Synthesis and Characterization of Pt-Polyaniline Composite

A Thesis Submitted

In Partial Fulfillment of the Requirements
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in

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by

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CERTIFICATE

This is to certify that the thesis entitled "Synthesis and Characterization of Pt-Polyaniline Composite", submitted by Mr. Neeraj Kumar is in the partial fulfillment of the requirement for the degree of Master of Technology in Materials Science and Engineering of this university. This work has been done under the supervision of Dr. M. L. Singla and Dr. S. D. Tiwari.

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DECLARATION

I hereby declare that the entitled work "Synthesis and Characterization of Pt-Polyaniline Composite" is the original work carried out by me under the supervision of Dr. M. L. Singla and Dr. S. D. Tiwari. Synthesis and characterization of all the samples are done at Central Scientific Instrument Organization, Chandigarh by me under the supervision of Dr. M. L. Singla. I am responsible for all the content of this thesis. The matter embodied in this thesis has not been submitted to any other degree of this or any other university.

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ABSTRACT

Polyaniline and Pt-polyaniline composite samples are synthesized by chemical routes. The samples are characterized by X-ray diffractometer and thermogravimetric analyzer. I-V characteristics of the sample are also studied. Results and analysis indicate for increase in conductivity of the Pt-polyaniline composite in comparison to polyaniline.

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CHAPTER-1

INTRODUCTION

1.1 Polyaniline

Polyaniline has been an extensively studied system due to its unique and interesting properties. It shows reversible metal to insulator transition and electrochromic behavior depending on its oxidation state and pH. It is stable in air and humidity. These characteristics make polyaniline very useful for use in various applications such as molecular sensors [1], transistors [2] etc. Polyaniline exists in various oxidation states i.e. Leucoemeraldine base, Emeraldine base, Emeraldine salt and Pernigraniline.

Polyaniline is a phenylene based polymer. There is a chemically flexible –NH group in the polymer chain flanked either side by a phenylene ring. It can also be defined as the simple 1, 4- coupling product of monomeric aniline. The various physico-chemical properties of polyaniline are because of the presence of the –NH- group. Polyaniline is one of the most known and extensively investigated conducting polymers. It exists in many different oxidation states. Conductivity of polyaniline strongly depends on protonation with organic or inorganic acids. The commonly used green protonated emeraldine has conductivity in a range that of semiconductor.

1.1.1 Synthesis of Polyaniline

The most common synthesis of polyaniline involves oxidative polymerization. In this method the polymerization and doping occurs at the same time and may be accomplished either electrochemically or chemically. Electrochemical methods have lower yields than chemical yields.

Synthesis of polyaniline by chemical oxidative method involves the use of either hydrochloric or sulfuric acid and the presence of ammonium peroxo-di-sulfate (as the oxidizing agent) in the aqueous medium. In this method the oxidant withdraws a proton from an aniline molecule without forming a strong coordination bond with the substrate, intermediate or with the final product. A smaller quantity of oxidant is used to avoid oxidative degradation of the formed polymer. It has been reported that the propagation of polymer chains proceeds by a redox process between the growing chain and aniline with addition of monomer to the chain end [3]. The high concentration of a strong oxidant at the initial stage of the polymerization enables the fast oxidation of oligomer and polyaniline, as well as their existence in the oxidized form.

Polyaniline can also be synthesized by electrochemical route [4]. This method is regarded as a novel and simple method for the synthesis of conducting polymers. In this method the polymerization in appropriate electrolytic medium directly gives doped polymer in form of a flexible film. The film is produced on the electrode surface by oxidative coupling. Therefore this method is somewhat similar to the electrochemical deposition of metal. Electrochemically synthesized polyaniline is a good method to obtain a clean and ordered polymer in form of thin film.

1.1.2 Composites of Conducting Polymers

Conducting polymer composites are physical mixtures of nonconductive polymer and conducting material. Conductivity of such composite is governed by the percolation theory. Here the percolation theory describes the movement of electrons between metallic phases and exhibits a sudden drop in conductivity at the point where the dispersed conductive phase no longer provides a continuous path for the transport of electrons through the material [5]. These days research has been carried out to synthesis the composites of polymer with nanoparticles of conducting materials. The aim to synthesize nanostructures that combine the mechanical flexibility, optical and electrical properties of conducting polymers with the high electrical conductivity and magnetic properties of metal nanoparticles has inspired the development of several techniques for the controlled fabrication of metal nanoparticle conducting polymer composites. Three main types of inorganic nanomaterials are used as inorganic fraction. The first type is metal oxide. This can improve the properties of polyaniline in the area of electricity, magnetism etc. The second type is metal nanoparticles. Many polyaniline-metal composite systems such as polyaniline-Au, polyaniline-Ag and polyaniline-Ni nanocomposites have been prepared using chemical or electrochemical method. The third type of inorganic nanomaterials is carbon nanotube. This could improve the conductivity of polyaniline.

