Electrochemical Impedance Spectroscopic Study of Electrodeposited Polyaniline Thin Films

B. P. Relekar, G. M. Lohar, V. J. Fulari*

Holography and Material Research Laboratory,

Department of Physics, Shivaji University,

Kolhapur-416 004 (MH), India

*Corresponding author's Tel.: +91-231-2609224, E-mail address: vijayfulari@gmail.com,

Abstract

In the present investigation, polyaniline thin films have been prepared by potentiostatic mode of electrodeposition. The effects of different potentials on structural and electrochemical properties of polyaniline thin films have been investigated. For the structural properties Raman spectroscopy has been used and morphological study was done using field emission scanning electron microscope (FE-SEM) technique. Electrochemical properties were studied by electrochemical impedance spectroscopy (EIS). The electrochemical properties of polyaniline thin films have been studied in 1M Na_2SO_4 electrolyte. The less charge transfer resistance has been observed for 1.6V/SCE.

Keywords- Electrodeposition, FT-Raman, Electrochemical Impedance Spectroscopy etc

1. Introduction

In recent years, polymer nanostructures, particularly conducting polymer nanowires and nanofibers [1], have received rising interest in applied and fundamental research. Among the known types of polymers, conjugated polymers have attracted a lot of attention due to their unique electrical properties and they have been classified as a conducting polymer, having a framework of alternating single and double carbon-carbon bonds [2]. As compared with bulk, nanostructured conducting polymers are expected to display improved performance in technological applications [3]. Among the whole conducting polymer family, polyaniline is special due to its, ease of synthesis, inexpensive monomer, environmental stability and simple proton doping / dedoping chemistry. Polyaniline can be synthesized by enzymatic, template, chemical oxidation or electrochemical polymerization of aniline under mild conditions [4].

Recently, it is found that so many researchers have synthesized polyaniline thin films using the electrodeposition method. Electrodeposition is widely accepted technique because, it is an isothermal process and controls easily surface morphology and thickness [5-6].

Electrochemical properties highly depend on surface morphology and modification of surface using electro deposition. To study its electrochemical properties for device fabrication is an important task. Cordova et al [7] developed porus morphological thin films with porus network. Singh et al. [8] reported dense and sphere like morphology for polyaniline thin film. Similarly the impedance spectroscopic study has been reported by many researchers [5, 8, 9].

In the present study, the polyaniline thin films are deposited using the potentiostatic mode of electrodeposition with different potentials such as 1.6 V/SCE, 1.7 V/SCE, 1.8 V/SCE and 1.9 V/SCE. The characteristic vibrations of polyaniline thin films are confirmed using Fourier transform Raman spectroscopy. The surface morphology of thin film deposited at 1.6 V/SCE has studied using the FESEM and electrochemical properties of polyaniline have been studied using the electrochemical impedance spectroscopy.

2. Experimental details

The polyaniline thin films are prepared using AR grade chemicals. The bath consists of 0.1M aniline and 0.1M H_2SO_4 for to maintain the pH. The polyaniline thin films are deposited on the stainless still (SS) substrates. The stainless still (SS) substrates are cleaned using zero polish paper. The potentiostatic deposition has been carried out for -1.6 V/SCE, -1.7 V/SCE, -1.8 V/SCE and -1.9 V/SCE and studied

Raman scattering experiments were performed in air at room temperature with Raman system from Bruker AXE Analytical Instruments PVT, Germany. The Raman spectra were excited with Nd:YAG Laser source at wavelength 1064 nm from 200 to 2000 cm^{-1} and Ge detector was used. Surface morphology was studied using a Mira 3, Tescan, Czech Republic using field emission scanning electron microscope (FE-SEM). The electrochemical impedance spectroscopy has been studied using the CH608E instrument.

3. Results and discussion

3.1 FT-Raman spectroscopic study

The vibrational spectroscopic studies are carried out by Raman spectroscopy [10]. Fig. 1 shows Raman spectrum of potentiostatically deposited polyaniline thin film. The bands close to 570 cm^{-1} can be assigned to the presence of phenazine structures. The band at 1194 cm^{-1} assigned to C–N stretching in benzene diamine units, at 1370 cm^{-1} C–N+ stretching of cation radicals, The N–H vibration band of protonated amine at 1503 cm^{-1} and 1625 cm^{-1} is assigned to

C–C stretching in benzenoid rings [11]. The ring of quinoid are mostly coupled at C and N position, because the C=N stretching band is relatively stronger than that of benzonoid.

