Effect of Manganese (Mn) Doping On Electrochemical Behavior of Polyaniline

CHAPTER FOUR

Outline

Pure and Mn doped Polyaniline (PANI) thin films were deposited on stainless steel substrates by chemical polymerization. Films deposition was done using dip coating technique. To study the Mn doping effect on the specific capacitance of PANI, concentration of Mn was varied from 0.4 to 1.6 weight percent. The Fourier Transform-Infrared and Fourier Transform- Raman spectroscopy techniques have been used for the phase identification and determination of the Mn in the PANI films. Surface morphology was examined by using Field Emission Scanning Electron Microscopy which showed nanofiber aggregate structure of pure PANI and porous and well distributed nanofibers for the doped PANI. The supercapacitive behavior of the electrodes was tested in three electrode system with 1.0 M H₂SO₄ electrolyte by using cyclic voltammetry (CV). The specific capacitance value increases from 285 Fg⁻¹ to 474 Fg⁻¹ as the Mn concentration was increased.
4.1 Introduction

In the previous chapter we optimized the number of deposition cycles of the PANI films to obtain the high specific capacitance. This optimized deposition cycles are used for the preparation of further electrodes. As mentioned previously the electronic conductivity of PANI is less than metal oxides. So in the present chapter we tried to enhance the electronic conductivity of PANI electrode by doping Mn metal ion.

Extensive research work has been focused on enhancing electronic conduction of the electrodes by using metal doping [1]. Gosk et al. and Xuebing Wu et al. studied the magnetic properties of FeCl$_3$ and oxidized ferrocenesulfonic acid doped PANI respectively [2, 3]. Ghosh et al. studied the electrical properties of cobalt doped PANI [4]. Xiaoxuan Li et al. reported the excellent electrochemical properties of PANI co-doped with titanium & protonic acids [5].

Although several researchers have worked on different metal ion dispersion in PANI [6-10], very few studies have been attempted to dope PANI with the transition metals. Recently Li et al. have demonstrated the capacitive behavior of H$^+$ and Zn$^{2+}$ doped with PANI. They reported the specific capacitance values 415 Fg$^{-1}$ and 427 Fg$^{-1}$ at 30 mVSec$^{-1}$ respectively [11].

We have synthesized Mn doped PANI films by a chemical polymerization method via dip coating technique for supercapacitor application. The aim of the synthesis of Mn doped PANI films as electrode for supercapacitor is to improve the electronic conductivity of PANI films with acceptable level of specific capacitance [12]. The doping concentration was varied to determine its effect on the magnitude of specific capacitance of the PANI films. In comparison to a well-known RuO$_2$, Mn doped PANI is a better choice for supercapacitor application because of its ecofriendly nature.

4.2 Experimental Details

A synthetic route was employed to obtain monodispersed and highly stable PANI and Mn doped PANI solution. PANI solution was prepared by
standard recipe as described in the previous chapter. Appropriate quantity of Manganese chloride (MnCl$_2$.H$_2$O) 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 30 minute. Uniform depositions of the PANI and Mn doped PANI thin films were obtained on stainless steel substrates by dip coating technique. The solution was kept under constant stirring for proper dispersion of Mn in PANI throughout the film deposition process. The weight percent of the dopant was varied as; 0.4, 0.8, 1.2 and 1.6 and the samples are referred as PANIM$_{0.4}$, PANIM$_{0.8}$, PANIM$_{1.2}$ and PANIM$_{1.6}$, respectively. Further increase in doping concentration resulted in decreased film quality. Pure PANI film prepared by above method without addition of MnCl$_2$.H$_2$O solution is referred as PANIM$_{0}$.

Raman studies were conducted using Bruker make FT-Raman spectrometer. Infrared (IR) spectroscopy was also used to confirm the PANI phase, in which the powdered material collected from the deposited film was characterized by infrared spectrometer (Perkin-Elmer, model 783, USA). The surface morphology of the films was examined by analyzing the Field emission scanning electron microscope (FE-SEM), JEOL JSM JSM-6500F equipped with an energy dispersive x-ray spectrometer (EDS).