1.1.3 Applications of Polyaniline

The conductivity of polyaniline makes it useful as a shield against discharges of static electricity. Because of this reason the polyaniline based composites and compounds have been used in the packaging of electronics products. Polyaniline composites are being tested for use against electromagnetic radiation. People hope that polyaniline compounds may be useful in printed circuit boards, electro chromic windows in houses and cars and conductive fabrics in future.

Polyaniline shows metal to insulator transition and electrochromic behavior depending on its oxidation state and pH. It is stable in air and humidity. These reasons makes polyaniline useful for many applications such as in rechargeable batteries, light emitting diodes, transistors, molecular sensors, nonlinear optical devices, corrosion protection, electromagnetic interference shielding and electro chromic displays. However problems like poor solubility in common solvents and infusibility limit its use into industrial applications. Synthesis of composites of conducting polymer has been considered to provide a suitable solution to the process ability problem. These composites have the ability to enhance their material properties along with desirable mechanical and physical characteristics.

1.2 Aim of the Thesis

The aim of this thesis is to synthesize and study the I-V characteristics of polyaniline and Pt-polyaniline composite samples.

CHAPTER-2

EXPERIMENTAL TECHNIQUES

2.1 X-ray Diffratometer

X-ray diffractometer works on the principle of Bragg's law [6]. A crystal consists of parallel atomic planes. If a beam of X-ray falls on such a plane then according to Bragg's law the diffracted beam will have a maximum intensity if

$$2d\sin\theta = n\lambda$$

where d is spacing between atomic planes, λ is wavelength of X-ray used, θ is angle of diffraction and $n = 1, 2, \ldots..$

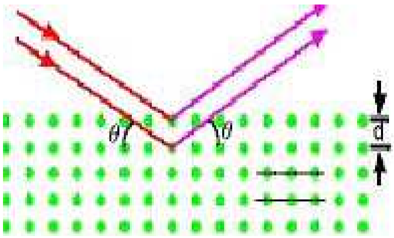

Fig. 2.1: Beam of X-ray reflected by the set of parallel planes.

The X-ray diffractometer gives a plot of intensity of diffracted beam as a function of the angle 2θ. Using this plot the values of d can be calculated and thus the material can be characterized.

2.2 Thermogravimetric Analyzer

Thermogravimetric analysis (TGA) is an analytical technique used to determine the thermal stability and fraction of volatile components in a material by monitoring the weight change that occurs as the material is heated. The measurement is normally carried out in air or in an inert atmosphere and the weight is recorded as a function of increasing temperature. The maximum temperature is selected so that the specimen weight is stable at the end of the experiment.

In differential thermal analysis (DTA) the sample and an inert reference material are heated under identical conditions. The temperature difference between the sample and reference material is continuously recorded during this process. The difference in temperatures is then plotted against temperature. By this the changes in the sample due to the absorption or evolution of heat can be detected.

Systematic sketch of a DTA is shown in Figure 2.2 [7]. It mainly consists of sample holder, thermocouples, furnace, temperature programmer and recording system. The sample holder is in form of a crucible and usually made of platinum. The thermocouples are not placed in direct contact with the sample to avoid contamination and degradation. The furnace should provide a stable hot zone. The temperature programmer is required to obtain desire constant heating rates.