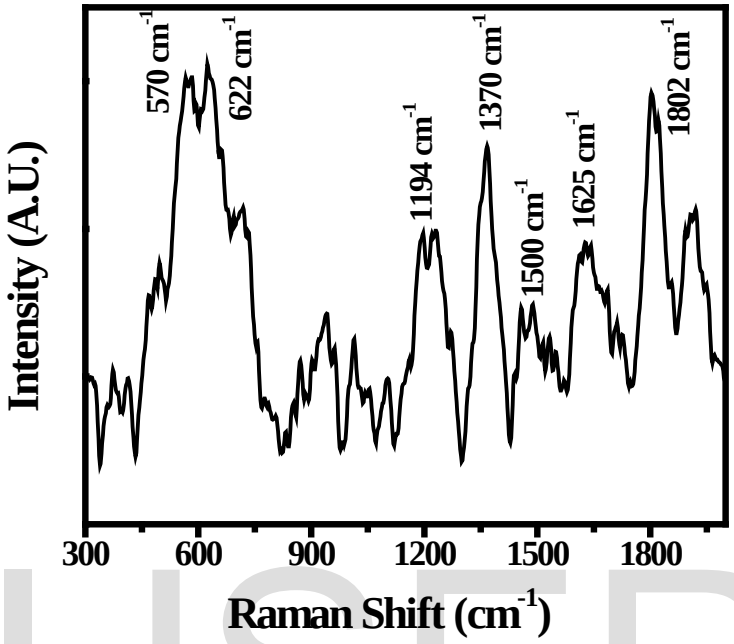

Fig. 1 FT-Raman spectrum of potentiostatically deposited polyaniline thin film

Field emission scanning electron microscopic study (FE-SEM)