The electrochemical measurements were performed in an electrolyte of 1.0 M H$_2$SO$_4$ in a conventional three electrode arrangement comprising of graphite as the counter electrode and saturated calomel electrode (SCE) serving as the reference electrode, using electrochemical quartz crystal (EQCM) measurements (model- CHI-400A) made by CH Instrument, USA.

4.3 Results And Discussion

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

4.3.1 Fourier Transform Infra-Red (FT-IR)

Fig. 4.1 (a-e) shows the FTIR spectra of the powder collected from the PANIM$_{0}$ to PANIM$_{1.6}$ samples over 450-2000 cm$^{-1}$.
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**Fig. 4.1** FT-IR transmittance spectra of the (a) PANIMn₀, (b) PANIMn₀.₄, (c) PANIMn₀.₈, (d) PANIMn₁.₂, (e) PANIMn₁.₆ samples recorded in the wavenumber range of 450–2000 cm⁻¹.

The PANIMn₀ (Fig. 4.1 (a)) spectrum consists of seven distinct peaks at 1560, 1492, 1304, 1131, 821, 735 & 687 cm⁻¹. The bands obtained at 1560, 1492, 1304 & 1131 cm⁻¹ are attributed to the N=Q=N stretching, N-B-N stretching (where Q & B denotes the quinoid & Benzenoid), N-H bending and –N= vibration which are similar to those obtained by Jie Li *et al.* [11]. The band at 821 cm⁻¹ is attributed to the CH-out of plane bending on 1,4- disubstituted benzene and the two peaks at 735 cm⁻¹ and 687 cm⁻¹ are assigned to the C-H out of plane bending on 1-2 disubstituted benzene. The samples containing Mn (PANIMn₀.₄ to PANIMn₁.₆) exhibit all these peaks and two additional peaks at 1404 cm⁻¹ and 638 cm⁻¹. The peaks corresponding to 1560, 1492 and 1304 cm⁻¹ showed a shift towards the higher wavenumber designating the doping of Mn in the PANI.

It is well known that in the PANI backbone there are two sites available for proton or metal ion bonding via either protonation or complexation: amine (–NH₂) and nitrogens (–N=).
NH-) and imine (-N=) nitrogen atoms [5,11]. These two peaks are observed at 1304 cm\(^{-1}\) 1131 cm\(^{-1}\). From Fig.4.1 (b-e) it can be seen that the peak at 1131 cm\(^{-1}\) in PANIMn\(_0\) gets gradually shifted to 1101 cm\(^{-1}\) after doping of Mn. This means that Mn gets preferentially bonded with the imine nitrogen atoms. From this it is clear that the characteristic absorption bands shifted according to the doping level in PANI. Importantly, in doped PANI two more peaks are observed, one at 1404 cm\(^{-1}\) and another at 638 cm\(^{-1}\). The new band at 1404 cm\(^{-1}\) around 1492 cm\(^{-1}\) are assigned to radical cation species C-N\(^+\). In the present case the band appears at 638 cm\(^{-1}\) indicate the interaction between organic and inorganic materials. The intensity of this peak increases with increasing the Mn doping concentration. Presence of above peak in doped PANI shows the relative amount of Mn present in our samples.

4.3.2 Fourier Transform Raman (FT-Raman)

In order to get insight about the bending and stretching vibrations, the films were characterized for their FT-Raman spectra. The Raman spectra were recorded by a laser radiation at an excitation wavelength of 1064 nm. Fig.4.2 (a) shows the characteristic bands at 1590, 1505, 1359 and 1175 cm\(^{-1}\) corresponding to C-C stretching of quinoid units, C-C stretching of benzene ring, C-N\(^+\) stretching and C-N stretching respectively [13]. The observed bands agree well with the chemical structure of PANI. Similar bands were also observed for the PANIMn\(_{1.6}\) samples (Fig. 4.2). But there was decrease in intensity of the bands with the Mn doping in PANI. The band corresponding to C-N\(^+\) stretching shifted by 2 cm\(^{-1}\) towards the lower wavenumber and the band corresponding to C-N stretching broadens as the doping percentage increases. This decrease in intensity, shifting and broadening of bands indicate the presence of Mn content in PANI. Similar arguments were used to demonstrate the doping of metal in other oxides/polymers.
Fig. 4.2 FT-Raman spectra of the (a) PANIMn$_0$ (b) PANIMn$_{0.4}$ (c) PANIMn$_{0.8}$ (d) PANIMn$_{1.2}$ (e) PANIMn$_{1.6}$ samples recorded in the wave number range of 450–2000 cm$^{-1}$.

