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Synthesis and Characterization of Manganese (Mn) Doped Polyaniline

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Abstract

To study the Mn doping effect on the specific capacitance of PANI, concentration of Mn was varied from 0.3 to 1.5 weight percent. Surface morphology was examined by using Scanning Electron Microscopy (SEM) which showed nanofiber aggregate structure of pure PANI and porous and well distributed nanofibers for the doped PANI. The DC electrical resistivity (ρ) of pure PANI and Mn doped PANI films were measured which shows semiconducting behavior of pure PANI and Mn doped samples.

Keywords: PANI; Dopant; SEM; Resistivity

Introduction

We know that the electronic conductivity of PANI is less than the metal oxides. So, in this paper we tried to enhance the electronic conductivity of PANI electrode by doping Mn metal ion [1]. Extensive research work has been focused on enhancing electronic conduction of the electrodes by using metal doping [2].

Although several researchers have worked on different metal ion dispersion in PANI, very few studies have been attempted to dope PANI with the transition metals. Transition metals are malleable and ductile, they conduct heat and electricity, and they form positive ions. Transition metals are more electronegative than the main group metals. When the manganese atom is oxidized, it becomes more electronegative. In the greater specific oxidation state, this atom is electronegative enough to react with water to form a covalent oxide, MnO_4^-. It is useful to have a way of distinguishing between the charge on a transition-metal ion and the oxidation state of the transition metal. We have synthesized Mn doped PANI films by a chemical polymerization method via dip coating technique [3].

The aim of the synthesis of Mn doped PANI films as electrode for super capacitor is to improve the electronic conductivity of PANI films. Mn doped PANI is a better choice for super capacitor application because of its eco-friendly nature behaviour of H^+ and Zn^{2+} doped with PANI [4].

Experimental Details

A synthetic route was employed to obtain mono-dispersed and highly stable PANI and Mn doped PANI solution. Appropriate quantity of Manganese chloride ($MnCl_2.H_2O$) solution (0.2 M) was dissolved in the PANI solution. In order to obtain the uniform distribution of Mn ions in the PANI solution the mixture was ultrasonicated for 45 min. Uniform depositions of the PANI and Mn doped PANI thin films were obtained on glass substrates (Blue Star) by dip coating technique [5]. The solution was kept under constant stirring (Tarsons Magnetic Stirrer) for proper dispersion of Mn in PANI throughout the film deposition process. The weight percent of the dopant was varied as; 0.3, 0.6, 0.9 and 1.5 and the samples are referred as $PANIM_{0.3}$, $PANIMn_{0.6}$, $PANIMn_{0.9}$ and $PANIMn_{1.5}$ respectively. If we further increase in doping concentration then it results in decreased film quality. Pure PANI film prepared by above method without addition of $MnCl_2.H_2O$ solution is referred as $PANIMn_0$.

The surface morphology of the films was examined by analyzing the scanning electron microscope (SEM), equipped with an energy dispersive x-ray spectrometer (EDS) [6].

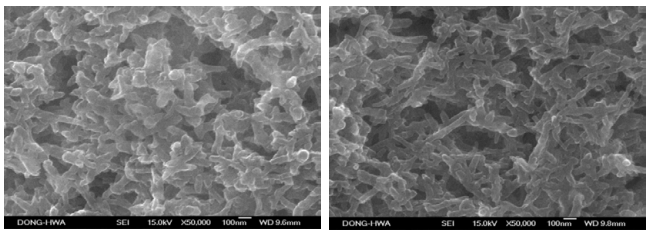
Results and Discussion

All the samples of the deposition were subjected to the structural, optical, and morphological.

Scanning electron microscopy (SEM)

To investigate the effect of Mn doping on the morphology, the films were characterized by SEM. Figure 1a and 1b shows surface morphologies of $PANIMn_0$ and $PANIMn_{1.5}$ samples. The nanofiber structure is observed for $PANIMn_0$ sample Figure 1a. However $PANIMn_{1.5}$ sample revealed well distributed nanofibers with nanoporous. In both the cases, the average diameter of the nanofibers is about 40-60 nm. The nanofibers structure provides large surface to volume ratio leading to a high charge/discharge rate. Well distributed nanofibers with nanoporous offered relatively larger surface area in Figure 1b.

A transition metal ion (Mn) has multiple positions for doping and tends to bind several nitrogen sites of PANI to form inter-chain linkage among several adjacent PANI chains by coordination [7]. This nanofibers and porous structure is beneficial for super capacitor, because it reduces the diffusion resistance of the electrolyte into electrode matrix. The diffusion resistance factor (μ) shows the vapor permeability of a material. It indicates how many times it will be more



(a) (b)

Figure 1: FE-SEM images of the (a) $PANIMn_0$ (b) $PANIMn_{1.5}$ samples at X50000 magnification.

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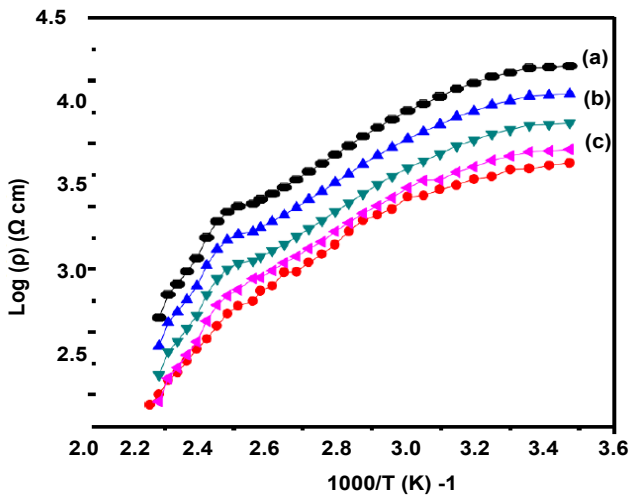

Figure 2: Electrical resistivity of the (a) $PANIMn_0$, (b) $PANIMn_{0.3}$ (c) $PANIMn_{0.6}$ (d) $PANIMn_{0.9}$ (e) $PANIMn_{1.5}$ samples.

difficult to pass the water vapor through the material then through the air [8].

Electrical resistivity

The DC electrical resistivity (ρ) of pure PANI and Mn doped PANI films were measured in the temperature range over 300-450 K. The room temperature ρ for pure PANI film decreases with increase in Mn content in PANI. Further, decrement in ρ with temperature confirms semiconducting behavior of pure PANI and Mn doped samples shown in Figure 2.

Conclusion

We have successfully synthesized pure PANI and Mn doped PANI films onto glass substrate by a chemical polymerization method via dip coating technique for super capacitor application. Synthesis of Mn doped PANI films as electrode for super capacitor is important to decrease the resistivity of the PANI electrode. DC electrical resistivity (ρ) decreases with increase in Mn samples.

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