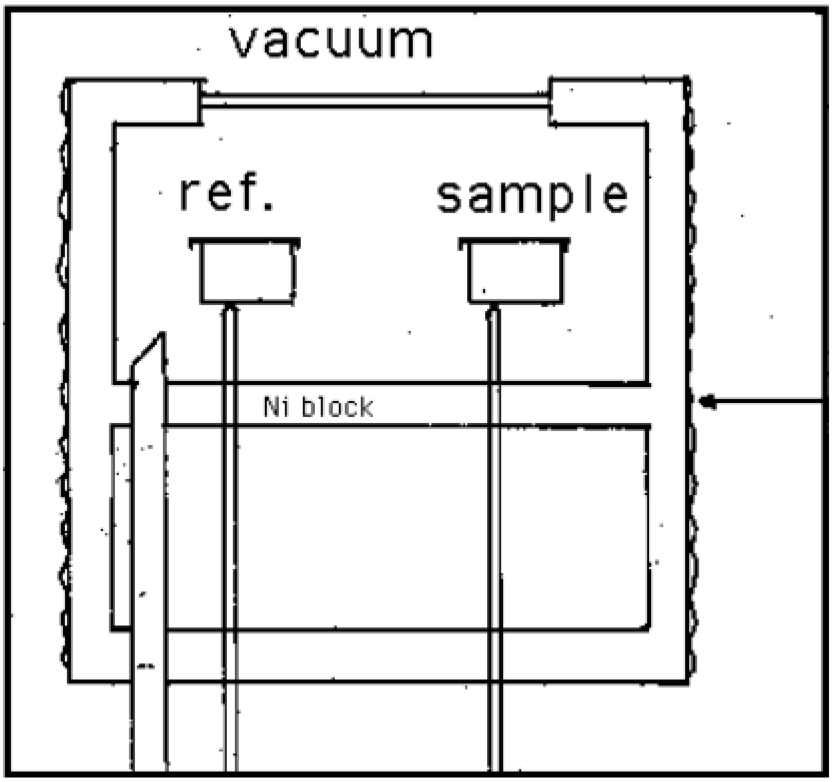

Fig. 2.2: Schematic diagram of a DTA cell [7].

The main applications of DTA are in finding transition temperature, heat capacity, identification of materials etc. An endothermic or exothermic transition will give rise to a peak in the DTA curve. The endothermes are along negative direction and exotherms are along positive direction in the plot.

CHAPTER-3

EXPERIMENTS, RESULTS AND DISCUSSIONS

3.1 Sample Preparation

Polyaniline is synthesized using commercially available aniline monomer following a procedure as described elsewhere [8]. This polyaniline is further used to synthesize Pt-polyaniline composite following a method reported in literature [9]. For this the polyaniline is dispersed in ethylene and water solution containing the platinum precursor. The mixture is sonicated for 1 minute and then polyvinylpyrrolidone is added. The mixture is heated at 100 ^{0}C for 2 hours. After this the mixture is cooled to room temperature and water is added. The precipitate is centrifuged and washed several times with water. Finally the solid is washed with acetone.

3.2 X-ray Diffraction

X-ray diffraction pattern of synthesized sample of polyaniline is shown in Figure 3.1. This pattern clearly indicates for amorphous nature of the polyaniline.

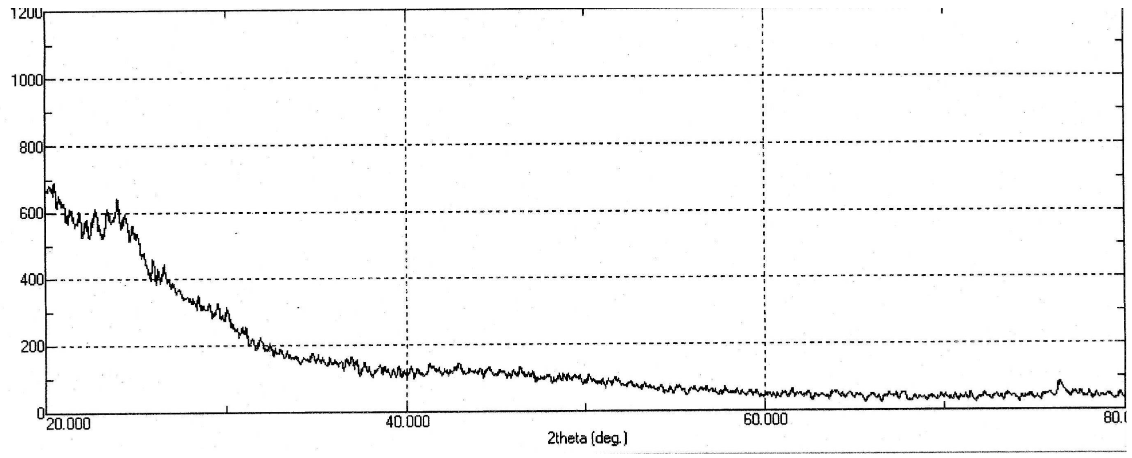

Figure 3.1: Room temperature X-ray diffraction pattern of polyaniline.

