

Doped Polyaniline for Promising Supercapacitor

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Abstract.

In the present work, doping effect of metal ions (Mn, Ag) in PANI films is investigated. Undoped and Mn and Ag doped PANI thin films are deposited on stainless steel substrates by sonochemical method via dip coating technique. To study the Mn or Ag doping effect on the specific capacitance of PANI, concentration of Mn or Ag was varied. Fourier Transform-Infrared, Fourier Transform-Raman Spectroscopy and Energy Dispersion X-ray techniques were used for the phase identification and determination of the doping content in the PANI films respectively. Surface morphology of the films was examined by Field Emission scanning electron microscopy and revealed nanofiber aggregate structure for undoped PANI, well distributed nanofibers for Mn doped PANI and well distributed nanofibers with bright spots of Ag particles for the Ag doped PANI films. The electrical resistivity of the doped PANI films decreased with increasing metal ion concentration. The supercapacitive behavior of the electrodes was tested in three electrode system with 1.0 M H₂SO₄ electrolyte by using cyclic voltammetry. The highest specific capacitance value 474 Fg⁻¹ and 512 Fg⁻¹ were observed for Mn and Ag doped PANI film, respectively.

Keywords: Supercapacitor, Polyaniline, Mn ion, Ag particles.

INTRODUCTION

Polyaniline is one of the most promising material which is frequently used as electrode material for supercapacitor due to its four oxidation states (Leucoemeraldine, Emeraldine base, Emeraldine salt and Pernigraniline) which contribute to its high specific capacitance. The excellent electrode required for the supercapacitor consists of good electronic conductivity, electrochemical stability and high surface area. The electronic conductivity of green protonated emeraldine form of polyaniline is lower than that of metals [1]. So, one of the challenging issues in development of high performance supercapacitor is to improve its electronic conductivity of the PANI electrode which is reversibly controlled both by the charge transfer doping and by protonation. Extensive research work has been focused on enhancing electronic conduction of the electrodes by using metal doping.

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. Recently Jie Li et al. have demonstrated the capacitive behavior of H⁺ and Zn²⁺ doped with PANI. They reported the Specific capacitance values 415 Fg⁻¹ and 427 Fg⁻¹ at 30 mVSec⁻¹ respectively [2]

On the other hand silver nanoparticles have applications in conductive inks, catalysis photonics, thick film pastes and adhesives for various electronic components due to their unique optical, electrical, electrochemical and catalytic properties [3]. Hence it is achievable to develop specific properties with the selection of the organic and inorganic phases and produce novel materials which exhibit both organic and inorganic characteristics.

So in our study, we attempt to use Mn and silver doped PANI as electrode material for the supercapacitor. The doping concentration of Mn and Ag is varied to determine its effect on the magnitude of specific capacitance of the PANI films. The electrical resistivities of the prepared films are discussed. The electrochemical performance of undoped, Mn and Ag doped PANI films are investigated.

EXPERIMENTAL

Pure PANI solution was prepared by using a chemical bath. Appropriate quantity of Silver nitrate (AgNO₃) for Ag doped PANI and Manganese chloride (MnCl₂) for Mn doped PANI solution (0.2 M) was dissolved in the PANI solution to obtain the Ag doped PANI films. Uniform depositions of the PANI, Mn and Ag doped PANI thin films are obtained on steel

substrates by a sonochemical method via dip coating technique. The weight percent of the dopant was varied as; 0.4, 0.8, 1.2, and 1.6 and the samples are referred as PANIMn_{0.4}, PANIMn_{0.8}, PANIMn_{1.2} and PANIAg_{1.6} for Mn doped PANI respectively whereas 0.3, 0.6, 0.9 and 1.2, and the samples are referred as PANIAg_{0.3}, PANIAg_{0.6}, PANIAg_{0.9} and PANIAg_{1.2} respectively for Ag doped PANI. Undoped PANI film without addition of AgNO₃ or MnCl₂ solution is referred as PANIMnAg₀.

RESULTS AND DISCUSSION

Fig. 1 (C) shows EDS spectrum of PANIMn_{1.2} and PANIAg_{0.9} sample which inform the presence of Mn, Ag ions respectively.