Shaikh et al. synthesized Ru doped CuO by colloidal solution method. They observed that Ru doped CuO films show a peak of Ag mode and two peaks of Bg mode with small shift in wavenumber as compared to pure CuO film and hence the presence of Ru in CuO films is confirmed [14]. The Krishna et al. chemically synthesized metal ion (Fe, La, and Ni) doped PANI. They observed that the decrease in intensity of peaks in doped PANI compared with the pure PANI indicates the doping of PANI with metal ions [15].

4.3.3 Field Emission Scanning Electron Microscopy (FE-SEM) And Energy Dispersive X-Ray Spectroscopy (EDS)

To investigate the effect of Mn doping on the morphology, the films were characterized by FESEM. Fig.4.3 (a, b) shows surface morphologies of PANIMn$_0$ and PANIMn$_{1.6}$ samples. The nanofibers aggregate structure is observed for PANIMn$_0$ sample Fig.4.3 (a). However, PANIMn$_{1.6}$ sample
revealed well distributed nanofibers with nanoporous. In both the cases, the average diameter of the nanofibers is about 30-50 nm. The nanofibers structure provides large surface to volume ratio leading to a high charge/discharge rate and specific capacitance. Well distributed nanofibers with nanoporous offered relatively larger surface area in Fig.4.3 (b). 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 [42]. This organic-inorganic interaction prevents the aggregation of PANI during film deposition. This nanofibers and porous structure is beneficial for supercapacitor, because it reduces the diffusion resistance of the electrolyte into electrode matrix.

![Fig. 4.3](image)

**Fig. 4.3** FE-SEM images of the (a) PANIMn$_0$, (b) PANIMn$_{1.6}$ samples at X50000 magnification

![Fig. 4.3](image)

**Fig. 4.3** (C) EDS spectrum of PANIMn$_{1.6}$. 
Fig. 4.3 (c) shows EDS spectrum of PANIMn\textsubscript{1.6} sample which reveals the presence of Mn metal ions. The obtained atomic weight percent of Mn in the sample is 0.195%. The atomic weight percent calculations affirm alleviation of oxide phases of Mn.

4.3.4 Electrical Resistivity

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4_4}
\caption{Electrical resistivity of the a) PANIMn\textsubscript{0}, (b) PANIMn\textsubscript{0.4}, (c) PANIMn\textsubscript{0.8}, (d) PANIMn\textsubscript{1.2}, (e) PANIMn\textsubscript{1.6} samples.}
\end{figure}

The DC electrical resistivity ($\rho$) of pure PANI and Mn doped PANI films were measured in the temperature range over 290 – 440 K, using two point probe method (Fig. 4.4). The room temperature $\rho$ for pure PANI film is $1.14 \times 10^4$ $\Omega$ cm, it decreases with increase in Mn content in PANI. The room temperature $\rho$ decreases over $1.14 \times 10^4$ to $4.9 \times 10^3$ $\Omega$ cm. Further, decrement in $\rho$ with temperature confirms semiconducting behavior of pure PANI and Mn doped samples.

MnCl\textsubscript{2} forms tetrahedral complex on reaction with PANI and this structure is shown in Fig. 4.5. The nitrogen atoms of PANI act as donor atoms during complexation. The electron density on the nitrogen atoms of PANI decrease upon formation of tetrahedral complex making the nitrogen atoms...
electron deficient. This enhances P-type conductivity in the resultant complex. Hence the increase in the conductivity of the electrodes with increase in the doping concentration of Mn, which further may help to enhance the specific capacitance.