Figure 3.2 shows room temperature X-ray diffraction pattern of synthesized Pt-polyaniline composite sample. This pattern shows diffraction peaks for platinum. These peaks are also found to be broadened. This indicates that the platinum in the composite material is in nanocrystalline form.

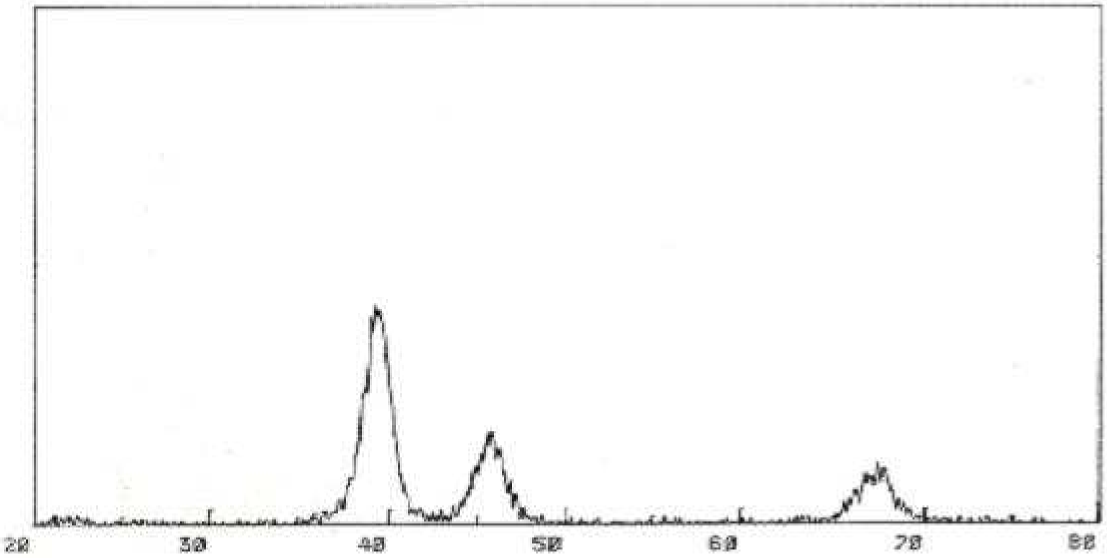

Figure 3.2: Room temperature X-ray diffraction pattern of Pt-polyaniline composite.

The average crystallite size *d* of the platinum nanoparticles is calculated using the modified Scherrer formula [10]

$t = 0.9\,\lambda / \mathrm{Cos}\,\theta_B\,(B_M - B_S)$

Here λ = wavelength of X-ray used

θ_B = Bragg's angle

B_M = Full width at half maximum of the peak

B_S = Full width at half maximum of the same peak from a standard material

Using the modified Scherrer formula the average crystallite size turns out to be about 6 nm.

3.3 Thermo Gravimetric Analysis

Many compounds are not stable at higher temperatures and decompose into other compounds on heating. Keeping this thing in mind the prepared samples are characterized with the help of a thermogravimetric analyzer.

In thermogravimetric analysis the mass of a given material is measured as a function of temperature by keeping the material at a constant heating rate. The prepared sample of polyaniline is heated at a rate of 10 ^{0}C per minute for this analysis. The variation of mass of the sample as a function of temperature is shown in Figure 3.3. This figure shows that the mass of the sample decreases with increasing temperature continuously up to 650 ^{0}C. After this the mass becomes constant. In other words the decomposition of the polyaniline is almost complete at about 650 ^{0}C.