The DC electrical resistivity (ρ) of from PANIMn₀ to PANIMn_{1.6} and PANIAg₀ to PANIAg_{1.2} is shown in Fig. 1 (A)(a-e) and (B)(a-e) respectively. The room temperature ρ for undoped PANI film is $1.14 \times 10^4 \Omega \text{ cm}$, it decreases with increase in Mn and Ag content in PANI. The room temperature ρ decreases over 1.14×10^4 to $4.9 \times 10^3 \Omega \text{ cm}$, $5.19 \times 10^2 \Omega \text{ cm}$ for Mn and Ag doped PANI respectively. Hence the increase in the conductivity of the PANI electrodes with increase in the doping concentration of Mn and Ag, which further may help to enhance the specific capacitance.

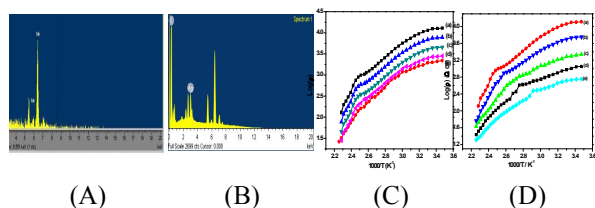


FIGURE 1. EDS of (A) PANIMn_{1.2} (B) PANIAg_{0.9} Resistivity of (C) PANIMn₀ to PANIMn_{1.6} (D) PANIAg₀ to PANIAg_{1.2}

To identify the oxidation and reduction potentials and the effect of Mn and Ag on the electrochemical performance of polyaniline, cyclic voltammograms (CV) of all samples have been recorded over -0.2 to 0.8 V versus SCE at 5 mVs^{-1} in $1.0 \text{ M H}_2\text{SO}_4$ [Fig. 2 (A)(B)]. The oxidation peak corresponding to the leucoemeraldine to emeraldine salt at about 0.22 V . The small peaks between 0.3 V to 0.55 V potential are attributed to transformation of PANI charge carriers consisting of polaron (radical cation) and bipolaron (dication) forms delocalized on PANI chains. All peaks are observed in Mn and Ag doped PANI electrodes. No any additional peak observed in Mn doped PANI electrodes. But one additional dominant anodic peak observed at 0.25 V Versus SCE in Ag doped PANI. This is recognized due to the oxidation of silver. Also, for PANIAg_{0.6}, PANIAg_{0.9} and PANIAg_{1.2} samples another minute cathodic peak observed near to the leucoemeraldine reduction peak

which is due to the reduction of the silver nanoparticles.

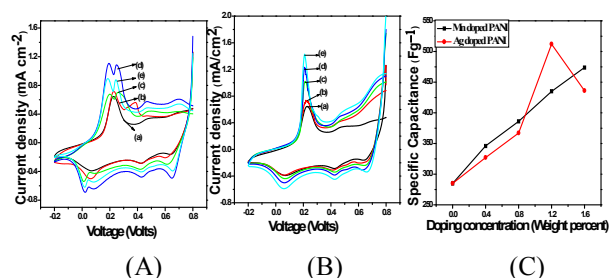


FIGURE 2. CV of (A) PANIMn₀ to PANIMn_{1.6} (B) PANIAg₀ to PANIAg_{1.2} (C) variation of sp.capacitance w. r. t Ag doping concentration

As the doping concentration of the Ag increases there is a shift in oxidation and reduction peaks is observed.

The plot of specific capacitance with respect to doping concentration is shown in Fig. 2(C). As the doping concentration increases the specific capacitance increases from 285 to 474 Fg^{-1} for Mn doped PANI and 285 to 512 Fg^{-1} for Ag doped PANI electrodes.

4. CONCLUSIONS

We have synthesized Mn and Ag incorporated PANI electrodes by sonochemical method via simple and cost effective dip coating technique for supercapacitor application. Synthesis of Mn and Ag doped PANI films as electrode for supercapacitor is important to decrease the resistivity of the PANI electrode with acceptable level of specific capacitance. The highest specific capacitances of 474 Fg^{-1} , 512 Fg^{-1} are observed at 5 mVs^{-1} for PANIMn_{1.2} and PANIAg_{0.9} samples respectively in $1.0 \text{ M H}_2\text{SO}_4$.

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