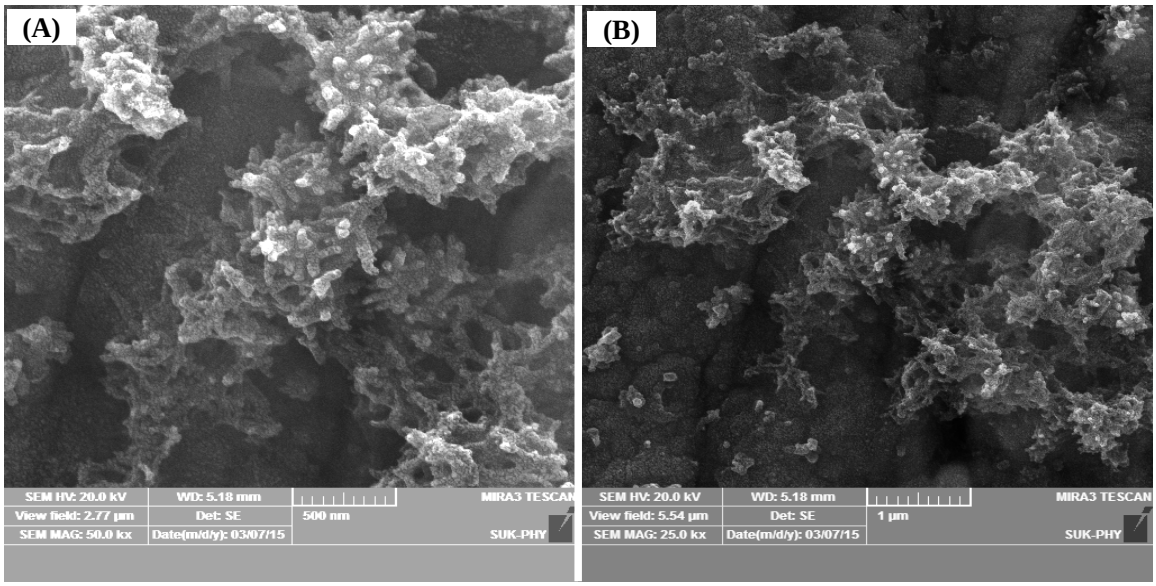

Fig. 2 FE-SEM images of potentiostatically deposited polyaniline thin film

Fig. 2 shows FE-SEM images of potentiostatically deposited polyaniline thin film. The morphology of the resultant PANI was observed under an electron microscope. As shown in Fig. 2, FE-SEM images consistently indicate that the resultant PANI consists of uniform nanofibers with diameter around 35 nm, and the length of the fibers range from hundreds of nanometers to several micrometers. In addition, it is observed that many fibers join with others and form branched structures or interconnected networks. These fibers are curved and entangled, demonstrating that the PANI nanofibers are very flexible [12].

3.3 Electrochemical impedance spectroscopic study (EIS)

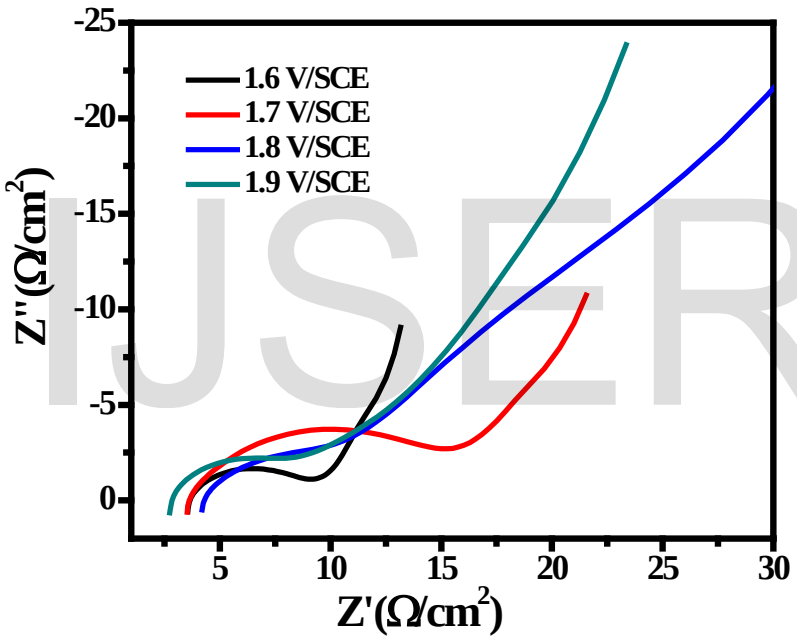

Fig.3 Nyquist plot of potentiostatically deposited polyaniline thin film

The electrochemical impedance spectroscopic study of polyaniline thin films has been studied using Na_2SO_3 electrolyte. The EIS gives the information about the solid liquid interface. Mostly, EIS technique has been used for to understand the charge transfer resistance [1-4]. The Nyquist plot is a parametric plot of a frequency response used in automatic control and signal processing as well as a Bode plot is a graph of the frequency response of a system. Fig. 3 shows the Nyquist plot of polyaniline thin film. The observed solution resistance (R_s) and charge transfer resistance (R_{ct}) with respect to different potential are mentioned in Table.1. The less charge transfer resistance has been observed for a thin film deposited at 1.6 V/SEC. The

observed charge transfer resistance is 7.74 Ω/cm^2. It indicates that a thin film deposited at 1.6 V/SCE is a comparatively better film for supercapacitor application. This better charge transfer resistance is due to the nanofibers like nature of polyaniline thin film.

Table. 1 EIS parameters of polyaniline thin film

Sr. No.	**R_s (Ω/ cm^2)**	**R_{ct} (Ω/ cm^2)**
1	3.58	7.74
2	3.53	13.21
3	4.17	8.69
4	2.74	8.20

4. Conclusions

In the present study, we have successfully deposited polyaniline thin films using electrodeposition method and confirmed using the FT-Raman spectroscopic study. The FESEM study shows that deposited thin films show the nano-fiber like structure. The thin films deposited at 1.6 V/SCE show better charge transfer resistance than the other deposition potentials. The thin films deposited at 1.6 V/SCE are more useful for supercapacitor application.

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