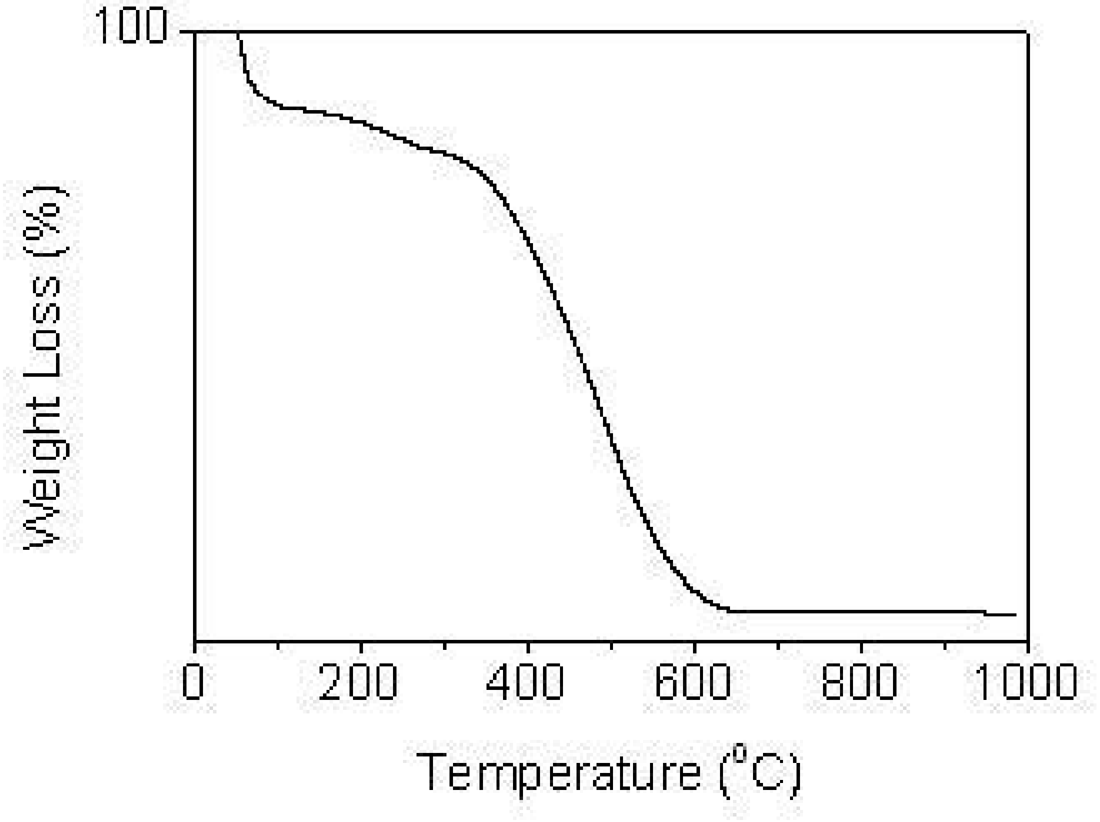

Figure 3.3: Weight loss as a function of temperature for the polyaniline.

