studied the influence of electrochemical process parameters for optimal results such as uniformity, conductivity etc. It has been observed that the amount of P(NMP) deposited on platinum during electrochemical polymerization increases with increasing current density and the pH of the electrolyte. It has

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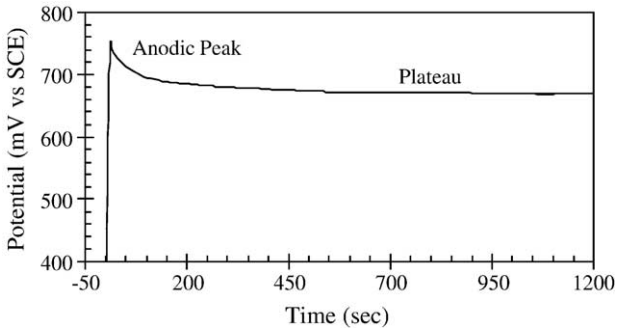

Fig. 1. A typical chronopotentiogram (E–t curve) obtained by galvanostatic polymerization.

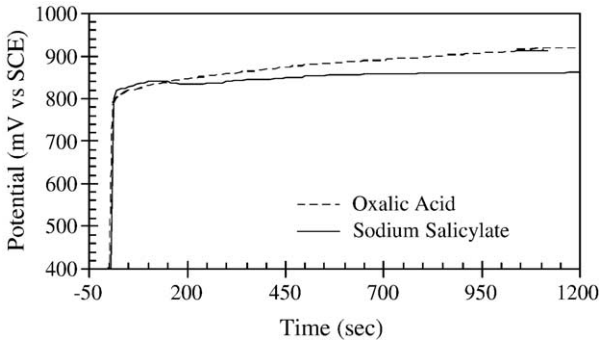

Fig. 3. Potential vs. time at pH 1.5, current density 1 mA/cm^2 and T=27 °C for oxalic acid and sodium salicylate with 0.05 : 0.1 molar concentration ratio of NMP and electrolytes.

also been observed that, the pH of the solution strongly influences the synthesis of P(NMP).

The electrochemical synthesis of conducting polymer with controlled thickness and enzyme activity in galvanostatic conditions offers numerous advantages, especially in the fabrication of micro-sensors and arrays of micro-sensors [17]. Conducting polymers have attracted a lot of interest as a suitable matrix for entrapment of enzyme, which leads to the development of biosensor [18].

2. Experimental

The NMP monomer was distilled twice before use. Potassium nitrate, nitric acid, sodium nitrate, oxalic acid, sodium salicylate, hydrochloric acid, potassium chloride, and sodium chloride were used as electrolytes. All above reagents were obtained from Rankhem, Ranbaxy, New Delhi (INDIA). An aqueous solution of *N*-methylpyrrole (99%) and various electrolytes were prepared in deionized water. The 0.05 M concentrations of *N*-methylpyrrole and electrolyte were kept constant. The pH was adjusted by adding nitric acid or sodium hydroxide.

The electropolymerization of NMP was carried out by galvanostatic technique in one compartment electrochemical cell. Platinum rectangular sheet (20 × 40 × 0.25 mm) was used as a counter electrode and another platinum rectangular sheet (20 × 10 × 0.25 mm) was used as a working electrode. The reference electrode was a saturated calomel electrode (SCE). 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 a calibrated pH meter. The concentrations of *N*-methylpyrrole and various electrolytes were held constant in all runs while pH and applied current densities have been changed at room temperature. The deposited P(NMP) film was tested for adherence, surface uniformity and morphology.

The characterization of P(NMP) film was carried out by electrochemical techniques, solubility tests, FTIR spectra and scanning electron micrograph. The electrochemical characterization was carried out by galvanostatic polymerization, which maintains a constant current throughout reaction. FTIR spectra were recorded, using Testscan Shimadzu FTIR-8000 series, using KBr pellets in the region between 500 and 4000 cm^{-1}. Scanning electron micrographs were recorded at various magnifications using JEOL JSM-6360 A Analytical SEM.

3. Results and discussions

A typical galvanostatic electropolymerized chronopotentiogram [19] is as shown in Fig. 1. It shows the anodic peak at which the polymerizations process starts and the plateau at which the polymerization process reaches the stable state with time, indicating the completion of the process. In fact during polymerization the polymerization potential should be as

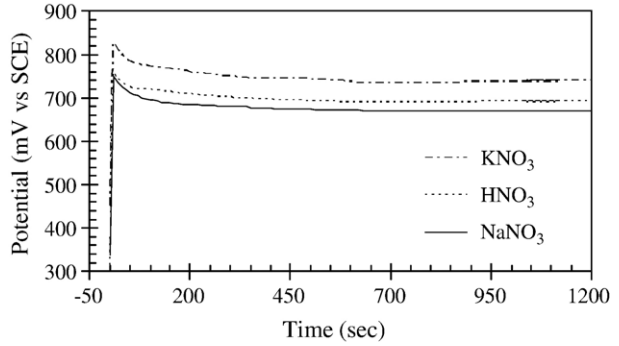

Fig. 2. Potential vs. time at pH 1.5, current density 1 mA/cm^2 and T=27 °C for potassium nitrate, nitric acid and sodium nitrate with 0.05 : 0.1 molar concentration ratio of NMP and electrolytes.

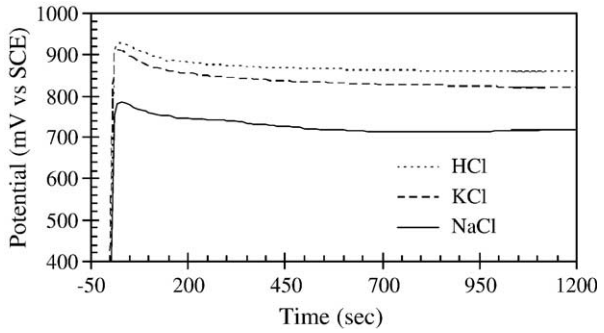

Fig. 4. Potential vs time at pH 1.5, current density 1 mA/cm^2 and T=27 °C for hydrochloric acid, potassium chloride and sodium chloride with 0.05 : 0.1 molar concentration ratio of NMP and electrolytes.