![Reaction mechanism of complex formation between Mn and PANI.](image)

**Fig. 4.5 Reaction mechanism of complex formation between Mn and PANI.**

### 4.3.5 Electrochemical Measurements

In order to identify the oxidation and reduction potentials and the effect of Mn on the electrochemical performance of PANI, cyclic voltammograms (CVs) of PANIMn$_0$ to PANIMn$_{1.6}$ thin films have been recorded. Fig. 4.6 (a-e) shows CV curves for PANIMn$_0$ to PANIMn$_{1.6}$ electrodes over $-0.2$ to $0.8$ V versus SCE at scan rate of $5$ mVSec$^{-1}$ in $1.0$ M H$_2$SO$_4$. The oxidization peak corresponding to the leucoemeraldine to emeraldine salt at about $0.22$ V versus SCE was observed in pure PANI sample. As the doping concentration of the Mn increases the peak is shifted to lower potential and the area under the curve increases. The peak at $0.7$ V is due to the transformation of emeraldine to pernigraniline. The reduction peaks corresponding to the leucoemeraldine and
emeraldine base are found to be at 0.05 V and 0.65 V respectively and these peaks are similar to pure PANI. The small peaks between 0.3 V to 0.55 V potential is attributed to transformation of PANI charge carriers consisting of polaron (radical cation) and bipolaron (dication) forms delocalized on PANI chains.

The specific capacitance of each film was calculated from cyclic voltammogram by using the following formula:

$$ C_s = \frac{\int idV}{2m\Delta V \times S} $$

Where,

- $C_s$ is the specific capacitance,
- $\int idV$ is the integrated area of the CV curve,
- $m$ is mass of active material,
- $\Delta V$ is the potential range,
- $S$ is the scan rate.
Fig. 4.6  CVs of the (a) PANIMn₀, (b) PANIMn₀.₄, (c) PANIMn₀.₈, (d) PANIMn₁.₂, (e) PANIMn₁.₆ samples within a potential window of -0.2 to 0.8 V versus SCE at 5 mVSec⁻¹. Insets show the CVs of respective different scan rate.

The plot of specific capacitance with respect to Mn doping concentration is shown in Fig.4.7. As the Mn doping concentration increases the specific
capacitance increases from $285 \text{ Fg}^{-1}$ to $474 \text{ Fg}^{-1}$ at $5\text{mVSec}^{-1}$. This is due to the increase in Mn ion concentration which increases the electrical conductivity of the films.

![Graph of capacitance vs. Mn doping concentration]

**Fig. 4.7** Variation of specific capacitance with respect to Mn doping concentration of samples.

The variation of specific capacitance with respect to scan rates is as shown in Fig.4.8. Generally, the specific capacitance decreases with the increase of potential scan rate. It is accepted that at a low scan, the presence of inner active sites which undergo the redox transitions completely, can lead to produce specific capacitance to that at high scan rate because of the diffusion effect of proton within the electrode.
Fig. 4.8 Variation of specific capacitance with respect to scan rate.

Fig. 4.9 Variation of specific capacitance with respect to cycle numbers
(a) PANIMn_0, (b) PANIMn_{1.6} samples.

The cyclic stability of PANIMn_0 and PANIMn_{1.6} were recorded up to the 2000 cycles. The specific capacitance of the samples (PANIMn_0 and
PANIMn$_{1.6}$) changed along with the cycles as shown in Fig.4.9. It is observed that the specific capacitance of electrode decreases sharply for first 200 cycles, after that there is no drastic change observed up to 2000 cycles it indicates that the film becomes stable.

### 4.4 Conclusions

We have successfully synthesized pure PANI and Mn doped PANI films onto stainless steel substrate by a chemical polymerization method via dip coating technique for supercapacitor application. Synthesis of Mn doped PANI films as electrode for supercapacitor is important to decrease the resistivity of the PANI electrode with acceptable level of specific capacitance. The porous and well distributed nanofibers structure of Mn doped PANI increases the surface to volume ratio of electrode provide short diffusion path lengths to ions enhance the charge/discharge rate and hence the specific capacitance. The highest specific capacitance of 474 Fg$^{-1}$ is observed at 5 mVSec$^{-1}$ for PANI film having 1.6 weight percent Mn doping concentration in 1.0 M H$_2$SO$_4$. 
4.5 References