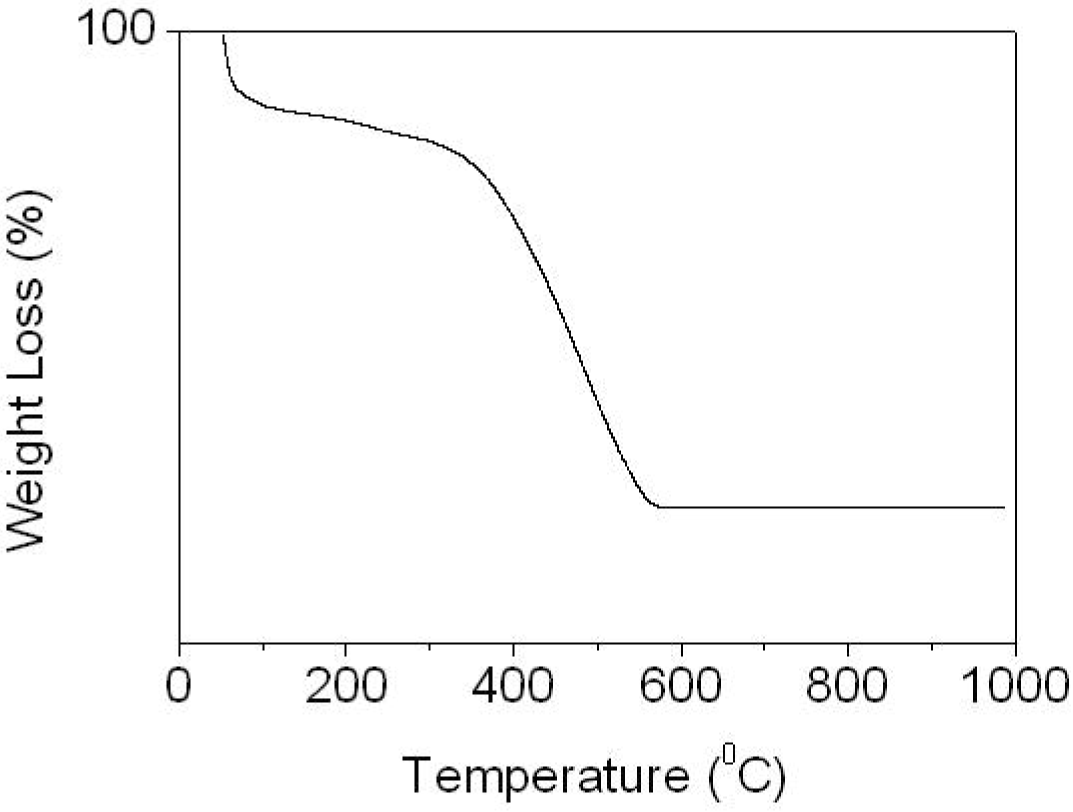

Figure 3.4: Weight loss as a function of temperature for the Pt-polyaniline composite.

The weight loss as a function of temperature for the Pt-polyaniline composite at a heating rate of 10 ^{0}C per minute is shown in Figure 3.4. This figure shows that the mass of sample decreases with increasing temperature up to about 600 ^{0}C. After this, mass of the sample becomes constant. From this figure it is also clear that the mass of the undecomposed material, the Pt in this case, is about 20% of the initial mass of the composite. In other words the concentration of Pt in the composite sample is about 20 wt %.

3.4 Electrical Characterization

I-V characteristic of the polyaniline sample at room temperature is shown in Figure 3.5. This figure shows that the current increases with increasing voltage across the sample. The resistance of the sample is about 1.4×10^4 ohm at a potential difference of 1 V.

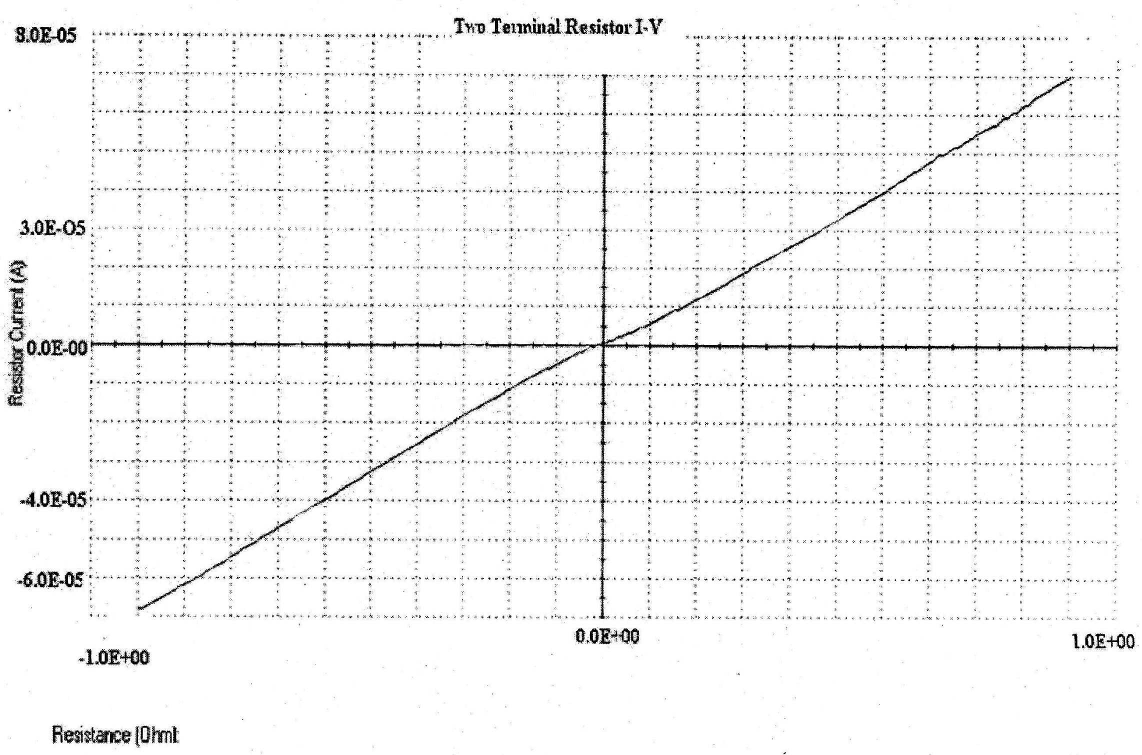

Figure 3.5: Room temperature I-V characteristics of the polyaniline.

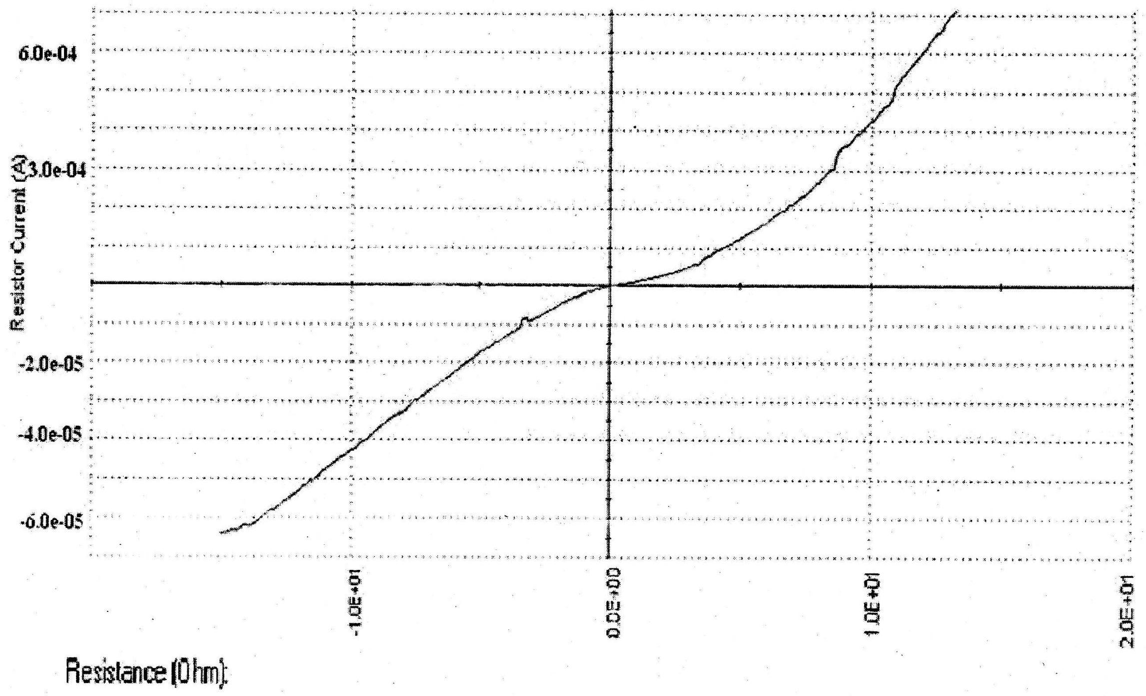

Figure 3.6: Room temperature I-V characteristics of Pt-polyaniline composite.

I-V characteristic of the Pt-polyaniline sample at room temperature is shown in Figure 3.6. This figure shows that the current increases with increasing voltage across the sample. The resistance of the sample is about 2.5×10^3 ohm at a potential difference of 1 V across the sample.

CHAPTER-4

CONCLUSIONS

In the present study, polyaniline and Pt-polyaniline composite are prepared following chemical routes. X-ray diffraction confirms the amorphous nature of the polyaniline. Also X-ray diffraction of Pt-polyaniline composite shows Bragg's diffraction peaks corresponding to platinum. Thermogravimetric analysis on the polyaniline sample shows that its decomposition is almost complete at about 650 ^{0}C. Concentration of Pt in the Pt-polyaniline composite sample is confirmed to be about 20 wt % from the thermogravimetric analysis. From the I-V characteristics of the sample it is found that the conductivity of the Pt-polyaniline composite increases by about one order of magnitude compared to polyaniline sample.

The present work was aimed to study the effect of doping the polyaniline by Pt nanoparticles on its conductivity. For this purpose only one sample of Pt-polyaniline composite having concentration of Pt of about 20 wt% was prepared. One may further synthesize the Pt-polyaniline composites with different concentrations of Pt nanoparticles and study the conductivity of these samples.

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